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TALANTA MINI-REVIEW*

THE APPLICATION OF TERNARY COMPLEXES TO SPECTROFLUOROMETRIC ANALYSIS

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Summary—The use of ion-association and co-ordination-unsaturated ternary complexes for the spectrofluorometric determination of trace elements is reviewed.

Ternary complexes, wherein a central ion reacts with two different ligands, have aroused considerable interest in recent years. West[1] has classified ternary complexes into two major categories, these being the co-ordination-unsaturated type and ion-association type. The co-ordination-unsaturated ternary complex results when a binary complex ("binary" here refers to a complex containing one type of central ion and one type of ligand, regardless of their stoichiometric ratio) has free co-ordination positions available on the central ion, allowing further reaction with a different ligand. Alternatively, if the binary complex is charged, then ion association with an ion of the opposite charge (usually a dyestuff) may occur. The modes of formation of both types of ternary complex, together with improvements in selectivity and sensitivity which accompany their formation, have been extensively discussed in a series of reviews.[2–9]

These articles have been primarily concerned with the use of ternary complexes in spectrophotometric analysis, while making only passing reference to fluorometric application of ternary complexes. Some further information on fluorometric use of ternary complexes may be extracted from two general reviews on fluorescence analysis.[10,11] In view of the fact that publications describing the use of ternary complexes in spectrofluorometry are rapidly increasing in frequency in the chemical literature, it is appropriate to present in this paper a collation of existing methods and theory in this subject. Table 1 presents a summary of fluorometric methods which are based on ternary complex formation.

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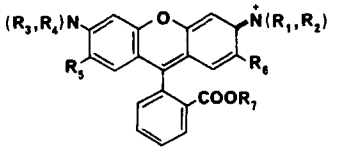
ION-ASSOCIATION TERNARY COMPLEXES

Anionic binary complexes

Ternary complexes formed by ion association of an anionic binary complex with a basic dye cation comprise the vast majority of ternary complexes used for spectrophotometric analysis. The same is true for fluorometric analysis where fluorescent dyes of the xanthene series (*i.e.*, rhodamine dyes) serve as the cationic counter-ion in the ternary complex. The structures of the various rhodamine dyes are listed in Fig. 1.



NAME	R_1	R_2	R_3	R_4	R_5	R_6	R_7
Rhodamine B	C_2H_5	C_2H_5	C_2H_5	C_2H_5	H	H	H
Rhodamine 3B	C_2H_5	C_2H_5	C_2H_5	C_2H_5	H	H	C_2H_5
Butylrhodamine B	C_2H_5	C_2H_5	C_2H_5	C_2H_5	H	H	C_4H_9
Rhodamine 3GO	C_2H_5	C_2H_5	H	H	CH_3	H	C_2H_5
Rhodamine 4G	C_2H_5	C_2H_5	C_2H_5	H	H	H	C_2H_5
Rhodamine 6G	H	C_2H_5	H	C_2H_5	CH_3	CH_3	C_2H_5
Rhodamine 6J	H	C_2H_5	H	C_2H_5	H	H	C_2H_5

Fig. 1. Structures of rhodamine dyes.

The considerable fluorescence displayed by xanthene dyes has been attributed to the rigidity of their molecular structure arising from the oxygen bridge between the benzene rings.[3] Within the xanthene dye series, fluorescence increases in the order Rhodamine B (RhB) < Rhodamine 3B (Rh 3B) < Rhodamine 4G (Rh 4G) < Butylrhodamine B (BuRhB) < Rhodamine 6G (Rh 6G),[3,64,132] whilst stability and extractability of their ion-association complexes increase in the order RhB < Rh 6G < Rh 3B < BuRhB.[133] Although RhB and the asymmetrical dye Rh 4G are less sensitive than Rh 6G, they have been shown to be more selective.[64,134] The dyes can be arranged in the following order with respect to their selectivity: BuRhB > RhB > Rh 6G.[135]

Each of the xanthene dyes has an upper limit to

Table 1. Summary of fluorometric methods using ternary complexes

A	Aqueous fluorometric method.
A/E	Method suitable for both aqueous and extraction fluorometry.
Q	Aqueous fluorescence-quenching method.
OQ	Organic phase fluorescence-quenching method.
λex	Excitation wavelength.
E	Extraction—fluorometric method.
ES	Extraction—fluorometric method incorporating exchange of the associated dye ion.
IE	Indirect extraction—fluorometric method.
λem	Emission wavelength.

Note: This table does not include some older, superseded methods, as these are listed elsewhere.[3]

Element	Reagents	Type of Method	Reaction Conditions	λex/λem (nm)	Determinable Limits (μg)/ Final aqueous or organic volume (ml)	Interferences	Ref.
Ag	Butylrhodamine B + Br^-	E	C_6H_6 from 6N H_2SO_4 + 0.1N Br^-, preliminary separation of Ag^+ with dithizone	565/590	0.6-6.0/6	Many cations	12-15
	Eosin + 1,10-phenanthroline	E	$CHCl_3$-acetone (7:3) from pH 6. Preliminary separation of Ag^+ with dithizone	540/580	0.5-10/6	Fe(III),In,Co	16
	Eosin + 1,10-phenanthroline	Q	pH 3-8. EDTA used as a mass masking agent	546/560	0.1-1.0/25	Pd	17
	Erythrosin + 1,10-phenanthroline	E	$CHCl_3$ from pH 6	510/570	0.5-10/6	Many cations	18
Ag	Rhodamine 6G + Br^-	E	C_6H_6 from 4.2N H_2SO_4 + 0.17N Br^-	535/560	0.3-3/6	As above	19-22
	Rose Bengal + 1,10-phenanthroline	E	$CHCl_3$ from pH 6	535/580	0.5-10/6	As above	18
	3,4,5,6-tetrachlorofluorescein + 1,10-phenanthroline	Q	pH 10.5-11.8, EDTA used as a mass masking agent	540/ -	0.5-6.0/-	I^-,CN^-,$S_2O_3^{2-}$	23
Al	Antipyrine + quercetin	E	$CHCl_3$ from pH 5 + $NaClO_4$	365/509	-	Ga,In,Zr,Th, Fe(III)	24
As	Rhodamine B + Cl^-	IE	C_6H_6 from 1.2N HCl + 2×10^{-5}M KIO_3. The complex I Cl_4 (Rhod) is extracted as an indirect estimate of As(III)	565/590	0.3-1.5/5	Fe,Cu,Ga,Sn	25
Au	Butylrhodamine B + Cl^-	E	C_6H_6-acetone from 12N H_2SO_4 + 0.5% NaCl	565/590	0.12-1.2/6	NO_3^-, Tl	26-30
	Crystal Violet + butylrhodamine B + Br^-	ES	C_6H_6 from 0.5N H_2SO_4 + 0.1% KBr + 0.0025% Crystal Violet, then shake with Butylrhodamine B in 11.5N H_2SO_4	560/595	0.01-2/6	Sb,Tl	31
	Rhodamine B + Br^-	E	C_6H_6-$(C_2H_5)_2O$ from 3.8N HBr + 0.5N KBr	366/590	1.0-100/20	Many cations	32
	Rhodamine B + Br^-	E	Isopropylether from 0.8N HCl	550/575	< 0.23/10	Sb,Tl,In,Ga	33
	Rhodamine B + Cl^-	E	C_6H_6 from 0.25-0.4N H_2SO_4 + 0.5% NaCl + 0.005% Rhodamine B	575/ -	0.1-1/6	-	26
Au	Rhodamine B + Cl^-	E	C_6H_6-acetone from 3.1N H_2SO_4 + 0.4N NaCl	560/580	0.5-4.0/5	Many cations	34

B	Butylrhodamine B + F^-	E	C_6H_6 from 0.1N H_2SO_4 + 0.05N F^-	336/590	0.01-0.5/10	As above	35,36
	Rhodamine 6G + salicylic acid	E	C_6H_6 from 0.001N HCℓ	368/560	0.001-1/10	Pt,Ru,Mo,V,W	37,38
Be	Tetracycline + diethylthiobarbituric acid	A	pH 9	407/506	5-15/50	-	39
Cd	Erythrosin + 1,10-phenanthroline	E	$CHCℓ_3$ from pH 8; add acetone to extract	530/570	0.6-9/6	Many cations	40
	Iodoeosin or Eosin + 1,10-phenanthroline	E	As above	540/570	0.3-6/6	As above	40
Co	Eosin + 1,10-phenanthroline	E	$CHCℓ_3$ from pH 9; add acetone to extract	540/580	0.1-1.0/10	As above	41
	Pyridine-2-aldehyde-2-pyridyl hydrazone (PAPHY) + Eosin	E	$CHCℓ_3$-acetone (7:3) from pH 5.6 + 0.0025% PAPHY	530/558	0.08-4/10	Cu,Ni,Fe,Pd,Hg	42
	Salicylfluorone + H_2O_2	A	pH 11	366/540	0.0005-0.01/5	-	43
Cu	Eosin + 1,10-phenanthroline	E	$CHCℓ_3$ from pH 9; add acetone to extract	540/580	0.1-1.0/10	Many cations	41
	Rose Bengal + 1,10-phenanthroline	E	$CHCℓ_3$ + 2% NH_3 in acetone from pH 9	560/570	0.1-6.0/100 ml	As above	44
Dy	Iminodiacetic acid + Tiron (1,2-dihydroxybenzene-3,5-disulphonic acid	A	pH 12.5-13.0	- /577	From 0.0001	-	45
Eu	Dibenzoylmethane + diethylamine	A	pH 9.2 (precipitate suspension)	365/613	From 0.002	-	46
	2 Naphthoyltrifluoroacetone + trioctylphosphine oxide	E	C_6H_6 from pH 5.5-6.5	365/613	0.01-500/10	Sm,Fe(III)	47
	Hexafluoroacetylacetone + trioctylphosphine oxide	E	Methylcyclohexane from pH 3	360/615	0.001-4.5/3	Sm,Tb	48
	1,10-phenanthroline + salicylate	E	C_6H_6 from pH 6-7	366/612	0.05-25/10	Rare Earth Ions	49
	Thenoyltrifluoroacetone + collidine	A/E	pH 6-7 or C_6H_6 from pH 6-8	366/612	0.0001-1.0/5	As above	50
	Thenoyltrifluoroacetone + diphenylguanidine	A/E	As above	366/612	As above	As above	50
	Thenoyltrifluoroacetone + hydroxyethylethylenediaminetriacetic acid	A	pH 8.2	365/613	0.05-3/10	-	51
	Thenoyltrifluoroacetone + 1,10-phenanthroline	A/E	pH 6-8 or C_6H_6 from pH 6-8	366/612	0.002-5.0/5	Rare Earth Ions	50,52,53
F^-	Zirconium + Calcein Blue	A	pH 2.5	315/410	0.9-6.0/100	WO_4^{2-},PO_4^{3-},Aℓ, Mn,Ag	54
Fe	Eosin + 1,10-phenanthroline	E	$CHCℓ_3$ from pH 9; add acetone to extract	540/580	1-10/10 ml	Many cations	41
Ga	Acridine Orange + $Cℓ^-$	E	$C_2H_4Cℓ_2$ from 6M HCℓ	305/525	0.025-0.5/5	-	55
	Antipyrine + quercetin	E	$CHCℓ_3$ from pH 5.0 + $NaClO_4$	365/509	0.05-0.5/5	Aℓ,In,Zr,Th, Fe(III)	24
	Rhodamine B + $Cℓ^-$	E	C_6H_6 from 5-6M HCℓ	560/580	0.02-6/5	Many cations	56-60
	Rhodamine B + $Cℓ^-$	E	9:1 C_6H_6-acetone from 6N HCℓ	560/580	0.01-2/6	-	61-63
	Rhodamine 3GO + $Cℓ^-$, Br^-	E	C_6H_6 from 6M HCℓ, 4.5 M H_2SO_4 + 0.2-0.5M HBr	538/558	From 0.19/10	-	64,65
	Rhodamine 4G + $Cℓ^-$, Br^-	E	As above	557/572	From 0.025/10	-	64,65
	Rhodamine 6G + $Cℓ^-$	E	C_6H_6 from 13N H_2SO_4 + 1N HCℓ (or 1N NaCℓ)	530/555	0.01-0.2/5	Au,Hg,Sb,Tℓ,Fe	66,67
	Rhodamine 6G + $Cℓ^-$	E	C_6H_6 from 6M HCℓ	535/560	0.02-1.6/10	Many cations	58

Gd	Salicylate + rhodamine B	E	C_6H_6 from pH 6.0-6.5	546/571	1.5-15/10	Rare Earth Ions	68
Hf	Morin + $C\ell^-$	A	7N HCℓ + 30% CH_3OH	420/501	From 0.04/5	Zr	69
	Quercetin + $C\ell^-$	A	7N HCℓ or 0.5N H_2SO_4 + 38% CH_3OH	436/505	From 0.2/5	Zr	70
Hg	Crystal Violet + butylrhodamine B + Br^-	ES	C_6H_6 from 0.25N H_2SO_4 + 10^{-4}M KBr + Crystal Violet, then butylrhodamine B in 11N H_2SO_4 + KBr	560/590	0.03-2/10	Au	71
	Eosin + 1,10-phenanthroline	E	$CHC\ell_3$ from pH 9; add acetone to extract	540/580	0.5-10/10	Many cations	41
	Rhodamine B + Br^-	E	C_6H_6 from 4.5N H_2SO_4 + 0.2N Br^-	560/590	1.0-10/6	As above	21,72
	Rhodamine B + $C\ell^-$	A	2N H_2SO_4 + 0.2N NaCℓ	565/590	0.25-10/10	-	73
	Rhodamine B + I^-	Q	pH < 4	486/586	5-50/5	Cd,Pd,Te,Sb,Bi, Tℓ,Pt	74
In	Rhodamine B + Br^-	E	C_6H_6 + acetone (5:1) from 2.5N HBr	560/580	From 0.03/10	Many cations	75
	Rhodamine B + Br^-	E	C_6H_6 from 3-6N H_2SO_4 + 2N KBr + 5% acetone	560/580	0.2-4/10	As above	76
	Rhodamine 3B + Br^-	E	C_6H_6 from 1N HBr	565/590	0.02-2.0/6	Sb,Sn	61
	Rhodamine 3B + Br^-	E	C_6H_6 from 2.5N HBr	565/590	0.04-0.4/6	Many cations	77
	Rhodamine 3B + Br^-	E	C_6H_6 from 2-6N H_2SO_4 + 2N KBr	565/590	0.1-3.0/5	As above	78
	Rhodamine 3GO + $C\ell^-$	E	C_6H_6 from 6M HCℓ or 4-5M H_2SO_4 + 0.2-0.5M HBr	536/552	7/10	-	65
	Rhodamine 4G + $C\ell^-$	E	As above	546/565	2/10	-	65
	Rhodamine 6G + Br^-	E	C_6H_6 from 13N H_2SO_4 + 0.2 N KBr	530/570	From 0.01/6	Many cations	79
	Rhodamine 6J + Br^-	E	As above	535/560	2-1000/5	Cu,Fe,Sn	80
La	2 phenylquinoline-4-carboxylic acid + rhodamine B	E	C_6H_6 from pH 5-6	555/590	-	Rare Earth Ions	81
Lu	Morin + diantipyrylmethane	E	$CHC\ell_3$ from pH 6.2-6.8	365/508	0.1-50/5	Many cations	82
Mn	Eosin + 1,10-phenanthroline	E	$CHC\ell_3$ from pH 9; add acetone to extract	540/580	1-10/10	As above	41
Mo	Rhodamine B + SCN^-	Q	1.6N H_2SO_4 + 0.8N HCℓ + 0.8% SCN^-	350/578	0.05-5/25	None	83
Nb	Lumogallion + H_2O_2	A	pH 5.6-7.1	546/640	1-10/5	-	84
Nb	Lumogallion + oxalate	A	pH 5-6.5, 0.02N $H_2C_2O_4$	336/630	1-2.5/10	Ga,Fe,Ti,Ta	85
	Morin + H_2O_2	A	pH 3, 50% CH_3OH or 25% C_2H_5OH or acetone	436/505	0.02-2.0/5	Aℓ,Ga,In	86
	Quercetin + H_2O_2	A	pH 2.1, 50% C_2H_5OH	430/500	0.5-4.5/5	Ta	87
	Sulphonaphtholazoresorcinol + H_2O_2	A/E	pH 3.2-4.7, 30% CH_3OH, 1-1.5 hour reaction time; complex may be extracted in presence of diphenylguanidine by C_4H_9OH	540/680	0.2-2.0/5	Ta,EDTA, $C_2O_4^{2-}$	88
	Sulphonaphtholazoresorcinol + oxalate, tartrate or F^-	A/E	pH 5-6.5, 10-30% CH_3OH, 30-80 min reaction time; complexes may be extracted in presence of diphenyl-guanidine by C_4H_9OH	540/640-700	0.2-2.0/5	-	89
Ni	Eosin + 1,10-phenanthroline	E	$CHC\ell_3$ from pH 9; add acetone to extract	540/580	1-10/10	Many cations	41
Pb	Eosin + 1,10-phenanthroline	E	As above	540/580	1-10/10	As above	41
PO_4^{3-}	Molybdophosphate + Quinine	A	0.05M H_2SO_4 in 90% acetone	352/445	0.02-1.2/2	As,W,Ge	90
	Molybdophosphate + Rhodamine B	E	1N HCℓ. Excess dye extracted with $CHC\ell_3$, then $CHC\ell_3/C_4H_9OH$ (4:1) used to extract the ternary complex	350/575	0.04-0.6/2	As,V,Cr	91

Re	Perrhenate + Acridine Orange	E	$C_2H_4Cl_2$ from 0.5-2.5M H_3PO_4 + 6×10^{-6}M Acridine Orange	505/520	0.05-40/10	-	92,93
	Perrhenate + rhodamine 3B	E	C_6H_6 from 1M H_3PO_4	560/590	0.1-2.0/6	Fe,W,Cl^-	94
	Perrhenate + rhodamine 6J	E	C_6H_6 from 1N H_2SO_4	535/560	1-30/6	Hg,Cr,Mn,W, + anions	95
	Perrhenate + safranin T	E	$C_2H_4Cl_2$ from pH 4-8; add acetone to extract (40%)	515/546	0.02-1/10	-	96
Sb	Crystal Violet + rhodamine 3B + Cl^-	ES	C_6H_6 from 9N HCl + 0.005% Crystal Violet; shake extract with 6.5M H_2SO_4 + 0.002% rhodamine 3B; add acetone to extract	565/595	0.05-0.25/6	Au,Tl	97
	Rhodamine 6G + Cl^-	E	C_6H_6 from 6N H_2SO_4 + 0.5N NaCl	532/555	1-20/10	-	98
	Safranin T + Cl^-	E	C_6H_6 from 2N HCl; dilute extract 7:3 with acetone	510/570	0.2-15/15	Au,Th,Ga	99
Sc	Morin + antipyrine	E	$CHCl_3$ from pH 3.3-3.4 + 0.1M $NaClO_4$	365/510	0.1-2/10	Many cations	100
	2-phenylquinoline-4-carboxylic acid + rhodamine B	E	C_6H_6 from pH 4.2	556/580	1-45/10	As above	101
Sm	Hexafluoroacetylacetone + trioctylphosphine oxide	E	Methylcyclohexane from pH 3	365/565	0.02-4.5/3	Eu,Tb	48
	2-naphthoyltrifluoroacetone + trioctylphosphine oxide	E	C_6H_6 from pH 5.5-7.0	365/565	0.01-500/10	Fe(III),Eu	47
	Thenoyltrifluoroacetone + collidine, diphenylguanidine or 1,10-phenanthroline	A/E	pH 6-7 or C_6H_6 from pH 6-7	366/562	0.25-5/5	Rare Earth Ions	50
	Thenoyltrifluoroacetone + 1,10-phenanthroline	E	C_6H_6 from pH 5-7	366/562	0.05-5/5	As above	52,53
Sn	Rhodamine B + Br^-	E	Diethyl ether from 4N HBr; evaporate extract; C_6H_6 from 2N HBr + rhodamine B	565/580	2-5/5	-	102
	Rhodamine B + Br^-	E	C_6H_6 from 2N HBr	560/580	0.5-10/5	Au,Cr,Tl,In,Hg, WO_4^{2-}	103
Ta	Brilliant Green + butylrhodamine B + F^-	ES	C_6H_6 from 1N H_2SO_4 + 0.2% F^- + Brilliant Green; shake extract with butylrhodamine B in 10N H_2SO_4; add acetone (to 30%) to extract	560/595	0.1-2/5	Ti,Cr,Zr,Re,Nb	104
	Morin + H_2O_2	E	C_4H_9OH from pH 3	436/509	0.03-0.35/5	Nb,Ti	105
	Rhodamine 6G + F^-	E	C_6H_6 from F^- solution	- /530	From 0.5	-	106
	Rhodamine 6J + F^-	E	C_6H_6 from 0.1M F^-	530/570	From 0.002/5	-	107
Tb	Acetylacetone + EDTA	A	pH 10.0-11.5	250/546	0.04-40/25	-	108
	Antipyrine + sodium tetraphenylborate	A	pH 5.0-6.3	296,302/543	0.5-10/10	Dy,Eu,Sm	109
	2,3-dihydroxynaphthalene + EDTA	A	pH 10.5-12.0	365/545	0.01-4/10	-	110
	Hexafluoroacetylacetone + trioctylphosphine oxide	E	Methylcyclohexane from pH 3	350/545	0.005-4.5/3	Eu,Sm	48
	Iminodiacetic acid + Tiron (1,2-dihydroxybenzene-3,5-disulphonic acid)	A	pH 12.5-13.0	- /546	0.0001-1000/25	-	45
	Salicylate + antipyrine	E	C_6H_6 from pH 5-6	366/544	0.05-25/5	Eu,Nd,Pr	111
	Salicylate + EDTA	A	pH 12.0-12.7	289/546	0.007-5/10	-	112
	Salicylate + 1,10-phenanthroline	E	C_6H_6 from pH 6-7	366/543	0.5-25/10	-	49
	Sulphosalicylic acid + EDTA	A	pH 11.7-11.9	350/545	0.16-80/25	Many cations	113

Te	Butylrhodamine B + Br^-	E	C_6H_6 + $CH_3COOC_4H_9$ from 11N H_2SO_4 + 0.07N Br^-	366/590	0.02-1/5	Sn,Bi,In,Tℓ,As	114
	Butylrhodamine B + Br^-	E	C_6H_6 + $CH_3COOC_4H_9$ from 9.2N H_2SO_4 + 0.1N Br^-	565/590	0.1-1/5	Many cations	13
	Rhodamine B + $Cℓ^-$	E	C_6H_6 + acetone (2:1) from 5.7% HCℓ	560/590	0.5-1.0/15	As above	115
	Rhodamine 3GO	E	C_6H_6 from 3.5-4M HCℓ	365/ -	4.5-600/6	-	116
	Rhodamine 4G	E	As above	365/ -	1-80/6	Ga,In	116
	Rhodamine 6J + Br^-	E	C_6H_6 from 8N H_2SO_4 + 0.8N Br^-	535/560	0.5-5/5	Many cations	13
Th	5,7-dibromo-8-hydroxyquinoline + rhodamine B	OQ	C_6H_6 from pH 4.5-7.0	544/570	0.2-6/5	-	117
	5,7-dinitro-8-hydroxyquinoline + rhodamine B	E	C_6H_6 from pH 1.8	560/580	0.07-15/10	-	118
Tℓ	Acridine Orange + $Cℓ^-$	E	$CH_3COOC_4H_9$ from pH 0.8-2.5	495/520	0.02-3/6	Hg,Au,Sb,In	119
	Acridine Yellow + $Cℓ^-$	E	$C_2H_4Cℓ_2$ from pH 0.4-1.0 HCℓ	- /495	From 0.05/10	Sb,Au,Hg,NO_3^-	120
	Acriflavine + $Cℓ^-$	E	$C_2H_4Cℓ_2$ from pH 1.5-1.7 HCℓ	- /490	0.025-5.0/10	Sb,Hg,Au	121
	Crystal Violet + butylrhodamine B + $Cℓ^-$	ES	C_6H_6 from H_3PO_4 (1:7) + $Cℓ^-$ + Crystal Violet; shake extract with butylrhodamine B in 12N H_2SO_4	560/595	0.02-1.6/6	-	122
	Rhodamine B + $Cℓ^-$,Br^-	E	C_6H_6 from 5N HCℓ,HBr	366/580	From 0.1/500	Au,Hg,Sb,Fe, SCN^-	123, 124
	Rhodamine 6J + Br^-	E	C_6H_6 from 5N HBr	366/560	0.02-1.0/4	Many cations	125, 126
UO_2^+	Rhodamine B + benzoic acid	E	C_6H_6 from pH 5	366/590	2.5-4000/10	As above	127
W	Tungstate + rhodamine B	Q	0.01N HCℓ	366/580	0-1000/50	As above	128, 129
Zn	Eosin + 1,10-phenanthroline	E	$CHCℓ_3$ from pH 9; add acetone to extract	540/580	1.0-10/10	As above	41
	Rhodamine B + SCN^-	E	Diethyl ether from pH 3.5-5.0	366/580	1.0-25/5	-	130
	Rhodamine B + SCN^-	Q	pH 4.2 + 0.1M SCN	366/580	0.5-10/6	-	131

the acidity of the aqueous phase at which it may be employed; beyond this maximum acidity the dyes tend to form doubly-charged cationic species which are much less likely to form extractable ion-association complexes than are singly-charged dye cations.[136] The esters of RhB may be used over a much wider range of acidity than RhB itself (largely because of the unfavourable effect of the carboxylic acid group of RhB) and have the additional advantage of forming ion-association complexes of low solubility, thereby considerably assisting the extraction of these into organic solvents.[133] It has been found that an alkyl substituent containing four carbon atoms produces esters of RhB which have optimal properties for extraction fluorometric procedures. The basicity of xanthene dyes decreases in the order RhB < Rh 6G < BuRhB[137,138] and the optimal acidity increases in the same order.[135]

Ion-association ternary complexes formed from these dyes may be classified into two groups; those containing an anionic binary complex formed between a metal and an electronegative ligand, and those formed from an anionic chelate binary complex.

Extraction–fluorometric procedures utilizing the first group are based on metal complexes with the ligands chloride, bromide, iodide, fluoride and thiocyanate. The metals studied most are gallium(III),[56] tin(IV),[102] gold(III),[26] tantalum(V),[106] tellurium(IV)[115] and indium(III),[65] most usually as chloro or bromo complexes. These metals have been extensively investigated and variations produced by alteration of the nature of the dye and electronegative ligand have been exploited. The anionic complexes are generally formed in strongly acid media and in many cases mutual interference occurs, reflecting the poor selectivity of rhodamine dyes. Fluorescence quenching often accompanies the formation of an ion-association ternary complex in aqueous solution and this has been utilized in highly sensitive fluorescence-quenching procedures based on thiocyanate complexes of zinc[131] and molybdenum(V)[83] as ion-association complexes with RhB. The poor selectivity of these quenching techniques was overcome in the case of the molybdenum method, because of the unusually high stability of the $MoO(SCN)_5(RhB)_2$ complex which permits the use of an acidity so high that potentially interfering elements cannot form stable complexes and can therefore be tolerated. Indirect fluorometric procedures using ion-association complexes are also possible and such a method has been described[25] for arsenic(III) wherein potassium iodate reacts quantitatively with arsenic(III) and RhB in hydrochloric acid solution to produce the ternary complex $ICl_4(RhB)$, which is extractable into benzene. The

fluorescence of this extract is used as an indirect measure of the concentration of arsenic(III) originally present in the solution.

Anionic binary chelate complexes have been utilized in the formation of ion-association complexes with xanthene dyes for use in fluorometric analysis. The ligands used include 8-hydroxyquinoline derivatives,[117,118] salicylic acid[68] and 2-phenylquinoline-4-carboxylic acid,[81] but these methods exhibit poor selectivity, necessitating routine use of masking agents or prior separation of the analyte. In such unselective procedures, experimental parameters must be strictly controlled if the blank value is to be minimized; a mathematical design[118] whereby parameters are simultaneously optimized is particularly useful. It is noteworthy that many ion-association ternary complexes involving anionic binary chelate complexes with rhodamine dyes have been applied only to spectrophotometric analysis,[139,140] and it is possible that these same complexes could prove suitable for fluorometry.

The selectivity of extraction procedures involving ion-association ternary complexes has been discussed with regard to aqueous phase pH and nature of dye, electronegative ligand and solvent,[141] and the effects of the concentration of the metal to be determined and of the organic cation have also been considered.[142,143] These last two papers were particularly concerned with intermolecular aggregation of dyes in solution and the effect this has on linearity of the calibration curve and ultimately, therefore, on the sensitivity of the determination. In brief, it was concluded that too high a concentration of dye leads to a high degree of intermolecular aggregation of dye molecules and a reduction in the number of molecules present in the protonated form (which is essential for reaction with the anionic binary complexes). Decreases in sensitivity are therefore observed with excessive dye concentrations. The same effect was observed for the anionic binary complexes, which tend to become aggregated at higher concentrations, thereby considerably departing from adherence to Beer's law.

The choice of solvent is an important aspect, and extractability of ion-association complexes of xanthene dyes generally increases along the series of solvents toluene, benzene, nitrobenzene, chloroform, dichloroethane.[133] Solvents such as alcohols, esters, ketones, aldehydes and many nitro-compounds tend to extract the dye itself (usually as a simple salt with a halide ion) and accordingly are of little value.[135,136] Diethyl ether has been used[130] but is not recommended for analytical work because of its high volatility. An alternative to selective extraction of ternary complexes is the prior separation of excess of the dye with solvent different from that employed for extraction of the ternary complex. Thus, in the determination of orthophosphate as molybdophosphate–RhB, chloroform is used to extract excess of RhB before extraction of the ternary complex with a mixture of butanol and chloroform.[91] In general, choice of solvent must be tempered by considerations of selectivity as well as sensitivity, although prior separation of the analyte is often the only solution to the problem of selectivity. The effect of the nature of the extracting solvent on the fluorescence and extractability of rhodamine dyes and their ion-association complexes with chlorotellurate has been reported.[144] The addition of alcohols and acetone to benzene increased both the tellurium(IV) extraction and the fluorescence of the extracted complex, and accordingly was recommended for the fluorometric determination of tellurium.

There are many examples of the use of acetone, ethanol, methanol or butyl acetate, in mixtures with benzene, as solvents for extraction fluorometric analysis. These solvents result in increasing the fluorescence (by a factor of as much as 80 relative to the fluorescence of benzene extracts)[97] as well as improving the stability and reproducibility of the fluorescence of the organic extract.[31] Acetone is the most widely used enhancing solvent and the increase in fluorescence observed on its addition has been attributed to dissociation of the ternary complex.[97] Addition of acetone to extracts is not advisable in cases where poor selectivity is observed since the accompanying increase in blank fluorescence negates any advantage gained through enhancement of the sample fluorescence. For example, the addition of acetone is not beneficial in the unselective determination of gadolinium with salicylic acid and RhB.[68]

Other binary mixtures of solvents have been studied as extractants for xanthene dye ion-association complexes[135,136,145] These mixtures are composed of a low activity (inert) solvent, usually benzene or carbon tetrachloride, and a donor-active (polar) solvent such as nitrobenzene, ketones, alcohols, dichloroethane and chloroform. Such solvent mixtures can achieve significant increases in extraction of the three-component complex, with very little corresponding effect on the extraction of simple salts of the dyes.[135] The magnitude of this synergistic effect is strongly dependent on the dielectric constant of the active solvent, and decreases with decreasing dielectric constant, although this rule does not hold for alcohols.[136]

Other factors which must also be considered in the selection of an optimum solvent mixture include volatility, speed of separation of phases and the dependence of extraction on the acidity of the aqueous phase. The range of suitable acidities over which an ion-association complex may be extracted has been shown to be dependent on the type of solvent used. For example, when benzene is used for extraction of the complex of $SbCl_6^-$ with BuRhB, the optimal acidity is 8–9*M* hydrochloric acid, whereas when carbon tetrachloride is the extractant, the optimal acidity is 6*M* hydrochloric acid.[135] The suitable range of acidity may be expanded when solvent mixtures are used in preference to a single solvent.[136]

The sensitivity threshold of fluorometric determination is governed by two independent values, these being the analytical threshold, resulting from the intrinsic fluorescence of the reagents used in the course of the determination, and the instrumental threshold which results from instability and variable response characteristics of electronic components of the fluorometer.[146] These two thresholds may be separately estimated, and in practice the analytical threshold is the more significant of the two. Calculations show that the theoretical detection limits of fluorometric methods are 1/50–1/25 of those obtainable for equivalent photometric methods using the same ternary complexes. Practically, however, fluorometric methods generally prove to be only about twice as sensitive as equivalent photometric methods[83,130] although there are, of course, some exceptions. The main reason why discrepancies are observed between calculated and practical detection limits of fluorometric methods using xanthene dye ion-association complexes is the increase in blank levels caused by co-extraction of complexes of interfering elements.[45] The sensitivity of these extraction–fluorometric methods where an acid is used to provide both acidity and an electronegative ligand (as is often the case) is limited largely by the amount of impurities introduced by the acid even when especially purified reagents are used.[97,104]

An extraction system for ternary complexes, involving additional operations of back-extraction, washing and repeated extraction has been suggested as a means of improving the separation of an analyte from interfering ions.[61] This process is based on differences in the stabilities and solubilities of ternary complexes and has proved effective in reduction of interferences in the extraction of rhodamine complexes of indium, tellurium and gallium.[61] The procedure may not be applicable to compounds which are extracted from nearly neutral aqueous solution, since there is considerable transfer of the colourless (lactone) form of RhB to the extractant;[130,147] this lactone form may, under suitable conditions, be readily transformed into the coloured, fluorescent form of RhB (*e.g.*, when acetone is added[3]) and could cause difficulty.

A further effort to overcome the limitations of the use of ternary complexes of xanthene dyes in fluorometric analysis has involved development of a technique wherein selectivity and sensitivity of a determination are optimized by exchange of the dye molecule in the ternary complex. The triphenylmethane dyes generally show greater selectivity in the extraction of a particular complex anion than do the dyes of the xanthene series.[145] On the other hand, the ability of xanthene dyes to fluoresce provides the opportunity for a more sensitive determination than is possible with triphenylmethane dyes, provided the "background" fluorescence can be reduced. The advantages of each method have been combined in a procedure involving extraction of a complex anion formed with a triphenylmethane dye for which a fluorescent xanthene dye cation is then substituted, the resulting complex being used for fluorescence analysis. The usual problems of poor selectivity and high blank values were largely overcome, mainly because the substitution solution could be readily purified by washing with a suitable organic solvent. This technique has been applied to mercury(II) (as $HgBr_4^{2-}$),[71] gold(III) (as $AuCl_4^-$),[31] and thallium(III) (as $TlCl_4^-$)[122] with Crystal Violet followed by substitution with BuRhB, antimony(V) (as $SbCl_6^-$)[97] with Crystal Violet followed by substitution with Rh 3B, and tantalum(V) (as TaF_6^-)[104] with Brilliant Green followed by substitution with BuRhB.

In these methods, the dye substitution technique resulted in elimination of the interference of platinum and boron in the determination of tantalum[104] also achieved a 50-fold and 25-fold improvement sensitivity for the determination of mercury[71] and antimony[97] respectively. The method was, however, not entirely successful for elimination of interferences in the determination of gold,[31] since prior separation of the analyte was still necessary. The full potential of each method was realized through the use of acetone as enhancing solvent after extraction of the complexes.

The acridinium dyes Acridine Orange, Acridine Yellow and acriflavine, and the azine dye Safranin T (3,6-diamino-2,7-dimethyl-10-phenylphenazine hydrochloride) may be used as the fluorescent counter-ion in ion-association ternary complexes. Safranin T bears a much stronger charge on the central nitrogen atom than does RhB and consequently is considerably more basic. The presence of two primary amino groups in this dye greatly increases its hydrophilic nature, while its rigid structure results in an ability to fluoresce.

Each of the acridinium dyes has been employed for the extraction–fluorometric determination of thallium(III) (as $TlCl_4^-$).[119–121] These methods were subject to interference by antimony(V), mercury(II) and gold(III), although these elements could be removed from solution by cementation on a copper wire or the thallium could be separated by extraction from 3*M* hydrochloric acid.[119] Detection limits were similar for Acridine Orange and acriflavine (0.003 ppm Tl), but Acridine Yellow was much less sensitive (5 ppm Tl). Solvents used for extraction of these complexes include dichloroethane,[120,121] butyl acetate[119] and benzene;[99] solvents such as acetone, ethanol and methanol have been found to enhance the fluorescence of the extracts when added either to the aqueous phase before extraction,[96] or to the extract itself.[99] However, a larger enhancement is observed in the latter case.

The effect of these enhancing solvents has been attributed to the solvating action of the organic solvent on the ternary complex.[96] Fluorescence reaches a maximum in 30–40% acetone medium[96,99] but at higher acetone concentrations the more thorough sol-

vation results in a partial breakdown of the complex, leading to a slight decrease in fluorescence intensity. The addition of acetone can also affect the precision and selectivity of fluorometric methods based on ternary complexes with acridinium dyes (or Safranin T); the improvement in selectivity is presumably due to decomposition of complexes of the dyes with interfering ions. Thus the amounts of thallium and gallium which may be tolerated in the determination of antimony with Safranin T are increased by factors of 10 and 23 respectively on addition of acetone up to a concentration of 30% in the benzene extract,[99] and the precision is also improved.

Considering that all the basic dyes discussed in this section are strongly coloured, it is not surprising that a spectrophotometric method was often developed simultaneously with the fluorometric method. As a general rule, however, the fluorometric method has proved more sensitive than the equivalent spectrophotometric method by at least a factor of two. This has enabled the same method to be used for a wide range of concentrations of analyte, with a spectrophotometric finish for higher concentrations and a fluorometric finish for lower concentrations; greater versatility of the analytical method was therefore achieved.

Cationic binary complexes

The availability of fluorescent anionic dyes of the fluorescein series has led to the possibility of fluorescent ion-association ternary complexes wherein the binary complex is cationic. Fluorescein dyes (often referred to as phthalein dyes) are very closely related in structure to the xanthene (rhodamine) dye series.

The quantum efficiency of fluorescence of the halogenated fluoresceins shows a marked decrease with increase in the degree of halogenation, and the halogens increase the fluorescence efficiency in the order $Cl > Br > I$.[148] This latter effect may be explained by the relative strengths of the nuclear fields of these ions, which promote increased triplet state degeneration of the singlet excited state of the molecule.[44] As a general rule, the degree of extraction of ternary complexes with fluorescein dyes decreases with decrease in halogenation and with decrease in the atomic number of the halogen substituent. Thus the dyes eosin (2′,4′,5′,7′-tetrabromofluorescein), erythrosin (2′,4′,5′,7′-tetraiodofluorescein) and Rose Bengal Extra (4,5,6,7-tetrachloro-2′,4′,5′,7′-tetraiodofluorescein) find most use in this work.

Cationic binary complexes may be formed by reaction of many metal ions with the ligands pyridine, 1,10-phenanthroline (phen), 2,2′-bipyridyl and substituted hydrazones such as pyridine-2-aldehyde-2-pyridylhydrazone (PAPHY).[149] These binary complexes form extractable ion-association complexes with fluorescein dyes and can be suitable for extraction–fluorometric analysis. Metals which form extractable complexes include silver,[16] cadmium,[40] zinc,[150] lead[44] and copper(I)[44,151] the reactions of which are in accordance with the "d^{10}" theory of fluorescence wherein complexes which use vacant d orbitals from the cation for bonding are non-fluorescent. Thus transition metal ions [with the exception of manganese(II) which has a relatively stable d^5 configuration] produce coloured non-fluorescent ternary complexes with phen and eosin. The weak fluorescence of the silver, cadmium and copper(I) complexes of phen and eosin may be considerably enhanced by addition of acetone to the chloroform extracts of these complexes; moreover, such an addition can also cause the coloured (but non-fluorescent) extracts obtained with iron(III), cobalt(II), nickel and copper(II) to become fluorescent.[41] Addition of acetone therefore improves sensitivity, but by producing fluorescent extracts for many metals otherwise suitable only for photometric analysis, considerably reduces the selectivity of these procedures. In spite of this, silver is particularly suited to determination in this way because of the possibility of masking most other metal ions with EDTA, this reagent having no effect on the reaction of silver with phen and eosin.[16]

In aqueous solution, the formation of a ternary complex with eosin usually results in quenching of the fluorescence of the dye, presumably because the ternary complex is only sparingly soluble. This fact has been utilized in a fluorescence-quenching procedure for silver in aqueous solution after reaction with phen and eosin; again, EDTA is employed as a general masking agent.[17] A recent development has been the use of PAPHY as the ligand in the cationic binary complex:[42] the ion-association ternary complex formed between eosin and a Co(II)–PAPHY complex was used for the fluorometric determination of cobalt after extraction of the ternary complex into an acetone–chloroform mixture.

Various solvents, including alcohols, ketones, esters, ethers, hydrocarbons, chlorinated hydrocarbons and aromatic hydrocarbons, have been examined for their efficiency in extracting the ternary complexes containing fluorescein dye derivatives.[16] In general, alcohols and ketones have been found to dissolve the dye itself, esters and ethers achieve slight extraction but cause the complexes to float at the interface, and extraction of the complex is only achieved with aromatic or chlorinated hydrocarbons, usually nitrobenzene or chloroform.

As indicated above, the addition of acetone to a chloroform extract of a metal–phen–eosin ternary complex increases the fluorescence, sometimes by as much as a factor of 100.[64] Acetone also has the advantage of preventing film formation at the aqueous–organic interface,[16] but can cause a decrease in reproducibility of the fluorescence of the extract.[40] The optimum concentration of acetone in the final extract usually lies in the range 30–45%,[40,42] and the enhancement is generally explained in terms of dissociation of the ternary complex caused by increasing the dielectric constant of the organic solvent.[44] In view of this explanation, it should prove beneficial

to encourage complete dissociation of the complex in the organic phase, perhaps by the use of a complexing agent to react with the metal ion involved. Such an approach has been successful for the Cu–phen–eosin[44] complex where addition of ammoniacal acetone produces a considerably larger fluorescence enhancement than that of acetone alone.

Alternative fluorescent species which can serve as the anionic counter-ion in a fluorescent ternary complex include the flavones quercetin (3,3′,4′,5,7-pentahydroxyflavone) and morin (3,5,7,2′,4′-pentahydroxyflavone), the azo dye sulphonaphtholazoresorcinol (SNAR), and lumogallion. The cationic component in these ternary complexes can be of the type metal–auxiliary complexing agent (ACA), where ACA can be oxalate,[85] fluoride,[84] tartrate[84] or hydrogen peroxide,[87] whilst the metal is typically niobium[87] or tantalum.[105] Alternatively, cationic complexes of antipyrine with gallium, indium or scandium may be used.[24,100] The ternary complexes formed between these complex cations and the fluorescent counter-ions mentioned above are only extractable if a neutral ion-association complex results; if this is not the case, addition of a further counter-ion such as perchlorate[100] or diphenylguanadinium ion[89] is necessary.

The fluorescence of these ternary complexes may be measured either in aqueous solution (since in this case the fluorescence is actually produced by the ternary complex as a whole) or in the organic extract. Addition of acetone, ethanol or methanol to the aqueous solution to give a final organic solvent concentration of 25–50% increases the fluorescence intensity.[86,87,89] Excess of organic solvent causes decomposition of the ternary complex and consequently decreases the fluorescence.[89]

As with the anionic binary complexes, the use of coloured dyes as the fluorescent counter-ion in the ternary complex has resulted in the development of many spectrophotometric methods of analysis. These, however, are generally less sensitive than the corresponding fluorometric procedures. For example, the fluorometric determination of copper(II) with Rose Bengal Extra and phen is ten times as sensitive as the spectrophotometric method,[44] while the sensitivities of determination of silver as Ag–phen–eosin by fluorescence-quenching[17] and extraction–fluorometric[23] procedures are 25 and 10 times, respectively, that of the extraction–photometric method.

CO-ORDINATION-UNSATURATED TERNARY COMPLEXES

Co-ordination-unsaturated ternary complexes do not suffer from the lack of selectivity often experienced with the ion-association type. This is generally attributed to reduction in the likelihood of unwanted side-reactions, because of the increased complexity in conditions required for two ligands to react. Improvement in precision is often observed[152] and this is thought to be due to suppression of hydrolysis and of polycondensation by formation of the ternary complex. It is noteworthy that high-valence elements such as niobium and tantalum appear very frequently in the co-ordination-unsaturated group of ternary complexes. The reason for this is the tendency of such elements to form polymeric hydroxo-complexes which must be suppressed by using an activator such as EDTA or tartaric acid.[89] Such activators are usually complexing agents and their presence encourages ternary complex formation.

The relationship between the number of ligand atoms in the complexant and the co-ordination number of the metal ion plays a special part in promoting ternary complex formation and improving the selectivity of such complexes. The reaction of niobium with catechol (*o*-dihydroxybenzene) and sexidentate α-aminopolycarboxylic acids gives ternary complexes whereas quadri- or octadentate α-aminopolycarboxylic acids give only binary complexes. Since Nb(V) has a co-ordination number of 8, reaction with the octadentate ligands completely fills the co-ordination sphere of the metal ion, thereby prohibiting ternary complex formation. In this same reaction, the interferences of iron(III) and titanium(IV) (which also react with catechol) are eliminated by addition of EDTA, which reacts with these metals, completely filling their co-ordination spheres (C.N. = 6) and preventing ternary complex formation.[153]

The complexes of niobium and tantalum with auxiliary complexing agents (oxalate, tartrate *etc.*) and quercetin, morin or SNAR which were discussed under "Ion-Association Ternary Complexes", might well have been classified as co-ordination-unsaturated ternary complexes. For example, during formation of the niobium complex with oxalate and SNAR,[89] the hydroxyl groups present in the co-ordination sphere of the binary Nb-ACA complex are replaced by SNAR; this suggests a co-ordination-unsaturated mechanism. However, since the binary complex is charged and a counter-ion is necessary for extraction, this complex may also be classified as ion-association.

Of the rare earth elements, only lanthanum, gadolinium, scandium, yttrium and lutetium are able to form fluorescent compounds, in which it is the organic part of the molecule which is responsible for the fluorescence.[82] The reason for this is that when complexed, these ions do not contain energy levels which could contribute to fluorescence quenching through radiationless decay.[77] Thus, scandium and lutetium form fluorescent ternary complexes with morin and antipyrine derivatives.[82,100] The remainder of the rare earth series, which cannot form fluorescent complexes of this type, can, however, exhibit a fluorescence which is characteristic of the metal ion itself.[154] This fluorescence takes the form of a line-like spectrum and may be considerably enhanced if the metal ion is complexed with certain organic ligands, since the metal ion is excited as the result of intramolecular energy transfer from the organic part of the molecule which has absorbed the light

energy. An example of this is the fluorometric determination of terbium as its binary complex with tiron (1,2-dihydroxybenzene-3,5-disulphonic acid).[155] Unfortunately, the fluorescence from such a complex is subject to quenching caused by collision with solvent molecules, resulting in reduction in sensitivity of methods based on this type of complex. This adverse effect may be minimized, and the fluorescence consequently enhanced, by reaction of the binary complex with a further reagent (called a "synergic reagent") which fills the co-ordination sphere of the metal ion and therefore excludes close contact of solvent molecules.[156] The synergic reagent should be a poor energy-acceptor and ideally should possess a lone oxygen atom available for co-ordination to the metal ion, combined with a bulky saturated hydrocarbon tail directed away from the metal ion. In this way, an "insulating sheath" is established around the metal ion. Reagents which can serve as synergic agents include trialkyl Group V oxides [such as trioctylphosphine oxide (TOPO)], trifluoroacetylacetone, tributyl phosphate and dihexylsulphoxide. Fluorescent ternary complexes of rare earth ions are typified by the reaction of samarium and europium with 2-naphthoyltrifluoroacetone and TOPO,[47] and of europium, samarium and terbium with hexafluoroacetylacetone and TOPO.[48] Interferences can be eliminated by the use of EDTA as a general masking agent and this reagent has also been used both for masking and for inclusion in the complex for the determination of terbium.[112,113] Interference, however, is not always a difficult problem in the fluorometric determination of rare earths by use of these ternary complexes, since the line-like spectra reduce overlap of the emission from other rare earth ions and separate identification and determination of each species is possible.

CONCLUSIONS

Despite the increased use of fluorescent ternary complexes, it is evident that there exist many further unexamined possibilities for such complexes. The development of new fluorescent dyes and new techniques, particularly that using exchange of the associated dye cation, has opened the way for reinvestigation of existing spectrophotometric methods, with a view to applying them to fluorescence analysis.

A notable feature which arises from consideration of the literature is the large number of extraction–fluorometric procedures which have used addition of acetone to enhance the fluorescence of an extracted ternary complex. Wider application of acetone and other enhancing solvents, together with use of suitable solvent mixtures for extraction of ternary complexes, could lead to significant improvements in the sensitivity, selectivity and precision of extraction fluorometric procedures. This would increase the advantages of such procedures over the corresponding spectrophotometric methods.

The use of synergic agents has made possible the sensitive fluorometric determination of rare earth ions as ternary complexes. Further development of this aspect, for example by using a synergic agent with a chromophore, could lead to increases in sensitivity.

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SELEKTIVITÄTSSTEIGERUNG KATALYTISCHER BESTIMMUNGSVERFAHREN—EXTRAKTIONSKATALYMETRISCHE MOLYBDÄNBESTIMMUNG

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Zusammenfassung—Zur Erhöhung der Selektivität katalytischer Analysenverfahren wird eine Kombination von Solvent-Extraktion und katalytischer Bestimmung vorgeschlagen. Anhand der katalytischen Mo-Bestimmung mittels der 1-Naphthylamin–Bromat-Reaktion kann gezeigt werden, daß bei Auswahl eines geeigneten Extraktionssystems der Katalysator direkt im organischen Extrakt bestimmbar ist. Nach Testen verschiedener Molybdänkomplexe hinsichtlich ihrer katalytischen Aktivität in der Indikatorreaktion wurde die Extraktion von Molybdän als Oxinat für eine analytische Anwendung gewählt. Die Methode gestattet, Molybdän bis zu einer Grenzkonzentration von $2{,}7 \times 10^{-9} M$ bei einem mittleren relativen Fehler von 10% zu bestimmen. Die Mo-Bestimmung wird von Konzentrationen des Vanadiums bis zu $10^{-4} M$, von Chrom bis zu $2 \times 10^{-4} M$, von Wolfram bis $5 \times 10^{-5} M$ und von Mn, Ni, Cu, Co, Fe, Mg, Zn, Cd, Al und Pb jeweils bis zu $10^{-2} M$ nicht gestört. Mit dem extraktionskatalymetrischen Verfahren wurde Molybdän in Meerwasser bestimmt.

Molybdän macht als Spurenelement, insbesondere als essentieller Bestandteil von Enzymen,[1] zunehmend auf sich aufmerksam. Der Gehalt an Molybdän in der Biosphäre liegt bei einigen ppm, und das Interesse an nachweisstarken, spezifischen Bestimmungsverfahren für dieses Element ist groß. Das Nachweisvermögen photometrischer oder atomspektroskopischer Analysenmethoden genügt aber oftmals nicht, um Molybdän im ppm-Bereich ohne Anreicherung bestimmen zu können.

Nachweisstärker sind katalytische Bestimmungsmethoden.[2] Ihre praktische Anwendung wird allerdings durch eine ungenügende Spezifität, insbesondere gegenüber den chemisch verwandten Elementen Wolfram und Vanadium begrenzt. In der Praxis macht sich eine Abtrennung des Molybdäns von den störenden Elementen erforderlich. Wir untersuchten deshalb die Möglichkeiten einer extraktiven Abtrennung des Molybdäns von störenden Begleitionen mit nachfolgender katalytischer Bestimmung des separierten Molybdäns direkt im organischen Extrakt (siehe dazu auch Zitat[22]).

Als Indikatorreaktion zur katalytischen Molybdänbestimmung wurde die von Yatsimirskii und Filippov[3] untersuchte Redoxreaktion zwischen 1-Naphthylamin (1-Naph) und Bromat ausgewählt. Diese Reaktion ist nicht sehr spezifisch, besonders V, W und Cr katalysieren sie im vergleichbaren Ausmaß. Molybdän wurde deshalb als Neutralchelat extrahiert und dann direkt im organischen Extrakt bestimmt. Voraussetzung dafür ist allerdings, daß der extrahierte Molybdänkomplex katalytisch aktiv ist. Ausgehend von komplexkatalytischen Wirkungen des Molybdäns in Enzymreaktionen[4] untersuchten wir die katalytische Wirkung verschiedener Molybdänkomplexe auf die Indikatorreaktion, um den geeignetsten Komplex und damit das günstigste Extraktionsverfahren auswählen zu können. Mit der ausgearbeiteten extraktionskatalymetrischen Methode wurde Molybdän im Meerwasser bestimmt.

EXPERIMENTELLER TEIL

Geräte

Zur Registrierung der Extinktions–Zeit-Kurven verwendeten wir das Spektralphotometer Spekol in Verbindung mit dem Extinktionsmeßansatz EK 5 Aut und einem Standardkompensationsschreiber GlBl (alle vom VEB Carl Zeiss Jena, DDR) (Aufbau siehe Zitat[5]).

Der Meßansatz EF 5 Aut ermöglicht einen automatischen Küvettenwechsel in einem wählbaren Zyklus (in unseren Versuchen aller 15 s). Der Extinktionsmeßansatz ist thermostatierbar und kann gleichzeitig 4 Küvetten der Schichtdicke 0,1 bis 5 cm aufnehmen. Die Lampenspannung für das Spektralphotometer wurde durch einen Wechselspannungsregler Statron 220/0,45 (PGH Statron Fürstenwalde, DDR) stabilisiert. Zur Thermostatierung der Reagenzien bzw. des Meßansatzes verwendeten wir einen Ultrathermostaten U 10. Die Reaktanten wurden in vierschenkligen Glasgefäßen mit Schliffstopfen thermostatiert und gemischt.

Reagenzien

Alle nicht gesondert angeführten Reagenzien waren vom Reinheitsgrad "p.A." oder "reinst". Es wurde bidestilliertes Wasser verwendet.

Die Mo(VI)-Stammlösung wurde durch Einwägen von $Na_2MoO_4 \cdot 2H_2O$ (Chemapol, Prag) und entsprechender Verdünnung erhalten. $NaBrO_3$ erhielten wir durch doppelte Umsetzung wäßriger Lösungen von $NaClO_4$ mit $KBrO_3$.

Die Darstellung der untersuchten Molybdänkomplexe erfolgte nach bekannten Arbeitsvorschriften $MoO_2(Oxin)_2$,[6] $MoO_2(Thioxin)_2$,[7] $MoO_2(DÄDTC)_2$,[8] $(NH_4)_2MoS_4$,[9] und Komplexe mit 1,2-Dithiolat-Liganden $[MoOS_4C_4(CN)_4][N(C_2H_4)_4]_2$,[10] $[MoS_6C_6(C_6H_5)_6][As(C_6H_5)_4]_2$,[11] $[MoS_6C_6(CN)_6][N(C_4H_9)_4]_2$,[12] $[MoS_6C_6(C_6H_5)_6]$[13] (siehe dazu Zitat[14]). Alle Komplexe

wurden durch Elementaranalysen und Schmelzpunkte charakterisiert.

Katalytische Bestimmung

Als Lösungsmittel für die Komplexe bzw. als Extraktionssolvens diente Chloroform. Zur Messung der katalytischen Aktivitäten wurden die in Chloroform gelösten Komplexe bzw. der Chloroformextrakt in eine wäßrig-alkoholische Lösung gebracht. Die Einstellung des günstigsten pH-Wertes erfolgte durch Säurezusatz. Da die Löslichkeit des Oxydationsmittels Kaliumbromat in der organisch-wäßrigen Reaktionsmischung begrenzt ist, verwendeten wir Natriumbromat bei Volumenanteilen der organischen Lösungsmittel über 50%.

Durchführung. Die Ausgangslösungen wurden in zwei verschiedenen Mischungsverhältnissen in ein vierschenkliges Reaktionsgefäß gegeben.

Reaktionsmischung I. (Konzentrationen siehe Tabelle 1), 4.5 ml alkoholische 1-Naph-Lösung, 6 ml wäßrige Lösung, die $KBrO_3$, H_2SO_4 und Na_2MoO_4 enthält, und 0,4 ml $CHCl_3$ mit gelöstem Mo-Komplex bzw. Extrakt der Solvent-Extraktion.

Reaktionsmischung II. (Konzentrationen siehe Tabelle 5), 5 ml alkoholische 1-Naph-Lösung, 4 ml wäßrige Lösung die $NaBrO_3$ und H_2SO_4 enthält, und 1 ml Extrakt der Solvent-Extraktion.

Die Reaktionsgefäße thermostatiert man 10 min bei 25°. Neben der Blindprobe (I) werden gleichzeitig 3 weitere Proben (II–IV) mit Katalysator angesetzt. Zum Zeitpunkt $t = 0$ wird die Blindprobe gestartet und nach jeweils 15 s die weiteren Proben (II–IV). Die Messung erfolgt in 5-cm Küvetten bei einer Wellenlänge von 530 nm und einer Temperatur von 25°. Die Registrierung beginnt nach 3 Minuten durch Einschalten des Papiertransportes und der Antriebswelle für den Küvettenwechsel und wird nach 20 Minuten beendet.

Die analytische Auswertung erfolgt nach einer Zweipunktmethode, d.h. nach dem Starten der Reaktion wird bei 2 Zeiten t_1 und t_2 die Extinktionsänderung der Gesamtreaktion $(\Delta E_{t_2-t_1})_{ges}$ und die der Blindreaktion $(\Delta E_{t_2-t_1})_0$ gemessen. Die Extinktionsdifferenz zwischen beiden Reaktionen entspricht der der katalysierten Reaktion und hängt linear von der Molybdänkonzentration ab.

$$\Delta E_{t_2-t_1} = (\Delta E_{t_2-t_1})_{ges} - (\Delta E_{t_2-t_1})_0 \propto [Mo]$$

Die Verfolgung der Indikatorreaktion über einen längeren Zeitraum ($t_2 - t_1 > 17$ min) bedingt auf Grund der relativ hohen Geschwindigkeit der Blindreaktion[15] Messungen bei Extinktionswerten über 1. Um hohe Extinktionswerte zu vermeiden, glichen wir bei der simultanen Vermessung von 3 Proben die Extinktionen zum Zeitpunkt t_1 auf die Blindreaktion (Probe I) ab.

Extraktionsverfahren

Zehn Volumenteile wäßrige Phase, die 0,06*M* an H_2SO_4 ist und neben Molybdän ($1–50 \times 10^{-8}M$) als Maskierungsreagenzien ÄDTA ($6 \times 10^{-3}M$ bzw. bei der Bestimmung im Meerwasser $2 \times 10^{-3}M$) und NaF ($2,5 \times 10^{-2}M$) enthält, werden mit 1 Volumenteil 0,1*M* Oxin in $CHCl_3$ 2 min geschüttelt. Anschließend wird die wäßrige Phase durch Zugabe weiterer Schwefelsäure auf 0,33*M* Säurekonzentration eingestellt und nochmals geschüttelt, um die Konzentration von überschüssigem Oxin in der Chloroform-Phase zu verringern. Die organische Phase wird abgetrennt und 0,4 ml davon in die Reaktionsmischung I bzw. 1 ml in die Reaktionsmischung II (bei der Meerwasseruntersuchung) gebracht. Die nachfolgende katalytische Bestimmung erfolgt wie beschrieben.

Zur Bestimmung von Molybdän im Meerwasser wurde die in Behältern aus Polyäthylen aufbewahrte Probe mit Schwefelsäure auf pH 1 gebracht, durch eine Fritte (Porenweite 8 μm) filtriert und 16 ml bzw. ein Vielfaches davon in Gegenwart von ÄDTA, NaF und H_2SO_4 (Konzentrationen wie oben beschrieben) auf 20 ml aufgefüllt. Danach wurde das Molybdän wie oben angegeben extrahiert. Als Blindprobe verwendeten wir eine Meerwasserprobe, aus der das Molybdän durch Extraktion entfernt worden war.

ERGEBNISSE UND DISKUSSION

Die Geschwindigkeit der katalytischen Reaktion hängt stark vom pH-Wert der Reaktionsmischung ab.[15] Die im Reaktionsgemisch Chloroform–Alkohol–Wasser aufgenommene Abhängigkeit der Geschwindigkeit der katalytischen Reaktion von der Wasserstoffionenkonzentration (Abb. 1) hat einen ähnlichen Verlauf wie die Reaktion in einer wäßrig–alkoholischen Reaktionsmischung.[15] Durch Variation der Säurekonzentration oder der Bromatkonzentration, von der die Reaktionsmischung nach erster Ordnung abhängt,[15] kann die gleiche Empfindlichkeit erreicht werden, wie sie in Abwesenheit von Chloroform gemessen wird. Wir arbeiteten deshalb bei $-\log[H^+]$-Werten zwischen 1,4 und 1,75.

Katalytische Aktivitäten von Molybdänkomplexen

Um das optimale Extraktionsreagens zu finden, ermittelten wir die katalytische Aktivität verschiedener Molybdänkomplexe. Dazu wurden die in Substanz isolierten Komplexe in Chloroform (Wasser bzw. Aceton) gelöst und in die Reaktionsmischung mit jeweils gleicher molarer Konzentration eingesetzt. Die so ermittelten katalytischen Aktivitäten wurden auf die unter gleichen Bedingungen ermittelte Aktivität von MoO_4^{2-} bezogen (siehe Tabelle 1).

Die Auswertung der Reaktion erfolgte zwischen der 7. und 17. Minute. Dem Molybdat katalytisch ähnlich verhalten sich die Komplexe 2–6 (Tabelle 1). Sie kommen für eine extraktive Abtrennung des Molybdäns in Frage.

Erste Untersuchungen über den Reaktionsmechanismus weisen darauf hin, daß alle katalytisch aktiven Molybdänkomplexe unter den angegebenen Reaktionsbedingungen zerstört werden und daß die katalytische Wirkung auf dem dabei entstehenden

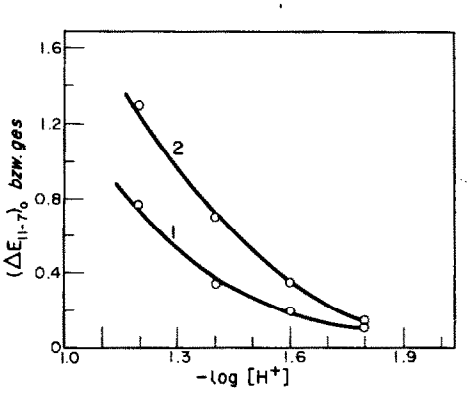

Abb. 1. Abhängigkeit der katalytischen Reaktion von der Säurekonzentration in organisch-wäßrigem Milieu. $1,2 \times 10^{-2}M$ 1-Naphthylamin; $0.07M$ $NaBrO_3$; $2,4 \times 10^{-7}M$ Mo(VI); (1)—Blindreaktion; (2)—Reaktion in Anwesenheit von Mo(VI).

Tabelle 1. Relative katalytische Aktivitäten von Molybdänkomplexen bei der Oxydation von 1-Naphthylamin durch Bromat

Nr.	Komplex	Relative katalytische Aktivität in% bezogen auf die MoO_4^{2-}-Aktivität (mittlere Schwankung in %)	
1	MoO_4^{2-}†	100	(±2,9)
2	$MoO_2(Oxin)_2$	100	(±5,2)
3	$MoO_2(Thioxin)_2$	89,3	(±4,8)
4	$MoO_2(DÄDTC)_2$	89,5	(±4,8)
5	$[MoOS_4C_4(CN)_4][N(C_2H_5)_4]_2$*	97,0	(±3,3)
6	$(NH_4)_2MoS_4$†	95,6	(±3,4)
7	$[MoS_6C_6Ph_6][AsPh_4]_2$	54,0	(±1,5)
8	$[MoS_6C_6(CN)_6][NBu_4]_2$	23,0	(±3,2)
9	$MoS_6C_6Ph_6$	0,0	(±1,2)

Ph = Phenyl, Bu = Butyl, *in Aceton–$CHCl_3$ gelöst, †in Wasser gelöst.
Reaktionsbedingungen: $1{,}2 \times 10^{-2}M$ 1-Naphthylamin; $6{,}2 \times 10^{-2}M$ $KBrO_3$; $-\log [H^+] = 1{,}75$; $2 \times 10^{-7}M$ MoO_4^{2-} bzw. Komplex; 3,67 Vol% $CHCl_3$; 41,3 Vol% Alkohol.

MoO_4^{2-} beruht. Die Arbeiten darüber werden fortgesetzt.

Katalytische Bestimmung von Molybdän nach Extraktion als Oxinat

Wir wählten für eine analytische Anwendung die gut untersuchte Extraktion von Molybdän mit Oxin in Chloroform.[16] Mitextrahiertes Oxin gelangt bei der angegebenen Arbeitsweise in die Reaktionsmischung und inhibiert bei Konzentrationen über $10^{-3}M$ die molybdänkatalysierte Reaktion. Wir verringerten deshalb seine Konzentration durch einen Reextraktionsschritt bei 0,33M Schwefelsäure auf ein Zehntel. Das Molybdänoxinat verbleibt dabei neben einer geringen Menge an freiem Oxin, die die katalytische Reaktion nicht mehr beeinflußt, vollständig in der organischen Phase.

Ein anderes Problem ergibt sich durch die begrenzte Mischbarkeit des Extraktionssolvens mit der Reaktionsmischung. Chloroform löst sich in der Reaktionsmischung (wäßrig-alkoholische Lösung) nur zu etwa 10%.[17] Um gegenüber einer katalytischen Bestimmung ohne Extraktion die gleiche absolut bestimmbare Molybdänmenge zu ermöglichen, reicherten wir Molybdän bei der Extraktion um den Faktor 10 durch entsprechende Volumenverhältnisse der Phasen an.

Als Eichkurve ergab sich $\Delta E_{17-9} = 0{,}062 \times 10^8$ [Mo] + 0,018 (mit [Mo] in M) bei folgenden Bedingungen: $1{,}2 \times 10^{-2}M$ 1-Naphthylamin; $7 \times 10^{-2}M$ Kaliumbromat; $-\log [H^+] = 1{,}43$; 3,67 Vol% Chloroform und 41,3 Vol% Alkohol. Die Reproduzierbarkeit des Verfahrens testeten wir bei einer Molybdänkonzentration von $5 \times 10^{-9}M$. Gefunden wurde ein Mittelwert von $5{,}05 \pm 0{,}53 \times 10^{-9}M$. Die Standardabweichung betrug 10,5% für $n = 11$. Als Standardabweichung für Blindwert erhielten wir aus 8 Bestimmungen 0,010 Extinktionseinheiten. Daraus wurde für die angegebenen Bedingungen für eine Doppelbestimmung eine Grenzkonzentration[18] von $2{,}7 \times 10^{-9}M$ berechnet.

Vergleicht man das hier angegebene Verfahren mit der katalytischen Bestimmung von Molybdän ohne vorherige Extraktion (in reinen Lösungen), dann haben sich durch die zusätzliche Abtrennung hinsichtlich der katalytischen Bestimmung keine nachteiligen Veränderungen ergeben: der zeitliche Aufwand ist durch den Extraktionsschritt um ein geringes gestiegen, die Grenzkonzentrationen und Reproduzierbarkeiten sind bei beiden Methoden gleich, die absolut bestimmbare Molybdänmenge ist der ohne vorherige Extraktion vergleichbar. Inwieweit die Spezifität der katalymetrischen Molybdänbestimmung erhöht werden konnte, zeigt der Fremdioneneinfluß auf die Bestimmung.

Fremdioneneinfluß

Ziel unserer Untersuchungen war es, die Spezifität des katalytischen Bestimmungsverfahrens durch Vorschalten eines Extraktionsschrittes zu erhöhen. Die Spezifität der katalytischen Reaktion ist dabei vorgegeben. Die katalytische Reaktion stören insbesondere die dem Molybdän verwandten Elemente Wolfram und Vanadium.[3] Der Extraktionsschritt sollte daher vor allem zur Abtrennung des Molybdäns von W(VI) und V(V) dienen.

Wolfram stört durch ausfallende Polywolframsäure, die Molybdän mitreißt. Durch Zusatz von Fluorid wurde diese störende Fällung verhindert. Gegenüber Vanadium ist die Molybdän-Extraktion ohne Einsatz von Maskierungsmitteln nicht spezifisch und es ist deshalb eine Beeinflußung der Indikatorreaktion durch mitextrahiertes Vanadium zu erwarten. Bei Anwesenheit von ÄDTA wird die Mitextraktion von Vanadium stark verringert, und bei der anschließenden Reextraktion des Oxins mit Schwefelsäure wird mitextrahiertes Vanadium weiter abgereichert, da das Vanadiumoxinat im Gegensatz zum Molybdänoxinat gegenüber 0,33M Schwefelsäure nicht stabil ist.

Der Einfluß von Fremdionen auf die extraktionskatalymetrische Molybdänbestimmung ist in Tabelle 2 angeführt. Angegeben sind die Konzentrationen, die

Tabelle 2. Einfluß von Fremdionen auf die extraktionskataly metrische Molybdänbestimmung, [Mo] = $2 \times 10^{-7} M$

Fremdion	Konz. in Probe, M	[Mo] gefunden, $10^{-7} M$
ohne		2,0 ± 0,16
Mn(II)	10^{-2}	2,16
Ni(II)	10^{-2}	2,07
Cu(II)	10^{-2}	2,13
Co(II)	10^{-2}	1,84
Fe(III)	10^{-2}	2,11
Mg(II)	10^{-2}	2,12
Zn(II)	10^{-2}	2,12
Cd(II)	10^{-2}	2,12
Al(III)	10^{-2}	2,09
Pb(II)*	10^{-2}	2,04
Hg(II)	6×10^{-3}	1,97
Fe(II)	5×10^{-3}	1,98
Cr(VI)	2×10^{-4}	2,06
V(V)	10^{-4}	2,02
Ce(IV)	5×10^{-5}	1,95
W(VI)	5×10^{-5}	2,08

$1{,}2 \times 10^{-2} M$ 1-Naphthylamin; $7 \times 10^{-2} M$ $KBrO_3$, $-\log[H^+] = 1{,}75$; 3,67 Vol% $CHCl_3$; 41,3 Vol% Alkohol
Die Störionen wurden in Form der Sulfate eingesetzt, Wolfram als $Na_2WO_4 2H_2O$; Vanadium als NH_4VO_3, Blei als $Pb(NO_3)_2$.
* aus HNO_3 in Abwesenheit von F^- extrahiert.

die Bestimmung gerade noch nicht stören. Höhere Konzentrationen beeinflussen den Meßwert und stören so die Bestimmung.

Den Einfluß von Cadmium, Magnesium und Zink bestimmten wir im Gemisch. Gleichfalls als Summe wurde der Einfluß eines Gemisches aus Ni(II), Cu(II), Fe(III), V(V), W(VI) und Cr(VI) mit einer Gesamtkonzentration von $3 \times 10^{-3} M$ auf die Bestimmung von $2 \times 10^{-7} M$ Molybdän getestet. Gefunden wurde $(2{,}01 \pm 0.01) \times 10^{-7} M$ Molybdän.

Durch Extraktion von Molybdän vor seiner katalytischen Bestimmung konnte die Spezifität des Verfahrens gegenüber einer katalytischen Bestimmung ohne Vorschalten eines Trennschrittes erhöht werden. Während Molybdän in Gegenwart von Vanadium ohne Extraktion nur bei Konzentrationen kleiner als $10^{-8} M$ Vanadium bestimmt werden konnte,[3] ist extraktionskatalymetrisch eine Bestimmung in Gegenwart von bis zu $10^{-4} M$ Vanadium möglich. Die Spezifität der Bestimmung ist in Bezug auf Vanadium um *ca.* das 10^4-fache gestiegen. Molybdän kann somit in Pflanzen[19] oder im Meerwasser, das Vanadium in einem Konzentrationsbereich von (0,5–5) × $10^{-8} M$ enthält,[20] bestimmt werden. Ebenfalls erhöht werden konnte die Selektivität der Molybdänbestimmung gegenüber W(VI) und Cr(VI). Vorteilhaft ist auch die Tatsache, daß Molybdän in Anwesenheit einer Vielzahl von Elementen von hohen Konzentrationen (untersucht bis $10^{-2} M$) extraktionskatalymetrisch bestimmt werden kann und sich das Verfahren daher zur Bestimmung von Molybdän in hochreinen Metallen, Salzen u. a. eignen sollte. Die Methode wurde anhand der Molybdänbestimmung im Meerwasser getestet.

Molybdänbestimmung im Meerwasser

Zur Bestimmung von Molybdän im Meerwasser werden gewöhnlich spektralphotometrische bzw. atomspektroskopische Analysenmethoden verwendet. Die Bestimmungen sind allerdings nicht empfindlich genug, um Molybdän ohne Anreicherung erfassen zu können.[20]

Empfindlicher sind katalytische Molybdänbestimmungen. Hierbei ist keine Anreicherung des Molybdäns erforderlich. Die Spezifität solcher Verfahren genügt allerdings nicht, Molybdän im Meerwasser ohne Abtrennung zu bestimmen. Kuroda und Tarui[21] verwendeten zur Abtrennung von Molybdän vor seiner katalytischen Bestimmung ein Ionenaustauschverfahren, das eine beträchtliche Probenmenge (300 ml pro Analyse) und einigen zeitlichen Aufwand erfordert. Die von uns verwendete Extraktionstechnik

Tabelle 3. Molybdänbestimmung im Meerwasser*

[Mo], $10^{-8} M$ zugesetzt	[Mo], $10^{-8} M$ gefunden	[Mo]Meerw., $\mu g/l$ berechnet	[Mo], $10^{-8} M$ zugesetzt	[Mo], $10^{-8} M$ gefunden	[Mo]Meerw., $\mu g/l$ berechnet
0	3,27	4,48	0	3,74	5,13
0	3,11	4,26	0	3,54	4,86
0	3,75	5,14	0	3,54	4,86
0	3,90	5,34	0	2,92	4,00
0	3,62	4,91	2	5,80	5,21
2	5,65	5,01	2	5,11	4,27
2	5,84	5,23	4	7,37	4,62
4	7,08	4,22	4	8,06	5,57
4	7,94	5,40	6	9,70	5,08
6	8,82	3,86	6	10,20	5,76
6	10,57	6,26	8	11,35	4,60
6	9,62	4,96	8	11,55	4,87
8	12,57	6,26			
8	10,89	3,96			
		$\overline{[Mo] = 4{,}94}$			$\overline{[Mo] = 4{,}90}$
		$\pm s\overline{Mo} = 0{,}40$			$\pm s\overline{Mo} = 0{,}50$

* westliche Ostsee, der ufernahen Zone bei Zingst, DDR, entnommen. $1{,}2 \times 10^{-2} M$ 1-Naphthylamin; $2 \times 10^{-2} M$ $NaBrO_3$; $-\log [H^+] = 1{,}4$; 10 Vol% $CHCl_3$; 50 Vol% Alkohol.

kommt mit kleinen Probevolumina (15 ml) aus. Das Verfahren ist einfach und schnell durchführbar. Die Ergebnisse einer Molybdänbestimmung in zwei Meerwasserproben der westlichen Ostsee mit der Zusatzmethode[2] sind in Tabelle 3 angeführt.

Sie stimmten mit Literaturwerten[20,21] über den Molybdängehalt im Meerwasser überein. Die Reproduzierbarkeit des Verfahrens ist mit anderen Molybdänbestimmungsmethoden im Meerwasser vergleichbar.

Anerkennungen—Herrn Dr. W. Dietzsch (Sektion Chemie der Karl-Marx-Universität Leipzig, DDR) danken wir für die Überlassung der Mo-1,2-Dithiolat-Chelate, Herrn Doz. Dr. P. Hupfer (Sektion Physik der Karl-Marx-Universität Leipzig, DDR) für die Bereitstellung der Wasserproben.

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Summary—To increase the selectivity of catalytic methods, a solvent extraction and catalytic determination have been combined. By means of the determination of molybdenum based on the catalytic oxidation of 1-naphthylamine by bromate, it is shown that by selection of a suitable extraction system the catalyst can be determined directly in the organic extract. The catalytic activity of different complexes of molybdenum was tested and for an analytical application the extraction of molybdenum as oxinate was chosen. The method enables molybdenum to be determined down to $2.7 \times 10^{-9} M$. The relative error of the determinations is 10%. $10^{-4} M$ V, $2 \times 10^{-4} M$ Cr, $5 \times 10^{-5} M$ W and $10^{-2} M$ Mn, Ni, Cu, Co, Fe, Mg, Zn, Cd, Al and Pb cause no interference. The method has been used for the determination of molybdenum in sea-water.

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A MODIFIED OXIDATIVE MICROCOULOMETRIC METHOD FOR DETERMINATION OF SULPHUR IN HYDROCARBONS CONTAINING LARGE AMOUNTS OF CHLORINE

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Summary—The oxidative coulometric method for trace sulphur determinations has been modified and a procedure is described which includes the elimination of the interferences caused by chlorine whilst retaining a high recovery of sulphur. The liquid hydrocarbon sample is combusted in an excess of oxygen at 1000 K followed by dilution with a proper flow of carbon monoxide at 1300 K. In this way the partial pressure of oxygen is kept small and the interfering chlorine compounds are effectively converted into hydrogen chloride which does not interfere with the coulometric titration. A recovery of sulphur of 96 ± 1% was found for thiophene in mixtures of chlorobenzene (0–10%) and cyclohexane, thus indicating the absence of significant interference.

During the last years microcoulometry has become widely accepted as the most convenient technique for the determination of sulphur in petroleum products.[1] A review of the most important methods for determining sulphur will be found in the three volumes by Karchmer.[2] The flame photometric method[3] seems to be unsuitable for the determination of total sulphur because it gives different responses for different sulphur species.

There are two types of microcoulometric method, namely the oxidative and the reductive. Comparisons between the methods have been reported.[4,5] According to these reports it seems to be difficult to recommend one of the methods without knowing the type of sample to be analysed. The oxidative method is known to be easier to perform and there is little interference from nitrogen but it suffers from severe interference from chlorine.[4] The main drawback concerned with the reductive method seems to be the interference from nitrogen.[4]

The work presented in this paper deals with an experimental study of the interference from chlorine in the oxidative method. In a recent paper[6] the author studied the combustion step theoretically by calculations of the high-temperature equilibria. The aim of these calculations was to find conditions for a high recovery of sulphur with no formation of interfering chlorine compounds. It was shown that these requirements can be met by addition of carbon monoxide to the combustion gas mixture at 1300 K. Moreover, it was found that the amount of carbon monoxide should be kept as small as possible in order to avoid the formation of COS but large enough to prevent the formation of interfering chlorine compounds. Some additional calculations have been performed in this work in order to make it easier to compare the theoretical and experimental results.

EXPERIMENTAL

A block diagram of the experimental arrangement is shown in Fig. 1. The ovens were provided with thermoelements coupled to electronic temperature regulators. The gases were taken from high-pressure cylinders *via* reduction valves, needle valves and rotameters. The gas flows were calibrated by use of a soap-bubble meter. Silica gel was used to purify the gases. The injection system consisted

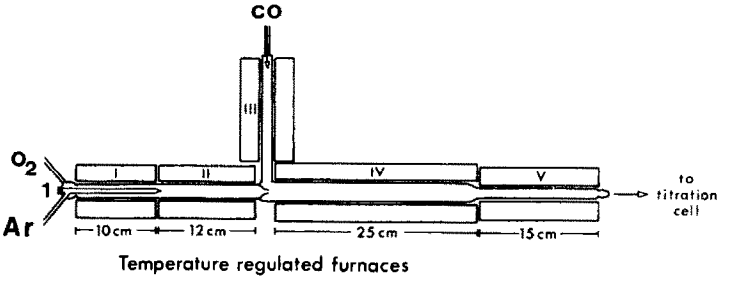

Fig. 1. Experimental arrangement. (1) Motor-driven 10-μl Hamilton syringe, (I–V) temperature-regulated furnaces at 300–1400 K. The diameters of the quartz tube in zones II and IV were 1.4 and 1.8 cm respectively.

of a motor-driven 10-μl Hamilton 701 N syringe. The variation of speed of sample delivery was about 1% at a rate of 0.1 μl/sec. The sample is vaporized in oven No. I at 650 ± 100 K followed by combustion at 1000 K in oven No. II. The oven No. III is used to preheat the carbon monoxide before entering the equilibrium zone IV which is held at 1300 K. The gas is then cooled somewhat in the zone V before entering the titration vessel. This cooling results in a slightly better stability of the titration system, as also reported by Killer.[1]

The coulometric cell consisted of three chambers, one for the platinum auxiliary electrode, one for the generating platinum anode and the platinum indicating electrode, and one for the radiometer K 401 calomel electrode. Electrolytic contacts between the chambers were made by means of asbestos-filled liquid junctions. The sample compartment was provided with a gas-inlet tube and a magnetically driven stirrer bar. The electrodes were connected to an LKB 16300 Coulometric Analyzer the function of which has been described before.[7]

The titration medium contained 0.40% potassium iodide and 0.68% acetic acid. In some experiments 0.055% of sodium azide was added.

The coulometric system measures the sum of sulphur dioxide and hydrogen sulphide, both of which consume two equivalents of iodine. It has been shown by Avdeeva[8] that there is no reaction between carbonyl sulphide and iodine in the titration medium.

Hydrogen sulphide was determined in separate experiments by coulometric titration with silver ions in 0.1*M* sodium acetate at pH 11. One ng of sulphur could be determined with a standard deviation of 0.2 ng.

GENERAL

Calculation of high temperature equilibria

The calculations of the high-temperature equilibria reported in this paper were performed in the same way as recently described by the author.[6] The input amounts of the elements used for the equilibrium calculations corresponded to the rate of sample injection and to the flow-rates of oxygen, argon and carbon monoxide (see Fig. 1). The total pressure was supposed to be 1 atm. The following gases were earlier[6] found to be the main combustion products: CO(g), CO_2(g) COS(g), H_2S(g), HCl(g), HClO(g), ClO(g), Cl_2(g), Cl(g), H_2O(g), SO_2(g), SO_3(g), H_2(g), O_2(g) and Ar(g).

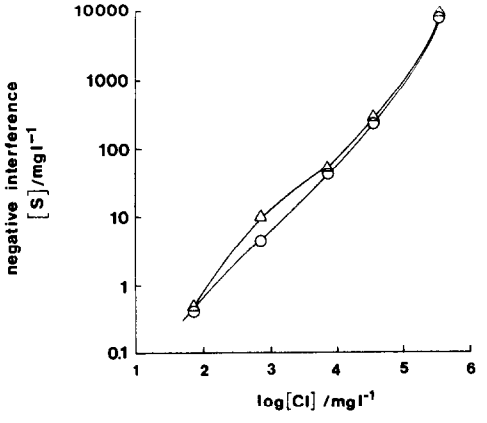

Fig. 2. The extent of negative interference on the sulphur determination caused by various concentrations of chlorine in the sample. (○) Theoretical results obtained at 1300 K for equal flows of oxygen and argon (85 ml/min); a 0.1-μl/sec injection rate of a sample containing thiophene and various concentrations of chlorobenzene in cyclohexane was used for the calculations. (△) Experimental results (zone IV at 1300 K).

Interference from chlorine

Interference from chlorine in the oxidative microcoulometric sulphur method is negative because compounds such as Cl(g), Cl_2(g) and HClO(g) oxidize the iodide present in the titration medium to iodine. The iodine reacts with sulphur dioxide without being measured coulometrically, according to the reaction:

$$SO_2 + 2H_2O + I_3^- \rightarrow SO_4^{2-} + 3I^- + 4H^+$$

Since Cl(g) $\equiv \frac{1}{2} I^-_{3(aq)}$, Cl_2(g) $\equiv I^-_{3(aq)}$ and HClO(g) $\equiv I^-_{3(aq)}$ the theoretical error caused by the interfering chlorine-containing combustion products Cl(g), Cl_2(g) and HClO(g) could be calculated.

RESULTS AND DISCUSSION

Interference from chlorine in a normal oxidative sulphur method

The extent of interference from chlorine in the sample was first studied for the normal oxidative procedure, *i.e.*, no addition of carbon monoxide was made. The experimental and calculated values are compared in Fig. 2. The flows of argon and oxygen were both 85 ml/min, which could be considered to be representative values for the oxidative procedure, and the temperatures of the zones were as follows (see Fig. 1): I 650 K, II 1000 K, III 1300 K, IV 1300 K and V 800 K. The calculations represented in Fig. 2 correspond to 1300 K, so the equilibrium is considered to be frozen in the outlet zone V. The samples consisted of various combinations of chlorobenzene, thiophene and cyclohexane. The points in Fig. 2 showing the experimental results represent the mean of three determinations. The results show that the concentration of sulphur in the sample must be at least as large as that of chlorine if there is to be less than 1% decrease in the recovery of sulphur dioxide. The presence of 0.055% sodium azide in the titration solution had no significant effect on the extent of interference, which was surprising because this substance is reported to suppress the interference from chlorine in the oxidative coulometric method.[4]

Combustion in CO-buffer

It was calculated earlier by the author,[6] that the interference from chlorine can be reduced by adding a proper amount of carbon monoxide to the gas mixture. The calculations showed that the flow-rate of carbon monoxide should be rather critical with respect to the recovery of sulphur, because of the formation of carbonyl sulphide. The influence of carbon monoxide on the recovery of sulphur ($H_2S + SO_2$) is shown in Fig. 3 where a comparison between experimental and theoretical results is given. The flow-rates of argon and oxygen were chosen to be 100 and

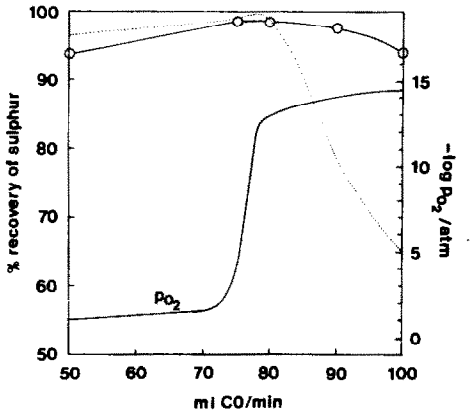

Fig. 3. Recoveries of sulphur (SO_2 + H_2S) for various flow-rates of carbon monoxide added to 50 ml/min of oxygen and 100 ml/min of argon. A cyclohexane sample (sulphur content 192 mg/l.) was injected at a rate of 0.10 µl/sec. (O) Experimental results, (···) calculated results. The solid curve shows the partial pressure of oxygen and is referred to the right-hand scale.

50 ml/min respectively. The total gas flow, *i.e.*, the sum of oxygen, argon and carbon monoxide, should not exceed about 250 ml/min since higher total flow-rates will affect the stability of the titration system. The temperatures of the zones were as follows (see Fig. 1): I 650 K, II 1000 K, III 1300 K, IV 1300 K and V 800 K. A cyclohexane sample with a sulphur content of 200 mg/l. was injected at a rate of 0.10 µl/sec.

As can be seen in Fig. 3 the agreement between theoretical and experimental results is good for oxygen pressures larger than 10^{-13} atm. These results indicate that the equilibrium between sulphur dioxide, oxygen and sulphur trioxide is obtained at 1300 K.

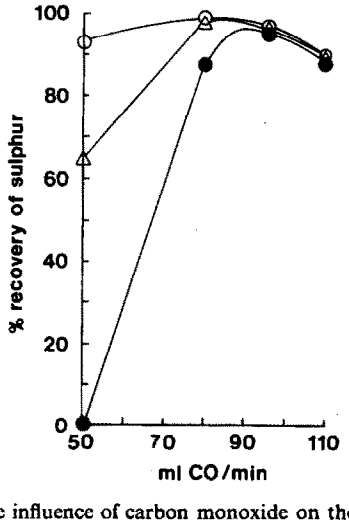

Fig. 4. The influence of carbon monoxide on the recovery of sulphur from cyclohexane samples containing 200 mg/l. of sulphur and 0% (O), 2% (△) and 10% (●) of chlorobenzene respectively. Except for the compositions of the samples the experimental conditions used were the same as those described in the caption to Fig. 3.

For lower values of the partial pressure of oxygen, however, there is a large difference between the curves. This is evidently due to the slow reaction between sulphur dioxide and carbon monoxide to form COS. The calculated distribution of sulphur compounds at 1300 K for a carbon monoxide flow-rate of 100 ml/min is 15% SO_2, 50% H_2S, and 35% COS. A coulometric titration with silver ions was made and at this gas composition only 6% of hydrogen sulphide was found. Obviously, the rate of formation of hydrogen sulphide is also slow under these conditions.

For carbon monoxide flows larger than 78 ml/min the interference from chlorine should be eliminated, according to the calculations. The fact that the formation of COS is slow means that the flow of carbon monoxide is not so critical with respect to the recovery of sulphur as is predicted by the calculations. However, the deviations from the expected equilibrium compositions do not affect the overall calculations since sulphur is present in a very small amount.

Modified oxidative procedure

The influence of carbon monoxide on the recovery of sulphur from cyclohexane samples containing 0, 2 and 10% (v/v) of chlorobenzene and 192 mg/l. of sulphur (as thiophene) was studied and the result is shown in Fig. 4. Except for the compositions of the samples, the experimental conditions used for the determinations represented in the figure were the same as those given for Fig. 3. As can be seen from the figure, the addition of carbon monoxide has a very favourable influence on the recovery of sulphur. However, it was found necessary to use a somewhat higher flow of carbon monoxide than that theoretically predicted. For example at a carbon monoxide flow of 80 ml/min the recovery of sulphur for the 10% chlorobenzene sample was only 87%, compared to the theoretical 99%. The recovery of sulphur over the range 95–100 ml/min of carbon monoxide was found to be 96 ± 1%.

It is thus possible to select the conditions suitable for a modified oxidative sulphur method for samples containing large amounts of chlorine. The method is as follows. The hydrocarbon sample is injected at a constant rate of 0.1 µl/sec into the quartz tube. For use of the combustion system described in this paper suitable flows of oxygen, argon and carbon monoxide are 50, 100 and 95 ml/min respectively. The temperatures of the zones I–V (see Fig. 1) are 650, 1000, 1300, 1300 and 800 K respectively. Results obtained with the described method are shown in Table 1. As seen from the Table the recovery of sulphur was reasonable and did not change significantly when the concentration of chlorine in the sample was varied between 0 and 35 g/l.

According to the results given in this paper it is thus possible to overcome the interference from chlorine in the oxidative sulphur method. However, the

Table 1. Determination of sulphur in solutions containing thiophene, chlorobenzene and cyclohexane

Sulphur taken, * *mg/l.*	Conc. of chlorine, *g/l.*	Sulphur found mean value, *mg/l.*	Recovery of sulphur, %	Number of detns.	Std. devn., *mg/l.*
$76._8$	34.9	$74._4$	$95._5$	3	2.0
	0	185	$96._3$	5	2.0
192	7.0	185	$96._3$	3	1.8
	34.9	183	$95._3$	5	2.1

* Sample size 3–4 μl.

suggested procedure is more elaborate than the normal procedure, since parameters such as the gas flows and sample injection rate must be carefully controlled. Another disadvantage is the necessity of using the toxic gas carbon monoxide. However, only a very small amount of carbon monoxide is vented into the air as long as the flow-rate of carbon monoxide does not exceed twice the flow-rate of oxygen. The hazard of using carbon monoxide can be minimized by producing the gas by reaction between solid carbon and carbon dioxide at about 1300 K. In this way the maximum amount of carbon monoxide vented to atmosphere is limited by the amount of carbon present in the generating tube.

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ELECTROREDUCTION OF MOLYBDENUM(VI) AT A PREHYDROGENATED PLATINUM ELECTRODE

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Summary—The use of hydrogenated platinum electrodes allows observation of the electroreduction of some oxygenated ions, which is otherwise masked by the reduction of the hydrogen ion. The present paper deals with the reduction of molybdenum(VI) at a prehydrogenated platinum electrode in acid solutions. The experimental conditions for the electrode hydrogenation process are the following: 90 min at a cathodic current density of about 7 A/cm^2 for microelectrodes with an area of 0.02–0.03 cm^2; about 120 min at a current density of 1.5–2 A/cm^2 for microelectrodes with an area of 0.25–0.35 cm^2. The reduction of molybdenum(VI) in 0.8–1.6M H_2SO_4 occurs in two consecutive steps: the more cathodic wave [Mo(V) to Mo(III)] is for the most part masked by the reduction of the solvent; the less cathodic wave [Mo(VI) to Mo(V)] takes place at $E_{1/2}$ values of about +0.07 V, is well shaped, diffusion-controlled and usable for the determination of molybdenum down to $4 \times 10^{-5}M$ or $6 \times 10^{-5}M$ if a rotating disk electrode is used. Interferences from diverse ions have been studied. A generalization of the effect of electrode hydrogenation on the reduction of those oxygenated ions so far studied [*i.e.*, vanadium(IV), uranium(VI) and molybdenum(VI)] is presented.

The polarographic and coulometric behaviour of molybdenum in various media is a matter of continuing interest and has been reviewed by many authors,[1–4] as have the analytical applications of these phenomena.[5–8] The use of solid electrodes presents severe limitations because of the evolution of hydrogen at the potential needed for the reduction of molybdenum(VI). Massart and Souchay[9] have employed a rotating platinum electrode, but they had recourse to the complexation of molybdenum as silicomolybdic acid. An indirect determination,[10] involving measuring the limiting current of the titrant, makes use of vibrating platinum electrodes. Use of the rotating graphite disk electrode[11] to exhibit the catalytic wave of bromate ions in the presence of molybdenum(VI) at pH 2–3 has been reported.

The present work demonstrates that the platinum electrode, both smooth and platinized, can be used for the direct voltammetric determination of molybdenum(VI) in strongly acidic solutions and in the presence of diverse ions, when it has first been subjected to a vigorous hydrogenation.[12] Both a rotating platinum disk electrode and one with periodic renewal of the diffusion layer have been employed. The proposed techniques are sensitive, easy to use and give good reproducibility.

EXPERIMENTAL

Apparatus

Unless otherwise specified, the measurements on the molybdenum(VI) reduction were carried out at 25 ± 0.1° with a three-electrode cell and a PAR model 170 Electrochemistry System. The potentiostatic current–times curves were measured on the screen of a Tektronix Type 502 dual-beam oscilloscope.

The study makes use of a platinum electrode either with periodic renewal of the diffusion layer (DLPRE),[13] or with the rotating disk electrode (RDE).

The characteristics of the dropping mercury electrode used were: m = 1.35 mg/sec, t_d = 4.83 sec.

In the cell of the DLPRE a Teflon-finned piston containing an iron core is moved at regular intervals of time by an external magnetic coil, causing a rapid laminar flow of the solution around a hemispherical microelectrode. The period of time during which the flowing solution reduces the diffusion layer thickness around the electrode almost to zero (washing period) is about 30 msec. The washing period is followed by a much longer period of time (3–9 sec), during which the solution around the electrode is perfectly still and the depolarizer reaches the electrode by simple diffusion. Owing to the periodical renewal of the diffusion layer, the current–potential curve recorded when the cell of the DLPRE is connected with a polarograph is similar to a polarographic wave. The only difference is that in the present case the average current is recorded at a stationary spherical electrode rather than at a growing drop.

A saturated mercury(I) sulphate electrode was used as reference, and was connected to the polarographic cell through a bridge filled with saturated sodium sulphate solution. The auxiliary electrode was of platinum, with an area of 1 cm^2. The platinum working microelectrode was, when necessary, platinized by cathodic treatment at a current density of 1.2 A/cm^2 in a 3% solution of chloroplatinic acid containing 0.025% of lead acetate. For coulometric measurements a smooth platinum working electrode with a large area (5 cm^2) was used, together with a mercury(I) sulphate auxiliary electrode.

Oxygen was removed from the solutions by passing pure nitrogen through them.

The potentials reported are referred to the saturated calomel electrode.

Reagents

Ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Merck "*pro analysi*"), was used. The molybdenum content was determined according to an established procedure.[14]

All other chemicals were of reagent grade.

Pretreatment of the electrode

As will be seen in the subsequent section, in order to obtain a well-formed cathodic wave for molybdenum(VI) at a platinum electrode it is necessary first to hydrogenate the electrode itself. This pretreatment must be carried out in sulphuric acid. During the voltammetric measurements it is convenient to avoid any handling of the solution that may cause the electrode to come into contact with air, because of the possible oxidation of adsorbed hydrogen. The best conditions are the following:[1,2] with nitrogen passing through a known volume of 1*M* sulphuric acid, keep the DLPRE (with an area of 0.02–0.03 cm^2) at a constant cathodic current and a current density of 6–9 A/cm^2 for at least 90 min, or the RDE (with an area of 0.25–0.35 cm^2) at a current density of 1.5–2 A/cm^2 for at least 120 min.

Because of the prolonged electrolysis, it is advisable to work with aqueous solutions of sulphuric acid prepared in doubly distilled water.

After the last determination the electrode is washed with concentrated nitric acid, then rinsed and stored in demineralized water.

In the rest of this paper any reference to the electrode pretreatment implies following these procedures.

RESULTS AND DISCUSSION

Voltammetric behaviour

Figure 1 shows the voltammogram obtained from a deaerated $6.0 \times 10^{-4}M$ molybdenum(VI) solution in 1*M* sulphuric acid, on applying potentials decreasing from +0.325 to −0.250 V (scan-rate 60 mV/min) to a smooth platinum electrode (DLPRE); an ill-defined cathodic wave is obtained, distorted by the beginning of electrolyte break-down. When decreasing voltages are applied to a smooth platinum electrode, prehydrogenated as previously described, under the same experimental conditions as for Fig. 1, a current-voltage curve is recorded (Fig. 2, curve 1) which exhibits a well-formed cathodic wave (*a*)

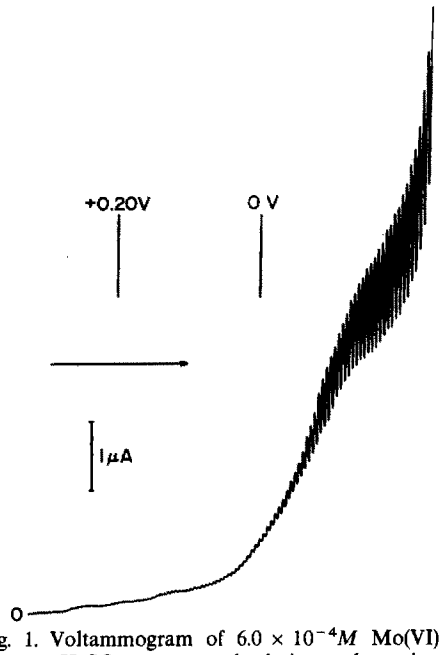


Fig. 1. Voltammogram of $6.0 \times 10^{-4}M$ Mo(VI) in 1*M* H_2SO_4 at a smooth platinum electrode.

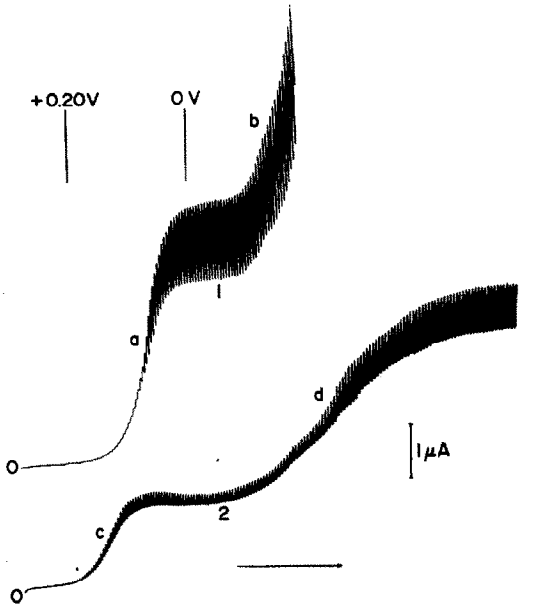


Fig. 2. Voltammetric curves of $6.0 \times 10^{-4}M$ Mo(VI) in 1*M* H_2SO_4 on a prehydrogenated platinum electrode (curve 1); the same solution polarographed with a DME (curve 2).

($E_{1/2}$ = +0.071 V) and, at more negative potentials, a rising portion (*b*) of a successive cathodic wave, eclipsed by the hydrogen evolution. At a dropping mercury electrode, the same solution gives the curve 2 of Fig. 2, characterized by the presence of two distinct cathodic waves: the first (*c*) which falls at slightly more positive potentials ($E_{1/2}$ = +0.13 V) than (*a*), and the second (*d*) that starts at the same potentials as portion (*b*) on curve 1.

The resemblance between the cathodic behaviour of molybdenum(VI) on prehydrogenated platinum and on mercury electrodes has been verified in the sulphuric acid concentration range 0.5–5*M*; in more acidic solutions (above 2.5*M*) the analogy becomes even more evident. In Fig. 3 the voltammograms with prehydrogenated platinum (curve 1) and mercury (curve 2) electrodes of a deaerated $6.0 \times 10^{-4}M$ molybdenum(VI) solution in 4*M* sulphuric acid, are given for comparison (scan-rate 60 mV/min). The wave (*c*) of Fig. 2 now splits (curve 2) into two waves [(c_1) and (c_2)], with ill-defined plateaus, while wave (*d*) remains well defined. As regards the platinum electrode, curve 1 exhibits a point of inflection, (a_1)(a_2), corresponding to the above-mentioned splitting, and a wave portion (*b*) [relatively better defined than (*b*) of Fig. 2] at the same potential as (*d*), curve 2. In this case too, the first wave [(c_1)(c_2)] appears at potentials slightly less cathodic than the corresponding wave [(a_1)(a_2)] on a platinum electrode.

It has been ascertained[1,2,7] that the polarographic behaviour under these experimental conditions corresponds, for decreasing potentials, to the reduction of molybdenum(VI) to (V) and of molybdenum(V) to

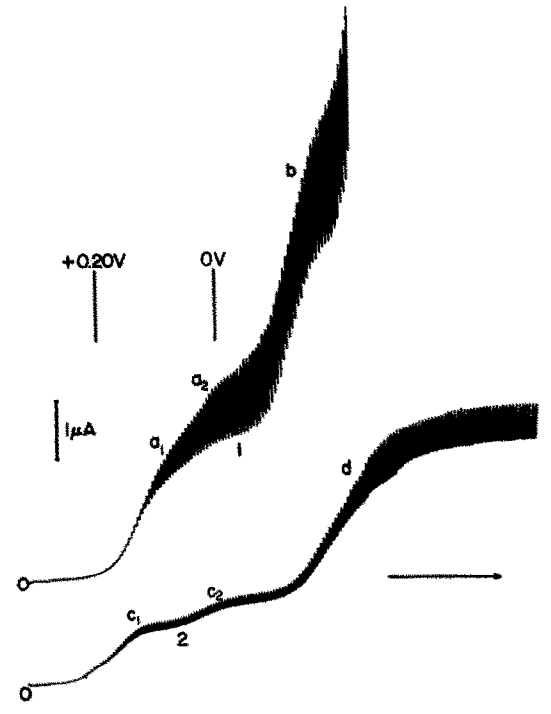


Fig. 3. Comparison of voltammograms of $6.0 \times 10^{-4}M$ Mo(VI) in $4M$ H_2SO_4 on a prehydrogenated platinum (curve 1) and a mercury electrode (curve 2).

(III); the splitting at high sulphuric acid concentrations is attributed to the reduction of different species of molybdenum(VI).

But let us return to $1M$ sulphuric acid solutions; on a prehydrogenated platinum electrode the cathodic wave of molybdenum(VI) [(*a*) in Fig. 2, and neglecting portion (*b*)] is well shaped and strictly proportional to molybdenum(VI) concentrations down to $4 \times 10^{-5}M$.

Potentiostatic curves show that the mean reduction currents for molybdenum(VI) remain practically constant for about 180 min, when the platinum electrode has been prehydrogenated according to the procedure described. Then gradually the cathodic wave shifts towards negative potentials, so that it is necessary to repeat the hydrogenation cycle.[12]

The results of coulometric measurements, performed on a large prehydrogenated electrode, show that the cathodic electrode process is characterized by the transfer of one electron per molecule: $Mo(VI) + e^- \rightarrow Mo(V)$.

The limiting current of the wave is controlled by diffusion; in fact, an oscillographic examination of the corresponding instantaneous current shows that it obeys the Cottrell equation[15] corrected for sphericity:

$$i = \text{const}\left(\frac{1}{\pi^{1/2}t^{1/2}} + \frac{D^{1/2}}{r}\right)$$

where t is the electrolysis time, D is the diffusion coefficient of the reactant,[1] and r the radius of the spherical electrode (0.097 cm).

The $\log [\bar{i}/(\bar{i}_d - \bar{i})]$ *vs.* E plot derived from the wave is a straight line with a slope of 67 mV, compared with 59 mV expected for a reversible process.

Voltammetric curves were also recorded over the temperature range 10–50°: the half-wave potential of the cathodic wave exhibits a mean shift to a more positive value of 0.65 mV/degree; the mean limiting diffusion current increases by 0.87% per degree.

Essentially the same results have been obtained over the whole range 0.5–5M. The more acidic the medium, the less negative was the $E_{1/2}$ value for the wave. We have omitted any quantitative examination of the dependence of the half-wave potential on the pH of the solution because of the incomplete knowledge of the degree of polymerization of molybdenum(VI) at varying pH.[16]

From these results it is reasonable to suppose that the reduction of molybdenum(VI) on a hydrogenated platinum electrode occurs through consecutive steps as on a DME; therefore the portion (*b*) of Figs. 2 and 3 can be attributed to the electroreduction of molybdenum(V) to (III).

The best-shaped waves were obtained in 0.8–1.6M sulphuric acid, when the curves were registered for increasingly negative potentials, after the working electrode had been held for 1 min at the starting potential of +0.325 V.

Effect of supporting electrolytes and hydrogenation conditions

Previous investigations[12] have showed that sulphuric acid is the best supporting electrolyte for the electrode prehydrogenation. Other strong acids proved less effective, because seemingly the hydrogen is not as strongly adsorbed on the electrode surface as in sulphuric acid medium. Sulphuric acid (1–2M) and the cited current densities represent the best conditions for the hydrogenation process. Lower current densities require a more protracted time of hydrogenation. More acidic solutions or higher current densities cause the auxiliary electrode to produce some peroxodisulphuric acid, electroreducible near to the potential of the molybdenum(VI) to (V) reduction.[17] The screening of the counter-electrode from the solution by a sintered-glass disk prevented this harmful effect, but many difficulties arose in constructing sintered-glass disks with electrical resistance low enough to cause no fall of the hydrogenation current. No further detectable shifts towards positive potentials were observed for longer electrolysis times.

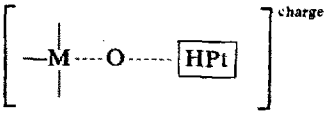
Effect of platinizing the electrode

Essentially the same results have been obtained with the platinum electrode platinized for times varying from 2 to 8 sec. The prehydrogenation times required for the display of a well-formed cathodic wave, are not appreciably shortened. At platinizing time greater than 8 sec the capacity of the electrode-solution condenser becomes too high, and this distorts the wave.

An approach to the electrode hydrogenation effect

The experimental necessity of hydrogenating the platinum electrode for the appearance of the reduction process of such oxygenated ions as VO^{2+} and UO_2^{2+}, besides Mo(VI), has been reported.[12,18]

In the previous investigations it was observed that on a hydrogenated electrode the reduction processes for the VO^{2+}/V^{3+} and UO_2^{2+}/U^{4+} couples took place at more positive potentials than on the DME. The reason has been attributed to the presence of adsorbed hydrogen on the platinum surface, which forms a hydrogen bridge with the oxygen coordinated to the central metal atom. The transition state might be depicted as in the scheme



where one or more oxygen atoms could be bonded to the metal atom M, and PtH also participates in the charge transfer. The weakening of the M–O bond, due to the hydrogen bridge, causes the reduction process to occur at more positive potentials than on a non-hydrogenated platinum electrode or a mercury electrode, which does not adsorb hydrogen in the potential range considered.

Apparently the molybdenum(VI) behaviour seems inconsistent with this explanation; in fact the hydrogenation of the electrode shifts its electroreduction to more positive potentials than on a non-hydrogenated platinum electrode, but the results, summarized in Fig. 4, show that on a DME the reduction of molybdenum(VI) is favoured. It can be deduced from Fig. 4 that the reduction processes for UO_2^{2+} (like VO^{2+})[18] and Mo(VI) on hydrogenated platinum electrodes take place at about the same potential (within a range of 100 mV) and in the middle of the "hydrogen region" (a broad discussion of hydrogen adsorption on platinum electrodes is reported in reference 19). The curve *C* of Fig. 4 shows the inflections corresponding to the deposition of the suggested two discrete "types" of hydrogen (in the figure the process has been intentionally slightly enlarged through a more rapid scan-rate: 300 mV/min).

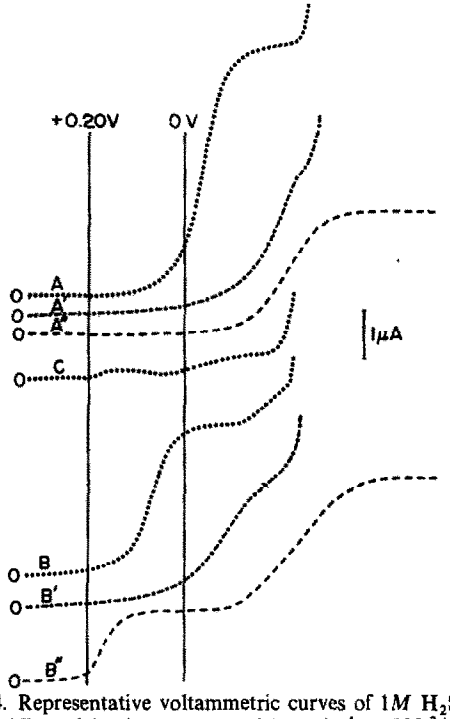


Fig. 4. Representative voltammetric curves of 1*M* H_2SO_4 alone (*C*), and in the presence of $5 \times 10^{-4}M$: UO_2^{2+} (*A*, A^{I}, A^{II}) or Mo(VI) (*B*, B^{I}, B^{II}); (·····) on a prehydrogenated platinum electrode; (—·—·—·—) on a non-pretreated platinum electrode; (——) on a DME.

In our opinion this gives credence to the hypothesis that hydrogenation of the platinum electrode shifts the electroreduction of the ions mentioned, in a positive direction, up to the potential range corresponding to the two types of adsorbed hydrogen. For the sake of brevity we shall call this potential range the hydrogenation border. Structures for "weakly" and "strongly" bound hydrogen have been suggested;[19] it has also been reported[20] that the hydrogen type deposited at more positive potentials is less active, while the other is very active. Therefore our electrode pretreatment offers an improvement over the DME for those oxygenated ions, such as UO_2^{2+} and VO^{2+}, that are reduced on the mercury electrode at potentials more negative than the hydrogenation border; for ions such as Mo(VI), electroreducible on the DME at potentials more positive than the hydrogenation border, hydrogenation of the electrode causes only a slight shift, because at more positive potentials the hydrogenation effect fails (whatever the reason may be, *e.g.*, adsorbed hydrogen weakly bound to the platinum surface and/or less active).

The above accounts for the apparent discordance of molybdate behaviour and, at the same time, can clarify and make it possible to generalize on, and define the limits of the hydrogenation shifts.

ANALYTICAL APPLICATIONS

Voltammetric determination of molybdenum(VI)

As shown above, molybdate ions give a well-shaped cathodic wave at a hydrogenated platinum microelectrode, the limiting current of which is proportional to molybdenum(VI) concentration. Sulphuric acid of about 1*M* concentration is the most convenient medium.

The proposed method gives reproducible results for molybdenum(VI) concentrations down to $4 \times 10^{-5}M$ if the DLPRE is used.

As an analytical example we deal with the determination of molybdenum(VI) in 1*M* H_2SO_4, with an electrode prehydrogenated for 90 min ($E_{1/2} = +0.07$ V).

The effects of foreign ions on the determination of molybdenum(VI) are summarized in Table 1. Strongly oxidizing ions such as permanganate and dichromate

Table 1. Effect of diverse ions on the determination of molybdenum(VI)

Cation	$E_{1/2}$, V	Tolerance limit, mg	Anion	Tolerance limit, mg
Aluminium	—	100	Acetate	100
Bismuth	−0.08	0.2	Arsenate	30
Cadmium	−0.22	30	Borate	100
Calcium	—	100	Chloride	0.5
Cerium(IV)	+1.1	6	Fluoride	30
Chromium(III)	—	50	Nitrate	70
Cobalt(II)	—	50	Perchlorate	1
Copper(II)	−0.1	1.5	Phosphate	30
Iron(III)	+0.4	3		
Magnesium	—	100		
Manganese(II)	—	100		
Nickel	—	50		
Silver	+0.37	5		
Titanium(IV)	−0.2	20		
Thorium	—	100		
Uranium(VI)	−0.04	1		
Vanadium(V)	+0.7	5		
Zirconium	—	100		

Initial solution: volume 40 ml, Mo(VI) 60 μg/ml, 1*M* H_2SO_4.

interfere because of oxidation the H_{ads}. Chloride ion suppresses the molybdenum reduction wave on the hydrogenated electrode because of the modification of the platinum surface due to its complexing action on platinum oxides.[21] It has been reported[5,6] that nitrate and perchlorate ions give rise to catalytic waves on the DME in the presence of molybdenum(V) reduced to molybdenum(III); we have verified such a behaviour on the platinum electrode for the nitrate ion, so that at high concentrations the reduction process Mo(VI)/Mo(V) is almost masked from the Mo(V)/Mo(III) catalysed process; on the contrary, we have observed that the catalytic effect of perchlorate ions also affects the Mo(VI)/Mo(V) reduction process. Seemingly the arsenate acts like nitrate, that is, it catalyses the Mo(V)/Mo(III) reduction process. As previously noted,[12] the phosphate ion weakens the adsorption of hydrogen on the electrode surface, so that, even though to a lesser extent, it resembles chloride, since it is possible that it also complexes the platinum surface.

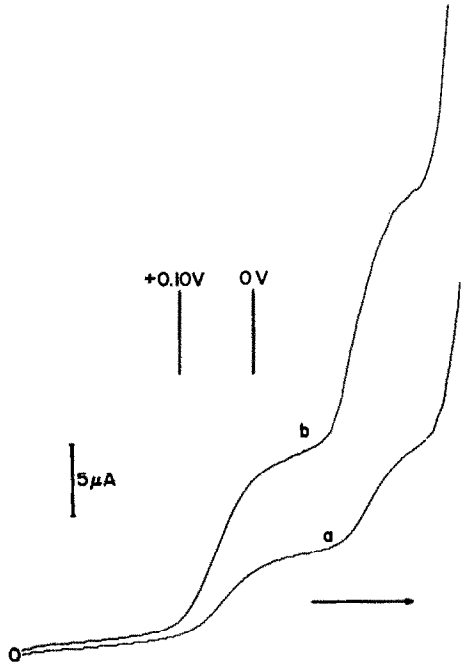


Fig. 5. Application of the standard addition method (hydrogenated RDE). (*a*) Wave given by $3.5 \times 10^{-5}M$ Mo(VI) in 1*M* H_2SO_4 solution; (*b*) after addition of Mo(VI) standard solution.

Rotating platinum disk electrode. The use of a hydrogenated platinum disk electrode gives the same results as the DLPRE. The wave portion corresponding to the Mo(V)/Mo(III) reduction process is better defined, but remains useless for any quantitative consideration. The wave-height is proportional to the molybdenum concentration and the sensitivity of the method is increased by about an order of magnitude, allowing the determination of molybdenum(VI) down to $6 \times 10^{-6}M$.

Recommended procedure. During the determination pass nitrogen through the solution. Precondition the working electrode, as previously indicated, in 40 ml of 1*M* H_2SO_4 (doubly distilled water solution). Replace 20 ml of the acid with 20 ml of deaerated test-solution. Record the polarogram of the solution over the potential range from +0.30 to −0.30 V at a scan-rate of 60–120 mV/min. When the rotating-disk electrode is used, it should rotate at about 800 rpm. Determine the molybdenum(VI) by the standard addition method. Figure 5 shows the curves for a determination of $3.5 \times 10^{-5}M$ molybdenum(VI) with the RDE.

Amounts of 0.05–15 mg of molybdenum(VI) were determined with a relative standard deviation of 4.7–0.3% and a maximum relative error of 2.2%.

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MECHANISTIC INTERPRETATION OF THE REDOX BEHAVIOUR OF DIPHENYLAMINE

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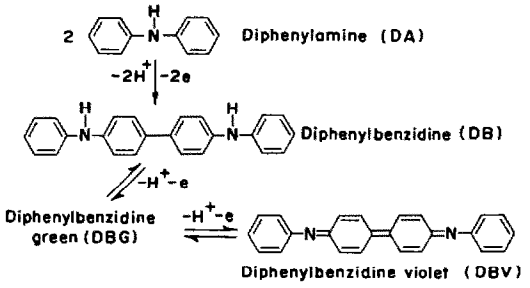
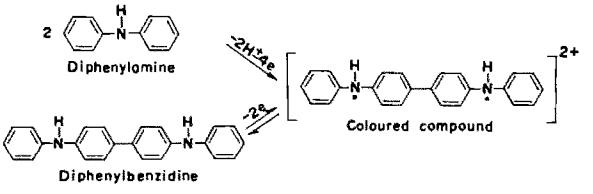
Summary—The oxidative mechanism of diphenylamine does not seem to involve the formation of diphenylbenzidine or diphenylbenzidine green (DBG) as intermediates, but these are observed in the reduction of diphenylbenzidine violet. The diphenylbenzidine green is generally obtained as an insoluble solid. It is a free radical. It is concluded that for kinetic reasons the different oxidation products of diphenylamine may not necessarily appear together nor in fixed generic sequence in an oxidation or reduction reaction but may be obtained individually under appropriate experimental conditions. The decay of diphenylbenzidine violet seems to involve a disproportionation reaction to give DBG, rather than a polymerization reaction.

Hoffmann[1] is credited with the discovery of colour formation on oxidation of diphenylamine (DA). However, its cause is still a subject of discussion. Some attribute the colour to a structural change in the molecule and others to formation of addition compounds.[2] Though the former view has gained general acceptance, it was believed until recently that the blue colour is due to the quinonoid salt of diphenylbenzidine called diphenylbenzidine violet (DBV). However, opinions differ regarding the intermediate steps in the oxidation. Wieland[3] and Thiel[4] assumed the formation of a bivalent radical, $C_6H_5—N=C_6H_4<$, as an intermediate which dimerizes rapidly to give the quinone-imonium salt of diphenylbenzidine. Kehrmann and Micewicz,[5] and Marqueyrol and Muraour[6] showed that diphenylbenzidine (DB) and diphenylbenzidine green (DBG) could be prepared from DA by procedures involving oxidation and reduction. A more detailed mechanistic study was made by Kolthoff and Sarver,[7] who concluded that DB and DBG are indeed the intermediate products as shown in the following scheme:



DBG was first considered a meriquinone but was later thought to be a semiquinone in accordance with the theory of Michaelis. Similar mechanisms were assumed for the oxidation of some derivatives of DA, without further experimentation.

Recently, Bishop and Hartshorn[8] have shown that the oxidation of DA in sulphuric acid is an irreversible single-step two-electron process with no detectable evidence for the formation of either a benzidine or semiquinone intermediate; DB is also oxidized to the same blue compound by a reversible one-step two-electron process without formation of the presumed semiquinone intermediate. The coloured compound is believed to be a doubly charged biradical (triplet state).



There was no evidence, however, for the formation of a semiquinone on the decay of the coloured compound in the case of some derivatives of DA, except *N*-phenylanthranilic acid. Contrary to an earlier report[9] that first DBG and then DB can be obtained by reducing the coloured compound with zinc dust and sulphuric acid, these authors[8] report only the benzidine form as the reduction product. The present paper seeks to explain the difference in the two mechanistic approaches in the light of further experimental study.

Hereafter in this paper, DBV will be taken to mean the blue oxidation product, without regard to its structure.

EXPERIMENTAL

Reagents

Diphenylamine solution in 20N sulphuric acid, 0.002M. Prepared from analytical reagent grade material.

Cerium(IV) sulphate solution in 1M sulphuric acid, 0.05M. Prepared from iron-free cerium(IV) oxide and standardized against sodium oxalate.

Sodium vanadate solution, 0.05M and iron(II) ammonium sulphate solution, 0.05M. Prepared and standardized as described earlier.[10]

DBG powder samples. Samples containing DBG and used in the spectrophotometric and e.s.r. studies were prepared as follows.

Portions of diphenylamine (0.1 g) were treated with an equivalent amount of cerium(IV) sulphate (for oxidation to DBV) in 1*M* sulphuric acid, the solutions being kept at 3° during the experiment. After thorough stirring of the mixtures, the DBV was reduced (*a*) with a little zinc dust, (*b*) with iron(II) and (*c*) with excess of diphenylamine. The green solids formed were filtered off separately and repeatedly washed with ice-cold 1*M* sulphuric acid. The products were finally dried over concentrated sulphuric acid in a vacuum desiccator. They will be referred to as A, B and C respectively.

The sulphuric acid used was nitrate-free analytical-reagent grade.

Apparatus

The potentiometric assembly used was described earlier.[10] The e.s.r. spectra were measured on a Varian E-4 spectrometer.

Potentiometric investigation

The reaction of DA with cerium(IV) sulphate is quite fast. However, in titration of DA (1–2.5 mg in 50–100 ml of 2*N* sulphuric acid) with 0.01*M* cerium(IV) sulphate at 29°, the potentials generally drifted, and no inflection was obtained on a potentiometric plot (Fig. 1), presumably because of side-reactions similar to those assumed by Kolthoff and Sarver. Titration at 3° (keeping both half-cells at this temperature) was successful, however (Fig. 1).

From several titrations, it was found that 2.3 equivalents of oxidant are consumed per mole of DA, close to the value of 2.0 for oxidation of DA to the blue product. The discrepancy is probably due to the irreversible oxidation of part of the blue product. The curve shows no break corresponding to the formation of DB (at 1 eq/mole) like the one reported by Kolthoff and Sarver. Attempts to titrate DA with potassium dichromate or sodium vanadate at either 3° or 29° were unsuccessful because the reaction was too slow and gave no sharp potential break.

In view of the peculiar behaviour of the chromium(VI)/(III) system[11] and the higher oxidation potential of the cerium(IV)/(III) system causing irreversible oxidation of

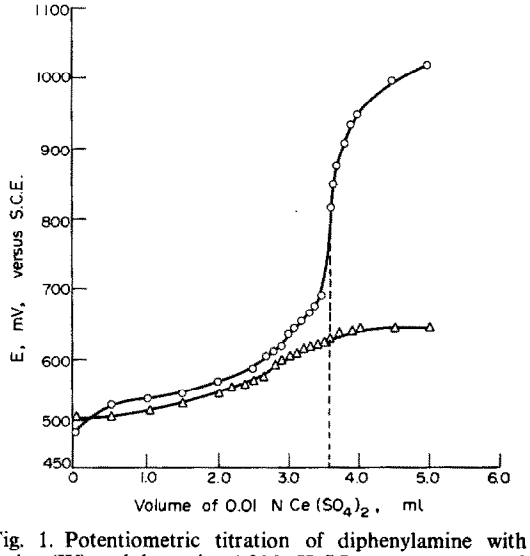


Fig. 1. Potentiometric titration of diphenylamine with cerium(IV) sulphate in 1.0*M* H_2SO_4 ⊙——⊙ at 3° △——△ at 29°.

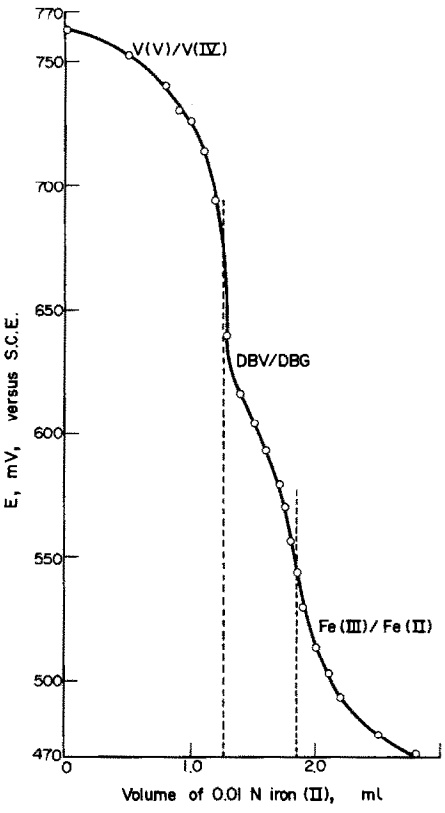


Fig. 2. Potentiometric titration of diphenylbenzidine violet and excess of vanadium(V) with iron(II) in 1.0*M* H_2SO_4 + 0.5*M* H_3PO_4 at 3°.

DBV more rapidly, the author used vanadate in the potentiometric back-titration at 3° to minimize the extent of side-reactions. The first break in the curve in Fig. 2 corresponds to the reduction of excess of vanadate and the second to the reduction of DBV to DBG by iron(II). The results indicate that DA requires 2.15 equivalents of oxidant per mole (theory 2.00) to give the coloured compound and 0.45 equivalents of iron(II) (theory 0.50) are required per mole of DA to reduce the blue to the green compound, in agreement with the conclusions of Kolthoff and Sarver regarding formation of the green intermediate.

Spectrophotometric investigation

Absorption spectrum of DBV. The absorption spectrum of the blue compound in 2.0*N* sulphuric acid had a maximum at 560 nm. The shape of the curve and λ_{max} were similar to those reported by Sarver and Kolthoff.[12]

Spectrophotometric titration. In a rapid spectrophotometric titration of DA (40–80 μg in 20–40 ml of 2.0*N* sulphuric acid) with cerium(IV) sulphate, monitored at 560 nm, the curve was linear up to the break. Since the volume change is small, this shows that the blue product obeys Beer's law in this concentration range. Excess of titrant would be expected to produce no more increase in absorbance, but a slight fall is observed, perhaps due to further oxidation of the blue product. The break in the curve (Fig. 3) corresponds to consumption of 2.15 equivalents of oxidant per mole of DA (theory 2.0). Again no formation of the colourless DB is evident.

Absorption spectrum of DBG. The solid samples A, B and C were insoluble in non-polar solvents such as benzene and carbon tetrachloride but gave red solutions in dimethylformamide (DMF), dimethylsulphoxide (DMSO)

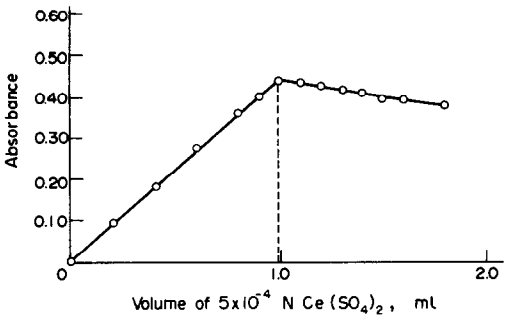


Fig. 3. Spectrophotometric titration of diphenylamine with cerium(IV) sulphate in 1.0*M* H_2SO_4. Absorbance at 560 nm.

and pyridine, and blue-green in tributyl phosphate (TBP) and acetic acid; a small residue left after the dissolution was thought to be a product of side-reactions in the preparation. The absorption spectra of all three TBP solutions had a broad band around 635 nm. The differences in Fig. 4 may be due to soluble products of side-reactions in the preparation.

Electron spin resonance study. The powder samples A, B and C gave a signal that showed a Landé splitting factor (*g*-factor) of 2.0035, indicative of a free radical with an unpaired electron. The appearance of a sharp signal at the same field strength for all three implies identity of the paramagnetic species in the three samples.

Spectra of the samples in solution in DMF and DMSO were obtained with a view to gaining information about the structure of the free radical. The similarity found in the resolved hyperfine structure indicates that the mechanism is influenced either not at all or to about the same extent by the two solvents. There is a difference in the intensity of the signals which may be due to a difference in the spin concentration of the samples. The central line occurs at a field strength corresponding to a *g*-value of 2.0035. The samples were found to give the signal even after six months, showing the extraordinary stability of the paramagnetic species.

DISCUSSION

DA is a useful reagent for the colorimetric determination of a number of oxidizing agents. The validity of Beer's law when excess of DA is present shows that no DB is produced. When DA is used as a redox indicator the blue colour is visible even though insufficient excess of oxidant is added for conversion of all DA into DB. The results of the present potentiometric and spectrophotometric titrations prove that the blue colour is due to a two-electron oxidation product of DA, with no detectable formation of DB or DBG as intermediates. The low solubility of DB is a drawback in its potentiometric oxidation titration because it delays attainment of equilibrium and thereby upsets the measurement of potentials.[7,13] However, Sarver and Kolthoff[12] argue that the different rate of reaction of DB in the oxidation of DA is due to the former being formed in a finely divided suspension. Their analytical study did not unequivocally prove that DB is the direct oxidation product. The reaction of DA with dichromate is slow; elevated temperature and slow titration are likely to promote DB formation through a secondary reaction between DA and DBV. However, Kolthoff and Sarver believe that the direct dichromate oxidation product of DA is DB although DBV is observed before the completion of this change, but that DBG is formed only through a secondary reaction during oxidation of DB to DBV. They report two potential jumps corresponding to DA → DB and DB → DBV. Although the potential in the direct titration drifted, it was claimed that the results were reproducible under similar conditions. The slow potential equilibration with dichromate may be due to the peculiar behaviour of the chromium (VI)/(III) system at the platinum indicator electrode.[11] In contrast the reaction of DA with cerium(IV) sulphate is fast, the potential equilibration is also rapid and only one potential jump is observed, corresponding to DA → DBV in the potentiometric titration at 3°. Another argument advanced by Kolthoff and Sarver in support of their theory is that both DA and DB yield DBV on oxidation and DB is obtained by reduction of DBV under suitable conditions. The theory of Bishop and Hartshorn also suggests that the blue oxidation products of DA and DB are the same, although the difference in the half-lives of these products (96 and 188 min respectively)[8] remains unexplained. However, these authors rule out DB as an intermediate in the oxidation of DA to DBV.

Though the present results do not conclusively disprove the mechanism proposed by Kolthoff and Sarver, if DB and DBG are treated as undetectable transient intermediates instantly being oxidized to the blue compound, the theory of Thiel,[4] and of Bishop and Hartshorn,[8] gives a more plausible explanation. As pointed out earlier,[10] the two-electron oxidation product of DA may be a biradical, $C_6H_5—N{=}C_6H_4<$ which dimerizes to the diquinonedi-imine (singlet state) which is in equilib-

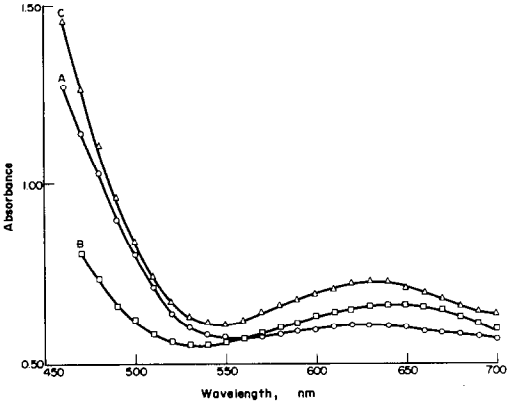
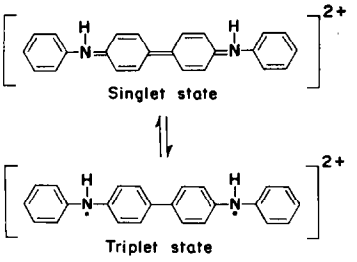


Fig. 4. Absorption spectra of DBG in tributyl phosphate *A* ⊙——⊙ Prepared by reduction of DBV with zinc dust; *B* ⊡——⊡ prepared by reduction of DBV with iron(II); *C* △——△ prepared by treatment of DBV with DA.

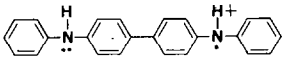
rium with the biradical (triplet state) proposed by Bishop and Hartshorn.



The equilibrium probably favours the singlet state in terms of energy. Basically, the difference in the two mechanisms seems to arise in some of the initial steps that were not considered. One-electron transfer reaction of DA with oxidant results in formation of DA free radicals ($Ph_2^+\dot{N}H$) which avoid N–N coupling and prefer C–C coupling at the *para*-position to maximize the separation of the two positive charges in yielding DB as the product on condensation;[3,15] alternatively, if the DA or DB free radicals in solution react faster with the oxidant the corresponding biradicals will result, with no evidence provided for the formation of DB or DBG.

The back-titrations have established that DBG is the first product of DBV reduction with iron(II). It has already been reported[7] that formation of DBG can be prevented by rapid addition of iron(II), the reduction then going as far as DB, although it is hard to reduce precipitated DBG to DB with iron(II); however, a more powerful reducing agent such as stannous chloride reduces it to colourless DB rapidly. DBG is not observed[8] in the reduction of DBV with *excess* of zinc or in the oxidation of DA or in the decay of DBV. However, DBG has been prepared[6,9] from DBV by reduction and characterized[5] by oxidation, or by reduction with zinc dust to DB.[9]

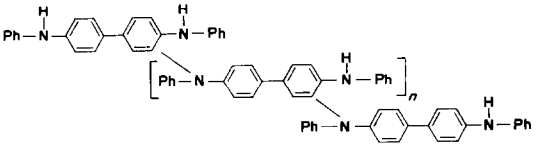
The *g*-values of the polycrystalline or amorphous samples of DBG are 2.0035, indicative of an unpaired electron in the structure, and the spectra are isotropic. The spectra of the solid matrices indicate that the paramagnetic species in the samples is not a biradical. The hyperfine structure in the spectra of the samples in solution has five major components symmetrically disposed. The spectra indicate the presence of the same paramagnetic material in the reaction products, with one unpaired electron. It is difficult to say whether there is further splitting of the major components, because of noise. Analysis of the e.s.r. data indicates that the unpaired electron spends most of its time at the two N-sites and hence the following structure may be proposed for the free radical:



The unpaired electron and "lone" electron-pair delocalization in the symmetrical ion are important in explaining the stability of the radical since both the unpaired electron and the lone-pair electrons are present in *p*-orbitals of the respective nitrogen atoms.

The spectra of the solutions do not conclusively rule out the possibility that the paramagnetic species is a biradical. If the electron exchange coupling between the two molecular fragments is fast and strong, the ground state of the biradical could be a singlet (diquinonedi-imine) or a triplet. The electron exchange in the triplet state might then allow the interaction of each electron with both the N-nuclei to give a similar quintet line spectrum. However, the biradical can be expected to behave differently from a free radical in the powder spectrum. Only in a single crystal with radicals in identical orientation, can it give a widely separated three-line spectrum (fine structure). Even so it is not possible for any line to occur exactly at a field corresponding to a *g*-value of 2.0035 for the free radical except when the biradical is a large molecule. In any such molecule that can be proposed with unpaired electrons on the terminal non-hydrogen-bearing nitrogen atoms,[14] the electrons are too far apart to interact with each other or with both nuclei and this should result in only a triplet (or a quartet if H in –NH– has a coupling equal to that of N in a protonated species) spectrum in solution, but the observed spectrum has five lines. The other evidence, such as stability of the radical and the stoichiometry of the reaction leading to formation of the radical is also not in favour of the green product being a biradical monomer.

In the absence of an accurate estimate of the molar absorptivity of DBG (because of lack of purity in the sample), the broad band around 635 nm in the DBG spectra is difficult to interpret beyond inference of the existence of a common species in all the samples. A green amorphous solid obtained from an acid-catalysed transformation of DBV, and considered to be a polymer, was reported by Hammond *et al.*,[15] who also obtained the green product in the oxidation of more concentrated solutions of DA. A tentative structure,[14]



has been proposed for this compound. The spectrum showed maxima at 250 and at 610–650 nm (in concentrated sulphuric acid). The spectrum of the polymer is reported to contain components of DB (250 nm) and DBV (610–650 nm) and addition of dichromate is found to increase the long wavelength absorbance and decrease the other. The reported paramagnetic behaviour of the green material suggests the presence of unpaired electrons in the structure. Since the monomer, DBV, can have a biradical structure, the polymer may also be a biradical. Instead of the terminal "nitrogen" hydrogens in the chain,[14] two unpaired electrons satisfy the biradical structure of the

polymer. This also satisfies the chemical balance of the polymerization reaction. However, these authors[15] do not seem to have studied the e.s.r. spectra of the polymer-designates in solution. Also the inference from their spectral study that increase of biradical polymer chain is promoted by dichromate oxidation is interesting and requires further investigation.

Hammond *et al.* further reported that partial oxidation of DB in media of low acidity resulted in the formation of the semiquinone (460–480 nm band). In a more acid medium, however, formation of the semiquinone was not observed, and this was attributed to its disproportionation. A careful oxidation of DA in more acid medium was found to yield DB without a trace of the green insoluble product whereas oxidation of more concentrated solutions resulted in the formation of the green precipitate. This latter experimental condition is similar to the one used in the preparation of sample C.

The appearance of the 610–650 nm band with the reported high molar absorptivity (in concentrated sulphuric acid) of the green products obtained by Hammond *et al.* suggests, however, that this is a charge-transfer band; if so, it may be attributed to a dimer of the semiquinone, DBG, which is likely to exist as a charge-transfer complex of DB and DBV (probably in their conjugate acid forms, AH_4^{2+} and AH_2^{2+} where A stands for a diquinonedi-imine unit) in 1:1 proportion. The same remarks may apply to the behaviour of the green products (obtained by the author by the reduction of DBV) in TBP and acetic acid but not in DMF and DMSO, where no such bands were observed.

It is significant that the increased rate of DBV decay in dilute sulphuric acid is attributed to autocatalysis by DB; Bishop and Hartshorn, however, seem to believe that the insoluble compound obtained on the addition of DB to a solution containing DBV is the irreversible oxidation product (derived from accelerated decay of DBV). It is apparent from their results that this decomposition of DBV, autocatalysed by DB, is curiously absent during the reduction of DBV to DB by zinc, so that the stoichiometry of this latter reaction is preserved; but then the results of the present back-titration procedure should be interpreted to mean that the autocatalytic effect by DB is so predominant as to affect by about 50% the stoichiometry of the reduction of DBV by iron(II) (to the presumptive DB). Further, the decay of DBV is considered by Hammond *et al.* to be a result of polymerization, while Bishop and Hartshorn consider it a disproportionation. These apparently contradictory results may be explained if the green compound is treated as an intermediate oxidation state of DB. The sparingly soluble semiquinone obtained during partial oxidation of DB is reported to be stable in media of low acidity but to undergo disproportionation:

$$2\,\mathrm{DBG} \overset{\mathrm{H^+}}{\rightleftharpoons} \mathrm{DB} + \mathrm{DBV}$$

with increasing acidity of the medium.[15] The increased rate of disproportionation with acid and the relatively slow kinetics of solution of the green product do not allow the DBG absorption band to appear in the decaying solutions of DBV in a strongly acid medium. Inability to detect DBG spectrally in solutions of decayed DBV in the experiments of Bishop and Hartshorn may be because its rate of formation is comparable to the rate of its disproportionation at these concentrations. No large quantity of insoluble green product was reported. One of the final products is DB but the small residue observed may be the insoluble DBG which has escaped disproportionation, although these authors seem to feel that it is another decomposition product. The results of Hammond *et al.* for the decay of DBV to give the insoluble green product may be the result of a difference in the concentration of DBV changing the rate of formation of DBG intermediate. The production of DBG in the present back-titration procedure may be due to the rate of formation [reduction of DBV by iron(II)] predominating over the disproportionation of DBG and to its insolubility.[7,9] Evidence for the various insoluble green products is in favour of their existing as the free radical monomer or dimer but not as a long-chain polymer or polymer biradical.

The various reactions that occur during the oxidation of DA or reduction of DBV in dilute sulphuric acid may conveniently be built up from the following half-cell reactions:

$$2\mathrm{DA} \overset{-2\mathrm{H^+}}{\rightleftharpoons} \mathrm{DBV} + 4\mathrm{e} \qquad (i)$$

$$\mathrm{DB} \rightleftharpoons \mathrm{DBG} + \mathrm{e} \qquad (ii)$$

$$\mathrm{DBG} \rightleftharpoons \mathrm{DBV} + \mathrm{e} \qquad (iii)$$

$$p\mathrm{DBV} \overset{\text{disproportionation}}{\rightleftharpoons} q\mathrm{DB} + \text{unidentified irreversible oxidation products} \qquad (iv)$$

where $p > q$ (exact values not known), and appropriate charges on DBV and DBG are implied. Then the formation of DB and DBG from interactions of DA and DBV, and the oxidation of DBV with oxidant, account for the side-reactions in the oxidative titrations. The reduction of DBV to DB involves semiquinone (DBG) formation but this may not be detectable if the reaction between DBG and the reductant used is fast enough. The apparently slower decay of DBV with excess of cerium(IV) indicates reaction (*iv*) as the main path but other side-reactions also occur.[8]

DB, DBG and DBV may be viewed as different oxidation states of DA that can be prepared under different experimental conditions but neither occurring together nor always in the same generic sequence in an oxidation or reduction process, possibly for kinetic reasons. It is also possible that some of the intermediate states are thermodynamically unstable but are in a metastable state, again for kinetic reasons. The near-denial of the existence of the semiquinone form[8] because of inability to detect it in the zinc reduction or decay of DBV, or in the oxidation of DA or DB, and the insistence[7,16] on DB and DBG

as intermediates in oxidation of DA because of their preparation from DBV reduction, seem to be two extreme positions in the mechanistic interpretation. It may not be difficult to use a kinetic result to postulate a rate-determining slow step in a reaction but it is not possible to be conclusive in predicting or ruling out a fast step in a reaction, because this is all based on chemical intuition; all one can do under these circumstances is to give a plausible interpretation.

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CONSTRUCTION AND ANALYTICAL APPLICATIONS OF AN EXTRACTIVE ELECTRODE SENSITIVE TO MERCURY(I)

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Summary—The construction and characteristics of a new type of extractive electrode sensitive to Hg_2^{2+} are described. The performance of the electrode is compared with that of an ion-selective electrode with mercurous dithizonate as the active substance. The Hg_2^{2+}-extractive electrode contains $Pd(HDz)_2$ in its membrane. Its stability and sensitivity are remarkable. It has been used as indicator electrode for the titration of halides alone and in mixtures, and for determination of mercury(I), mercury(II), silver, and of substances containing or reacting with mercury. The basis of the electrode response is discussed.

Because of the instability of insoluble mercurous compounds, the construction of solid-state Hg_2^{2+}-selective membrane electrodes is not possible. Our attempts to obtain a liquid-state electrode for this ion, using feebly dissociated mercury chelates, led us to the conclusion that such electrodes are not practicable because their characteristics change with time and/or use, and they finally become completely insensitive. We have therefore tried to construct an Hg_2^{2+}-sensitive extractive electrode, suitable for the determination of the equivalence point in a mercurometric titration, but not containing the species Hg_2^{2+} in its membrane.

Such an electrode should be stable, selective and sensitive, have a Nernstian response and attain equilibrium rapidly. Also by addition of a species R^{n-} which converts the M^{m+} species into non-extractable form, the ion-exchanger should be easy to regenerate.

Thus in the presence of M^{m+} an active agent appears in the membrane and the electrode becomes M^{m+}-sensitive. When placed in a solution containing species R^{n-}, the electrode becomes inactive because species M^{m+} is released from the membrane. Under such conditions it can be stored and used for very long periods of time. Obviously, for each titration of R^{n-} with M^{m+} (or *vice versa*), the electrode goes through the same "inactive"–"active" cycle. The chemical structure of the membrane is reversibly changed at the equivalence point, and with an accompanying large potential change.

In order to check these assumptions, we constructed an Hg_2^{2+}-extractive electrode, using palladium dithizonate $Pd(HDz)_2$ as ion-exchanger.

EXPERIMENTAL

Apparatus

The potential was measured *vs.* a double-junction Orion electrode (No. 90-02-00) with a 15% potassium nitrate solution in the outer compartment, with an Orion Research Digital Ion-Analyzer 801 A. For pH measurements and argentometric titrations of chlorides we used the Orion glass electrode (No. 91-01-00) and the solid-state electrode for Cl^- (No. 94-17 A).

Reagents

The following analytical-grade reagents were used without further purification: dithizone, sodium chloride, nitric acid, potassium nitrate, mercurous nitrate, potassium iodide, potassium bromide and palladium chloride.

The 10^{-2}–$10^{-6}M$ mercurous nitrate solutions were made by diluting a $0.1M$ stock solution made by grinding mercurous nitrate with metallic mercury with dropwise addition of 20 ml of $2M$ nitric acid, followed by addition of 800 ml of distilled water, stirring for about 1 hr, filtration, and dilution to 1 litre. Metallic mercury was added as preservative. Working solutions were prepared weekly. The stock solution was standardized gravimetrically.

Primary palladium dithizonate $Pd(HDz)_2$, $5 \times 10^{-4}M$ solution, was obtained by mixing the stoichiometric amounts of dithizone and palladium chloride. The dithizone was dissolved in a minimum amount of chloroform, and the palladium chloride in a minimal amount of conc. hydrochloric acid. Both solutions were transferred to a separating funnel, 100 ml of distilled water and 10 ml of $2M$ nitric acid were added, and the mixture was shaken vigorously for 5 min. The organic layer, which was green-brown, was washed thrice with distilled water, dried with anhydrous sodium sulphate, transferred to a standard flask (100 ml) and made up to the mark with chloroform.

Secondary palladium dithizonate, PdDz, was prepared by using excess of palladium.

For the preparation of mercurous dithizonate, $Hg_2(HDz)_2$, solution, $5 \times 10^{-4}M$, an excess of mercury(I) (1 ml of $0.15M$ mercurous nitrate in $0.2M$ nitric acid) was treated with the requisite amount of dithizone dissolved in chloroform, and the extraction and dilution were completed as for the palladium complex.

2,4-Dichlorophenoxyacetic acid solution, $0.1N$, was made by dissolving the "2,4-D acid" in 30 ml of ethanol, then adding 40 ml of n-propanol and diluting to 100 ml with Michaelis buffer (pH = 4.62).

"Regenerating solution" was made by adding 1 ml of 0.1*M* nitric acid to 50 ml of 2*M* potassium iodide. Between titrations the electrode was stored in this solution.

Construction, use and storage of the electrodes

The body of the electrode was machined from a PTFE bar. The interior of the electrode was filled with chloroform solutions of $Pd(HDz)_2$ or $Hg_2(HDz)_2$ prepared as described above. The membrane was of graphite as previously described.[1]

The electrodes were stored in hermetically closed test-tubes containing the appropriate solutions. The test-tubes and electrode reservoirs were refilled whenever necessary.

After each use the Hg_2^{2+}-extractive electrode that contained the $Pd(HDz)_2$ internal solution was washed with 0.1*M* potassium iodide made slightly acid with nitric acid. Before being replaced in the test-tubes, the electrodes were washed with distilled water and dried thoroughly with filter paper to avoid any danger of Hg_2^{2+}-contamination of the test-tube and/or the internal solution. This treatment inactivates the electrode during storage and prevents the pores from becoming clogged with precipitate.

RESULTS AND DISCUSSION

Characterization and mechanism of the electrode

The calibration curve (Fig. 1) shows that the Hg_2^{2+}-selective electrode (S), which has mercurous dithizonate as the active substance, has a Nernstian response of 30 mV/decade in the 10^{-1}–$10^{-6}M$ range. It also has the general characteristics of dithizonate electrodes,[2] but is less stable. After a week of use in pure mercurous solutions it becomes practically inactive, probably because of disproportionation. With 2,4-dichlorophenoxyacetic acid the electrode becomes insensitive after the first titration. Obviously such shortcomings make the electrode unattractive.

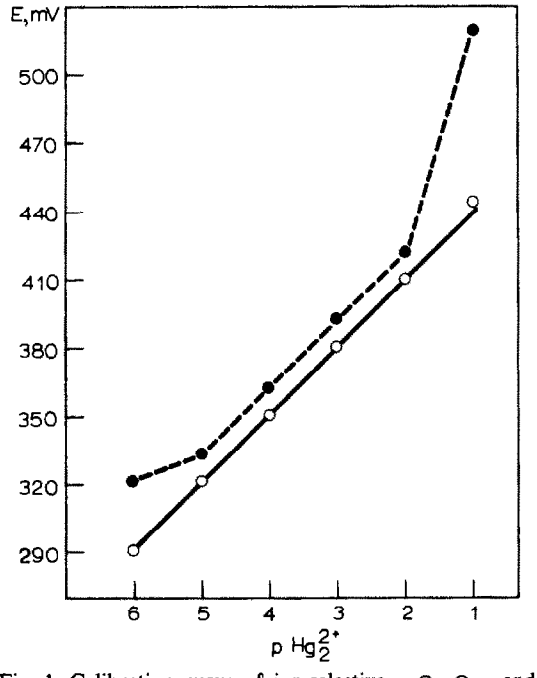

Fig. 1. Calibration curve of ion-selective —O—O— and ion-extractive —●—●— electrodes in 1*M* HNO_3 and at ionic strength 2.2*M* (KNO_3).

However, the Hg_2^{2+}-extractive electrode (E), which contains $Pd(HDz)_2$ as the active substance, has considerably different characteristics. First, the calibration curve (Fig. 1) has three distinct portions. In the 10^{-6}–$10^{-5}M$ range the response is unstable, and dependent on the sample volume. This instability range can be narrowed or widened by diluting or concentrating the internal solution. In the 10^{-5}–$10^{-2}M$ range the response of the electrode is Nernstian. Between 10^{-2} and $10^{-1}M$ mercury(I) concentrations the slope changes again, reaching 100 mV/decade. This latter phenomenon signals the occurrence of another chemical change in the membrane.

In mercury(I) solutions more concentrated than $10^{-5}M$ the response of the electrode is instantaneous and independent of the ionic strength of the solution (Fig. 1), but dependent on pH (Fig. 2).

The behaviour of the electrode can be explained if we assume the following equilibrium:

$$2Pd(HDz)_2 + Hg_2(NO_3)_2 \overset{K_1}{\rightleftharpoons} 2PdDz + Hg_2(HDz)_2 + 2HNO_3. \quad (1)$$

If this lies to the right, $Hg_2(HDz)_2$ appears in the membrane. Thus the sensitivity of the electrode is dependent on the magnitude of K_1. The existence of this equilibrium is confirmed by the following experimental facts.

(*a*) The absorption spectra of the Hg_2^{2+}-saturated internal solution and of a synthetic mixture of PdDz and $Hg_2(HDz)_2$ in the ratio given by equation (1) are identical.

(*b*) The response of electrodes (S) and (E) to Hg_2^{2+} has about the same absolute potential value (Fig. 1).

(*c*) The pH-dependence of the response of both electrodes is similar (Fig. 2).

On this basis we conclude that the $Hg_2(HDz)_2$ chelate is responsible for the functioning of the electrode, so the theoretical considerations[2] for the dithizonate electrodes will apply.

The selectivity constants were calculated by using a simplified form[3] of the Eisenman equation:

$$\log K_{Hg_2^{2+}/M^{z+}} = \frac{(E_2 - E_1)nF}{2.303\,RT} - \log a^{(n/z-1)} \quad (2)$$

and show the differences in the selectivity of the two electrodes (Table 1).

Palladium and silver give the same selectivity values for both electrodes; the interference from Hg^{2+} is about 20 times as high for (E) as for (S) whereas (E) is the most selective towards all other ions studied. Thus the extractive electrode becomes sensitive to Ag^+ or Hg^{2+} when placed in solutions containing these ions, because of formation of the corresponding dithizonate in the membrane.

In the presence of halides equilibrium (1) shifts to the left, the active species disappearing from the membrane according to the reaction:

$$2MX^- + 2HNO_3 + 2PdDz + Hg_2(HDz)_2 \overset{K_2}{\rightleftharpoons} 2Pd(HDz)_2 + Hg_2X_2 + 2NO_3^-. \quad (3)$$

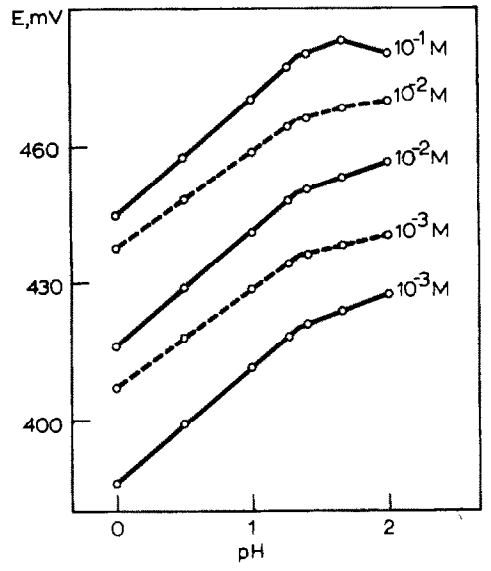

Fig. 2. Influence of pH on the response of the electrodes —O—O— selective electrode (S), (mercurous dithizonate), and —O--O— extractive electrode (E), (palladium dithizonate).

The reaction is confirmed experimentally by detection of the compound $Pd(HDz)_2$ and gravimetric determination of the mercurous halide.

The extractive electrode has a remarkable stability in time and towards chemical agents, making possible its use in solutions up to 4*N* in acid. It cannot be poisoned and the internal solution keeps its properties even after boiling for 8 hr. We have used three such electrodes daily for 14 months for potentiometric titrations in aqueous and organic media, and so far no deterioration of the performance has been observed. The only maintenance required has been the sporadic addition of internal solution to the electrode.

Although both electrodes utilize the same active substance there are important differences between them. One is unusable because of its instability, while the other is exceptionally stable and has improved selectivity. We conclude that the ion-exchanger used satisfies all the conditions outlined except for high selectivity.

Because Hg^{2+} and Ag^+ cannot be extracted in presence of halides, pseudohalides, sulphides, carbamates *etc.*, the extractive electrode can be used to advantage for end-point detection in argentometric and mercurimetric titrations. As the mercurous halides are less dissociated, mercurometric titrations give better sensitivity than argentometric or mercurimetric titrations.

A peculiar case is the operation of the extractive electrode in the presence of palladium ions: an inactive secondary dithizonate appears in the membrane, according to the equation:

$$Pd(HDz)_2 + Pd^{2+} \underset{K_2}{\overset{K_1}{\rightleftharpoons}} 2PdDz + 2H^+. \quad (4)$$

However, in titrations with Pd^{2+} the equivalence point is still accompanied by a slight variation of the potential, which is due to the change in the chemical nature of the membrane.

Because iodides interfere with the extraction of Pd^{2+} in the membrane, when I^- is titrated in presence of high concentrations of Br^- or Cl^- the electrode can furnish useful information (Fig. 3). In this case the regeneration of the electrode can be done rapidly with a dilute sulphide solution.

The ion-extractive electrode can be used for potentiometric titration with or of the species Hg_2^{2+}, Hg^{2+} and Ag^+ because it has a remarkable stability and a better selectivity than the liquid electrode based on mercurous dithizonate.

Some of the applications are presented below.

APPLICATIONS

Determination of mercury compounds

The use of the ion-extractive electrode for the analysis of inorganic and organic mercury compounds has substantial advantages. Such analyses are both accurate and sensitive, and sometimes give more information than other techniques. The error does not exceed 0.1%.

Mercuric chloride. To a sample containing about 0.1 meq of $HgCl_2$ add a known volume of an alkaline standard iodide solution, with vigorous stirring. Stop adding the iodide when the precipitate initially formed is redissolved according to the equation

$$HgCl_2 + 4\,I^- \rightarrow HgI_4^{2-} + 2Cl^-. \quad (5)$$

Acidify with 0.05*M* nitric acid and titrate with 10^{-1}–$10^{-2}N$ $Hg_2(NO_3)_2$ standard solution. The tit-

Table 1. Values of the selectivity coefficients for the Hg_2^{2+}-selective electrode (S) and Hg_2^{2+}-extractive electrode (E) (ionic strength 1*M*, HNO_3)

Interfering cation ($10^{-3}M$)	Salt used	$K_{S_{Hg_2^{2+}}/M^{n+}}$	$K_{E_{Hg_2^{2+}}/M^{n+}}$
Ag^+	$AgNO_3$	1.0×10^2	1.0×10^2
Cu^{2+}	$Cu(NO_3)_2.5H_2O$	2.2×10^{-1}	3.2×10^{-2}
Cd^{2+}	$Cd(NO_3)_2.4H_2O$	1.2×10^{-3}	7.8×10^{-4}
Hg^{2+}	$Hg(NO_3)_2.2H_2O$	1.0×10^{-1}	2
Pb^{2+}	$Pb(NO_3)_2$	1.3×10^{-2}	3.2×10^{-3}
Ni^{2+}	$Ni(NO_3)_2.6H_2O$	2.3×10^{-2}	6.9×10^{-3}
Co^{2+}	$Co(NO_3)_2.6H_2O$	3.2×10^{-2}	7.9×10^{-3}
Pd^{2+}	$PdCl_2$	0.14×10^2	0.15×10^2

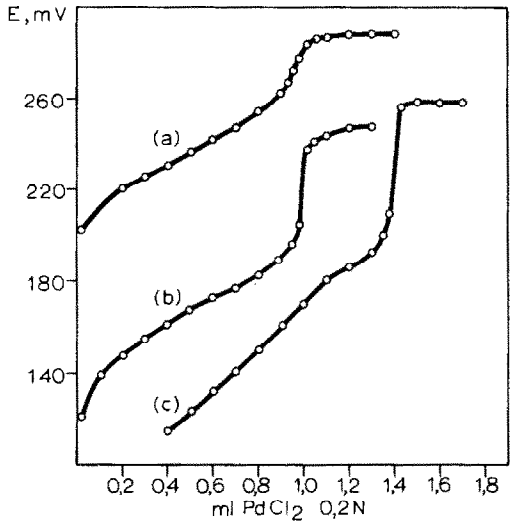

Fig. 3. Titration of 2 ml of 0.1*M* KI with 0.1*M* $PdCl_2$, in presence of 80 ml of 1*M* HCl (curve *a*), 80 ml of 0.1*M* HCl (curve *b*), 80 ml of 0.1*M* HCl and 10 ml of 0.1*M* KBr (curve *c*).

ration curve has two potential jumps, the first jump corresponding to the titration of the excess of iodide, and the second to titration of the chloride and the tetraiodomercurate according to the equation

$$2\,Hg_2^{2+} + HgI_4^{2-} + 2Cl^- = HgI_2 + Hg_2I_2 + Hg_2Cl_2. \quad (6)$$

The volume of Hg_2^{2+} solution used for the titration gives the chloride content of the compound, while the difference between the iodide added and found gives the mercury content of the sample.

Mercurous chloride. Hg_2Cl_2 can be analysed in the same way as $HgCl_2$, but the reaction (7) is very slow.

$$Hg_2Cl_2 + 4\,I^- \rightarrow HgI_4^{2-} + 2Cl^- + Hg. \quad (7)$$

However, the rate of reaction is increased considerably by addition of 5–15 ml of acetone. From the titration curve we can again determine simultaneously the chloride and the mercury content.

Mercuric oxide. To a beaker containing 0.01–2 meq of HgO add 1–10 ml of methyl ethyl ketone (in proportion). From a burette add with continuous stirring *A* ml of 10^{-1}–$10^{-2}M$ standard iodide solution until the solution becomes clear owing to formation of tetraiodomercurate:

$$HgO + H_2O + 4I^- \rightarrow HgI_4^{2-} + 2OH^-. \quad (8)$$

Add 10–100 ml of distilled water and acidify with 0.05–0.1*M* nitric acid. Titrate the excess of iodide with *B* ml of 10^{-1}–$10^{-2}N$ standard mercurous nitrate solution. In the titration the tetraiodomercurate complex is also destroyed:

$$HgI_4^{2-} + Hg_2^{2+} \rightarrow Hg_2I_2 + HgI_2. \quad (9)$$

From the difference $A - B$ calculate the mercury content of the sample.

Other inorganic mercury compounds. The determination of mercury in inorganic compounds and complexes can easily be done by appropriate treatment of the sample followed by titration with iodide or Hg_2^{2+}.

In the case of the chloro and bromo-complexes the mercury and the halide can be determined simultaneously, the actual problem being the titration of a mixture of I^- or Cl^-, which is dealt with below.

Organomercury compounds. The analysis of organomercury compounds consists in a titration with Hg_2^{2+} or I^- after wet-ashing of the sample. Wet-ashing can be done in many ways,[4] but the use of sulphuric acid with hydrogen peroxide or potassium nitrate is to be preferred.

We have analysed in this way all the organomercuric compounds used in agriculture, because the technique needs only between a hundredth and a tenth of the sample required by the CIPAC methods,[4] without loss of accuracy.

Determination of Hg_2^{2+}, Hg^{2+} and Ag^+ alone and in mixtures

Hg_2^{2+}, Hg^{2+} and Ag^+ alone can be easily titrated potentiometrically with a halide or sulphide standard solution and the extractive electrode, the results being remarkably accurate, but the extraction constants of these ions in the membrane are not sufficiently different to allow differential titration of these species in mixtures, and only the total metal ion concentration can be measured by simple titration. However, suitable treatment of the sample makes it possible to determine all three in mixtures.

Determination of Hg_2^{2+} in presence of all other ions. Dilute an aliquot containing 0.05–1 meq of Hg_2^{2+} to 20–100 ml with distilled water and adjust the pH to 2–4.5 with Michaelis buffer. Add, with stirring, an alcoholic solution of 2,4-D acid until a slight excess is present. Collect the precipitate on a rapid-filtration paper and wash until the washings give no reaction with diphenylcarbazone. Dissolve the precipitate and transfer it quantitatively (with or without the paper) with 10–250 ml of 2*M* nitric acid into the beaker used for the precipitation, and titrate the solution with 0.01–0.1*M* standard bromide solution.

Under these conditions Hg_2^{2+} can be determined with satisfactory precision in presence of all other ions with which it is compatible in solution (Table 2).

If the Hg^{2+} concentration is high, too large an excess of reagent should be avoided, or the quantity of n-propanol in the solution of 2,4-D acid should be increased.

Mixtures of Hg^{2+} and Ag^+. To a volume of about 10–80 ml containing 0.01–1 meq of Hg^{2+} and Ag^+ add 10–15 ml of 0.1*M* EDTA and adjust the pH to 5–8.5 with ammonia or sodium acetate buffer. Titrate with 0.01–0.1*M* standard bromide solution. Under these conditions only Ag^+ is titrated. The error does not exceed $\pm 0.1\%$. For the determination of the sum of Hg^{2+} and Ag^+ the titration is done in acid medium (0.01–1*M* nitric acid) with 0.01–0.1*M* standard iodide solution.

Table 2. Determination of Hg_2^{2+} in presence of Ag^+ and Hg^{2+}

No.	Hg_2^{2+} taken	Ag^+ added	Hg^{2+} added	Hg_2^{2+} recovered, %
	ml (0.1*N* solutions)			
1	1	5	5	98.8
2	2	5	5	99.2
3	3	5	5	99.6
4	4	5	5	99.5
5	5	10	7	99.8
6	7	10	7	100.2
7	9	10	7	100.5
8	11	15	9	99.6
9	13	15	9	99.4
10	15	15	9	100.1

Mixtures of Hg_2^{2+} and Ag^+. A titration with iodide will give the sum of both compounds. Hg_2^{2+} is then determined by the method involving precipitation with 2,4-D acid. Alternatively Hg_2^{2+} is oxidized to Hg^{2+} and Ag^+ is then determined as just described.

Mixtures of Hg_2^{2+} and Hg^{2+}. The sum of the two components is determined in one aliquot, and then Hg_2^{2+} is determined in another aliquot by titration after precipitation with 2,4-D acid.

When a more accurate determination is needed we convert the Hg_2^{2+} and Hg^{2+} into the chlorides, separate them by filtration, and determine them as described for analysis of the chlorides.

Mixtures of Hg_2^{2+}, Hg^{2+} and Ag^+. The sum of the three components is determined by titration with a standard iodide solution. Hg_2^{2+} is determined after separation as mercurous phenoxyacetate. For silver the procedure is the same as for its mixtures with Hg_2^{2+}.

The analysis of organic substances

Its use for the determination of organic substances is a most important feature of the ion-extractive electrode, and is based on the fact that many organic compounds contain chlorine, bromine or iodine, or can react with Hg_2^{2+}, Hg^{2+} or the mercury(II)–EDTA complex, giving reduction, addition or precipitation reactions.

Determination of mercury added in excess or contained in the precipitate gives the amount of organic compound in the sample. A few examples of determinations of some compounds are given here.

Phthalic acid. Adjust an aliquot containing 0.4–2 meq of phthalic acid to pH 1–3 with sodium acetate or acetic acid, and dilute to 25–100 ml. Heat to 60–90° and add an excess of mercurous nitrate solution. Cool and filter (medium-pore paper). Wash the mercurous phthalate precipitate until the washings show no reaction with bromide. Transfer the precipitate quantitatively (with or without the filter paper) into a beaker containing 100–200 ml of 2*M* nitric acid. Titrate with 0.1*M* potassium bromide.

The method is accurate (Table 3) even in the presence of halides, pseudohalides and sulphides.

Pyrethrins and formic acid. Crizantemic acid[4] and formic acid[5] reduce Hg^{2+} to Hg_2^{2+}. The mercury(I) thus formed is precipitated, separated and determined gravimetrically as Hg_2Cl_2. Of practical importance is the determination of pyrethrins after hydrolysis to crizantemic acid.[4] Determination of Hg_2Cl_2 by the method already described is a convenient and accurate means for the determination of pyrethrins and formate.

Aldehydes, hydroxylamine, hydrazine and its derivatives. Aldehydes, hydroxylamine and hydrazine and its derivatives reduce the mercury(II)–EDTA complex

Table 3. Determination of phthalic acid in presence of halides

No.	Phthalic acid taken, *mg*	KCl	KBr	KI	Phthalic acid recovered, %
		ml (0.1*N* solutions)			
1	33.2	—	—	—	99.3
2	41.5	—	—	—	99.6
3	66.4	—	—	—	99.5
4	66.4	5	—	—	99.7
5	83.0	5	—	—	100.1
6	99.6	—	5	—	100.0
7	116.2	—	5	—	99.8
8	132.8	—	—	5	100.1
9	166.0	—	—	5	99.8
10	166.0	5	5	5	99.9

in alkaline medium. Titration with Pb^{2+} of the complexone thus liberated (Methylthymol Blue as indicator) is an excellent method of determination.[6] An alternative is to determine the Hg^{2+} from the unreduced mercuric complexonate, with potassium iodide solution, in acid medium; this improves the sensitivity and accuracy of the method, thus making possible applications even to coloured samples.

To an aliquot containing 0.05–0.4 meq of reducing agent add 10–15 ml of distilled water, 10 ml of 0.01–0.1*M* mercuric complexonate and 2–10 ml of 10*M* potassium hydroxide. Leave the sample standing for 20–60 min, depending on the nature of the reducing agent.[6] Add an excess of 0.5*M* nitric acid and titrate with 0.01–0.1*M* potassium iodide. The presence of the EDTA does not affect the titration.

Potentiometric titration of I^-, Br^-, and Cl^- alone and in mixture

The existence of equilibria (1) and (2) in the membrane explains the functioning of the electrode in titration of halides with Hg_2^{2+} and *vice versa*. The sensitivity of the electrode and the insolubility of the mercurous halides lead to potential jumps at the equivalence point that are about twice as great as those obtained with the solid-state Orion 94-17 A electrode (about 120 mV for Cl^-, 240 for Br^-, 360 for I^-). Titration of $10^{-3}M$ bromide with $5 \times 10^{-4}M$ mercurous nitrate will give a potential break of about 30 mV.

The three halides must be titrated in 0.01–4*N* acid media, as outside this range the response of the electrode to Hg_2^{2+} is unstable. In choosing the acidity and concentration of the solution to be titrated, account must be taken of the influence of pH on the response of the electrode, the low stability of iodides towards acidity and the complexing of mercurous halides by alkali metal halides. Increasing the pH of the medium increases the potential jump at equivalence.

At acidities $< 1N$ the titration curves for Cl^- and Br^- suggest the initial formation of mercurous complexes which disappear with dilution or increased acid concentration.

Because of complexing by the disproportionation reaction

$$Hg_2X_2 + 2X^- \rightarrow [HgX_4]^{2-} + Hg \qquad (10)$$

in the titration of iodide Hg^{2+} species appear, leading to the formation of both Hg_2I_2 and HgI_2. However this phenomenon does not modify the stoichiometry of the reaction nor the precision, as the two salts have approximately the same solubility.

During the titration of Cl^- and/or Br^-, conditions leading to reaction (4) should be avoided if possible.

The values of K_2 varies with the halide: $K_{2_{I^-}} > K_{2_{Br^-}} > K_{2_{Cl^-}}$ and accordingly the three halides can be titrated in mixtures (Fig. 4). Such titrations are very accurate if before the first potential jump (titration of iodide), the acidity of the medium is increased to a maximum of 3*N* (nitric acid).

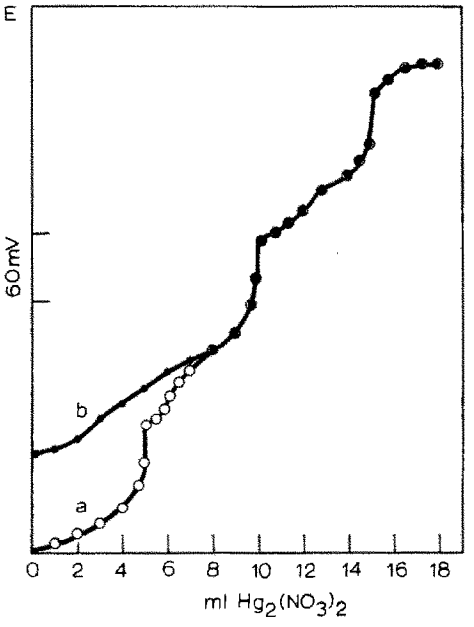

Fig. 4. Titration of mixtures of halides in 250 ml of 0.4*M* HNO_3. Curve (a) —●—●— 5 ml each of 0.1*M* KI, KBr, and KCl. Curve (b) —○—○— 5 ml each of 0.1*M* KCl and KBr.

CONCLUSIONS

We have proposed a new type of electrode (Hg_2^{2+}-extractive). The active substance of this electrode is formed in the membrane by extraction of Hg_2^{2+} from solution, whenever the electrode is used. The electrode can be used as indicating electrode in mercurometric and other titrations.

The construction of other such electrodes could widen the field of application of ion-selective electrodes, as they would make possible the use of less stable active substances.

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SHORT COMMUNICATIONS

INDIRECT DETERMINATION OF FLUORIDE BY EDTA BACK-TITRATION OF LANTHANUM

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Summary—Semimicro to macro amounts of fluoride ion (0.4–100 mg) are determined rapidly and accurately by precipitation with an excess of lanthanum at pH 2.5–2.8 by digestion on a water-bath, cooling to room temperature, addition of excess of EDTA and back-titration of the excess with zinc solution to the Xylenol Orange end-point at pH 5.8–5.9. Large amounts of chloride, acetate and perchlorate, and small amounts of sulphate and silicate do not interfere, but phosphate does. This method is much superior to the usual thorium nitrate titration method and can be applied after preliminary separation of fluorine by steam distillation or pyrolysis.

The thorium nitrate titration with Alizarin S as indicator[1–3] has widely been used for the determination of semimicro amounts of fluoride. However, the end-point is not very clear, and the range of concentration of fluoride for which the reaction is stoichiometric is rather narrow. Various indirect complexometric determinations of fluoride ion based on the low solubility of lanthanide fluorides have been reported. Combs and Gove[4] used samarium(III) for indirect determination of fluorine in various inorganic compounds. The reaction between fluoride and samarium was very slow, and the end-point became indistinct if a large amount of precipitate was present. Yamamura *et al.*[5] precipitated cerium(III) fluoride and titrated the excess of cerium(III) in the supernatant with EDTA after centrifuging. The procedure was time-consuming. Mizuno and Miyaji[6] determined micro-amounts of fluorine (0.05–2 mg) in organic compounds by EDTA titration of lanthanum after combustion in an oxygen-flask. When we tried this method, we found that the end-point was indistinct for larger amounts of fluoride ion, owing to adsorption of the indicator chelate on the precipitate. Hubicka and Sawicki[7] precipitated lanthanum fluoride at pH 2 and titrated the excess of lanthanum by adding an excess of EDTA and titrating with zinc at pH 8 with Eriochrome Black T as indicator. In our opinion, however, it is preferable to do the precipitation at pH 2.5–2.8 and the titration at pH 5.8–5.9.

In the present study, lanthanum was proved to be the most suitable of scandium, yttrium, and the lanthanides for indirect complexometric determination of semimicro and macro amounts of fluoride, and this method was compared with the thorium nitrate titration method.

EXPERIMENTAL

Reagents

Standard fluoride solution, 0.02*M*. Dissolve 0.8398 g of analytical grade sodium fluoride, dried to constant weight at 120–130°, in water and dilute accurately to 1000 ml.

Lanthanum nitrate solution, 0.01*M*. Dissolve 1.63 g of lanthanum oxide (99.99% purity) in 30 ml of nitric acid (1 + 10) and dilute to 1000 ml with water. Standardize against standard EDTA solution.

Cerium(III) nitrate solution, 0.01*M*. Dissolve 4.34 g of cerium(III) nitrate hexahydrate in 50 ml of nitric acid (1 + 30) and dilute to 1000 ml with water. Standardize against standard EDTA solution.

Yttrium, samarium, ytterbium and scandium nitrate solutions, 0.01*M*. Prepared from the oxides (99.9% purity).

Standard EDTA solution, 0.01*M*. Dissolve 3.74 g of disodium ethylenediaminetetra-acetate dihydrate in water and dilute to 1000 ml. Standardize against standard zinc solution.

Standard zinc solution, 0.01*M*. Dissolve 0.6537 g of metallic zinc (99.999% purity) in 30 ml of nitric acid (1 + 10) and dilute accurately to 1000 ml with water.

Monochloroacetic acid solution, 1*M*. Dissolve 47 g of monochloroacetic acid in water and dilute to 500 ml.

Hexamine buffer solution, 1*M*. Dissolve 35 g of hexamethylenetetramine in 200 ml of water and adjust the pH to 5.8–5.9 with hydrochloric acid (1 + 10) and dilute to 250 ml with water.

Xylenol Orange indicator solution, 0.05 *w*/*v*%. All other reagents were of analytical grade.

Procedure

To the solution containing 0.4–100 mg of fluoride, add a 40–130% excess of lanthanum nitrate solution and 2 or 3 drops of 1*M* monochloroacetic acid solution, and adjust the pH to 2.5–2.8 with dilute nitric acid or ammonia solution. Digest the mixture on a water-bath for 10–15 min and cool to room temperature. Add an excess of EDTA solution (equivalent to 1.0–2.5 times the amount of lanthanum added) and 5 ml of hexamine buffer solution, and adjust the pH to 5.8–5.9. Titrate with standard zinc solution to the Xylenol Orange end-point, the final volume of the solution being approximately 100–150 ml.

RESULTS AND DISCUSSION

Effect of pH on the precipitation of lanthanum fluoride

For the stoichiometric precipitation of rare earth metal fluorides, rather close pH control is required, because the hydrolysis of rare earth metals and the protonation of fluoride depend on pH. The optimum pH is reported to be 3.00 for samarium(III)[4] and 1.75 for cerium(III)[5]. It was determined experimentally for scandium, yttrium, lanthanum, cerium(III), samarium, and ytterbium, and the results are summarized in Fig. 1.

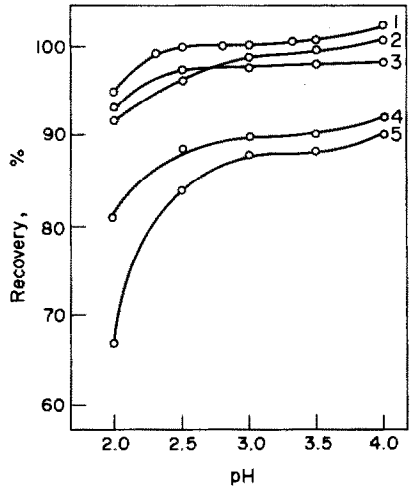

Fig. 1. 1: La, 2: Ce(III), 3: Y, 4: Sm, 5: Yb; Digestion time: La, Y: 10 min, Ce(III)., Sm, Yb: 30 min; $C_F = 2.10^{-3}M$, $C_M = 1.10^{-3}M$, $C_{EDTA} = 1.10^{-3}M$

With lanthanum, the precipitation of the fluoride was so rapid that digestion for only 10–15 min was sufficient. With metals other than yttrium, the precipitation was slower, especially with scandium, no precipitate being observed even after 2–3 hr. The optimum pH for the precipitation of lanthanum fluoride was in the range 2.5–2.8. Below pH 2.3, the precipitation was incomplete, and at pH 1.5, no precipitate was observed even after 2–3 hr. Increasingly positive errors were obtained as the pH was increased above 3.0.

Effect of the buffer

The effect of the buffer is shown in Table 1. The precipitation of lanthanum fluoride was more rapid when monochloroacetic, formic, or acetic acid was added. Monochloroacetic acid was the most efficient, and the optimum amount was 0.1–0.2 ml of 1*M* solution. Without it, no precipitate was observed even after 1 hr, for 4 mg of fluoride. With 1.0 ml, a colloidal precipitate appeared immediately at room temperature, but large positive errors resulted. With acetic acid, a larger amount was necessary, and the results were worse. Formic acid gave slightly better results than acetic acid.

Effect of the digestion time

The results were slightly low (by up to 2%) for digestion times shorter than 10 min but recovery was complete and practically constant for 10–60 min digestion times.

Effect of the excess of lanthanum

With 40–125% excess of lanthanum added, the recovery was almost constant, with relative error ±0.2%.

Dissolution of lanthanum fluoride in aqueous EDTA

As shown in Fig. 1, the results were best with lanthanum, and progressively poorer with cerium(III), yttrium, samarium and ytterbium. This may be related to the stability constants of their EDTA chelates and the solubility products of their fluorides. The stability constant of lanthanum–EDTA is the smallest (log *K*: Sc 23.1, Y 18.1, La 15.5, Ce(III) 16.0, Sm 17.1, Yb 19.5),[8] and lanthanum fluoride is the least soluble [K_{sp}: La $(1.4 \pm 0.1) \times 10^{-18}$, Ce $(1.4 \pm 0.2) \pm 10^{-18}$ Eu 2.2×10^{-17}, Gd $(6.7 \pm 0.2) \times 10^{-17}$][9]. Lanthanum fluoride is, therefore, the most difficult to dissolve in aqueous EDTA. Addition of up to a 200% or more excess of EDTA relative to the free lanthanum had no effect on the recovery. The recovery was constant up to 2 hr standing and decreased gradually as the standing time was increased.

Table 1. Effect of the buffer

pH	1*M* acid solution added, *ml*	Recovery %
	Monochloroacetic acid	
	0.1	99.4
2.3	0.2	99.2
	0.5	99.4
	1.0	99.5
	0.1	99.8
	0.2	100.0
2.5	0.5	100.7
	1.0	101.4
	1.0*	100.7
	0.1	100.0
	0.2	100.1
2.8	0.5	101.1
	1.0	102.5
	1.0*	102.0
	0.1	100.1
3.0	0.2	101.1
	0.5	101.8
	1.0	102.6
	Acetic acid	
	0.5	97.6
2.8	1.4	100.5
	2.8	102.5
	5.6	103.3
	Formic acid	
	0.3	99.8
	0.5	101.2
	1.4	102.7
	2.8	104.0

* Without digestion, F: 4 mg.

Indicator

Xylenol Orange, Methylthymol Blue, and arsenazo III were compared as indicators for the back-titration of the excess of EDTA with zinc solution. Xylenol Orange was the most suitable and yielded a sharp colour change from yellow to red-purple even when a large amount of lanthanum fluoride was present.

The excess of lanthanum could not be titrated directly with EDTA because of adsorption of the indicator chelate on the precipitate. Yamamura *et al.*[5] avoided the interference by centrifugation, as stated above. The adsorption could not be prevented by addition of various surfactants and coagulants, or oleic acid,[10] but if an excess of EDTA was added before the indicator, as suggested in the present method, the indicator chelate was not adsorbed.

Determination of various amounts of fluoride ion

The results of titration of 0.4–100 mg of fluoride ion are shown in Table 2. The relative error increases with amount of fluoride. The positive errors may be due to the adsorption or co-precipitation of lanthanum ion, and the negative ones to dissolution of some of the lanthanum fluoride precipitate. As the error increases uniformly with increase in the amount of fluoride, a correction can be applied.

Table 2. Results of determination of fluoride ion

F taken, *mg*	F found, *mg*	Difference, *mg*	Relative error, %
0.38_3	0.38_0	-0.00_3	−0.8
0.57_5	0.57_3	-0.00_2	−0.4
0.94_9	0.94_8	-0.00_1	−0.1
1.90_1	1.89_9	-0.00_2	−0.1
3.80_2	3.80_2	0.00_0	0.0
5.70_2	5.73_1	$+0.02_0$	+0.5
9.50_4	9.56_1	$+0.05_7$	+0.6
19.8_0	19.9_8	$+0.1_8$	+0.9
39.6_0	39.9_2	$+0.3_2$	+0.8
98.9_9	100.6_7	$+1.6_8$	+1.7

Table 3. Effect of foreign ions

Anion	Added ([Anion][F])	Recovery, %
Chloride	17	99.6
	48	98.7
Acetate	6	100.0
	25	100.4
Perchlorate	18	99.8
	36	99.4
Sulphate	0.5	99.8
	1.5	99.4
Silicate	1.0	99.8
	2.5	99.2
Boric acid	10	99.9
	40	100.2
Monohydrogen phosphate	2	—

F: 4 mg.

Effect of foreign ions

The effect of foreign ions is shown in Table 3. Large amounts of chloride (17-fold molar ratio to fluoride), acetate (25-fold), perchlorate (36-fold), boric acid (40-fold) and small amounts of sulphate (1.5-fold) or silicate (2.5-fold) do not interfere. Phosphate interferes remarkably, but the interference can be avoided by the steam distillation method.

Comparison with the thorium nitrate method

The present method was compared with the thorium nitrate titration method. The conditions in the present method, such as pH, amount of neutral salts and of anions which complex thorium, are not so severe as in the latter method. For comparison of the deviation from stoichiometry, the results of the photometric titration are shown in Fig. 2. The deviation from stoichiometry was very large when the amount of fluoride ion was decreased. The reaction ratio was 1:3.88 (La:F) for 3.8–7.6 mg of fluoride,

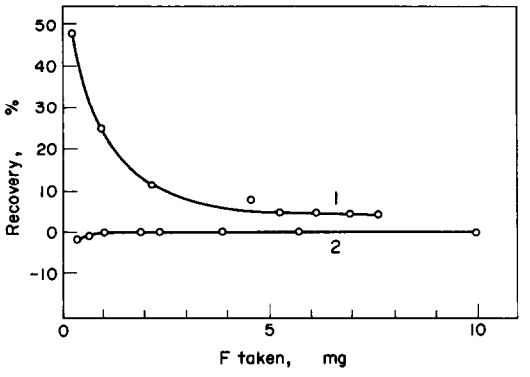

Fig. 2. 1: the thorium nitrate titration method, 2: the present method

where the titration error was within 1%, but below this range it changed remarkably. When the solution containing fluoride is titrated with metal ion M^{n+}, m in the complex ion $[MF_m]^{n-m}$ is at its maximum at the beginning, since the fluoride ion is present in large excess. As the titration proceeds, m decreases gradually as a mixture of complexes is formed. When a small excess of the metal ion is added to determine the end-point, especially when an insensitive indicator such as Alizarin S is used in the thorium nitrate titration, $n - m$ becomes positive. This is the reason why most direct titration methods for fluoride are accurate only for a narrow range of fluoride concentration.

On the other hand, in the present method, the deviation from stoichiometry is very small, the reaction ratio being 1:3 over the range 0.4–100 mg, increasing slightly with increase in fluoride ion.

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DETERMINATION OF STRONTIUM IN HUMAN TOOTH ENAMEL BY FLAMELESS ATOMIC-ABSORPTION SPECTROMETRY

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Summary—The determination of strontium in human tooth enamel by flameless atomic-absorption spectrometry was found to be subject to interference from the calcium/phosphate matrix of the enamel. The standard addition method was used to compensate for this interference. Hydrochloric acid and nitric acid did not affect the strontium absorption, but perchloric acid caused a significant reduction in the absorption. The sensitivity of the flameless atomic-absorption enabled 1-mg samples of enamel to be analysed. Hence, the proposed method can be used to determine the distribution of strontium through the tooth. An average recovery of 100.4% for amounts of strontium added to enamel showed that the proposed method was reliable.

A number of trace elements, including strontium,[1,2,3] have been reported to reduce the prevalence of dental caries. The strontium content of human tooth enamel varies according to the geographical origin[4,5] of the strontium and appears to be correlated with the levels present in food and drinking water.

The analysis of calcified tissues for strontium both by emission and atomic-absorption spectrometry has been found to be subject to serious interferences. Webb and Wordingham[6] observed interference from calcium and phosphate in the flame emission analysis of strontium in bone and teeth and overcame it by surrounding the oxygen–propane flame with a mantle of oxygen. Atomic-absorption determination of strontium in human tooth enamel[7] has also been found to be influenced by interference from calcium and phosphate in both air–acetylene and nitrous oxide–acetylene flames. This has been overcome to some extent in air–acetylene flames by the addition of perchlorate. The sensitivity is such that 0.1 g of tooth enamel is required for each analysis, which prevents the technique being used to assess the distribution of strontium through the tooth.

Recently, flameless atomic-absorption spectrometry has been applied to the analysis of human tooth enamel. Reda *et al.*[8] analysed surface enamel for zinc, copper, aluminium, iron, lead and manganese after digestion of the sample with hydrochloric acid. Langmyhr and Sundli[9] atomized cadmium and lead in human tooth enamel directly from the solid state. Dolinšek *et al.*[10] determined aluminium in both *in vitro* and *in vivo* human tooth enamel samples. Strontium has been determined in biological[11] and geological[12] samples by flameless atomic-absorption spectrometry. In the analysis of silicate rocks,[12] chemical interference was found to be caused by calcium.

EXPERIMENTAL

Apparatus

A Perkin-Elmer model 303 atomic-absorption spectrophotometer fitted with a recorder–read-out accessory and a Hitachi 165 recorder was used in conjunction with a Perkin-Elmer graphite cell HGA 74. The graphite tube was purged by argon at a pressure of 1.2 kg/cm,^{2} resulting in external and internal flow-rates of 900 and 300 ml/min respectively. The internal gas flow was stopped for the first 8 sec of the atomization stage of the heating programme. The spectral source was an "Intensitron" strontium hollow-cathode lamp, the 460.7-nm line being used. Eppendorf pipettes were used for the transfer of sample and standard solutions to the graphite tube.

Reagents

A 1000 μg/ml stock solution of strontium, prepared from strontium chloride, was used for the preparation of standards. Calcium and phosphate solutions used in the interference studies were prepared from analytical-reagent grade calcium chloride and orthophosphoric acid. Perchloric acid, nitric acid and hydrochloric acid used in the interference studies were B.D.H. "Aristar" grade.

Procedure

Separate the enamel and dentine from the tooth by mechanical means, and dry the enamel at 105° for 48 hr in an air-oven. Pulverize the enamel in an agate mortar and pestle to pass through a 100-mesh (149 μm) nylon-meshed sieve. Digest 1.0 mg of enamel in 0.5 ml of 1.0*M* hydrochloric acid at room temperature. When dissolution is complete, dilute to 2 ml with demineralized water.

Prepare standards with strontium concentrations of 0, 0.1, 0.2, and 0.3 μg/ml for the standard addition method. Transfer a 10-μl aliquot of the standard solution to the graphite tube and dry for 30 sec at 100°. On completion of the drying stage, add a 10-μl aliquot of the sample solution to the graphite tube. Atomize according to the conditions given in Table 1. By extrapolation of the graph of absorbance against strontium added, obtain the level of strontium in enamel.

RESULTS AND DISCUSSION

Interference by enamel matrix

In a preliminary investigation, the heating programme for maximum sensitivity was established. It is shown in Table 1.

Strontium standards (0.1 μg/ml) were prepared, containing either calcium or phosphate in a concentration range corresponding to the minimal and maximal levels possible in an aqueous solution of tooth enamel. Standards containing both calcium and phosphate in the same ratio as in enamel were also prepared. A 10-μl aliquot of the standard

Table 1. Heating programme for strontium

	Temp, °C	Time, *sec*
Drying	100	60
Charring	900	20
Atomization	2600	10
Clean-out	2700	10

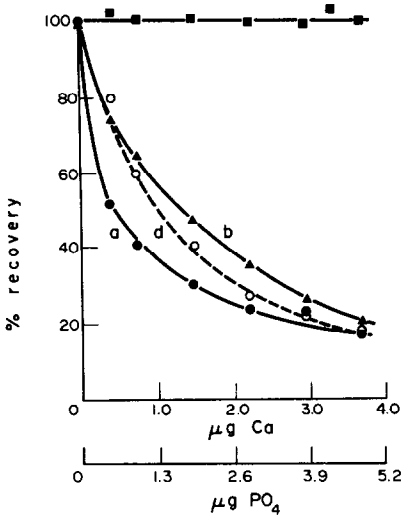

Fig. 1. Depression of strontium (1.0 ng) absorption due to increasing concentrations of (*a*) calcium, (*b*) calcium/phosphate, (*c*) phosphate, (*d*) calcium after charring at 1240°.

solution was transferred to the graphite tube and treated according to the conditions given in Table 1.

The results of these interference studies are shown in Fig. 1. Interference was produced by calcium alone (curve *a*) or in presence of phosphate (curve *b*), whilst phosphate (curve *c*) produced no interference. The calcium/phosphate interference was considerably less than the calcium interference. In the presence of calcium a small absorption peak occurred as the temperature increased from the charring temperature (900°) to the atomization temperature (2600°), and a second larger absorption peak occurred at the atomization temperature. This two-stage loss of strontium is shown in peak *a* in Fig. 2. No additional absorption peaks were observed in the presence of phosphate or calcium/phosphate. It is possible that in the presence of calcium/phosphate the two-stage atomization of strontium observed when calcium is present does not occur owing to some influence by the phosphate ions or to the formation of calcium phosphate (which would reduce the number of free calcium atoms available for interference).

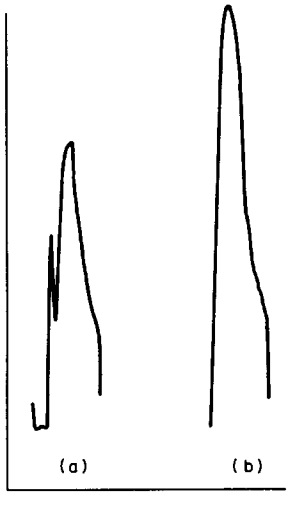

Fig. 2. Absorption peak of strontium (2.0 ng) in the presence of calcium (0.73 μg) after charring at (*a*) 900° (*b*) 1240°.

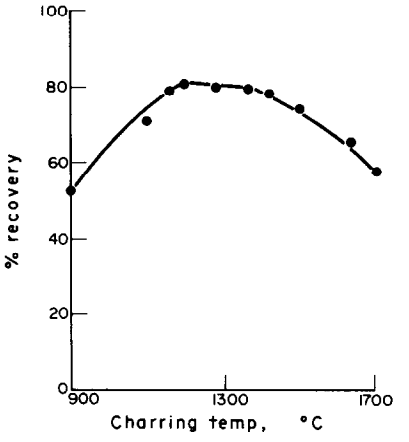

Fig. 3. Effect of increasing charring temperature on strontium (1.0 ng) absorption in the presence of calcium (367 ng).

Strontium standards (0.1 μg/ml) were prepared, containing either calcium (37 μg/ml) or calcium (37 μg/ml)/phosphate (52 μg/ml). A 10-μl aliquot of the standard solution was transferred to the graphite tube and atomized, at various combinations of charring and atomization temperatures.

Figure 3 shows the effect on the calcium interference when the charring temperature was increased. A significant reduction occurred in the calcium interference. A plateau region occurred between 1160° and 1420°. At temperatures above 1420°, strontium was probably lost during the charring stage; this was observed in the preliminary investigation at charring temperatures greater than 1500°. The optimum charring temperature for strontium in the presence of calcium and absence of phosphate was considered to be 1240°. Curve *d* in Fig. 1 shows the recovery of strontium in the presence of increasing calcium concentrations after charring at 1240°. Increase of the charring temperature from 900° to 1240° prevented the two-stage atomization of strontium, which had previously been observed in the presence of calcium. This is shown by peak *b* in Fig. 2. The charring temperature had no effect on the calcium/phosphate interference. Neither the calcium nor calcium/phosphate interference was reduced by increasing the char-

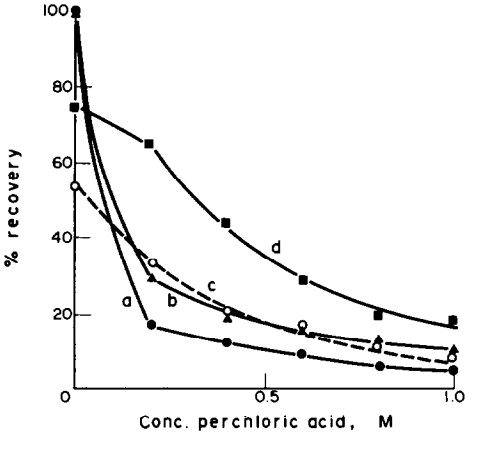

Fig. 4. Effect on strontium (1.0 ng) absorption of increasing concentrations of perchloric acid: (*a*) no additions, (*b*) +520 ng of phosphate, (*c*) +367 ng of calcium, (*d*) +367 ng of calcium and 510 ng of phosphate.

Table 2. Recovery studies (strontium present in enamel 102.4 ppm)

No of detns.	Added, *ppm*	Found, *ppm*	Recovery, %
3	40	142.5 ± 2.2	100.1 ± 1.6
4	100	204.7 ± 9.9	101.4 ± 4.9
4	140	241.6 ± 3.9	99.7 ± 1.6

ring time or by altering the atomization stage of the heating programme.

Interference by acids

Perchloric acid has previously been found to be a highly suitable digestion medium for enamel. Hence, its suitability for flameless atomic-absorption was investigated. Strontium standards (0.1 μg/ml) containing increasing concentrations of perchloric acid (up to 1.0*M*) were prepared with or without the presence of calcium (37 μg/ml), phosphate (52 μg/ml) or the calcium (37 μg/ml)/phosphate (52 μg/ml) combination. A 10-μl aliquot of the standard was transferred to the graphite tube and atomized according to the conditions given in Table 1. The results are shown in Fig. 4. In addition to the serious reduction in the strontium absorption it was observed that the variation between duplicate absorption measurements could be as great as 40%. Similar investigations were carried out to evaluate the interference effects of increasing concentrations of either nitric acid (up to 1.5*M*) or hydrochloric acid (up to 1.0*M*). Both acids were found not to interfere. Interferences produced by calcium, phosphate and calcium/phosphate in dilute solutions of hydrochloric acid (0.5*M*) and nitric acid (0.5*M*) were investigated for a range of interferent concentrations and found to follow the same trends as in aqueous solution (Fig. 1).

Calibration

The analysis of materials which are subject to serious chemical interference requires the use of calibration standards matched to the sample with respect to the concentration of the interferents. Alternatively, the method of standard addition can be employed, but use of this method requires a certain amount of caution. A bulk enamel sample of known strontium content was analysed by the procedures described, with use of the method of standard addition. Accurate and reproducible results were obtained for enamel samples of 0.5–2.0 mg.

Recovery studies

The recoveries of strontium added to samples of dried, powdered enamel before the digestion with hydrochloric acid are summarized in Table 2; the analysis was carried out by the procedure described. Analysis of enamel without any addition gave a mean strontium content of 102 ± 2.5 ppm (5 determinations, coefficient of variation 2.4%). An estimate of the precision was obtained from the results for five aqueous solutions of enamel, each containing 0.63 ng of strontium. These samples gave a mean absorbance of 0.0515; the standard deviation was 0.0006 and the coefficient of variation 1.3%.

CONCLUSION

In the flameless atomic-absorption determination of strontium in human tooth enamel, the calcium/phosphate matrix of the enamel results in a reduction in the strontium absorption. This interference can be compensated for by the use of the standard addition method, which ensures that both sample and standard are matched with regard to amount of interferents and total solids. Of the acids investigated, hydrochloric and nitric acid do not interfere, but perchloric acid significantly reduced the absorption and results in non-reproducible absorption measurements. The sensitivity for strontium by flameless atomic-absorption was found to be 0.006 μg/ml for 1% absorption. This shows a significant improvement over the sensitivities[7] obtained with either air–acetylene or nitrous oxide–acetylene flames, 0.36 and 0.26 μg/ml for 1% absorption respectively. This improved sensitivity allows enamel samples of 1.0 mg to be analysed. Hence, flameless atomic-absorption can be used to follow the distribution of strontium through the tooth, whereas the flame atomic-absorption methods are limited to the determination of strontium in whole enamel.

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AN IMPROVED TURBIDIMETRIC PROCEDURE FOR THE DETERMINATION OF SULPHATE IN PLANTS AND SOILS

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Summary—A rapid turbidimetric procedure for the determination of sulphate in soils and plants has been developed with sorbitol as stabilizing agent. When used in a concentration of 20% in the final volume, the sorbitol regulates the size of the $BaSO_4$ particles formed and stabilizes them against sedimentation, growth and aggregation for long periods of time. The conditions of precipitation are not rigorous, as they are in similar procedures. Linearity of the calibration curve up to 50 ppm of sulphate and good reproducibility are special attributes of the procedure.

The importance of sulphur as a bioelement in agriculture is receiving considerable attention in the developing countries, because of the rapid depletion of this element in the soils as a result of the changeover to sulphur-free fertilizers. Among the various methods of determination of sulphate in soils and plants, the turbidimetric procedure offers much in the way of rapidity and suits best for routine tests. The major criteria for the reliability of turbidimetry consist in (*i*) a uniform finely distributed solid phase in the dispersing medium; (*ii*) stability of the suspension with time; (*iii*) absence of aggregation of the suspensoid during the analysis time. The procedures described in the literature[1–5] all involve the use of protective colloids such as gums, gelatine, glycerol or peptone to confer a certain degree of stability on the suspension, but leave much to be desired in respect of the other criteria, as the empirical conditions prescribed such as time limits for the reading, regulation of temperature, particle size of the precipitant, *etc.*, are rather too stringent for routine analysis.

In our search for a reagent that would stabilize the barium sulphate suspension, and at the same time control the fineness and uniformity of the suspended particles and prevent their growth or aggregation with time, we found sorbitol to meet our requirements. Sorbitol, commercially available either as a powder or as a 70% aqueous solution possesses a high viscosity even after further dilution of the solution[6] and is not attacked by dilute acids and alkalis, such as those usually present in soil and plant extracts. When used in concentrations of about 20% in the final volume, it regulates the formation of fine-sized barium sulphate particles, preserves the suspension against rapid sedimentation and also hinders growth and aggregation of the particles for as long as 6 days, irrespective of the conditions of precipitation, *i.e.*, temperature of the solution, size of the barium chloride crystals, method of precipitant addition, shaking routine, *etc.*

EXPERIMENTAL

Reagents

Hydrochloric acid, 6*M*.
$BaCl_2 \cdot 2H_2O$ *crystals.*
Sorbitol, 70% *aqueous solution.*

Procedure

To a 10 ml-aliquot of the extract in a 19-mm test tube, or to a smaller aliquot diluted to 10 ml with demineralized water, add 1 ml of 6*M* hydrochloric acid followed by 5 ml of 70% sorbitol solution from a pipette with an enlarged jet and finally about 1 g of $BaCl_2 \cdot 2H_2O$ crystals (from a measuring spoon). Shake vigorously to dissolve the barium chloride and allow to stand for at least 5 min, then read the turbidity of the suspension in a photoelectric colorimeter at 470 nm, along with standards prepared in the same way and covering the sulphate concentration range 0–50 ppm. If the suspension has had to stand for a particularly long time it is advisable to shake the tube gently before reading.

Table 1. Statistical evaluation of calibration curves

Test parameters	Chesnin and Yien	Blancher *et al.*	Bardsley and Lancaster	Proposed method	Steinbergs	Obermer and Milton
Approximate range of linearity, *ppm*	20	20	15	50	30	30
Variance for difference between replicates, sampling error, s^2	37.6	24.0	21.4	0.6	11.7	4.3
Slope of the curve, *b*	3.2	2.8	1.9	1.1	1.2	1.0
Expected precision when linear portion of curve is used, $s/b = \lambda$	1.9	1.8	2.5	0.7	2.8	2.1

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Table 2. Recovery of added sulphate

Material	Ammonium sulphate dressing in the field, *ton/hectare*	Mean sulphate content in the original material *ppm*	Mean sulphate content in the enriched material, *ppm*	Recovery, %
Potato leaf	0	658	1643	98.8 ± 0.7
	0.5	1479	2453	99.0 ± 0.9
	1.0	1850	2840	99.2 ± 0.8
Potato tuber	0	395	1345	96.4 ± 1.8
	0.5	488	1451	97.5 ± 1.0
	1.0	511	1481	98.0 ± 1.2

RESULTS AND DISCUSSION

The proposed procedure was compared with five of the earlier turbidimetric methods of determination of sulphate, with the relevant statistical test parameters[7] given in Table 1.

The data show that the proposed method is superior to the others tested, for the following reasons: (*i*) the value of λ is the lowest, which gives it the greatest precision, (*ii*) the linear working range is the widest, and (*iii*) the standard deviation of the measurement is the lowest.

The proposed procedure has a wide range of tolerance for the reagents used; no cognizable variation in the colorimeter readings for a given concentration of standard sulphate solution was noted with the addition of 0.5–3 ml of the acid, 0.5–4.0 g of barium chloride, and 2–10 ml of sorbitol solution. The size of the barium chloride crystals used had no pronounced effect, unlike the other reported methods. No influence of the working temperature, up to 30°, on either the reproducibility or the sensitivity was observed.

None of the normal constituent ions of soil and plant extracts was found to interfere; under the conditions of the procedure, nitrate and phosphate did not appear to be co-precipitated even at as high a concentration as 5000 ppm, so the proposed procedure is particularly suited to the determination of sulphate in plants after digestion with nitric and perchloric acids, or in soils after extraction with 0.1*M* potassium dihydrogen phosphate.[8]

Another attribute is the stability of the dispersed phase. The rate of settling of the suspension was extremely slow, complete sedimentation taking about 20 hr, and microscopic examination of the suspensoid showed no increase in the size of the particles, even after 6 days, and the turbidity readings were highly reproducible during the same period if the suspension was gently shaken before being read. The suspensions obtained by other procedures settled within an hour and invariably aggregated after long standing, the most unsatisfactory in this respect being the one prepared according to Steinbergs[3] with glycerol as stabilizer.

Recovery studies were made to evaluate the procedure for the determination of sulphur in the leaves and tubers of the potato. Samples of the dry materials from a field experiment, 0.5 g each in weight, were digested with a 9:4 mixture of nitric and perchloric acids, with and without the prior addition of 0.5 mg of sulphate (as a solution of potassium sulphate) to the samples. The digest was diluted to 25 ml and sulphate was determined in aliquots by the proposed procedure. The results (Table 2) show good recovery of the added sulphate, establishing the suitability of the procedure.

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TITRIMETRIC ESTIMATION OF PHOSPHATE, MOLYBDATE, TUNGSTATE AND SULPHATE WITH LEAD NITRATE SOLUTION, USING 1,2-NAPHTHOQUINONE-2-SEMICARBAZONE-4-SULPHONIC ACID (NQS-4S) AND 1,2-NAPHTHOQUINONE-2-THIOSEMICARBAZONE-4-SULPHONIC ACID (NQTS-4S) AS VISUAL INDICATORS

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Summary—The use of 1,2-naphthoquinone-2-semicarbazone-4-sulphonic acid and 1,2-naphthoquinone-2-thiosemicarbazone-4-sulphoic acid as indicators in the titrimetric estimation of phosphate, molybdate, tungstate and sulphate with lead has been examined. The precision, accuracy and applicability of the methods have been evaluated.

Püschel *et al.*[1–7] have reported the use of PAR as indicator in titrimetric estimation of molybdate, tungstate, phosphate and sulphate with lead nitrate solution under specified conditions. Sommer and Janošcová[8] have established the conditions under which PAR, TAR, TAMP and 1-PAN-4S can be used as indicators in titrimetric estimation of phosphate, molybdate, tungstate and sulphate. They have also mentioned the difficulty in estimation of tungstate and sulphate.

The present study shows that NQS-4S and NQTS-4S can be used successfully as visual indicators for rapid titrimetric estimation of these anions by titration with lead nitrate solution. The titration of sulphate and tungstate by precipitation with lead nitrate solution is easy and accurate under specified conditions.

EXPERIMENTAL

Reagents

Standard lead nitrate solution. Prepared in doubly distilled water containing a few drops of dilute nitric acid. Standardized complexometrically with EDTA (Xylenol Orange as indicator).

Sodium molybdate solution. Standardized gravimetrically.

Sodium tungstate solution. Standardized gravimetrically.

Dipotassium hydrogen phosphate solution, 0.1*M*.

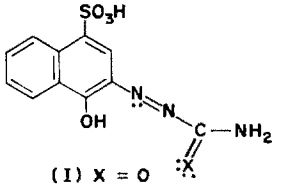
Potassium sulphate solution, 0.1*M*.

Indicator solution, 0.1%.

Buffers, 0.5*M*. Hexamine buffers of pH 6.0 and 7.0, and pyridine buffers of pH 5.0–7.0 were prepared[8] by adjusting the pH with nitric acid under control with a pH-meter.

Analytical-grade reagents and doubly distilled water were used for the standard solutions.

NQS-4S and NQTS-4S. Prepared by the method of Gummerus,[9] by condensing semicarbazide hydrochloride or thiosemicarbazide hydrochloride with sodium 1,2-naphthoquinone-4-sulphonate. The compounds were isolated, purified and characterized. NQS-4S: found C 43.9%, N 14.1%; required C 44.7%, N 14.3%. NQTS-4S: found C 42.6%, N 13.3%; required C 42.4%; N 13.5%; the infrared and NMR spectra are similar to those of the potassium salts of NQS-4S and NQTS-4S[10] and justify the structures I and II for NQS-4S and NQTS-4S respectively.



(I) X = O
(II) X = S

Titration procedures

NQS-4S (0.1–0.5 ml of 0.1% solution) is suitable for titration of 0.5–30 mg of phosphate, 1–50 mg of molybdate, 9–18 mg of tungstate in 20 ml of solution or 10–50 mg of sulphate in 10 ml of 30% methanol solution, with 0.01 or 0.1*M* lead nitrate, at a temperature of 20–80°. The pH of the titrant should be 6–7 for phosphate, molybdate and tungstate (1 ml of buffer) and ~5 for sulphate (2 ml of buffer). The colour change is from greenish yellow to pink. In the tungstate titration the concentration of the lead solution must be at least five times that of the tungstate. In the sulphate titration the results are satisfactory only for 0.1*M* sulphate; more dilute solutions need great care in the titration.

NQTS-4S (0.1–0.4 ml of 0.1% solution) is equally suitable for the same ranges of phosphate, molybdate and tungstate, but the end-point occurs prematurely for sulphate. The solution should be heated to 60° for titration, 2 ml of buffer should be added, and the colour change is from yellow to pink.

The relative error is generally in the range 0.2–0.8%.

Interferences

Fluoride, sulphate, sulphite, persulphate, borate, oxalate, and tartrate interfere, as do any ions that form precipitates or complexes with lead (thus phosphate will interfere with the other titrations, *etc.*). Nitrate, nitrite, thiocyanate, thiourea (50 mg of each), bromide, chloride and acetate (20 mg of each) do not interfere.

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EXTRACTIVE SEPARATION OF TUNGSTEN AS PHOSPHOTUNGSTATE

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(*Received* 10 *March* 1976. *Accepted* 25 *August* 1976)

Summary—Tungsten can be extracted quantitatively as phosphotungstate in micro as well as milligram concentrations by extraction with MIBK from 0.1–1*M* hydrochloric acid if the w/w tungsten:phosphorus ratio = 7, and separated from Fe, Ni, Co, Cr, Mn, Cu, Ca, U, Th, As, Sb, Bi and Si, after reduction of Fe(III) and Cr(VI) with thiosulphate, in natural and industrial samples. Mo and V suppress the extraction of tungsten and therefore require prior separation. The method takes 15 min for a single separation and gives highly satisfactory results with an overall error of about 0.1–0.2% over the range 10–100 mg tungsten in the sample.

Tungsten has been extracted in microgram amounts as its complex with oxine,[1a,2] thio-oxine,[3] polyphenols,[4,5,6] dithiols,[1b,7] or xanthate[8] into organic solvents for its determination, and with substituted hydroxylamines[1c,1d] for its separation. Its complexes with thiocyanate,[9] peroxide,[10] chloride,[11] fluoride[12] and phosphate[13] have also been shown to be extractable into organic solvents. Extraction of the thiocyanato complex with various solvents has been used for determination of tungsten[9,14] and that with tribenzylamine for its separation from other elements, both in microgram and milligram quantities.[15] Extraction of the peroxo-complex with a quarternary amine[10] and of the chloro-complex with tributyl phosphate[11] can separate tungsten from many elements; extraction of the fluoro-complex with octylamine[12] can separate it from molybdenum. Extraction of the phosphato-complex[13] with 1-pentanol is, however, neither quantitative, especially at lower concentrations of tungsten, nor selective.

We report below our studies on extraction of the phosphato-complex, which show that both microgram and milligram amounts of tungsten can be quantitatively extracted and separated from almost all analytically important elements.

EXPERIMENTAL

Reagents and solutions

Tungsten solution. Sodium tungstate was dissolved to give a tungsten concentration of about 1 mg/ml, and the solution was standardized volumetrically with iron(III).[16]

Phosphate solution. Trisodium orthophosphate was dissolved to give a phosphorus concentration of 10 mg P/ml, and further dilutions were made as desired.

Methyl isobutyl ketone (MIBK). Distilled, and the 114–115° fraction used.

Sodium thiosulphate solution, 40%.

Procedure

Solvent extraction of tungsten. To a solution of the sample in a separating funnel, add phosphate solution to give a W/P w/w ratio = 7 and adjust with hydrochloric acid to a suitable acidity and volume as given below, depending on the amount of tungsten. Extract with three 20-ml portions of MIBK, shaking for 1 min each time.

(a) For >20 mg of tungsten, neutralize the initial aqueous phase to litmus with sodium hydroxide, then add enough hydrochloric acid and water to give 20 ml of 1*M* hydrochloric acid solution. After the second extraction add 1.7 ml of 10*M* sodium hydroxide and 3.3 ml of water to reduce the acidity to 0.1*M*.

(b) For 8–20 mg of tungsten, make the aqueous phase 1*M* in hydrochloric acid with a volume of 20 ml, as in (*a*). After the first extraction adjust the acidity to 0.5*M* by addition of 1.0 ml of 10*M* sodium hydroxide, and after the second extraction adjust again to 0.1*M* by adding 0.7 ml of 10*M* sodium hydroxide and 3.3 ml of water.

(c) For 1–8 mg of tungsten, make the initial phase 0.5*M* in hydrochloric acid with a volume of 20 ml. After the first extraction adjust the acidity to 0.1*M* by addition of 0.7 ml of 10*M* sodium hydroxide and 4.3 ml of water.

Back-extraction of tungsten. Combine the three extracts in a separating funnel and back-extract with 20 ml of water at pH 10, shaking for 2 min. Combine the aqueous extracts, heat just to the boil and filter off any traces of hydroxide precipitate, washing the precipitate with three 5-ml portions of water.

Modification for iron(III) and chromium (VI)

These should be reduced to iron(II) and chromium(III) by dropwise addition of sodium thiosulphate solution (2 and 3 ml respectively for each 100 mg[17]) to the sample solution having an acidity of 1*M* hydrochloric acid before the tungsten is extracted.

Modification for silicon

Before separating the layers after each extraction, add 3 drops of alcohol and mix them into the solvent phase by gentle swirling, to clarify the solvent layer. Filter the combined solvent phases through Whatman No. 41 paper before back-extraction.

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Before separating the layers after each extraction, add 3 drops of alcohol and mix them into the solvent phase by gentle swirling, to clarify the solvent layer. Filter the combined solvent phases through Whatman No. 41 paper before back-extraction.

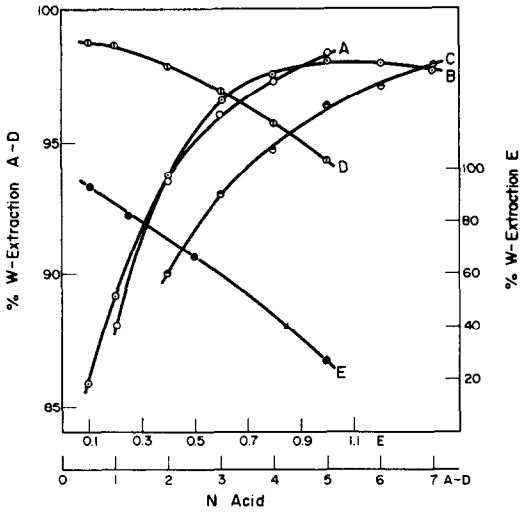

Fig. 1. Dependence of phosphotungstate extraction with MIBK on acid (curves and corresponding scales on axes indicated by same letter). *A* to *E*—10, 5, 5, 1, 0.02 mg W/ml and 7, 10, 10, 7, 0.06 W/P respectively. *C*—H_2SO_4 medium, others HCl medium.

Samples

Industrial samples. Ferrotungsten A and B (100 mg) were opened out by standard methods,[1e,14] the solutions were made up accurately to 50 ml, and aliquots were used for analysis.

Synthetic samples. Prepared by mixing solutions of the ions to give the compositions shown in Table 4.

Determination of the elements

Less than 5 mg of tungsten was determined by the Hg–SCN method.[14] Higher amounts were determined volumetrically[16] after destruction of any thiosulphate by hydrogen peroxide in ammoniacal medium.[18] Other elements were tested for by conventional sensitive colorimetric methods.[19,20]

RESULTS AND DISCUSSION

Morrison and Cosgrove[13] extracted phosphotungstate with 1-pentanol from 3*M* sulphuric acid. They showed that the extraction was 99% complete at 6.6 mg/ml but decreased with tungsten concentration, and that other elements such as iron and chromium were also well extracted under the conditions used.

The extraction of phosphotungstate depends on the nature and concentration of the acid, the W/P ratio and concentration of tungsten. The extraction is higher in hydrochloric acid than in sulphuric acid up to nearly 7*M* (Fig. 1, curves B and C). The acidity of maximum extraction depends on the tungsten concentration. Higher tungsten concentrations require higher acidity (Fig. 1, curves A and B) and lower concentrations require lower acidities (Fig. 1, curves D and E); in both cases, the extraction increases with concentration of tungsten, reaching a maximum of about 98.5% at 0.5 mg/ml in 1*M* hydrochloric acid and 5.0 mg/ml in 5*M* hydrochloric acid (Fig. 2, curves C and D). At lower concentrations of tungsten, the extraction is nearly constant for W/P w/w ratios from 2 to 20 with a slight increase at W/P <2 (Fig. 2, curve B). For higher tungsten concentrations, the extraction is erratic for different W/P ratios; however, it is above 98% for W/P ≤ 1 and 3–10, decreasing at still higher values (Fig. 2, curve A). The extraction procedure has been arranged on the basis of these studies, taking into account the lowering of the tungsten concentration in the aqueous phase after each extraction, and the range of 4–75% tungsten found in various samples ranging from steels to ferrotungstens. A small amount of acid is extracted by MIBK and this is taken into account in readjusting the acidity for later extractions. If the instructions are followed, over 90% of the tungsten is extracted after each equilibration with the solvent and after the three extractions over 99.9, 99.8 and 99.5% tungsten is extracted in the procedures *a*, *b* and *c* respectively.

Though the water immiscible oxygenated solvents extract tungsten efficiently and to about the same extent (Table 1), either MIBK or amyl acetate can be recommended because of their selectivity, and the former because of its lower boiling point. Solutions of the tertiary amines in chloroform extract tungsten almost equally well but do

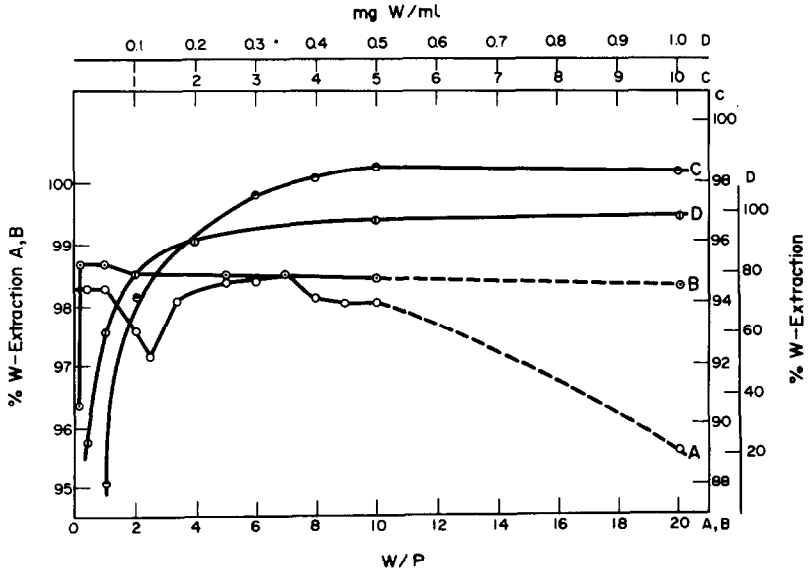

Fig. 2. Dependence of phosphotungstate extraction with MIBK on W/P and W/ml (curves and corresponding scales on axes indicated by same letter). *A*, *B*—5, 0.5 mg W/ml, 5*M*, 1*M* HCl respectively. *C*, *D*—5*M*, 1*M* HCl respectively at W/P = 7.

Table 1. Extraction of phosphotungstate into various solvents*

Solvent	Extraction,† %
Chloroform + ethanol	88.8
Isoamyl acetate	98.4
Methyl isobutyl ketone	98.5
Isoamyl alcohol	99.1
Tri-n-octylamine§	96.6
Tri-n-hexylamine§	97.2
Tri-n-butylamine§	99.0

* W = 5 mg/ml; acidity = 5*M* HCl.
† By difference; W determined in aqueous phase by Hg–SCN method.[14]
§ 1% v/v in chloroform.

not offer any advantage. They form a stable emulsion at the interface, and this has to be filtered off for separation of the solvent layer. Tribenzylamine forms unbreakable emulsions.

Acetate, chloride and sulphate (5% w/v) enhance the extraction by 5–7%. Tartaric acid (15% w/v) almost completely suppresses the extraction but up to 1.5% w/v can be tolerated. Citrate, fluoride and oxalate almost completely suppress the extraction (Table 2). Hydrogen peroxide has little effect.

Fe(III), Cu(II), Bi(V). Sb(V), As(V), after reduction with thiosulphate, and Mn(II), Si(IV). U(VI) and Ca(II), affect the extraction of tungsten by ±1%; Cr(III), Co(II), Ni(II) suppress the extraction by about 3% and Th by about 13% (Table 3). These elements are only slightly extracted (Table 3) and are either completely removed by filtration of the alkaline back-extract or remain in traces at the level of around 0.5% of their original amount. Molybdenum and vanadium considerably suppress the extraction of tungsten, perhaps by formation of ternary heteropoly complexes. Reducing agents should be oxidized to avoid formation of "heteropoly blue". Tungsten is not lost by adsorption on the small amount of hydroxide precipitate filtered off from the back-extract.

Applications

The method is applicable for quantitative separation of tungsten both in microgram and milligram amounts in various samples from other analytically important elements, by use of ordinary, inexpensive reagents and solvents. Only thorium, molybdenum and vanadium interfere, by strongly suppressing the extraction, and require prior separation. For >50 mg of tungsten in the sample this method is preferable to the thiocyanate separation method.[16] The usefulness and wide applicability of the method are shown by the satisfactory results for analysis of several samples (Table 4). A single separation requires only 15 min.

Table 2. Effect of anions on the extraction of phosphotungstate*

Salt	Amount *g*	Extraction,† %
None	—	90.1
Sodium chloride	1.0	97.3
Sodium sulphate	1.0	97.7
Sodium acetate	1.0	95.8
Potassium citrate	1.0	10.8
Potassium hydrogen fluoride	1.0	4.0
Potassium oxalate	1.0	2.6
Tartaric acid	0.3, 3.0	94.4, 0.8
Hydrogen peroxide (20 vol.)	1.5 ml	90.7

* W = 5 mg/ml; acidity = 1*M* HCl.
† By difference; W determined in aqueous phase by Hg–SCN method.[14]

Table 3. Coextraction of cations and their effect on the extraction of phosphotungstate (50 mg of W; [HCl] 1*M*)

Cation	Amount (mg)	% Extraction of Cation†	% Extraction of Tungsten§
None	—	—	98.4
Fe(III)*	950	0	98.2
Mn(II)	25	0	97.5
Cu(II)	200	0.6	98.9
Cu(II)*	50	0.6	99.0
Bi(V)	10	1.1	94.5
Bi(V)*	10	0.7	98.7
Sb(V)	10	1.4	92.6
Sb(V)*	10	0.1	97.2
As(V)	10	1.2	99.5
As(V)*	10	0.4	99.5
Si(IV)	50	1.1	99.4
U(VI)	50	0.2	98.5
Ca(II)	50	0.02	98.8
Ni(II)	350	0	95.1
Co(II)	300	0	95.0
Cr(III)	250	0.05	94.1
Th(IV)	50	0.3	85.7

* Reduced with sodium thiosulphate solution.
† Determined in the back-extract from the solvent phase[19,20] after filtering off any hydroxide precipitate.
§ By difference; W determined in aqueous phase by Hg–SCN method.[14]

Table 4. Analysis of samples by the proposed method

Sample composition Other elements,* *mg*	Tungsten, *mg*	Tungsten found, *mg*
Fe(54), Co(40), Cr(3)	2.0	1.99
Fe(92), Cr(0.7), Mn(0.3), Si(0.3)	5.0	4.98
Fe(68.1), Cr(20), Ni(7), Mn(0.5),	4.0	3.98
Co(60), Cr(22.5)	15.0	14.96
Fe(189)	10.0	9.98
Fe(28), Mn(0.2), Si(0.4), Cu(0.5), As(0.05)	70.0	69.9
Ferrotungsten A, 75.2% W	—	75.1%
Ferrotungsten B, 73.3% W	—	73.2%

* Samples 1–6 are analogous to K.S. Magnet steel, low-alloy instrument steel CHV5, Midvale HR, stellite, tungsten steel and ferrotungsten USSR respectively.

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Summary—Amperometric titration has been applied to study parameters determining the extent of mutual co-precipitation of lead and barium in the formation of their chromates. The anomalous behaviour of dichromate due to repulsion at the dropping mercury electrode, which severely affects the precision of the measurements, has been eliminated by addition of tetrabutylammonium hydroxide. By this modification the amperometric end-point detection has been extended to higher concentrations of the reagent and a wider pH range of the medium as required for this study. Shifts in the distribution of chromium species, slow evolution of the precipitate and, in the case of lead, its varying composition, all depend on pH and ionic strength. They have been identified as limiting factors in the amperometric titration of lead and barium and optimum conditions found for their determination. The applicability of the technique to practical analysis is limited, but in the absence of ions which precipitate at the required pH, it permits precise and accurate titration of lead in the presence of barium at pH 2–3 and of their sum at pH 5–6.

Amperometric determination of lead and barium with chromate was proposed by Kolthoff *et al.*[1] who also drew attention to the mutual interference of these two ions because of co-precipitation. Titrations of lead as well as of barium were later recommended by several authors[2–9] as accurate and precise and the barium titration was also used for indirect determination of sulphate.[6,8] Its applicability, however, is seriously limited by the solubility of barium chromate, and in this study several parameters which influence the accuracy and precision have been considered, leading to optimum conditions for precipitation and for amperometric titrations of the two ions with potassium dichromate.

EXPERIMENTAL

Apparatus

The apparatus, consisting of a 6-V battery coupled to a 200-ohm (ten-turn) potentiometer, glass cells with "Teflon" covers carrying a dropping mercury electrode, an electrolytic junction, saturated calomel electrode, tubing for bubbling with nitrogen, and the tip of 10-ml piston burette (Metrohm E274 accurate to ± 0.02 ml and with reproducibility of ± 0.005 ml), was assembled in the laboratory. The diffusion current was measured with a galvanometer.

Reagents

Standard solutions were prepared from barium and lead nitrates; potassium dichromate solution (0.0167*M*) was made by diluting the contents of an ampoule ("Fixanal") to appropriate volume and was used without further standardization. Other reagents included potassium nitrate, sodium acetate buffer (0.5*M*), Triton X-100, tetrabutylammonium hydroxide and ethanol.

RESULTS AND DISCUSSION

The composition of the electrolyte has to fulfil the requirements of the amperometric end-point detection, *viz.* it should not interfere with the electrode reaction of the depolarizer at the selected potential and must simultaneously act as a buffer. The presence of the electrolytes necessary to keep the conductivity of the solution constant results in an increase in solubility of the precipitate, which cannot be entirely avoided. There is considerable discrepancy in the literature as to their effect. Tenkovtsev,[6] who studied the effect of several chlorides of uni- and bivalent metals in concentrations between 0.5 and 1.0*M*, claims that their effect on the accuracy is less than 1.0%; according to his observations precipitation is rapid and quantitative

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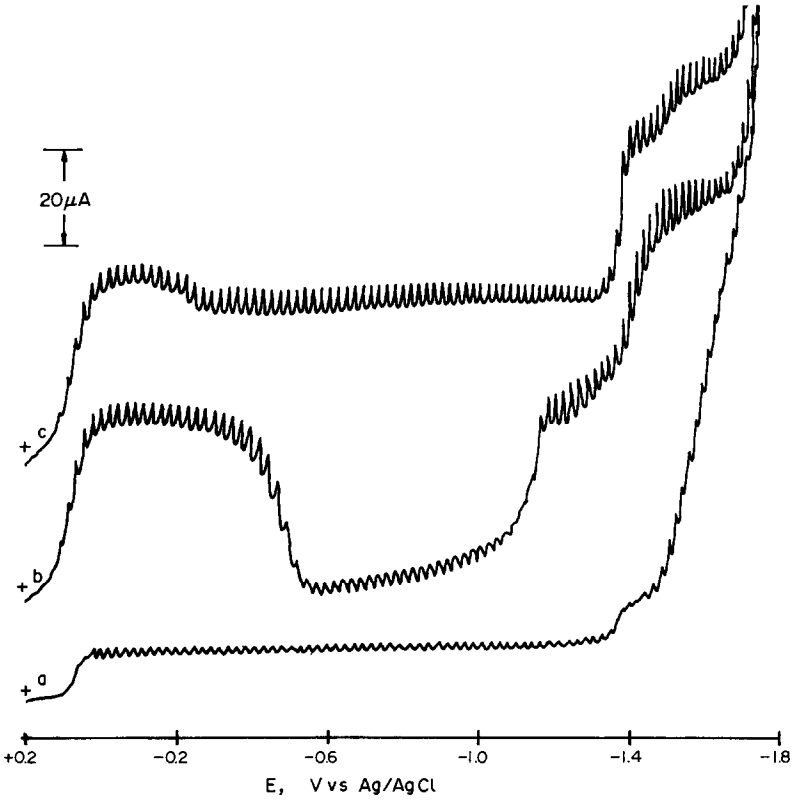

Fig. 1. Polarographic curves for reduction of potassium dichromate in 0.1*M* potassium nitrate and 0.2*M* acetate buffer of pH 5.5. (*a*) $6.0 \times 10^{-4}M$ potassium dichromate, (*b*) $2.0 \times 10^{-3}M$ potassium dichromate, (*c*) $2.0 \times 10^{-3}M$ potassium dichromate and 0.01% tetrabutylammonium hydroxide.

in the presence of 1.0*M* acetate buffer and 20% ethanol. Vasilyev and Popel' investigated the interferences of potassium nitrate (up to 0.5*M*), ammonium chloride (up to 0.6*M*) and sodium acetate (up to 1.5*M*) but did not notice serious effects on accuracy. Only Warshovski *et al.*[8] found low results in the presence of chloride and nitrate. The concentration of the potassium nitrate and acetate buffer chosen as electrolyte had to be accommodated to the concentration level of the ion titrated. For the range of ionic strengths used in our experiments the calculated activity coefficients should result in a tenfold increase in the solubility product. Accordingly the electrolyte concentration was kept at the lowest possible level, not exceeding that of the titrated ion by more than a factor of twenty.

Very little is known about the polarography of dichromate in acid medium. At the potential of titration, −1.0 V *vs.* S.C.E. as proposed in the original paper by Kolthoff and Pan,[1] results for lead and barium are good only at pH lower than 5 and at low concentrations of excess of reagent. At higher concentration of dichromate the linearity is lost (Fig. 1*b*), making the amperometric titration impossible. With potassium chloride as supporting electrolyte, Lingane and Kolthoff[10] found four polarographic waves. According to these authors the first wave at −0.3 V represents reduction of dichromate on the electrode, accompanied by the formation of chromium(III) hydroxide. An investigation of the reduction of dichromate at lower pH revealed that at higher dichromate concentrations there is a well in the polarographic curve, similar to that reported by Lingane and Kolthoff, which appears also in acid solution, although at another potential. Since maximum suppressors did not straighten the shape of the curve, it can be concluded that the effect is due to electrostatic interferences, which are frequently observed in the reduction of anions,[11] and have their origin in the electro-

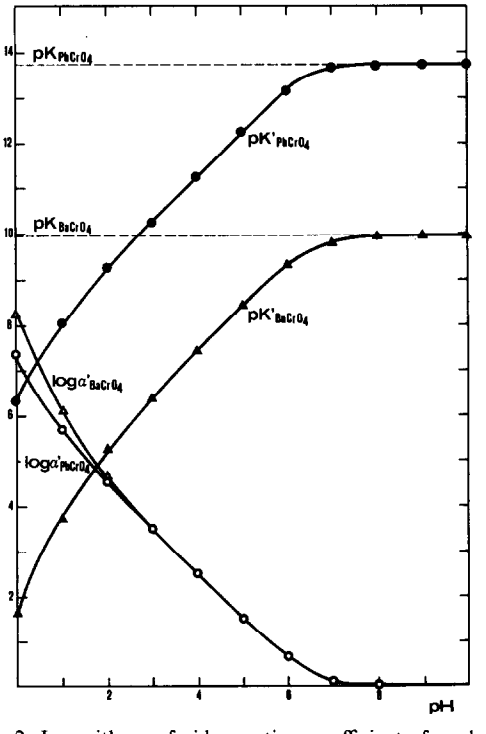

Fig. 2. Logarithms of side-reaction coefficients for chromate ($\alpha_{CrO_4(H)}$) and negative logarithms of conditional solubility products of barium and lead chromates as a function of pH calculated for $1.0 \times 10^{-3}M$ concentrations of metal ions.

static repulsion because of changes in the structure of the electric double layer, after the potential of the electrocapillary maximum has been reached. A proof of the validity of this assumption is the fact that this interference can be efficiently eliminated by the addition of tetrabutylammonium hydroxide in concentrations between 0.001 and 0.02%. In its presence, diffusion currents are proportional to concentration in the range between −0.5 and −1.3 V vs. S.C.E. (Fig. 1c).

Another essential factor, the importance of which has been underestimated in the earlier papers, is constituted by the equilibria between various ionic and molecular species, in particular the dimerization equilibrium important at higher total concentration, and protonation of the chromate ions formed in the dissociation of the precipitate, at different pH. Among conditions to be fulfilled im amperometric titration is the requirement that in the last 25% of the titration the solubility of the precipitate should not contribute more than 1% of the initial concentration of the titrated ion. The solubility product for lead chromate is $10^{-13.75}$ and the side-reaction coefficient, calculated from the revised dissociation and dimerization constants of chromic and dichromic acids[12] for a $10^{-3}M$ solution of lead is $10^{4.53}$ at pH 2. Hence pK'_{sp} becomes 9.22 which satisfies the criterion above for precipitation of lead, and leaves a sufficient gap with respect to the critical pH for precipitation of barium chromate. Figure 2 represents the relevant diagram for lead and barium chromates. Obviously mixtures of lead and barium will not behave strictly according to theory because of co-precipitation. and their behaviour will depend on the concentrations, and ratios, of lead to barium or *vice versa*.

Figure 3 illustrates the influence of the phenomena discussed above. Sections 1 and 3 represent titrations of 10^{-2} and $10^{-3}M$ solutions, respectively, of lead (*a*) or barium (*b*), at pH 3. The end-point detection of lead is precise at the concentrations involved and presents no problems. Incipient precipitation of barium is noticeable only in $10^{-2}M$ solution and at higher excess of the reagent. At pH 6.8 (sections 2 and 4), there is a bending of the left-hand part of the curve during the titration of lead, accompanied by a shift of the apparent end-point towards lower values, indicating precipitation of hydroxo-chromates. The distortion of the final, right-hand part of the titration curve

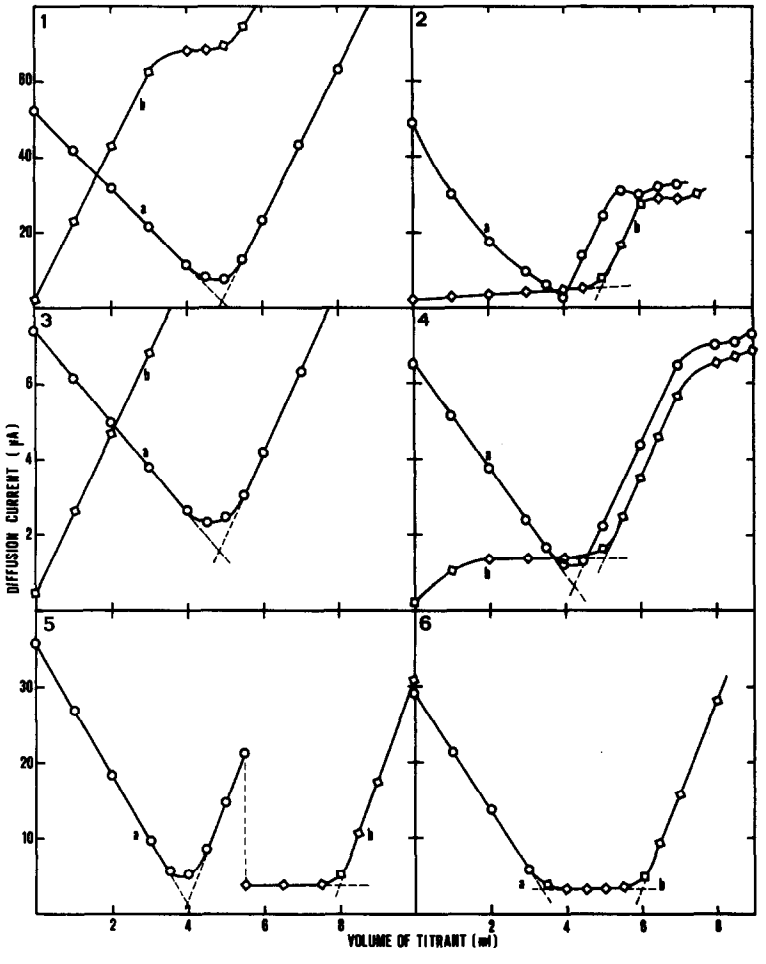

Fig. 3. Titration of lead (○) and barium (◇) with potassium dichromate in 0.1*M* potassium nitrate and 0.2*M* acetate buffer at −0.9 V *vs.* S.C.E. Theoretical end-points in diagrams 1–4 are at 5.00 ml of reagent. In diagrams 5 and 6 they are theoretically at 4.00 ml and 3.00 ml for lead and at 8.00 ml and 6.00 ml for barium, respectively. Diagrams 1 and 3 represent titrations at pH 3.0, 2 and 4 at pH 6.8, diagram 5 at pH 2.5 and then with the pH raised to 5.7 at the point indicated by the dashed line, and 6 at pH 5.7. Concentrations of lead and/or barium are $1.0 \times 10^{-2}M$ in diagrams 1 and 2, $1.0 \times 10^{-3}M$ in diagrams 3 and 4, $5.0 \times 10^{-3}M$ in diagram 5 and $3.0 \times 10^{-3}M$ for lead and for barium in diagram 6. Tetrabutylammonium hydroxide and ethanol were added only during the titrations represented by diagrams 5 and 6.

representing the increasing excess of reagent after the end-point, is due to the anomalous behaviour of chromate at the electrode as discussed above. It is noticeable particularly at higher concentration of titrant and at higher pH. If the pH is maintained at 5.7 throughout the titration of mixtures of lead and barium (section 6) the second end-point representing the sum can be determined accurately and precisely. The first end-point, however, is always shifted towards higher values because of co-precipitation. Both end-points are accurate if the pH is kept between 2 and 3 during titration of lead and then raised for the titration of barium (section 5) provided that the amount of barium exceeds that of lead.

Optimization of the measurements

As a result of these observations, the following procedure has been found to give optimum results for either lead or barium or for their sum in mixtures. Appropriate amounts of lead and/or barium standard solution (or sample) are pipetted into a 25-ml volumetric flask and neutralized to Methyl Orange with sodium hydroxide. Acetate buffer of pH 5.5–6.0 is added, followed by potassium nitrate and ethanol, and the solution is diluted with water to the mark. Portions of the solution (10 ml) are pipetted into the titration cell and 10 μl of 10% tetrabutylammonium hydroxide solution are added. Nitrogen is bubbled through the solution for 5 min at the beginning and later for 30 sec after each addition of titrant. Diffusion currents measured at -1.0 V *vs.* S.C.E. and corrected for dilution are plotted against volume of added reagent and the end-point is determined graphically.

Under these conditions (0.01M potassium nitrate in 0.02M acetate buffer of pH 5.7, containing 20% v/v ethanol and 0.01% tetrabutylammonium hydroxide) the relative standard deviation for titration of $10^{-3}M$ lead in a set of seven measurements was 1.2%. For an equal concentration of barium, the relative standard deviation in a similar set was 2.3%.

Although of limited applicability in practical analysis, amperometric titration can prove useful at intermediate concentration levels for determining lead, barium and their sum as well as chromate and indirectly sulphate, especially since it has been shown that strontium, magnesium and calcium do not interfere if present in 10–20-fold ratio to lead and barium. The technique permits an easy detection of co-precipitation and appears promising for its evaluation in quantitative terms. In this respect it complements the radiometric procedure in the study of co-precipitation phenomena.

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APPLICATION OF ZONE-MELTING TECHNIQUE TO METAL CHELATE SYSTEMS—X*

ZONE-REFINING OF BIS(ACETYLACETONATO)BERYLLIUM(II), TRIS(ACETYLACETONATO)ALUMINIUM(III) AND BIS(DI-ISOVALERYLMETHANATO)COPPER(II)

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(*Received* 27 *January* 1976. *Accepted* 16 *June* 1976)

Summary—Bis(acetylacetonato)beryllium(II), tris(acetylacetonato)aluminium(III) and bis(di-isovalerylmethanato)copper(II) were zone-refined. Also crude beryllium(II), aluminium(III) and copper(II) salts were purified by zone-melting the above-mentioned chelates, obtained by precipitation from aqueous methanol solutions. Some contaminants were excluded at the stage of chelate formation and the remainder were concentrated at the terminal end of a zone-refining column.

In continuation of previous work[1–3] this paper deals with three metal chelates found stable enough to withstand the prolonged heating of a zone-melting process.[4,5] The results show that all three can be freed from various foreign metal ions.

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representing the increasing excess of reagent after the end-point, is due to the anomalous behaviour of chromate at the electrode as discussed above. It is noticeable particularly at higher concentration of titrant and at higher pH. If the pH is maintained at 5.7 throughout the titration of mixtures of lead and barium (section 6) the second end-point representing the sum can be determined accurately and precisely. The first end-point, however, is always shifted towards higher values because of co-precipitation. Both end-points are accurate if the pH is kept between 2 and 3 during titration of lead and then raised for the titration of barium (section 5) provided that the amount of barium exceeds that of lead.

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Summary—Bis(acetylacetonato)beryllium(II), tris(acetylacetonato)aluminium(III) and bis(di-isovalerylmethanato)copper(II) were zone-refined. Also crude beryllium(II), aluminium(III) and copper(II) salts were purified by zone-melting the above-mentioned chelates, obtained by precipitation from aqueous methanol solutions. Some contaminants were excluded at the stage of chelate formation and the remainder were concentrated at the terminal end of a zone-refining column.

In continuation of previous work[1–3] this paper deals with three metal chelates found stable enough to withstand the prolonged heating of a zone-melting process.[4,5] The results show that all three can be freed from various foreign metal ions.

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EXPERIMENTAL

Materials

Bis(acetylacetonato)beryllium(II), Be(AA)$_2$, contaminated with iron and aluminium. To 100 ml of water–methanol mixture (95 : 5 v/v) containing 12.5 g of beryllium nitrate, 3.0 mg of iron(II), 25.0 mg of aluminium(III) and 26.8 g of acetylacetone, 6*M* aqueous ammonia was added with vigorous stirring till the pH was 5. The pale red precipitate was collected by filtration, and dried over phosphorus pentoxide (m.p. 108–110°; yield 17.2 g).

Tris(acetylacetonato)aluminium(III), Al(AA)$_3$, contaminated with iron and other metals. To 100 ml of water–methanol mixture (95 : 5 v/v) containing 15.0 g of acetylacetone, 12.1 g of aluminium chloride hexahydrate, and 5.0 mg each of nickel(II), cobalt(II), zinc(II), iron(II), copper(II) and manganese(II), 6*M* aqueous ammonia was added with vigorous stirring till the pH was 4. The pale red precipitate was collected by filtration, and dried at 100° for 5 hr (m.p. 196–197°; yield 10.0 g).

Bis(di-isovalerylemethanato)copper(II), Cu(DIVM)$_2$, contaminated with iron and other metals. From 150 ml of aqueous methanol (95 : 5 v/v) containing 18.4 g of di-isovalerylmethane, 10.0 g of copper acetate monohydrate and 5.0 mg each of nickel(II), cobalt(II), zinc(II), iron(II), and manganese(II), a pale grey precipitate was obtained at pH 4 by addition of ammonia; it was collected and then dried at 100° for 5 hr (m.p. 161–162°; yield 21.0 g).

Other metal chelates used in the present work were prepared as described previously.[4,5]

Zone melting apparatus

The home-made zone-melting apparatus has been described previously.[6] The molten zone was stirred by spinning the column at 35 rps with reversal of the direction of rotation every 1.0 sec. The column container was a Pyrex tube of i.d. 4 mm, and o.d. 6 mm. Molten chelate at a temperature 10–15° higher than its melting point was sucked into the column container and cooled to give a solid column 21 cm long, which was then subjected to zone-melting.

Determination of foreign metals

A sample cut from a zone-refined column was decomposed with a hot mixture of hydrochloric acid (4 parts), perchloric acid (3 parts) and fuming nitric acid (3 parts). The resulting solution was analysed for the trace metal components by atomic-absorption spectrophotometry in an air–acetylene flame, except for aluminium, which was measured in a nitrous oxide–acetylene flame. The instrument was a Jarrel–Ash model AA-1.

RESULTS AND DISCUSSION

In all the preparations, the iron(II) originally added appeared to be converted into iron(III) during the chelation reaction, and the iron is referred to below as being in this oxidation state, though the analytical method used does not differentiate between the two states. In terms of contamination, the oxidation state seems immaterial.

Table 1. Effective distribution coefficient k_{eff} of Fe (AA)$_3$ in Be (AA)$_2$ *vs.* zone travelling speed, v

v, mm/hr	k_{eff}
864	0.58
575	0.47
470	0.45
432	0.40
344	0.38

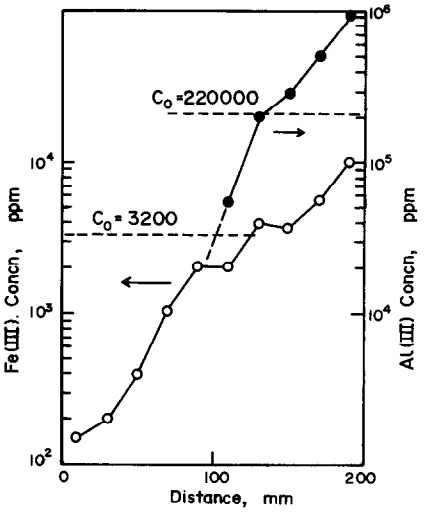

Fig. 1. Distribution of Fe(AA)$_3$ (—○—) and Al (AA)$_3$ (—●—) in Be(AA)$_2$ after zone-melting. Number of reciprocations = 10.^{7} Zone travelling speed v = 344 mm/hr.

Zone-melting of the beryllium chelate

In the preliminary work[3] on the zone-melting of Be(AA)$_2$, the zone travelled at a speed of 864 mm/hr, which was considered too fast to afford efficient zone-refining of the chelate. As shown in Table 1, a slower travelling speed gives a smaller effective distribution coefficient, k_{eff}, for Fe(AA)$_3$, resulting in more efficient refining.

Figure 1 shows the distribution of iron and aluminium on a column after zone-melting of a model mixture of Be(AA)$_2$ containing trace amounts of Fe(AA)$_3$ and Al(AA)$_3$. Both contaminants are effectively removed from the top of the column and concentrated at the other end.

With a crude beryllium salt as starting material, the chelate complex must be prepared first. Analyses of the chelate precipitated from an inorganic beryllium(II) salt solution indicate that the main component was refined to a great extent in the precipitation itself, *e.g.*, 440 ppm of iron and no aluminium were detected in the precipitate from a beryllium(II) salt deliberately contaminated with 2500 and 20,600 ppm of iron and aluminium respectively (metal/metal ratio). Figure 2 shows that the distribution of iron

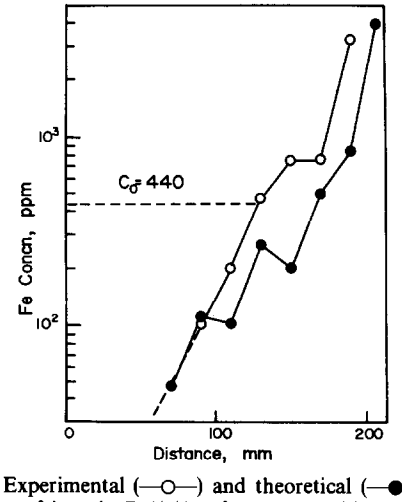

Fig. 2. Experimental (—○—) and theoretical (—●—) distribution of iron in Be(AA)$_2$ after zone melting. Number of reciprocations = 10.^{7} Zone travelling speed: v = 344 mm/hr. Theoretical distribution was calculated for k = 0.38.

Table 2. Metal ions in the $Al(AA)_3$ charge before and after zone melting

Metal	Conc., μg of metal/g of aluminium: Initial charge	Top fraction, 0.2L long	End fraction, 0.2L long
Fe	3100	80	13,600
Cu	70	*	310
Zn	50	*	160
Ni, Co, Mn	*	*	*

Zone travelling speed 344 mm/hr; 10 reciprocations by the intermittent method,[7] total length of the charge, L, 210 mm.

* Undetectable.

after the zone-melting is similar to that obtained in the model mixture. The initial concentration, C_0, of the contaminant iron was much lower than that in the model mixture, and its distribution after zone melting was much closer to that calculated for a solute of $k = 0.38$, especially in the top half of the column. At a higher concentration of impurity the refining effect seems less efficient.

Table 3. Analyses before and after zone-refining of $Cu(DIVM)_2$, which contained initially various metal chelate contaminants.

Contaminant	Concn., μg of metal/g of copper: Initial charge	Top fraction, 0.2L long	End fraction, 0.2L long
$Fe(DIVM)_3$	2700	120	12,000
$Co(DIVM)_3$	2500	95	12,000
$Mn(DIVM)_3$	2800	90	11,500
$Ni(DIVM)_2$	3300	140	15,600

v 470 mm/hr; 10 reciprocations; L 210 mm.

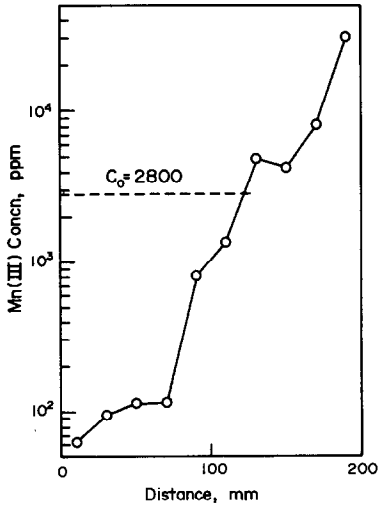

Fig. 3. Distribution of $Mn(DIVM)_3$ in $Cu(DIVM)_2$ after zone-melting. Number of reciprocations = $10.^7$ Zone travelling speed: v = 470 mm/hr.

Table 4. Analyses before and after zone-refining of $Cu(DIVM)_2$

Metal	Concn., μg of metal/g of copper: Initial charge	Top fraction, 0.2L long	End fraction, 0.2L long
Fe	610	60	2920
Zn	35	*	130
Ni, Co, Mn	*	*	*

v 344 mm/hr; 10 reciprocations; L 210 mm; initial copper solution contaminated with trace metal ions at 1560 ppm each.

* Undetectable.

Zone-melting of $Al(AA)_3$

In the chelate obtained from Al(III) solution containing trace Fe(III), Cu(II), Zn(II), Ni(II), Co(II) and Mn(II) at 3600 ppm each, only iron, copper and zinc (at concentrations of 3100, 70 and 50 ppm, respectively) were found. Obviously the other contaminants were removed during the precipitation. Analyses of the precipitate before and after zone-refining (Table 2) show that iron, copper and zinc were concentrated towards the bottom of the column; no nickel, cobalt and manganese were detected.

Zone-melting of $Cu(DIVM)_2$

Figure 3 shows the distribution of $Mn(DIVM)_3$ on the column of a model mixture with $Cu(DIVM)_2$. The contaminant $Mn(DIVM)_3$ was removed from the top and concentrated at the bottom. Other minor components showed similar behaviour (Table 3).

Precipitation with di-isovalerylmethane from a contaminated copper solution effectively separated copper from trace contaminants (Table 4); iron and zinc were reduced to the level of 610 and 35 ppm, respectively, and nickel, cobalt and manganese to below the detection limit.

Conclusions

For the metal ions and chelating agents discussed, a considerable fraction of contaminants can be removed at the stage of precipitation, presumably in consequence of the stabilities or solubilities of the chelate complexes of the trace elements, most probably the solubilities at the trace levels used.

The last traces of contaminating metal ions, however, can be removed only by the zone melting process, giving pure metal chelates. As the apparatus can be readily enlarged to a preparative scale, the present method might be promisingly applied to the production of highly pure metal chelates or pure reference materials of various metallic elements by use of suitable chelating agents.

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APPLICATION OF ZONE-MELTING TECHNIQUE TO METAL CHELATE SYSTEMS—XI

REFINING OF TETRAKIS(DI-n-PROPIONYLMETHANATO)ZIRCONIUM(IV) FROM HAFNIUM AND TRACE AMOUNTS OF SOME OTHER METALS*

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Summary—The zone-melting method was applied to purification of tetrakis(di-n-propionylmethanato)-zirconium(IV) which contained copper(II), nickel(II), cobalt(II and III), iron(III) and hafnium(IV) in the forms of their chelates with the common ligand. All minor components having effective distribution coefficients < 1 in the zirconium(IV) chelate were concentrated toward the terminal end of the refining column. When an aqueous solution of zirconium(IV) containing zinc(II) and manganese(II) in addition to the metal contaminants above was treated with di-n-propionylmethane to precipitate the chelate complexes, only zinc, iron and hafnium were found in the precipitated zirconium chelate. The first two were effectively removed by zone-melting. Though the separation of hafnium was poorer, the technique was efficient enough for practical purposes.

Practically available zirconium contains 1–2% of hafnium owing to the difficulty of their mutual separation, and this trace of hafnium is known to affect the properties of zirconium as a material for various uses.[1] However, we have found di-n-propionylmethane (DNPM) to afford thermally stable chelate complexes with various metal ions, including zirconium and hafnium, even on prolonged heating. This system was therefore considered suitable for application of our method of zone-melting, for purification of zirconium.

EXPERIMENTAL

Materials

The metal di-n-propionylmethanates were prepared in a similar manner to those described previously.[2–4] The zirconium chelate, deliberately contaminated with other metal ions, was prepared as follows. To 50 ml of a cooled aqueous solution containing 10.74 g of zirconium oxychloride and 500 μg each of copper(II), nickel(II), cobalt(II), zinc(II), manganese(II), and iron(II) were added 17.1 g of DNPM in 20 ml of methanol. With vigorous stirring, 3*M* aqueous sodium carbonate was added dropwise to adjust the pH to 2. The light red precipitate was filtered off and dried *in vacuo* over phosphorus pentoxide for 2 days (m.p. 58–59°; yield 18.4 g).

A sample of the zirconium chelate, highly contaminated with hafnium was prepared by the same procedure but with 19.6 g of DNPM and 1 g of hafnium tetrachloride in place of the trace metals.

Procedure and apparatus

Two types of zone-melting apparatus were used, both constructed in our laboratory.[5,6] One was a high-speed apparatus, in which an array of ring heaters travelled up the tube, in the intermittent mode, at 120–840 mm/hr. The tube was Pyrex, i.d. 4 mm. The charge length, *L*, was fixed at 213 mm and five molten zones were produced on the charge at equal spacings. The tube was rotated at 2500 rpm (maximum) around its longitudinal axis, with reversal of rotation direction every 0.5 sec.

Another apparatus was equipped with an array of five ring heaters. The molten zones moved downward at 20.3 mm/hr by the normal mode of zone-travel.

Trace analysis for the contaminant metals

A small amount (200–300 mg) of a sample cut out from a zone-refined column was decomposed in 6–8 ml of a hot mixture of perchloric acid (3 parts), fuming nitric acid (3 parts) and hydrochloric acid (4 parts). An aliquot of the resulting solution was diluted to the mark in a volumetric flask with 0.01*M* hydrochloric acid, and analysed for trace metals (except hafnium) by atomic-absorption spectrophotometry in a 10-cm acetylene–air flame on a Jarrel-Ash AA-1 apparatus. An aliquot diluted with 0.3*M* ammonium fluoride and 0.07*M* iron(III) was analysed for hafnium by atomic absorption in a 5-cm acetylene–nitrous oxide flame.

RESULTS AND DISCUSSION

Effective distribution coefficients, k_{eff}, of the contaminants in the zirconium chelate

The k_{eff} values of the metal diketonates in the zirconium diketonate were determined by the Sorensen method[7] by use of a high-speed zone-melting apparatus. Operating conditions were the same as for the zone-refining except

Table 1. The k_{eff} values of various metal dipropionylmethanates in $Zr(DNPM)_4$

Minor component	*v*, mm/hr*	k_{eff}
$Cu(DNPM)_2$	864	0.73
$Ni(DNPM)_2 . H_2O$	864	0.54
$Co(DNPM)_2 . H_2O$	864	0.53
$Fe(DNPM)_3$	864	0.86
$Co(DNPM)_3$	864	0.89
$Hf(DNPM)_4$	864	0.92
	575	0.80
	470	0.72
	432	0.76
	344	0.69
	120	0.65
	20†	0.93

* Zone travel speed.
† The zone travels downward without stirring.

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Table 2. Zone melting of the model mixtures of $Zr(DNPM)_4$ with traces of various metal dipropionylmethanates

Minor component	Zone melting*	Ratio of metal to zirconium, % Initial charge	Top fraction, 0.2 L long	End fraction, 0.2 L long
$Fe(DNPM)_3$	III	0.40	0.06	1.40
	IV		0.24	0.66
	V		0.24	0.65
$Cu(DNPM)_2$	III	1.00	0.10	4.34
	IV		0.59	1.64
	V		0.69	1.58
$Co(DNPM)_2$	III	1.00	0.13	3.94
	IV		0.56	1.74
	V		0.79	1.78
$Ni(DNPM)_2$	III	0.40	0.07	1.58
	IV		0.33	0.75
	V		0.33	0.66
$Hf(DNPM)_4$	III	11.2	9.0	12.5
	IV		11.0	11.6
	V		9.2	11.8

* Conditions of zone melting: III, zone travel speed $v = 470$ mm/hr, reciprocation number of heater assembly $m = 10$; IV, $v = 864$ mm/hr, $m = 10$; V, slow and normal zone melting, without mixing of zone, $v = 20$ mm/hr, number of zone passes $n = 15$.

the zone-travel speed. The k_{eff} values are summarized in Table 1. Each value is less than unity, indicating that the minor components should segregate toward the terminal end of a charge.

The zirconium diketonate, which has an archimedean square antiprismatic co-ordination, forms a eutectic binary system with tris(di-n-propionylmethanato)cobalt(III) which has octahedral co-ordination. Since the other metal di-n-propionylmethanates except hafnium have co-ordination structures different from that of the zirconium chelate, they would probably also form eutectic systems with it.[2] If so, their equilibrium distribution coefficients, k_{eq}, in the zirconium chelate should be essentially zero. The hafnium and zirconium chelates have the same co-ordination structure and form a solid solution.[2] The k_{eq}-value for the hafnium in the zirconium chelate, estimated from the phase diagram, is 0.5 for hafnium content < 10%.

Zone-refining of the contaminated zirconium chelate

Table 2 shows the analyses for the contaminant metal ions after the zone refining. The trace components were concentrated toward the terminal end of the column as expected from the k_{eff} values, though the extent of refining was not always in agreement with theory. Slow zone speed and vigorous stirring seem essential for efficient refining.

Table 3. Analyses for metal ions in the $Zr(DNPM)_4$ charge before and after zone melting

Metal	Zone* melting	Ratio of metal to zirconium, % Initial charge	Top fraction, 0.2 L long	End fraction, 0.2 L long
Fe	III	—†	—	0.17
Zn	III	0.026	—	0.13
Cu, Co, Ni, Mn, Al, Cr	III	—	—	—
Hf	I	15.1	6.6	18.3
	II			17.1
	IV		13.3	15.9
	V		13.8	15.8

* Condition of zone melting. I: $v = 120$ mm/hr, $m = 10$. II: $v = 344$ mm/hr, $m = 20$.

† Undetectable.

Table 4. The separation of hafnium by the zone melting of $Zr(DNPM)_4$

Zone melting	Ratio of hafnium to zirconium, % Initial charge	Top fraction 0.2 L long	End fraction, 0.2 L long
I	1.5	0.36	2.2
II		0.86	1.7
III		0.91	1.7
IV		0.87	1.5
V		1.0	1.5

Separation of metal contaminants from zirconium salts

Most of the metal ion impurities are removed during preparation of the chelate, as with other diketonates;[8] the chelate from a solution of zirconium containing 164 ppm each of Cu(II), Ni(II), Co(II), Zn(II), Mn(II), and Fe(II) and 17.7% of Hf, contained 26 ppm of Zn(II) and 15.1% of Hf (metal/metal w/w). No other contaminant metal ions were detected. Zone-refining of the precipitate thus obtained gave the results shown in Table 3. Zinc and iron were concentrated at the terminal end, while at the starting end no trace of these impurities was detected. Hafnium was also concentrated at the terminal end, but to a much lower extent and a considerable level of hafnium still remained near the start.

Commercially available zirconium oxychloride, (Wako Pure Chemicals, Sp. Grade) with a hafnium content of 1.3% (w/w/Hf/Zr) was subjected to precipitation with DNPM and zone-refining. Results are shown in Table 4. No foreign metal ions other than Hf(IV) were detected over the entire range of a charge before and after zone refining.

If a system containing a solute of $k = 0.65$, at an initial concentration C_0 of 1.5% w/w, is assumed to be zone-refined to the ultimate stage, the final average solute concentration in the starting region of length 0.2 L is expected to be 1.7×10^{-3}% w/w. This means removal of $100(1.5 - 0.0017)/1.5 = 99.89\%$ of the original contamination in this zone. In the best of the separations (Table 4) where the residual hafnium in this zone was 0.36%, about 75% of the original contamination was removed, and further refining would give no advantage in terms of time.

For the same system after 10 reciprocations the theoretical residual contamination in this zone would be 0.097%, so on similar reasoning the purification experimentally obtained is about 80% of the theoretical $[100(1.5 - 0.36)/(1.5 - 0.097)]$. Therefore to remove 99% of the hafnium content would require four repetitions of the proposed zone-refining separation, at every repetition the top 0.2 L fractions from several charges being combined to form a new column of length L. As 5^4 such fractions would be needed to give one final 0.2 L fraction, the yield of purified chelate would be 0.16%, which is not very economic.

In comparison with other techniques for purifying zirconium, the method gives no better yield, but is so much faster (separation takes only 3.3 hr) that it might be worth operation on the preparative scale.

Acknowledgement—The authors thank the Nippon Kogyo Co. Ltd. for the gift of primary standards of hafnium and zirconium metal.

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LIQUID–LIQUID EXTRACTION OF ARSENIC(III) WITH DILUTED TRIBUTYL PHOSPHATE

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Department of Chemistry, Indian Institute of Technology, Powai, Bombay-400076, India

(*Received* 18 *November* 1975. *Revised* 21 *June* 1976. *Accepted* 1 *July* 1976)

Summary—A 40% tributyl phosphate solution in xylene was used for the quantitative extraction of arsenic(III) from 4*M* hydrochloric acid/2*M* lithium chloride. It was stripped from the organic phase with water and determined volumetrically with potassium bromate. The period of equilibration was 3 min. Arsenic was extracted in presence of copper, cobalt, nickel, tin, bismuth, iron, cadmium and other elements which are usually associated with it in sulphide minerals and alloys.

Arsenic is extracted with 8-mercaptoquinoline[1] from neutral solutions. Sodium diethyldithiocarbamate[2] has been used for the extraction of arsenomolybdenum blue. By ligand exchange in the organic phase, a mixed dithizone–diethyldithiocarbamate complex[3] has been obtained. Diethylammonium dithiocarbamate[4] and ethyl xanthates[5] facilitate extractive separations. Chloride media have proved effective for the extraction of the halo-complexes into chloroform, carbon tetrachloride, benzene or diethyl ether.[6,7] An ether–butanol mixture has been used for the extraction of arsenomolybdic acid.[8] Diethyldithiophosphoric acid[9] and trioctylphosphine oxide[10] have proved to be poor extractants. Arsenic has also been separated from tin and bismuth with bis(2-ethylhexyl)phosphorodithioate.[11]

Tributyl phosphate has been explored in this laboratory (among others) for the solvent extraction separation of many elements. Extension of these studies reveals that 40% tributyl phosphate in xylene quantitatively extracts arsenic from 4*M* hydrochloric acid containing 2*M* lithium chloride as salting-out agent. The arsenic can be stripped from the organic phase with water and determined volumetrically[12] with potassium bromate. The proposed method is simple, rapid and selective.

EXPERIMENTAL

Reagents

Tributyl phosphate, b.p. 143°.

Stock solution of arsenic. Prepared by dissolving 3.09 g of analytical grade arsenious oxide in sodium hydroxide solution, neutralizing with hydrocholoric acid, and making up to 250 ml with distilled water. The solution, standardized volumetrically with potassium bromate,[12] was found to contain 9.37 mg of arsenic per ml, and was diluted tenfold.

General procedure

To an aliquot of the solution containing 937 μg of arsenic, enough hydrochloric acid and lithium chloride were added to make their concentrations 4*M* and 2*M* respectively in a volume of 25 ml. The solution was transferred into a 125-ml separatory funnel, 10 ml of 40% TBP in xylene were added, and the mixture was shaken briskly for about 3 min. The layers were allowed to separate, and the aqueous layer was withdrawn. Arsenic was stripped from the organic phase with two 10-ml portions of water, and determined titrimetrically[12] with potassium bromate.

RESULTS AND DISCUSSION

Effect of TBP and acid concentration

The concentration of TBP was varied from 20 to 100% (0.71–3.66*M*) with xylene as diluent. The acid concentration was varied from 1 to 6*M*. Lithium chloride solution (2*M*) was used throughout as the salting-out agent (Table 1). With 100% TBP the extraction was quantitative from 5*M* hydrochloric acid even in the absence of salting-out agent. However, the optimum conditions for quantitative extraction were 40% TBP and 4–6*M* hydrochloric acid that was 2*M* in lithium chloride as the salting-out agent.

The composition of the extractable species was investigated by plotting log *D* *vs.* log [TBP] at a fixed acidity of 2*M* hydrochloric acid. The slope was 2.6, suggesting that the composition of the extractable species is a 1:2 or 1:3 arsenic:TBP adduct, the arsenic being in the form of $AsCl_3$ or $HAsCl_4$.

Effect of salting-out agents

Various salting-out agents, such as the chlorides of lithium, sodium, potassium, ammonium, magnesium and aluminium were tested (Fig. 1). With 2*M* lithium or magnesium chloride, the extraction was quantitative. The other salting-out agents were not very effective.

The period of equilibration was varied from 0.5 to 15 min. The extraction was quantitative with 2 min equilibration or more.

Effect of diverse ions

Several ions were tested for their effect on extraction of arsenic. The tolerance limit was taken as the amount of foreign ion required to cause ±2% error in arsenic recovery. It was observed that alkali and alkaline earth metal

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Table 1. Distribution ratio as a function of acidity [As(III) = 937 μg; 2M LiCl]

[TBP]	Initial [HCl], M	Extraction %	Distribution ratio, D
20% (0.71M)	1	13.6	0.4
	2	21.6	0.7
	3	46.4	2.2
	4	68.0	5.3
	5	76.8	8.3
	6	84.8	14.0
40% (1.46M)	1	56.8	3.3
	2	67.2	5.1
	3	85.6	14.9
	4–6	100.0	∞
60% (2.19M)	1	55.2	3.1
	2	84.0	13.1
	3	92.0	28.8
	4–6	100.0	∞
75% (2.74M)	1	60.0	3.8
	2	88.8	19.8
	3	97.4	93.7
	4–6	100.0	∞
90% (3.29M)	1	68.8	5.5
	2	92.8	32.2
	3	99.2	310
	4–6	100.0	∞
100% (3.66M)	1	76.0	7.9
	2	96.0	60.0
	3–6	100.0	∞
40% (1.46M) (without salting-out agent)	1	32.1	1.2
	2	44.0	2.0
	3	51.3	2.6
	4	58.2	3.5
	5	76.8	8.3
	6	92.0	28.8
100% (3.66M) (without salting-out agent)	1	40.0	1.7
	2	53.6	2.9
	3	76.8	8.3
	4	96.8	75.6
	5–6	100.0	∞

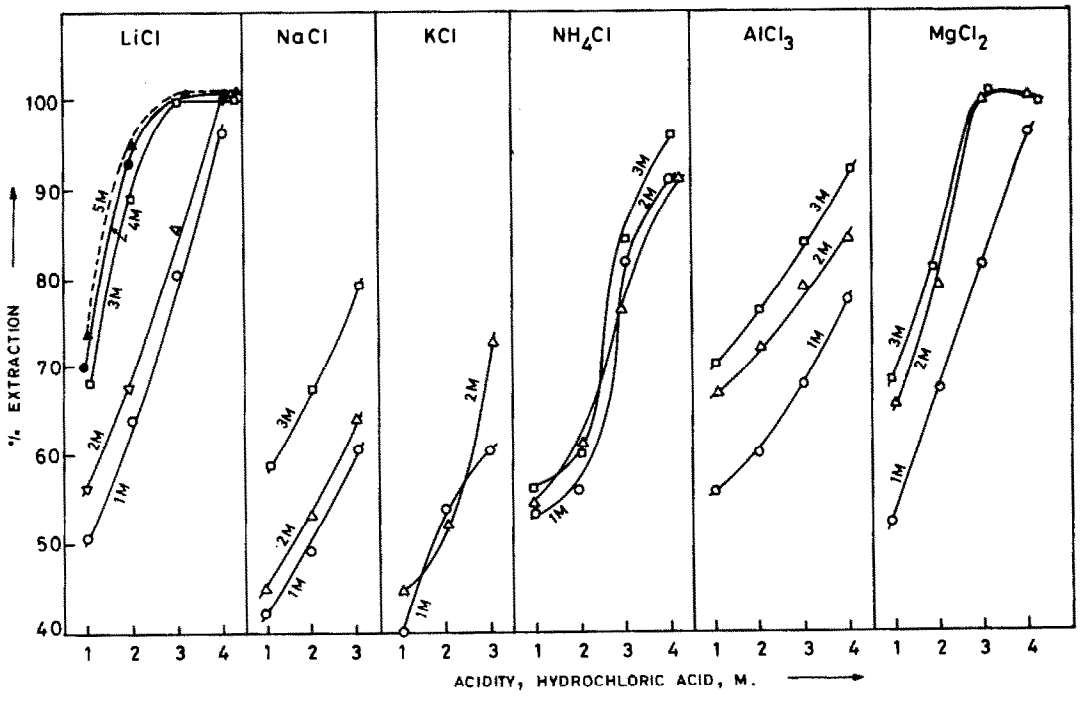

Fig. 1. Effect of salting-out agents.

ions, bismuth, beryllium, citrate, tartrate, malonate, sulphate, EDTA, phosphate and sulphite were tolerated in ratios of at least 25:1 w/w relative to arsenic. Uranyl, chromium(III), zinc and manganese(II) were tolerated in 15:1 ratio to arsenic; copper(II), mercury(II), cadmium, palladium(II), iridium(III), platinum(IV), gold(III), iron(III), thorium, yttrium, cobalt(II), nickel, gallium, indium, tellurite and vanadate in 10:1 ratio; ruthenium(III), osmium(VIII), rhodium(III), zirconium, germanium, barium and selenite in 5:1 ratio; molybdate and tungstate in 2:1 ratio and chromate in 1:1 ratio. Antimony, fluoride, thiocyanate and this urea must be completely absent.

Many of these ions show no interference because they are not extracted, others because they would not interfere with the bromate determination in any case.

Arsenic is usually associated with sulphide ores of tin, iron, cobalt, copper and nickel, and a separation is required before it can be determined. The present method is rapid and permits extraction and determination of small amounts of arsenic in less than 30 min, and is simple as it needs only diluted tributyl phosphate and a redox titration. The relative standard deviation is 0.8%.

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TERNARY COMPLEXES IN ANALYTICAL CHEMISTRY—I THE NIOBIUM–PYROCATECHOL–SPARTEINE COMPLEX

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Summary—A ternary complex of niobium with pyrocatechol and sparteine has been investigated as a sensitive and selective system for the spectrophotometric determination of niobium. The complex is formed rapidly over a wide range of pH and is stable for several days. It is extracted quantitatively by some organic solvents. The interference from 40 cations and 10 anions has been examined, and synthetic mixtures and niobium ores have been analysed.

Several investigations have been made into the use of ternary complexes of metal ions with electronegative ligands and organic bases for the quantitative determination of metal ions. A number of organic bases such as pyridine, quinoline, acridine, pyrimidine, antipyrine, diantipyrylmethane, phenanthroline and sparteine have been used,[1,2,3] often with pyrocatechol as the third component. Niobium has been shown to form a coloured complex with pyrocatechol and oxalic acid,[4] extractable into butanol, and a second complex with pyrocatechol and tribenzylamine[5] which can be extracted into chloroform. As pointed out by Babko,[1] the field of ternary metal complexes is in need of systematic investigation, and several other studies have been initiated in our laboratory. The aim of the present work is the development of a convenient technique for the quantitative determination of niobium. The applicability of the niobium–pyrocatechol–sparteine complex for quantitative determination of niobium has been investigated over the range 5–200 ppm of niobium.

EXPERIMENTAL

Reagents

Niobium(V) solution, 1% *w/v*. Add to 1.000 g of niobium metal in a Teflon beaker 5 ml of concentrated hydrofluoric acid. Add concentrated nitric acid dropwise until the metal has just dissolved. Dilute to 100 ml with demineralized water and store in a polyethylene bottle. Dilute as required.[6]

Pyrocatechol solution, 5% *w/v*. Fresh solution should be made every few days, with newly resublimed pyrocatechol stored in a cool, dark place.

Sparteine solution, 2.5% *w/v*.

Ammonium acetate buffer solution, *pH* 3.5. Add small amounts of 0.2*M* ammonia solution to 100 ml of 0.2*M* acetic acid until pH 3.5 is reached.

Procedure

Transfer 2 ml of sample solution containing 500–2000 μg of niobium(V), with 0.1–0.2 ml of 1% thiourea solution (for masking iron or vanadium if present), 2 ml of 5% pyrocatechol solution, 0.5 ml of 2.5% sparteine solution and 4 ml of pH 3.5 acetate buffer, into a 50-ml separating funnel and dilute to 10 ml. Add 10 ml of chloroform and shake for about 20 sec. Filter part of the organic phase into a 1-cm cuvette and measure the absorbance at 342 nm against either chloroform or a reagent blank. Construct a calibration curve under identical conditions.

Niobium ores. Fuse a sample of the finely ground mineral with 10 times its weight of potassium pyrosulphate at 650–700° until a transparent melt is obtained. Dissolve the cooled melt in 1*M* hydrochloric acid by heating, transfer the solution to a 200-ml volumetric flask and dilute it to

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ACID–BASE TITRATIONS BY STEPWISE ADDITION OF EQUAL VOLUMES OF TITRANT WITH SPECIAL REFERENCE TO AUTOMATIC TITRATIONS—III*

PRESENTATION OF A FULLY AUTOMATIC TITRATION APPARATUS AND OF RESULTS SUPPORTING THE THEORIES GIVEN IN THE PRECEDING PARTS

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Summary—This paper forms Part III of a series in which the first two parts describe methods for evaluating titrations performed by stepwise addition of equal volumes of titrant. The great advantage of these methods is that they do not require an accurate calibration of the electrode system. This property makes the methods very suitable for routine work, *e.g.*, in automatic analysis. An apparatus for performing such titrations automatically is presented. Further, results of titrations of monoprotic acids, a diprotic acid, an ampholyte, a mixture of an acid with its conjugate base, and mixtures of two acids with a small difference between the stability constants are given. Most of these titrations cannot be evaluated by the Gran or Hofstee methods but yield results having errors of the order of 0.1% if the methods proposed in Parts I and II of this series are employed. The advantages of the method of stepwise addition of equal volumes of titrant combined with the proposed evaluation methods, in comparison with common methods such as titration to a preset pH, are that all the data are used in the evaluation, permitting a statistical treatment and giving better possibilities for tracing systematic errors.

In the two earlier papers[1,2] in this series, methods for the evaluation of titrations performed by stepwise addition of titrant were introduced. A great advantage of these methods is that they do not require an accurate calibration of the electrode system. In most cases a very rough calibration is enough and the electrode system may then be used for months without recalibration. This makes the methods very suitable for routine work when many similar samples are titrated, *e.g.*, in automatic analysis.

In comparison with traditional titration methods our methods have the following advantages. They make possible the titration of very weak acids that cannot be titrated in an aqueous medium by conventional methods. Also, titration of a mixture of two acids with a small difference between the stability constants is possible. Further, as the results are obtained from several titration points and not only from the point of maximum slope of the titration curve, it is possible to treat the results statistically and to trace systematic errors.

This paper gives experimental results for titrations of:

(*a*) some monoprotic acids: formic acid (log K_{HA} = 3.38), 2.5-diethylbarbituric acid (log K_{HA} = 7.61) and β-alanine (log K_{HA} = 10.05);
(*b*) formic acid in a mixture with propionic acid (log K_{HA} = 4.53);
(*c*) a diprotic acid: tartaric acid (log $K^{H}_{H_2A}$ = 2.48 and log K_{HA} = 3.32);
(*d*) an ampholyte: potassium hydrogen phthalate (log K_{HA} = 4.32);
(*e*) formic acid in the presence of formate.

The values given in brackets are the logarithms of the stability constants $K_{HA} = [HA]/[H][A]$ and $K^{H}_{H_2A} = [H_2A]/[H][HA]$ of the acids in barium chloride medium at an ionic strength of 0.5.

The titrations were performed by using a fully automatic apparatus with a loading capacity of 200 samples. The apparatus is an improved version of that described by Johansson and Pehrsson.[3] It was designed to perform the following operations:

(*a*) pipetting of sample and addition of a neutral salt solution; a preset volume of a sample is transferred to a titration vessel and diluted with a neutral salt solution in order to give a constant, rather high ionic strength;
(*b*) thermostatic control of the temperature of the diluted sample solution to 25 ± 0.1°;
(*c*) titration by adding titrant in equal portions and measuring the electrode potential after each addition;
(*d*) rinsing of the titration vessel and the electrode couple;
(*e*) sample change-over.

EXPERIMENTAL

Apparatus

The layout of the apparatus is shown in Fig. 1 and schematically in Fig. 2. It is comprised of units for solu-

* Part II—*Talanta*, 1976, **23**, 781.

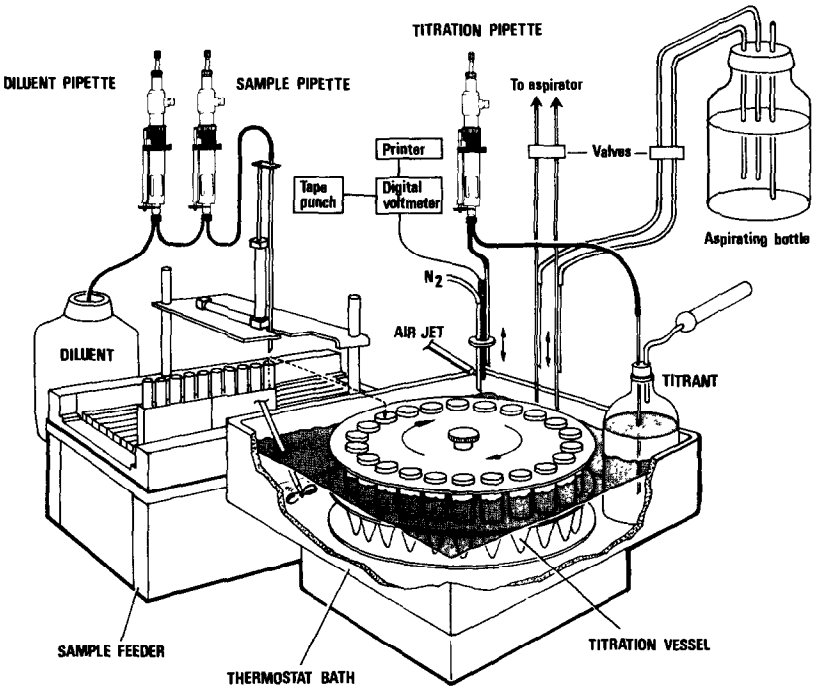

Fig. 1. The titration apparatus.

tion handling, measurement of the electrode potential, and operation control.

The *solution handling unit* is in principle built up from three automatic pipettes, two fraction-collectors, a thermostatic bath and three pneumatically driven pistons. The automatic pipettes (AutoChem Instrument AB, Lidingö, Sweden) are driven by compressed air and controlled by magnetically operated valves. One of the fraction-collectors (LKB 7000 A Ultro Rac, LKB-Produkter AB, Stockholm-Bromma, Sweden), having a capacity for 200 sample-tubes, is used as a sample-feeder. A traditional circular fraction-collector is used as a turntable for the titration vessels. It is combined with a thermostatic bath so that the titration vessels are partly immersed in the bath. The titration vessels consist of polypropene centrifuge-tubes (30 mm diameter, 130 mm length, 50 ml volume). Necessary movements of, for example, the electrode and the outlet tubes of the pipettes, are performed by the pneumatically driven pistons.

The *unit for measuring potentials* consists of a small combination glass and silver–silver chloride electrode (HA-401 M5, Dr. ing. chem. W. Ingold, Zürich, Switzerland), a digital voltmeter and a tape-punch (or printer).

Operation of the apparatus

The samples are added to sample-tubes which are placed in the sample-feeder. The apparatus then automatically performs the following operations (refer to Figs. 1 and 2).

(*a*) *Pipetting of sample and dilution with a neutral salt solution.* Samples and diluent are added at position 1 (Fig.

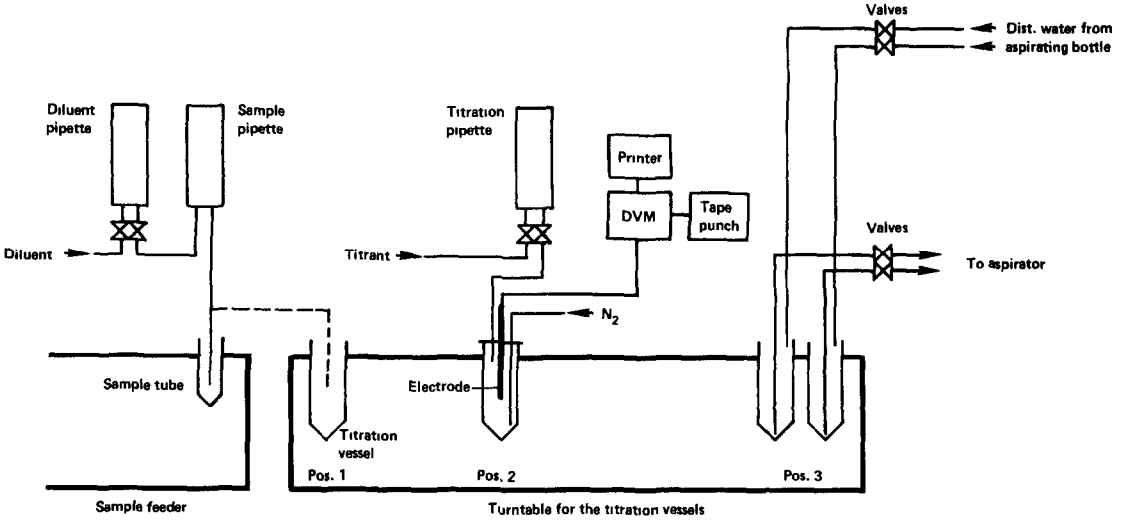

Fig. 2. Diagram of the titration apparatus

2) to every second titration vessel. The remaining vessels are filled with distilled water at position 3 as described later.

The tip of the sample-pipette tube (made of Teflon and having an external diameter of 1.8 mm) is lowered into the sample and 5 ml of the sample are sucked up. Subsequently, the tip of the tube is raised, moved across to the titration turret and lowered into a titration vessel. The sample is introduced into the vessel followed by 5 ml of neutral salt solution from the diluent-pipette, which rinses the sample-pipette tube. The sample carry-over[3] from one sample to the next as a result of this procedure was determined and found to be less than 0.02%.

(*b*) *Temperature control.* The titration vessels are immersed in a thermostatic bath kept at 25° and the diluted sample solution is brought to bath-temperature while it is moved from position 1 to position 2 for titration (Fig. 2). If, for example, the difference in temperature between the sample plus diluent and the thermostatic bath is 5°, 10–15 min are required for the diluted sample solution to reach a temperature of 25 ± 0.1°. The time taken to move the samples from position 1 to position 2 should in this case be at least 15 min. The titrant, kept in a bottle immersed in the bath, is also at a temperature of 25°.

(*c*) *Titration.* The diluted sample solution is titrated at position 2 of the turret The electrode and the outlet tubes for titrant and nitrogen are lowered into the titration vessel (the outlet tube for the titrant is not allowed to dip into the solution). A cover is at the same time lowered onto the titration vessel in order to prevent the titration mixture from taking up carbon dioxide from the air while titrations are performed in the alkaline pH range.

A stream of nitrogen is passed through the solution both before and during the titration to exclude carbon dioxide and to ensure rapid mixing during the titration. Traces of carbon dioxide are removed from the nitrogen stream by letting it pass through a column of "Ascarite". Subsequently, the stream of nitrogen is equilibrated with distilled water by passage through an efficient gas-washing bottle immersed in the thermostatic bath.

The titration is not started until the electrode couple has attained a stable potential in the sample solution. The titrations for which results are given below were started when the drift in the electrode potential was ≤ 0.1 mV during the approximate time required for performing one titration. The control unit samples the potential at preset regular intervals and stores the last ten readings in a memory. When the difference between the first and last of these ten readings is less than a preset value (this criterion must be fulfilled twice in sequence) the titration is started.

The titration is carried out by adding titrant stepwise in portions of 0.5 ml by means of the titration pipette and measuring the electrode potential after each addition.

The time required for the electrode couple to reach a stable potential, *i.e.*, to attain a stable value of E'_0 (refer to Part I in this series), after it has been immersed in the sample solution, is the most time-consuming step of this titration technique. After each titrant addition, however, the electrode couple in a well-buffered solution will attain within 15–25 sec a potential that is stable to ±0.1 mV. The time delay between the additions of titrant is preset by use of the control unit and should not be longer than necessary, in order to eliminate a systematic error due to a slow drift in E'_0.

When the change in potential after a titrant addition is large, particularly when going from the acid to the alkaline pH-range, the time required for the electrode to reach a stable potential is longer than mentioned and not very reproducible. In such cases a potential may be preset, and when the electrode potential passes this potential the titration is interrupted. The titration is then not continued until a stable value of the electrode potential is again attained.

When a weak acid is titrated there is a large potential change when the first addition of titrant is made. In order to speed up the titrations in such cases, one addition of titrant is therefore made immediately after lowering the titrant outlet tube into the titration vessel. Owing to low buffer capacity the very first titration point (at $V = 0$ ml) is uncertain and should be discarded anyway.

The titration is terminated when a preset potential has been passed or when a preset number of additions of titrant has been made. For each titration the tape-punch (or printer) records a sample identification number and the measured potential values. The data are then treated according to the principles given in Parts I and II.

(*d*) *Rinsing.* When a titration is finished the combination electrode and the outlet tube for nitrogen are rinsed by dipping them briefly into the subsequent vessel on the turret, containing distilled water. Nitrogen is bubbled through the water during this operation. Before introduction of the electrode into the next vessel containing sample, it is dried in a jet of compressed air. The carry-over from one sample to the next because of incomplete rinsing of the electrode is less than 0.001%.

The titration vessels are rinsed at position 3 (Fig. 2) in the following way. Two tubes are lowered into two neighbouring vessels to draw off the titrated mixture and the rinse water, respectively. The vessel that contained the titrated mixture is then completely filled with distilled water and this is subsequently drawn off. The other vessel is filled with about 20 ml of distilled water so that every second vessel will again contain rinse water. The water is supplied by an aspirator bottle (capable of giving a constant flow of water) *via* two magnetically operated valves.

The carry-over from one sample to the next titrated in the same titration vessel is less than 0.001%. Small droplets of distilled water will adhere to the inside wall of the titration vessel. The volume of this residual water was determined to be ≤0.01 ml. In order to keep this value as small as possible the vessels should be cleaned regularly, preferably once a day, with a detergent.

RESULTS

All titrations were performed in barium chloride medium at a constant ionic strength of 0.5. Since the volumes of the sample- and diluent-pipettes in this case were equal, the diluent should thus be 0.333*M* barium chloride (assuming the sample to have negligible ionic strength). The titrant consisted of 0.03*M* sodium hydroxide in 0.157*M* barium chloride solution.

In this medium, j_H in the equation

$$E = E'_0 + RT/nF \ln (H) + E'_j \qquad (1)$$

where

$$E'_j = j_H(H) + j_{OH}(OH)$$

was determined and found to be –40 mV.l.mole^{-1} [refer to Part I, Eq. (2)]. Determination of j_{OH} is more difficult since the glass electrode yields erroneous results at pH values where the term $j_{OH}(OH)$ is big enough for an accurate determination of j_{OH}. Because of the alkali error of the electrode no titration points were taken at pH values higher than 11.3. For lower values of pH the term $j_{OH}(OH)$ was found to be negligible.

The sodium hydroxide solution used as titrant was standardized by running samples of 0.01*M* hydrochloric acid, which had been assayed by gravimetric determination as silver chloride. This quite laborious standardization procedure was chosen because evaluation of titrations of strong acid by using the Gran method[4] has been carefully tested and found to yield correct results. As the term E_j' in most cases must be taken into account when titrating strong acids, the iteration technique described in Part I, p. 771, was used.

It will be shown in this paper that the method proposed in Part II for the evaluation of ampholytes such as potassium hydrogen phthalate yields accurate results. This substance may thus also be used as a primary standard for titrations performed by stepwise addition of the titrant.

When titrations are evaluated by the methods proposed in Parts I and II a very approximate value of E_0' for the electrode system is enough. However, when the aim is to determine an accurate value of the stability constant of an acid by the Hofstee method,[1,5] an accurate determination of E_0' is required. As was described in Part I, the value of E_0' may be accurately determined by an E_0'-titration. We have determined E_0' by running samples of 0.01*M* hydrochloric acid. The concentration of either the sample or the titrant must then be known. The other concentration is calculated according to Gran. The titration points taken before the equivalence point are used for the calculation of an E_0'-value for use in the acid pH-range. An E_0'-value for use in the alkaline range is calculated from points taken after the equivalence point (refer to Part I, pp. 771 and 778).

A drawback of this titration method is that the ionic strength must not vary by more than a few per cent, in order that the activity coefficients and the liquid junction potential remain constant during the course of the titration. Because the ionic strength of the sample is most often unknown, neutral salt should be added so as to make the ionic strength high enough to render the contribution from the sample negligible. Neutral salts are, however, not quite free from contaminating weak acids even when analytical grade reagents are used. These impurities may generally be neglected when acids in about 0.01*M* concentration are titrated. Problems may arise, however, in very accurate analyses and at lower concentrations of the acids.

The barium chloride used to make the ionic medium was Merck *p.a.* grade. (Chemicals of "Suprapur" grade are not attractive for use in routine analyses because of their high price. It would, however, seem possible to manufacture neutral salts such as barium chloride that are relatively free from contaminating protolytes, though not necessarily "Suprapur" in other respects.) Distilled water from which carbon dioxide had been removed by boiling was used to make the barium chloride solution.

The concentration of the acidic impurities in the 0.167*M* barium chloride medium (ionic strength 0.5) was determined by titrating 100 ml of the solution by adding titrant from a burette and measuring the amount used to reach a pH of 6, 7, 8 and 9. (Initially the pH of the solution was between 5 and 6.) The theoretical additions of titrant needed to yield these pH-values in a pure $BaCl_2$-solution (assuming $pK_w = 13.61$)[6] were then subtracted from the respective experimentally determined values. The difference was taken as a measure of the impurity concentration. The amounts of titrant used to reach pH = 6 corresponded to an impurity concentration of $1.5 \times 10^{-5}M$, to pH = 7 of $2.5 \times 10^{-5}M$, to pH = 8 of $3 \times 10^{-5}M$ and to pH = 9 of $4.5 \times 10^{-5}M$.

The total concentration of the acidic impurities in the 0.167*M* barium chloride medium was also determined by adding 0.1*M* sodium hydroxide (in 0.133*M* barium chloride) in 1-ml portions to 100 ml of the solution and measuring the electrode potential after each addition. The titration data were then treated by the Gran method for use after the equivalence point.[1,4] The plot of $(V_0 + V)/(H)$ against V for the titration gave an intercept with the V-axis corresponding to a total impurity concentration of acids of $4–5 \times 10^{-5}M$.

These results and the fact that the Gran function yielded a perfectly straight line lead to the following conclusions. The impurities may be completely neglected when acids having $\log K_{HA} \leq 5$ and $C_{HA} \geq 0.01M$ are titrated *and only points taken before the equivalence point* are used. Further, when very weak acids ($\log K_{HA} \geq 9.5$) are titrated, the total concentration of impurities found by Gran's method may in accurate determinations be subtracted from the calculated concentration of the sample. (Using the titration apparatus, the total concentration of impurities is determined by running a sample of distilled water from which carbon dioxide has been expelled by boiling.) In the range $5 \leq \log K_{HA} \leq 9.5$ there is no universal solution to the problem. If the ionic strength of the sample is known to be very low it is possible to work at a lower ionic strength. The contribution of the acid to the ionic strength is negligible at these $\log K_{HA}$ values.

In the following, the results of some titrations performed to test the evaluation methods that were proposed in Parts I and II will be presented. The results are summarized in Tables 1 and 2. All the titrations were performed in a 0.167*M* barium chloride medium (having an ionic strength of 0.5). The stability constant values given in the tables are valid for this medium.

Titration of formic acid

Formic acid is a moderately strong acid that cannot be satisfactorily evaluated by Gran's method using titration points before the equivalence point, and Hofstee's method requires an accurate determination of E_0' (refer to Part I). Therefore, some titrations of formic acid were run and evaluated by the methods

Table 1. Results of titrations

	Formic acid		Barbital	β-Alanine	Potassium hydrogen phthalate	Formic acid in presence of 0.02*M* formate	Tartaric acid
log K_{HA}	3.382		7.61	10.050	4.316‡	3.382	2.476 and 3.316
Conc. of the acid, *M*	0.01332*	0.02220*	0.01995†	0.00998§	0.02299¶	0.02215*	0.01154¶
Number of titrant additions	4	7	6	6	7	7	7
Average time per titration, *min*	5	6	6	6	5	6	6
Time between titrant additions, *sec*	20	20	25	20	20	20	20
Number of samples titrated	10	10	10	10	10	10	10
Mean value of the acid conc found, *M*	0.01331 (0.01331)	0.02221 (0.02219)	0.01999 (0.01998)	0.00995	0.02299	0.02216	0.01154
Error, %	<0.1	<0.1	+0.2	−0.3	<0.1	<0.1	<0.1
Coefficient of variation, %	0.10 (0.10)	0.09 (0.12)	0.17	0.30	0.07	0.06	0.13

* Found by titration to a preset pH.
† Found by titration to the inflexion point.
§ Found by perchloric acid titration.
‡ log K_{HB} = 2.58 (refer to Part II)
¶ Weighed.

proposed in Part I. Samples of the acid at two different concentrations were run. The results without brackets in Table 1 were obtained by method B, and the results in brackets with method A (refer to Part I).

Method B does not require a value of K_{HA}, which is an advantage. When many similar samples are to be run, it may, however, be worthwhile to determine the value of K_{HA} by the Hofstee method and then use method A. The number of parameters will then decrease from three to two, resulting in reduced computing time. For formic acid, K_{HA} was determined by running an E'_0-titration before and after the titration of a sample of the acid. The Hofstee method was then used with the mean E'_0-value to calculate a value of K_{HA}. Three such determinations yielded log K_{HA} = 3.383, 3.380 and 3.383, mean value 3.382.

Titration of 2,5-diethylbarbituric acid (barbital)

The log K_{HA} value for barbital in 0.167*M* barium chloride is about 7.6. Assuming normal concentrations (about 0.01*M*) this lies within the relatively narrow range where the Gran method for weak acids gives satisfactory results. Results are given in Table 1. The same titrations were, for comparison, evaluated by using method A and the results are given in brackets in Table 1. (The value of log K_{HA} was first determined as 7.61 by the Hofstee method. For this acidic strength, and C_{HA} = 0.01*M*, method A gives accurate results even when the error in log K_{HA} is large, refer to Part I, Table 8.)

Titration of β-alanine

Evaluation by both methods A and B yields the results given in Table 1. Three additions of titrant were made before and three after the equivalence point. The value of log K_{HA}, as required by method A, was determined as 10.050 by using the Hofstee method in conjunction with E'_0-titrations in the alkaline range. A pK_w-value[6] of 13.610 was used in the determination (refer to Part I, p. 778). When titration points are taken both before and after the equivalence point, method B yields an accurate value of 10.050 for log K_{HA} in these titrations (standard deviation 0.002).

Preliminary results of titrations of *piperidine hydrochloride*—which is a still weaker acid, having log K_{HA} = 11.2—indicate that while method A is still capable of giving results with errors not higher than a few per cent provided that an accurate value of K_{HA} is used, method B gives much greater errors (assuming ≤10 titration points and $C_{HA} \leq 0.01M$,

Table 2. Results of titrations of mixtures of formic and propionic acid

	Mixture I	Mixture II
Formic acid conc., *M*	0.01110	0.01664
Propionic acid conc., *M*	0.00999	0.00600
Total acid conc., *M*	0.02109	0.02264
Number of titrant additions (all made before the equivalence point)	7	7
Average time per titration, *min*	6	6
Time between titrant additions, *sec*	20	20
Number of samples titrated	10	10
Mean value of the formic acid conc found, *M*	0.01104	0.01660
Error, %	−0.5	−0.2
Coefficient of variation %	0.26	0.21
Mean value of the propionic acid conc found, *M*	0.01003	0.00607
Error, %	+0.4	+1.2
Coefficient of variation, %	0.25	0.6
Mean value of the total acid conc found, *M*	0.02107	0.02267
Error, %	−0.1	+0.1
Coefficient of variation, %	0.1	0.08

and the measuring accuracy of our experimental set-up).

Titration of formic acid in the presence of formate

Neither the Gran method nor the Hofstee method is capable of yielding acceptable results for the titration of an acid in presence of its conjugate base, using titration points taken before the equivalence point. A method for use in this case was therefore proposed in Part II. In order to test that method, samples containing formic acid in a mixture with formate were titrated and the titration data evaluated by the proposed method. Approximate values of E'_0 and K_{HA} are required. Only the value of E'_0 was refined (*i.e.*, *f*, refer to Part II) since a large error in K_{HA} may be tolerated without impairing the resulting equivalence volume even when the value of the stability constant is not refined (refer to Part II). The results are given in Table 1.

Titration of potassium hydrogen phthalate

Neither the Gran nor the Hofstee method can be used in this case either The method proposed in Part II requires approximate values of E'_0 and K_{HA} but not of K_{HB}, the value of which may be put equal to zero. The condition for convergence is $|\Delta \log K_{HA}| \lesssim 0.3$. In spite of the large permissible error the calculations did not converge for the value of $\log K_{HA} \approx 5.1$ given in common text books.[7] Therefore, the value was changed in steps of $+0.3$ and -0.3 units until convergence was obtained. The results then contained a value of K_{HA} which could be used in subsequent evaluations. (An approximate value of K_{HA} may be obtained by use of the Hofstee method. This K_{HA} value is sufficiently accurate to yield convergence of the calculations.)

The results are given in Table 1. As is seen, the accuracy and precision of the results are good. Potassium hydrogen phthalate may thus be used as a primary standard even for titrations performed by stepwise addition of titrant.

Titration of tartaric acid

The evaluation method proposed in Part II requires approximate values of E'_0 and the stability constants (or rather the titration constants, refer to Part II). If the calculation does not converge with values taken from the literature, the approach given for the titration of potassium hydrogen phthalate may be used.

Results are given in Table 1. (The logarithmic titration constants $\log K_1$ and $\log K_2$ were determined by using an E'_0-value obtained by an E'_0-titration and not refining *f* during the further calculations. The resulting logarithmic titration constant values were 2.559 and 3.233, respectively, for 0.167*M* barium chloride medium. The corresponding logarithmic stability constants may be calculated to be 2.476 and 3.316, respectively.[2,8])

Titration of a mixture of formic acid and propionic acid

The values of the logarithmic stability constants of formic and propionic acid differ by about one unit. As shown in Part II it is not possible to obtain satisfactory results even from theoretically calculated titration data if all parameters, *i.e.*, $C^0_{HA_1}$, $C^0_{HA_2}$, K_{HA_1}, K_{HA_2} and *f* are calculated or refined (assuming a moderate number of titration points). The method proposed in Part II implies reducing the parameters by determining the stability constants by the Hofstee method. The stability constants of the acids were determined in the same way as described for formic acid. The mean values of $\log K_{HA}$ for formic acid and propionic acid obtained from three determinations of each were 3.383 and 4.528, respectively. Samples of two different mixtures of the acids were titrated and the results are given in Table 2.

Contrary to previous results in this laboratory[9] the values of K_{HA} obtained by the Hofstee method for formic acid and propionic acid were found to be valid also for mixtures of the two acids. This was found by evaluating titrations of known concentrations of the acids and using accurately determined E'_0-values in the evaluation. The only quantities refined were K_{HA_1} and K_{HA_2}. The results were consistent for both 0.167*M* barium chloride and 0.5*M* potassium chloride ionic media, though the values of the constants were different in the different media.

It can be seen from Table 2 that the individual acid concentrations show increasing errors with decreasing proportion of the acid in the mixture and this is according to expectations. The sum of the acids is, however, accurately determined in both cases.

CONCLUSIONS

As can be seen from Tables 1 and 2, the proposed evaluation methods used in conjunction with the automated apparatus presented in this paper are capable of yielding results of remarkable accuracy and precision even in the cases where neither the Gran nor the Hofstee method gives satisfactory results. Thus, a wide variety of analyses is rendered feasible by the method of stepwise addition of equal volumes of titrant. Still more analytical titration problems can be solved along the same lines as those presented in Parts I and II of the present series of papers.

The main reason for the consistency of the results is, in addition to the fact that the evaluation methods are non-approximative, the approach to the problem of a varying E'_0 from one titration to the next. This variation arises when the electrode couple is transferred from one solution to another and is a source of systematic error in titrations of the type discussed, when evaluation methods requiring an accurate calibration of the electrode system are used. Electrode calibrations are time-consuming and impractical except for special purposes such as determining stability constants accurately. The approach used here, which implies using an approximate E'_0-value which

is then refined during the evaluation and used as the starting value for the next titration, provides a practical solution to the problem and its success is evident from Tables 1 and 2.

It is demonstrated in this paper that the method of stepwise addition of equal volumes of titrant is very suitable for automation. Both the control and the evaluation of the titrations along the lines discussed in this series of papers could conveniently be carried out by a mini computer; operation and data handling could then be accomplished by one rather compact system.

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ACID–BASE TITRATIONS BY STEPWISE ADDITION OF EQUAL VOLUMES OF TITRANT WITH SPECIAL REFERENCE TO AUTOMATIC TITRATIONS—IV*

PHOTOMETRIC TITRATION OF AN ACID

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Summary—In Part I of this series, evaluation methods for potentiometric titrations of acids performed by stepwise addition of titrant were introduced. These methods are non-approximative and may therefore in principle be applied to titrations of acids of any strength. This paper demonstrates that photometric titrations performed by stepwise addition of titrant may also be evaluated by the proposed methods. The photometric method is compared with the potentiometric method of monitoring the course of a titration.

In the preceding parts[1–3] of this series methods for the evaluation of potentiometric titrations of acids performed by stepwise addition of titrant were introduced. These methods are non-approximative and can therefore be applied to titrations of acids of most strengths (from strong acids to weak acids having stability constants up to 10^{10}–10^{11} and at $0.01M$ concentration). Another advantage is that a very rough calibration of the electrode system is enough when the evaluation methods are used, which makes the methods very suitable for routine work.

Photometric titrations by stepwise addition of titrant can also be evaluated by the proposed methods. In this paper, titrations of monoprotic acids are discussed and experimental results are given for titrations of formic acid, done with a semiautomatic titration apparatus.

THEORY

Photometric measurement of hydrogen-ion concentration

The hydrogen-ion concentration, [H], of a solution can be determined by measuring the absorbance of an added acid–base indicator. If [HI] denotes the concentration of the acid form of the indicator and [I] the concentration of its base form, then the stability constant of the indicator is

$$K_{HI} = \frac{[HI]}{[H][I]} \tag{1}$$

which gives

$$[H] = \frac{1}{K_{HI}} \frac{[HI]}{[I]}. \tag{2}$$

Assuming absorption cells having unit path-length, the absorbance, A, is

$$A = a_I[I] + a_{HI}[HI] \tag{3}$$

where a_I and a_{HI} are the absorptivities of the indicator species I and HI. If all of the indicator is present in the form of I the absorbance is

$$A_I = a_I C_{HI} \tag{4}$$

where C_{HI} is the total concentration of the indicator. Further, if all of the indicator is present as HI, then the absorbance is

$$A_{HI} = a_{HI} C_{HI}. \tag{5}$$

Since $C_{HI} = [HI] + [I]$, equations (3), (4) and (5) give

$$A_I - A = (a_I - a_{HI})[HI] \tag{6}$$

and

$$A - A_{HI} = (a_I - a_{HI})[I]. \tag{7}$$

Equations (6) and (7) give

$$\frac{[HI]}{[I]} = \frac{A_I - A}{A - A_{HI}}. \tag{8}$$

Equations (2) and (8) give

$$[H] = \frac{1}{K_{HI}}\left(\frac{A_I - A}{A - A_{HI}}\right). \tag{9}$$

When an acid is titrated it is most practical to follow the change of [I] during the titration. The absorbance measurements should therefore be performed at a wavelength where a_I is large and a_{HI} is small.

A_I can be calculated from titration points taken after the equivalence point. A_{HI} can then be calculated as kA_I, where $k = a_{HI}/a_I$. The value of k is determined once and for all in a separate experiment. Before in-

* Part III—*Talanta*, 1977, **24**, 79.

sertion of A_I and A_{HI} into equation (9), these quantities must be corrected for dilution. Often it is possible to find an indicator for which $a_I \gg a_{HI}$ so that A_{HI} may be neglected.

It should be noted that K_{HI} is a concentration constant. The value of K_{HI} will therefore depend upon the nature of the medium in which the titrations are performed. However, the medium not only affects K_{HI} but often also the values of a_I and a_{HI}.[4] It is therefore important to carry out the titrations in a defined medium of constant ionic strength.

If the titrations are performed by the method of stepwise addition of equal volumes of titrant and all titration points are used in the evaluation, the highest precision is obtained if the absorbance of the titration mixture changes linearly with the addition of titrant. This condition is best fulfilled if half of the indicator is in its acid form (and the other half in the base form) at the point where half of the acid sample has been neutralized, in other words at the so-called half-neutralization point.[5] For weak acids this condition is valid if the stability constant, K_{HA}, of the acid is equal to K_{HI}. However, good results can be obtained even if there is a difference of about 0.3–0.5 logarithmic units between the constants.

Calculation of the equivalence volume from photometric titration data

In Part I of this series, the applications of the Gran method[6] and the Hofstee method[7] have been discussed and two non-approximative methods have been proposed for the evaluation of potentiometric titrations of acids. In this communication it is demonstrated that these methods can also be used for the evaluation of photometric titrations involving the stepwise addition of titrant.

From the titration data (V, A), where V is the volume of added titrant and A the absorbance, (V, [H])-values are calculated by use of equation (9). To calculate [H] it is necessary to know the value of K_{HI}. An incorrect value of K_{HI}, denoted by K'_{HI}, will result in an incorrect value of [H], which may be denoted by [H']. Consequently,

$$[H'] = \frac{1}{K'_{HI}} \frac{A_I - A}{A - A_{HI}}. \quad (10)$$

Combination of equations (9) and (10) yields

$$[H] = \frac{K'_{HI}}{K_{HI}}[H'] = f[H'] \quad (11)$$

where

$$f = \frac{K'_{HI}}{K_{HI}}. \quad (12)$$

If the error in log K_{HI} is denoted by $\Delta \log K_{HI}$ so that

$$\log K'_{HI} = \log K_{HI} + \Delta \log K_{HI} \quad (13)$$

then

$$f = 10^{\Delta \log K_{HI}}. \quad (14)$$

Photometric titrations of acids and bases have been evaluated by Higuchi,[8] Johansson[5] and Anfält and co-workers,[9] using the Gran method. This method has the great advantage that it does not require absolute [H]-values but only values proportional to [H]. This means that K_{HI} in equation (9) may be unknown. The Gran functions are, however, approximative and therefore they are applicable only to narrow ranges of acidic strengths.[1]

The method given by Hofstee is non-approximative but requires the use of absolute [H]-values, which means that K_{HI} must be known. An error in K_{HI} gives rise to an error in the equivalence volume calculated by using the Hofstee method. The order of this titration error depends upon the stability constant K_{HA} and the concentration of the acid, as demonstrated in Part I. Table 7 in Part I may be used to estimate the titration error for $\Delta \log K_{HI} = \pm 0.01$ at different values of K_{HA} and concentrations of the acid. Approximate proportionality exists between the titration error and $\Delta \log K_{HI}$.

Methods A and B presented in Part I are also non-approximative. These methods require an approximate value of K_{HI}. However, a very approximate value is sufficient and such a value must be known anyway in order to make possible the choice of a suitable indicator for the titration. (If Δph is exchanged for $\Delta \log K_{HI}$, Part I gives the tolerable error in log K_{HI} that still gives convergence of the calculations.) When these evaluation methods are used, a value of f is obtained as well. Since $K_{HI} = K'^{guess}_{HI}/f$ a corrected value of K_{HI} may be calculated and used in the evulation of subsequent titrations.

EXPERIMENTAL

Titration apparatus

The layout of the titration apparatus is shown in Fig. 1. The apparatus consists mainly of a pneumatically driven piston pipette (AutoChem Instrument AB, Lidingö, Sweden), a photometer (AutoChem Instrument AB) and a control unit. The filter photometer is a double-beam unit equipped with a cylindrical absorption cell. The cell is fitted with a pneumatically driven plunger and a two-way valve so that solution can be sucked up into the cell through one piece of tubing and pumped out through another.

The titrations are performed automatically. Titrant is added in equal portions by means of the titration-pipette and the absorbance of the titration mixture is measured after each addition. Before each measurement of the absorbance, the titration mixture is pumped through the absorption cell twice to rinse the cell. After the equivalence point has been reached, one or more portions of titrant are added and the corresponding absorbance values measured in order to determine the value of A_I [see equation (9)]. The indicator is completely converted into its base form in the vicinity of the equivalence point. Further additions of titrant will only lower the absorbance of the titration mixture because of dilution. When an absorbance reading is less than the preceding value the control unit stops the titration. A preset number of further titrant additions beyond the equivalence point may also be chosen to obtain a more accurate value of A_I.

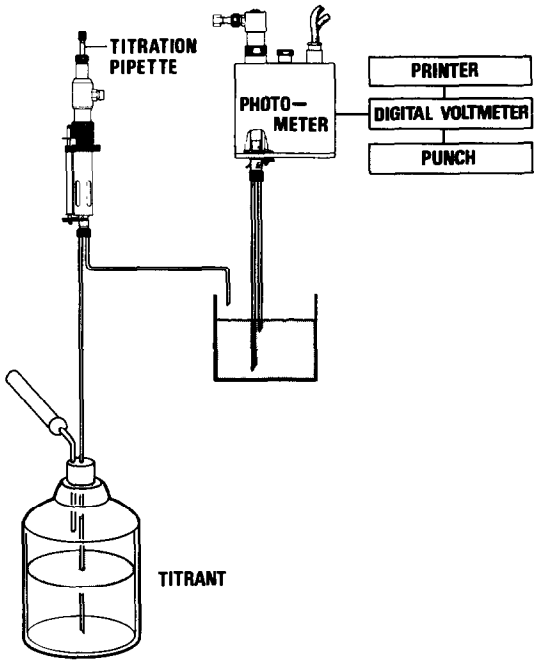

Fig. 1. The titration apparatus.

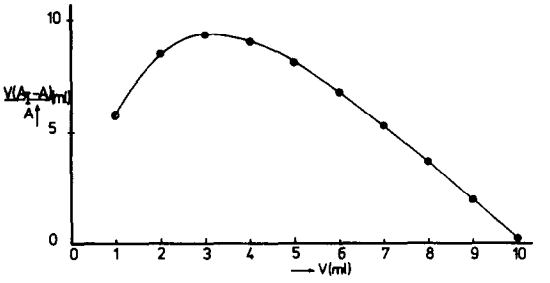

Fig. 2. A Gran plot, $V(A_I\text{-}A)/A = f(V)$, of the data obtained from titration of 100 ml of 0.01 M formic acid with 0.1 M NaCH.

RESULTS

Samples of formic acid were titrated and the titrations were evaluated by method B presented in Part I. The titrations were performed in a barium chloride medium having an ionic strength of 0.5. In this medium, formic acid has a stability constant of about $10^{3.4}$ at 25°. A suitable indicator is therefore Bromophenol Blue, having log $K_{HI} \approx 3.7$ in the same medium. The base form of the indicator has an absorbance maximum at 590 nm. An interference filter giving maximum transmittance at 588 nm was chosen. At this wavelength a_{HI} is negligible compared to a_I. The base form of the indicator was found to obey the Lambert–Beer law within the linear range of the photometer, which is limited to $A = 0$–0.4. The indicator was added to the sample solutions so that the concentration of indicator was about 0.0005% ($\sim 7 \times 10^{-6} M$).

Samples (100 ml) of 0.01006M formic acid were titrated by adding 0.1M sodium hydroxide in portions of 1 ml. Four additions of titrant followed by absorbance measurements were made after the equivalence point. Ten consecutive titrations were evaluated by method B, which gave 0.01007M as the mean value and 0.12% as the coefficient of variation.

For comparison, Fig. 2 shows a Gran plot of the data of one of the titrations. As is evident, it is difficult to calculate an accurate value of the equivalence volume for this titration by using the Gran method.

CONCLUSION

The evaluation methods for potentiometric titrations performed by the method of stepwise addi- of titrant presented in the preceding parts of this series can also be used for evaluating photometric titrations. In contrast to the Gran method, these methods are non-approximative and may therefore in principle be used for evaluating titrations of acids of any strength.

The method of photometric titration by stepwise addition of titrant offers the following advantages compared with potentiometric titration by the same technique.

1. The titrations can be carried out much faster. When the hydrogen-ion concentration is measured potentiometrically, the electrode couple must attain a stable potential in the sample solution before the titration is started (refer to Part III). Photometric titrations may be started immediately after the addition of indicator to the sample solution.

2. When using evaluation methods that do not require the exact value(s) of one or more stability constants, it is not necessary to thermostat the titration mixture to a given temperature. The only requirement is that the temperature does not change during the titration.

The disadvantages are as follows:

1. Each indicator can only be used within a rather narrow pH-range.

2. For some pH-ranges it may be difficult to find a suitable indicator.

3. Some indicators are unstable, particularly in strongly alkaline solution, which makes it difficult to determine an accurate value of A_I. When acids having log $K_{HA} \lesssim 6$ are titrated, this problem may, however, be overcome by adding a weaker acid to the sample solution. The difference between the stability constants of the acids must be at least 4 logarithmic units and the concentration of the added acid should be of the same order as that of the sample. When the equivalence point of the sample is passed the titration mixture will attain pH-values that are lower than if no addition of the weaker acid had been made, but still high enough for the determination of A_I. At these pH-values the risk of decomposition or rearrangement of the indicator is generally much less than in strongly alkaline solution.

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EINFLÜSSE DRITTER PARTNER BEI DER LÖSUNGSSPEKTRALANALYSE NACH DEM ZERSTÄUBERVERFAHREN—II

EINFLÜSSE ORGANISCHER LÖSUNGSMITTEL

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Zusammenfassung—An einem Zerstäuberverfahren für die spektrographische Bestimmung von Aluminium und Silicium in metallurgischen Produkten (Gehalte: 0,1% bis 10%) wurde geprüft, ob Zusätze organischer Lösungsmittel zur Probelösung das Nachweisvermögen dieser Arbeitsweise verbessern. Die Ergebnisse zeigen, daß Zusätze von Äthanol, Methanol, Aceton, Essigsäure oder Ameisensäure die Oberflächenspannung der Lösung herabsetzen, zu einem verminderten mittleren Tropfendurchmesser des Aerosols führen und damit den Durchsatz des Zerstäubers und die Intensität der Spektrallinien verstärken. Ein hoher Dampfdruck der Solventien begünstigt diese Erscheinung. Sehr hohe Viskositäten wirken diesem Effekt entgegen, obwohl die in diesem Zusammenhang verminderte Zerstäubungsgeschwindigkeit das Verhältnis der Strömungsgeschwindigkeiten von Zerstäubergas und Lösung vergrößert und sich damit günstig auf eine Bildung kleinerer Tropfen des Primäraerosols auswirkt. Entsprechend ausgewählte Zusätze führen zu einer entscheidenden Verbesserung des Nachweisvermögens für die Bestimmung von Aluminium und Silicium.

In einer vorangegangenen Arbeit[2] wurden bereits eine Meßeinrichtung und ein Verfahren für die spektrographische Bestimmung von Aluminium und Silicium in metallurgischen Produkten vorgestellt. Die angewandte Zerstäubertechnik gestattet es, Gehalte zwischen 0,1% und 10% mit Variationskoeffizienten $\leq 5\%$ zu erfassen. Die in diesem Zusammenhang durchgeführten Untersuchungen zum Einfluß dritter Partner zeigen, daß Zusätze von Alkali- und Erdalkalisalzen das Nachweisvermögen des Verfahrens verbessern, ohne die Reproduzierbarkeit der Meßergebnisse nachteilig zu beeinflussen.

Weiterhin ist bekannt, daß man bei flammenspektrometrischen Bestimmungsverfahren den zu zerstäubenden Probelösungen mit Wasser mischbare organische Lösungsmittel zusetzt und damit eine entscheidende Verbesserung des Nachweisvermögens erreicht.

Daraus ergibt sich die Frage, ob derartige Effekte auch bei der Anregung im Hochspannungsfunken, einer Lichtquelle, die sich in ihrem Charakter sehr stark von einer Flamme unterscheidet, auftreten. In diesem Falle wäre eine zweite Möglichkeit gegeben, die Bestimmungsgrenzen für Aluminium und Silicium und auch für andere Elemente unter Beibehaltung der gewählten Arbeitsweise[2] in Richtung kleinerer Konzentrationen zu verschieben. Um den Sachverhalt zu überprüfen, wurden die nachfolgend beschriebenen spektrographischen Untersuchungen durchgeführt.

EINFLUSS VON ZUSÄTZEN ORGANISCHER LÖSUNGSMITTEL AUF DIE LINIENINTENSITÄTEN

Für diese Untersuchungen wurden den Lösungen mit 0,1 mg Al/ml organische Lösungsmittel (Methanol, Äthanol, Ameisensäure, Essigsäure und Aceton) in den Abstufungen 2, 5, 10, 20, 40, 60, 80 und 90 Vol-% zugegeben. Die spektrographische Aufnahme dieser Proben erfolgte nach der bereits dargelegten Arbeitsvorschrift.[2] Die Meßpunkte stellen Mittelwerte aus drei Aufnahmen dar. Die Änderung der Linie-Untergrund-Verhältnisse (ΔY) für Al I 3082,16 Å mit dem Zusatz ist in den Abb. 1 bis 3 in logarithmischer Darstellung wiedergegeben. Alle Kurven durchlaufen nach einem mehr oder weniger starken Anstieg der Linienintensität ein Maximum, das je nach Art des Zusatzes zwischen 20 und 80 Vol.-% des zugesetzten Solvens liegt. Am Beispiel von Lösungen mit 0,1 mg Si/ml und steigendem Acetongehalt (Abb. 3) läßt sich ein völlig analoges Verhalten für die Linie Si I 2516,12 Å ablesen.

Die Ergebnisse zeigen, daß die Zusätze organischer Lösungsmittel nicht nur in der Flamme, sondern auch bei Anwendung einer Funkenanregung zu einem

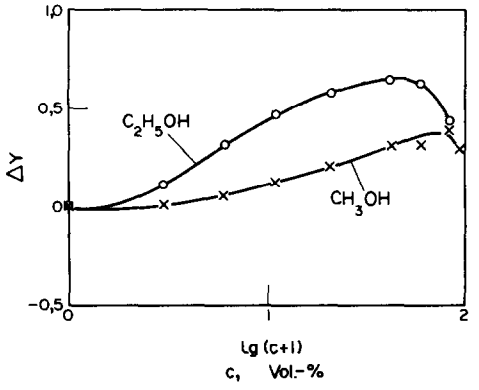

Abb. 1. Einfluß von Äthanol- und Methanolzusätzen auf die Intensität der Linie Al I 3082,16 Å (Al: 0,1 mg/ml).

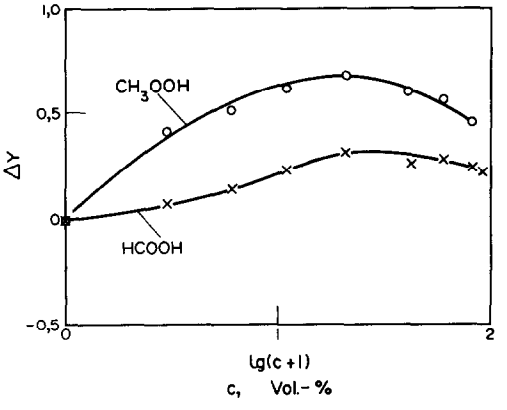

Abb. 2. Einfluß von Ameisen- und Essigsäurezusätzen auf die Intensität der Linie Al I 3082,16 Å (Al: 0,1 mg/ml).

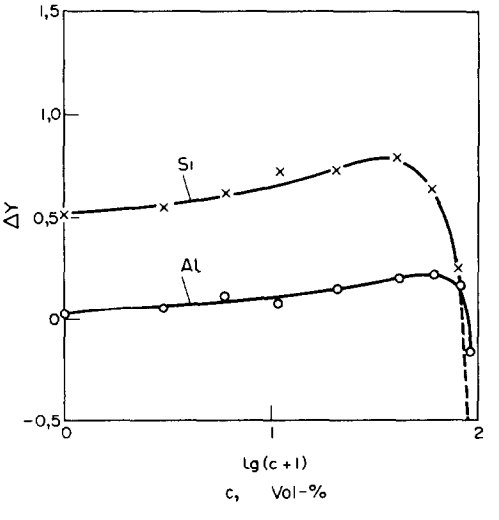

Abb. 3. Einfluß von Acetonzusätzen auf die Intensität der Linien Al I 3082,16 Å und Si I 2516,12 Å (Al: 0,1 mg/ml; Si: 0,1 mg/ml).

erhöhten Nachweisvermögen des Bestimmungsverfahrens führen können.

Auf der Suche nach den Ursachen dieses Befundes lassen sich von vornherein Abgrenzungen treffen. So kann ein, wie bei Anwesenheit von Alkaliionen festgestellter, spektroskopischer Puffereffekt[2] nicht auftreten, da die mit dem Zusatz der Entladung zugeführten Elemente nicht dazu fähig sind, den Anregungs- und Ionisationsgrad von Aluminium und Silicium zu verändern. Eine merkliche Erhöhung der Plasmatemperatur, hervorgerufen durch die vom Zusatz gelieferte Verbrennungsenergie ist ebenfalls nicht zu erwarten.[3,4] Außerdem dürfte eine solche Erscheinung nach unseren Ergebnissen[2] zu keiner Intensitätserhöhung der Linie Al I 3082,16 Å führen.

Hieraus läßt sich schließen, daß die Ursachen für die gemessene Steigerung der Linienintensitäten nur in den veränderten physikalischen Eigenschaften der Lösungen und ihren Einflüssen auf den Zerstäubungs- und Verdampfungsvorgang zu suchen sind.

Die physikalischen Eigenschaften der Lösungen

Die Oberflächenspannung (α), die Dichte (d_f) und die Viskosität (η) der Lösung haben auf die Ausbildung des Aerosols einen entscheidenden Einfluß. Ihre Änderung für Lösungen mit 0,1 mg Al/ml bzw. 0,1 mg Si/ml und mit den entsprechenden steigenden Zusätzen an organischen Lösungsmitteln wurden mit einem Aerometer (d_f), über die kapillare Steighöhe (α) und mit Hilfe eines Höppler-Viskosimeters (η) gemessen. Die Abb. 4 bis 6 zeigen die ermittelten Werte am Beispiel von Aluminiumlösungen mit Zusätzen von Äthanol, Ameisensäure und Essigsäure, wobei die Abhängigkeiten als Funktion $f[\lg(c+1)]$ dargestellt sind. Für Methanol und Aceton ergeben sich ähnliche Kurven wie für Äthanol.

Die Änderung der physikalischen Eigenschaften der Lösungen ist erheblich. So führen die Zusätze bei

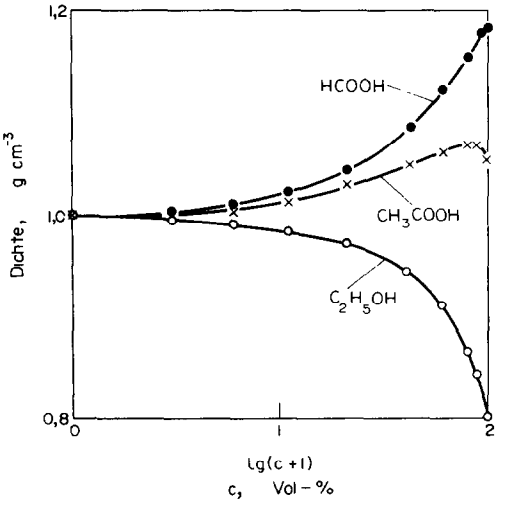

Abb. 4. Abhängigkeit der Dichte d_f einer Lösung mit 0,1 mg Al/ml vom Zusatz an Äthanol, Ameisensäure und Essigsäure.

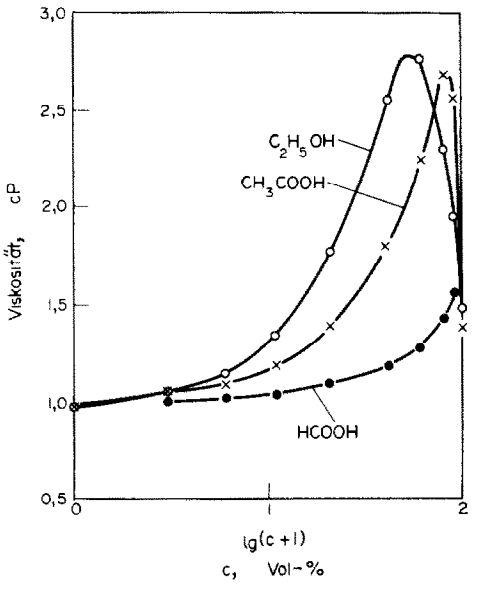

Abb. 5. Abhängigkeit der Viskosität η einer Lösung mit 0,1 mg Al/ml vom Zusatz an Äthanol, Ameisensäure und Essigsäure.

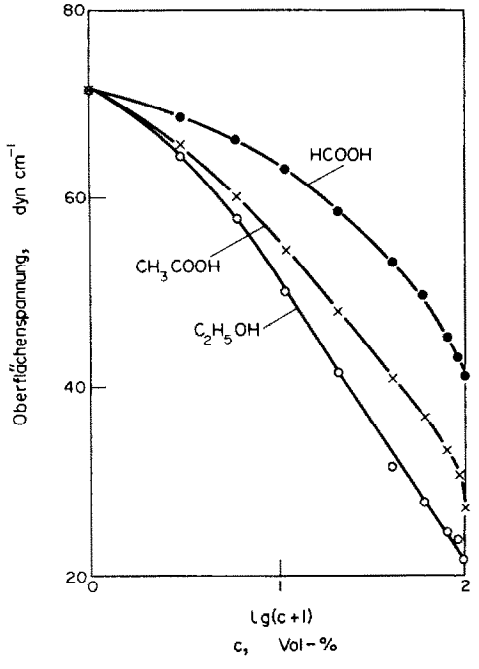

Abb. 6. Abhängigkeit der Oberflächenspannung α einer Lösung mit 0,1 mg Al/ml vom Zusatz an Äthanol, Ameisensäure und Essigsäure.

allen fünf Solventien zu einem steilen Absinken der Oberflächenspannung. Ein ähnliches Verhalten zeigen die Dichten der Proben mit steigenden Gehalten an Äthanol, Methanol bzw. Aceton. Essigsäure und Ameisensäure führen hingegen zu erhöhten Werten. Unterschiedlich verhalten sich auch die Viskositäten in ihrer Abhängigkeit vom Zusatz. Die Kurven für Äthanol und Essigsäure zeigen einen steilen Anstieg, durchlaufen ein Maximum bei etwa 60 Vol.-% (Äthanol) bzw. 80 Vol.-% (Essigsäure) und sinken dann auf Viskositätswerte von etwa 1,4 cP wieder ab. Zusätze von Methanol und Aceton führen zu Maxima, die bei 40 Vol.-% liegen. Der sich anschließende Viskositätsabfall endet bei Werten von 0,6 cP (Äthanol) bzw. 0,4 cP (Aceton) für das reine organische Lösungsmittel. Zusätze von Ameisensäure führen zu einem kontinuierlichen Anstieg der Viskosität, ein Maximum tritt nicht auf.

Die an Siliciumlösungen mit den gleichen Zusätzen durchgeführten Untersuchungen ergaben Daten, die mit den für die Aluminiumlösungen erhaltenen weitgehend übereinstimmen. Tabelle 1 zeigt dies am Beispiel der Acetonzusätze. Nur dieses Lösungsmittel zeigt gelegentliche Abweichungen der Meßwerte, die jedoch so gering sind, daß ihr möglicher Einfluß auf die Linienintensität in den nachfolgenden Darlegungen vernachlässigt werden kann.

Zerstäubungsgeschwindigkeit, Durchsatz und Wirkungsgrad

Um den Einfluß der veränderten physikalischen Eigenschaften auf die Parameter der Zerstäubung zu überprüfen, wurden die Zerstäubungsgeschwindigkeit (v), der Durchsatz (v_d) und der Wirkungsgrad (κ) des angewendeten Zerstäubersystems in Abhängigkeit vom Zusatz organischer Lösungsmittel bestimmt.

Grundlage hierfür war die Beziehung

$$\kappa = \frac{v_d \cdot 100}{v} = \frac{v - v_r}{v} \cdot 100[\%] \qquad (1)$$

in der v_d der pro Zeiteinheit der Entladung zugeführten Lösungsmenge entspricht, während die Meßgrößen v und v_r (Rücklaufgeschwindigkeit) die Lösungsvolumina darstellen, die pro Zeiteinheit vom

Tabelle 1. Physikalische Eigenschaften von Lösungen mit 0,1 mg Al/ml bzw. 0,1 mg Si/ml und Zusätzen von Aceton

Element	Zusatz, *Vol.-%*	η, *cP*	d_f, *g/cm³*	α, *dyne/cm*
Al	0	0,98	0,998	71,6
	2	1,01	0,996	63,8
(0,1 mg/ml)	5	1,07	0,993	57,5
	10	1,17	0,988	50,9
	20	1,35	0,977	43,8
	40	1,54	0,953	35,1
	60	1,38	0,918	30,6
	80	0,87	0,870	26,9
	90	0,59	0,841	25,8
	100	0,39	0,790	23,2
Si	0	1,01	0,997	71,5
	2	1,01	0,995	63,7
(0,1 mg/ml)	5	1,07	0,992	57,3
	10	1,17	0,987	50,4
	20	1,35	0,977	43,5
	40	1,66	0,958	36,3
	60	1,56	0,928	31,2
	80	1,10	0,885	27,2
	90	0,81	0,858	26,2
	100	0,39	0,790	23,2

Zerstäuber angesaugt und versprüht werden (v) bzw. sich an den Wänden der Zerstäuberglocke abscheiden und zurückfließen (v_r). Die Messungen erfolgten an Lösungen mit 0,1 mg Al/ml und steigenden Zusätzen an Äthanol, Aceton bzw. Essigsäure (0–80 Vol.-%).

Refraktometrische Analysen der Probelösungen vor und nach der Zerstäubung bestätigten,[1] daß bei geschickter Versuchsführung keine Verarmung an der leichtflüchtigen Komponente während des Meßvorganges in den Lösungen eintritt. Die an Lösungen mit Äthanolzusatz gemessenen Werte sind in der Abb. 7 dargestellt; Aceton und Essigsäure führen zu analogen Ergebnissen. Der Verlauf der Kurvenzüge bestätigt die bei gleichbleibender Geräteanordnung nach dem Hagen–Poiseuille'schen Gesetz

$$\eta = \frac{\pi \cdot r^4 \cdot t}{8v} \cdot \frac{p_1 - p_2}{l} = \frac{\text{const}}{v} \qquad (2)$$

erwartete umgekehrte Proportionalität zwischen der Zerstäubungsgeschwindigkeit und der Viskosität (Abb. 5). Bezeichnend ist, daß das Maximum der Viskosität und das Minimum der Zerstäubungsgeschwindigkeit bei der gleichen Konzentration des Zusatzes zu finden sind.

Besonders Beachtung verdient weiterhin, daß trotz abnehmender Probenzufuhr in allen Fällen die Intensität der Linie Al I 3082,16 Å ansteigt. Eine Erklärung hierfür geben die Änderungen von Durchsatz und Wirkungsgrad. Beide Größen steigen kontinuierlich mit dem Zusatz an, d.h. der Anteil der Probe, der als Sekundäraerosol in die Entladungszone des Funkens getragen wird, erhöht sich trotz sinkender Zerstäubungsgeschwindigkeit. Unter diesen Bedingungen ist der gemessene Intensitätsanstieg der Aluminiumlinie verständlich. Die Ursache für dieses Verhalten muß in einer veränderten Tropfenverteilung

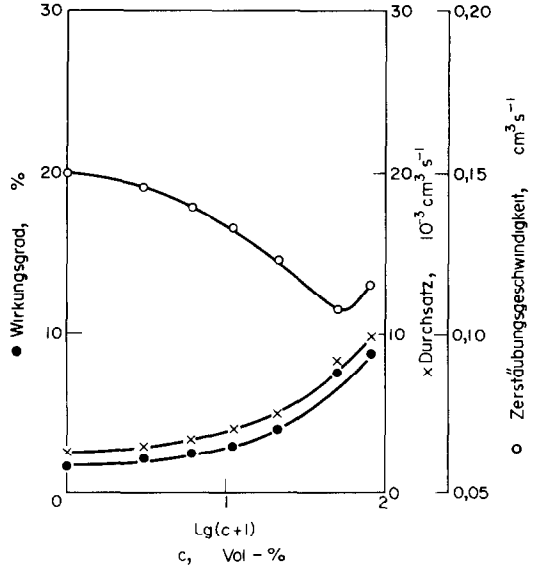

Abb. 7. Wirkungsgrad κ. Zerstäubungsgeschwindigkeit v und Durchsatz v_d in Abhängigkeit vom Äthanolzusatz für eine Lösung mit 0,1 mg Al/ml.

Tabelle 2. Siedepunkte der Lösungsmittel sowie Oberflächenspannungen und Wirkungsgrade von Lösungen mit 80 Vol.-% Zusatz

Lösungsmittel	Siedepunkt, °C	κ, %	α, *dyne/cm*
Aceton	56,3	17,3	26,9
Äthanol	78,3	8,7	24,8
Essigsäure	118,1	4,5	33,2
Wasser	100,0	1,6	72,5

des an der Zerstäuberdüse erzeugten Primäraerosols liegen. Offensichtlich führt die bereits bei geringen Zusätzen stark herabgesetzte Oberflächenspannung (Abb. 6) zu einem verminderten mittleren Tropfendurchmesser und damit zu den in der Abb. 7 dargestellten Ergebnissen.

Wäre das Absinken der Oberflächenspannung die einzige Ursache für die Erhöhung des Wirkungsgrades, so müßten alle organischen Lösungsmittel, die zu gleichen Änderungen der Oberflächenspannung führen, auch übereinstimmende Wirkungsgrade ergeben. Die Werte der Tabelle 2 zeigen, daß die Ergebnisse dieser Annahme widersprechen. So sind z.B. die für Äthanol und Aceton auftretenden unterschiedlichen Wirkungsgrade nicht durch Abweichungen in der Oberflächenspannung erklärbar. Bezieht man jedoch die Siedepunkte der Zusätze in die Betrachtung ein, so wird ersichtlich, daß Einflüsse des Verdampfungsverhaltens der Lösungsmittel auf den Wirkungsgrad vorliegen müssen.

Es ist vorstellbar, daß leicht verdampfbare Zusätze den mittleren Tropfendurchmesser frühzeitig, d.h. unmittelbar nach der Zerstäubung reduzieren und damit den Wirkungsgrad und den Durchsatz erhöhen.

Weiterhin ist in diesem Zusammenhang die bereits bei Schwefelsäurezusätzen[2] festgestellte intensitätsmindernde Wirkung hoher Viskositäten auf die Aluminiumlinien zu berücksichtigen. Dieser Einfluß wird durch Messungen, die an Lösungen mit 0,1 mg Al/ml und mit steigenden Mengen von 6*M* Trichloressigsäure (0 bis 90 Vol.-%) durchgeführt wurden, besonders deutlich (Abb. 8 und 9).

Der steile Anstieg der Viskosität mit dem Zusatz führt, wie erwartet, zu einem starken Absinken der Zerstäubungsgeschwindigkeit. Obwohl ein steiler Abfall der Oberflächenspannung vorliegt, ergibt sich, verglichen mit den bei Äthanol- bzw. Acetonzusätzen erhaltenen Ergebnissen, nur eine geringfügige Erhöhung des Wirkungsgrades. Der Durchsatz des Zerstäubers bleibt dabei annähernd konstant. Dementsprechend ist auch nur ein geringer Anstieg der für das Nachweisvermögen maßgebenden ΔY-Werte bis zu 20 Vol.-% Trichloressigsäure festzustellen. Oberhalb dieser Konzentration sinken die Linienintensitäten wieder ab. Die Ursache für dieses Verhalten liegt darin, daß die nachweisverbessernde Wirkung der verminderten Oberflächenspannung durch sehr hohe Viskositäten und die damit verbundene

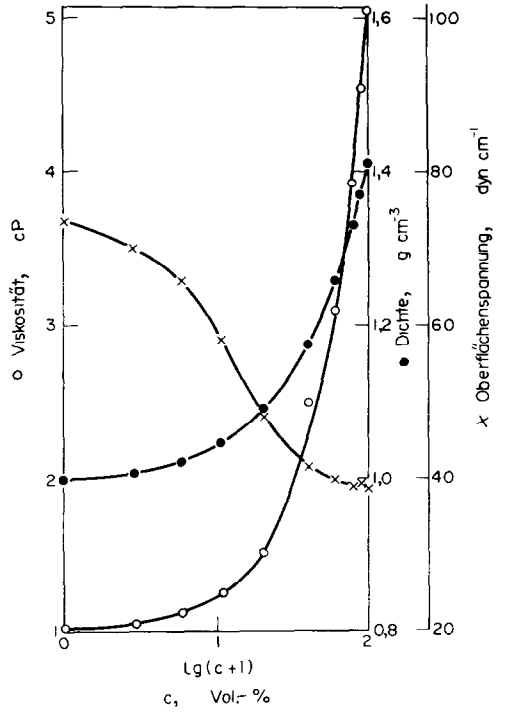

Abb. 8. Einfluß des Zusatzes an Trichloressigsäure auf die physikalischen Eigenschaften einer Lösung mit 0,1 mg Al/ml.

Beeinträchtigung des Zerstäubungsvorganges weitgehend aufgehoben wird.

Da die festgestellten Änderungen des Durchsatzes und des Wirkungsgrades ausschließlich vom Zusatz der organischen Lösungsmittel verursacht werden, sind die für Aluminium erhaltenen Ergebnisse ohne weiteres auf Silicium übertragbar. Eine Überprüfung zeigt, daß z.B. Lösungen mit 0,1 mg Al/ml und 0,1 mg Si/ml sowie 20 Vol.-% Äthanol mit κ_{Al} = 3,96% und κ_{Si} = 3,87% weitgehend übereinstimmende Wirkungsgrade bei der Zerstäubung aufweisen.

Einflüsse der Zerstäubungsgeschwindigkeit auf die Linienintensität

Die mit steigender Viskosität verminderte Zerstäubungsgeschwindigkeit wirft die berechtigte Frage auf, ob die herabgesetzte Probenzufuhr bei konstantem Zerstäuberdruck bereits Ursache für die Änderung des Tropfenspektrums und damit der Linienintensität sein kann.

Um dies zu prüfen, wurden die spektrographischen Messungen an Aluminiumlösungen mit Äthanolzusatz mit einer geänderten Geräteanordnung[1] wiederholt. Hierbei wurde als Probebehälter ein Niveaugefäß verwendet, das auch bei wechselnder Viskosität die Einstellung einer konstanten Zerstäubungsgeschwindigkeit gestattet. Die Meßergebnisse (Abb. 10) zeigen einen kontinuierlichen Anstieg der ΔY-Werte mit wachsendem Zusatz an Äthanol. Dieser Kurvenverlauf weicht stark von dem in Abb. 1 dargestellten ab; das bei Messungen mit veränderlicher Zerstäubungsgeschwindigkeit (Abb. 1) gefundene Maximum der Kurve tritt nicht auf. Diese Erscheinung ist weder mit der Oberflächenspannung noch mit dem Verdampfungsverhalten der Lösungen zu erklären. Offenbar führt auch das bei steigender Viskosität und damit sinkender Probenzufuhr erhöhte Verhältnis der Strömungsgeschwindigkeiten von Luft und Flüssigkeit zu einem verminderten mittleren Tropfendurchmesser und somit zu erhöhten Linienintensitäten des Aluminiums. Daß bei Zusatz von Äthanol auch dieser Einfluß wirksam wird und sich mit denen der verminderten Oberflächenspannung und des veränderten Verdampfungsverhaltens überlagert, zeigen die Ergebnisse in Abb. 1. Bezeichnend dafür ist, daß die Maxima der Linienintensität und der Viskosität (Abb. 5) bei dem gleichen Äthanolgehalt (40 bis 60 Vol.-%) auftreten.

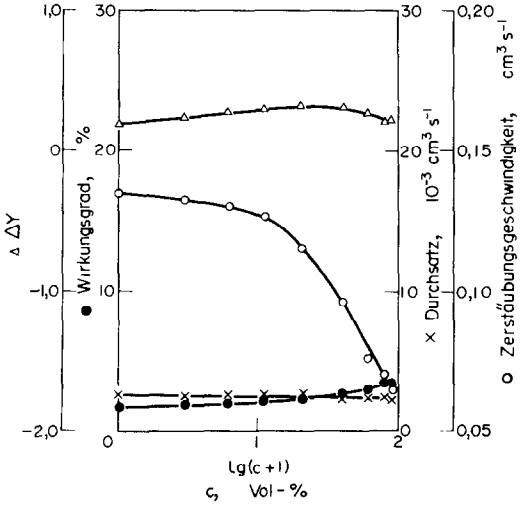

Abb. 9. Einfluß von Trichloressigsäurezusätzen auf die Zerstäuberdaten und auf die Intensität der Linie Al I 3082.16 Å (Al: 0,1 mg/ml).

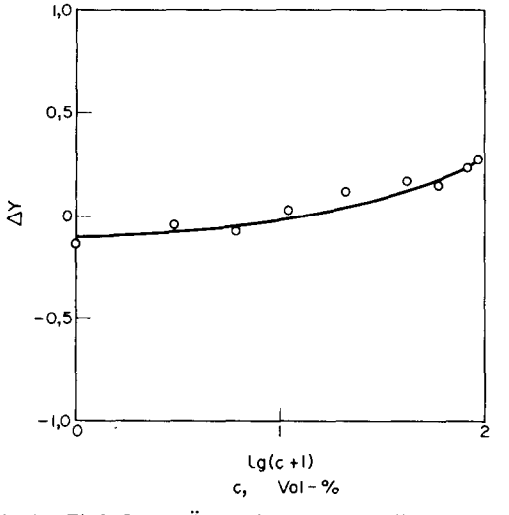

Abb 10 Einfluß von Äthanolzusätzen auf die Intensität der Linie Al I 3082.16 Å bei konstanter Zerstäubungsgeschwindigkeit (Al: 0,1 mg/ml).

Der Einfluß der angesaugten Lösungsmenge allein läßt sich leicht überprüfen, wenn man eine Lösung mit 0,1 mg Al/ml und 50 Vol.-% Äthanol spektrographiert und dabei unter sonst konstanten Bedingungen (Druck, Viskosität, Oberflächenspannung, Dichte usw.) mit Hilfe des Niveaugefäßes unterschiedliche Zerstäubungsgeschwindigkeiten (zwischen 0,077 und 0,13 cm^3/s in zehn Stufen) vorgibt. Die Messungen[1] zeigen, daß die ΔY-Werte unabhängig von der Zerstäubungsgeschwindigkeit sind. Sie liefern keine Erklärung für den in den Abb. 1 und 10 dargestellten unterschiedlichen Kurvenverlauf. Eine Bestätigung des Verhaltens der Linienintensitäten geben die unter den gleichen Bedingungen ermittelten Zerstäubungsdaten. Während die Rücklaufgeschwindigkeit mit der Zerstäubungsgeschwindigkeit ansteigt, bleibt bei abnehmendem Wirkungsgrad der für die ΔY-Werte maßgebliche Durchsatz des Zerstäubers konstant.

DEUTUNG DER MESSERGEBNISSE

Kocsis, Gegus und Erdey[5,6] untersuchten die Tropfenverteilungen an indirekten pneumatischen Zerstäubern, die in ihrer Konstruktion mit der von uns gewählten Anordnung weitgehend übereinstimmen. Die für wässrige Lösungen bestimmten mittleren Tropfendurchmesser betrugen 30 μm für das Primär- und 5 μm für das Sekundäraerosol. Die damit verbundene Oberflächenvergrößerung pro Volumeneinheit um den Faktor 6,0[1] der in die Entladungszone eingebrachten Lösungsmenge ist die Ursache dafür, daß auch indirekte Zerstäuber—verglichen mit Direktzerstäubern—mit Wirkungsgraden von wenigen Prozent zu akzeptablen unteren Bestimmungsgrenzen führen. Die vergrößerte Oberfläche des Sekundäraerosols gewährleistet eine schnellere Verdampfung des Lösungsmittels, führt zu einer feineren Verteilung des Lösungsrückstandes und erhöht als Folge davon den Anteil der angeregten Atome. Die direkte Abhängigkeit der Tropfengröße von der Oberflächenspannung für recht unterschiedliche Zerstäubersysteme[7,8] und experimentelle Untersuchungen[5,6] bestätigen, daß geeignete Zusätze organischer Lösungsmittel zu einer höheren Dispersion des Primäraerosols führen. Damit steigen—konstante Selektionsbedingungen des Zerstäubergefäßes vorausgesetzt—der Wirkungsgrad und der Durchsatz entscheidend an; es wird eine größere Menge des zu bestimmenden Elementes der Anregungsquelle zugeführt. Dies ist eine entscheidende Ursache für die Erhöhung der Linienintensitäten bei Zusatz organischer Lösungsmittel.

Darüber hinaus spielt das Verdampfungsverhalten der Lösungen eine wichtige Rolle. Setzt man einer Probe Solventien wie Äthanol oder Aceton zu, so ergibt sich neben der vergrößerten Oberfläche, hervorgerufen durch den verminderten mittleren Tropfendurchmesser, auch eine beschleunigte Verdampfung der Lösung durch den erhöhten Dampfdruck über den Tropfen, wie sich über eine grobe Abschätzung[1] nach einer von Langmuir[9] abgeleiteten Beziehung leicht zeigen läßt. Dies bewirkt, daß die zu bestimmenden Elemente in konzentrierterer Lösung, d.h. in angereicherter Form, in die Lichtquelle gelangen, womit eine zweite Ursache für den emissionssteigernden Einfluß organischer Lösungsmittel gegeben ist.

Wie bereits bei der Darlegung der Meßergebnisse zum Ausdruck kam, kann auch die Viskosität und damit das Verhältnis der Strömungsgeschwindigkeiten von Zerstäubergas und Probelösung einen Einfluß auf die Tropfengröße ausüben. Zur Klärung des gesamten Sachverhaltes sei hier eine Beziehung (3) nach Nukiyama und Tamasawa[7] herangezogen,

$$D_0 = \underbrace{\frac{586}{w_1}\cdot\frac{\sqrt{\alpha}}{\sqrt{d_f}}}_{\text{I}} + \underbrace{597\left(\frac{\eta}{\sqrt{\alpha\cdot d_f}}\right)^{0{,}45}\cdot\left(\frac{1000v}{v_1}\right)^{1{,}5}}_{\text{II}} \qquad (3)$$

in der neben den bereits bekannten Größen D_0 den mittleren Tropfendurchmesser in μm, w_1 die Geschwindigkeit der Preßluft in der Austrittsöffnung der Düse in m/s und v_1 den Luftverbrauch in cm^3/s darstellen.

Obwohl (3) streng genommen nur für Ringspaltzerstäuber gilt, muß für den von uns angewendeten Knierohrzerstäuber die Abhängigkeit des Tropfendurchmessers des Primäraerosols von den physikalischen Eigenschaften der Lösung und von den Zerstäubungsbedingungen einer Funktion $D_0 = f(\alpha,\eta,d_f,v,v_1,w_1)$ genügen, die der Formel (3) sehr nahe kommen kann. Nachfolgend soll versucht werden, für die beschriebenen Meßergebnisse eine (zumindestens halbquantitative) Erkläring zu finden.

Betrachten wir zuerst Term I der Gleichung (3) und berücksichtigen, daß w_1 bei allen Versuchen konstant bleibt und daß d_f selbst in ungünstigen Fällen (Äthanol, Methanol, Aceton) nur auf 0,8 g/cm^3 absinken kann, so wird deutlich, daß durch die direkte Proportionalität zwischen α und D_0 ein Absinken des Tropfendurchmessers mit der Oberflächenspannung erfolgen muß, denn α sinkt weit stärker ab als d_f. Dies bestätigt die vorangegangenen Überlegungen. Term I verkörpert den Effekt der Verfeinerung des Aerosols bei sinkender Oberflächenspannung. Ansteigende Dichten (Ameisensäure, Essigsäure) begünstigen diese Erscheinung.

Term II wird wie Term I niemals < 0, ist mit diesem additiv gekoppelt und gibt die Einflüsse der Viskosität und des Verhältnisses v_1/v auf die Tropfengröße wieder.

Für den Fall, daß $v_1/v > 5000$ beträgt, dieser tritt ein, wenn w_1 in der Nähe der Schallgeschwindigkeit liegt, kann Term II vernachlässigt werden. Dann wird die Tropfengröße eine reine Funktion von Oberflächenspannung und Dichte. Unsere Versuchsanordnung führt unter normalen Betriebsbedingungen (Düse: 0,4 mm Durchmesser, $p = 0{,}45$ atü) zu Werten von $v_1/v \approx 500$; d.h. Term II muß bei unserer Betrachtung berücksichtigt werden. Im vereinfachten Ausdruck B sind η und v zwei mit dem Zusatz von

organischen Lösungsmitteln

$$B = \frac{\text{II}}{597} = \left(\frac{\eta}{\sqrt{\alpha \cdot d_f}}\right)^{0,45} \cdot \left(\frac{1000v}{v_l}\right)^{1,5} \qquad (4)$$

veränderliche Größen, die einander umgekehrt proportional sind, d.h. nach dem Maß ihrer Änderung kann B mit steigendem Zusatz einen sinkenden oder anwachsenden additiven Anteil zur Tropfengröße liefern.

Nachfolgend sollen diese Zusammenhänge am Beispiel des Äthanol (Tabelle 3, Abb. 11) gezeigt werden. Unter Zugrundelegung der beschriebenen Meßergebnisse läßt sich B für den in Abb. 1 dargestellten Fall ohne weiteres berechnen. Dies gilt ebenfalls für die in Abb. 10 dargestellten Messungen, bei denen $v = 0{,}15$ cm³/s mit Hilfe eines Niveaugefäßes konstant gehalten wurde. In diesem Fall ergibt sich ein B':

$$B' = 3\left(\frac{\eta}{\sqrt{\alpha \cdot d_f}}\right)^{0,45} \qquad (5)$$

da $(1000v/v_l)^{1,5} = \text{const.} = 3{,}0$ für die gewählten Versuchsbedingungen ist.

Die Änderungen von B und B' mit dem Äthanolzusatz sind in Abb. 11 graphisch dargestellt. Bei geringen Zusätzen sinkt B schwach ab, was der steilen Abnahme von Term I mit der Oberflächenspannung entgegenkommt. Die damit verbundene Abnahme des Tropfendurchmessers führt zu einem Anstieg der Linienintensität (Abb. 1). Erst bei Zugaben über 10 Vol.-% beginnt B, bedingt durch die Viskosität, anzusteigen und damit der Abnahme der Oberflächenspannung bzw. des Term I entgegenzuwirken. Für Zusätze über 50 Vol.-% ändert sich Term I nur noch geringfügig; hingegen steigt B trotz sinkender Viskosität noch an. Dies ergibt einen vergrößerten Tropfendurchmesser, d.h. ein Absinken der Linienintensität. Nach dieser Abschätzung müssen die Intensitätswerte ein Maximum durchlaufen, das durch die Ergebnisse in Abb. 1 bestätigt wird.

Betrachtet man den Verlauf von B', der den Messungen mit konstanter Zerstäubungsgeschwindigkeit (Abb. 10) entspricht, so ergibt sich ein veränderter Sachverhalt. B' zeigt, da $v = \text{const.}$, einen steilen

Tabelle 3. Die Änderung der physikalischen Eigenschaften der Lösung, der Zerstäubungsgeschwindigkeit und der Ausdrücke B und B' mit dem Zusatz an Äthanol

Zusatz, Vol.-%	α, dyne/cm	d_f, g/cm³	η, cP	v, cm³/s	B	B'
0	72,0	1,000	1,00	0,150	0,1444	0,1444
2,0	64,5	0,995	1,05	0,145	0,1437	0,1514
5,0	58,0	0,990	1,14	0,139	0,1426	0,1608
10,0	50,4	0,984	1,34	0,133	0,1492	0,1789
20,0	41,6	0,974	1,77	0,123	0,1569	0,2123
50,0	30,0	0,930	2,78	0,108	0,1734	0,2828
80,0	24,8	0,866	2,30	0,114	0,1815	0,2755

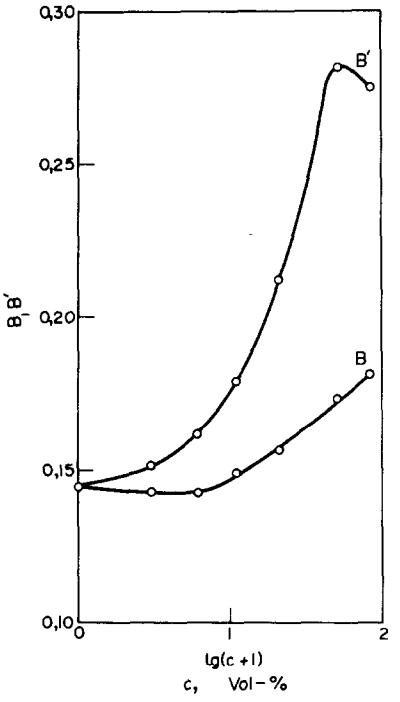

Abb. 11. Änderung der Ausdrücke B und B' (Gleichung (4) und (5)) mit steigenden Zusätzen an Äthanol.

Anstieg mit der Viskosität, begünstigt durch die sinkenden Werte von α und d_f, bis zum Viskositätsmaximum bei 50 Vol.-% Äthanol. Oberhalb dieser Konzentration, wo sich α nur noch geringfügig ändert und η wieder steil absinkt, nimmt auch B' wieder ab. Dies erklärt den in Abb. 10 dargestellten Verlauf der Intensitätsänderung. Mit $B' \gg B$ wächst Term II so stark an, daß die Abnahme von Term I mit der Oberflächenspannung stark ausgeglichen wird und sich nur geringe Intensitätserhöhungen mit steigendem Äthanolgehalt ergeben. Erst bei Zusätzen über 50 Vol.-% ergibt sich, wie aus dem Verlauf von B' zu erwarten ist, eine etwas stärkere Empfindlichkeitserhöhung. Daß B und B' ebenso wie die Kurven in den Abb. 1 und 12 bei 50 Vol.-% die größten Abweichungen voneinander zeigen, ist ein zusätzlicher Beweis für die Richtigkeit dieser Schlußfolgerungen.

Diese Ergebnisse lassen noch die Frage offen, ob die Änderung von B bei hohen Zusätzen auch einen Einfluß auf den Wirkungsgrad und auf den Durchsatz des Zerstäubers hat. Tatsächlich zeigt für Äthanol (Abb. 7) der Meßpunkt bei 50 Vol.-% eine reproduzierbare Abweichung aus dem Kurvenverlauf, der in diesem Sinne gedeutet werden könnte. Allerdings wird bei hohen Zusätzen leicht flüchtiger organischer Lösungsmittel eine gesteigerte Verdampfungsrate wirksam, die diesen Effekt weitgehend überdeckt.

In diese Betrachtungen lassen sich auch die mit anderen Zusätzen durchgeführten Messungen einbeziehen. So steigt z.B. bei Zugabe von Trichloressigsäure (Abb. 8 und 9) der Ausdruck B so stark an, daß die Abnahme von Term I mit der Oberflächen-

spannung nahezu ausgeglichen wird und nur ein äußerst flaches Intensitätsmaximum festzustellen ist.

Als Ergebnis dieser Betrachtungen läßt sich schließen, daß bei Zusätzen geeigneter organischer Lösungsmittel eine Erhöhung der Linienintensität durch eine verminderte Oberflächenspannung eintritt. Dieser Effekt kann durch einen erhöhten Dampfdruck der Lösung noch verstärkt werden. Sehr hohe Viskositäten wirken dieser Erscheinung entgegen, obwohl die in diesem Zusammenhang verminderte Zerstäubungsgeschwindigkeit sich günstig auf eine Bildung kleinerer Tropfen auswirkt.

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Summary—A nebulizer procedure, used in spectrographic determination of aluminium and silicon in metallurgical products at levels of 0.1–10%, has been investigated to find whether adding an organic solvent to the sample solution will improve the sensitivity of the handling. Results indicate that addition of ethanol, methanol, acetone, acetic acid or formic acid leads to a smaller mean drop-size in the aerosol, by lowering the surface tension of the solution, and hence increases the throughput of the nebulizer and therefore also the intensity of the spectral line. The effect is more marked with solvents of high vapour pressure. Very high viscosity of the mixed solvent is disadvantageous, although the reduced rate of nebulization increases the ratio of the velocities of the nebulizer gas and solution, and therefore has a beneficial effect in producing smaller droplets in the primary aerosol. Suitably chosen additions of solvent result in a significant improvement in the sensitivity for the determination of aluminium and silicon.

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PHOTOMETRISCHE BESTIMMUNG VON QUECKSILBER(II) IM NANOGRAMMBEREICH MIT THIO-MICHLERS KETON

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Zusammenfassung—Die auf der Grundlage des roten Hg–TMK-Komplexes entwickelte photometrische Methode zur Hg(II)-Bestimmung im Nanogrammbereich arbeitet in einem wäßrig-n-propanolischen Medium (30 Vol.% n-Propanol), dessen pH-Wert durch Acetatpuffer auf pH 5,8 eingestellt wird. Bei einer Wellenlänge von 560 nm erreicht der molare Extinktionskoeffizient einen Wert von $1{,}51 \cdot 10^5$ $1 \cdot mole^{-1} \cdot cm^{-1}$, was einem Sandell-Index von 0,0013 μg Hg/cm^2 entspricht. Das Lambert-Beersche Gesetz gilt von 0,007 bis 1,5 μg Hg/ml. Die Nachweisgrenze liegt bei Verwendung von 5-cm Küvetten bei 4,2 ng Hg/ml und die Erfassungsgrenze bei 7,1 ng Hg/ml. Neben statistischen Angaben werden Richtwerte für das Störverhalten einer Vielzahl von Ionen gegeben.

Das 4,4′-Bisdimethylaminothiobenzophenon, ein im Jahre 1886 von A. Kern patentierter Farbstoff,[1] der in Anlehnung an das 4,4′-Bisdimethylaminobenzophenon (Michlers Keton) als Thio-Michlers Keton (TMK) bezeichnet wird, stellt ein empfindliches Reagens für die photometrische Quecksilberbestimmung dar, das in der Vergangenheit nur wenig beachtet wurde. Gehauf und Goldensen geben eine colorimetrische Methode an,[2] die auf der Ausnutzung des blauen Hg–TMK-1:1-Komplexes und der Extraktion des überschüssigen Reagens in Athyläther beruht, in dem der Quecksilberkomplex selbst unlöslich ist. Cheng und Goydish[3] entwickelten zwei photometrische Verfahren, die beide auf dem roten Hg–TMK-1:3-Komplex basieren, der sich bei Reagensüberschuß bildet. Dieser Quecksilberkomplex wird entweder nach Extraktion in Isopentanol oder direkt in der wäßrig-äthanolischen Phase photometriert. Das im folgenden beschriebene Verfahren, in dem ein Wasser–n-Propanol-Medium angewandt wird, soll anschließend mit bisherigen photometrischen Quecksilberbestimmungsverfahren verglichen werden.

EXPERIMENTELLER TEIL

Lösungen

Hg-Stammlösung, 0,01*M*. $Hg(NO_3)_2 \cdot 2H_2O$ *p.a.* Hg-Gehalt wurde komplexometrisch geprüft.

Reagenslösung, $2{,}5 \cdot 10^{-4}$*M*. TMK in chromatographisch reinem n-Propanol.

pH-Einstellung. Verdünnte HNO_3 (*p.a.*) bzw. KOH (*p.a.*); Acetatpuffer (0,2*M* Essigsäure *p.a.* und 0,2*M* Natriumacetat *p.a.*).

Eigenschaften des Reagens

TMK stellt eine dunkelrote, feinkristalline, wasserunlösliche Substanz dar, deren alkoholische Lösungen eine intensiv gelbe Farbe aufweisen. Zu Vergleichszwecken wurde das Reagens auf zwei Wegen selbst synthetisiert. Der erste Weg führt nach Wallach[4] über die Umsetzung von 4,4′-Bisdimethylaminodiphenylmethan mit Schwefel zum TMK, während man auf dem zweiten Weg über die Reaktion zwischen Auramin und Schwefelwasserstoff nach Graebe[5] zum Ziel gelangt. Der erste Weg erwies sich als weniger günstig, da es große Schwierigkeiten bereitet, den entstehenden teerigen Kristallbrei zu einem analytischen Erfordernissen gerecht werdenden Produkt aufzuarbeiten. Die Synthese nach Graebe liefert hingegen eine gut kristalline Substanz, welche sich mühelos durch weiteres Umkristallisieren entsprechend reinigen läßt. In Tab. 1 sind die Werte der Elementaranalysen für die drei TMK-Sorten aufgeführt.

Die Absorptionsspektren der wäßrig-n-propanolischen Lösungen der drei TMK-Sorten und ihrer Quecksilberkomplexe zeigt Abb. 1. Obwohl das handelsübliche TMK die größte Extinktion aufweist, besitzt der dazugehörige Quecksilberkomplex eine niedrigere Extinktion als der entsprechende Quecksilberkomplex mit TMK nach Graebe. Es ist weiter auffallend, daß das Extinktionsmaximum des Handelsproduktes gegenüber dem der beiden anderen TMK-Sorten deutlich hypsochrom verschoben ist und eine zusätzliche Schulter aufweist. Da auch dünnschichtchromatographische Untersuchungen (Kieselgur/Al_2O_3 im Verhältnis 1:1 auf Glasplatten; Fließmittel Benzol) zeigten, daß neben dem intensiven Haupttüpfel beim handelsüblichen TMK stärkere Folgetüpfel auftraten, be-

Tabelle 1. Ergebnisse der Elementaranalyse von 3 Sorten Thio-Michlers Keton

Element	% theoret	TMK handelsubl	% praktisch TMK nach Graebe	TMK nach Wallach
C	71,80	71,9	68,2	63,2
H	7,08	7,1	6,8	6,2
N	9,85	10,7	9,7	8,9
S	11,27	7,5	11,4	10,0

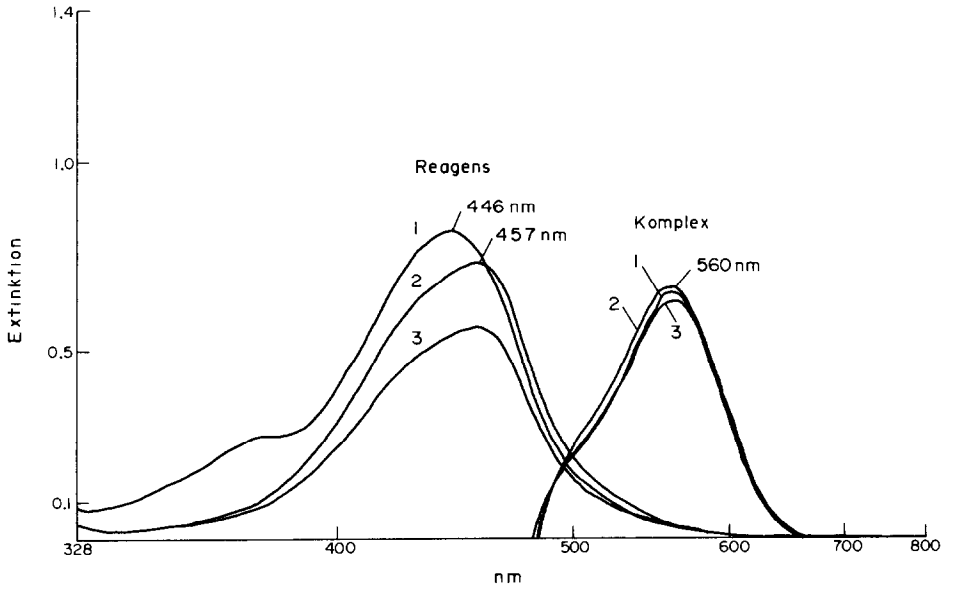

Abb. 1. Absorptionsspektren von 3 Proben des Thio-Michlerschen Ketons und deren Quecksilber(II)-Komplexe. [Hg] $5 \cdot 10^{-6} M$; [TMK] $5 \cdot 10^{-5} M$; pH = 5,8; 30 Vol% n-Propanol; 1-cm Küvette. 1—Handelsprodukt des TMK; 2—TMK nach Graebe; 3—TMK nach Wallach.

steht Grund zur Annahme, daß dieses noch durch weitere farbige Substanzen–möglicherweise Auramin–verunreinigt ist. Dies wird noch durch den niedrigen Schwefelgehalt und den zu hohen Stickstoffgehalt der Elementaranalyse unterstrichen. Offensichtlich stellt das nach Graebe synthetisierte TMK die reinste der drei Proben dar, obwohl auch hier—trotz sorgfältiger Reinigung—bei der dünnschichtchromatographischen Untersuchung noch zwei, wenn auch sehr schwache, Folgetüpfel beobachtet wurden. Die getroffenen Aussagen konnten durch IR-spektroskopische Untersuchungen erhärtet werden, in denen das Spektrum von TMK nach Graebe einen wesentlich schwächeren Untergrund aufwies. Für das Reagens TMK sollen auf der Grundlage des nach graebe synthetisierten Produktes folgende spektralphotometrischen Daten angegeben werden: $\lambda_{max} = 457$ nm; $\epsilon = 2{,}92 \cdot 10^4 \, l \cdot mole^{-1} \cdot cm^{-1}$. Da die Verunreinigungen im handelsüblichen TMK sich im folgenden bezüglich der Komplexbildungsreaktion zwischen Hg(II) und TMK als weitgehend indifferent erwiesen und darüberhinaus der Anwender photometrischer Analysenverfahren meist auf handelsübliche Reagenzien angewiesen sein wird, wurde im folgenden dieses TMK benutzt.

Die Untersuchungen zeigten, daß die Reagenslösung und auch die des Quecksilberkomplexes vor allem gegen direktes Sonnenlicht empfindlich sind. Mit schwarzer Lackfarbe angestrichene Maßkolben gewährleisteten ein störungsfreies Arbeiten. Die im Dunkeln aufbewahrte n-propanolische Reagenslösung bleibt bei Zimmertemperatur mindestens 40 Tage verwendbar. Dies wurde durch Extinktionsmessungen des Reagens bei 446 nm und des Quecksilberkomplexes bei 560 nm bestätigt. Da sich trotz intensiven Schüttelns bei der Bereitung der Reagenslösung nicht sofort alles TMK löst, empfiehlt sich, die Lösung im Interesse konstanter Extinktionen einige Stunden vor Gebrauch anzusetzen.

Charakteristik der Reaktion

Wahl des Mediums. Der Hg–TMK-Komplex zeigte in wäßrig-äthanolischer Lösung bei 560 nm eine deutlich höhere Extinktion als in reinen organischen Medien wie z.B. Isopentanol. Trotz des Arbeitens im verdunkelten Maßkolben blieb die zeitliche Stabilität der Komplexlösung unbefriedigend (0,01 Extinktionseinheiten Abfall in 5 min). Daraufhin wurden weitere wäßrig-organische Medien bezüglich ihrer Einflüsse auf die Komplexzeitstabilität untersucht. Neben dem bereits angewandten Äthanol (vergällt) wurden reines Äthanol, Methanol, n-Propanol, Isopropanol, Äthylenglykol, Glycerin, Aceton, Pyridin und Dioxan getestet. Unter vergleichbaren Bedingungen lagen die Extinktionen, die in wäßrig-alkoholischen Medien erreicht wurden, teilweise mehr als doppelt so hoch wie bei Verwendung von Aceton, Pyridin oder Dioxan. Bezüglich der Komplexzeitstabilität erwies sich das wäßrig–n-propanolische Medium als besonders geeignet. Nach einer sonst nicht beobachteten kurzen Phase konstanter Extinktion erwies sich der Extinktionsabfall nur etwa halb so groß, wie es vom wäßrig-äthanolischen Medium her bekannt ist.

Einfluß des pH-Wertes. Die Abhängigkeit der Extinktion des Komplexes und des Blindwertes vom pH-Wert zeigt Abb. 2. Das Extinktionsmaximum des Komplexes befindet sich im Bereich von pH 4 bis pH 5,5, während das Blindwertminimum bei pH 6 bis pH 7 liegt. Für die Versuche erwies sich die pH-Einstellung mit Acetatpuffer als besonders günstig. In Tab. 2 sind die Farben der Komplex- und Blindlösungen bei verschiedenen pH-Werten zusammengestellt.

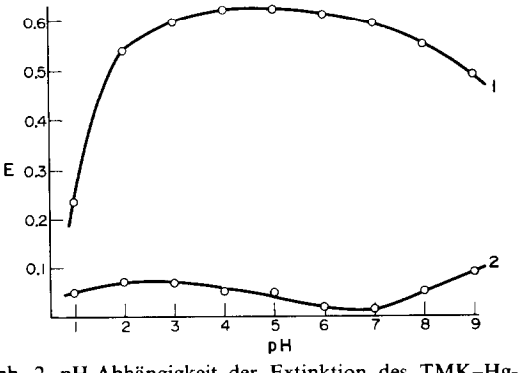

Abb. 2. pH-Abhängigkeit der Extinktion des TMK–Hg-Komplexes (*1*) und des Blindwerts (*2*). [Hg] $5 \cdot 10^{-6} M$; [TMK] $2{,}5 \cdot 10^{-5} M$; 20 Vol.% n-Propanol; $\lambda = 568$ nm; 1-cm-Küvette.

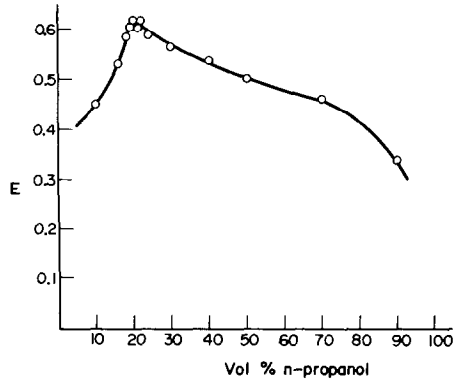

Abb. 3. Abhängigkeit der Extinktion des Hg–TMK-Komplexes vom n-Propanolgehalt der Lösung. [Hg] $5 \cdot 10^{-6} M$; [TMK] $2{,}5 \cdot 10^{-5} M$; pH = 5,0; λ = 572 nm; 1-cm-Küvette.

Einfluß der n-Propanolkonzentration. Die Abhängigkeit der Extinktion des Komplexes vom n-Propanolgehalt der Lösung ist in Abb. 3 dargestellt. Maximale Extinktionswerte werden bei Gehalten von etwa 20 Vol.% erreicht. Es muß besonders darauf hingewiesen werden, daß nur chromatographisch reines n-Propanol zu verwenden ist. Geringste Spuren von Aldehyden, welche sich sogar einem IR-spektroskopischen Nachweis entziehen, führen infolge Reduktion des Hg(II) zu erheblicher Extinktionsminderung. Es empfiehlt sich, neue n-Propanolchargen stets gaschromatographisch zu prüfen.

Molarer Reagensüberschuß. Die Abhängigkeit der Extinktion von Komplex und Blindwert vom Reagensüberschuß zeigt Abb. 4. Man kann erkennen, daß sich der Quecksilberkomplex quantitativ bei etwa 10-fachem molarem Reagensüberschuß bildet. Die Komplexbildung ist weitgehend von der Puffermenge unabhängig und wird durch Ionenstärken bis zu J = 0,9 ($NaClO_4$) nicht beeinflußt.

Untersuchungen zur Zeitstabilität von Komplex und Blindwert. Die Untersuchungen zeigten, daß die zeitliche Stabilität von Komplex und Blindwert sowohl von der n-Propanolkonzentration als auch vom pH-Wert abhängt. Hohe Zeitstabilitäten können lediglich auf Kosten einer Extinktionserniedrigung realisiert werden, d.h. es muß ein Kompromiß zwischen Höhe der Zeitstabilität und der Höhe der Extinktion eingegangen werden. Im folgenden wurde ein n-Propanolgehalt von 30 Vol.% gewählt, da dieser einen konstanten Blindwert über mindestens 60 min gewährleistet. Geringere n-Propanolgehalte führen zu einer Abnahme der Extinktion des Blindwertes und zu einer Verkürzung der Stabilitätsphase des Komplexes. Die pH-Abhängigkeit der Zeitstabilität zeigt Abb. 5. Als optimaler pH-Wert wurde pH 5,8 gewählt.

Weiterhin zeigte sich, daß die Temperatur einen entscheidenden Einfluß auf die Komplexzeitstabilität ausübt. Während die Extinktion des Komplexes bei 5°C nahezu 60 min konstant bleibt, nimmt die Extinktion bei Lösungstemperaturen von >25°C merklich ab (0,01 Extinktionseinheiten Abfall in 5 min und darüber). Auf eine Kühlung der Proben wurde jedoch verzichtet, da bei größeren Temperaturunterschieden zwischen Lösung und Außentemperatur sich infolge unkontrollierter Erwärmung beim

Tabelle 2. pH-Abhängigkeit der Farbe der TMK- und der Hg-Komplex-Lösung

pH	Farbe des Komplexes*	Farbe des Blindwertes
1–2	dunkelgrun	lindgrun
3–7	weinrot	gelb
8–10	hellrot	gelb

* bei Reagensüberschuß

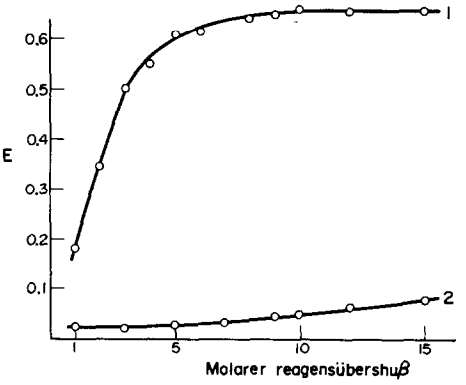

Abb. 4. Abhängigkeit der Extinktion des Hg–TMK-Komplexes und des Blindwerts vom molaren Reagensüberschuß. *1*—Komplexlösung; *2*—Blindlösung. [Hg] $5 \cdot 10^{-6} M$; [TMK] $2{,}5 \cdot 10^{-5} M$; pH = 5,8; 30 Vol% n-Propanol; λ = 568 nm; 1-cm-Küvette.

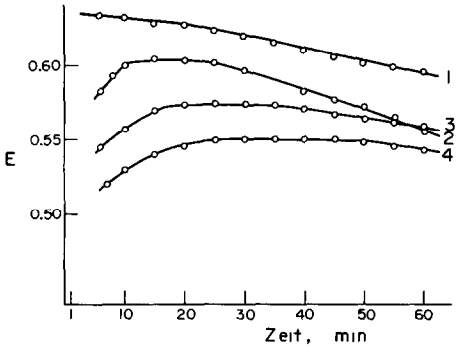

Abb. 5. pH-Abhängigkeit der Komplex-Zeit-Stabilität. *1*—pH = 4,2; *2*—pH = 5,4; *3*—pH = 5,8; *4*—pH = 6,2. [Hg] $5 \cdot 10^{-6} M$; [TMK] $2{,}5 \cdot 10^{-5} M$; 30 Vol.% n-Propanol; λ = 568 nm; 1-cm-Küvetten.

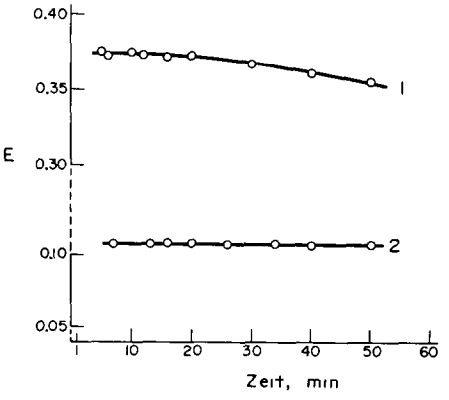

Abb. 6. Zeitabhängigkeit der Extinktion des Hg–TMK-Komplexes unter optimalen Bedingungen. *1*—Komplexlösung; *2*—Blindlösung. [Hg] $2{,}5 \cdot 10^{-6} M$; [TMK] $7{,}5 \cdot 10^{-5} M$; 30 Vol.% n-Propanol; pH = 5,8; λ = 560 nm; 1-cm Küvetten.

Auffüllen der Küvetten stark schwankende Meßwerte ergaben. Es erwies sich zur Abschwächung des Temperatureinflusses als günstiger, die TMK-Konzentration um die Hälfte zu erhöhen. Durch diese Maßnahme wird praktisch gleichzeitig die sofortige maximale Ausbildung der Extinktion erreicht. In Abb. 6 sind die unter optimalen Bedingungen des Verfahrens ermittelten Zeitstabilitätskurven für Komplex und Blindwert bei einer Lösungstemperatur

von 20°C dargestellt Die Messung sollte unter diesen Bedingungen nach etwa 5 bis 15 min erfolgen. Weicht die Temperatur der Lösung stärker von 20°C nach oben ab, ist sofort zu messen, während bei stärkeren Abweichungen nach unten die Zeit bis zur Entwicklung der maximalen Extinktion zu berücksichtigen ist.

Arbeitsvorschrift

Bis zu 10 ml der zu bestimmenden Lösung werden in einem mit schwarzem Lackanstrich versehenen 50-ml-Maßkolben eingefüllt und 20 ml Acetatpuffer (0.2*M* CH_3COOH/0,2*M* $NaCH_3COO$ = 1:4) zugegeben. Daraufhin werden 15 ml Reagenslösung einpipettiert; anschließend wird der Maßkolben gut geschüttelt und schließlich mit dest. Wasser bis zur Marke aufgefüllt. Parallel dazu wird eine Reagenzienblindprobe hergestellt. Die so bereiteten Proben besitzen bei 30 Vol.% n-Propanolgehalt den gewünschten pH-Wert von 5,8. Die Quecksilberprobe wird etwa 5 bis 15 min nach Reagenszugabe entsprechend dem Quecksilbergehalt in 1-oder 5-cm-Küvetten bei einer Wellenlänge von 560 nm gegen den Blindwert photometriert. Zur Herstellung der Lösungen ist bidestilliertes Wasser zu verwenden. Vermeidet man beim Füllen der Küvetten direktes Sonnenlicht, liegt bei zügigem Arbeiten der durch Lichteinflüsse entstehende Fehler innerhalb der Fehlergrenze des Verfahrens.

DISKUSSION DER ERGEBNISSE

Charakteristik der Methode

Infolge hoher Konstanz der Blindwerte ist es möglich, neben 1-cm-Küvetten auch 5-cm-Küvetten zu verwenden. Dadurch konnte die Nachweisgrenze noch weiter gesenkt und die Präzision bei der Bestimmung sehr kleiner Quecksilbergehalte erhöht werden. Die mit 5-cm-Küvetten aufgenommene Eichkurve wurde einer Regressionsberechnung unterworfen, in welche 21 Extinktionswerte (7 Meßpunkte im Bereich von 0,010 bis 0,3 μg Hg/ml jeweils dreifach bestimmt) Eingang fanden. Ein Meßwert (0,010 μg Hg/ml) wurde auf Grund des 2σ-Kriteriums vom Rechner eliminiert. Für die allgemeine Geradengleichung $y = bx + a$ ergaben sich folgende Werte:

$$b = 3{,}774 \pm 0{,}0106$$

$$a = -0{,}0151 \pm 0{,}00196$$

Mittlere Standardabweichung der Extinktion der Eichgeraden:	0,00451
Korrelationskoeffizient:	0,99993
Bestimmtheitsmaß:	0,99986

Die Eichkurve kann durch Division durch die Küvettenstärke von 5,008 cm auf 1-cm-Küvetten umgerechnet werden. Für den Fall einer Doppelbestimmung von beispielsweise 0,1 μg Hg/ml unter Verwendung von 5-cm-Küvetten besitzt der Mittelwert beider Quecksilbergehalte bei einer statistischen Wahrscheinlichkeit von 95% einen Fehler von weniger als $\pm$ 2%. Durch Mehrfachbestimmungen kann die Genauigkeit der Analysenergebnisse weiter erhöht werden. In Tab. 3 sind charakteristische Kenngrößen des Verfahrens zusammengestellt und mit denen bekannter photometrischer Quecksilberbestimmungsverfahren verglichen.

Selektivität der Reaktion

In Tab. 4 werden für eine größere Anzahl von Kationen und einigen Anionen Richtwerte für deren Störverhalten gegeben, wobei festgelegt wurde, daß ein Ion dann stört, wenn die entstehende Abweichung der Extinktion mehr als die zweifache Standardabweichung des Quecksilberwertes beträgt ($\pm$0,006 Extinktionseinheiten; 1-cm-Küvetten). Wie erwartet, zeigen die Edelmetalle, welche selbst mit TMK intensiv gefärbte Komplexe bilden, die stärksten Störungen, vor allem Pd, Au, Ag und Pt. Weiterhin stören alle

Tabelle 3. Verfahrensbewertung

Kenngröße	neues TMK-Verfahren	bisherige TMK-Verfahren[3]	Dithizonverfahren[6]	Verfahren mit Bindschedlers Grün[7]
Lambert-Beersches Gesetz (μg/ml)	0,007 bis 0,3 (5-cm-Küv.) bis 1,5 (1-cm-Küv.)	0,0 bis 2,5 (Isopentanol)	0,1 bis 4 (485 nm, CCl_4) 0,08 bis 3 (620 nm CCl_4)	0,16 bis 0,8* (1,2-Dichlorathan)
molarer Extinktionskoeffizient ($l\ mole^{-1}\ cm^{-1}$)	$1{,}51\ 10^5$ (560 nm)	$1{,}17\ 10^5$ (560 nm) (wäßrig-athanol Medium) $8{,}8\ 10^4$ (550 nm) (Isopentanol)	$7{,}12\ 10^4$ (485 nm)	$1{,}70\ 10^5$ (740 nm)
Sandell-Index ($\mu g/cm^2$ für $E = 0{,}001$)	0,0013	0,0017 (wäßr. Phase) 0,0023 (Isopentanol)	0,0044 (485 nm) 0,003 (620 nm)	0,0012*
Nachweisgrenze nach Kaiser u. Specker[8] (ng/ml)	4,2 (5-cm-Küv.) ($x = \bar{x}_B + 3s_B$)			
Erfassungsgrenze nach Svoboda u. Gerbatsch[9] (ng/ml)	7,1 (5-cm-Küv.) ($x_l = \bar{x}_B + 6s_B$)		11,0 (485 nm)† 7,5 (620 nm)† (auf Basis von $E = 0{,}025$ berechnet)	
Präzision des Verfahrens (Standardabweichung der Extinktion von n gleichen Meßwert)	0,003 (n = 24) (0,1 μg Hg/ml, 5-cm-Küv.) 0,003 (n = 26)§ (0,5 μg Hg/ml, 1-cm-Küv.)			$\pm$0,005 (n = 10) (0,4 μg Hg/ml)*
relative Standardabweichung	0,9% (für beide Meßreihen)			$\pm$1,5%*

* Umgerechnete oder selbst berechnete Werte.

† Diese Werte sind mit der Erfassungsgrenze des neuen Verfahrens etwa vergleichbar, welcher ein Wert von $E = 0{,}027$ zugrunde liegt.

§ Im Zeitraum von mehreren Wochen am "Spekol" gemessene Werte.

Tabelle 4. Störungen—Nicht störende Gewichtsüberschüsse bei [Hg] = 0,50 μg/ml

Storelement	Überschuß, μg/ml	Storelement	Überschuß, μg/ml	Storelement	Überschuß, μg/ml
Li	35*	Se(IV)	80	Ni	280
Na	>9200	Te(IV)	25	Pd(II)	0,001
K	13600	Sc	400	Pt(IV)	0,5
Rb	8500	La	660*	Cu(II)	20
Cs	4300	Ti(IV)	30	Ag	0,05
Be	>3600	Zr	80	Au(III)	0,05
Mg	5400	V(V)	30	Zn	10800
Ca	>16300	Cr(III)	40	Cd	45000
Sr	35000	Mo(VI)	10	Ce(IV)	20
Ba	5500	W(VI)	300	Th	7000
Al	3400	Mn(II)	>22000	NH_4^+	7200
In	90*	Fe(III)	20	NO_3^-	>24800
Tl(I)	>400	Ru(III)	<1	SO_4^{2-}	>38400
Ge	44	Co(II)	290	ClO_4^-	>40000
Sn(II)	0,006	Rh(III)	10	CO_3^{2-}	2400
Pb	830	Ir(III)	<1	Cl^-	180
As(V)	80			CH_3COO^-	5900
Bi	70			ReO_4^-	830

* Störung wird vermutlich durch Cl^- verursacht.

auf Hg(II) reduzierend wirkenden Ionen wie beispielsweise Sn(II) und alle Ionen, welche mit Hg(II) zu undissoziierten Verbindungen reagieren können, (z.B. Chlorid). Dies gilt sicher auch für die hier nicht untersuchten Anionen wie SO_3^{2-}, $S_2O_3^{2-}$, Br^- oder J^-. Über Maskierungsmöglichkeiten soll in einer späteren Veröffentlichung berichtet werden. Es sei hier lediglich unter Hinweis auf die Maskierungsversuche von Cheng und Goydish[4] bemerkt, daß unter diesen Bedingungen (pH 5,8) der Quecksilberkomplex von ÄDTA schon stark angegriffen wird.

Empfindlichkeit der Methode

Im wäßrig-n-propanolischen Medium erfolgt eine beachtliche Erhöhung der Empfindlichkeit der Reaktion zwischen Hg(II) und TMK gegenüber den bisher bekannten Arbeitsvorschriften. Gleichzeitig wird die Verwendbarkeit der Reagenslösung durch n-Propanoleinsatz wesentlich verlängert. Die beschriebene Methode gestattet infolge guter Blindwertkonstanz bei hoher Präzision die photometrische Bestimmung von Quecksilber(II)-Spuren im Nanogrammbereich. Eine Erhöhung der oberen Bestimmungsgrenze sollte durch Variation der Bedingungen möglich sein. Auf Grund der Einsparung des Extraktionsschrittes gestaltet sich das Verfahren sehr einfach und zeitsparend. Nachteilig ist die relativ geringe Komplex-Zeit-Stabilität. Die störend wirkende Lichtempfindlichkeit kann durch geeignete Maßnahmen ausgeschaltet werden. Die Grundselektivität des Verfahrens ist zufriedenstellend. Unter Zuhilfenahme geeigneter Maskierungsmittel sollte eine praktische Anwendung der Methode in einer Reihe von Fällen möglich sein. Besonders vorteilhaft erscheint ein Einsatz des Verfahrens bei Quecksilberanalysenmethoden, die auf thermisches Austreiben des Quecksilbers aus der Probe und Überführung desselben in die wäßrige Phase beruhen. Darüberhinaus wäre eine Anwendung nach selektiver Hg(II)-Extraktion denkbar.

Im Vergleich zur gegenwärtig meist angewendeten Dithizonmethode[6] ist das entwickelte Verfahren nicht nur erheblich empfindlicher, sondern vor allem auch weniger störanfällig. Die von Tsubouchi[7] ausgenutzte Reaktion von Hg(II), Br^- und Bindschedlers Grün ist zwar noch empfindlicher, jedoch infolge des nur sehr engen Gültigkeitsbereiches des Lambert-Beerschen Gesetzes bezüglich sehr kleiner Quecksilberkonzentrationen lediglich begrenzt einsetzbar.

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Summary—A photometric method for the determination of nanogram amounts of mercury based on formation of the red complex with thio-Michler's ketone in 30% aqueous propanol is described. The pH is adjusted to 5.8 with acetate buffer. When measured at 560 nm, the molar absorption coefficient is $1.51 \times 10^5\ l \cdot mole^{-1} \cdot cm^{-1}$, corresponding to a Sandell index for Hg of 0.0013 μg/cm². The Lambert-Beer law is obeyed for Hg from 0.007 to 1.5 μg/ml. With 5-cm cells, the limit of detection is 4.2 ng/ml, and the limit of determination 7.1 ng/ml. A statistical analysis of the performance is presented, along with the results of a study of interferences.

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SPECTROPHOTOMETRIC DETERMINATION OF ARSENIC IN CONCENTRATES AND COPPER-BASE ALLOYS BY THE MOLYBDENUM BLUE METHOD AFTER SEPARATIONS BY IRON COLLECTION AND XANTHATE EXTRACTION

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Summary—A method for determining 0.0001–1% of arsenic in copper, nickel, molybdenum, lead and zinc concentrates is described. After sample decomposition, arsenic is separated from most of the matrix elements by co-precipitation with hydrous ferric oxide from an ammoniacal medium. Following reprecipitation of arsenic and iron, the precipitate is dissolved in ~2 *M* hydrochloric acid and the solution is evaporated to a small volume to remove water. Arsenic(V) is reduced to the tervalent state with iron(II) and separated from iron, lead and other co-precipitated elements by chloroform extraction of its xanthate from an 11*M* hydrochloric acid medium. After oxidation of arsenic(III) in the extract to arsenic(V) with bromine–carbon tetrachloride solution, it is back-extracted into water and determined by the molybdenum blue method. Small amounts of iron, copper and molybdenum, which are co-extracted as xanthates, and antimony, which is co-extracted to a slight extent as the chloro-complex under the proposed conditions, do not interfere. The proposed method is also applicable to copper-base alloys.

The certification of various sulphide concentrates for major and minor elements and for trace elements in concentrations as low as 1 ppm is a current facet of the Canadian Certified Reference Materials Project sponsored by the Canada Centre for Mineral and Energy Technology. As part of this project, the present investigation was undertaken to develop a method for determining minor and trace amounts of arsenic in a variety of concentrates.

The most widely used method for determining small amounts of arsenic is based on its separation by distillation as arsenic(III) chloride, followed by spectrophotometric measurement of its molybdenum blue complex. Other methods using the same spectrophotometric finish involve prior separation of arsenic by evolution as the hydride by the action of zinc in hydrochloric or sulphuric acid, or by precipitation as elemental arsenic in acid solution by reduction with stannous chloride or hypophosphite.[1] More recently, methods have been reported which are based on the evolution of arsenic hydride by reduction with sodium borohydride in an acid medium, followed by an atomic-absorption finish in which the hydride is combusted in a tube furnace or atomizer placed in the light-path of the instrument.[2,3] Neither the distillation nor the evolution methods were considered in the present work, because they require special apparatus. Furthermore, the evolution method is subject to interference from numerous elements, regardless of the type of finish employed,[1–3] and the method based on precipitation of elemental arsenic is reported to result in incomplete recovery of arsenic.[1] Recent work by the author on the extraction of metal xanthate complexes,[4] and the subsequent development of a method for tellurium in ore concentrates,[5] suggested the possibility of a similar method for arsenic. This method would involve a preliminary separation of arsenic by co-precipitation with hydrous ferric oxide from an ammoniacal medium, followed by its separation from iron by chloroform extraction as the xanthate. Although xanthate–chloroform extraction of arsenic has been used previously for its isolation and subsequent determination in foods,[6] zinc- and lead-base materials,[7] pyrite and pyrite ashes,[8] natural water, silicates and biological materials,[9] it has been found that numerous elements [antimony(III), bismuth, tin(IV), iron(III), nickel, copper(II), molybdenum(VI) and thallium(III)] are co-extracted appreciably as xanthate complexes under the dilute acid conditions used in these methods.[4] Because the co-extraction of these elements is minimal from 10–12*M* hydrochloric acid media,[4] the extraction of arsenic from >10*M* acid media was investigated in the present work.

This paper describes the determination of arsenic in copper, nickel, molybdenum, lead and zinc concentrates and copper-base alloys after its separation from the matrix elements by co-precipitation with hydrous ferric oxide and chloroform extraction as the xanthate from 11*M* hydrochloric acid medium. Arsenic is ultimately determined spectrophotometrically by a modification of a molybdenum blue method reported by

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the American Society for Testing and Materials (ASTM).[10] It is to be noted that the subsequent determination of trace amounts of arsenic by flameless (carbon rod) atomic-absorption spectroscopy was also investigated but was ultimately abandoned because of the poor reproducibility obtained by this technique.

EXPERIMENTAL

Reagents

Standard arsenic solution, 10 μg/ml. Dissolve 0.1320 g of pure arsenic trioxide in 10 ml of warm 2% sodium hydroxide solution. Dilute the solution to ~50 ml with water and add 2 drops of 0.2% (ethanolic) phenolphthalein indicator solution. Add 10% v/v sulphuric acid dropwise until the solution is colourless, dilute to 1 litre with water, and transfer the solution to a polyethylene bottle. Dilute 10 ml of this stock solution to 100 ml with water. Prepare fresh as required.

Ammonium molybdate, 1% w/v solution in 2.3M sulphuric acid. Add 128 ml of concentrated sulphuric acid to ~800 ml of water and cool to room temperature. Dissolve 10.00 g of ammonium molybdate tetrahydrate in ~50 ml of warm water and cool to room temperature. Transfer both solutions to a 1-litre volumetric flask, dilute to volume with water, and transfer the resultant solution to a polyethylene bottle.

Hydrazine sulphate, 0.5% w/v solution. Prepare a fresh solution every five days.

Iron(III) sulphate solution (1 ml ≡ ~20 mg of iron). Dissolve 25 g of ferric sulphate monohydrate in hot water, add 10 ml of 50% v/v sulphuric acid, cool and dilute to 250 ml with water.

Iron(II) sulphate, 5% w/v solution. Dissolve 5 g of the reagent in 100 ml of hot concentrated hydrochloric acid and cool to room temperature. Prepare fresh as required.

Potassium ethyl xanthate, 20% w/v solution. Prepare fresh as required.

Bromine, 20% v/v solution in carbon tetrachloride.

Bromine water.

Sulphuric acid, 50% v/v.

Hydrochloric acid, 15% v/v.

Ammonia, 5% v/v.

Chloroform, analytical-reagent grade.

Procedures

Calibration curves. Add 15 ml of bromine water to each of eight 150-ml beakers; then, by burette, add to the last seven beakers 0.5, 1, 2.5, 5, 7.5, 10 and 15 ml, respectively, of standard 10 μg/ml arsenic solution. The first beaker contains the blank. Heat each solution until it is free of bromine and, if necessary, evaporate to ~20 ml. Transfer each solution to a 50-ml volumetric flask and dilute to ~40 ml with water. Add 5 ml of 1% ammonium molybdate solution and 1 ml of 0.5% hydrazine sulphate solution, dilute to ~48 ml with water, stopper, and mix thoroughly. Loosen the stopper and place the flask in a boiling water-bath for 30 min. Remove the flask, cool the solution to room temperature in a water-bath and dilute to volume with water. Determine the absorbance of the blank and each of the three solutions of lowest arsenic content, at 845 nm, against water as the reference solution, using 40-mm cells. Determine the absorbance of the blank and each of the five solutions of lowest arsenic content in a similar manner, using 20-mm cells, then determine that of the blank and the six solutions of highest arsenic content, using 10-mm cells. Correct the absorbance value obtained for each arsenic-molybdenum blue solution by subtracting that obtained for the blank. Plot μg of arsenic *vs.* absorbance for each series of measurements.

Concentrates. Depending on the expected arsenic and/or iron content (Note 1), transfer 0.2–1 g of powdered sample, containing not more than ~150 mg of iron, to a 250-ml beaker. Add 10 ml of 20% bromine–carbon tetrachloride solution, cover and add 15 ml of concentrated nitric acid. Allow the solution to stand for ~15 min, then heat gently to remove the bromine and carbon tetrachloride. Cool, add 10 ml of concentrated hydrochloric acid and 25 ml of 50% v/v sulphuric acid, heat until the evolution of brown oxides of nitrogen ceases, then remove the cover, wash down the sides of the beaker with water, and carefully evaporate the solution to fumes of sulphur trioxide. Cool, add ~100 ml of water, 5 ml of concentrated hydrochloric acid, and sufficient iron(III) sulphate solution, if necessary, so that at least 80 mg of iron are present. Cover and heat to dissolve the soluble salts.

Add sufficient concentrated ammonia solution to precipitate iron as the hydrous oxide, then add 5 ml in excess and boil the solution to coagulate the precipitate. Allow it to settle, then filter the hot solution (Whatman No. 40 paper) and transfer the bulk of any insoluble material (and lead sulphate) to the filter paper with a jet of 5% v/v ammonia solution. Wash the paper and precipitate twice with 5% ammonia solution and discard the filtrate. Place the original beaker under the funnel and dissolve the precipitate with hot 15% v/v hydrochloric acid added from a wash-bottle. Wash the paper three times with the acid solution and discard the paper. Wash down the sides of the beaker with the hot acid solution, then reprecipitate the iron and filter as described above. Wash the beaker twice and the paper and precipitate three times with 5% ammonia solution, then again dissolve the precipitate into the original beaker with hot 15% hydrochloric acid, and wash the paper three times with the hot acid solution (Note 2). Discard the paper. Wash down the sides of the beaker with the hot acid solution and evaporate the resultant solution to ~25 ml on a hot-plate (Note 3), then evaporate it to ~3 ml in a hot water-bath. Cool to room temperature and add 20 ml of concentrated hydrochloric acid and 3 ml of water. Detach any salts adhering to the bottom of the beaker with a rubber-tipped stirring rod ("policeman") and wash down the rod with concentrated hydrochloric acid from a plastic wash-bottle. Carry a blank, with ~80 mg of iron(III) added, through the whole procedure.

Allow the blank and sample solutions to stand at room temperature (Note 4) until the salts are dissolved (Note 5), then add 10 ml of freshly prepared 5% iron(II) sulphate solution in concentrated hydrochloric acid and mix thoroughly. Transfer each solution to a 125-ml separatory funnel, marked at 50 ml, using concentrated hydrochloric acid to wash the beaker, and dilute to the mark, if necessary, with the concentrated acid. Add 10 ml of chloroform, followed by 1 ml of freshly prepared 20% potassium ethyl xanthate solution, stopper, and extract immediately (Note 6) by shaking for 1 min. Allow several minutes for the layers to separate, then drain the chloroform phase into a 125-ml separatory funnel. Extract the aqueous phase twice more, in a similar manner, with 10- and 5-ml portions of chloroform and 1 and 0.5 ml of xanthate solution, respectively, then wash the aqueous phase by shaking it for ~30 sec with 5 ml of chloroform. Add 5 ml of 20% bromine–carbon tetrachloride solution to the combined extracts, stopper, and mix thoroughly. Allow the solution to stand for ~5 min to ensure the complete oxidation of arsenic(III) to arsenic(V), then add 15 ml of water, stopper, and shake for 1 min. Allow several minutes for the layers to separate, then drain off and discard the chloroform–carbon tetrachloride phase. Drain the aqueous phase into a 150-ml beaker and wash the funnel three times with small portions of water. Heat the resultant solution gently to remove bromine and the excess of chloroform, evaporate it to ~20 ml, and cool to room temperature.

If the sample contains 150 μg or less of arsenic, transfer both the sample and blank solutions to 50-ml volumetric flasks, dilute to ~40 ml with water, and proceed with the determination of arsenic as described above.

If the sample contains more than 150 μg of arsenic, transfer both the sample and blank solutions to volumetric flasks of appropriate size (50–200 ml) and dilute to volume with water. Transfer suitable aliquots (up to 40 ml) of both solutions to 50-ml volumetric flasks, and proceed with the determination of arsenic as described above.

Copper-base alloys. Depending on the expected arsenic content, transfer 0.2–1 g of sample to a 250-ml beaker. Add ~15 ml of water, cover and add 15 ml of concentrated nitric acid and 10 ml of concentrated hydrochloric acid. Heat gently until the sample is dissolved, then add 25 ml of 50% sulphuric acid and proceed with the evaporation of the solution to fumes of sulphur trioxide, the separations of arsenic by co-precipitation with hydrous ferric oxide and by chloroform extraction of its xanthate complex, and the subsequent determination of arsenic as described above.

Notes

1. The use of samples containing more than ~150 mg of iron is not recommended because the filtration step becomes unduly slow.
2. Any lead chloride that is present at this stage will redissolve during the subsequent evaporation of the solution.
3. Low results will be obtained for arsenic if the solution is allowed to evaporate to dryness on a hot-plate.
4. Because arsenic(V) is reduced by chloride[11] in relatively concentrated hydrochloric acid media, arsenic(III) will be lost by volatilization if the solution is heated to dissolve the salts.
5. If only a small amount of salts is present, add the recommended volume of iron(II) sulphate solution and transfer the solution and the salts to the separatory funnel as described. The salts will dissolve during the subsequent extraction procedure. If a large amount is present, it may be necessary to allow the solution to stand overnight.
6. Because of the known instability of many metal xanthate complexes, extraction immediately after the addition of chloroform and xanthate solution is recommended.

RESULTS

Spectrophotometric determination of arsenic by the molybdenum blue method

Low results were obtained for arsenic in initial tests in which the ASTM method[10] was applied to arsenic(III) xanthate extracts after oxidation of the arsenic with nitric acid, removal of the chloroform by evaporation, and evaporation of the solution to dryness in a hot water-bath followed by heating at ~150° to remove nitric acid as recommended. This was found to be caused by the small amount of sulphuric acid that is formed during the nitric acid oxidation of xanthate in the extract; this presumably results in the partial formation of an insoluble arsenic compound when the solution is evaporated to dryness. Low results were also obtained in subsequent work in which an attempt was made to oxidize and back-extract moderate amounts of arsenic (1 mg) by shaking the xanthate extract with bromine water (20 ml) as recommended by previous investigators.[7,8] Although this method is effective for up to ~250 μg of arsenic, an inordinately large volume of bromine water is required for the back-extraction of larger quantities. Subsequent work showed that up to at least 2 mg can be back-extracted into water after treatment of the extract with 5 ml of 20% bromine–carbon tetrachloride solution. Because this procedure only necessitates the removal of excess of bromine from the solution by heating, the ASTM method was modified so that the requisite volumes of ammonium molybdate and hydrazine sulphate solutions were added separately. This method of addition is also advantageous because the mixed ammonium molybdate–hydrazine sulphate solution recommended in the method is stable for only ~1 hr. The molar absorptivity of the complex, at 845 nm, is 25.5×10^2 $l.mole^{-1}.mm^{-1}$, and the absorbance remains constant for at least 24 hr.

Separation of arsenic by co-precipitation with hydrous ferric oxide

In previous work[5] in which tellurium was separated from the matrix constituents by co-precipitation with hydrous ferric oxide from an ammoniacal medium, the precipitate was dissolved in 12*M* hydrochloric acid before the reduction and subsequent separation of tellurium(IV) by chloroform extraction as the xanthate. However, in corresponding tests with arsenic it was found that arsenic(III), formed by reduction with fairly concentrated hydrochloric acid,[11] was lost by volatilization, presumably because of the heat generated during the dissolution procedure. Further work, in which the precipitate was dissolved in 25% nitric acid, followed by the removal of nitric acid by evaporation to dryness in a hot water-bath in the presence of formic acid, and dissolution of the salts in 12*M* hydrochloric acid, also yielded low results for arsenic in the presence of tin. This was found to be caused by the formation of an insoluble tin–arsenic compound in the presence of metastannic acid.[12] Consequently, in subsequent work, the precipitate was dissolved in ~2*M* hydrochloric acid and the resultant solution was evaporated to a small volume to remove excess of water before the addition of 12*M* hydrochloric acid and the ultimate separation of arsenic from iron by extraction as the xanthate. Complete recovery of arsenic is obtained under these conditions because arsenic(V) is not reduced by chloride in <4*M* hydrochloric acid media,[11] and arsenic(III) is not volatilized from 12*M* hydrochloric acid media at room temperature.

Separation of arsenic by extraction of its ethyl xanthate complex

Previous investigators[11,13,14] have shown that arsenic(III) can be quantitatively extracted as the chloro-complex from >8*M* hydrochloric acid into volumes of carbon tetrachloride, chloroform or benzene that are either equal to or larger than that of the aqueous phase. However, recent work by the author,[4] in which it was found that arsenic(III) ethyl

xanthate can be quantitatively extracted into chloroform from 0.1–10*M* hydrochloric acid medium, suggested the possibility of an alternative solvent extraction method using small volumes of solvent. It was also found in that and subsequent work dealing with the extraction of tellurium xanthate[5] that the co-extraction of iron(III), copper(II), molybdenum(VI) and certain other elements [antimony(III) and (V), bismuth, tin(IV) and nickel] is minimal from $\geq 10M$ hydrochloric acid media. Consequently, it was considered that extraction from such media might be an effective means of separating small amounts of arsenic from large amounts of iron and from other co-precipitated elements following the collection of arsenic by co-precipitation with hydrous ferric oxide from an ammoniacal medium.

Preliminary experiments showed that, in the absence of iron(III), up to at least 2 mg of arsenic(V) is quantitatively reduced to arsenic(III) in 12*M* hydrochloric acid, and can be quantitatively extracted as the xanthate into chloroform under the proposed extraction conditions. In the absence of xanthate, only about 2% of the arsenic(III), at the 2-mg level, was extracted as the chloro-complex under the same conditions. Subsequent tests carried out on 12*M* hydrochloric acid containing up to 200 mg of iron(III) yielded low results because of incomplete reduction of arsenic(V). However, further work showed that arsenic(V) is rapidly and completely reduced to the tervalent state in this medium in the presence of iron(III) if an excess of iron(II) sulphate is also present [hence the use of the iron(II) solution in concentrated hydrochloric acid]. Previous investigators[6–8] have used potassium iodide as a reductant for arsenic(V) in dilute sulphuric acid media. However, this reductant could not be used in the present work because the sodium thiosulphate or sulphite used to destroy the liberated iodine cannot be added as a solution in concentrated hydrochloric acid.

Extraction from 11*M* hydrochloric acid was chosen for subsequent work with concentrates because the presence of a small amount of water was advantageous in dissolving the salts remaining after the evaporation of the solution obtained from the dissolution of the mixed hydrous oxide precipitate with $\sim 2M$ hydrochloric acid.

Effect of diverse ions

Previous work[4] showed that platinum(IV), gold(III) and rhenium(VII) are partly extracted into chloroform as xanthate complexes from 10*M* hydrochloric acid media, palladium(II), selenium(IV) and tellurium(IV) are completely extracted as xanthates, and germanium is partly extracted as the chloro-complex. As stated previously, small amounts of iron(III), copper(II) and molybdenum(VI) are also co-extracted as xanthate complexes from 12*M* hydrochloric acid, and antimony(V) is co-extracted to a slight extent as the chloro-complex.[5] Consequently, an investigation was made of the effects of these ions on the determination of 50 μg of arsenic. Results showed that up to at least 500 μg of rhenium(VII) and 3 mg each of iron(III) and copper(II) will not interfere in the proposed method. Although moderate amounts of selenium(IV) (400 μg) and tellurium(IV) (500 μg) do not interfere during complex formation, these species are reduced to the elemental state by iron(II) during the reduction of arsenic. Small amounts of platinum(IV) and palladium(II) (~ 25 μg) and more than 300 μg of gold(III) interfere during complex formation, but they are almost completely separated from arsenic during its co-precipitation with hydrous ferric oxide. Up to at least 200 μg each of platinum and palladium and 1 mg of gold will not interfere after a single ammonia separation of iron and arsenic. Residual molybdenum retained in the hydrous oxide precipitate does not interfere.

Table 1. Recovery of arsenic from synthetic concentrate samples

Matrix	Total As present, %	As found, %
Cu concentrate	0.0054_0	0.0052_5
	0.0059_0	0.0059_0
	0.0099_0	0.0098_5
	0.0149	0.014_9
	0.1049	0.104_0
	0.505	0.50_3
	1.005	0.99_8
Ni–Cu concentrate	0.0008_5	0.0008_5
	0.0013_5	0.0016_0
	0.0053_5	0.0053_0
	0.0104	0.009_8
	0.1004	0.100_1
	0.500	0.49_8
	1.000	1.00_0
Mo concentrate, NBS 333	0.0017_2	0.0015_5
	0.0022_2	0.0020_8
	0.0062_2	0.0061_8
	0.0112	0.011_1
	0.1012	0.101_0
	0.501	0.50_1
	1.001	1.00_5
Pb concentrate	0.0020_4	0.0020_3
	0.0025_4	0.0024_8
	0.0065_4	0.0065_0
	0.0115	0.010_7
	0.1015	0.099_9
	0.502	0.50_0
	1.002	0.99_4
Zn concentrate, NBS 113	0.0008_0	0.0007_5
	0.0013_0	0.0012_5
	0.0053_0	0.0051_5
	0.0103	0.010_1
	0.1003	0.099_9
	0.500	0.49_8
	1.000	0.99_8

Duplicate determinations of arsenic in the Cu, Ni, Mo, Pb and Zn concentrates by the proposed method gave 0.0048_5 and 0.0049_5, 0.0003_5 and 0.0003_5, 0.0012_0 and 0.0012_2, 0.0015_0 and 0.0015_8, and 0.0003_0 and 0.0003_0%, respectively. The iron contents of the concentrates were 31.94, ~38, 1.15, 0.27 and 1.18% respectively.

Germanium, phosphorus and silicon are known to interfere in the determination of arsenic by the molybdenum blue method because they form similar reduced heteropoly molybdic acid complexes under the conditions employed for arsenic.[1] However, these elements do not interfere in the proposed method because phosphorus and silicon are not extracted as xanthate complexes, and germanium is volatilized as the tetrachloride during the decomposition step. Antimony(V), tin(IV) and bismuth are completely co-precipitated with arsenic and iron from an ammoniacal medium. Small amounts of antimony(V), which are co-extracted as the chloro-complex during the xanthate extraction of arsenic, and large amounts of bismuth (50 mg) do not interfere. Tin, if present as insoluble metastannic acid before the separation of arsenic by co-precipitation with hydrous ferric oxide, causes low results for arsenic because of the formation of an insoluble tin–arsenic compound.[12] This interference is eliminated during sample decomposition by dissolving metastannic acid with concentrated hydrochloric acid and evaporating the solution to fumes of sulphur trioxide. Although it was found in previous work[5] that small amounts of copper, particularly in the presence of iron(III), inhibit or completely prevent the extraction of tellurium xanthate, a similar effect does not occur during the extraction of arsenic as the xanthate. Up to at least 50 mg of copper(II) and 150 mg of iron(III) will not interfere with the extraction of arsenic. Large amounts of sulphate salts that are retained in the hydrous oxide precipitate after a single precipitation and separation of arsenic may interfere by remaining insoluble in 11*M* hydrochloric acid after dissolution of the precipitate and evaporation of the solution to a small volume. Consequently, a double precipitation is recommended.

Table 2. Determination of arsenic in N.B.S. and B.C.S. copper alloys and in reference ores MP-1 and CD-1

Sample	Nominal composition, %	Certified value and range, % As	As found, %
NBS-C1101 Cartridge brass B	69.5 Cu, 30.3 Zn	0.009	0.0098
NBS-C1102 Cartridge brass C	72.9 Cu, 27.1 Zn	0.004	0.0048
NBS-C1118 Aluminium brass A	75.1 Cu, 21.9 Zn, 2.8 Al, 0.1 P	0.007	0.0074
NBS-C1119 Aluminium brass B	77.1 Cu, 20.5 Zn, 2.1 Al, 0.1 P	0.040	0,040
NBS-C1120 Aluminium brass C	80.1 Cu, 18.1 Zn, 1.5 Al, 0.1 Sb	0.090	0.090
NBS-62B Manganese bronze	57.4 Cu, 38.0 Zn, 1.3 Mn, 1.0 Al, 1.0 Sn, 0.8 Fe, 0.3 Pb, 0.3 Ni	0.004	0.0046
NBS-63c Phosphor bronze bearing metal	80.5 Cu, 9.4 Pb, 9.0 Sn, 0.5 Sb 0.3 Ni, 0.2 P, 0.1 Zn	0.023 (0.017–0.029)	0.023
NBS-124d Ounce metal	83.6 Cu, 5.2 Pb, 5.1 Zn, 4.5 Sn, 1.0 Ni, 0.2 Fe, 0.2 Sb	0.02†	0.015
BCS-Manganese brass "B"	58.8 Cu, 33.9 Zn, 1.0 Mn, 0.9 Fe, 1.6 Al, 1.8 Sn, 0.8 Pb, 1.0 Ni	0.03§ (0.02–0.04)	0.019
BCS-207 Bronze "C"	86.8 Cu, 9.8 Sn, 2.5 Zn, 0.4 Pb	0.05 (0.04–0.07)	0.057
BCS-183/1 Bronze	84.8 Cu, 5.0 Sn, 5.2 Zn, 3.5 Pb, 0.5 P, 0.5 Ni, 0.2 Sb	0.14 (0.12–0.14)	0.127, 0.129
MP-1-Zinc-tin-copper-lead ore	16.3 Zn, 2.5 Sn, 2.2 Cu, 1.9 Pb, 5.7 Fe	0.79 (0.768–0.814)*	0.764‡
CD-1-Antimony ore	3.6 Sb	0.65‖	0.684¶

* 95% Confidence limits of the recommended mean value.
† N.B.S. provisional result.
‡ Mean of 3 values, *viz.* 0.765, 0.768 and 0.758%.
§ Certified value based on 4 results, *viz.* 0.03, 0.04, 0.02 and 0.03%.
‖ Tentative mean value of 100 results from an incomplete certification programme (8 laboratories reporting).
¶ Mean of 10 values ranging from 0.680 to 0.690%.

Applications

The proposed method was applied to the analysis of a series of five synthetic concentrates (200-mesh commercial grade sulphide concentrates) in which arsenic, added to the powdered samples in the form of a standard solution, was varied from 0.0005 to 1%. It was also applied to certified reference copper-base alloys and to a certified reference zinc–tin–copper–lead ore, MP-1. An antimony ore, CD-1, which is currently undergoing certification for arsenic by the Canadian Certified Reference Materials Project, was also analysed. The results of these analyses are given in Tables 1 and 2.

DISCUSSION

Table 1 shows that the results for the synthetic concentrate samples agree favourably with the calculated amount of arsenic present. The results (Table 2) for the National Bureau of Standards and British Chemical Standards copper-base alloys are also in good agreement with the certified values. The result of 0.764% for the certified reference ore, MP-1, is very close to the lower 95% confidence limit of the recommended mean of 0.79%. Because a recognized "standard" method for arsenic in ores does not exist, MP-1 was certified by a consensus scheme in which participants used a variety of methods (X-ray fluorescence, titrimetry and spectrophotometry),[15] many of which have not been examined for bias as closely as the one proposed here. Therefore, it is possible that certain of these methods (*e.g.*, volumetric) may be prone to positive interference from constituents of the mineralogically complex ore. A further examination of this problem may be undertaken later in this laboratory. The result obtained for the antimony ore, CD-1, is higher than the tentative consensus mean value of the results hitherto reported in the interlaboratory programme of certification. However, more data are required from participating laboratories before this result can be evaluated.

The proposed method is suitable for samples containing $\geq 0.0001\%$ of arsenic. Probably samples containing approximately 0.02% or more can be analysed by flame atomic-absorption spectroscopy after removal of the excess of bromine and chloroform from the final solution by heating, and dilution of the resulting solution to an appropriate volume (25 ml or more) with water. The method is sensitive, reasonably specific, requires no special apparatus, and the technique required is simple.

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LIMITS OF DETECTION AND SELECTIVITY COEFFICIENTS OF LIQUID MEMBRANE ELECTRODES

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Summary—An equation has been derived theoretically describing the emf of a liquid membrane electrode: $E = E_0 - (RT/F)\ \ln[(C + \sqrt{C^2 + A_X})/2]$. Experimental data are in good agreement with this equation. The parameter A_X is related to the limit of detection. When the ion-exchanger dissociates completely in the membrane phase, A_X is given by $4\sigma^2/b_X$. Here σ represents the concentration of the ion-exchanger in the liquid membrane and b_X is a quantity related to the ion-selectivity.

A liquid membrane electrode makes use of an ion-exchanger dissolved in a suitable organic solvent which should preferably have a very low solubility in water.[1–3] Ion-exchangers are substances consisting of an ionogenic group attached to an organic molecule, and are sparingly soluble in water. A number of both experimental and theoretical investigations on the origin of the membrane potential of liquid membrane electrodes have been carried out,[4–9] but these have been mainly concerned with selectivity. For a comprehensive understanding of the origin of the potential of a liquid membrane electrode, the limit of detection must also be understood. Bonner *et al.*[10] and Ishibashi *et al.*[11] have suggested that the limit of detection is determined by the leakage of the ion-exchanger into the aqueous solution, but no quantitative study has been reported. The present work deals with the limit of detection for a liquid membrane electrode, and shows that a close correlation exists between the limit of detection and the ion-selectivity of a membrane electrode.

THEORETICAL

The system under consideration consists of two aqueous solutions denoted by (′) and (″) which are separated by an organic solution containing a positively charged ion-exchanger. The limits of the organic solution phase are given by $x = 0$ and $x = L$, and this region is referred to hereafter as the membrane. First, we consider the case where the whole system contains only one kind of anion with concentrations in the two aqueous solutions denoted by C' and C'', respectively. In the membrane, the following three mobile species exist: the positively charged ion-exchanger S, the anion X, and the associated ion-exchanger SX, which is supposed to be electrically neutral. Species S and X considered here are a univalent cation and anion, respectively. The flux equations for these species in the membrane phase are written as follows;

$$FJ_S = -\bar{U}_S\bar{C}_S\frac{d\tilde{\mu}_S}{dx} = -\bar{U}_S\bar{C}_SF\frac{d\varphi}{dx} - \bar{U}_SRT\frac{d\bar{C}_S}{dx} \quad (1)$$

$$FJ_X = -\bar{U}_X\bar{C}_X\frac{d\tilde{\mu}_X}{dx} = \bar{U}_X\bar{C}_XF\frac{d\varphi}{dx} - \bar{U}_XRT\frac{d\bar{C}_X}{dx} \quad (2)$$

$$FJ_{SX} = -\bar{U}_{SX}\bar{C}_{SX}\frac{d\mu_{SX}}{dx} = -\bar{U}_{SX}RT\frac{d\bar{C}_{SX}}{dx} \quad (3)$$

where J_i, $\bar{U}_i$, $d\bar{\mu}_i/dx$, X, and $\bar{C}_i$ ($i = S$, X, and SX) represent the flux, the mobility, the gradient of the electrochemical potential, the electrical potential, and the concentration of the ith-species at a position x in the membrane, respectively. In these equations, activity coefficients and the movement of the local centre of mass relative to the membrane are neglected. According to the Curie principle,[12] the dissociation reaction of SX introduces no extra driving force in the set of flux equations described above. The dissociation constant of SX, α_X, is defined as

$$\bar{C}_S\,\bar{C}_X/\bar{C}_{SX} = \alpha_X \quad (4)$$

Since the membrane potential is measured under such conditions that no electrical current passes through the membrane, *i.e.*, $J_X = J_S$, the gradient of electrical potential is given by

$$d\varphi/dx = \left(\frac{RT}{F}\right)[(\bar{U}_X d\bar{C}_X/dx - \bar{U}_S d\bar{C}_S/dx)]/(\bar{U}_S C_S + \bar{U}_X C_X)$$

Substitution of this equation into equations (1) and (2)

leads to the following equation for J_S and J_X:

$$J_S = J_X = -\frac{RT}{F}\frac{\bar{U}_S\bar{C}_S\bar{U}_X\bar{C}_X}{\bar{U}_S\bar{C}_S + \bar{U}_X\bar{C}_X}\frac{\mathrm{d}\ln(\bar{C}_S\bar{C}_X)}{\mathrm{d}x}$$

$$= -\frac{RT}{F}\frac{\bar{U}_S\bar{C}_S\bar{U}_X\bar{C}_X}{\bar{U}_S\bar{C}_S + \bar{U}_X\bar{C}_X}\frac{\mathrm{d}\ln\bar{C}_{SX}}{\mathrm{d}x}$$

$$= \frac{\bar{U}_S\bar{C}_S\bar{U}_X\bar{C}_X}{(\bar{U}_S\bar{C}_S + \bar{U}_X\bar{C}_X)\bar{U}_{SX}\bar{C}_{SX}}J_{SX} \qquad (5)$$

where equations (3) and (4) are used with the assumption that α_X is independent of x. The dissociated ion-exchanger, S is able to leak out into the aqueous phase, but the associated ion-exchanger, SX, is assumed to be insoluble in water, and hence is restricted to the organic membrane phase. For the steady state, this assumption leads to the equation that $J_{SX} = 0$ at the two boundaries $x = 0$ and L. Combining this equation with equation (5), we obtain the following equation for the steady state;

$$J_S = J_X = 0 \quad 0 < x < L \qquad (6)$$

By incorporating equation (6) and assuming continuity of electrochemical potential at the membrane–solution interface, we can integrate equations (1) and (2) with respect to x from 0 to L to obtain

$$E = -\frac{RT}{F}\ln\frac{C''_S}{C'_S} = \frac{RT}{F}\ln\frac{C''_W}{C'_W} \qquad (7)$$

where E stands for the difference in the electrical potentials of the two bulk solutions (′) and (″), *i.e.*, the membrane potential, and C_X and C_S represent the concentrations of anion X and the positively charged ion-exchanger S in the aqueous solutions, which leaked out from the membrane phase. In the experiments described below, the composition of the solution (″) is kept constant. Then, we obtain

$$E = E_0 - (\mathrm{RT}/\mathrm{F})\ln C'_X = E_0 + (RT/F)\ln C'_S \qquad (8)$$

where E_0 is a constant which depends only on the concentration of X or S in the solution (″). For the sake of simplicity, we will omit the prime ′ in the following discussion unless confusion would arise, since the composition of the solution (″) is kept constant. It should be noted that the concentration of anion C_X is different from C, the concentration of X added initially to the test solution. Since the amount of anion-exchanger leaked out from the membrane into the aqueous solution is equal to that of the anion, we have

$$C_X = C + C_S \qquad (9)$$

Continuity of electrochemical potential at the membrane–solution interface leads to

$$C_SC_X = \bar{C}_S\bar{C}_X/b_X = \alpha_X\bar{C}_{SX}/b_X \qquad (10)$$

where b_X is defined by the equation[13]

$$RT\ln b_X = (\mu_S^0 + \mu_X^0) - (\mu_S^{0,m} + \mu_X^{0,m}) \qquad (11)$$

Here, μ_i^0 and $\mu_i^{0,m}$ stand for the standard chemical potentials of the ith ion in the aqueous and membrane phases, respectively. The total concentration of the ion-exchanger in the membrane, σ, is given by

$$\bar{C}_S + \bar{C}_{SX} = \sigma \qquad (12)$$

Combination of equations (9), (10), and (12) yields

$$C_X = \frac{C + \sqrt{C^2 + A_X}}{2}; \quad C_S = \frac{A_X}{2C + 2\sqrt{C^2 + A_X}} \qquad (13)$$

where A_X is

$$A_X = 4(\alpha_X/b_X)\bar{C}_{SX}$$

$$= (2\alpha_X^2/b_X)\{1 + 2\sigma/\alpha_X - \sqrt{1 + 4(\sigma/\alpha_X)}\}. \qquad (14)$$

The meanings of the parameters in equation (14) are listed in Table 1. Substituting equation (13) into equation (8), we obtain the desired equation for the membrane potential, E:

$$E = E_0 - (RT/F)\ln[(C + \sqrt{C^2 + A_X})/2] \qquad (15)$$

When $A_X = 0$, equation (15) simplifies to the familiar Nernst equation. Figure 1 illustrates the relationship between E and C for various values of A_X, for C'' fixed at $10^{-2}M$. The figure shows that the membrane potential E begins to level off from the Nernstian relationship at higher concentrations as the value of A_X becomes larger. When C is infinitely dilute, the membrane potential E tends asymptotically to a constant E^∞, which is given by

$$E^\infty = E_0 + (RT/F)\ln 2 - (RT/2F)\ln A_X \qquad (16)$$

Then the parameter A_X governs the limit of detection, and is a function of both σ and b_X.

Table 1. Meanings of symbols used

A_X	Quantity defined by equation (14), governing the limit of detection
α_X	Dissociation constant defined by equation (4)
b_X	Difference of the standard chemical potential of the salt SX between aqueous and membrane phases; see equation (11)
C_S	Concentration of ion-exchanger in the aqueous solution, leaked out from the membrane
C_X	Concentration of anion X in aqueous solution
$\bar{C}_{SX}$	Concentration of the associated ion-exchanger in the membrane
$\bar{C}_S$	Concentration of dissociated ion-exchanger in the membrane
$\bar{C}_X$	Concentration of free anion X in the membrane
K_{XY}	Selectivity coefficient of Y with respect to the primary ion X
k_i	Difference between the standard chemical potentials of the ith ion in the aqueous and membrane phases; see equation (20).
P_X	Distribution ratio of CV between aqueous and membrane phases
σ	Total concentration of ion-exchanger in the membrane
$\bar{U}_X$	Mobility of X in the membrane phase

EXPERIMENTAL

Materials

Crystal Violet (abbreviated as CV hereafter) was used as the positively charged anion-exchanger: its concen-

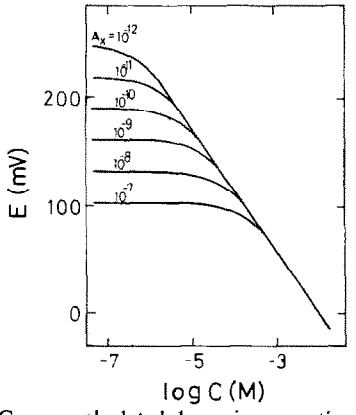

Fig. 1. Curves calculated by using equation (15) for a number of values of A_X. The concentration of the solution (') is taken as $10^{-2}M$.

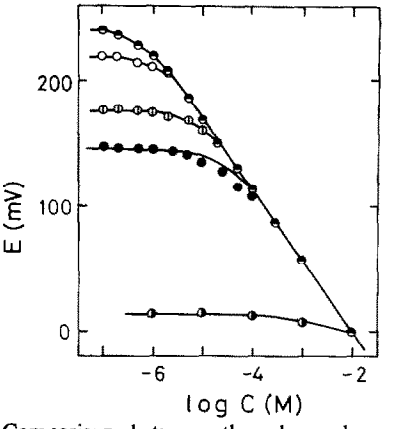

Fig. 2. Comparison between the observed membrane potential and equation (15) for a variety of anions. ⊖, ClO_4^-; ○, I^-; ⊕, Br^-; ●, Cl^-; ◑, F^-. Solid lines represent the curves calculated by using equation (15). The values of A_X used are given in the text.

tration was determined spectrophotometrically. Various salts (F^-, Br^-, I^-, NO_3^- and ClO_4^-) of CV were prepared as follows. The chloride, which was commercially available, was dissolved in dichloroethane (the concentration being about $10^{-2}M$) and the solution was filtered to remove undissolved CV. The solution was shaken vigorously with a concentrated electrolyte solution containing the desired anion (*ca.* $1M$) and the aqueous solution was discarded after separation of the two phases. This procedure was repeated 6 times to replace the chloride ion completely by the desired anion, and the dichloroethane was then removed completely by evaporation under reduced pressure. The CV salts thus prepared were stored in a desiccator.

The water used was obtained by passing distilled water through an ion-exchange column, and was saturated with nitrogen gas to eliminate interference from the bicarbonate ion. Analytical grade chemicals were used without further purification.

Measurements of the membrane potential

The liquid membrane was prepared by dissolving the CV salt of the desired counter-ion in nitrobenzene which was then placed in the bottom of a U-shaped glass tube. The emf arising between the two electrolyte solutions in the arms of the U-tube and separated by the liquid membrane was measured with an electrometer (Takeda Riken Co., Tokyo, Type TR-9651) through a pair of calomel electrodes. The tips of the salt bridges were placed far away from the organic membrane so as to avoid contamination by potassium chloride leaking out from the salt bridges. The electrometer was connected to a pen-recorder to confirm that the observed potentials remained constant. The potentials observed were reproducible to within $\pm$ 2 mV.

Distribution ratio of CV

The nitrobenzene solutions of CV with various counter-ions were shaken vigorously with pure water. After the organic and aqueous phases had separated, the concentration of CV in the aqueous phase, C_S, and that in the organic phase, $\bar{C}_S$, were determined by absorbance measurements at 560 nm. The values of C_S examined were between 2 and 20 μmole/l.

RESULTS AND DISCUSSION

In Fig. 2, the membrane potentials observed for the concentration cell are plotted as a function of the concentration for the various anions in the solution ('). The concentration of the solution (") was kept constant at $10^{-2}M$ consistent with conditions assumed in the calculations for Fig. 1, and the concentration of the ion-exchanger in the membrane, σ, was fixed at $10^{-3}M$. The solid lines represent the curves calculated from equation (15) with the values of A_X taken as 8×10^{-13}, 7.5×10^{-12}, 4×10^{-10}, 2.5×10^{-9} and 10^{-4} mole^2/l.^{2} for perchlorate, iodide, bromide, chloride and fluoride respectively. Figure 3 shows the membrane potentials for iodide solutions when the ion-exchanger concentration σ was varied. The solid lines are the curves calculated by using the appropriate values of A_X according to equation (16), which were 6.3×10^{-12}, 7.5×10^{-12}, 6×10^{-10} and 4×10^{-8}, respectively, from top to bottom. These figures signify the applicability of equation (15) for all the systems examined.

If the ion-exchanger dissociates nearly completely in the organic membrane, *i.e.*, the condition that $\sigma/\alpha_X \ll 1$ is satisfied, equation (14) is simplified to give

$$A_X \simeq 4\sigma^2/b_X \qquad (17)$$

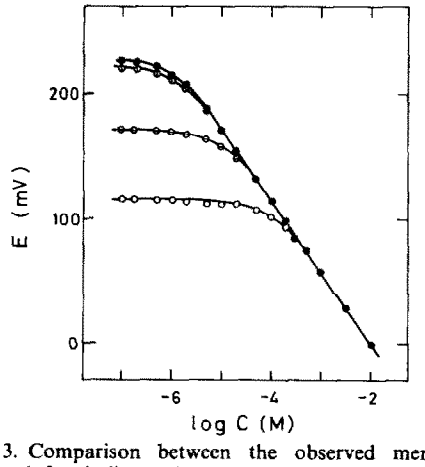

Fig. 3. Comparison between the observed membrane potential for iodide solutions and those calculated by using equation (15) for a range of ion-exchanger concentrations, σ. ●, $\sigma = 3.2 \times 10^{-4}$, $A_X = 6.3 \times 10^{-12}$; ⊕, $\sigma = 1 \times 10^{-3}$, $A_X = 7.5 \times 10^{-12}$; ⊖, $\sigma = 1 \times 10^{-2}$, $A_X = 6 \times 10^{-10}$; ○, $\sigma = 1 \times 10^{-1}$, $A_X = 4 \times 10^{-8}$.

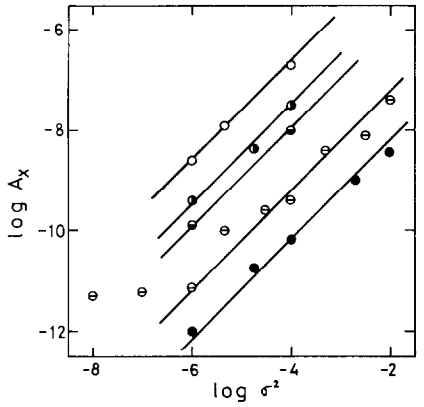

Fig. 4. Plots of log A_X against log σ^2 for various anions. ○, Cl^-; ◑, Br^-, ⊖, NO_3^-; ⊖, I^-; ●, ClO_4^-.

This equation predicts that the values of A_X obtained by measuring the membrane potentials with different concentrations of ion-exchanger σ are proportional to σ^2. Figure 4 shows the plots of log A_X against log σ^2 for chloride, bromide, nitrate, iodide and perchlorate. Except in the case of extremely small values of σ for iodide, log A_X is proportional to log σ^2, with unit slope. The value of b_X can be determined from this figure for each anion, and compared with the distribution ratio of CV at infinite dilution, P_X. The distribution ratios were found to be practically independent ($\pm 5\%$) of C_S over the range examined. Equation (10) and the electroneutrality condition enable one to predict[6] that $b_X = P_X^2$. The experimental points, however, lie on the straight line represented by the equation

$$\log b_X = 1.7 + 0.7 \log P_X^2 \tag{18}$$

Next, we consider the case where the solutions (′) and (″) contain two anionic species, X and Y. For such a system, Eisenman *et al.*[4] derived the equation of the membrane potential, assuming that the ion-exchanger is confined within the membrane phase, and that co-ions are perfectly excluded from the membrane phase. The first condition mentioned above is equivalent to stating that $C^2 \gg A_X, A_Y$. When the ion-exchanger dissociates completely in the membrane phase, the Eisenman equation can be simplified to give

$$E = \frac{RT}{F} \ln \frac{k_X \overline{U}_X C_X'' + k_Y \overline{U}_Y C_Y''}{k_X \overline{U}_X C_X' + k_Y \overline{U}_Y C_Y'} \tag{19}$$

where k_i ($i = X, Y$) is defined by the following equation;

$$RT \ln k_i = \mu_i^0 - \mu_i^{0,m} \tag{20}$$

If the salt composition in solution (″) is kept constant, equation (19) is rewritten as

$$E = E_0 - (RT/F) \ln (C_X' + K_{XY} C_Y') \tag{21}$$

with

$$K_{XY} = (\overline{U}_Y k_Y)/\overline{U}_X k_X) = (\overline{U}_Y b_Y)/\overline{U}_X b_X) \tag{22}$$

[where equation (11) has been introduced]. K_{XY} defined by equation (21) is referred to as the selectivity coefficient.[14] If the membrane potential is measured under conditions where $C_X'' = C_Y' = 0$ and $C_Y'' = C_X'$, equation (19) simplifies to

$$E = (RT/F) \ln K_{XY} \tag{23}$$

The value of K_{XY} for a given system can be determined from the measurement of the membrane potential under either multi-ionic conditions [equation (20)] or bi-ionic conditions [equation (23)].[9,15] In the system studied here, the values of K_{XY} determined from these two different approaches were in agreement.

The relationship between log $K_{Cl,X}$ and log $\overline{u}_X b_X$ was linear. The values of $\overline{U}_X$ were taken from Coetzee's data.[16] Coetzee *et al.* measured the mobilities of various anions which were used as counter-ions of tetraisoamylammonium dissolved in nitrobenzene. It was noted that the values of log $\overline{U}_X b_X$ are not altered substantially if the mobility is neglected.[8] Equation (22) predicts that the slope of this plot should be equal to unity, but the experimental data follow a straight line with slope equal to 0.7. The value of this slope is the same as that observed in equation (18) but as the ratio of K_{ClX} to P_X^2 remains constant for all the anions examined (as shown in the previous investigation),[8,9] the discrepancy is considered to arise from the improbable value of b_X. The reason for this discrepancy is not clear to us, though an explanation may lie in the incomplete restriction of the associated ion-exchanger SX or in neglecting the ion-association in the aqueous solutions. Further study may be necessary.

In conclusion, the membrane potential of a liquid membrane electrode is adequately described by equation (15) where A_X determines the limit of detection of the electrode, and is a function of both b_X and σ. The parameter b_X takes into account the differences between the standard chemical potentials of the anion and of the anion-exchanger in both the aqueous and the membrane phases. In fact, it is shown that the use of a more hydrophobic ion-exchanger lowers the limit of detection.[11,15] According to equation (17), log $\overline{U}_X b_X$ is equal to log$(4\overline{U}_X \sigma^2/A_X)$. For a given ion-exchanger, diluting the exchanger lowers the limit of detection. The plot of log $K_{Cl,X}$ vs log $\overline{U}_X b_X$ indicates that the limit of detection is closely related to the selectivity coefficient.

Buck[17] has derived an equation for the membrane potential of a solid-state membrane. His equation is quite similar to equation (15), except for the meaning of A_X. In his equation for a solid-state membrane, A_X in equation (15) is replaced by the solubility product of the sparingly soluble salt embedded in the membrane. The solubility product is a measure of the difference between the standard chemical potentials in the aqueous solution and in the pure solid.[18] The selectivity coefficient of a solid membrane electrode is determined by the solubility product. This fact suggests that the origin of the membrane potential is similar in the liquid and solid membrane types.

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DETERMINATION OF LOW LEVELS OF URANIUM IN SOLUTIONS OBTAINED BY ACID ATTACK ON PHOSPHATE ROCK

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Summary—The uranium present in the leach liquors obtained by attack on phosphate rock with sulphuric acid can be extracted with di(2-ethylhexyl)phosphoric acid and TBP after oxidation of any iron(II), and then stripped at 65° with iron(II) in 8.6*M* phosphoric acid. The uranium is finally determined with arsenazo III.

In recent years the phosphate fertilizer industry has developed rapidly and at the same time the amount of uranium dissolved in wet-process phosphoric acid has become important. An increased demand for uranium on the world market has led to the need to pay more attention to this important source. The phosphate rocks (Florida, North Africa, Israel, *etc.*) have a uranium content of 0.01–0.02%, and phosphoric acid solutions 0.1–0.2 g/l.

The recovery of uranium as a by-product in the wet phosphoric acid process results in a much cheaper uranium concentrate than that usually obtained from ores. The phosphoric acid solutions obtained in the first stage are 4–5*M*, and several other elements are present at much higher concentrations than the uranium, typical concentrations (g/l.) after sulphuric acid attack being Fe^{2+} 0.5–1.0, Fe^{3+} 2–5, Al^{3+} 1–2, Ca^{2+} 1–3, SO_4^{2-} 15–25, F^- 20. Organic matter (humic acids) is also almost always present when the phosphate rock is not calcined.[1,2] For nitric acid attack, prior calcination of the rock eliminates this inconvenience, but some of the uranium is rendered insoluble.

In determination of the uranium, many problems are to be expected because of the composition of the sample solution. Any iron(II) present after sulphuric acid treatment of the rock might lead to reduction of U(VI) to U(IV), because of complexation of Fe(III) by the phosphoric acid increasing the reducing power of the Fe(II).

In this study, it was intended to separate uranium by solvent extraction and determine it spectrophotometrically. The choice of extractant also poses problems related to the medium. It is well known that liquid cation-exchangers such as di(2-ethylhexyl)phosphoric acid (DEHP) are very effective for actinide extraction, but to attain high distribution coefficients a synergic system, involving a neutral phosphorus ester such as tributyl phosphate (TBP), was sought. Kerosene was found to be the most suitable diluent. The extraction system chosen was based on the behaviour of UO_2^{2+} and U^{4+} in phosphoric acid, and then the effect of the other impurities was examined. When the most suitable parameters had been determined, the method was applied to industrial phosphoric acid solutions containing all the impurities obtained in the phosphate rock acid process.

EXPERIMENTAL

All reagents were of analytical grade. For studies on the effect of temperature, separating-funnels fitted with a water-jacket connected to a thermostat were used, several minutes being allowed for temperature equilibration. The funnels were shaken by hand for 5 min, more than enough for equilibrium to be attained (preliminary experiments showed that 2 min are sufficient).

The uranium was determined spectrophotometrically as the arsenazo III complex or by the X-ray fluorescence of liquid or solid samples. In the case of liquid samples the intensity of the signal is affected by the uranium concentration. The calibration curves are linear but the slopes depend on the phosphoric acid concentration, which therefore has to be taken into account.

In most of the experimental work, 0.1-g/l. uranium(VI) solutions were used, prepared by calcining $UO_2(NO_3)_2 \cdot 6H_2O$ to the oxide to eliminate nitric acid, and dissolving the oxide in conc. phosphoric acid. In the extraction studies iron(II) or iron(III) was also present at a concentration of 25 mg/ml.

Pure uranium(IV) solutions not containing iron(II) were prepared by dissolving UO_2 in hydrochloric acid (containing traces of fluoride) or, more frequently, by dissolving UO_3 in 2*M* hydrochloric acid, followed by reduction in a Jones reductor. The effluent from the reductor was passed through a column of Dowex 50 × 8 cation-exchange resin and any uranyl(VI) ions were eluted with 1*M* hydrochloric acid, followed by elution of uranium(IV) with 4–6*M* hydrochloric acid.[3] The same operation was possible with sulphuric acid. The uranium(IV) solution was diluted to a uranium concentration of 0.1 g/l., with enough phosphoric acid to give 4.3*M* concentration. The final hydrochloric acid concentration was 0.04*M*, which was negligible. It should be remembered that industrial phosphoric acid solutions have a residual acidity due to sulphuric, hydrochloric or nitric acid, depending on the processing of the phosphate rock.

Iron(II) and (III) solutions in phosphoric acid were prepared by dissolving the sulphates in the desired medium.

Iron was determined by permanganate titration. The aqueous phase was titrated with alkali before and after extraction, and it was thus established that the extraction did not alter the phosphoric acid concentration. Uranium was determined directly in the stripping solution of 4.3 or 8.6*M* acidity by reduction with zinc and ascorbic acid followed by addition of arsenazo III (aqueous solution). Comparisons were made with standards which had been analysed by X-ray fluorescence. Uranium(VI) in pure phosphoric acid solutions was directly determined colorimetrically, by treatment with arsenazo III.

Finally the method was checked with industrial phosphoric acid solutions but in some cases known amounts of U(VI) were also added because of the low concentration of uranium. Some studies were performed in the presence of various concentrations of nitric acid. Iron(II) and uranium(IV) were generally oxidized by passing air through the solution, or more surely with sodium chlorate.

Procedure

Take 10 ml of raw phosphoric acid (about 4.3*M*), previously treated with enough sodium chlorate to oxidize the iron(II) present (determined separately), then extract uranium with three 7-ml portions of 1.2*M* DEHP/0.15*M* TPB at 25–30°. Strip the uranium with three 10-ml portions of 8.6*M* phosphoric acid containing 5–15 mg of Fe(II) per ml, at 65°. Take 1 ml of the combined strippings and stir for 5 min with several granules of zinc, then add 2 ml of 2% ascorbic acid solution, 15 ml of 0.006% arsenazo III solution in 0.6*M* acetic acid +0.5*M* sodium acetate buffer, and leave for 15 min for complex formation. Measure at 665 nm against a reference solution consisting of 1 ml of 8.6*M* phosphoric acid treated in exactly the same way with zinc *etc.*, and prepare a calibration curve with standards similarly treated (same acidity *etc.*).

RESULTS

The first set of experiments on U(IV) and U(VI) in pure 4.3*M* phosphoric acid solutions, at 25°, the extractant being DEHT + TBP in kerosene, is represented in Fig. 1, where the values of log *D* are plotted as a function of log [DEHP]. On the straight lines are given the concentrations of the TBP. All concentrations are expressed in mole/l. and *D* is the distribution coefficient defined as the ratio of the uranium concentrations in the organic and aqueous phases at equilibrium. Plots of log *D* *vs.* log [H_3PO_4] gave straight lines of slope −2 for 0.05–0.3*M* TBP + 0.3–1.8*M* DEHP, the value of *D* being higher at higher DEHP concentration.

The role of temperature is shown in Fig. 2 for 4.3*M* phosphoric acid and U(VI) or U(IV) (0.1 g/l.). The choice of extractant was generally based on the earlier results but other systems were also tried.

Owing to the important role played by iron(II) and (III) as major constituents in industrial phosphoric acid solutions, its behaviour during the extraction and its influence on the uranium recovery were investigated. It was added as pure Fe(II) or Fe(III) to 4.3*M* phosphoric acid solutions with and without U(VI). Distribution coefficients were plotted as log *D* *vs.* log [DEHP] at constant TBP concentrations of 0.05, 0.15 and 0.3*M*. Figure 3 shows the results only for Fe(II). The *D*-values for Fe(III) are only a tenth of those for Fe(II), and there is practically no Fe(III) in the industrial solutions.

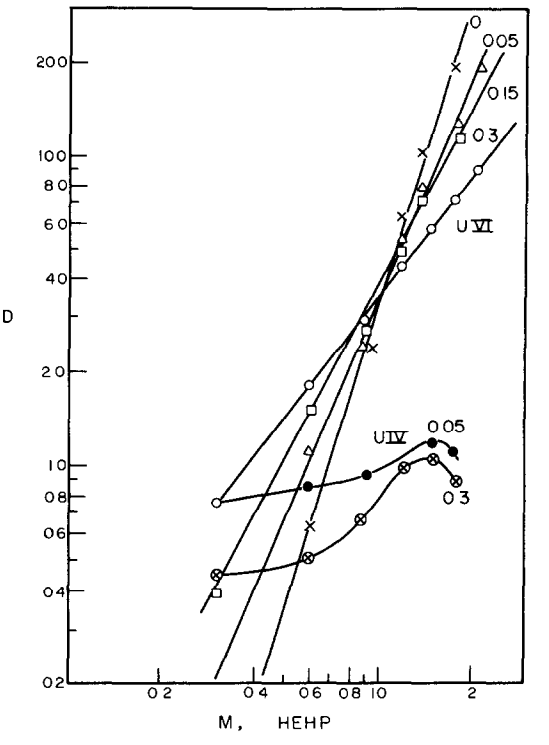

Fig. 1. Distribution coefficient as a function of DEHP concentration, for U(VI) and U(IV) and 4.3*M* H_3PO_4. Numbers by the lines refer to molarity of TBP.

Since the presence of Fe(II) leads to the reduction of U(VI) to U(IV) in phosphoric acid solutions, the log *D* *vs.* log [DEHP] functions are expected to be the same as those represented for U(IV) in Fig. 1. This is indeed so at medium and higher concentrations of DEHP, but at lower concentrations the effect of surplus Fe(II) is more marked (Fig. 3). In the presence of only Fe(III) the behaviour of U(VI) is practically the same as that shown in Fig. 1.

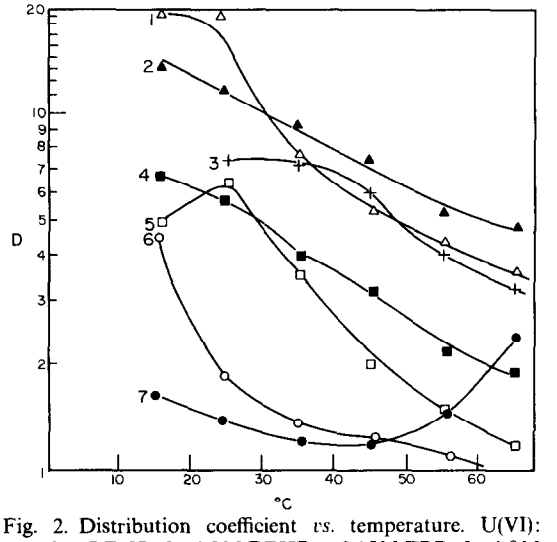

Fig. 2. Distribution coefficient *vs.* temperature. U(VI): *1*—1.8*M* DEHP; *2*—1.8*M* DEHP + 0.15*M* TBP; *3*—1.8*M* DEHP + 0.30*M* TBP; *4*—1.2*M* DEHP + 0.15*M* TBP. *5*—1.2*M* DEHP; *6*—0.6*M* DEHP + 0.30*M* TBP; U(IV) *7*—1.5*M* DEHP + 0.05*M* TBP.

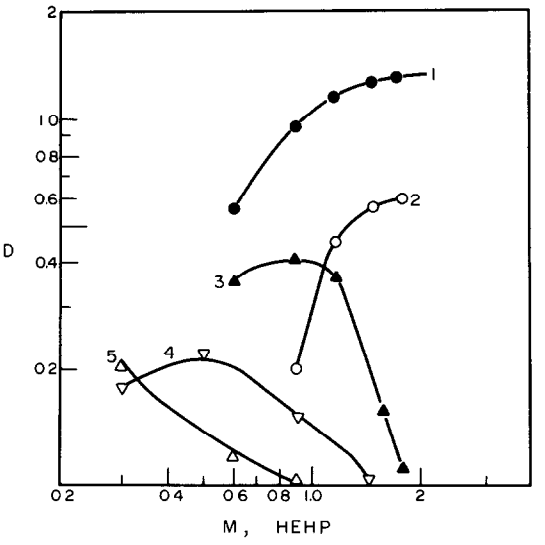

Fig. 3. Distribution coefficient *vs.* DEHP concentration. U(IV) in the presence of Fe(II): *1*—0.05*M* TBP; *2*—0.30*M* TBP. Fe(II): *3*—0.05*M* TBP; *4*—0.15*M* TBP; *5*—0.30*M* TBP.

Increase in temperature generally reduces the value of *D*. The presence of Fe(II) at a concentration of 5 mg/ml in 8.6*M* phosphoric acid decreases *D* to 0.10–0.15 at 50–65°. Thus a stripping solution of this composition is efficient for uranium recovery.

Finally the method was applied to industrial phosphoric acid solutions and the results compared with those of X-ray fluorescence (Table 1).

DISCUSSION

The fresh industrial phosphoric acid solution obtained by sulphuric acid attack on phosphate rock contains a significant amount of Fe(II) which reduces U(VI) to U(IV), which is less extractable at temperatures below 45° (Fig. 2). At higher temperatures this behaviour changes slightly and it is therefore desirable to convert all the uranium into U(VI).

The iron can be oxidized by bubbling air through the solution at 70–80° but the process is slow. The speed of reaction increases with temperature but the solubility of oxygen also decreases. It is better to add a reagent such as sodium chlorate. Sometimes the interval between sampling and analysis is long enough to ensure a partial oxidation of iron.

Table 1. Results from X-ray fluorescence and extraction-spectrophotometric methods

Sample	X-ray fluorescence, *g/l.*	Extraction-spectrophotometry, *g/l.*
1	0.231	0.228 (±2%)*
2	0.240	0.240 (±1%)
3	0.261	0.254 (±3%)
4	0.376	0.364 (±5%)
5	0.188	0.192 (±4%)
6	0.204	0.200 (±2%)
7	0.181	0.178 (±2%)

* Errors are the mean value from several determinations.

The dependence of uranium extraction on the concentration of DEHP and TBP in kerosene at 25° is given in Fig. 1. The slopes decrease from 2.6 for pure DEHP to 1 for 0.3*M* TBP in the case of U(VI). For U(IV) the values of *D* are much lower (at 25°) and no linear dependence appears. The presence of TBP in the organic phase exerts a synergic effect on the U(VI) extraction up to 1*M* DEHP concentration but at higher concentration an antagonistic effect is present. However the values of *D* always increase with DEHP concentration, therefore better uranium recoveries are obtained by extraction with 1.2–1.8*M* DEHP from 4.3*M* phosphoric acid at 25°. It is better to add TBP at lower concentrations of DEHP. A family of straight lines of slope −2 was obtained for plots of log *D* *vs.* log $[H_3PO_4]$ for various DEHP concentrations and 0.05–0.3*M* TBP. *D* should be given by

$$D = \frac{D_0}{1 + \Sigma_n K_n [H_2PO_4^-]^n} \quad (1)$$

where *D* refers to the distribution coefficient for uranium(VI) in presence of phosphoric acid and D_0 to the distribution in the absence of phosphoric acid. K_n is defined by

$$UO_2^{2+} + nH_3PO_4 \overset{K_n}{\rightleftharpoons} [UO_2(H_2PO_4)_n]^{(1-n)+} \quad (2)$$

The literature on UO_2^{2+} complexes in phosphoric acid medium mentions the existence of ions such as $UO_2H_3PO_4^{2+}$, $UO_2H_2PO_4^+$, $UO_2(H_2PO_4)H_3PO_4^+$, $UO_2(H_2PO_4)_2$.[4–7] In dilute phosphoric acid UO_2^{2+} predominates but at higher acid concentrations various complexes are formed. Over the phosphoric acid concentration range studied, the high value of *D* at lower acid concentrations supports the supposition that UO_2^{2+} is the major extractable species. The behaviour of DEHP (denoted by HX, and dimerized in the organic phase) in the extraction is described by the equation

$$UO_{2aq}^{2+} + 2(HX)_{2\,org} \rightleftharpoons UO_2X_4H_{2\,org} + 2H_{aq}^+ \quad (3)$$

and corresponds to an ion-exchange mechanism, and to the slope of −2 for log *D* *vs.* log $[H_3PO_4]$.

The mechanisms for other systems are described in the literature.[8–12] In the phosphoric acid system it is likely that there is a similar mechanism in the region where synergism exists. The antagonistic effect seems to play a minor role at concentrations higher than 1*M* DEHP and it is therefore rather difficult to believe that water is present in the organic phase when the synergic species is destroyed. The extraction coefficient becomes smaller when the TBP concentration is increased, because of a stronger interaction between HX and TBP through hydrogen-bonding, and a consequent reduction in the concentration of free HX.

The reaction mechanism chosen leads to a mathematical treatment like that of Sato[13] for $UO_2X_2 \cdot 2Y$

in sulphuric acid medium. From the slopes in Fig. 1 it is possible to assume that this mechanism is partly valid but other contributions are also present to a lower or higher degree, depending on the system studied.

The value of D for U(VI) and various DEHP–TBP mixtures decreases with temperature, Fig. 2, which explains the advantage of extraction at low temperature, say 20–25° and stripping at 65° with 4.3M phosphoric acid (or, even better, 8.6M). Both extraction and stripping should be done in three steps. The D value increases with DEHP concentration but the presence of TBP makes it less dependent on temperature. From this point of view it is better to use 1.2M DEHP in kerosene than 1.2M DEHP + 0.15M TBP. The D values in both cases are the same at 25° but stripping at 65° is favoured if TBP is absent. The behaviour of U(IV), as shown in Fig. 2, might partly be explained by oxidation but it is unlikely that this is the only process responsible for the increased extraction at temperatures higher than 45°. It is this behaviour that makes it necessary to oxidize Fe(II) and U(IV) before the extraction. However, it was found that stripping at 65° with 8.6M phosphoric acid is more efficient in presence of Fe(II), as U(IV) has much the lower extraction coefficient, $\sim$0.1. The role of iron in the extraction of uranium depends on its oxidation state. In the case of Fe(II), Fig. 3, the D values for iron are much lower than those of U(IV) and an increase of TBP concentration from 0.05 to 0.3M appreciably reduces the Fe(II) extraction. When uranium(VI) at a concentration of 0.1 mg/ml was extracted from 4.3M phosphoric acid in the presence of Fe(II) at a concentration of 25 mg/ml, the values of D (Fig. 3) indicated an extraction comparable with that of U(IV) in the absence of iron. It is thus clear that U(VI) was reduced by Fe(II) to U(IV) which then behaved as such. It seems that Fe(II), with lower D but higher amount extracted, say 7 mg/ml, exerts little influence at 1M DEHP concentration on the value of D for U(IV) from the point of view of reducing the concentration of active HX groups. Increasing the TBP concentration markedly reduces the extraction yield both for U(IV) and Fe(II).

The values of D for Fe(III) extraction are a tenth of those for Fe(II) under the same conditions. Therefore U(VI) will not be practically affected.

From the results of all these experiments, the choice of extractant depends on the case under study but sometimes it is preferable to employ pure DEHP in kerosene at say 1.2M concentration, because of the greater influence of temperature on D. Uranium must be in the sexivalent form, therefore oxidation of iron is required. At the same time, lowering the phosphoric acid concentration greatly increases the value of D. Stripping is best done in the presence of Fe(II) with 4.3–8.6M phosphoric acid. There will then be no organic matter in the stripping solution and hence no interference in the analysis.

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SHORT COMMUNICATIONS

DETERMINATION OF CADMIUM IN SOILS BY NEUTRON-ACTIVATION ANALYSIS

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Summary—A radiochemical neutron-activation method for the determination of cadmium in soils is presented. The irradiation is carried out in a neutron flux with a high epithermal component, taking advantage of the high ratio of the resonance-activation integral to the thermal-neutron cross-section for ^{114}Cd to obtain an increased sensitivity. The irradiated samples are decomposed with hydrofluoric acid–nitric acid and cadmium is separated by anion-exchange. Zinc may also be determined. There is good agreement with results obtained by atomic-absorption spectrophotometry based on solvent extraction separation of cadmium.

The high toxicity of cadmium to man has aroused great interest in recent years in studies of the concentration of this element in environmental samples. The greater part of the work has been performed by means of atomic-absorption spectrophotometry because of the very high sensitivity of the determination of cadmium by this technique. In a complex matrix such as soil where a low concentration level of cadmium is most often encountered, errors due to chemical interferences may occur if the absorption measurement is performed directly on the dissolved sample, or difficulties due to contamination or incomplete recovery may be evident if a chemical concentration step is used. It is therefore desirable to check the results by an independent analytical technique. Methods available for a reliable determination of cadmium in soils at natural concentration levels are, however, very few.

Neutron-activation analysis is not extensively used for cadmium determinations because of the low thermal-neutron activation cross-sections of the stable cadmium isotopes of interest. The preferred choice is in most cases a method based on the (n,γ) reaction of ^{114}Cd (28.9% isotopic abundance) followed by γ-activity measurements of the reaction product ^{115}Cd ($t_{1/2}$ = 53.5 hr) or its daughter nuclide ^{115m}In ($t_{1/2}$ = 4.5 hr). The thermal-neutron cross-section of this reaction is as low as 0.30 barn,[1] so the sensitivity for environmental sample analysis is not adequate unless a very high neutron flux, or an extensive radiochemical separation followed by a very long counting period, is employed.

Considerable improvement of the neutron-activation sensitivity for cadmium can be obtained if the irradiation is carried out in a flux with a high epithermal neutron component, because of the high resonance-activation integral of ^{114}Cd (20 barn),[2] relative to its thermal-neutron cross-section. In an irradiation position with a cadmium ratio of ^{197}Au equal to 1.7, the sensitivity of cadmium determination based on this reaction is improved by a factor of about 50 compared with that obtained in a well thermalized flux. If this fact is taken advantage of, the sensitivity of radiochemical neutron-activation analysis will approach that of the most sensitive atomic-absorption methods without the use of extreme conditions in the activation analsis. The application of neutron-activation analysis to the determination of cadmium in soils has not been reported previously. In the present paper, a radiochemical neutron-activation method, taking advantage of the epithermal component in the reactor neutron spectrum, is presented. The separation procedure is similar to those used previously in the author's laboratory for the analysis of other matrices,[3,4] and allows the simultaneous determination of the geochemically associated element zinc.

EXPERIMENTAL

Soil samples of about 0.5 g, wrapped in aluminium foil, were irradiated for 2 days in a central position of the JEEP-II reactor (Kjeller, Norway) with a thermal-neutron flux of about 1.5×10^{13} n.cm^{-2}.sec^{-1} and $R_{Cd}^{Au} = 1.7$. Standards were prepared by evaporating 100-μl aliquots of a standard solution on 3 × 3 cm squares of aluminium foil.[5] After a delay of 6 days to allow the decay of ^{24}Na, the samples were transferred to 100-ml Teflon beakers containing 10 ml of concentrated hydrofluoric acid, 2 ml of concentrated nitric acid and the following carriers: Cd, 1 mg; Zn, 1 mg; La, 1 mg; Sc, 1 mg. After evaporation to dryness on a hot-plate, 5 ml of concentrated nitric acid and 5 ml of concentrated hydrofluoric acid were added, and another evaporation to dryness was carried out. The residue was dissolved by gentle heating with 15 ml of 6*M* hydrochloric acid containing 30 mg of boric acid, and then applied to an anion-exchange column (Dowex 1-X8, 100–200 mesh, 10 mm diam., 8 cm height of resin bed, pre-equilibrated with 6*M* hydrochloric acid) through a "Blue ribbon" filter paper (Schleicher & Schüll). After the filter had been washed with 5 ml of 6*M* hydrochloric acid, elution with five 10-ml portions of 0.5*M* hydrochloric acid was performed in order to remove ^{59}Fe and other interfering activities. Cadmium (plus zinc) was then eluted with three 10-ml portions of 1*M* ammonium nitrate, and collected in a 100-ml polyethylene screw-cap bottle. The activity measurements were postponed to the next day to allow the growth of the ^{115m}In daughter activity. A Ge(Li) detector (5% efficiency, 2.5 keV FWHM, at 1.33 MeV) and a 2000-channel analyser based on a small digital computer were used, and the 335-keV γ-ray of ^{115m}In was made the basis for the determinations of cadmium. If zinc was to be determined, the 1115-keV γ-ray of ^{65}Zn was used. A counting period of 30 min was used. The recovery by the anion-exchange separation procedure was found to be

Table 1. Determination of cadmium by neutron activation (NAA) and atomic absorption (AA) and zinc by neutron activation in 15 soil samples

Sample no.	Cd, *ppm* AA[6]	Cd, *ppm* NAA	Zn, *ppm* NAA
1	0.58	0.56, 0.60	70.8, 72.4
2	0.70	0.50, 0.56	49.4, 51.2
3	3.70	3.30, 3.44	934, 1015
4	0.30	0.28, 0.24	57.4, 62.0
5	0.03	<0.05, <0.05	21.4, 20.9
6	0.24	0.20, 0.20	60.1, 60.2
7	0.41	0.34, 0.39	112, 102
8	0.04	0.05, 0.07	40.5, 46.0
9	0.05	0.05, 0.06	40.5, 37.3
10	0.24	0.17, 0.18	45.9, 46.5
11	1.25	1.23, 1.19	176, 177
12	0.18	0.16, 0.22	87.4, 87.3
13	0.15	0.07, 0.07	33.4, 31.4
14	0.02	<0.05, <0.05	32.9, 34.8
15	0.67	0.46, 0.52	144, 139

99 ± 1% for both elements, by separate radiotracer experiments.

RESULTS AND DISCUSSION

In connection with a programme on the determination of natural levels of cadmium in soils, conducted by the National Soil Survey of Norway, it was decided to carry out a comparison of atomic-absorption data for some samples with results from neutron-activation analysis, obtained by the present method. A flame method based on wet-ashing of the samples with nitric acid/perchloric acid, followed by solvent extraction at pH 3 with ammonium pyrrolidinedithiocarbamate in chloroform after removal of Fe by extracting with a chloroform solution of acetylacetone, was used in the atomic-absorption measurements.[6] Results for 15 soil samples are shown in Table 1. Results for determination of zinc by the present method are also given. In most cases the agreement between the two methods for cadmium is good, considering the low levels present in most samples. This would indicate that the accuracy of both methods is satisfactory for work at this level. In a few samples, minor amounts of ^{46}Sc were evident in the separated fractions. These amounts were, however, too low to cause any appreciable interference by the 1120-keV γ-ray of ^{46}Sc with the measurement of the 1115-keV γ-ray of ^{65}Zn. Other activities were present only at insignificant levels. Irradiation within a cadmium box to suppress the total activity of the sample as well as that of ^{46}Sc was considered. In view of recent experience[7] indicating a strong resonance absorption in the cadmium cover, leading to a reduction in ^{115}Cd activity by about a factor of 5 in the samples, it was decided to resort to the irradiation technique described above. In addition to the handling of significant amounts of radioactivity during the first part of the radiochemical procedure, the present method involves somewhat more work and under the conditions employed is slightly less sensitive than atomic-absorption methods based on chemical separation of cadmium. It is therefore not implied that neutron activation is going to play a major role in soil analysis for cadmium, but the present method may be useful for checking the accuracy of methods used routinely for its determination in soil and similar materials.

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ALL-*cis*-1, 2, 3, 4-CYCLOPENTANETETRACARBOXYLIC ACID FOR THE GRAVIMETRIC DETERMINATION OF ZIRCONIUM

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(*Received* 30 *June* 1976. *Accepted* 20 *July* 1976)

Summary—1, 2, 3, 4-Cyclopentanetetracarboxylic acid (CPTA) may be used for the gravimetric determination of zirconium. The procedure is simple and relatively free from interference.

Cyclopentanetetracarboxylic acid (CPTA) has been used for the preparation of resins and rubber,[1] its tetra-esters have been used for plasticizers[2] and its chromium complexes for surface treatment of metals and plasters.[3] Hitherto it has not found use as a gravimetric reagent, although as a quadridentate ligand it has been of great interest in co-ordination chemistry. This paper describes the gravimetric determination of Zr((IV) with selective separation from Th(IV) and other commonly associated ions.

EXPERIMENTAL

Reagent

CPTA (m.w. 246.17, m.p. 195–196°) is fairly soluble in water at room temperature and can be prepared by oxi-

Table 1. Determination of cadmium by neutron activation (NAA) and atomic absorption (AA) and zinc by neutron activation in 15 soil samples

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ALL-*cis*-1, 2, 3, 4-CYCLOPENTANETETRACARBOXYLIC ACID FOR THE GRAVIMETRIC DETERMINATION OF ZIRCONIUM

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EXPERIMENTAL

Reagent

CPTA (m.w. 246.17, m.p. 195–196°) is fairly soluble in water at room temperature and can be prepared by oxi-

Table 1. Interferences in the determination of Zr with CPTA

ZrO_2 taken, g	Substance added*	Weight, g	ZrO_2 found, g	Difference, g
0.0614	ThO_2	0.0660	0.0614	Nil
0.1228	ThO_2	0.2640	0.1226	−0.0002
0.0614	ThO_2	0.5280	0.0614	Nil
0.0614	ThO_2	0.6600	0.0622	+0.0008
0.0614	Cr_2O_3	0.3800	0.0612	−0.0002
0.0614	R_2O_3	0.6408	0.0616	+0.0002
0.0614	R_2O_3	1.6020	0.0614	Nil
0.0614	Y_2O_3	0.0240	0.0614	Nil
0.0614	Y_2O_3	0.1445	0.0612	−0.0002
0.0614	Al_2O_3	0.4076	0.0612	−0.0002
0.0614	Fe_2O_3	0.3992	0.0616	+0.0002
0.0614	TiO_2	0.3994	0.0616†	+0.0002
0.0614	BeO	0.06223	0.0614	Nil
0.0614	V_2O_4	0.3256	0.0612†	−0.0002
0.0614	U_3O_8	0.2026	0.0614	Nil
0.0307	SnO_2	0.1098	0.0308	+0.0001
	SnO	0.1063		
	CaO	0.4064		
	SrO	0.2879		
	ZnO	0.1588		
	MgO	0.5877		

* Weight of the oxide equivalent to the metal chloride or nitrate added.
† Double precipitation.

dation of the Diels-Alder adduct of cyclopentadiene and maleic anhydride.[4] Add 100 g of the adduct, over a 2-hr period, to 189 g of 60% w/v nitric acid solution, keeping the temperature at 60°. Stir the mixture for 2.5 hr and cool (~ 80% yield). Purify by recrystallization. Use as a 0.1*M* solution.

Procedure

To a solution containing 4-400 mg of zirconium, add 50 ml of saturated ammonium chloride solution. Heat this solution, add 50 ml of hot 0.1*M* reagent with continuous stirring, and dilute to 250 ml. Add enough hydrochloric acid to make its concentration in the solution 0.3*M*. Keep the mixture on a hot water-bath for 2 hr. A copious precipitate separates. Cool the mixture and filter (Whatman No. 42 paper). Wash the precipitate with 20 ml of a hot 2% solution of the reagent in 0.1% ammonium chloride solution and finally twice with water. Ignite the precipitate directly and weigh as ZrO_2.

RESULTS AND DISCUSSION

The acidity may be varied over the range 0.1–0.35*M* without deleterious effect. The relative standard deviation for the determination of zirconium at 0.3*M* acidity is 0.3% (7 replicates). Cations likely to be associated with zirconium have been investigated for interference. The results are shown in Table 1.

Applications

Standard zircon (63.55% ZrO_2)[5] obtained from Travancore, India, was analysed. The ore was brought into solution by fusion with sodium carbonate, employing the procedure of Holness and Kear.[6] The excess of acid left after removal of silica was neutralized with sodium hydroxide until it reached the required concentration (0.3*M*). Zirconium was also determined by the phthalic acid method.[7] The results (CPTA, 63.6, 63.45, 63.65%; phthalic acid 63.6, 63.5%) of determinations on three sample sizes, 0.1002, 0.1238 and 0.2000 g, were very satisfactory, being within the experimental limits of error and in agreement with each other and the certificate value.

A tenfold excess of thorium does not precipitate, or interfere with the method. However, after removal of the zirconium, thorium can be separated as $ThL.2H_2O$ at pH 2.6–3.8 and thus be determined.[8]

Elemental analysis of the zirconium complex with CPTA suggests the formula $(ZrO)_2$CPTA.

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COULOMETRIC DETERMINATION OF ASCORBIC ACID WITH ELECTROGENERATED OCTACYANOMOLYBDATE(V)

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Summary—A coulometric-potentiometric method is described for the estimation of ascorbic acid with octacyanomolybdate(V) generated electrolytically. The accuracy and precision are comparable with those of the other coulometric methods available.

The coulometric determination of ascorbic acid with electrogenerated bromine and iodine has been the subject of several investigations.[1–4] A potentiostatic method of determination has also been described.[5] The coulometric and titrimetric determination of ascorbic acid, and also the applications of ascorbic acid as a reductant, have all been carried out in acid media to avoid interference by oxygen and the subsequent oxidation of the dehydroascorbic acid formed.[6] The conditional standard potential of the dehydroascorbic–ascorbic acid system depends on pH, and ranges from −0.012 V (pH 8.7) to +0.326 V (pH 1.1) *vs.* N.H.E.[6,7]

Electrogenerated octacyanomolybdate(V) has been used as reagent in alkaline media in the determination of Tl(I),[8] Ce(III)[9] and Co(II).[10] Its electrogeneration from octacyanomolybdate(IV) can be attained with a current efficiency of 99–100% for different media and it is independent of the pH of the generating solutions.[9] The standard potential of the octacyanomolybdate(V)–octacyanomolybdate(IV) system is +0.73 V *vs.* N.H.E.[11]

As an extension of our previous work, we describe here the coulometric–potentiometric determination of microquantities of ascorbic acid with electrogenerated octacyanomolybdate(V). To avoid photodecomposition of the octacyanomolybdate(V) the reaction is carried out in the absence of sunlight.

EXPERIMENTAL

Reagents

Potassium octacyanomolybdate(IV) dihydrate. Prepared and purified according to the method of Willard and Thielke.[12]

Ascorbic acid solutions. Approximately 0.1 and 0.05*M* solutions were prepared by dissolution of the solid in water that had been twice distilled in glass apparatus; 0.1 g of EDTA and 3.6 g of formic acid (40%) were added per litre as preservative. The solutions were standardized iodometrically with 0.1000*N* potassium iodate solution immediately before use.

Buffer solutions of pH 2–10. Prepared from analytical-grade reagents. The acetate buffers (pH 2–5) were prepared by dissolving 68 g of sodium acetate trihydrate in water and adding enough concentrated hydrochloric acid to give the required pH after dilution to 1 litre with water. The same general technique was used for the other buffers. The phosphate buffers (pH 6 and 7) and borate buffers (pH 8–10) were prepared from $NaH_2PO_4 \cdot 2H_2O$ (15.6 g/l.) and H_3BO_3 (3.05 g/l.) respectively and 0.3*M* potassium hydroxide. The pH-values were measured with a glass electrode.

All solutions used as supporting electrolytes were made 0.5*M* in potassium chloride.

Apparatus and procedure

The apparatus and procedure were the same as described previously for cerium.[9]

RESULTS AND DISCUSSION

Effect of pH

The results obtained at different pH-values show that the determination of ascorbic acid is not possible at a pH less than 2 because of the increase in redox potential of the dehydroascorbic–ascorbic acid system.[7]

In general, the coulometric determination is possible in the pH-range studied (pH 2–10) but pH 5 is optimal and there is then no interference from oxygen. Oxygen interference occurs in the alkaline pH-range, but even at pH 6 and 7 in phosphate buffer solutions the results were in error by up to +5.0% and were not reproducible.

In the pH-range studied, the readings of the potential were unstable until a small excess of octacyanomolybdate(V) was present. This is attributed to irreversibility of the dehydroascorbic–ascorbic acid system when measured at the platinum electrode. The octacyanomolybdate system is reversible, and so the instability disappears when this is the potential-determining system. However, this phenomenon does not affect the accuracy and precision of the

Table 1. Coulometric determination of ascorbic acid with electrogenerated octacyanomolybdate(V)

Taken, *μmole*	Found, *μmole*
0.260	0.260
0.284	0.284
0.578	0.577
0.601	0.600
1.092	1.093
1.103	1.103
2.18	2.18
2.24	2.24
3.89	3.90
3.94	3.94
4.64	4.65
5.68	5.68
5.84	5.84
6.06	6.06

Table 2. Comparison of established methods for the coulometric determination of ascorbic acid

Method	Reagent electrogenerated	Ascorbic acid, *μmole*	Error, %
Foresti[1]	Br_2 or I_2	5.7–34.1	±0.4
Kalinowski[2]	I_2	5.7	±0.3
Jedrzejewski[3]	I_2	0.002–0.03	±0.3
Kawamura[4]	Br_2	0.3–2.8	±4 to ±0.4
Santhanam[5]	—	85.2–625	±4.6 to −0.6
This paper	$Mo(CN)_8^{3-}$	0.2–4.0	±0.3
		⩾5.7	±0.2

results. Higher pH-values than 10 are not suitable, because of the partial oxidation of the dehydroascorbic acid formed and the partial decomposition of the octacyanomolybdate(V):

$$Mo(CN)_8^{3-} + 2OH^- = \tfrac{1}{2}O_2 + H_2O + Mo(CN)_8^{4-}$$

Effect of the concentration of dehydroascorbic acid

Since dehydroascorbic acid is present along with ascorbic acid in natural products and because of the interest in developing a method that would allow successive determinations of ascorbic acid in the same cell, it was necessary to determine the effect of the presence of the dehydroascorbic acid. It was found that 6 μmoles of ascorbic acid can be determined in the presence of 60 μmoles of dehydroascorbic acid in a total volume of 20 ml with an error of ±0.2%. This means that 10 analyses can be performed in succession with the same electrolyte in the cell, provided the sample volumes added do not exceed about 0.1 ml (to avoid excessive dilution). If 130 μmoles of dehydroascorbic acid are present, the error for 6 μmoles of ascorbic acid is increased to ±1% and the potential-reading after the end-point becomes unstable, indicating a side-reaction with dehydroascorbic acid.

Effect of temperature

The temperature should not exceed 20°. Higher temperatures facilitate the partial oxidation of dehydroascorbic acid by octacyanomolybdate(V), producing an error as high as +21% at 50°. In addition, such conditions undoubtedly bring about decomposition of the oxidant,[9] and the end-point potential readings are unstable.

Interferences

A 100-fold molar ratio of glucose, fructose, sucrose, malic, oxalic, citric, tartaric, succinic and dehydroascorbic acids does not interfere. Dehydroascorbic acid interferes when its concentration is greater than 0.003*M*.

Effect of the amount of ascorbic acid

Table 1 presents the results for determination of various concentrations of ascorbic acid. It shows that this method, under the optimum experimental conditions [pH 5, acetate buffer, temperature below 20°, octacyanomolybdate(IV) concentration $7.5 \times 10^{-3}M$, dehydroascorbic acid less than 60 μmoles] permits the determination of 0.25–5 μmoles of ascorbic acid with an error of ±0.3% and with an error less than ±0.2% for higher amounts. The relative standard deviation was ±0.2% for the range studied (20 variates).

The results obtained with this method are comparable with those obtained by use of the other coulometric methods (Table 2). Unfortunately, the reagent is expensive and difficult to obtain, which limits the importance and applicability of the method.

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DETERMINATION OF CALCIUM IN URINE BY MANUAL MICROTITRATION WITH EDTA

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Summary—A simple, direct method for the determination of total calcium in urine by manual microtitration with EDTA at pH 12, with Calcein as fluorescent indicator, is proposed. By use of urine sample volumes of only 0.01–0.05 ml, interference from phosphate and natural fluorescence is minimized. For strongly naturally fluorescing urines the addition of potassium dichromate provides effective quenching. Agreement between results obtained by the proposed method and by atomic-absorption spectroscopy for a series of urine samples was satisfactory.

Total calcium in serum and urine can be determined by atomic absorption,[1–3] or by spectrophotometry with *o*-cresolphthalein complexone.[4–6] Recently, several automatic titrators employing titration by EGTA to a fluorometric end-point have been introduced for estimation of total calcium in biological samples. For urinary calcium direct manual titration without preliminary treatment has been reported to be unsatisfactory,[8–11] although results reported by Raman and Chong[12] and by Kleinman[13] indicate that use of an automatic fluorometric titrator gives results agreeing with those from other methods. In this paper we describe a procedure for a direct manual EDTA microtitration that is useful where the determination of calcium in urine is done only occasionally, or where special instrumentation is not available. The procedure is rapid and simple and gives results that compare favourably with those obtained by atomic absorption.

EXPERIMENTAL

Reagents and solutions

All chemicals were of reagent grade quality and used as supplied. Distilled water was used throughout in preparing the solutions.

Standard EDTA solution. A 0.005*M* solution was made by dissolving 1.861 g of $Na_2H_2EDTA \cdot 2H_2O$ in water and diluting to 1 litre. A 5-ml portion of this stock solution was diluted to 100 ml with water to give a 0.00025*M* working solution.

Standard calcium solution. Prepared by dissolving 2.497 g of calcium carbonate in 60 ml of 1*M* hydrochloric acid and diluting to 1 litre with water. This solution was then diluted by a factor of 100 to give a working solution containing 10 μg of calcium per ml.

Calcein indicator solution. Approximately 20 mg of Calcein was dissolved in 25 ml of water and the minimum amount of 0.1*M* potassium hydroxide, then diluted to 1 litre with water. This solution was found to deteriorate rapidly unless kept frozen and protected from light. It was convenient to freeze the solution in small sample bottles, each containing sufficient reagent for one day's use.

Potassium hydroxide–potassium cyanide solution. Approximately 1 g of potassium cyanide and 5.6 g of potassium hydroxide pellets were dissolved in 100 ml of water to give a solution 0.15*M* in potassium cyanide and 1*M* in potassium hydroxide.

Solutions for studies of interferences. Solutions of the compounds to be tested were prepared at the concentrations listed in column 2 of Table 1. Also, a simulated urine solution was prepared by dissolution of 4 g of sodium chloride, 8 g of urea, 0.168 g of magnesium chloride hexahydrate, 0.01 g of sodium oxalate, 0.100 g of citric acid and 5 mg of albumin in water to give a final volume of 1 litre. These solutions contained the components of interest at concentrations of about one tenth of those normally found in urine. The amounts actually present in the 1-ml aliquot taken for the titrations were higher than those generally found in the normal urine analyses, because real urine samples were diluted by a factor of at least 20 before an aliquot was taken for titration.

Procedures

Titrations were performed at a micro level because of greater convenience and reduced phosphate interference. The procedure can be carried out rapidly and without loss of accuracy by a weight-titration technique[14,15] using a 5-ml syringe with a 20-gauge stainless-steel needle as the burette.[16] The plunger was lightly lubricated with silicone grease to prevent loss of solution and to provide positive plunger action. All titration end-points were observed under ultraviolet radiation from a Chromatovue light enclosure (Ultraviolet Light Products Inc.), although any ultraviolet lamp providing excitation at 220 or 300 nm can be used.[17]

For the study of interferences the procedure used was as follows. To a small beaker or vial was added 1 ml of potassium hydroxide–potassium cyanide solution, 1 ml of working calcium standard solution, 1 ml of water (or the solution to be tested for interference) and 4 drops of Calcein indicator solution. A small magnetic-stirrer bar was added and the vessel placed on a magnetic stirrer inside the ultraviolet-light enclosure. The syringe, filled with titrant, was weighed on a top-loading balance to the nearest milligram. The EDTA solution was then added dropwise from the syringe to the titration vessel until the bright green fluorescence disappeared. The syringe was reweighed and the weight of titrant used was found by difference. Blank titrations were carried out in the same way but with omission of the calcium solution.

Determination of calcium in urine. Dilute a 5-ml portion of a fresh urine sample to 100 ml with distilled water and mix. In a 10-ml beaker place 1 ml of potassium cyanide–potassium hydroxide solution, 1 ml of distilled water, a 1.00-ml aliquot of the diluted urine sample and 4 drops of Calcein solution. Add a small stirrer-bar and titrate with 0.00025*M* EDTA under ultraviolet radiation until the green fluorescence disappears. If the end-point is interfered with by natural fluorescence in the sample, or if, near the equivalence point, the fluorescence of the indicator tends to disappear on addition of an increment of EDTA but then returns after a time owing to phosphate interference, repeat the titration on a smaller aliquot (0.5 or 0.25 ml). If natural fluorescence continues to block observation of the end-point, quench the interference by addition of 2–4 drops of 0.1% potassium dichromate solution

Table 1. Effects of selected constituents of urine on the EDTA titration of calcium

Compound tested for interference	Concentration, *g/l.**	Recovery of Ca, %†
Sodium chloride	4.0 (NaCl)	101.4
Urea	8.0 [$CO(NH_2)_2$]	101 1
Magnesium chloride	0.02 (Mg)	97.4
„ „	0.01 (Mg)	98.5
Sodium oxalate	0.008 ($C_2O_4^{2-}$)	99.2
Citric acid	0.1 ($C_6H_8O_7$)	100.2
Albumin (egg)	0.005 (albumin)	100.8
Disodium hydrogen orthophosphate	0.2 (P)	93§
„ „	0.07 (P)	97.1§
Simulated urine solution	contained all the above except phosphate	99.3

* The species to which the concentration refers is shown in brackets. A 1-ml portion of solution was used for each titration.
† Each result is the average of 5 titrations of 10 μg of calcium.
§ Poor end-point.

RESULTS AND DISCUSSION

Results for ten titrations of 10.0 μg of calcium gave a relative standard deviation of 0.9%. After subtraction of the blank value, an average of 10.0 μg of calcium, based on EDTA as standard, was found. Thus the accuracy and precision of the method at the microgram level appear satisfactory.

In a study of possible interferences the major constituents of normal urine[18] were tested individually and the results compared with those obtained for calcium in the absence of these substances (Table 1). It can be seen that sodium chloride, urea, oxalate, citric acid and albumin cause less than 2% error when present at concentrations typically found in urine. Magnesium causes results for calcium to be about 2.5% low at magnesium concentrations equivalent to high (but not abnormal) values for urine. The interference is probably the result of co-precipitation of some $Ca(OH)_2$ along with $Mg(OH)_2$ under the highly alkaline conditions of the titration. This same concentration of magnesium in the simulated urine solution, however, gave a reduction in the calcium value of less than 1%. The diminished error may be due partly to compensation of positive and negative interference effects, or possibly to partial complexation of the magnesium with oxalate and citrate.

Phosphate was found to interfere more seriously. Calcium recoveries were low by 3–7% and a "creeping" end-point was observed. This interference is the result of the presence of undissociated calcium phosphate or calcium hydroxyphosphate (apatite). On addition of each increment of EDTA in the region just before the equivalence point, calcium ions are removed from the calcium–Calcein complex and the fluorescence disappears. Upon standing, calcium ions are released to the solution by the slow dissolution of insoluble calcium phosphate species, and the calcium level increases to a point where sufficient calcium–Calcein complex is formed to cause a return of the fluorescence. It has been reported that a back-titration will eliminate this interference.[19] The recommended back-titration procedure was tested by addition of a known excess of EDTA to a solution containing calcium and phosphate, followed by back-titration with standard calcium solution. An unsatisfactory end-point was obtained for artificial urine solutions, however. It has also been reported that addition of citrate overcomes the interference from phosphate when Cal-red is used as indicator,[20] presumably because citrate forms a soluble complex with calcium that prevents formation of insoluble calcium phosphate. Addition of 10 mg of sodium citrate to the titration solution eliminated the creeping end-point caused by phosphate; however, the end-point was less sharp under these conditions and could not be determined with precision. The best method of minimizing the effects of phosphate is by use of smaller sample sizes to reduce the levels of calcium and phosphate to the point where the amount of insoluble calcium phosphate or calcium hydroxyphosphate formed is slight.

Real urine samples often possess a blue fluorescence under ultraviolet light, that causes difficulty in locating the end-point. This fluorescence was observed in samples from

Table 2. Analysis of urine samples by titration with EDTA and comparison with atomic-absorption analysis

Sample No.	Sample size, *ml*	Calcium concentration, *mg/100 ml* EDTA titration	Atomic absorption*
1	0.05	7.6	6.8
2	0.025	14	12
3	0.0125	21	18
4	0.0125	27	25
5	0.0125	29	23
6	0.05	2.7	3.1
7	0.05	2.6	2.0

* Results reported by University of Alberta Hospital clinical laboratory.

both normal individuals and hospital patients. Attempts to remove the fluorescing material by adsorption on a styrene–divinylbenzene copolymer macroreticular resin (XAD-2, Rohm and Haas) resulted in reduction of the fluorescence by only about half. It was found that addition of potassium dichromate eliminated the blue fluorescence, probably by a quenching mechanism rather than by oxidation, since reduction of the dichromate by addition of hydrogen peroxide resulted in a return of the fluorescence. Dichromate does not interfere with the EDTA titration or the functioning of the Calcein indicator and so can be used to block the natural fluorescence.

Use of small samples also reduces natural fluorescence to a point where the addition of potassium dichromate is not necessary. It was found that satisfactory end-points could be obtained when the weight of titrant was reduced to 0.5 g of 0.00025*M* EDTA or less by appropriate selection of sample size.

The procedure outlined above was applied to urine samples obtained from the University of Alberta Hospital and the concentration of total calcium in each sample was calculated. Corrections for a blank titration were applied. Results for single titrations of seven different samples are given in Table 2. Also, ten titrations were carried out on sample 3; a value of 21 mg Ca per 100 ml, with a relative standard deviation of 4.1%, was obtained. Results of analyses of these samples for calcium by atomic-absorption spectroscopy, carried out by the University of Alberta Hospital clinical laboratory, are included in the table for comparison. Reasonable agreement between the two methods was obtained for most samples. That the results by titration were somewhat higher than those by atomic absorption may be due in part to phosphate interference in the atomic-absorption method, as atomic-absorption results for calcium also tend to be generally lower than colorimetric values.

If desired, ethylene glycol bis(2-aminoethyl ether)-*N*,*N*,*N*′,*N*′-tetra-acetic acid (EGTA) can be used in place of EDTA as titrant, but the only apparent advantage is a slightly larger formation constant with calcium (log $K = 11.0$ compared with log $K = 10.7$ for calcium–EDTA). Since magnesium is essentially completely precipitated as magnesium hydroxide at pH 12, little interference from this element is encountered. By titration at a lower pH with EGTA the problem of magnesium interference, either by complexation with the titrant or by co-precipitation of calcium hydroxide with magnesium hydroxide, might be avoided, but unfortunately both Calcein and the Calcein–calcium complex fluoresce at pH values below 12, and no end-point is observed.

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2,2′-DIAMINODIPHENYLDISULPHIDE—A NEW SENSITIVE SPECTROPHOTOMETRIC REAGENT FOR PLATINUM

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Summary—2,2′-Diaminodiphenyldisulphide is a highly sensitive platinum chromogen. Platinum(IV) forms a complex with it in 50% aqueous ethanol at pH 5.0–6.0, having maximum absorption at 725 nm. The molar absorptivity of the complex is 5.48×10^4 l.mole^{-1}.cm^{-1} at 725 nm and the sensitivity is 0.0035 μg/cm^2. The colour system obeys Beer's law from 0.25 to 5 ppm with optimum concentration range 0.75–4 ppm of platinum. The relative error is 2.7%. The metal to reagent ratio is 1:2, and the stepwise formation constants K_1 and K_2 are 5.6×10^4 and 1.96×10^4 respectively.

both normal individuals and hospital patients. Attempts to remove the fluorescing material by adsorption on a styrene–divinylbenzene copolymer macroreticular resin (XAD-2, Rohm and Haas) resulted in reduction of the fluorescence by only about half. It was found that addition of potassium dichromate eliminated the blue fluorescence, probably by a quenching mechanism rather than by oxidation, since reduction of the dichromate by addition of hydrogen peroxide resulted in a return of the fluorescence. Dichromate does not interfere with the EDTA titration or the functioning of the Calcein indicator and so can be used to block the natural fluorescence.

Use of small samples also reduces natural fluorescence to a point where the addition of potassium dichromate is not necessary. It was found that satisfactory end-points could be obtained when the weight of titrant was reduced to 0.5 g of 0.00025*M* EDTA or less by appropriate selection of sample size.

The procedure outlined above was applied to urine samples obtained from the University of Alberta Hospital and the concentration of total calcium in each sample was calculated. Corrections for a blank titration were applied. Results for single titrations of seven different samples are given in Table 2. Also, ten titrations were carried out on sample 3; a value of 21 mg Ca per 100 ml, with a relative standard deviation of 4.1%, was obtained. Results of analyses of these samples for calcium by atomic-absorption spectroscopy, carried out by the University of Alberta Hospital clinical laboratory, are included in the table for comparison. Reasonable agreement between the two methods was obtained for most samples. That the results by titration were somewhat higher than those by atomic absorption may be due in part to phosphate interference in the atomic-absorption method, as atomic-absorption results for calcium also tend to be generally lower than colorimetric values.

If desired, ethylene glycol bis(2-aminoethyl ether)-*N*,*N*,*N*′,*N*′-tetra-acetic acid (EGTA) can be used in place of EDTA as titrant, but the only apparent advantage is a slightly larger formation constant with calcium (log $K = 11.0$ compared with log $K = 10.7$ for calcium–EDTA). Since magnesium is essentially completely precipitated as magnesium hydroxide at pH 12, little interference from this element is encountered. By titration at a lower pH with EGTA the problem of magnesium interference, either by complexation with the titrant or by co-precipitation of calcium hydroxide with magnesium hydroxide, might be avoided, but unfortunately both Calcein and the Calcein–calcium complex fluoresce at pH values below 12, and no end-point is observed.

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2,2′-DIAMINODIPHENYLDISULPHIDE—A NEW SENSITIVE SPECTROPHOTOMETRIC REAGENT FOR PLATINUM

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Summary—2,2′-Diaminodiphenyldisulphide is a highly sensitive platinum chromogen. Platinum(IV) forms a complex with it in 50% aqueous ethanol at pH 5.0–6.0, having maximum absorption at 725 nm. The molar absorptivity of the complex is 5.48×10^4 l.mole^{-1}.cm^{-1} at 725 nm and the sensitivity is 0.0035 μg/cm^2. The colour system obeys Beer's law from 0.25 to 5 ppm with optimum concentration range 0.75–4 ppm of platinum. The relative error is 2.7%. The metal to reagent ratio is 1:2, and the stepwise formation constants K_1 and K_2 are 5.6×10^4 and 1.96×10^4 respectively.

Many organic compounds employed for the colorimetric determination of platinum have been critically reviewed by Beamish.[1,2] Those with outstanding sensitivity are *p*-nitrosodimethylamine[3] ($\epsilon = 6.68 \times 10^4$ l.mole^{-1}.cm^{-1} at 525 nm) and *o*-phenylenediamine[4] ($\epsilon = 6.50 \times 10^4$ at 450 nm). However, these suffer from interference from associated base and platinum metals. The hexa-ammino platinum(IV) cation gives a red ion-association complex with 2,4,5,7-tetrabromofluoroescein ethyl ester[5] at pH 10 which can be used for the determination of platinum ($\epsilon = 8 \times 10^4$ at 555 nm); rhodium(III) and iron interfere seriously. Recently there has been a trend to employ sulphur-containing ligands for the determination of platinum, as these can form biologically active complexes of great stability. Amongst the thio-ligands, 1,4-diphenylthiosemicarbazide[6] ($\epsilon = 2.8 \times 10^4$ at 750 nm) and 2-mercaptobenzothiazole[7] ($\epsilon = 1.65 \times 10^4$ at 300 nm) are the most sensitive. The stability constants (stepwise and overall) are rarely quoted, but are all the more necessary on account of the recent interest in biological activity.

The present paper describes a highly sensitive and selective method of determination of platinum(IV) with 2,2′-diaminodiphenyldisulphide.

EXPERIMENTAL

Reagents

2,2′-Diaminodiphenyldisulphide. Air was passed through a solution of *o*-aminothiophenol in 60% aqueous ethanol containing a few drops of hydrogen peroxide.[8] The precipitate was filtered off and recrystallized from rectified spirit. A 0.5% w/v ethanol solution of the reagent was used for the study of the complex.

Standard platinum(IV) solution. Platinum wire was dissolved in *aqua regia* containing an excess of concentrated hydrochloric acid,[9] and diluted to the required concentrations with twice-distilled water. Other chemicals used in the spectrophotometric work were of the best available quality.

Standard procedure

An aliquot of platinum(IV) solution (0.25–5 ppm) was placed in a beaker and 4 ml of 0.5% reagent solution were added to it. Water and ethanol were added so as to make the solution 50% v/v ethanol. The pH of the solution was kept at about 5.5 by addition of very dilute hydrochloric acid. The solution was warmed for 10 min on a water-bath, then cooled and transferred into a 25-ml flask. The volume was made up to the mark. A reagent blank was prepared identically, except that the Pt(IV) solution was not added. Absorbances were measured at 725 nm against 50% aqueous ethanol.

RESULTS AND DISCUSSION

Sensitivity

The absorption spectrum of the platinum complex (Pt = 2 ppm) formed at pH 5.5, measured against a solvent blank in the wavelength region 660–765 nm showed maximum absorption at 725 nm.

Full colour development took place between pH 5.0 and 6.0. For 50 μg of platinum(IV) in 25 ml of solution, 3.0 ml of reagent solution (0.5%) proved sufficient. Addition of more reagent (up to 6.0 ml) had no effect on the absorbance. The colour was stable for more than 2 hr.

Beer's law was obeyed over the range 0.25–5 ppm of platinum(IV). Ringbom[10] curves revealed that the optimum concentration range was 0.75–4 ppm. The relative error per 1% absolute photometric error, as defined by Ayres[11], was 2.7%.

The sensitivity by Sandell's definition[12] is 0.0035 μg/cm^2. The molar absorptivity of the complex at 725 nm is 5.48×10^4 l.mole^{-1}.cm^{-1}.

Effect of diverse ions

For the study of the tolerance limits for diverse ions, 2-ppm solutions of platinum(IV) were prepared with varying concentrations of other ions. A large excess (400 ppm each) of the following ions–calcium, lithium, aluminium, strontium, barium, magnesium, zinc, lead, cadmium, copper(II), nickel, manganese(II), iron(III), chromium(VI), tungsten(VI), rare earths, nitrate, borate, chloride—had no effect. Iridium(IV), rhodium(III), ruthenium(III), vanadium(V), palladium(II), osmium(VI) and molybdenum(VI) in concentrations 10–50 times that of the platinum do not interfere.

Composition and stability constants of the complex

The modified Job method[13,14] and molar ratio method[15] showed that platinum(IV) combines with the reagent in a metal to reagent ratio of 1:2.

Yatsimirskii's method[16] of graphical extrapolation was used to evaluate the stepwise formation constants of the platinum(IV) diaminodiphenyldisulphide complex, and gave $K_1 = 5.64 \times 10^4$, $K_2 = 1.96 \times 10^4$. The Harvey and Manning method[17] gave a smaller value for β_2, namely 3.94×10^8.

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EVOLUTION DES SOLUTIONS AQUEUSES DE NIOBATES ALCALINS: EXISTENCE DE HAUTS POLYMERES

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(*Reçu le* 21 *mai* 1976. *Accepté le* 23 *août* 1976)

Résumé—Les auteurs attribuent à l'existence de polymères de masse molaire élevée la diminution de la réactivité et l'apparition de louche dans des solutions vieillies de niobates alcalins. L'ultracentrifugation et la perméation sur gel permettent de fixer l'ordre de grandeur (10^4 et $6 \cdot 10^4$) des masses de ces particules, ainsi que leur proportion (5%). Une explication à partir de l'édification structurale de ces ions est fournie pour expliquer cette évolution exceptionnelle des solutions.

Les conclusions de nombreux travaux sur la chimie des isopolyanions des éléments de transition de la 5e et 6e colonne du tableau périodique sont souvent contradictoires; au-delà du choix de la technique expérimentale (voir l'étude critique récente de Tytko et Schönfeld,[1] une des causes essentielles de ces divergences est la mauvaise définition de l'objet de l'analyse, c'est-à-dire la solution.

On se contente en général d'indiquer le mode de préparation de la solution (concentration, présence et concentration du sel de fond, nature du soluté, température) et d'indiquer comment est menée l'expérience (normalité du réactif et son mode d'addition, quelquefois temps de la réaction). Un facteur est en général négligé: l'âge de la solution.

Dans les travaux que nous avons effectués sur les solutions aqueuses de niobates alcalins,[2,3] nous notions que ces études étaient effectuées sur des solutions dont l'équilibre était suivi et minitieusement vérifié: le pH de la solution est stable après 5 à 30 mn d'agitation suivant la zone de pH et la nature du niobate. L'ensemble des mesures est alors reproductible. Nous précisions toutefois qu'il ne fallait pas laisser vieillir les solutions stock concentrées au-delà de quelques semaines. Un léger louche apparaît. De plus, nous observions une diminution de la réactivité de telles solutions. Ces observations nous ont fait rechercher les causes de ces phénomènes.

RESULTATS ET DISCUSSION

Le vieillissement de diverses solutions de niobates $K_8Nb_6O_{19} \cdot 16H_2O$; $K_7HNb_6O_{19} \cdot 12H_2O$ et $K_6H_2Nb_6O_{19} \cdot 11H_2O$ pour une même concentration est sensiblement le même. La densité optique croît avec le temps (fig. 1). Simultanément le pH décroît de l'ordre d'une unité pH pour de telles solutions, à la concentration $M/600$.

Ces évolutions sont par contre plus importantes dans le cas de solutions du niobate double $K_{15}H(Nb_6O_{19})_2 \cdot 24H_2O$. De plus, elles croissent avec la concentration en Nb des solutions.

Ces évolutions ne peuvent s'interpréter que par le lent déplacement d'un équilibre entre deux principales espèces: l'une possède un coefficient d'absorption plus important, donc une masse molaire différente. Cette conclusion suggère donc que dès la mise en solution des sels, deux espèces coexistent: l'une formée d'espèce dénommée Nb_x de masse molaire importante, de faible proportion devant l'autre espèce formée des isopolyanions $H_yNb_6O_{19}^{(8-y)}$—(où $y = 0, 1, 2, 3$) existant en solution dans le domaine de pH 14–9.

L'ultracentrifugation de telles solutions confirme l'existence d'une proportion plus importante d'espèces Nb_x pour des solutions vieillies, plus spécialement dans celles du niobate $K_{15}H(Nb_6O_{19})_2 \cdot 24H_2O$ (fig. 2). La présence de sel de fond (KCl) favorise toujours la séparation de deux polyélectrolytes: au cours de la centrifugation, les entités de signes opposés migrent différemment en raison de leur différence de masse, ce qui introduit une différence de potentiel ralentissant la migration de l'ion le plus lourd, effet annulé par l'addition d'un sel neutre en quantité suffisante.

Le spectre d'absorption d'une solution ultracentrifugée laissée au repos tend à reprendre son allure initiale en 70 h environ. Le temps est plus long si l'on suit l'évolution de la densité optique de la seule solution surnageante (environ 8 jours).

Par conséquent, le déplacement de l'équilibre entre ces deux espèces polyniobiques, créé par ultracentrifugation,

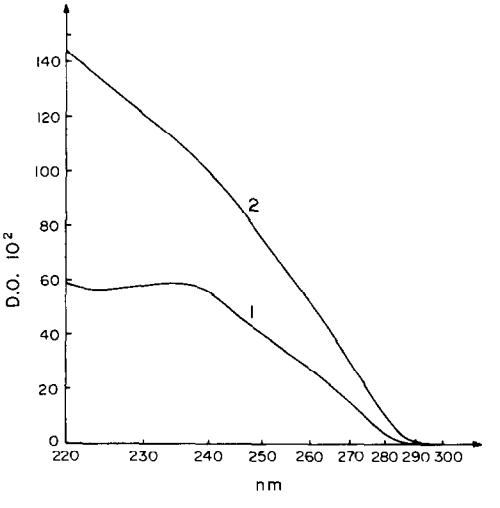

Fig. 1. Spectres U.V. de solutions $M/2000$ de niobate $K_7HNb_6O_{19} \cdot 12H_2O$ fraîchement préparée (courbe 1) et âgée de 16 mois (courbe 2) (cellule de 1 mm).

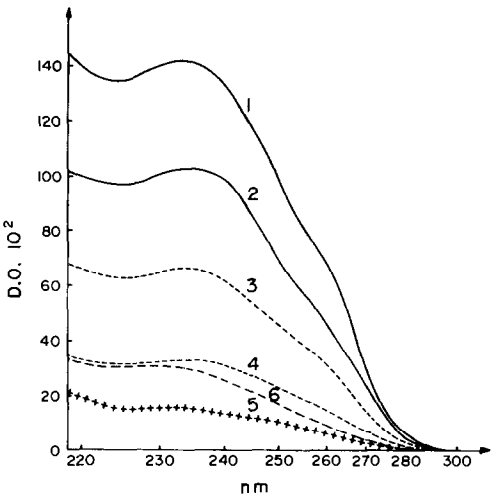

Fig. 2. Spectres U.V. de solutions $M/300$ de niobate $K_7HNb_6O_{19}\cdot 12H_2O$ fraîchement préparée (courbe 1), âgée de 3 mois (courbe 2), de 5 mois (courbe 3), de 5 mois dans KCl 1M (courbe 4), de 2 ans dans KCl 1M (courbe 5). Spectre U.V. de solutions $M/300$ de $K_{15}H(Nb_6O_{19})_2\cdot 24H_2O$ âgée de 5 mois (courbe 6). Toutes les solutions ont été ultracentrifugées à 39000 tours/minute pendant 20 heures.

tend à disparaître rapidement pour revenir à l'équilibre initial dépendant de la concentration en niobium et qui évolue lentement avec le temps.

Un tel déplacement peut aussi être obtenu par perméation sur gel: le volume d'élution d'une espèce déterminée est inversement proportionnel à la grosseur des molécules et donc à leur masse. Sur la figure 3 sont reproduites les variations d'absorption, à la longueur d'onde 232 nm de fractions de 3 ml d'une solution fraichement préparée de niobate $K_7HNb_6O_{19}\cdot 12H_2O$ et $K_{15}H(Nb_6O_{19})_2\cdot 24H_2O$ ayant traversé un gel de limite d'exclusion 10^4. Une limite d'exclusion plus faible (5×10^3) déplace ces courbes vers des volumes d'éluant plus faibles, du moins pour la zone relative à l'existence des seules espèces Nb_x. La comparaison de ces valeurs avec les résultats trouvés à partir d'un gel de limite d'exclusion supérieure (6×10^4) nous donne l'ordre de grandeur (10^4) de la masse des particules Nb_x présentes dans des solutions récentes de niobates alcalins (proportion 5%).

Si la concentration augmente notablement et si l'élution est effectuée sur des solutions ayant vieilli 5 mois, la masse croît jusqu'à $5\text{–}6\times 10^4$ environ, comme le montre la courbe 4 de la figure 3 provenant d'une élution à travers un gel de limite d'exclusion 6×10^4.

La présence de polymères de degré de condensation élevée semble due à la manière dont se protonnent les ions $Nb_6O_{19}^{8-}$: d'après une de nos études sur les spectres

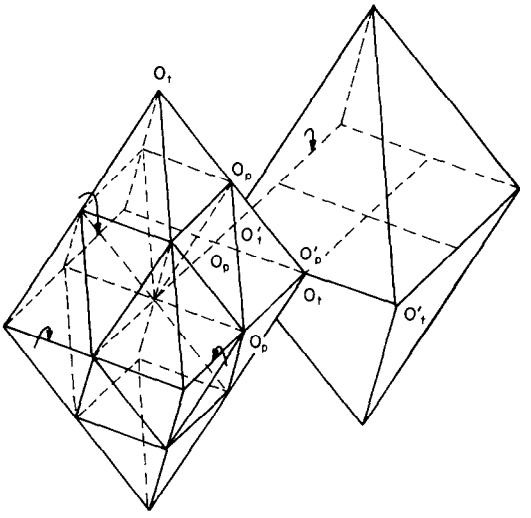

Fig. 4. Formation de polymères par mise en commun d'arêtes d'entités Nb_6O_{19}. O_t: atome d'oxygène terminal. O_p: atome d'oxygène ponté.

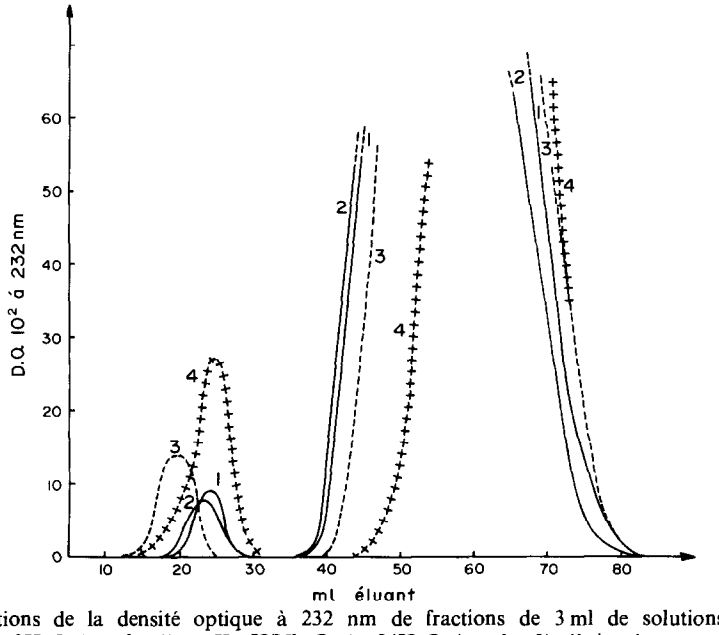

Fig. 3. Variations de la densité optique à 232 nm de fractions de 3 ml de solutions $M/80$ de $K_7HNb_6O_{19}\cdot 12H_2O$ (courbe 1) et $K_{15}H(Nb_6O_{19})_2\cdot 24H_2O$ (courbe 2), éluées à travers un gel de limite d'exclusion 10000 et de limite d'exclusion 5000 (courbe 3); la courbe 4 provient d'une solution $M/30$ de $K_7HNb_6O_{19}\cdot 12H_2O$ âgée de 5 mois ayant éluée à travers un gel de limite d'exclusion 60000.

Raman des solutions niobiques[4] et les conclusions de Müller,[5] la protonation s'effectue sur un oxygène terminal pour le niobate $Na_7HNb_6O_{19}\cdot 15H_2O$ et en position pontée pour les niobates $Na_6H_2Nb_6O_{19}\cdot 14H_2O$ et $Na_5H_3Nb_6O_{19}\cdot 13H_2O$ (fig. 4). L'addition d'une nouvelle entité Nb_6O_{19} protonnée s'effectue par la mise en commun d'une arête (et élimination de deux molécules d'eau) avec l'entité Nb_6O_{19} protonnée de base. Cette réaction d'addition est lente, ce qui explique l'évolution des solutions pendant plusieurs mois. La formation de polymères est plus importante dans les solutions du sel double $K_{15}H(Nb_6O_{19})_2\cdot 24H_2O$; en effet, sa structure implique l'existence d'une liaison hydrogène entre deux entités Nb_6O_{19}:[6] d'autres entités semblables peuvent s'adjoindre plus facilement que dans le cas précédent.

Ces observations corroborent celles que faisaient Guerchais[7] ou l'un d'entre nous:[2] la mise en solution de ce sel provoque initialement la formation d'un louche soyeux qui disparaît rapidement si le sel est fraichement préparé, plus difficilement (un chauffage est nécessaire) si le sel a vieilli ou si la solution n'est pas agitée immédiatement.

Conclusion

La proportion de ces espèces hautement polymérisées est faible dans les solutions de niobates alcalins. D'après des premières observations il semble qu'elle soit bien plus importante dans les solutions de niobates de tétralkylammonium récemment isolés:[8,9] la détermination précise de la masse molaire par ultracentrifugation, méthode Schlieren sera effectuée sur ces solutions.

L'existence de ces espèces permet enfin de comprendre pourquoi les recherches de la masse molaire par ultracentrifugation et par spectroscopie UV des espèces hexaniobiques conduisaient à des résultats dispersés.

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Summary—The authors attribute to the existence of high polymers the decrease in reactivity and the appearance of cloudiness in aged alkaline niobate solutions. Gel permeation and ultracentrifugation can be used to determine the order of magnitude (10^4 and 6×10^4) of the molecular weight of these particles and their proportion (5%). The structure of these ions is used to explain this exceptional behaviour of the solutions.

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MATRIX PROBLEMS IN THE DETERMINATION OF LITHIUM BY FLAMELESS (HGA) ATOMIC-ABSORPTION SPECTROMETRY, AND THEIR SOLUTION

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Summary—Flameless atomic-absorption analyses for Li in geological materials (limestones, carbonate-bearing cherts, calcium containing subsurface brines and sweet waters) result in low values, which may amount to less than 10% of the real lithium concentration in the sample. The observed signal decrease is caused by the reaction between gaseous Li and Cl and the consequent formation of LiCl (b.p. = 1325–1360°). The Cl vapour is produced by the dissociation of $CaCl_2$ molecules in the graphite-tube cavity. The interfering capacity of $CaCl_2$ is marked because of its survival in the graphite tube at temperatures above the boiling points of both LiCl and Li metal (= 1317°). Hydrochloric acid represses the Li signal in a similar manner but to a lesser extent because most of it is removed during the pre-atomizing drying and ashing stages. The addition of Ca^{2+} to the analytical solution lowers the absorption signal only if chloride is present. This interference of Cl has been completely overcome by addition of sulphuric acid in moderate excess relative to the quantity of chloride present. The release from interference is in strict accord with the stoichiometry of the reaction: $H_2SO_4 + CaCl_2 \rightarrow 2HCl + CaSO_4$. The same remedy overcomes Cl interference introduced by the presence of hydrochloric acid in the analytical solution. The addition of sulphuric acid itself has no effect on the intensity of the atomic-absorption signal of lithium. An analogous reaction with phosphoric acid takes place, but the Li signal is weaker and less reproducible. Solutions in which the Na/Li ratio exceeds 3×10^4 cannot be analysed for Li by the method described since a molecular sodium peak is superimposed on the major Li peak.

Raman des solutions niobiques[4] et les conclusions de Müller,[5] la protonation s'effectue sur un oxygène terminal pour le niobate $Na_7HNb_6O_{19}\cdot 15H_2O$ et en position pontée pour les niobates $Na_6H_2Nb_6O_{19}\cdot 14H_2O$ et $Na_5H_3Nb_6O_{19}\cdot 13H_2O$ (fig. 4). L'addition d'une nouvelle entité Nb_6O_{19} protonnée s'effectue par la mise en commun d'une arête (et élimination de deux molécules d'eau) avec l'entité Nb_6O_{19} protonnée de base. Cette réaction d'addition est lente, ce qui explique l'évolution des solutions pendant plusieurs mois. La formation de polymères est plus importante dans les solutions du sel double $K_{15}H(Nb_6O_{19})_2\cdot 24H_2O$; en effet, sa structure implique l'existence d'une liaison hydrogène entre deux entités Nb_6O_{19}:[6] d'autres entités semblables peuvent s'adjoindre plus facilement que dans le cas précédent.

Ces observations corroborent celles que faisaient Guerchais[7] ou l'un d'entre nous:[2] la mise en solution de ce sel provoque initialement la formation d'un louche soyeux qui disparaît rapidement si le sel est fraichement préparé, plus difficilement (un chauffage est nécessaire) si le sel a vieilli ou si la solution n'est pas agitée immédiatement.

Conclusion

La proportion de ces espèces hautement polymérisées est faible dans les solutions de niobates alcalins. D'après des premières observations il semble qu'elle soit bien plus importante dans les solutions de niobates de tétralkylammonium récemment isolés:[8,9] la détermination précise de la masse molaire par ultracentrifugation, méthode Schlieren sera effectuée sur ces solutions.

L'existence de ces espèces permet enfin de comprendre pourquoi les recherches de la masse molaire par ultracentrifugation et par spectroscopie UV des espèces hexaniobiques conduisaient à des résultats dispersés.

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Summary—The authors attribute to the existence of high polymers the decrease in reactivity and the appearance of cloudiness in aged alkaline niobate solutions. Gel permeation and ultracentrifugation can be used to determine the order of magnitude (10^4 and 6×10^4) of the molecular weight of these particles and their proportion (5%). The structure of these ions is used to explain this exceptional behaviour of the solutions.

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MATRIX PROBLEMS IN THE DETERMINATION OF LITHIUM BY FLAMELESS (HGA) ATOMIC-ABSORPTION SPECTROMETRY, AND THEIR SOLUTION

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Summary—Flameless atomic-absorption analyses for Li in geological materials (limestones, carbonate-bearing cherts, calcium containing subsurface brines and sweet waters) result in low values, which may amount to less than 10% of the real lithium concentration in the sample. The observed signal decrease is caused by the reaction between gaseous Li and Cl and the consequent formation of LiCl (b.p. = 1325–1360°). The Cl vapour is produced by the dissociation of $CaCl_2$ molecules in the graphite-tube cavity. The interfering capacity of $CaCl_2$ is marked because of its survival in the graphite tube at temperatures above the boiling points of both LiCl and Li metal (= 1317°). Hydrochloric acid represses the Li signal in a similar manner but to a lesser extent because most of it is removed during the pre-atomizing drying and ashing stages. The addition of Ca^{2+} to the analytical solution lowers the absorption signal only if chloride is present. This interference of Cl has been completely overcome by addition of sulphuric acid in moderate excess relative to the quantity of chloride present. The release from interference is in strict accord with the stoichiometry of the reaction: $H_2SO_4 + CaCl_2 \rightarrow 2HCl + CaSO_4$. The same remedy overcomes Cl interference introduced by the presence of hydrochloric acid in the analytical solution. The addition of sulphuric acid itself has no effect on the intensity of the atomic-absorption signal of lithium. An analogous reaction with phosphoric acid takes place, but the Li signal is weaker and less reproducible. Solutions in which the Na/Li ratio exceeds 3×10^4 cannot be analysed for Li by the method described since a molecular sodium peak is superimposed on the major Li peak.

The importance of lithium has steadily increased since its first discovery in 1817. Its classical and modern applications, as well as its geological occurrence, geochemical behaviour, prospecting and source materials, have been described and discussed by several workers.[1–6]

Although Li can easily be determined by other analytical methods, especially by flame emission photometry, its determination by flameless atomic-absorption spectrophotometry is at least as sensitive and accurate. The concentration levels of Li in inorganic natural materials (rocks and waters) vary greatly. Flame atomic-absorption spectrophotometry is normally sufficient for analysis of silicate rocks and brines for Li, but provides insufficient sensitivity for analysis of materials lower in Li, such as most sweet waters and certain sedimentary rock types (carbonates, cherts), for which the higher sensitivity of flameless atomic-absorption spectrometry is needed.

Our preliminary attempts to determine Li in such materials by flameless atomic-absorption spectrometry revealed a very substantial signal depression when *both* calcium and chloride ions were present in the analytical solution. The purpose of this study is to explain the nature of this interference and to delineate a way to remove it.

The physical constants of the chemical compounds used in the following discussion were taken from Weast.[7]

EXPERIMENTAL

Apparatus

The equipment used consists of a Perkin–Elmer model 403 atomic-absorption spectrophotometer, connected to a heated graphite atomizer, model HGA-72. The signal was fed into a model 56 potentiometric recorder. The original optics of the spectrophotometer were modified after Kerber *et al.*,[8] resulting in a significant improvement in the signal-to-background ratio. The spectrophotometer settings were as follows.

Wavelength: 670.8 nm.
Slit setting: 3 (= 0.4 nm spectral band-width).
Light source: Perkin–Elmer "Intensitron" Li hollow-cathode lamp, current 20 mA.
Scale expansion: 1A.
Recorder response-time setting: 1.
Signal output mode: absorbance.

The following programme for the HGA-72 was found by experiment to provide the optimal analytical conditions.

First drying stage: 1 min at 82° (digital setting = 030).
Second drying stage: 5 sec at 140° (digital setting = 045).
Heat-up stage: "Rate" was set to 7, so as to increase the temperature from 140° to 800° (digital setting = 169) within approximately 30 sec.
Ashing stage: 15 sec at 800°.
Atomizing stage: 12 sec at approximately 2660° (digital setting = 999).
Purge gas: argon (left to flow continuously through the graphite furnace).

Procedure

Stock solutions (1*N*) were prepared from the following analytical-grade reagents: H_2SO_4, HCl, $CaCO_3$ (dissolved in a minimal volume of hydrochloric acid before dilution to volume with water), H_3PO_4 and $Ca(NO_3)_2 \cdot 4H_2O$. A solution contaning 2.50×10^4 ppm sodium was prepared by dissolving sodium chloride in water. A stock solution containing 100 ppm lithium was prepared by dissolving Li_2CO_3 in a minimal amount of hydrochloric acid and diluting to volume.

All solutions were prepared in 50-ml Pyrex volumetric flasks and transferred, immediately after preparation, into 50-ml double-seal plastic bottles. Seven sets of solutions were made up.

(1) Aqueous solutions 0.1*N* in $CaCl_2$ and containing 60 ppM (parts per milliard) Li. Appropriate amounts of sulphuric acid were added to yield final concentrations in the range 0–0.26*N**.

(2) Same as set (1) but with half the $CaCl_2$ concentration. This set was used to check the constancy of the $H_2SO_4/CaCl_2$ ratio at which the interference of $CaCl_2$ with the Li signal is removed by sulphuric acid.

(3) Same as set (1) but chloride-free, calcium nitrate being added. These solutions served to show that the interference is caused by $CaCl_2$ rather than by Ca.

(4) Aqueous 0.1*N* HCl solutions, containing 60 ppM Li but no calcium. Sulphuric acid was added similarly as in (1).

(5) Aqueous solutions containing 60 ppM of Li plus various amounts of sulphuric acid similar to those applied in set (1).

(6) Sulphuric acid solution (0.2*N*) containing 60 ppM of Li, with Na^+ concentrations varying between 0 and 4000 ppm.

(7) A set of solutions similar to set (1), but containing, instead of sulphuric acid, phosphoric acid in the concentration range 0–0.2*N*.

A 50-ml portion of each solution was transferred into the graphite tube by means of an "Oxford" constant-volume micropipette. Calibration curves were prepared from solutions containing 20, 40, 60 and 80 ppM Li. This practice is superior to that of analysing different sizes of aliquot from the same standard, because equal-volume aliquots ensure a constant geometry of the graphite surface from which atomization takes place.

RESULTS AND DISCUSSION

The analytical results are presented in Table 1. It is obvious that the mere addition of sulphuric acid does not repress the atomic-absorption signal of Li. In fact, the signal yielded by a pure Li solution is increased by some 15% by addition of a very small amount of sulphuric acid. Introduction of $CaCl_2$, however, causes a marked decrease in the Li absorbance. On addition of sulphuric (or phosphoric) acid as well, the Li signal at first decreases even more, and stays low until the acid added is exactly equivalent to the $CaCl_2$ present in the solution, the Li signal then being restored to its full value and remaining steady regardless of further increase in acidity. It should be noted that the signal is steady with sulphuric acid but fluctuates considerably with H_3PO_4. This does not affect the proposed mechanism, but is of analytical significance. The exactly stoichiometric relationship between $CaCl_2$ and H_2SO_4 (or H_3PO_4) suggests that the $CaCl_2$ matrix interference is removed according to the two reactions

$$H_2SO_4 + CaCl_2 \rightarrow CaSO_4 + 2HCl \quad (1)$$

$$2H_3PO_4 + 3CaCl_2 \rightarrow 6HCl + Ca_3(PO_4)_2. \quad (2)$$

Reaction (2) will be disregarded in the following discussion, because of its poor analytical reproducibility.

Reaction (1) must take place anyway, because saturation with $CaSO_4$ is achieved during the drying stage of the analysis. The hydrochloric acid produced is removed on further heating at about 110°, long before the boiling point of metallic Li (1317°) or of LiCl (1325–1360°) is reached. The resultant $CaSO_4$ undergoes transformation into monoclinic anhydrite at around 1190–1200°, but does not melt below 1450°, *i.e.*, some 100° above the temperature at which Li boils off.

There is a drop in the instrumental signal obtained in the initial steps of addition of acid but the signal is

* It is advisable to add the sulphuric acid only after most of the water has been added to the volumetric flask, to minimize $CaSO_4$ precipitation. Also, analysis should be carried out as soon as possible after dilution. However, slight crystallization of $CaSO_4$ does *not* affect the Li results, because co-precipitation is negligible.

Table 1. The atomic-absorption signal of Li as a function of sulphuric acid concentration in various solutions

Li 60 ppM		Li 60 ppM in 0.1*N* $CaCl_2$		Li 60 ppM in 0.05*N* $CaCl_2$		Li 60 ppM in 0.1*N* $Ca(NO_3)_2$		Li 60 ppM in 0.1*N* HCl	
H_2SO_4, *N*	Absorbance	H_2SO_4, *N*	Absorbance	H_2SO_4, *N*	Absorbance	H_2SO_4, *N*	Absorbance	H_2SO_4, *N*	Absorbance
0.000	0.380	0.000	0.120	0.000	0.025	0.000	0.390	0.000	0.070
0.010	0.395	0.020	0.086	0.010	0.016	0.010	0.415	0.001	0.367
0.020	0.423	0.040	0.047	0.020	0.015	0.020	0.420	0.002	0.379
0.060	0.422	0.060	0.015	0.030	0.015	0.040	0.423	0.006	0.387
0.100	0.422	0.080	0.017	0.040	0.015	0.060	0.422	0.010	0.400
0.140	0.426	0.084	0.018	0.048	0.025	0.080	0.426	0.020	0.418
0.180	0.427	0.088	0.015	0.052	0.314	0.096	0.419	0.040	0.420
0.220	0.423	0.092	0.017	0.056	0.349	0.100	0.425	0.080	0.423
0.240	0.422	0.096	0.013	0.060	0.410	0.104	0.426	0.120	0.412
		0.100	0.018	0.080	0.429	0.108	0.428	0.160	0.423
		0.104	0.094	0.120	0.422	0.120	0.421	0.200	0.425
		0.108	0.239	0.160	0.425	0.160	0.422	0.240	0.422
		0.120	0.381	0.200	0.426	0.200	0.426		
		0.140	0.407	0.240	0.425	0.240	0.425		
		0.180	0.407						
		0.220	0.420						
		0.260	0.418						

stronger when a higher $CaCl_2$ concentration is used. It is suggested that this signal is produced by the residual unreacted $CaCl_2$ evaporating during the atomization stage, and causing light-scatter and/or molecular absorption.

That chloride is the interferent can be demonstrated directly. The replacement of chloride by nitrate (Table 1) removes the interference completely, although the Ca level is the same. When chloride is introduced into the system as HCl rather than as $CaCl_2$ (Table 1) a very substantial decrease in absorbance again occurs, but the effect is removed by addition of a very small amount of sulphuric acid.

The nature of the interference by chloride is easily explained. Li and LiCl have similar boiling points (1317° and 1325–1360°, respectively). The dissociation of LiCl, which is a prerequisite for atomic absorption is thus very sensitive to the vapour pressure of chlorine in the graphite tube. Any chloride capable of vaporization and dissociation at a temperature below 1320° will drive the reaction

$$LiCl \rightleftharpoons Li + Cl \qquad (3)$$

towards the undissociated, non-absorbing, molecular LiCl, which in the gaseous state is rapidly swept out from the graphite tube by the purge gas. $CaCl_2$ is an ideal agent for causing the observed interference. It melts at around 772° and boils at above 1600°. Thus, at the critical temperature range near 1320° it probably has sufficiently high vapour pressure to sustain a Cl-rich atmosphere in the graphite tube, but its high boiling point prevents its early selective volatilization.

The conclusions arrived at in this study have found successful application in the determination of Li in geological materials such as chert, silicates, limestones and sweet ground-waters. However, sodium at relatively high concentrations was also found to interfere with the Li signal. A secondary peak of a molecular sodium species is superimposed on the Li peak and cannot be entirely resolved from it (by changing the heating procedure) without a probable loss of some of the Li. Unless this interference can be removed, analysis of materials with Na/Li ratios exceeding approximately 3×10^4 should not be attempted.

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AN ABBREVIATED FIRE-ASSAY ATOMIC-ABSORPTION METHOD FOR THE DETERMINATION OF GOLD AND SILVER IN ORES AND CONCENTRATES

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Summary—A simplified scheme, combining aspects of the classical fire-assay with an atomic-absorption finish, is presented for the determination of gold and silver in ores and concentrates. The lead assay button is scorified to approximately 2 g and then parted in nitric acid. The filtrate is analysed by AAS for silver; the residue is dissolved in *aqua regia* and subsequently analysed for gold by AAS. The precision and accuracy of the method have been established by application to four diverse certified reference materials. The proposed method eliminates the need for such time-consuming steps as inquartation, multiple scorifications, and cupellation.

Within the past two decades several new specialized fire-assay schemes have been developed for collecting and concentrating the precious metals in the analysis of ores and concentrates.[1–5] These methods are used primarily for the platinum group metals, but of necessity include gold and silver because these metals are usually associated with platiniferous materials. However, in most laboratories, when only gold and silver determinations are required, the well-known classical lead-collection method of fire-assaying is used with either the customary gravimetric finish, or increasingly with an AAS finish. In both these cases pyrometallurgical operations involving fusion, scorification and cupellation are required to produce a precious metal bead having a silver:gold ratio that is suitable for parting or dissolution.

In routine work with ores of known behaviour, a direct acid decomposition can be used in conjunction with an AAS finish,[6,7,8] but when a wide range of materials of varying matrix composition and precious metal concentration is to be analysed, the classical fire-assay is necessary to ensure complete recovery of gold and silver.

This paper describes an abbreviation of the classical method which eliminates the tedious, time-consuming multiple scorifications required for lead buttons that are contaminated with base metals. A single scorification is used to obtain a lead button of approximately 2 g, which regardless of composition is parted directly in nitric acid, and gold and silver are separately determined by AAS. This procedure also eliminates the nuisance of inquartation and the expensive and time-consuming step of cupellation that is a fundamental part of the classical procedure.

That the new procedure is widely applicable is demonstrated by its successful application to a number of diverse reference materials.

EXPERIMENTAL

Apparatus

Assay furnace. A 15-kW "Globar" type.

Atomic-absorption spectrophotometer. Techtron Model AA-5. An oxidizing air–acetylene flame is used for the determination of gold and silver. Any instrument can be used provided it is equipped with scale expansion.

Assay crucibles. Catalogued as "30-gram" type.

Assay scorifiers. Catalogued as 7.5-cm diameter.

Reagents

Standard solutions of gold and silver. Gold standard prepared by dissolving accurately weighed quantities of Johnson Matthey "Specpure" gold sponge in *aqua regia*. Sodium chloride (25 mg) is added to the solution, which is then evaporated to dryness. The residue is dissolved in concentrated hydrochloric acid and the solution evaporated to dryness again, this being repeated several times. Finally, the salts are dissolved and diluted to volume with 1*M* hydrochloric acid. Silver standard prepared by dissolving accurately weighed quantities of pure silver foil in dilute nitric acid (4*M*) followed by dilution to volume with approximately 10% v/v nitric acid.

Mixed cadmium–copper sulphate solution.[9] Prepared by dissolving 98 g of $CuSO_4 \cdot 5H_2O$ and 57 g of $3CdSO_4 \cdot 8H_2O$ in 500 ml of 12*M* hydrochloric acid and 300 ml of water, followed by dilution to 1 litre with water.

Diethylenetriamine. Technical grade.

Flux for crucible fusion. PbO 90 g, Na_2CO_3 36 g, $Na_2B_4O_7$ 18 g, SiO_2 10–20 g (according to silica content of sample), flour 3–5 g (the larger quantity for samples high in iron).

Pretreatment of samples

Samples are roasted to convert sulphides into oxides and also to volatilize arsenic and antimony when present, to prevent the formation of matte or speiss during the subsequent fusion. All reference materials analysed in this investigation, except the South African ore, were roasted at 750–800° for approximately 1 hr. Because the major components of the South African ore are silica and magnesia, the roasting procedure was omitted.

The sample (200-mesh, weighing up to 1 assay-ton, *i.e.*, 29.1666 g) is placed in a shallow fire-clay dish and roasted with intermittent stirring. In cases where only a few grams of material (*e.g.*, sulphide concentrates) are to be roasted, the sample is placed on a bed of silica to prevent possible loss of the resultant calcine to the surface of the dish (the silica is included as part of that in the flux).

Preparation of assay charge

Powdered samples. For powdered samples, the standard assay practice of blending up to 1 assay-ton of sample with the flux on glazed paper is followed.

Solutions (synthetic samples for method development). When solutions of gold and silver were mixed with the flux, approximately one third of the flux was placed in the crucible and a 30-cm square of thin commercial wrapping film was pressed into the crucible to form an envelope, then the remainder of the flux was transferred into this envelope. With a spatula, a cavity was formed in the bed of flux and the sample solution was transferred slowly into the depression to avoid wetting the film or crucible

walls. The crucible was then heated in a drying oven at 110° for approximately 2 hr. After drying, the material in the wrapping film was ground in a mortar, mixed well and placed back in the film in the crucible.

Fusion. The crucible is placed in the assay furnace at 1250° for about 1 hr to fuse the charge. At the completion of the fusion period, the melt, which should pour freely, is transferred into a conical steel mould. When cooled, the lead button is separated from adhering slag by tapping with a hammer. The fusion conditions for both natural and synthetic samples (including solutions) were similar.

Treatment of lead assay button. The lead assay button, weighing 30–45 g, is reduced to approximately 2 g by a double scorification. This is done by placing the button in a scorifying dish, transferring the scorifier to the muffle at 1000°, and continuing heating in an oxidizing atmosphere until slag covers the molten lead. The melt is poured into a conical steel mould, allowed to cool, and the button separated from the slag. The button is increased in weight to 20 g with granulated test lead and transferred to a scorifier, and the scorification operation is repeated to obtain a final lead button for analysis.

NOTE. In routine control analysis where the mineralogical composition of the samples does not vary significantly, the weight of the lead assay button could be controlled at 19–22 g, and the second scorification omitted. This step would obviously reduce the time and cost per assay.

Analysis of lead button

The button, weighing approximately 2 g, is cleaned of adhering slag, flattened, and cut into pieces with a pair of snips.

Silver determination. The lead pieces are treated with 35 ml of nitric acid (1 + 3) in a 250 ml beaker. The beaker is covered and heated slowly for approximately 10 min to dissolve the lead alloy. The cover is removed, washed with 5% v/v nitric acid, then diethylenetriamine (5–7 ml) is added cautiously and with stirring to dissolve and complex silver and lead compounds, and produce a permanent hydrous oxide precipitate (Note 1). Sufficient concentrated nitric acid to dissolve the precipitate is added, then 10 ml in excess, and the solution is filtered by decantation through a Whatman No. 40 paper (9 cm) into a 200-ml volumetric flask. The filter paper and residue in the beaker are washed several times with 5% v/v nitric acid, then the filtrate and washings are combined and diluted to volume with water. Silver in the resulting solution is determined by AAS.

Gold determination. The original sample beaker is placed under its corresponding filter funnel, then the filter paper is treated with approximately 15 ml of *aqua regia* to dissolve any trapped gold, as well as the gold residue in the sample beaker. The filter paper is washed several times with 5% v/v nitric acid, 25 mg of sodium chloride are added to the sample solution, and this is then evaporated slowly to 1 ml.

To the cooled sample solution 5 ml of cadmium–copper sulphate solution are added to eliminate possible inter-element interferences from lead or from platinum-group metals that may have been present in the original sample. The solution is then diluted to 25 ml with water and the gold determined by AAS.

NOTES. 1. Treatment of the sample solution with diethylenetriamine is a modification of the procedure by Greaves.[6] Elements that precipitate as hydrous oxides under these conditions are, in general, those that form precipitates in slightly ammoniacal media.

2. In the analysis of lead buttons weighing more than 2.5 g problems were encountered in preventing the precipitation of lead salts with diethylenetriamine; this resulted in low values for gold and silver. In addition, blockage of the nebulizer occurred in the determination of silver by AAS.

Calibration for AAS

The calibration curves, based on various portions of the silver and gold stock solutions, were linear from 0.1 to 4 ppm and from 0.2 to 3 ppm respectively.

RESULTS AND DISCUSSION

Effect of scorification on gold and silver slag losses

The objective here was to compare the cumulative slag losses for gold and silver by both the proposed and classical scorification procedures. The classical procedure is not outlined in this paper, since it can be found in any fire-assay manual.

Fire-assay flux charges were salted with 4.4 g of Cu, 1.5 g of Fe (as oxides) and milligram quantities of gold and silver according to the procedure described above. The resultant assay buttons simulate those from 0.5-assay-ton samples containing 30% Cu and 10% Fe. Samples in this base-metal concentration range are considered the most troublesome for assay.

After completion of the required number of scorifications, slags obtained from each procedure were combined, crushed and assayed for gold and silver by the classical method using the assay flux charge. The resultant precious metal beads were weighed on a microbalance and results given in Table 1.

Table 1 shows that the loss of silver to the slag is not appreciably affected by the nature of the scorification procedure. It is apparent, however, that the loss of gold is an order of magnitude less in the proposed procedure. A likely explanation is that the classical method required up to seven scorifications to reduce the copper content of the button to a level at which there would be no interference

Table 1. Slag losses of gold and silver during scorification

Test No.	Silver taken *mg*	Gold taken *mg*	Slag loss, %			
			Proposed method		Standard method	
			silver	gold	silver	gold
1	61	30	0.9	0.05	1.7	0.35
	76	45	1.0	0.04	1.4	0.20
	46	60	1.2	0.03	1.2	0.20
2	—	30	—	0.06	—	0.50
	—	45	—	0.05	—	0.47
	—	60	—	0.06	—	0.58
3	61	—	0.9	—	1.6	—
	76	—	1.1	—	1.6	—
	46	—	0.7	—	1.1	—

Table 2. Application of proposed method to certified reference materials

Sample	Sample wt., *g*	Element	Mean found, *ppm*	Std. devn., *ppm*	Relative std. devn., %	Certified value, *ppm*
Silver ore KC-1[10]	14.58	Ag	1113	28.9	2.6	1138
Gold ore MA-1[11]	14.58	Au	17.9	0.32	1.8	17.8
Flotation concentrate	14.58	Ag	5.75	0.24	3.1	5.80
PTC-1[12]		Au	0.62	0.05	8.6	0.65
South African ore[13]	14.58	Ag	0.46	0.03	7.2	0.42
		Au	0.32	0.02	5.2	0.31

Concentration of base-metals in the sulphide reference materials: KC-1; Pb—6.98%; Zn—20.37%; S—28.0%. PTC-1; Cu—5.16%, Ni—9.42%; S—23.5%; Fe—26.9%.

during cupellation; each such scorification contributed to the overall loss.

Application to certified reference materials

To determine its reliability, the proposed method was applied to the analysis of three certified reference materials prepared by the Canadian Certified Reference Materials Project,[10,11,12] and also to a certified ore prepared by the National Institute for Metallurgy of South Africa.[13] Analytical results and precision data are presented in Table 2.

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Conclusions

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DIFFERENTIAL PULSE POLAROGRAPHY OF SOME BENZODIAZEPINES AND THEIR DETERMINATION IN URINE

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(*Received* 14 *October* 1975 *Revised* 20 *September* 1976. *Accepted* 10 *October* 1976)

Summary—A differential pulse polarographic method has been applied to the determination of diazepam, oxazepam, nitrazepam and flurazepam down to $2 \times 10^{-7} M$ (0.14 μg/ml). The method can also be used with biological materials such as urine, without prior extraction. Only a 2-ml volume of urine is necessary.

For the determination of the increasing group of benzodiazepine tranquilizers which are now extensively used in psychotherapy a number of different analytical methods have been suggested. Thus diazepam can be determined in various materials by spectrophotometry and chromatography.[1–4] Similar methods[4–6] can also be used for determining nitrazepam, which is used as a hypnotic. However, the analytical chemistry of benzodiazepines is a characteristic field of application of polarography, introduced by the Frankfurt school led by Oelschläger, and later studied by other research groups.[6–9]

One of the controlling factors in choosing a suitable

Table 2. Application of proposed method to certified reference materials

Sample	Sample wt., *g*	Element	Mean found, *ppm*	Std. devn., *ppm*	Relative std. devn., %	Certified value, *ppm*
Silver ore KC-1[10]	14.58	Ag	1113	28.9	2.6	1138
Gold ore MA-1[11]	14.58	Au	17.9	0.32	1.8	17.8
Flotation concentrate	14.58	Ag	5.75	0.24	3.1	5.80
PTC-1[12]		Au	0.62	0.05	8.6	0.65
South African ore[13]	14.58	Ag	0.46	0.03	7.2	0.42
		Au	0.32	0.02	5.2	0.31

Concentration of base-metals in the sulphide reference materials: KC-1; Pb—6.98%; Zn—20.37%; S—28.0%. PTC-1; Cu—5.16%, Ni—9.42%; S—23.5%; Fe—26.9%.

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One of the controlling factors in choosing a suitable

analytical method is the sensitivity of the assay. It has become evident—in particular with biological samples and low depolarizer concentrations—that d.c. polarography is not sensitive enough.

However, differential pulse polarography has a sensitivity comparable to that of gas chromatography with a flame ionization detector and is often more specific. That is why this polarographic method has been introduced in the analysis of diazepam in biological samples.[10] The present paper describes an investigation of the fundamental parameters and detection limits for the differential pulse polarography of the 4 major diazepines and the application of the results to a straight-forward determination of diazepam in urine without prior extraction.

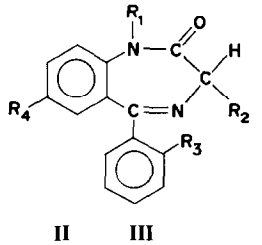
EXPERIMENTAL

The following benzodiazepine derivatives were investigated: oxazepam (**I**; 2,3-dihydro-3-hydroxy-5-phenyl-7-chloro-1*H*-1,4-benzodiazepine-2-one), produced by Thomae, Biberach a. d. Riss; diazepam (**II**; 1-methyl-2,3-dihydro-5-phenyl-7-chloro-1*H*-1,4-benzodiazepine-2-one), nitrazepam(**III**;1,3-dihydro-5-phenyl-7-nitro-2*H*-1,4-benzodiazepine-2-one), flurazepam [**IV**, 1-dimethylaminoethyl-5-(2-fluorophenyl)-7-chloro-2*H*-1,4-benzodiazepine-2-one], all produced by Hoffmann–LaRoche.

Reagents

All reagents used were of analytical grade purity. Doubly distilled water was used for the experiments and for washing the polarographic cell. Acetate buffer, pH 4.8, was prepared by mixing equal volumes of 0.2*M* acetic acid and 0.2*M* sodium acetate; the pH was checked and adjusted to 4.8 with the appropriate solution.

Standard solutions were prepared for each compound by dissolving an appropriate weight in acetate buffer (containing 10% v/v acetonitrile); the stock solutions were diluted with acetate buffer to the desired concentrations. The final solutions to be electrolysed contained only 0.5 or 1.0% acetonitrile. These standard solutions were also used as an internal standard, added to urine.



	I	II	III	IV
R_1	H	CH_3	H	$(CH_2)_2N(CH_3)_2$
R_2	OH	H	H	H
R_3	H	H	H	F
R_4	Cl	Cl	NO_2	Cl

Polarographic analysis

A P.A.R. Model 174 A Polarographic Analyser (Princeton Applied Research Corp.) equipped with a P.A.R. Model 172 Drop Timer electrode assembly was used.

The two-electrode cell contained a dropping mercury electrode as indicator and a saturated mercurous sulphate electrode as reference electrode. Polarography was performed in the differential pulse polarographic mode with a 100-mV pulse and a 5-sec drop.[11] The scans were started from a suitable potential according to the reduction potential of the substance studied; the scan-rate was 1 mV/sec with a full-scale range of 1.5 V. The current sensitivity was 2 or 10 μA for full-scale deflection.

RESULTS AND DISCUSSION

Differential pulse polarography (DPP) of substances I, II, III, IV

In the first stage of our experiments dimethylformamide was tested as solvent since it had proved to be very useful in d.c. polarography of benzodiazepine.[6,7,9] Unfortunately, it shows, especially at the high sensitivity used, a catalytic effect interfering with the accurate measurement of peak currents. Using purified acetonitrile as co-solvent resulted in a much better developed polarogram. Different supporting electrolytes were tested but the best development of the peaks was obtained with an acetate buffer of pH 4.8. When sulphuric acid was used as supporting electrolyte it was observed that decreasing its concentration led to a better defined peak, the optimal acid concentration being 0.05*N* (containing 1% acetonitrile). However, the pH-4.8 acetate buffer proved more favourable for quantitative evaluation. Differential pulse polarographic data for the four substances studied, *e.g.*, peak currents i_p and peak potentials E_p for the same conditions are given in Table 1.

A satisfactorily linear relationship was always obtained between the peak current recorded in the differential pulse mode and the concentration of the benzodiazepine derivative, down to the concentration range 2–10 $\times$ $10^{-7}M$ *i.e.*, down to 0.14 μg/ml. To illustrate the advantages of DPP over d.c. polarography, polarograms of two benzodiazepine derivatives, **III** with two peaks and **I** with a single peak, both at the 2 $\times$ $10^{-6}M$ level, were recorded by both techniques. Although the d.c. polarograms were recorded at a 10 times higher sensitivity setting than that for the differential pulse polarogram, a d.c. wave can scarcely be detected on the polarogram in Fig. 1.

The differences between the peak potentials of the four diazepines are rather small, because reduction of the 4,5-C=N double bond is involved in all cases. Consequently, in mixtures it is only possible to distinguish between oxazepam (**I**) and diazepam (**II**) or flurazepam (**IV**). In addition, however, the first four-electron reduction peak of nitrazepam (**III**) allows its easy determination in presence of any of the other three derivatives. However, determination of the four benzodiazepines in mixtures is not normally important, since they are always administered singly, though it would be useful in forensic work.

Table 1. Polarographic data for the benzodiazepine derivatives studied.

Compound	i_p, μA	E_p, V*	Bond reduced
Oxazepam (**I**)	2.7	−1.23	C=N– and C–OH
Diazepam (**II**)	1.4	−1.19	C=N–
Nitrazepam (**II**)	2.85	−0.61	$-NO_2$
	1.35	−1.23	C=N–
Flurazepam (**IV**)	1.4	−1.18	C=N–

* *vs.* satd. mercurous sulphate electrode.

Supporting electrolyte: 0.2*M* acetate buffer, pH 4.8; depolarizer concentration 2 $\times$ 10^{-5} *M*; polarographic parameters: differential pulse mode; pulse 100 mV; scan-rate 1 mV/sec; drop-time 5 sec; scan range 1.5 V.

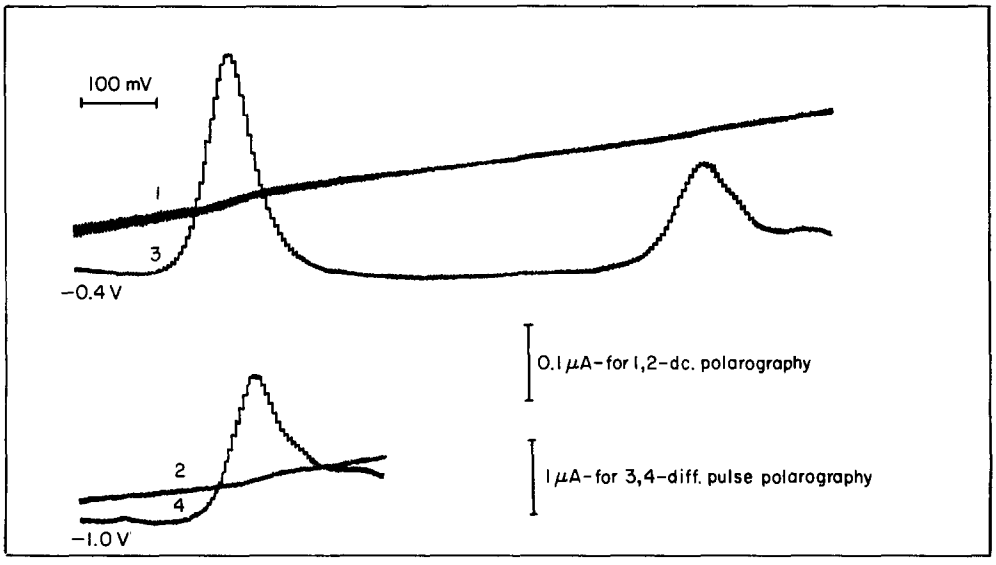


Fig. 1. Differential pulse and d.c. polarograms of $2 \times 10^{-6}M$ nitrazepam (1 and 3), and oxazepam (2 and 4) in pH-4.8 acetate buffer.

Table 2. Blood and urine levels of diazepam in the biological specimen described

Amount of diazepam added	Blood concentration level (calculated), *M*	Analysed urine level, *M*
5 mg in 90 ml	2.03×10^{-3}	4.1×10^{-5} (13 μg/ml) 4.2×10^{-5} [2.0×10^{-5}] 4.1×10^{-5}
1 mg in 90 ml	4.05×10^{-4}	0.6×10^{-7} (1.4 μg/ml) 0.55×10^{-7} 0.50×10^{-7} 0.55×10^{-7}

The polarographic behaviour of the corresponding metabolites depends on the state of the 4,5-double-bond. If it remains preserved in the metabolite the latter will not differ much from the original substance in its polarographic reducibility.

Application of the method to biological samples

When the differential pulse polarographic peak was registered for a solution containing human urine, well-defined peaks were obtained for the benzodiazepines at the same potentials as in absence of urine, but the peak currents were somewhat lower, though still a linear function of the depolarizer concentration.

In an attempt to apply this method to samples from humans a single high dose of diazepam (**II**) was administered and polarograms were recorded of the urine obtained at intervals from 3 to 10 hr after the drug intake. Only the urine collected 3 hr after administration of a single dose of 30 mg to an adult showed an indication of the presence of **II**; the height of the peak obtained increased on addition of a standard solution of diazepam. Nevertheless this straightforward procedure is not suitable for quantitative measurement at this dose level. This is in part due to the relatively low dose of the drug, in part to the ability of the tissues to bind and to metabolize the benzodiazepines.

The suitability of our method for toxicological analysis for benzodiazepines in biological materials without prior extraction was assessed in a special experiment. A rabbit kidney separated from the living animal was perfused with a solution composed of 45 ml of rabbit blood and 45 ml of Heinberg solution (150 ml of Heinberg physiological solution contains 2 ml of 1.13% KCl solution, 1.5 ml of 1.2% $CaCl_2$ solution, 0.5 ml of 0.9% KH_2PO_4 solution, 0.5 ml of 3.78% $MgSO_4$ solution, 10.5 ml of 1.29% $NaHCO_3$ solution and 130 mg of glucose). This mixture was circulated, and filtered by the kidney. Every 15 min about 5 ml of urine were obtained. Two sets of experiments were performed in this way; in the first 5 mg of diazepam were added to the 90 ml of circulated solution, in the other case only 1 mg was added. In each case, urine samples were collected every 15 min and diluted tenfold with the acetate buffer and differential pulse polarograms were recorded. The peaks appeared at −1.19 V *vs.* the saturated mercurous sulphate electrode. The curves were evaluated by the standard addition method, which proved more reliable than a calibration curve. The procedure is as follows: 2 ml of the urine sample were diluted to 20 ml with the acetate buffer; a part of this solution was used for rinsing the cell; the polarographic curve was recorded with exactly 10 ml of this solution after thorough deaeration with a stream of argon. After this an aliquot (0.5 ml) of a standard ($5 \times 10^{-5}M$) solution of **II** in acetate buffer was added. The solution was again deaerated and the second polarogram recorded. The concentration was calculated by use of the well-known relationship

$$c_1 = \frac{i_1 V_2 c_2}{i(V_1 + V_2) + i_1 V_2}$$

where V_1 is the original volume of the solution with concentration c_1, giving a current i_1, and V_2 is the volume of the added standard solution with concentration c_2 and

causing an increase of the current to i_2. The results are shown in Table 2.

The precision of the pulse polarographic determination of diazepam at the $10^{-6}M$ level, both in pure solutions and in presence of human urine, was tested by regression analysis. For the plot of $i_p = f(c)$ in the region 2×10^{-6}–$10^{-5}M$ the following values were obtained with aqueous pH 4.7 acetate buffer: intercept −0.185, slope 0.742, correlation coefficient 0.9989, standard deviation 0.1235. With analogous solutions containing 10% urine, these parameters had the values: intercept −0.300, slope 0.505, correlation coefficient 0.9917, standard deviation 0.0753.

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PHOSPHOMOLYBDIC ACID AS A REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF CERTAIN PHENOTHIAZINE DERIVATIVES OF PHARMACEUTICAL PRODUCTS

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(*Received* 25 *May* 1976. *Revised* 6 *September* 1976. *Accepted* 21 *October* 1976)

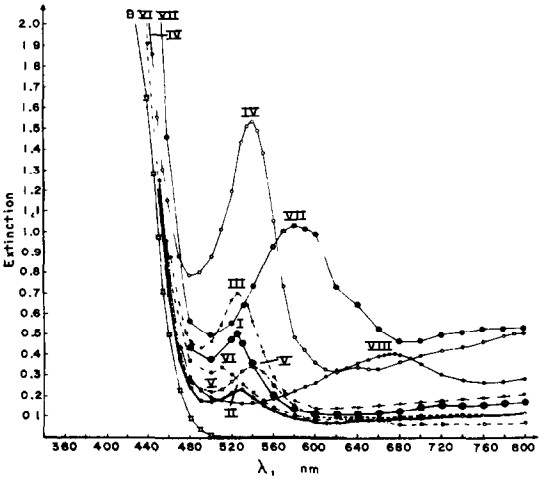
Summary—Phosphomolybdic acid is used as reagent for colorimetric determination of phenothiazine derivatives in various pharmaceutical products. The reagent oxidizes the derivative to a cationic free radical, with which it then forms a coloured salt. The method is simple and rapid. A preliminary extraction is necessary if certain reductants (sulphite or ascorbic acid) are present as stabilizers of the pharmaceuticals, as otherwise they reduce the reagent to phosphomolybdenum blue.

Phosphomolybdic acid has been used in chemical analyses for the identification and determination of several organic substances, among which are phenothiazine derivatives. Auterhoff[1–3] suggested its use as a reagent to identify certain antihistamines, including *N*-diethylaminoethylphenothiazine and *N*-diethylaminopropylphenothiazine. El-Dorry *et al.*[4] reported the interference of phenothiazine derivatives with the determination of phosphates as phosphomolybdates. Blazek and Travnicková[5] determined gravimetrically a series of phenothiazine derivatives with phosphomolybdic acid as reagent.

Our own investigations have shown that small amounts (< 300 μg) of phenothiazine derivatives react with an excess of phosphomolybdic acid to form soluble coloured compounds and we have applied this to the determination of certain phenothiazine derivatives used in therapeutics. Table 1 lists the derivatives studied and the wavelengths of maximum absorption.

Derivatives with a hydrogen atom at C_2 have their absorption maximum at 525 nm; a chlorine atom at C_2 causes a bathochromic effect, shifting λ_{max} to 540 nm, as do the groups $-OCH_3$ and $-SCH_3$ (λ_{max} = 580, 675 nm respectively), whereas $-CF_3$ causes a hypsochromic shift (λ_{max} = 510 nm). The absorption spectra are shown in Fig. 1.

Analysis of the infrared spectra shows that the reaction



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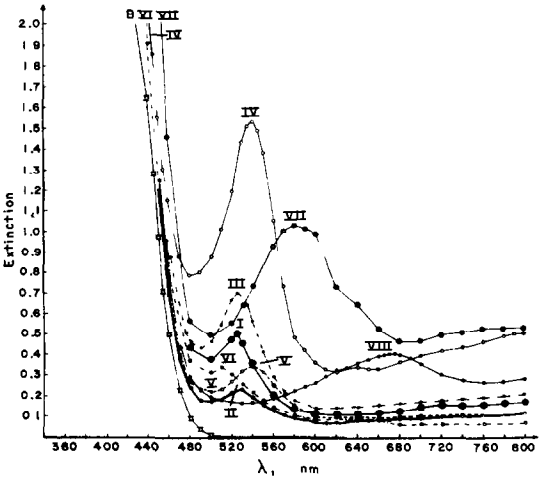

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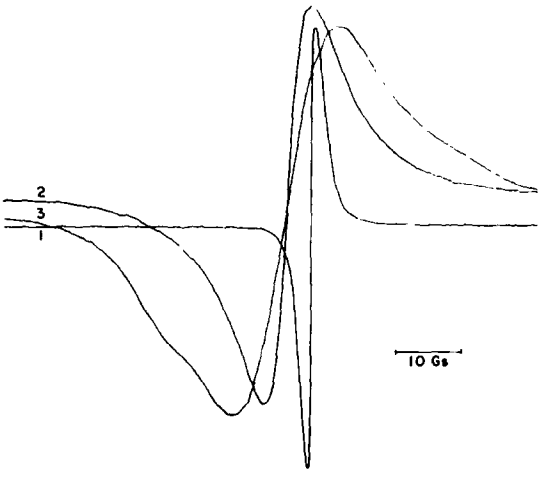


Fig. 2. ESR spectra. 1—Standard substance. 2—Chlorpromazine. 3—Promethazine.

between phenothiazines and phosphomolybdic acid is accompanied by anion-exchange at the main nitrogen atom in the side-chain, as for organic bases in general.[6] Thus, when levopromazine maleate reacts with phosphomolybdic acid, the characteristic band of the carboxylic acid C=O group (1695 cm^{-1}) disappears. The infrared spectra of the products all show the characteristic band of phosphomolybdic acid.

The ESR signals undoubtedly show that free radicals are formed by the oxidizing action of the phosphomolybdic acid on the phenothiazine nucleus (Fig. 2). Hence the coloured product obtained when an aqueous solution of a phenothiazine derivative is treated with phosphomolybdic acid is a phosphomolybdate of the cationic radical formed by this oxidation. This conclusion is lent further support by the colour obtained, the wavelength of maximum absorption in the visible region corresponding to that reported in the literature for the free radicals formed by oxidation.[7]

The solutions reach maximum absorbance in 10 min and the colour is stable for 60 min for compounds 1–6, but for only 25 min for 7 and 8. The optimum amount of phosphomolybdic acid for determination of 0–300 μg of phenothiazine derivative, is 1 ml of 10% solution.

The excipients used to make tablets or pills from phenothiazine do not interfere with the colour reaction. Therefore, the method can be applied to such pharmaceutical preparations. On the other hand, liquid preparations, such as solutions for injection or internal use, or syrups, generally contain reductants such as sulphite and ascorbic acid as stabilizers, and these reduce the phosphomolybdate to phosphomolybdenum blue, and thus interfere, the amounts tolerated being 1 mg and 25 μg respectively. This can be dealt with by use of a smaller sample, but for syrups containing a large amount of ascorbic acid a preliminary extraction of the phenothiazine with ether from alkaline medium is necessary.

EXPERIMENTAL

Reagents

Standard solutions of chlorpromazine hydrochloride, promethazine hydrochloride and maleate, promazine maleate, diethazine hydrochloride, fluphenazine hydrochloride and thioridazine hydrochloride were used, covering the concentration range 20–250 μg/ml.

Levopromazine maleate and prochlorperazine maleate, which have low solubility in water, were dissolved (0.1 g) in 4 and 10 ml of 1*M* hydrochloric acid respectively, then

Table 1.

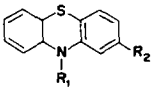
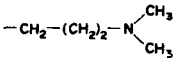
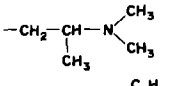
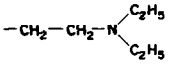
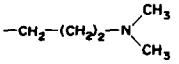
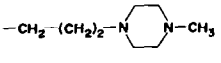
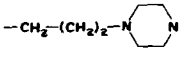
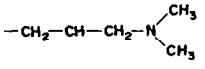
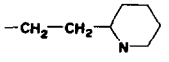
No. Derivatives studied	 R_1	R_2	λ_{max}, *nm*
1 Promazine (maleate)		—H	525
2 Promethazine (hydrochloride and maleate)		—H	525
3 Diethazine (hydrochloride)		—H	525
4 Chlorpromazine (hydrochloride)		—Cl	540
5 Prochlorperazine (maleate)		—Cl	540
6 Fluphenazine (hydrochloride)		$—CF_3$	510
7 Levopromazine (maleate)		$—OCH_3$	580
8 Thioridazine (hydrochloride)		$—SCH_3$	675

Table 2.

Pharmaceutical form analysed	Content of active substance	Content of active substance found
1. *Solutions*		
Plegomazin	0.5% chlorpromazine hydrochloride	0.513%
Romergan	2.5% promethazine hydrochloride	2.46%
Romthiazin	0.6% promazine maleate	0.606%
Diparcole	5.0% diethazine hydrochloride	4.99%
2. *Pills*		
Chlordelazin	0.025 g chlorpromazine hydrochloride	0.0237 g
Romergan	0.03 g promethazine maleate	0.0297 g
Romthiazin	0.025 g promazine hydrochloride	0.0248 g
Emethiral	0.005 g prochlorperazine maleate	0.0046 g
3. *Tablets*		
Levomepromazin	0.025 g levopromazine maleate	0.0247 g
4. *Syrups*		
Romergan	0.1% promethazine	0.093%
5. *Suppositories*		
Emethiral	0.025 g prochlorpromazine maleate	0.0249 g

diluted to 100 ml with water. Appropriate dilutions were made of these solutions.

A 10% phosphomolybdic acid solution was made by dissolving 10 g of phosphomolybdic acid in hot water with continuous stirring, then cooling and diluting to 100 ml, and filtering if necessary.

Calibration curve

To 1 ml of standard solution containing 20–250 μg of phenothiazine derivative 1 ml of phosphomolybdic acid solution is added; 10 min later the solution is diluted accurately with water to 5 ml, and the absorbance at the appropriate wavelength (Table 1) measured in a 1-cm cell. A blank is prepared under the same conditions. The calibration curves are linear but may not all pass through the origin.

Determination of phenothiazines in pharmaceutical products

An amount of the product to be analysed (tablets, pills, solutions) containing up to 10 mg of phenothiazine derivative is dissolved in water and filtered, then the solution is diluted to 100 ml with water. A 1-ml aliquot of this solution is treated in the same way as the standards.

With syrups, unguents and suppositories, a preliminary extraction with ether from 10% sodium hydroxide medium is made. The organic phase is then back-extracted with 1*M* hydrochloric acid and this acid extract diluted to 100 ml with water. A 1-ml aliquot is then used for the determination.

Table 2 gives typical results for pharmaceutical products.

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CHEMICAL SEPARATION AND SPECTROGRAPHIC ESTIMATION OF RARE EARTHS AND YTTRIUM IN PuO_2 AND $(U,Pu)O_2$

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Summary—An emission spectrographic method for the estimation of rare-earth impurities in plutonium oxide and the mixed oxide $(U,Pu)O_2$ (30% PuO_2–70% UO_2) has been developed. Rare-earth impurities are separated from the matrix by solvent extraction with tri-n-octylamine in xylene and are estimated after concentration. Thulium is used as internal standard and LiF–AgCl as carrier. The spectra are excited in a d.c. arc. The detection limits lie in the range 0.004–0.1 μg and the coefficient of variation ranges from 5 to 23%.

Plutonium oxide and the mixed oxide of uranium and plutonium have become important in recent years as nuclear fuel for Fast Breeder Test Reactors (FBTR). The concentrations of the metallic impurities in the fuel must be below the maximum permissible levels specified to obtain the required density for the pellets and also to reduce the loss of neutrons because of absorption by impurities having high neutron cross-sections. The estimation of metallic impurities in the fuel thus becomes an essential part of the chemical quality control programme. Estimation of common impurities in these materials is carried out routinely by carrier distillation techniques, first developed by Scribner and Mullin for uranium samples. The rare earths, however, are estimated after their chemical separation from the matrix.[2–7] Joshi *et al.*[2] and Faris[3] used ion-exchange techniques for separation of rare earths from plutonium, whereas solvent extraction methods were used by Vantuyl[4] and Dhumwad *et al.*[5] Ko used solvent extraction techniques for separation of the rare earths in the mixed oxide and estimated them by the copper spark method.[6,7] This paper describes a d.c. arc spectrographic method for estimation of rare earths in plutonium oxide and the mixed oxide after separation of rare earths by extraction of uranium and plutonium into tri-n-octylamine (TOA) in xylene. Thulium is used as internal standard and is assumed to be absent from the samples. All the elements except Tb could be determined at less than 1 ppm, the lower limit for Tb being 1 ppm.

EXPERIMENTAL

Reagents

All the chemicals used for the preparation of individual stock solutions were of spectroscopically pure grade (Johnson Matthey). Analytical grade concentrated nitric acid and hydrochloric acid and water were distilled twice in a quartz distillation unit before use. Tri-n-octylamine (K & K Laboratories) was used without further purification. The xylene was guaranteed reagent grade [Sarabhai (M) Chemicals, India]. "Ultrapurity" graphite powder U.C.P.-2 (200 mesh) supplied by Ultra Carbon Corporation, was used for preparation of the carrier.

Preparation of standards

Individual stock solutions for rare-earth elements and the internal standard thulium solution, with a concentration of 5 mg/ml, were prepared by dissolving the oxides (ignited at 800° for 1 hr), in 3*M* hydrochloric acid, and used to make a master solution with composition Y, Yb, 0.1 mg/ml; Eu, Gd, Dy, Er, Ho, Lu, La, 0.25 mg/ml; Ce, Nd, Sm, Tb 1 mg/ml.

A set of seven standards in 6*M* hydrochloric acid was prepared by taking different volumes of the master solution to give the concentration range 0.2–200 μg/ml for different elements. The concentration of Tm in all standard solutions was 25 μg/ml.

Preparation of carrier. A carrier mixture of LiF, AgCl and graphite powder in the ratio 1:1:2 was prepared by grinding weighed amounts in an agate mortar.

Chemical separation procedure

A solvent extraction technique (with 20% TOA in xylene) was used for the separation of PuO_2 or the mixed oxide $(U,Pu)O_2$ (30% PuO_2–70% UO_2) from rare earths. The mixed oxide or plutonium oxide, free from rare earths, was used for the standardization of the chemical procedure. The mixed oxide or the PuO_2 pellet was dissolved by heating in concentrated nitric acid that was 0.05*M* in hydrofluoric acid. After complete dissolution of the sample the solution was evaporated almost to dryness and taken up in 6*M* hydrochloric acid; this was repeated several times to remove traces of nitric and hydrofluoric acids. Known amounts of impurities and 2.5 μg of thulium were added to a solution containing 1 g of PuO_2 or $(U,Pu)O_2$ in 6*M* hydrochloric acid. This solution was evaporated to dryness and the residue dissolved in 10 ml of 6*M* hydrochloric acid. The plutonium was made quadrivalent by addition of a few drops of hydrogen peroxide (30%) and the excess of peroxide was destroyed by heating under an infrared lamp. The resulting solution was stirred vigorously (magnetic stirrer) with 10 ml of 20% TOA in xylene, pre-equilibrated with 6*M* hydrochloric acid. The Pu and U were extracted. Five such extractions gave complete removal of U and Pu. The aqueous phase was then rinsed twice with 10 ml of xylene. Finally the aqueous phase containing the rare earths was evaporated nearly to dryness, 2 ml of a 1:1 mixture of concentrated nitric acid and perchloric acid were added and the solution was evaporated to dryness. The residue was heated at 400° for 1 hr to destroy any organic matter and was then used for spectrographic analysis.

The Pu and U were stripped by vigorously stirring the organic phase with an equal volume of 5*M* perchloric acid. Two back-extractions gave complete removal of Pu and U from the organic phase. The plutonium and uranium were then precipitated as the hydroxides which were then dissolved in nitric acid for the separation of U and Pu by anion-exchange.

Table 1. Equipment and operating conditions

Spectrograph	Hilger 3.4-m Ebert plane grating spectrograph
Grating	30,000 lines/in. blazed at 1 μm in first order
Reciprocal linear dispersion	0.8 Å/mm in third order, 1.25 Å/mm in second order
Wavelength region	3570–4130 Å in second order, 3150–3500 Å in third order
Excitation unit	Hilger source unit FS 131
Arc current (d.c.)	13 A
Exposure time	45 sec—third order, 35 sec—second order
Electrodes	Graphite rods (Ultra Carbon Corporation, U.S.A.)
Anode	"Ultrapurity" graphite ST-45, 4.76 mm dia. 2 cm long, 2.5 mm crater depth and 3.17 mm crater diameter
Cathode	Ultrapurity graphite ST-40, 3.17 mm dia. and 2.5 cm long, pointed
Arc chamber atmosphere	80% argon + 20% oxygen at a flow-rate of 20 l./min for second-order setting
Analytical gap	4 mm (not constant during arcing)
Slit width	15 μm (third order) and 20 μm (second order)
Slit height	2.5 mm
Photographic material	Two 10.2 × 25.4 cm Kodak plates (SA-1)
Developer and development time	Kodak D-19 at 18° for 3 min
Fixer	Kodak acid fixing salt solution for 3 min
Plate calibration	Seven-step rotating sector with iron arc exposure of 20 sec. with current 4A
Microphotometer	Hilger non-recording microphotometer
Calculator	Respectra

Table 2. Recovery results for tracers

Tracer	Recovery, %	Average recovery, %
^{141}Ce	99.8	99.9
	100.0	
$^{152-154}Eu$	99.5	98.2
	97.0	
^{170}Tm	99.8	99.8
	99.8	
^{91}Y	97.3	96.8
	96.4	

Sample preparation and spectrographic conditions

The residue containing the rare earths, after chemical separation of Pu and U, was dissolved in 200 μl of 6*M* hydrochloric acid. An aliquot of 20 μl of each standard and 40 μl of sample were loaded in duplicate on 10 mg of carrier mixture in the electrode crater. The electrodes were dried under an infrared lamp.

The samples and standards were arced in a glass chamber inside a glove box. The spectra of the standards and the samples were photographed on the same plate in duplicate under the conditions given in Table 1

RESULTS AND DISCUSSION

The solvent extraction technique using 20% TOA in xylene removed all traces of the matrix elements, uranium and plutonium, as required for the spectrographic estimation of impurities in PuO_2 and $(U,Pu)O_2$ samples. This was established by the absence of alpha-activity in the aqueous phase after the five extractions.

The recovery of the rare-earth impurities was checked by using radioactive traces. Known amounts of the tracers, $^{152-154}Eu$, ^{170}Tm, ^{141}Ce and ^{91}Y were added to the solution containing 1 g of sample, then separated by the method discussed above and estimated, $^{152-154}Eu$, ^{170}Tm

Table 3. Precision and accuracy

Element	Analytical line, Å	Amount added, μg	Amount recovered, μg	Recovery, %	Coefficient of variation, %
Ce	3942.7	0.4	0.36	91.6	7
Dy	4015.9	0.1	0.096	96.5	8
Er	3264.78	0.1	0.106	105.6	10
	4007.9	0.1	0.095	95.0	9
Eu	3971.99	0.1	0.098	95.4	3
Gd	3422.5	0.1	0.107	107.0	11
	3768.9	0.1	0.099	99.5	9
Ho	3456.0	0.1	0.108	108.6	7
	3891.02	0.1	0.095	94.9	7
	4015.4	0.1	0.094	94.2	5
La	3337.5	0.1	0.121	121.1	9
Lu	3359.8	0.1	0.106	105.8	10
Nd	4012.4	0.4	0.406	101.5	6
Sm	3634.27	0.4	0.39	99.4	6
Tb	3324.4	0.4	0.42	105.7	6
Y	3242.28	0.04	0.049	123.3	23
Yb	3289.37	0.04	0.041	102.5	16

Table 4. Analytical line pairs and estimation ranges

Element	Analytical line, Å	Internal standard line, Å	Estimation range, ppm	Estimation limits, μg
Cerium	3942.1	3949.28	0.5–20.0	0.1
Dysprosium	4015.9	3949.28	0.125–2.5	0.025
Erbium	3264.78	3425.6	0.125–5.0	0.025
	4007.9	3949.28	0.125–1.25	0.025
Europium	3971.99	3949.28	0.05–1.25	0.01
Gadolinium	3422.5	3425.6	0.05–5.0	0.01
	3768.9	3734.12	0.125–2.5	0.025
Holmium	3456.0	3425.6	0.125–5.0	0.025
	3891.02	3949.28	0.125–2.5	0.025
	4015.4	3949.28	0.125–2.5	0.025
Lutecium	3359.8	3235.5	0.05–5.0	0.01
Lanthanum	3337.5	3235.5	0.05–5.0	0.01
Neodymium	4012.25	3949.28	0.5–5.0	0.1
Samarium	3634.27	3734.12	0.20–10.0	0.04
Terbium	3324.4	3235.5	1.0–20.0	0.2
Yttrium	3242.28	3235.5	0.02–2.0	0.004
Ytterbium	3289.37	3235.5	0.02–2.0	0.004

Table 5. Comparison of detection limits for the mixed oxide

Rare earth	Estimation limit, ppm: Literature method[6]*	Present method†
Ce	50	0.5
Nd	50	0.5
Sm	5	0.2
Eu	5	0.05
Gd	5	0.05
Tb	25	1.0
Dy	2.5	0.125
Ho	3	0.125
Er	5	0.125
Tm	5	Int. std.
Yb	2.5	0.02
Lu	5	0.05
Le	3	0.05
Y	Int. std.	0.02

* No details given of amount of sample used for separation and amount of separated impurities arced.

† Values based on arcing $\frac{1}{3}$ of the impurities separated from 1 g of sample.

and ^{141}Ce by gamma-counting with an NaI(Tl) detector, and ^{91}Y by the liquid scintillation technique. The results obtained are shown in Table 2. The recovery was also obtained by the spectrographic method after chemical separation from the matrix. These results are shown in Table 3. It can be seen from the results in Tables 2 and 3 that the recoveries are quantitative within experimental error.

Analytical lines and internal standard lines used are given in Table 4. Working curves were drawn by plotting the ratio of the intensities of the sample and standard lines against the logarithm of the sample concentration and were found to be linear.

The coefficient of variation for the estimation of rare-earth impurities (12 replicate samples with duplicate determinations) is shown in Table 3 and is below 16% except for yttrium, for which it is 23%.

The lowest concentration at which the working curve is linear is considered to be the lower estimation limit (Table 4). Table 5 gives a comparison of the estimation limits for the present method with others reported for mixed oxide samples. The limits obtained in the present work are all lower than those so far reported. The maximum permissible levels of rare earths specified for plutonium oxide and mixed oxide fuel used for FFTR reactors[7] are given as 100 ppm for the sum of four elements, *viz.* Sm, Eu, Gd and Dy. The low estimation limits obtained suggest that the sample size may be reduced below 1 g for the chemical quality-control analysis of rare earths in FBTR fuel.

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ROOM-TEMPERATURE PHOSPHORESCENCE OF SEVERAL POLYAROMATIC HYDROCARBONS*

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Summary—The room-temperature phosphorescence of several polyaromatic hydrocarbons (anthracene, coronene, phenanthrene, pyrene, benzo[*a*]pyrene) and carbazole on paper support has been investigated. Heavy-atom solvents such as silver nitrate and sodium iodide were found to have specific effects in inducing phosphorescence emission from these compounds.

Since the first report on room-temperature phosphorescence emission from the salts of some ionic organic compounds[1] adsorbed on filter paper, silica gel, alumina and polycellulose, "Room-Temperature Phosphorimetry" (RTP) has been investigated and developed in this laboratory into a sensitive spectroscopic method of analysis.[2–4] However, until now, the applications of this technique were limited to compounds of ionic nature, which were the only ones found to show strong phosphorescence emission, especially when they were examined in strongly acidic or basic solvents. It was therefore believed that the ionic state of the molecules resulted in an increased molecular rigidity through adsorption on the substrate, thus reducing collisional radiationless deactivation. Under the experimental conditions used, compounds which were not ionizable showed no significant phosphorescence at room temperature.

In order to explore new possibilities and improvements of the RTP method, the room-temperature phosphorescence behaviour of several polyaromatic hydrocarbons (anthracene, coronene, phenanthrene, pyrene, benzo[*a*]pyrene) and an important representative of heterocyclic molecules (carbazole) was investigated. Pyrene, benzo[*a*]pyrene, and carbazole are known to be carcinogenic and are found to be present in tar, cigarette smoke, polluted water and urban air.[5] The use of heavy-atom perturbers, such as sodium iodide and especially silver nitrate, was found to be very effective in inducing phosphorescence emission from several polyaromatic hydrocarbons. These results indicate that the simple and rapid RTP technique has a large potential in analytical spectrometry, in the coal and petroleum technology and in environmental pollution control, as well as in biological applications.[2–4]

EXPERIMENTAL

Apparatus

The experimental arrangement was described in detail previously.[2] An Aminco-Bowman spectrophotofluorimeter with an Aminco-Keirs phosphoroscope attachment (American Instrument Co., Silver Spring, MD) was used for room-temperature phosphorescence measurements. The excitation light-source was a 150-W xenon arc lamp, and the detection system was an R446S photomultiplier tube (Hamamatsu TV Co., Ltd., Hamamatsu, Japan) having a photocathode spectral response range from 185 to 850 nm. All spectra were recorded with 5-mm monochromator slit-widths.

Reagents

The sample support was Eaton Dikeman 613 filter paper. All compounds investigated were purchased and used without purification. All solutions were prepared in ethanol.

Procedure

Described in detail previously,[2–4] the experimental procedure consists of spotting 5 μl of the sample solution on 0.25-in. diameter filter paper circles and drying with an infrared lamp and warm-air blower (60°). For some measurements, a novel feature was pretreatment of the substrate by spotting with 0.1*M* silver nitrate before the usual sample preparation procedure.

RESULTS AND DISCUSSIONS

Choice of solvent for polyaromatic hydrocarbons

Previous studies on RTP indicated that ionic molecules show intense phosphorescence signals only when they are dissolved in aqueous solvents containing a large excess of a strong acid or base. The use of these types of solvents did not provide any successful results in the present studies on polyaromatic hydrocarbons, one main reason being the low solubility of these compounds in water ($\sim 10^{-6}M$). To overcome this problem, a 1:1 v/v mixture of ethanol and water was used. This solvent gave a solubility of up to $\sim 0.005M$ for most of the polyaromatic hydrocarbons investigated except for benzo[*a*]pyrene ($\sim 10^{-4}M$), thereby extending the range of analytical studies. In addition, the quantum yields for these compounds in ethanol were found to be generally equal to the values for them in water;[6] therefore the solvent composition is not critical in quantitative spectroscopic analysis. The aqueous nature of the solvent easily allows further addition of metal ion salts for "heavy-atom effect" studies.

Room-temperature phosphorescence of a typical compound, pyrene

Previous RTP studies dealing with ionic compounds indicated that the strength of the ionic bond between the analyte and the substrate might provide the necessary rigidity to reduce radiationless deactivation. This work reports the phosphorescence properties of pyrene under various experimental conditions, and the results are given in Table 1. A solution of pyrene in the water–ethanol solution showed no significant phosphorescence signal at room temperature, as expected (sample 1). Replacement of water by 1*M* sodium hydroxide in the solution gave no emission enhancement (sample 6). This is in agreement with the assumption[1–4] that ionic compounds must have molecular rigidity, through adsorption on the substrate, to give rise to phosphorescence emission. It is well known that the introduction of a heavy atom into a matrix enhances the phosphorescence signal owing to the increase in the spin–orbit coupling of the singlet and triplet excited states.[7] This external heavy-atom effect with sodium iodide was previously[4] successfully used to enhance the phosphorimetric

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Table 1. Room temperature phosphorescence of pyrene under various experimental conditions
(λ_{em} = 600 nm; λ_{ex} = 330 nm)

Sample	Sample environment				Relative phosphorescence intensity
	$AgNO_3$	Paper pretreated with $AgNO_3$	NaOH	NaI	
1					0
2a	0.05*M*				2
2b	0.1*M*				100
3		0.1*M*			0.1
4	0.05*M*	0.1*M*			0.1
5	0.05*M*			0.5*M*	Precipitate
6			0.5*M*		0
7			0.5*M*	0.5*M*	$\ll$0.1
8	0.05*M*		0.5*M*	0.5*M*	Precipitate
9		0.1*M*	0.5*M*	0.5*M*	1

limits of detection of several compounds of ionic nature. With polyaromatic hydrocarbons, the addition of sodium iodide induced only a weak phosphorescence signal (sample 7).

However, when silver nitrate was used, an intense phosphorescence emission could be observed, indicating that the silver ion is a more efficient heavy-atom perturber for these compounds (samples 2a and 2b). The use of support paper pretreated with silver nitrate also led to the observation of a weak phosphorescence signal (sample 3). Different combinations of the various experimental parameters were also investigated; the simultaneous use of silver nitrate and pretreated paper did not improve the phosphorescence (sample 4), whereas experiments with pretreated paper and solvent containing sodium hydroxide and iodide gave rise to a phosphorescence signal of moderate intensity (sample 9). Although general conclusions cannot yet be drawn from these preliminary investigations, some observations are made which should be helpful in future research. In contrast to the case with ionic molecules, strongly basic (or acidic) solvents will probably not be helpful in increasing the phosphorescence intensity of polyaromatic hydrocarbons unless other kinds of substrate are used. On the other hand, the heavy-atom effect of specific metal ions should be quite efficient in inducing triplet radiative emission (internally bound heavy atom).[8,9]

Influence of silver nitrate concentration

The phosphorescence of pyrene was found to be directly proportional to the concentration of silver nitrate present, but it was necessary to measure also the emission from the paper itself, as this was also dependent on the heavy-atom concentration. The limited solubility of silver nitrate in the ethanol–water mixture did not allow measurements with silver concentrations higher than 0.05*M* when fairly large amounts ($\sim 10^{-4}M$) of the analyte were also present.

Analytical calibration curve

The calibration curve for pyrene on filter paper pretreated with 0.05*M* silver nitrate in 1:1 ethanol–water mixture is shown in Fig. 1. The slope of the linear part of the log–log curve is close to unity. The range of linearity is approximately 10^{-5}–$10^{-4}M$, the upper limit being set by the solubility of pyrene in the solvent used.

Phosphorescence of carbazole

Carbazole was chosen for the present studies for several reasons. Compared with the other heterocyclic compounds which have been investigated,[4] this molecule has a simpler structure with only one nitrogen atom. It has two benzenoid rings and like the polyaromatic hydrocarbons its lowest triplet is $\pi\pi^*$. However, owing to the presence of

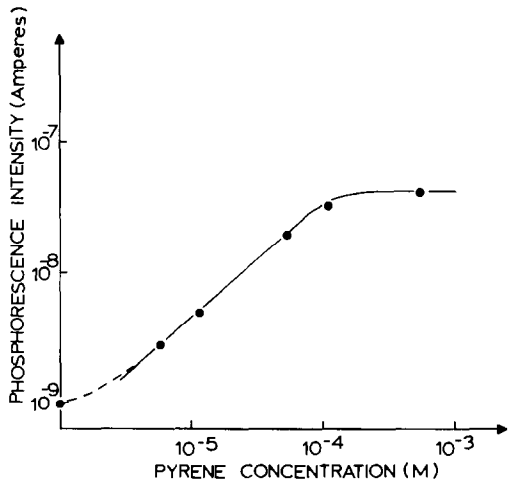

Fig. 1. Analytical calibration curve of pyrene (phosphorescence signal *vs.* pyrene concentration).

the nitrogen atom, this compound has phosphorescence properties at room temperature which are similar to those of molecules of ionic nature. The room-temperature phosphorescence spectra of carbazole adsorbed on filter paper from 0.5*M* sodium hydroxide–sodium iodide or 0.05*M* silver nitrate are shown in Fig. 2. In 0.5*M* sodium hydroxide alone, carbazole shows only a weak phosphorescence emission. However, the phosphorescence intensity was greatly increased by the addition of sodium iodide. This heavy-atom solvent has proved to be much less effective in enhancing the phosphorescence emission of polyaromatic hydrocarbons. On the other hand, silver ion, which is a very efficient heavy-atom perturber for the polyaromatic hydrocarbons, has a less significant effect than the sodium iodide–hydroxide system with carbazole. Carbazole has similar spectroscopic behaviour to ionic compounds because in strongly basic solvents it can be deprotonated at the nitrogen position, thus becoming an ionic species which could be rigidly adsorbed on the substrate.

Limits of phosphorimetric detection

Table 2 reports the limits of phosphorimetric detection of carbazole and five polyaromatic molecules. A comparison with spectroscopic data obtained without heavy-atom perturbers is not given, because in most cases the phosphorescence emissions were not significant when solvents containing heavy atoms were not used. Phenanthrene,

Table 2. Phosphorometric limits of detection for several aromatic hydrocarbons

	λ_{ex} (nm)	λ_{em} (nm)	LOD (M)	LOD (ng)	Remarks
Phenanthrene	345	510	1×10^{-6}	0.9	$AgNO_3$(0.05M)
			3.5×10^{-5}	31.0	
Pyrene	330	600	1.3×10^{-6}	1.3	$AgNO_3$
			W.S.	—	NaOH:NaI(1M)
Carbazole	323	435	8×10^{-7}	0.7	NaOH:NaI(1M)
			W.S.	—	$AgNO_3$
Benzo(a)pyrene	360	680	W.S.		$AgNO_3$
			W.S.	—	NaOH:NaI
Coronene	340	520	W.S.		$AgNO_3$
			no signal	—	NaOH:NaI
Anthracene	375	500	W.S.		$AgNO_3$
			W.S.	—	NaOH:NaI

λ_{ex} = excitation wavelength, in nm; λ_{em} = emission wavelength, in nm; LOD = limit of detection; the limit of detection is defined as the concentration of analyte resulting in a signal-to-noise ratio of 2; W.S. = weak signal–analyte intensity ($10^{-4}M$ solution) less blank which is less than 20% of the intensity of the blank at the emission wavelength of the analyte.

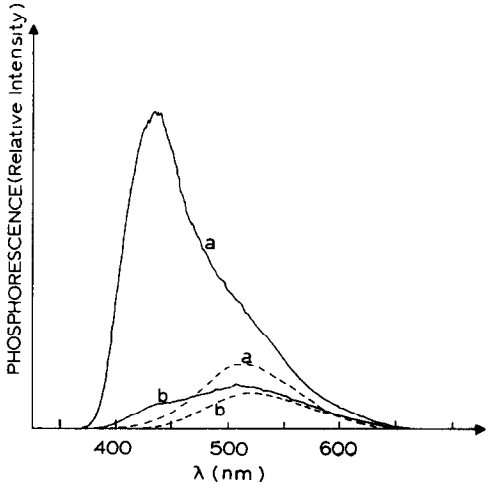

Fig. 2. Room-temperature phosphorescence spectra of carbazole (concentration: $3 \times 10^{-4}M$). a. Carbazole with 0.5M NaOH:NaI (1:1) (solid line), blank emission (dashed line); b. Carbazole with 0.05M $AgNO_3$ (solid line), blank emission (dashed line).

pyrene and carbazole show low limits of detection; the absolute limits quoted are calculated for a 5-μl sample. On the other hand, benzo[a]pyrene, coronene and anthracene produce only weak phosphorescence signals even in the presence of heavy atom solvents. These results show that the RTP processes depend not only on the nature of the emitting species (ionic or non-ionic) but also on the molecular structure of compounds of the same class.

Conclusion

This study has shown that room-temperature phosphorimetry should be applicable not only to ionic molecules but also to other types of organic compounds, such as polyaromatic hydrocarbons. Although those polyaromatic hydrocarbons which have high fluorescence quantum yields can be easily detected by fluorimetric techniques,[6] phosphorimetry would provide complementary data and permit the use of time-resolved and phase-resolved methods.[10] The heavy atom effects also suggest that the technique of using various heavy atom perturbers which interact differently with specific types of compounds should be applicable in the analysis of multicomponent mixtures

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TALANTA ADVISORY BOARD

The Publisher and Editorial Board of *Talanta* have great pleasure in welcoming Professor Olga Songina to the Advisory Board.

Professor Songina was born in Leningrad and educated there at the Polytechnical Institute, then because of the war worked in Alma-Ata. In 1950 she joined the Chemical Division of the Kazakh State University, and in 1958 obtained the Doctor of Chemical Sciences degree from Moscow University. She is now Professor at the Kazakh State University and leader of the section on the chemistry of the rare elements. She is also a corresponding member of the Kazakh Academy of Sciences. Professor Songina's main speciality is electrochemical analysis, especially amperometric titration of rare elements. She has written two books, "The Rare Elements", Moscow 1951, 1955 and 1963, and "Amperometric Titration", Moscow 1957 and 1967, Polish edition 1973, and is an associate member of IUPAC Section V-5 (electrochemical analysis).

TAL 24/3—A

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GUEST EDITORIAL

Analytical chemistry satisfies two general demands. One is the analytical requirement in different fields of practical life, the other is that of scientific research.

The demand of scientific research is connected with the special requirements of the given research, while that of practical life is more general and it is obvious that analysts should investigate the practical requirements of the various fields of application.

It is interesting to consider as an example the effects of theory in the past and practice in the present on the development of ion-selective electrodes. Theoretically it was necessary to prove whether the Nikolskii equation is valid for the extended scale of the new electrodes, and even now many questions are still open in spite of the further development of our picture of electrode processes.

In the beginning, ion-selective electrodes were only of theoretical interest, but several fields of practical application gave inspiration to further development. In water examination hydrogen-ion, cyanide, chloride and nitrate electrodes have gained wide application, for example. Current research has several objectives, one of them being to ensure and develop the long-term stability of these electrodes, one of the most important of their parameters. At the same time medical and clinical investigations have urged the improvement of microelectrodes; on the one hand it was important to develop micro and tubular electrodes in order to examine reliably small quantities of solutions; on the other, significant research has been done on submicroelectrodes employed for investigations in single cells. In this case 2, 3 or even 4 electrodes are placed in a circle 1–2 μm in diameter. The research on submicroelectrodes is directed partly towards the technology of their preparation, and partly to the solution of the problems of electrical measurements in a system having high input resistance. Further, various types of enzyme-electrode have been developed, primarily to satisfy the practical requirements of biochemistry, and from this has sprung the improvement of electrodes with covered surfaces sensitive to different types of molecules.

Environmental analysis in general has also had an effect on covered-surface electrodes, especially on those with non-active surfaces. In this field the development of gas-sensitive electrodes is of great importance.

All this demonstrates, from a special field of analytical chemistry, how practical life affects research work in analytical chemistry.

Similarly, examples can be given of the opposite side of the interaction: how the improvement of theory in analytical chemistry influences the demands of practical life. It can be demonstrated, over a wide spectrum of present applications, how complete have been the changes caused by development in the various branches of life. The study of the effects of trace elements in agriculture and biochemistry in general, semiconductor technology and fluorescent powders are all examples of fields in which development has been influenced by the extremely rapid improvement of ultramicro analysis. It is not necessary to enumerate further examples, because a genuine analytical chemist who devotes his life to his science always takes into the focus of his work the practical application of his theoretical findings. Even if he works purely in the theoretical field, he always considers the advantages and limits of application of his methods.

Prof. E. Pungor

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TALANTA MINI-REVIEW*

DETERMINATION OF THE CHEMICAL FORMS OF TRACE METALS IN NATURAL WATERS, WITH SPECIAL REFERENCE TO COPPER, LEAD, CADMIUM AND ZINC

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Summary—Methods used to differentiate between the various chemical forms of a metal in a natural water are critically reviewed. The methods range from simple procedures which discriminate between weakly and strongly complexed forms of the metal, to comprehensive analytical schemes which can determine as many as seven species of each metal. The many problems involved in this exacting area of trace analysis are discussed in detail.

Environmental scientists are becoming increasingly aware of the need for reliable methods which can differentiate and determine the chemical forms of trace metals, especially the toxic heavy metals, in natural waters. The common procedure of measuring the *total* concentration of a particular metal in a water sample (*e.g.* by atomic-absorption spectrophotometry) can be very misleading because, depending on the chemical forms of the metal, a water with a high total metal concentration may in fact be *less* toxic than another water with a lower total metal concentration. For example, most workers[1–3] have concluded that ionic copper is far more toxic towards aquatic organisms than organically-bound copper, and that the more stable the copper complex, the lower is its toxicity. Steeman Nielsen and Wium-Andersen[2] have suggested that deep sea-water has a higher ratio of ionic copper to organically-complexed copper than has surface water, and that this could explain why upwelling water is unsuitable for the growth of phytoplankton, even though it is rich in nutrients. In support of this hypothesis, Barber and Ryther[4] found that the addition of a strong chelating agent to upwelling water considerably improved the productivity, a result that was confirmed by Lewis *et al.*[5] who used EDTA to simulate a powerful natural chelating agent.

In general, the toxicity of metals towards aquatic organisms decreases in the order mercury > silver > copper > cadmium > zinc > lead > chromium > nickel > cobalt,[1] although there are some exceptions to this scale. It is often assumed that dissolved metal is the form which is toxic towards fish,[6,7] on the basis that suspended or particulate metal forms (*i.e.*, retained by a 0.45-μm membrane filter) are effectively unavailable to their gills. There is no doubt, however, that *ingested* particles (*e.g.*, sediment eaten with food) can contribute significantly to the body burden of heavy metals in fish, since these metals are rapidly absorbed from the stomach fluids.[8] With bottom-feeding fish, sediments may be more important than water as a source of heavy metals.

Laboratory experiments designed to measure the level of a heavy metal toxic to aquatic organisms have little meaning unless the chemical forms (speciation) of the metal in the test water are known, and extrapolation of results from an experimental test tank to a natural water system (ocean, lake, pond or river) may not be possible if the chemical speciation of the metal in the natural system is unknown.[9] In evaluating the environmental impact of the discharge of heavy metal compounds into an aquatic environment, it is important to determine the extent and rate at which the foreign metal species equilibrate with the natural pool of dissolved metal species in the water. This is equally true whether the metal is non-radioactive, *e.g.*, zinc salts from a zinc refinery, or is a radioactive nuclide from the cooling water of a nuclear power station. Unless the chemical distribution of the polluting metal is known, predictions cannot be made about its effect on aquatic organisms.

In the area of water treatment, knowledge of the chemical forms of dissolved metals is important for efficient operation of the treatment plant. The efficiency of the treatment operation often depends on whether the metal is in ionic, complexed, colloidal or particulate form.

The chemical speciation of trace heavy metals in natural waters is quite obviously a very difficult analytical problem. It is only in the last ten years that reliable techniques have become available to measure metals below the μg/l. level, and even now, few laboratories are competent to work in this area of sub-trace analysis. To attempt then to subdivide each

* For reprints of this Mini-Review see Publisher's announcement near end of this issue TALMR 6.

metal concentration into several chemical fractions is a task of considerable magnitude. Contamination problems are extreme, and the purity of all reagents used is critical. Some of the most sensitive analytical techniques, *e.g.*, neutron-activation analysis and atomic-absorption spectrophotometry, are not applicable to speciation studies because they measure only the *total* metal concentration. Another problem is that most analytical methods and separation procedures used to measure chemical speciation may disturb, to some extent, the equilibria between the various chemical species in solution. Many of these changes in equilibrium may be so slow that significant errors are not incurred, but nevertheless, it is important to attempt to minimize them by choosing rapid separation and analysis procedures.

Although several reviews have been written on the solution equilibria which cause metal speciation in natural waters,[10–13] no comprehensive review is available on the measurement of trace metal speciation. In this paper we have critically reviewed published methods for trace metal speciation in natural waters, with particular reference to the common toxic metals copper, lead, cadmium and zinc. The discussion concerns only the *dissolved* species in the waters, which by convention means that fraction of the metal which is not retained by a 0.45-μm membrane filter.

The methods can be grouped under five broad headings.

Calculation methods

These methods use published stability constant data, together with known concentrations of various ions in the natural water, to compute equilibrium concentrations of the heavy metal species. Until recently, most workers used stability constants singly or in pairs to enable them to calculate the equilibrium concentration of a particular species. This procedure is invalid, because any natural water contains many metals capable of reacting with each ligand, and many ligands which can react with each metal. The correct equilibrium concentration of any species can be computed only by simultaneously taking into account all of the competing equilibria. This task is too laborious for manual calculation, and computer programs are now available for application to the problem.[14–17]

Despite these advances in computational techniques, they are still of very limited value when applied to natural waters, mainly because of our imperfect knowledge of these systems. No data are available on metal ion interactions with many of the natural organic ligands present in the waters, and indeed even the nature and concentration of these ligands is usually unknown. More important perhaps, almost nothing is known about the concentration of organic and inorganic colloidal particles or their metal-binding ability. For these reasons the results from even the most sophisticated computer model of trace metal speciation in natural waters bear little, if any, relation to reality.

Separation methods

Dialysis, ultrafiltration and centrifugation have been used to separate "ionic" metal in natural waters from metal associated with colloidal material. Benes and Steinnes, in two authoritative and comprehensive papers[18,19] studied a large number of elements in river and lake waters by using dialysis (including *in situ* dialysis), ultrafiltration, centrifugation, ion-exchange and electrophoresis. Their results indicated that most uni- and bivalent metals exist in water predominantly as simple cationic species. Tervalent and quadrivalent metals (*e.g.*, Al^{3+} and Th^{4+}) are mostly adsorbed on colloidal particles.

Hooper[20] used dialysis to separate colloidal and dissolved iron in an acid bog lake (pH 4–5). He found that in surface samples most of the iron was in the tervalent state and was adsorbed on organic colloids. The concentration of ionic ferrous iron increased with depth.

Rona *et al.*[21] studied the chemical forms of zinc and manganese in sea-water, by using dialysis and ultrafiltration. They found that a high percentage of zinc and manganese exists in sea-water in the form of high molecular-weight complexes. These authors concluded that rapid co-precipitation with ferric hydroxide is effective for collecting zinc and colloidal and particulate forms of manganese from sea-water, but that very slow precipitation of ferric hydroxide is needed to collect ionic manganese quantitatively.

Slowey and Hood[22] applied dialysis and solvent extraction to separate different forms of zinc in sea-water. They found that 70% of the dissolved zinc was dialysable, and concluded that the non-dialysable zinc was associated with organic matter.

There are several experimental difficulties associated with the use of dialysis and ultrafiltration for the analysis of natural waters for trace metals.[23] Adsorption on the membrane can seriously affect the results from both techniques, and in dialysis, diffusion of negatively-charged complexes may be very slow.[19] We have found that metal contamination is also a vexing problem. Dialysis tubes need to be washed for an exceptionally long time before acceptable blanks are obtained, and ultrafiltration cells are likewise liable to contaminate the sample. Rubber O-rings contain high concentrations of readily leachable zinc and cadmium, and must always be avoided.

Slowey *et al.*[24] found that when 500-ml samples of filtered sea-water were extracted with three 15-ml portions of chloroform, 10–60% of the total copper present was transferred into the organic phase. There was no relationship between chloroform-extractable copper and the depth at which the sample was taken. This technique probably gives low results for organically-bound copper. Charged copper complexes would not be extracted and copper adsorbed on organic colloids may be only partially extracted. On the other hand, some of the copper adsorbed on inorganic colloidal particles may be included in the

measurement, since these colloids tend to accumulate at the phase interface.

Ion-exchange techniques have been applied to metal speciation in natural waters. Filby *et al.*[25] passed the filtered water sample sequentially through anion- and cation-exchange resins. Dissolved metal was divided this way into anion-exchangeable, cation-exchangeable and neutral (adsorbed by neither resin). In three rivers studied, the majority of the zinc was adsorbed on the cation-exchanger, but in a fourth river, 87% of the zinc was retained by the anion-exchange resin.

Florence and Batley[17,26] applied the chelating resin Chelex-100 to the determination of the chemical forms of copper, lead, cadmium and zinc in sea-water. The chelating resin was found to remove these metals only partially from sea-water, even though ionic spikes were adsorbed with nearly 100% efficiency. Muzzarelli and Rochetti[27] also reported that Chelex-100 resin removes only a small fraction of the total copper present in sea-water. Florence and Batley[17] suggested that most of the trace metal which is not removed by the resin is associated with organic and inorganic colloidal particles, since these colloids are too large to enter the resin pores. These authors pointed out the danger of using ionic spikes (either radioactive or inactive) to measure the recovery of trace metals in natural waters. The recovery of an ionic spike may bear no relation to the recovery of a metal naturally present in the water.

Bender *et al.*[28] used gel filtration chromatography (Sephadex G-50) to study the forms of copper in sewage effluents. No free copper was found in the samples, which produced two distinct chromatographic peaks; the first contained about 13% of the copper in the sample and was associated with molecular weights of 10^4 or greater, while the remaining copper was in the second peak, equivalent to molecular weights in the range 500–1000.

Gel filtration is very difficult to use for determining metals in unpolluted natural waters[29] because of the small sample volumes that can be used, and the high ratio of solvent/sample volume, which usually results in large blanks.

Direct physicochemical measurements

Some electrochemical techniques have been used directly in an attempt to differentiate between chemical forms of metals in natural waters. The copper ion-selective electrode was used[30] to measure free cupric ion activity in sea-water at concentrations as low as 0.6 μg/l. The application of these electrodes to copper concentrations lower than $10^{-7}M$ is, however, fraught with many difficulties,[31] and great care must be exercised in their use and in the interpretation of the potential-readings. At the concentration of copper in natural waters it may take 30–60 min before stable potentials are obtained. The ion-selective electrodes which are available for zinc, lead and cadmium are unsuitable for use in natural waters.

The shift in polarographic half-wave potential with change in pH has been studied for natural waters, and the shifts related to the nature and stability of complex metal species present.[32,33] Other workers[34–37] have used the position, height and shape of anodic stripping voltammetric (a.s.v.) peaks to make similar calculations on the chemical forms of copper, lead and zinc in natural waters.

While polarographic half-wave potential shifts have been successfully used to determine metal–ligand stability constants in synthetic solutions, it is extremely doubtful whether this technique can be extended to trace heavy metals in natural waters. Besides having very low concentrations of the metal under study, the natural systems contain a wide variety of complexing agents. Hume and Carter[38] attempted to repeat Matson's[34] results, but failed to do so. They found that many of the effects that Matson attributed to complex formation could be explained on the basis of variations in the preparation of the thin-film mercury electrode. They concluded that it was very unlikely that quantitative information about complex formation in natural waters could be obtained by direct a.s.v. techniques.

Physicochemical measurements after chemical treatment

Various workers have used selective chemical reaction techniques in attempts to distinguish between chemical forms of a metal in natural waters. Corcoran and Alexander[39] determined copper in sea-water by extraction with dithizone before and after oxidation with perchloric acid. The difference in copper concentration was equated to organically-bound copper. These same workers carried out another study on copper in sea-water, but used neocuproine instead of dithizone.[40] Williams[41] and Foster and Morris[42] performed similar experiments but used diethyldithiocarbamate to determine copper, and ultraviolet irradiation to destroy organic matter. These methods generally showed that 5–30% of the copper was present in organic form. Fukai and co-workers[43,44] determined "extractable" and total zinc in sea-water by using dithizone extraction before and after oxidation of the sample with persulphate. Morris[45] studied the concentrations of ionic and organically-associated zinc, copper and nickel in water from the Menai Straits. A portion of each water was irradiated with ultraviolet light before it was passed through a column of Chelex-100 chelating resin. After elution, the metals were determined by X-ray fluorescence. A second aliquot of each water was treated in the same way, but without the irradiation, and the difference between the two results was ascribed to strongly bound organically-associated metal.

As pointed out by Kamp-Neilsen,[46] the chelation–extraction methods probably seriously underestimate the percentage of organic copper in the waters. Dithizone and diethyldithiocarbamate form exceptionally strong complexes with copper, and would decompose

most, if not all, copper complexes with natural ligands. Kamp-Nielsen calculated that the stability constant of a natural copper complex would have to be greater than 10^{30} to avoid decomposition by diethyldithiocarbamate. Perhaps the only form of organic copper that would partially escape extraction would be that which is occluded in, or adsorbed on, colloidal organic particles.

Florence[47] determined "reactive" iron in fresh water by reacting the sample with bismuth–EDTA complex. Bismuth was displaced from the complex by iron, and the liberated Bi^{3+} was determined with high sensitivity by a.s.v. Total iron was measured in the same way after the sample had been fumed with perchloric acid. Less than 1% of the iron in demineralized water, and only 9% of that in tap-water, was found to be in a reactive form.

The simplest a.s.v. procedure for chemical speciation in waters is the determination of labile (*i.e.*, weakly complexed) and total metal. Total copper, lead, cadmium and zinc have been measured by a.s.v. after ultraviolet irradiation,[48] persulphate oxidation[49] and heating with dilute nitric acid.[17,26] Acid-exchangeable metal is sometimes used in place of total metal.[50] Labile metal is measured in faintly acid solution, often with an acetate buffer, by direct a.s.v.;[17,26,49,51] the result represents free metal ion plus metal dissociated at the electrode surface from complexes and colloids. The difference between total and labile metal has been called "bound" metal (*i.e.*, strongly complexed),[26] and as a crude approximation may be regarded as metal bound in inert complexes and other inert forms such as colloidal particles. Florence and Batley[52] found, using a.s.v. techniques, that most of the copper present in sea-water is complexed with or adsorbed on organic matter,[53] and that a smaller percentage is associated with inorganic colloids. Equilibration studies with ionic copper-64 added to sea-water showed that after 6 hr only 50% exchange had taken place with the naturally present copper, thus confirming the inert nature of the bound fraction.

Piro *et al.*[54] described an a.s.v. technique for differentiating between ionic, particulate and complexed zinc in sea-water. The first a.s.v. measurement at the natural pH (pH 8.1) gave ionic zinc. The pH was then lowered to 6, and the increase in peak height represented particulate zinc. Finally the pH was lowered to 2, and the increase over the pH 6 result was attributed to complexed zinc. In one sample of sea-water this method indicated that 40% of the total zinc was complexed, and 42% associated with particulate matter. Small *et al.*[55] used this technique to determine the chemical forms of zinc excreted by prawns.

The assigning of ionic, particulate and complexed zinc to the three pH ranges is somewhat arbitrary. Certainly there could be some particulate forms from which zinc would not be released at pH 6. Also, adjusting sea-water to pH 2 at room temperature does not yield total zinc. The sample must be oxidized[56] or boiled after acidification to below pH 2 to liberate all the zinc present.[17,26]

Stiff[57] presented a comprehensive scheme for the chemical speciation of dissolved copper in polluted fresh water. The analysis scheme involves the following operations. (*a*) Measurement of the free cupric ion activity with a copper ion-selective electrode. (*b*) After measurement of the pH and bicarbonate concentrations, calculation of the concentration of $CuCO_3$ from the known equilibrium constant. (*c*) Determination of copper complexed by "cyanide-like" ligands, from the difference between spectrophotometric copper determinations using neocuproine after nitric acid digestion, and the reagent 3-propyl-5-hydroxy-5-D-*arabino*-tetrahydroxybutyl-3-thiazolidine-2-thione (PHTTT) directly; cyanide and other powerful ligands interfere quantitatively in the reaction between copper and PHTTT, whereas neocuproine, after acid digestion, gives total copper. (*d*) Extraction of the water with hexanol; hexanol-soluble copper was assumed to be associated with humic substances. (*e*) Ascription of the difference between total copper and Cu^{2+} + $CuCO_3$ + Cu-cyanide complexes + Cu-humic complexes to copper present as amino and polypeptide complexes, and carbonate complexes other than $CuCO_3$.

Stiff applied this scheme only to polluted waters containing 100–1000 μg/l. levels of copper, *i.e.*, copper concentrations two orders of magnitude higher than those found in most natural waters. Considerable modification would be necessary before it could be used at natural levels of copper. Also, several questionable assumptions were made, *e.g.*, in the calculation of $CuCO_3$ concentration, in the description of all hexanol-soluble copper as being complexed by humic substances, and in the assigning of all remaining copper to amino and polypeptide complexes.

Fukai and Huynh-Ngoc[56] reviewed methods used to determine the chemical forms of zinc in sea-water, and compared dithizone extraction, chelating resin separation, co-precipitation on ferric hydroxide, and anodic stripping voltammetry for the determination of reactive and non-reactive zinc in sea-water. As a result of this comprehensive study they concluded that (*a*) the zinc concentration measured by dithizone extraction at pH 7 is similar to that determined by a.s.v. at pH 8, and corresponds to ionic plus other labile forms of zinc, (*b*) separation of zinc from sea-water by chelating resin adsorption or ferric hydroxide precipitation measures labile zinc plus some of the zinc combined as colloids and organic complexes, and yields results similar to those obtained by a.s.v. at pH 4. With all methods tested, total zinc could be determined only after strong oxidation of the sea-water, *e.g.*, with persulphate. Fukai and Huynh-Ngoc believed that strong oxidation was necessary to release zinc from "bound" forms such as colloids and strong organic complexes, although Florence and Batley[17] found that acidification of the sea-water sample to pH 1.5 with nitric acid, followed by heating

to boiling, was sufficient to convert all the metal into a form which could be measured by a.s.v.

All work with μg/l. levels of zinc is beset by contamination problems. Zinc contamination seems to occur more frequently than contamination by most other metals, and very careful technique is needed to minimize this problem.

The chemical speciation technique developed in our laboratories for copper, lead, cadmium and zinc in natural waters[17,58–60] involves the conventional a.s.v. labile–total metal differentiation, but also includes an ultraviolet irradiation step to destroy organic matter, as well as passage through a chelating resin column to separate metal contained in colloidal matter from metal which is chelated by the resin. The sequence of operations (Fig. 1) is as follows.

(*a*) Three 100-ml aliquots of the filtered water are treated with 0.05 ml of 30% H_2O_2 per 100 ml, then irradiated in silica tubes for 6 hours with ultraviolet light from a 550-W lamp. Total organic carbon measurements showed that this procedure completely oxidized organic matter in both fresh-water and sea-water. (*b*) While the ultraviolet irradiation is proceeding, labile and total metal measurements for Cu, Pb, Cd and Zn are made by a.s.v. on another aliquot of filtered water. Labile metal is measured[17] in 0.016*M* acetate buffer (pH 4.8), while total metal is determined in sea-water after boiling of the sample (acidified with 0.16*M* nitric acid), and in fresh-water after fuming with perchloric acid–nitric acid mixture. Labile and total metal are then measured on the irradiated water. (*c*) Aliquots of both the original filtrate and the irradiated filtrate are passed through 10 × 0.8 cm columns of 100–200 mesh Chelex-100 (Na^+-form for sea-water, NH_4^+-form for fresh-water) chelating resin. Labile and total metal measurements are made on the column effluents.

This a.s.v. scheme yields four labile and four total metal results for each metal. By subtraction, four bound metal results (bound = total minus labile) are also obtained. From these eight measurements, seven groups of species can be quantified (Fig. 1).

M + *ML*1 + *MA*1. In sea-water at natural pH this group will consist principally of simple inorganic complexes[17] such as chloride, sulphate, carbonate and hydroxide. In fresh-water, citrate and amino-acid complexes may be present.

*MA*2, *MA*4, *ML*2, *ML*4. Since significant concentrations of metal complexes stronger than the corresponding metal–Chelex-100 complexes are unlikely to be present in sea-water,[61] these species would be mainly metal adsorbed on, or occluded in, organic and inorganic colloidal particles. The situation may be different in fresh-water, which generally has a higher organic content, and hence possibly higher concentrations of strongly chelating organic ligands such as humic and fulvic acids.[12,29]

*MA*3, *ML*3. There is undoubtedly some overlap between the experimental classes determined in this speciation scheme. The MA3 and ML3 species may include some metal dissociated from colloids and retained by the resin. This group could also include some of the humic and fulvic acid complexes, which should be at least partially dissociated by Chelex-100 resin.[61–63]

Oxidation state determination

Determination of the ratio of two oxidation states of a metal in solution is a special case of speciation. In natural waters the main interest in oxidation state determination has been directed towards chromium, because of the high toxicity of chromium(VI) compared with chromium(III). Fukai and Vas[64] made use

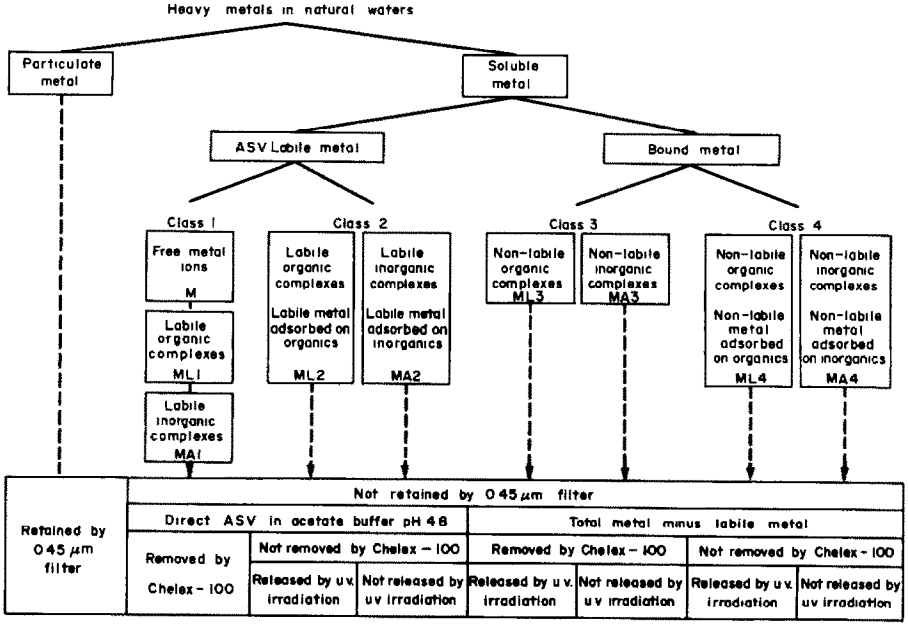

Fig. 1. Analytical scheme for the chemical speciation of trace metals in natural waters.

of the observation that Cr(III) is quantitatively co-precipitated on ferric hydroxide, whereas Cr(VI) shows little tendency to co-precipitate. They found that in most samples of sea-water studied, the concentration of Cr(VI) exceeded that of Cr(III), whereas Chuecas and Riley,[65] using a similar method, found the reverse to be true. Elderfield[66] pointed out that thermodynamic considerations predict that Cr(VI) should predominate in sea-water in equilibrium with the atmosphere. However, when he applied the method of Fukai and Vas[64] to samples of coastal sea-water he found, in fact, that most of the chromium was present as Cr(III).

Gohda[67] studied the oxidation states of arsenic and antimony in sea-water, using solvent extraction and co-precipitation. He found that both of these elements are predominantly in the quinquevalent state.

Batley and Florence[68] calculated from thermodynamic data that thallium in sea-water should exist almost entirely as Tl(III). Anion-exchange studies on sea-water tended to confirm that thallium is present mainly as Tl(III) chloro-complexes.

Metal-complexing ability of waters

The metal-complexing capacity of natural waters can be determined by an a.s.v. titration technique.[69–71] Successive additions of a standard copper solution are made to a sample of the water, and the a.s.v. peak height is plotted as a function of added copper concentration.[23] When all copper-complexing material has been consumed, there will be a sudden increase in the slope of the curve. The break-point represents the copper-complexing capacity of the water.

Florence and Batley[52] found that the copper-complexing capacity of surface sea-water was about $1 \times 10^{-8} M$, whereas Chau *et al.*[69] found that various river and lake waters had values in the range $1–7 \times 10^{-7} M$ Cu. Davey *et al.*[72] determined the copper-complexing ability of artificial sea-water by measuring the effect of copper additions on the growth of *Thalassiosira pseudonana*.

Storage of water samples for speciation measurements

The storage of water samples for chemical speciation measurements poses a difficult problem, because normal preservation methods, such as acidification, cannot be used since they would affect the speciation. Even freezing may irreversibly alter the distribution of the chemical forms of trace metals, yet if no preservation is used, significant changes in the water can occur quite rapidly.[18,73]

Preliminary work in our laboratory suggests that storage of the samples at 4° may enable both fresh-water and sea-water samples to be kept for a considerable time without alteration of the speciation of copper, lead, cadmium or zinc.[74]

DISCUSSION

The *total* concentrations of dissolved copper, lead, cadmium and zinc in many unpolluted fresh-water rivers throughout the world appear to be very similar,[75–77] and are in the range (μg/l.): zinc, 2–10; cadmium, 0.1–0.5; lead, 0.2–2; copper, 0.3–3. The distribution of the chemical forms of these metals, however, may vary considerably. Table 1 lists examples of some of the dissolved species that may exist in natural waters.

In the past, the presence of soluble, stable, metal–organic complexes in natural waters has been overemphasised at the expense of appreciation of the influence of colloidal particles, both organic and inorganic. Breger[78] has presented persuasive arguments that most of the dissolved organic matter in natural waters exists as colloidal particles. Inorganic colloids, including hydrated iron and manganese oxides, silica, clays and sulphides[79–81] and organic colloids from humic substances and animal and plant detritus[78,81,82] are powerful reagents for the adsorption and occlusion of trace heavy metals.

It is difficult at the present time to conceive of an analytical scheme which will unambiguously define all the various dissolved metal species present in a natural water. The analytical problems appear to be too complex, and some disturbance of the solution equilibria by the analytical measurements must inevitably take place. Nevertheless, considerable progress has been made in recent years in our ability to define certain classes of metal species in natural waters, *e.g.*, labile (weakly complexed) and bound (strongly complexed). These two main divisions can be further sub-

Table 1. Speciation of dissolved copper, lead, cadmium and zinc in natural waters

Chemical form	Examples
Particulate matter	retained by 0.45-μm filter
Simple hydrated metal ions	Cu^{2+}, Zn^{2+}
Simple metal–inorganic complexes	$CdCl_4^{2-}$, $PbSO_4$, $ZnCO_3$
Simple metal–organic complexes	Cu–glycinate, Zn–citrate
Stable metal–inorganic complexes	CuS, $PbSiO_3$, Cu–pyrites
Stable metal–organic complexes	Cu–humate, Zn–cysteinate
Metal adsorbed on, or occluded in, inorganic colloids	Pb^{2+}–Fe_2O_3, Cd^{2+}–MnO_2, Zn^{2+}–clay, Cu^{2+}–apatite
Metal adsorbed on, or occluded in, organic colloids	Cu^{2+} humic acid, Cu^{2+}–organic detritus

divided into inorganic, organic, ionic and colloidal fractions. Detailed analysis of a water sample in this way will prove of considerable value to chemists and biologists in their studies of trace metal toxicity towards aquatic organisms, and of the fate of metal pollutants added to natural waters.

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IMPROVED SCHEME FOR THE ANALYSIS OF HIGH-PURITY TALC

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Summary—An improved method is proposed for the determination of silica, magnesium oxide, R_2O_3, ferric oxide, calcium oxide, and aluminium oxide in high-purity talc. In the method for silica and magnesium oxide, the sample is fused with sodium carbonate and the cooled melt is dissolved with perchloric acid in such a manner that it floats free from the crucible (in previous schemes for the analysis of talc there are frequently mechanical losses due to the difficulty of removing the magnesium silicate melt from the crucible). The solution is then evaporated to fumes of perchloric acid and the silica is filtered off and ignited. The magnesium oxide is determined in the filtrate by precipitation as magnesium ammonium phosphate and a correction is made for the calcium which is precipitated along with the magnesium ammonium phosphate. R_2O_3 is determined after treatment of the sample with nitric and hydrofluoric acids and evaporation to fumes of perchloric acid. Iron oxide and calcium oxide are determined by atomic absorption, after treatment with nitric and hydrofluoric acids and evaporation to fumes of perchloric acid. Al_2O_3 is calculated by difference.

High-purity talc has many uses in explosives,[1–5] so this arsenal was interested in methods for its analysis.

Talc is a naturally occurring hydrated magnesium silicate with the approximate formula $3MgO \cdot 4SiO_2 \cdot H_2O$ [or $Mg_3Si_4O_{10}(OH)_2$], equivalent to 63.4% SiO_2, 31.9% MgO, and 4.7% H_2O.[6,7] It is not to be confused with artificially produced magnesium silicate which has the approximate formula $3MgSiO_3 \cdot 5H_2O$ (equivalent to 46.1% SiO_2, 30.9% MgO, and 23.0% H_2O).[6] Talc is very difficult to identify microscopically and positive identification is best made by a complete chemical analysis.[7]

Several schemes have been proposed for the analysis of talc. The ASTM[8] recommends the classical scheme for determining silica, R_2O_3, calcium oxide and magnesium oxide, in which the sample is fused with sodium carbonate, the cooled melt dissolved in water, and the silica dehydrated by evaporation to dryness with hydrochloric acid. The silica is ignited and treated with hydrofluoric acid in the usual manner, the residue is fused with potassium bisulphate, and the cooled melt is dissolved and combined with the silica filtrate. An R_2O_3 precipitation is then made and the calcium oxide is determined by the gravimetric oxalate method and the magnesium oxide by the phosphate method. The ASTM[8] also describes methods for moisture, loss on ignition, water-soluble matter, pH, and sieve analysis. The American Ceramic Society[9] determines silica, R_2O_3, calcium oxide and magnesium oxide somewhat similarly to the ASTM but the precipitated calcium oxalate is titrated with permanganate; also, the R_2O_3 precipitate is treated with hydrofluoric acid to eliminate the silica and the result for "carried silica" is added to the total silica. The American Ceramic Society[9] also describes methods for alkali metals, moisture, loss on ignition, acid-soluble matter, pH and sieve analysis. The government specification for technical-grade talc (used to simulate battlefield conditions)[10] describes methods for silica and magnesium oxide similar to the ASTM methods. TAPPI[7] determines silica, R_2O_3, magnesium oxide and calcium oxide by fusion with sodium carbonate, dissolution of the melt in hydrochloric acid, addition of gelatin to coagulate the silica, precipitation of the R_2O_3, and determination of calcium oxide and magnesium oxide in the R_2O_3 filtrate by EDTA titration. TAPPI[7] also describes methods for moisture, loss in ignition, pH and sieve analysis. Kysela[11] determined silica, R_2O_3, magnesium oxide and calcium oxide by fusion with a mixture of sodium carbonate, potassium carbonate and sodium borate, dissolution of the melt in hydrochloric acid, evaporation to dryness, addition of glycerol to coagulate the silica, precipitation of the R_2O_3 in the silica filtrate, and determination of the calcium oxide and magnesium oxide by EDTA titration. Yurist and Korotkova[12] determined silica, magnesium oxide, calcium oxide, iron oxide and aluminium oxide in talc by fusion with potassium bisulphate, dissolution of the melt in dilute sulphuric acid, collection of the silica, and determination of the magnesium, calcium, iron and aluminium in the filtrate by a rather intricate system of EDTA titrations. Ohtsuki, Nakagawa and Maeda[13] determined magnesium oxide, calcium oxide and iron oxide in talc by atomic absorption, after treatment with hydrofluoric and sulphuric acids and evaporation to dryness.

A disadvantage of methods that involve an initial fusion is the considerable difficulty encountered in

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bringing the melt into solution after the fusion. This trouble stems from the fact that the magnesium silicate makes the melt difficultly soluble in water, hydrochloric acid or sulphuric acid. Frequently, the melt can be removed from the crucible only by prolonged boiling with water or dilute acid, but when this technique is used the crucible becomes coated with a slimy mass of salts (magnesium silicate) that adhere tenaciously and cause significant mechanical losses. Another disadvantage of the common methods is that silica cannot be completely recovered by one evaporation with hydrochloric acid.

In the present paper an improved scheme is proposed for the analysis of talc. The silica and magnesium oxide are determined by fusion with sodium carbonate and dissolution of the cooled melt with perchloric acid in such a manner that it floats out of the crucible. The solution is then evaporated to fumes of perchloric acid and the silica is filtered off and ignited. The magnesium oxide is determined in the filtrate by precipitation as magnesium ammonium phosphate and a correction is made for calcium. R_2O_3 is determined after treatment of a sample with nitric and hydrofluoric acids and evaporation to fumes of perchloric acid. Ferric oxide and calcium oxide are determined by atomic absorption after treatment of a sample with nitric and hydrofluoric acids and evaporation to fumes of perchloric acid. The aluminium oxide is calculated by difference.

EXPERIMENTAL

Silica and magnesium oxide

Place 2 g of sodium carbonate on the bottom of a platinum crucible and weigh. Add about 0.5 g of the talc and weigh to obtain the exact weight of the sample. Mix the sample with the sodium carbonate by means of a small spatula and brush off the spatula. Place 2 g of sodium carbonate on top of the mixture, cover with a platinum lid, heat with a Méker burner at moderate heat for a few min, and then at highest heat for 30 min. Remove the lid and place it in a covered 1-litre beaker. While the crucible is still in the flame, grasp its outside with tongs (do not insert the tongs into the crucible) and tilt it in such a manner that the melt reaches to within 1/4 in of the top of the crucible. Keeping the crucible tilted the whole time, remove it from the flame and dip it intermittently every few seconds into a tray of tap water. Do not allow water to enter the crucible. When the melt has completely solidified, turn the crucible upright and dip it into the water a few more times. Allow the melt to cool thoroughly to room temperature (this is important). Place the crucible upright in the 1-litre beaker.

Pour 75 ml of perchloric acid (5 volumes of 70% perchloric acid mixed with 1 volume of water) onto the crucible and immediately cover the beaker with a clock-glass. Wait about 1 min, tip over the crucible and swirl the beaker. The melt will float free from the crucible. Wash down and remove the lid and the crucible. Add 20 ml of dilute hydrochloric acid (1 + 2) to the crucible and "policeman" the crucible with water, collecting the washings in the 1-litre beaker. Warm the 1-litre beaker on the hot-plate for a few min and break up the cake with a stirring rod. Evaporate to fumes of perchloric acid and fume at the highest heat of the hot-plate for 20 min. Allow to cool, add about 200 ml of water and stir to dissolve the salts. Filter (Whatman No. 41 paper) into a 400-ml beaker and wash with water. Save the filtrate for the determination of magnesium oxide. Char and burn off the filter paper in a platinum crucible and then ignite at 1100° for 30 min. Cool and weigh. Add 5 ml of hydrofluoric acid (48%) and 2 drops of sulphuric acid and evaporate to dryness. Ignite at 900° for 10 min, cool, weigh and calculate the amount of SiO_2 from the loss in weight.

Add 5 ml of hydrochloric acid to the crucible from the silica ignition, heat on the hot-plate a few minutes, and wash the solution into the filtrate from the silica determination. Heat the solution to about 90°, add ammonia solution (1 + 1) until the solution is alkaline to Methyl Red, and then 2 or 3 drops more. Boil for a minute, adding more ammonia, if necessary, to maintain alkalinity. Filter (Whatman No. 40 paper) into a 600-ml beaker and wash with hot 2% ammonium chloride solution. If the residue is very large, redissolve it in hot dilute hydrochloric acid (1 + 3) and reprecipitate the R_2O_3. Add hydrochloric acid to the (combined) filtrate(s) until the solution is just acid to Methyl Red, and then 5 drops more. Dilute to about 300 ml. Add 50 ml of 25% diammonium hydrogen phosphate solution and then immediately add ammonia solution dropwise with continual stirring until precipitation appears complete; then add 35 ml of ammonia solution and continue stirring intermittently for several min. Allow to stand for 3 hr or more. Filter off on Whatman No. 40 paper, transferring and washing the precipitate with dilute ammonia solution (1 + 19). Dissolve the precipitate into the original beaker with warm dilute hydrochloric acid (1 + 3) and wash the paper with water. Dilute to

Table 1. Effect of perchloric acid (ammonium perchlorate) and sodium chloride on the precipitation of magnesium ammonium phosphate

Added to 0.1600 g of MgO	No. of precipitations	MgO found, *g*
1 ml HCl	1	0.1597
5 ml $HClO_4$	1	0.1602
10 ml $HClO_4$	1	0.1605
20 ml $HClO_4$	1	0.1609
30 ml $HClO_4$	1	0.1591
5 g NaCl + 1 ml HCl	1	0.1680
5 g NaCl + 10 ml $HClO_4$	1	0.1670
5 g NaCl + 20 ml $HClO_4$	1	0.1683
5 g NaCl + 30 ml $HClO_4$	1	0.1654
5 g NaCl + 10 ml $HClO_4$	2	0.1596
5 g NaCl + 20 ml $HClO_4$	2	0.1597
5 g NaCl + 30 ml $HClO_4$	2	0.1600
5 g NaCl + 30 ml $HClO_4$	2	0.1598

Table 2. Results for magnesium oxide after correction for calcium oxide [deduction for $Ca_3(PO_4)_2$ in the ignited precipitate]

MgO present, g	CaO present, g	MgO found after correction, g
0.1600	0.0000	0.1601
0.1600	0.0000	0.1596
0.1600	0.0010	0.1598
0.1600	0.0050	0.1600
0.1600	0.0100	0.1604
0.1600	0.0200	0.1608
0.1600	0.0250	0.1606
0.1600	0.0500	0.1610
0.1600	0.1000	0.1611
0.0000	0.0100	0.0004
0.0000	0.0250	0.0003
0.0000	0.0500	−0.0001
0.0000	0.1000	0.0006

about 300 ml. Add 1 ml of 25% diammonium hydrogen phosphate solution and immediately add ammonia solution dropwise with continual stirring until precipitation appears complete; then add 10 ml of ammonia solution and continue stirring intermittently for several min. Allow to stand for 3 hr or more. Filter off and wash as before. Char and burn off the filter paper and then ignite at 1100° for 30 min. Cool and weigh. Calculate the magnesium oxide content as follows:

$$\%MgO = 36.21\ [\text{g of precipitate} - (0.01844 \times \%CaO \text{ in sample} \times \text{g of sample})]/\text{g of sample}$$

R_2O_3

Weigh a 2-g sample into a platinum dish and add 20 ml of nitric acid and 5 ml of hydrofluoric acid. Warm on the hot-plate until the sample is dissolved and then evaporate to a volume of about 15 ml. Add 8 ml of perchloric acid and heat at fuming point until the volume is about 5 ml. Add 50 ml of water and warm to dissolve the salts. Filter (Whatman No. 42 paper) into a 400-ml beaker and wash with water. Discard the filter paper. Dilute the filtrate to about 200 ml and add 5 ml of hydrochloric acid. Heat to about 90°, add ammonia solution (1 + 1) until the solution is alkaline to Methyl Red, and 3 drops more. Heat to boiling and boil for about a minute, adding more ammonia if necessary to keep the solution alkaline. Filter (Whatman No. 41 paper) and wash with water. Dissolve the precipitate into the original beaker with hot hydrochloric acid (1 + 3) and wash with water. Dilute to about 200 ml and reprecipitate and filter as before. Char and burn off the filter paper and then ignite at 1000° for 30 min. Cool, weigh, and calculate the R_2O_3 content.

Iron oxide, calcium oxide and aluminium oxide

Weigh a 2-g sample into a platinum dish and add 20 ml of nitric acid and 5 ml of hydrofluoric acid. Warm on the hot-plate until the sample is dissolved and then evaporate to a volume of about 15 ml. Add 8 ml of perchloric acid and evaporate to a volume of about 1 ml. Add 50 ml of water, warm to dissolve the salts, cool, and dilute to 100 ml in a volumetric flask. Dilute appropriate aliquots of standard solutions of iron and calcium to 100 ml in volumetric flasks, adjust the perchloric acid concentration to about 1 ml per 100 ml, and determine the absorbance of the samples and standards by atomic absorption, using an acetylene–air flame in accordance with the recommendations of the instrument manufacturer. It may be necessary to dilute the samples further before the atomic-absorption measurements. Calculate the iron oxide and calcium oxide content on the basis of the standard solutions, and then the aluminium oxide by difference ($R_2O_3 - Fe_2O_3$).

DISCUSSION AND RESULTS

The (5 + 1) perchloric acid was found by innumerable experiments to dissolve the melt away from the sides of the crucible so that the cake floats free when the technique described in this paper is used. Hydrochloric or sulphuric acid (no matter what the concentration) was not satisfactory.

The perchloric acid method for silica gave results that were about 0.3% higher than those obtained by the hydrochloric acid method.

The small amount of salts left after the hydrofluoric acid treatment (mostly sodium salts according to spectrographic analysis) dissolved readily in the hydrochloric acid and could be conveniently added to the solution before the magnesium oxide determination.

Experiments were conducted to establish the extent of the errors involved if only a single precipitation was made of the magnesium ammonium phosphate. For this study, a standard solution of magnesium was prepared by dissolving 1.9298 g of high-purity magnesium metal in hydrochloric acid (1 + 9) and diluting to 1 litre (50 ml ≡ 0.1600 g of MgO). Various amounts of hydrochloric acid, perchloric acid and sodium chloride were added and the magnesium was precipitated, by single and double precipitation. The results (Table 1) showed that surprisingly good results were obtained with one precipitation in the presence of the large amounts of perchloric acid (ammonium perchlorate) in the absence of sodium chloride. However, sodium chloride (5 g) caused rather high results whether the perchloric acid was present or not. Obviously, the reprecipitation of the magnesium ammonium phosphate is necessary.

As indicated by Hillebrand, Lundell, Bright and Hoffman,[14] any calcium oxide present when magnesium is precipitated as magnesium ammonium phosphate is converted essentially into $Ca_3(PO_4)_2$ on ignition. This was checked in this laboratory by adding various amounts of standard calcium solution (prepared by dissolution of calcium carbonate in dilute hydrochloric acid) to portions of the standard magne-

Table 3. Results for the analysis of three samples of high-purity talc

	Sample A	Sample B	Sample C
SiO_2, %	60.8; 61.0; 61.0	61.0; 61.3; 61.4	61.6; 61.5; 61.4
MgO, %	31.6; 31.3; 31.2	31.6; 31.4; 31.4	31.4; 31.6; 31.4
R_2O_3, %	1.16; 1.12	1.41; 1.43	1.16; 1.14
Fe_2O_3, %	0.38; 0.39	0.11; 0.11	0.22; 0.21
Al_2O_3, %	0.78; 0.74	1.30; 1.25	0.94; 0.92
CaO, %	0.02; 0.03	0.48; 0.48	0.43; 0.45

sium solution, precipitating the magnesium as described in the procedure, and making a correction for $Ca_3(PO_4)_2$, using the theoretical factor of 1.844 for conversion of weight of CaO into weight of $Ca_3(PO_4)_2$. The results obtained in this study (Table 2) showed that the correction is valid although slightly high results are obtained in the presence of more than about 0.02 g of CaO. It is probable that more accurate results can be obtained for the determination of magnesium oxide in the presence of calcium oxide by use of the correction technique than can be obtained by use of the conventional method involving prior separation of calcium as calcium oxalate, since this precipitation is never quite complete and the calcium oxalate tends to occlude magnesium.

It would be expected that the atomic-absorption method for calcium would be more accurate than the calcium oxalate precipitation method for the relatively small amounts of calcium oxide found in high-purity talc, because it eliminates the errors caused by incomplete precipitation of the calcium oxalate and occlusion of salts by calcium oxalate. In addition, the atomic-absorption method eliminates any error due to the hygroscopicity of the ignited CaO.

It has previously been established that calcium and iron can be determined by atomic absorption without difficulty, when a dilute perchloric acid solution is used.[15] If desired, zinc, lead, and other metals could be determined by atomic absorption at the same time as the calcium and iron. Aluminium could also be determined but this would necessitate the use of a nitrous oxide–acetylene flame.

The results obtained for SiO_2, MgO, R_2O_3, Fe_2O_3, Al_2O_3, and CaO in three samples of high-purity talc by the proposed procedures are shown in Table 3.

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ANION-EXCHANGE BEHAVIOUR OF METALS ON DEAE-CELLULOSE IN HYDROCHLORIC ACID–ACETIC ACID MEDIA

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Summary—The anion-exchange behaviour of 35 metal ion species on a weakly basic cellulosic ion-exchanger (DEAE-cellulose) in mixed hydrochloric acid–acetic acid media has been investigated. The sorption of metal chloro-complexes on DEAE-cellulose is greatly enhanced with increasing concentration of acetic acid. Differences in sorbability of metals allow many useful analytical separations to be conducted on short columns, containing ~1 g of DEAE-cellulose(Cl^-). Procedures for the chromatographic separations of two-, three-, four- and five-component mixtures are given.

In previous papers[1,2] it has been demonstrated that the sorption behaviour of many metals on DEAE-cellulose in aqueous hydrochloric acid can be greatly improved by the addition of a polar organic solvent to the acid medium, as demonstrated for Zn(II), Cd(II), Hg(II), Bi(III) and some platinum metals in hydrochloric acid–methanol[1] and for Te(IV) in hydrochloric acid–acetic acid media.[2]

Similarly, Th(IV) exhibits pronounced sorption on DEAE-cellulose in nitric acid–methanol[3] as well as nitric acid–acetic acid media,[4] although Th(IV) is not sorbed on DEAE-cellulose to any great extent from aqueous nitric acid. The addition of acetic acid to the nitric acid medium has also enhanced the sorption on DEAE-cellulose of a number of ions including Mo(VI), the lanthanide ions, W(VI), Re(VII), Bi(III) and U(VI).[4]

Kuroda *et al.*[5] have shown that several ions, including Cu(II), Zn(II), Cd(II), In(III), Bi(III) and U(VI), exhibit enhanced sorption on DEAE-cellulose from thiocyanate–hydrochloric acid–methanol mixtures. This is in contrast to aqueous thiocyanate–hydrochloric acid media, where only a very limited number of ions such as Hg(II) and those of some platinum group metals can be sorbed on DEAE-cellulose, so that this system provides a basis for the specific separation of these metals from several others.[6,7] Recently, Kawabuchi and Kuroda[8] have reported the effective sorption of Au(III) on DEAE-cellulose from hydrochloric acid–acetic acid mixtures, establishing a selective method for the separation of Au(III), which is only weakly sorbed on DEAE-cellulose from dilute hydrochloric acid solution.[9]

In this paper, results will be reported which demonstrate the effectiveness of acetic acid for increasing the sorption of a number of chloro-complexes on DEAE-cellulose from aqueous hydrochloric acid solution. The distribution coefficients of 35 metal species are given as a function of acetic acid concentration in mixed hydrochloric acid–acetic acid solutions. The differences in sorption allow many useful chromatographic separations to be conducted on short columns.

EXPERIMENTAL

Reagents and chemicals

Stock solution of metals. For most metals the stock solutions were prepared by dissolving the oxide, chloride or metal in enough hydrochloric acid to yield solutions 1*M* in hydrochloric acid. Exceptions were Sc(III), Zr(IV), Hf(IV) and Bi(III), their stock solutions being made 3*M* in hydrochloric acid. For V(V), Cr(VI), Ge(IV) and Mo(VI) the sodium, potassium or ammonium salts were dissolved in water to make the stock solutions. The metal concentrations were generally 0.05*M*. The stock solutions were standardized by standard chemical methods including complexiметric titration and gravimetry.

Ion-exchanger. "Selectacel" DEAE-cellulose (diethylaminoethylcellulose), (Brown Co., Berlin, N.H.), 0.95 meq/g was used. About 10 g of DEAE were treated with 1*M* ammonium chloride (pH 1) to convert it into the chloride form. The DEAE(Cl^-) thus obtained was washed with demineralized water by centrifugation until the supernatant liquid exhibited a pH of 3. Then the DEAE was dehydrated with sufficient anhydrous methanol and dried for 5 hr at 40°, and stored in a desiccator containing saturated potassium bromide solution.

Apparatus

A conventional ion-exchange column (1.5 cm bore) pulled to a tip and plugged with glass-wool at the outlet was used for the measurement of distribution coefficients and for the chromatographic separations. A Hitachi–Perkin Elmer 139 Spectrophotometer with 1-cm cells and a Yanagimoto Model PA-101 Polarograph were used for analyses. A Hitachi–Horiba pH Meter F-7SS was used for pH-measurements.

Determination of distribution coefficient

A batch equilibrium method was used to determine the distribution coefficient for metals showing higher sorbability (see Tables 2 and 3). Portions (1.0 g) of DEAE(Cl^-) were weighed and placed in glass-stoppered Erlenmeyer flasks containing 40.0 ml of appropriate hydrochloric acid–acetic acid mixtures and 5 μmole of the metal concerned. The mixtures were shaken mechanically for 24 hr at

25.1 ± 0.1°. The two phases were separated by filtration and the filtrate was analysed for each metal. The distribution coefficient was computed by the formula:

$$K_d = \frac{\text{amount of metal in DEAE phase/g of DEAE}}{\text{amount of metal in solution phase/ml of solution}}$$

For metals having lower distribution coefficients a column elution method was used. A short column containing 1 g of DEAE was loaded with 5 μmole of metal in as small a volume as possible; the metal was eluted with a hydrochloric–acetic acid mixture. The coefficient is given by

$$K_d = V_{max} - V_i$$

where V_{max} and V_i are the retention and interstitial volumes, respectively. The systems investigated were: (1–8*M*) HCl:HOAc(v/v) = 5:95; 10:90; 20:80; 30:70; 40:60; 60:40. For Fe(III), Zn(II), Te(IV) and U(VI) the coefficients on DEAE in 10% hydrochloric acid + 90% acetic acid mixtures were measured as a function of hydrochloric acid concentration (0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 8.0*M*).

Column separations

DEAE (1.0 g) was slurried with the mixture of hydrochloric acid and acetic acid to be used for sample preparation, and poured into an ion-exchange column (bore 1.5 cm); 40 ml of the mixture were used for the preparation. The resulting bed was about 6 cm long. For difficult separations a longer column (DEAE, 1.2 or 2.0 g) was used.

About 10 ml of a sample solution, in the appropriate mixture of acetic acid and hydrochloric acid, were loaded onto the top of the column and allowed to percolate, and then the metals were eluted at a flow-rate of 2 ml/min.

Table 1. Analytical methods used for effluent analysis

	Method used
Al	Back-titration with Zn(II) in excess of EDTA, XO indicator
Sc	Titration with EDTA, XO indicator
Cr	Colorimetrically as CrO_4^- or with diphenylcarbazide
Mn	Colorimetrically as MnO_4^-
Fe	Colorimetrically with *o*-phenanthroline
Co	Colorimetrically with nitroso R salt
Ni	Colorimetrically with dimethylglyoxime
Cu	Tritration with EDTA, 1-(2-pyridylazo)-2-naphthol indicator
Zn	Polarographically or colorimetrically with zincon
Ga	Titration with EDTA, 1-(2-pyridylazo)-2-naphthol indicator
Ge	Colorimetrically with phenylfluorone
As	Gravimetrically as As_2S_5. Traces determined colorimetrically with diethyldithiocarbamate
Se	Titration with Mn(II) in excess of EDTA after isolation as $PbSeO_4$
Zr	Back-titration with Bi(III) in excess of EDTA XO indicator
Cd	Polarographically
In	Polarographically
Te	Colorimetrically with $SnCl_2$
La	Titration with EDTA, XO indicator
Hf	Back-titration with Bi(III) in excess of EDTA, XO indicator
Pt	Colorimetrically with $SnCl_2$
Hg	Colorimetrically with dithizone
Bi	Colorimetrically with diethyldithiocarbamate
Th	Titration with EDTA, XO indicator
U	Polarographically

The analytical methods used for the effluent analyses are summarized in Table 1.

RESULTS AND DISCUSSION

Sorption of metals from hydrochloric acid–acetic acid mixtures

When the weakly basic cellulosic ion-exchanger DEAE is used as sorbent, only a few metals are sorbed from aqueous chloride and chloride–thiocyanate media,[6,7,9] However, the addition of acetic acid to the hydrochloric acid media markedly enhances the sorption of many metals on DEAE. In Table 2 the distribution coefficients of 35 metallic species in hydrochloric acid–acetic acid mixtures are given as a function of acetic acid concentration, for a hydrochloric acid concentration kept constant at 1, 3 or 8*M*, depending on the metal ion studied. Enhancement of sorption with increasing concentration of acetic acid is particularly marked for Pd(II), Pt(IV), Hg(II), Co(II), Cu(II), Zn(II), Cd(II), Te(IV) and U(VI). Au(III) behaves similarly, being sorbed sufficiently strongly from 10% 0.5*M* hydrochloric acid + 90% acetic acid medium[8] to allow column separation. The effect is more moderate for Fe(III), Ga(III) and Yb(III), and slight for V(IV), V(V), Cr(VI), Mn(II), Ni(II), Y(III), Mo(VI), In(III), Th(IV) and other metals. Oxy-anions, including Ge(IV), As(III), As(V), Se(IV) and Te(VI), do not show enhanced sorption with increasing concentration of acetic acid. Te(IV) behaves differently from these oxy-anions, presumably because it forms chloro-complexes in the mixed hydrochloric acid–acetic acid media and these are stabilized by an excess of acetic acid.

Korkisch and Hazan[11] have investigated the anion-exchange behaviour of the rare earths, Th(IV), U(VI) and several other elements in mixtures of 12 organic solvents (including acetic acid) with hydrochloric acid. The general trends of their distribution coefficients on Dowex 1 in 10% 6*M* hydrochloric acid + 90% acetic acid and in 5% 12*M* hydrochloric acid + 95% acetic acid media are similar to those on DEAE in the mixed acid media described here, but the K_d values for Dowex are much higher and the selectivity sequences differ considerably:

DEAE—5% 1*M* HCl + 95% HOAc: Zn(II), Cd(II), Hg(II) > U(VI) > Co(II) > Cu(II) > Fe(III) > Ga(III) > In(III).

Dowex 1—5% 12*M* HCl + 95% HOAc: U(VI) > Co(II), Cu(II) > Ga(III) > Mn(II), Zn(II) > Cd(II) > Hg(II) > Fe(III)

Table 3 shows the effect of hydrochloric acid concentration on the distribution coefficient of four metals in 10%*x M* hydrochloric acid + 90% acetic acid media. In general the sorbability decreases with increasing concentration of hydrochloric acid. The effect is different from metal to metal, depending perhaps on the stability of the dominant chloro-complex species in the conditions concerned. Such an effect

Table 2. Distribution coefficient of metals on DEAE(Cl^-) in HCl–HOAc media (25°C; [HCl] = 1.0*M*)

Metal	HOAc, % *v/v*						
	95	90	80	70	60	40	
Sc(III)	103	18	7	<2.5	<2.5	<2.5	a
V(IV)	128	50	14	7	4	4	a
V(V)	152	56	13	7	5	4	a
Cr(III)	>200	130	16	5	5	4	a
Cr(VI)	175	46	25	21	15	9	a
Mn(II)	100	20	10	6	5	3	a
Fe(III)	259	96	39	12[a]	3	1	a, b
Co(II)	2050	161	14	<1	<1	<1	b
Ni(II)	134	36	9	6	4	3	a
Cu(II)	450[b]	80	15	6	4	<2.5	a, b
Zn(II)	$>10^3$	664	259	77[a]	24	1	a, b
Ga(III)	221	48	12	4	<1	<1	b
Ge(IV)	<1	<1	<1	<1	<1	<1	b
As(III)	4	<2.5	<2.5	<2.5	<2.5	<2.5	a
As(V)	8	5	<2.5	<2.5	<2.5	<2.5	a
Se(IV)*	4	3	<2.5	<2.5	<2.5	<2.5	a
Se(VI)*	27	14	10	~5	4	4	a
Y(III)	148	96	20	6	4	<2.5	a
Mo(VI)†	180	90	39	21	14	10	a
Pd(II)	15200	5750	784	154	122[a]	45[a]	a, b
Cd(II)	$>10^3$	5260	558	62	23[a]	9	a, b
In(III)	165	180	40	11	3	<1	b
Te(IV)*	$>10^3$	550	67	13	4	<1	b
Te(VI)*	17	8	~5	4	3	3	a
La(III)	92	47	13	6	4	<2.5	a
Sm(III)	171	82	16	4	<1	<1	b
Yb(III)	269[b]	138	17	<2.5	<2.5	<2.5	a, b
Pt(IV)	$>10^3$	$>10^3$	1250	402	191	65[a]	a, b
Hg(II)	9660	4630	588	180	104	29	b
Th(IV)	150	79	16	4	<2.5	<2.5	a
U(VI)	3460	383	22	<1	<1	<1	b
	HCl concentration: 3 M						
Sn(IV)			104	38	24	13	a
Bi(III)			>250	90	70	14	a
	HCl concentration: 8 M						
Zr(IV)	81	49	15	6	<2.5	<2.5	a
Hf(IV)	101	28	11	9	6	3	a

* Coefficients published previously,[2] but included to provide complete list. HCl concentration kept at 0.93*M*.

† 0.4% H_2O_2 present. a: column method; b: batch method. For values by the column method there is an uncertainty of ± 2.5 owing to the fixed fraction-volume taken by fraction-collector.

generally means that chloride competes more effectively for ion-exchange sites as the hydrochloric acid concentration increases; this is well shown by the strongly basic anion-exchange resin–hydrochloric acid system.[1,2] In the system described here the overall hydrochloric acid concentration ranges only from 0.05 to 0.8*M*. However, the high concentration of acetic acid makes the formation of chloro-complexes easier even at low chloride concentrations, because the acetic acid lowers the dielectric constant of the

Table 3. Distribution coefficient of Fe, Zn, Te and U on DEAE in HCl–HOAc media (10:90, v/v) as a function of HCl concentration

Metal	[HCl], *M*								
	0.5	1.0	2.0	3.0	4.0	5.0	6.0	8.0	
Fe(III)	120	96		30		17		3	b
Zn(II)	1420	664		330		180		110	b
Te(IV)	710	550	530		470		310	280	b
U(VI)	480	383			370		293	174	b

a, b: see footnotes to Table 2.

medium ($\epsilon_{H_2O} = 80$, $\epsilon_{HOAc} = 6.2$), thereby increasing the attraction between ions. Therefore, ion association and complex formation are favoured. In agreement with this observation van den Winkel *et al.*[13] attributed the strong affinity of Dowex 1 for noble metal chloro-complexes, Zr(IV), Hf(IV) and Ta(V) fluoro-complexes, and Tl(III) and Bi(III) nitrates from 2–17.4*M* acetic acid to sorption of the chloro, fluoro and nitrato complexes, stabilized by the low ϵ value.

Column separations

More metals can be sorbed (with varying distribution coefficients) on DEAE from mixed hydrochloric acid–acetic acid media than from chloride-thiocyanate media, so this ion-exchange system provides a basis for many analytical separations.

Inspection of the relevant K_d values will show whether a separation is feasible and what the most favourable composition of eluent should be. In this way quantitative separations were accomplished for Al(III)–Cd(II), Al(III)–Zn(II), As(III)–Fe(III), Cu(II)–Bi(III), Cu(II)–Hg(II), Cu(II)–Zn(II), La(III)–U(VI), Ni(II)–Co(II), Ni(II)–Zn(II), Sc(III)–U(VI), As(V)–Cr(VI), As(V)–Pt(IV); Ge(IV)–Ga(III); Ge(IV)–Te(IV); Hf(IV)–U(VI); In(III)–Cd(II); Se(VI)–Cr(VI); Th(IV)–U(VI); U(VI)–Cd(II); Zr(IV)–U(VI); Mn(II)–Fe(III)–Zn(II). Amounts loaded were generally 10 mg for ions with low K_d and 1 mg for those with high K_d.

Two chromatographic separations are shown in Figs. 1 and 2. As can be seen, recoveries were quantitative, and there was no marked tailing.

Many other separations may be feasible by proper choice of acetic acid and/or hydrochloric acid concentration, as shown by Kawabuchi and Kuroda, for separation of Au(III) on a DEAE column.[8] The scope of separation on DEAE is much wider in hydrochloric acid–acetic acid media than in hydrochloric acid–methanol[1] or dilute aqueous chloride and chloride–thiocyanate media.[6,7,9] The sorption of metals in the present ion-exchange system is quite moderate and no irreversible sorption takes place such as that often found in anion-exchange resin–hydrochloric acid systems.

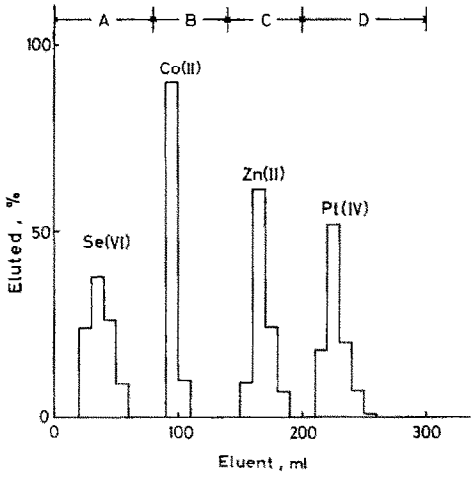

Fig. 1. Separation of chloro-complexes of Se(VI), Co(II), Zn(II) and Pt(IV). Column: 1.5 × 6.2 cm (DEAE, 1.0 g). Eluent A: 5% 1*M* HCl + 95% HOAc. Eluent B: 20% 1*M* HCl + 80% HOAc. Eluent C: 40% 1*M* HCl + 60% HOAc. Eluent D: 1*M* HCl.
Se(VI): 11.98 mg added, 11.63 mg recovered; Co(II): 325 μg added, 326 μg recovered; Zn(II): 501 μg added, 508 μg recovered; Pt(IV): 500 μg added, 489 μg recovered.

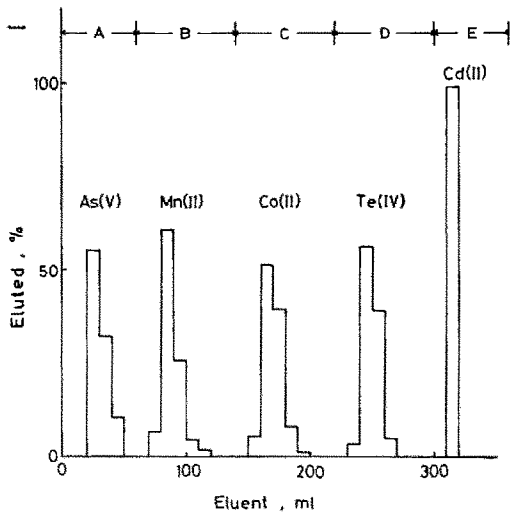

Fig. 2. Separation of As(V), Mn(II), Co(II), Te(IV) and Cd(II). Column: 1.5 × 7.6 cm (DEAE, 1.2 g). Eluent A: 5% 1*M* HCl + 95% HOAc. Eluent B: 10% 1*M* HCl + 90% HOAc. Eluent C: 15% 1*M* HCl + 85% HOAc. Eluent D: 25% 1*M* HCl + 75% HOAc. Eluent E: 1*M* HCl.
As(V): 9.95 mg added, 9.75 mg recovered; Mn(II): 288 μg added, 285 μg recovered; Co(II). 325 μg added, 341 μg recovered; Te(IV): 400 μg added, 407 μg recovered; Cd(II): 515 μg added, 508 μg recovered.

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SIMULTANEOUS DETERMINATION OF OXYGEN AND CADMIUM IN CADMIUM AND CADMIUM COMPOUNDS

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Summary—Cadmium and its compounds were analysed for oxygen and cadmium by a modification of the Schütze-Unterzaucher method. Oxygen in some compounds such as cadmium oxide, nitrate and sulphate could not be determined by the usual method. The method of adding carbon was employed for the determination of total oxygen. Total oxygen could be determined by the addition of 5 mg of carbon to a sample boat and heating at 950°. The determination was also carried out by addition of naphthalene (2 mg). It was found that the cadmium powder and cadmium flake used contained *ca.* 1 and 0.15% oxygen, respectively. Oxygen and cadmium in cadmium and its compounds were simultaneously determined by the addition of 2 mg of naphthalene. Cadmium was determined colorimetrically by use of glyoxal-bis-(2-hydroxyanil). Oxygen and cadmium in the samples could be determined simultaneously with an average error of −0.02 and −0.22%, respectively.

Holt and Goodspeed[1] determined oxygen in cadmium by the carbon-reduction method used at 1900°. However, methods for determination of oxygen in cadmium compounds have not hitherto been developed. The present study was designed to determine oxygen and cadmium simultaneously in cadmium and its compounds by the carbon-reduction method, the carbon being added directly or generated by pyrolysis of naphthalene.

EXPERIMENTAL

Samples

In addition to cadmium (flake and powder), inorganic and organic compounds or complexes were used. The composition of the organic samples was confirmed by analysis for carbon and hydrogen.

Reagents

Porous copper, sodium hydroxide, magnesium perchlorate, platinized carbon, and iodine pentoxide were obtained from Nakarai Chemicals, Ltd. Wire-form copper was prepared by reduction of wire-form copper oxide (Merck) with hydrogen. Carbon powder was purchased from Mitsubishi Chemical Industries Ltd.

Standard cadmium solution was prepared as follows and diluted before use: about 0.10 g of cadmium (not less than 99.99% pure), accurately weighed, was dissolved in 50 ml of dilute nitric acid, and the mixture was boiled to remove nitrogen oxide and, after cooling, was diluted with water to 100 ml.

Apparatus

The apparatus used was the same as that previously reported[2] except for a modification at the terminal part of the pyrolysis tube for the purpose of simultaneous determination of oxygen and cadmium (Fig. 1).

Procedures

(1) *Usual method of oxygen determination in organic compounds.* Nitrogen was passed through the apparatus as carrier gas at a rate of 10–15 ml/min, after purification by passage through a silica gel drying tube, a deoxidation tube filled with porous copper heated at 550°, and two absorption tubes, one containing sodium hydroxide and the other magnesium perchlorate. The combustion furnace, desulphurization furnace and heating furnace were maintained at 900°, 550° and 150°, respectively. A boat containing a weighed sample was put into the pyrolysis tube through the sample inlet, which was flushed with nitrogen to keep air out. The boat was moved up to the sample heater by means of an iron ball and magnet, and the sample was pyrolysed for a period of 15 min. Oxygen contained in the sample was completely converted into carbon monoxide by means of platinized carbon heated at 900°. The carbon monoxide was oxidized to carbon dioxide by iodine pentoxide, and the resulting carbon dioxide was absorbed in an absorption tube packed with sodium hydroxide. Thirty minutes after the beginning of pyrolysis, this absorption tube was disconnected and weighed. A blank was run and a correction applied:

$$\text{oxygen} = \frac{0.3636(a-b)}{s} \times 100\%$$

where s = sample weight (mg); a = increase in weight of the absorption tube (mg); b = blank value (mg). Carbon dioxide was determined coulometrically as well as gravimetrically.[3]

(2) *Determination by addition of a solid reaction agent.* This method was the same as that described in (1) except that carbon powder was sprinkled in the sample boat before and after placement of the sample.

(3) *Determination by addition of a reaction agent.* The procedure was the same as in (1), except for insertion of the sample boat and pyrolysis of the sample, which were carried out as follows. A weighed sample was placed in the sample boat which was then put in the sample inlet after the apparatus had been back-flushed with nitrogen. An iron ball and then a boat with a weighed reaction agent (2 mg of naphthalene) were inserted into the apparatus, and the apparatus was back-flushed for 3–5 min. The direction of flush was then reversed and the sample boat moved up to the sample heater by means of the iron ball and a magnet. During the pyrolysis, the iron ball was brought back to the other side of the boat with the reaction agent and the boat was moved up to about 2–3 cm

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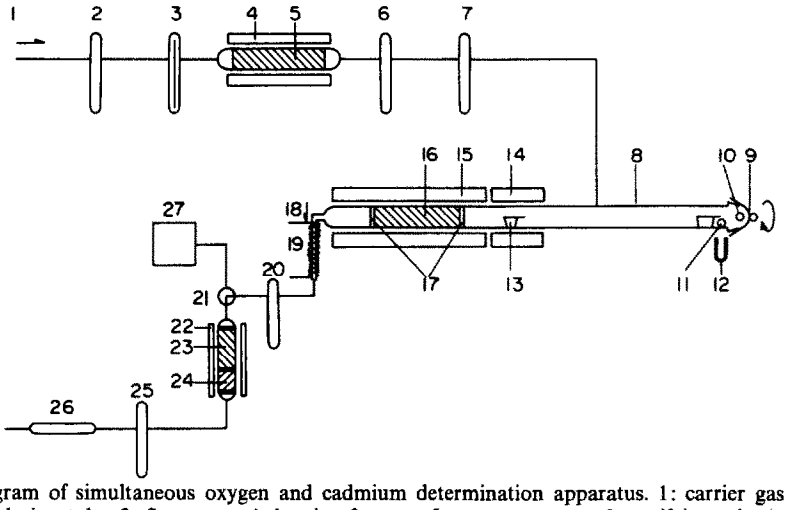

Fig. 1. Diagram of simultaneous oxygen and cadmium determination apparatus. 1: carrier gas inlet, 2: silica gel drying tube, 3: flowmeter, 4: heating furnace, 5: porous copper, 6: purifying tube (sodium hydroxide), 7: purifying tube (magnesium perchlorate), 8: pyrolysis tube, 9: sample inlet, 10: flushing hole, 11: iron ball, 12: magnet, 13: sample boat, 14: sample heater, 15: combustion furnace, 16: platinized carbon, 17: platinum wire, 18: heater, 19: cadmium absorption section, 20: purifying tube (sodium hydroxide), 21: stop-cock, 22: heating furnace, 23: iodine pentoxide, 24: porous copper, 25: purifying tube (magnesium perchlorate), 26: absorption tube, 27: coulometric apparatus.

from the sample heater. The naphthalene was vaporized by the sample heater and the gas carried by the nitrogen towards the sample heater. The sample or oxidation products remaining in the sample boat were allowed to react directly with the naphthalene vapour or its pyrolysis products. The resulting oxygen compounds were then allowed to react with platinized carbon at 900° in order to convert the oxygen into carbon monoxide.

(4) *Simultaneous determination of oxygen and cadmium by addition of a reaction agent (Fig. 1).* The method for oxygen determination was the same as the one just described. Cadmium was determined as follows.[4] At 15 or 30 min after the start of pyrolysis, according to whether oxygen was determined coulometrically or gravimetrically, the cadmium absorption section (19) was disconnected from the purifying tube containing sodium hydroxide (20) and its tip immersed in dilute nitric acid. With carrier gas flowing, the tube was heated by a heater (18) so that the cadmium deposit was evaporated and transferred into a receiver containing 5 ml of dilute nitric acid. The inner wall of the tube was washed with another 5-ml portion of dilute nitric acid and the washings were mixed with the cadmium solution, and the mixture was neutralized. To 2 ml of this solution (containing 30–40 μg of cadmium) were added 5 ml of potassium sodium tartrate solution (20%), 7 ml of sodium hydroxide solution (10%), and water up to a volume of 50 ml. Two ml of glyoxal-bis(2-hydroxyanil) solution in ethyl alcohol (about 8.5 mg/ml) were added to this solution, and the mixture was extracted with 5 ml of chloroform–pyridine solution (chloroform:pyridine = 5:1 v/v). The organic phase was separated, and the extraction repeated with 1 ml of glyoxal-bis(2-hydroxyanil) solution and 5 ml of chloroform–pyridine mixture. The organic phases were combined and dried with anhydrous sodium sulphate. The absorbance of this solution was measured at 610 nm against a reagent blank. The concentration of cadmium was determined from the calibration curve prepared with standard cadmium solution.

RESULTS AND DISCUSSION

Determination of oxygen in cadmium compounds by the usual method

Oxygen in cadmium compounds was determined according to the usual method for determination of oxygen in organic compounds, with heating at 900° for 15 min. The values for oxygen in cadmium oxide, hydroxide, carbonate, nitrate, and sulphate were 2–6% lower than the calculated values. Oxygen in cadmium acetate, 4-cyclohexylbutyrate, formate, nicotinate, propionate, salicylate, stearate and bis(8-quinolinolate), however, could be determined fairly accurately.

Cadmium oxide sublimes at 700° and at higher temperatures is converted into cadmium suboxide, giving off oxygen.[5] In addition, cadmium oxide is readily reduced to the metal by hydrogen at 270–300° or carbon monoxide at about 700°. Cadmium oxide is expected, from the thermodynamic data, to decompose into cadmium and oxygen:

$$CdO(s) \rightarrow Cd(g) + \tfrac{1}{2}O_2$$

Values of ΔG and K_p at temperatures above 700° are given in Table 1.

The relationship between ΔG and the pressure equilibrium constant K_p is

$$\log K_p = -\frac{\Delta G}{2.303\,RT}.$$

The K_p values indicate that cadmium oxide is very little decomposed at 800°–900°.

When cadmium oxide was heated at 900° for 15 min, the oxygen found was approximately 7%,

Table 1. ΔG and K_p of cadmium oxide

Temperature, °C	ΔG, *kcal/mole*	K_p
700	38.5	2.25×10^{-9}
800	36.1	4.46×10^{-8}
900	33.7	5.27×10^{-7}
1000	31.3	4.24×10^{-6}
2327	−0.2	2.25

Table 2. Influence of temperature on the determination of oxygen in cadmium oxide by addition of solid reaction agent (about 5 mg of carbon)

Temperature of sample heater, °C	Sample taken, mg	CO_2, mg	Oxygen found %	Oxygen calcd., %	Δ%
700	1.818	0.152	3.0_4		-9.4_2
750	1.727	0.195	4.1_1		-8.3_5
800	1.696	0.234	5.0_2		-7.4_4
850	1.570	0.439	10.1_7	12.46	-2.2_9
900	3.062	1.043	12.3_9		-0.0_7
950	1.740	0.594	12.4_1		-0.0_5
1000	2.001	0.680	12.3_6		-0.1_0
1050	1.996	0.685	12.4_8		$+0.0_2$

Table 3. ΔG and K_p in the reaction: $CdO(s) + C(s) \rightarrow Cd(g) + CO(g)$

Temperature, °C	ΔG Cd(g) kcal/mole	ΔG CO(g) kcal/mole	ΔG CdO(s), kcal/mole	ΔG C(s), kcal/mole	ΔG reaction, kcal/mole	K_p
700	−0.1	−47.2	−38.5	−1.2	−7.6	5.09×10
800	−2.9	−49.4	−36.1	−1.3	−14.9	1.08×10^3
900	−5.7	−51.5	−33.7	−1.3	−21.2	8.91×10^3
1000	−8.5	−53.6	−31.3	−1.5	−29.3	1.07×10^5

s: solid, g: gas.

whereas the calculated value is 12.46%. For compounds such as cadmium hydroxide and carbonate, the values found for oxygen were also low, presumably because pyrolysis of the compound led to the formation of cadmium oxide.

The influence of heating time and temperature was examined. The determination took *ca.* 70 min for cadmium oxide and *ca.* 100 min for cadmium hydroxide with heating at 900° and the values found were approximately correct. Next, on the assumption that increasing the temperature would decrease the determination time, cadmium oxide was heated for 15 min, the heating temperature being raised from 850° to 1050°. The values found did not show much variation with change in heating temperature. A glassy residue was left in the sample boat.

Table 4. Analytical results for oxygen in cadmium compounds, obtained by addition of solid reaction agent (about 5 mg of carbon). Heating temperature of sample: 950°

Sample	Sample taken, mg	CO_2, mg	Oxygen found, %	Oxygen calcd., %	Δ%
Cadmium carbonate	3.789	2.891	27.74	27.84	−0.10
	3.442	2.632	27.80		−0.04
	4.165	3.158	27.57		−0.27
Cadmium hydroxide	3.430	2.049	21.72	21.85	−0.13
	3.738	2.219	21.58		−0.27
	4.584	2.729	21.65		−0.20
Cadmium nitrate	4.117	5.868	51.82	51.87	−0.05
	3.688	5.235	51.61		−0.26
	3.422	4.856	51.60		−0.27
Cadmium oxide	3.973	1.348	12.34	12.46	−0.12
	3.187	1.096	12.50		+0.04
	3.657	1.228	12.21		−0.25
Cadmium sulphate	4.182	4.790	41.65	41.60	+0.05
	3.565	4.076	41.57		−0.03
	3.913	4.459	41.43		−0.17

Determination of total oxygen in cadmium compounds by addition of a solid reaction agent

Because total oxygen in some cadmium compounds cannot be determined by the usual method (for organic compounds) we used the method with

Table 5. Analytical results for oxygen in cadmium and cadmium compounds by addition of reaction agent (about 2 mg of naphthalene)

Sample	Sample taken, mg	CO_2, mg	Oxygen found, %	Oxygen calcd., %	Δ%
Cadmium powder	6.740	0.196	1.06		
	6.313	0.156	0.90		
	4.970	0.146	1.07		
Cadmium flake	8.104	0.031	0.14		
	7.260	0.020	0.10		
	8.109	0.045	0.20		
Cadmium carbonate	3.467	2.676	28.06	27.84	+0.22
	3.378	2.552	27.47		−0.37
Cadmium hydroxide	1.058	0.645	22.17	21.85	+0.32
	1.635	0.986	21.93		+0.08
	1.822	1.085	21.65		−0.20
Cadmium nitrate	6.442	9.154	51.67	51.87	−0.20
	2.361	3.382	52.08		+0.21
	1.347	1.920	51.83		−0.04
Cadmium oxide	1.569	0.547	12.68	12.46	+0.22
	3.082	1.050	12.39		−0.07
	2.632	0.906	12.52		+0.06
Cadmium sulphate	2.200	2.555	42.23	41.60	+0.63
	1.844	2.092	41.25		−0.35
	2.547	2.929	41.81		+0.21

Table 6. Simultaneous determination of oxygen and cadmium in cadmium and cadmium compounds by addition of reaction agent (about 2 mg of naphthalene)

Sample	Sample taken, mg	CO_2, mg	Oxygen found, %	Oxygen calcd., %	Δ%	Cd, mg	Cd found, %	Cd calcd., %	Δ%
Cadmium powder	5.905	0.166	1.02			5.802	98.2_6		
	5.230	0.196	1.36			5.123	97.9_5		
Cadmium acetate	4.012	3.989	36.15	36.02	+0.13	1.687	42.0_5	42.17	−0.1
	5.649	5.637	36.28		+0.26	2.365	41.8_7		−0.3
Cadmium carbonate	3.797	2.902	27.79	27.84	−0.05	2.461	64.8_1	65.20	−0.4
	4.653	3.543	27.69		−0.15	3.011	64.7_1		−0.5
Cadmium 4-cyclo-hexylbutyrate	5.825	2.256	14.08	14.19	−0.11	1.450	24.8_9	24.93	−0.0
	5.561	2.193	14.34		+0.15	1.400	25.1_8		+0.3
Cadmium formate	2.062	2.289	40.36	40.26	+0.10	0.975	47.2_8	47.15	+0.1
	1.792	1.992	40.42		+0.16	0.842	46.9_9		−0.2
Cadmium hydroxide	6.806	4.058	21.68	21.85	−0.17	5.200	76.4_0	76.77	−0.4
	4.611	2.756	21.73		−0.12	3.532	76.6_0		−0.2
Cadmium nicotinate	3.204	2.140	24.29	24.45	−0.16	0.959	29.9_3	30.02	−0.1
	4.688	3.172	24.60		+0.15	1.387	29.5_9		−0.4
Cadmium nitrate	4.951	7.053	51.80	51.87	−0.07	1.780	35.9_5	36.44	−0.5
	4.157	5.907	51.67		−0.20	1.527	36.7_3		+0.3
Cadmium oxide	4.894	1.668	12.39	12.46	−0.07	4.227	86.3_7	87.54	−1.1
	4.215	1.442	12.44		−0.02	3.649	86.5_7		−1.0
Cadmium propionate	3.958	2.718	24.97	24.75	+0.22	1.726	43.6_1	43.50	+0.1
	4.802	3.242	24.55		−0.20	2.106	43.8_6		+0.4
Cadmium salicylate	4.170	3.458	30.15	30.28	−0.13	1.103	26.4_5	26.59	−0.1
	4.393	3.672	30.39		+0.11	1.178	26.8_2		+0.2
Cadmium stearate	3.970	1.233	11.29	11.49	−0.20	0.629	15.8_4	16.14	−0.3
	4.014	1.274	11.54		+0.05	0.646	16.0_9		−0.1
Cadmium sulphate	5.611	6.393	41.43	41.60	−0.17	2.430	43.3_1	43.83	−0.5
	4.511	5.165	41.63		+0.03	1.956	43.3_6		−0.5
Bis(8-quinolino-lato)cadmium	4.390	1.783	14.77	14.65	+0.12	1.116	25.4_2	25.74	−0.3
	4.253	1.693	14.47		−0.18	1.087	25.5_6		−0.2

added carbon as reaction agent. To examine the influence of heating temperature, 5 mg of carbon were placed in the sample boat with cadmium oxide as test sample and the heating temperature varied. The analytical results are given in Table 2. It was found that oxygen in cadmium oxide can be determined fairly accurately when the sample is heated at 900° or above.

Cadmium oxide reacts with carbon as follows:

$$CdO(s) + C(s) \rightarrow Cd(g) + CO(g)$$

Values of ΔG, and K_p for this reaction at temperatures of 700–1000° are shown in Table 3. Thermodynamic considerations indicate that the reaction proceeds at 800–900°, and the results obtained here support this conclusion.

With the compounds which cannot be analysed for oxygen by the usual method, oxygen was also determined at 950°. Table 4 shows that the determination is quite accurate.

Determination of total oxygen in cadmium compounds by addition of a volatile reaction agent

We also tried the addition of naphthalene (2 mg) instead of carbon. The analytical results are given in Table 5 and are also satisfactory, as were those for oxygen in cadmium (Table 5). It was found that the cadmium powder and flake contained *ca.* 1% and 0.15% oxygen, respectively.

Simultaneous determination of oxygen and cadmium in cadmium and cadmium compounds

Total oxygen in cadmium compounds was determined more easily by the method using carbon than by the method with naphthalene, but the average error was smaller in the latter method than in the former. On this account, oxygen and cadmium in cadmium and its compounds were simultaneously determined by the naphthalene method. First, the recovery of cadmium from a sample of the metal (not less than 99.99% pure) was tested and found to be 98.9 ± 0.6% (6-mg samples). We then attempted simultaneous determination of oxygen and cadmium. The analytical results are given in Table 6. Oxygen and cadmium in all samples could be determined simultaneously with an average error of −0.02% and −0.22%, respectively.

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INTERPRETATION OF SELECTIVITY COEFFICIENTS OF SOLID-STATE ION-SELECTIVE ELECTRODES BY MEANS OF THE DIFFUSION-LAYER MODEL

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Summary—On the basis of a diffusion-layer model the selectivity coefficients of solid-state electrodes have been interpreted. In the Nernst equation the concentration of the principal ion may be expressed in terms of the diffusion coefficients D_B, D_C and the equilibrium constant K of the reaction $AB + C \rightleftharpoons AC + B$ where AB represents the membrane material and C the interfering ion, in the form of an equation:

$$[B]_0 = \frac{KD_B}{KD_B + D_C}[B] + \frac{KD_C}{KD_B + D_C}[C]$$

where the concentration with subscript "0" denotes the surface concentration directly influencing the electrode potential, and [B] and [C] are bulk concentrations of the species indicated. The differences between various literature data can be explained on the basis of this model.

The role of basic research in development of ion-selective electrodes is continuously increasing. Several models have been proposed[1–6] for the functioning of the electrodes, emphasizing various phenomena. Recently, more attention has been paid to the diffusion processes at the membrane surface[6–10] and leaving aside the processes inside the membrane, which are more difficult to investigate. The detailed picture of diffusion phenomena may be useful in treatment of relative electrode sensitivity on the basis of complex formation reactions between solution components and membrane material.[6,7,9]

The case of mixed phases, where two solid phases coexist in thermodynamic equilibrium with ions in solution has been mentioned by Buck,[3] but only Havas[11] has given a qualitative description of diffusion processes. In a previous paper[12] we have discussed this quantitatively for the copper ion-selective chalcocite electrode, but in this instance an exact experimental proof was difficult because of the necessity of working at very low concentration levels.

In this paper such an approach is developed in a more general form. This treatment gives a possibility of theoretical interpretation of selectivity coefficients for a number of electrodes. These values can be compared with those determined experimentally by the method of mixed and separated solutions, and differences occurring in some cases can be explained.

THEORETICAL CONSIDERATIONS

For simplicity we consider an electrode having a membrane-active component of 1:1 composition, *e.g.*, the AgCl or PbS electrode. The membrane may be a two-component material, such as in the Ag_2S–AgCl electrode, provided the solubility of one component is much the smaller. Also for simplicity, concentrations will be used throughout instead of activities, but this does not change the principal lines of the argument. The adsorption phenomena at the electrode surfaces are also neglected, and it is assumed that the concentration of ions originating from solubility equilibria of the membrane material are much smaller than those considered in the diffusion and exchange reactions. The necessary condition for the diffusion-layer model is the coexistence of both compounds, *e.g.*, AgCl and AgBr, at the electrode surface, *i.e.*, the case of mixed phases.

When the membrane material AB is placed in a solution containing the ion of interest at concentration [B] and the interfering ion at concentration [C], in the proper ranges of concentrations and with proper preparation of the membrane surface there exists the equilibrium (which is chemically reversible, and fast in comparison to the diffusional transport in the system):

$$AB + C \rightleftharpoons AC + B \tag{1}$$

characterized by the constant

$$K = \frac{[B]_0}{[C]_0} = \frac{K_{so(AB)}}{K_{so(AC)}} \tag{2}$$

where the subscript 0 denotes a concentration at the membrane surface, and K_{so} is the solubility product of the substance indicated by subscript. Independently of the reaction direction, the condition

$$J_B + J_C = 0 \tag{3}$$

must be fulfilled, where J_B and J_C are the fluxes of the ions indicated.

Assuming conditions typical for the diffusion model, *i.e.*, ion transport is diffusive only, concen-

tration changes in the diffusion layer are linear, and diffusion coefficients are independent of the thickness of the layer, from condition (3) the relationship

$$D_B([B]_0 - [B]) = D_C([C] - [C]_0) \quad (4)$$

is obtained, where D is the diffusion coefficient.

From equations (2) and (4) the concentration $[B]_0$ at the electrode surface may be calculated as a function of the concentrations of the principal and interfering ions in the bulk of the solution:

$$[B]_0 = \frac{KD_B}{KD_B + D_C}[B] + \frac{KD_C}{KD_B + D_C}[C] \quad (5)$$

It must be repeated here that this equation is valid when the concentration of C is not sufficient for complete coverage of the electrode surface with AC but not so small that no AC at all is formed.

The ratio of diffusion coefficients D_C/D_B is usually close to unity and certainly between 0.5 and 2.0 and is therefore of minor importance; hence for the value of K, three cases must be considered: $K \gg 1$, $K \approx 1$, $K \ll 1$. To these correspond the following three equations of the diffusion layer model:

$$\text{(A) } K \gg 1\text{: } [B]_0 = [B] + \frac{D_C}{D_B}[C] \quad (6)$$

$$\text{(B) } K \approx 1\text{: } [B]_0 = \frac{KD_B}{KD_B + D_C}[B] + \frac{KD_C}{KD_B + D_C}[C] \quad (7)$$

$$\text{(C) } K \ll 1\text{: } [B]_0 = \frac{KD_B}{D_C}[B] + K[C] \quad (8)$$

The experimental methods of selectivity coefficient evaluation are based on the use of so-called separate or mixed solutions. For these two procedures the following equations, based on particular forms of the Nikolsky–Eisenman equation, must be solved. For the method of separate solutions (I):

$$E_B = \text{const} + S\log[B] \quad (9)$$

$$E_C = \text{const} + S\log K_{BC}[C] \quad (10)$$

and for that of mixed solutions (II):

$$E_B = \text{const} + S\log[B] \quad (11)$$

$$E_{BC} = \text{const} + S\log([B] + K_{BC}[C]) \quad (12)$$

where S is the slope of the potential-response curve and K_{BC} is the selectivity coefficient for ion B in presence of interfering ion C.

When the selectivity coefficients are calculated from the diffusion-layer model equations (6)–(8), their values depend on the value of K and on which method was used.

These results are summarized in Table 1 and clearly indicate that the values of selectivity coefficients derived theoretically from other electrode models (*e.g.*, ref. 1) only in some limiting cases agree with the experimental value of the selectivity coefficient. It is also evident that both methods should generally give different results, which cannot be attributed solely to experimental error.

A more detailed treatment needs consideration of three main aspects.

The selectivity coefficients may be related to physical phenomena when the "mixed phases" system exists. In case (A) this is so until the membrane surface is covered with the layer of AC, irrespective of the method (I or II) used in the investigation. In case (C) it exists until the AC layer on the electrode dissolves completely as the result of the reaction with ion B (method II). In case (B) the coexistence of mixed phases is usually not disturbed by either of the two reverse processes. For case (A) the change from the mixed phases system to complete coverage of the surface by AC corresponds to change of the selectivity coefficient from D_C/D_B to K. When no second solid phase AC exists in equilibrium [mostly in case (C)] the selectivity coefficients may be experimentally evaluated but their physical meaning cannot be interpreted on the basis of our model. These are the reasons for the observed large discrepancies between the results for the same type of electrode. The proper value of the experimentally determined selectivity coefficient depends on the type of reaction occurring at the surface [(A), (B) or (C)] and on the initial state of the electrode.

It should be taken into account that the two methods (I and II) are not equivalent over the whole range of variability of K. The differences between the selectivity coefficients obtained by the separate-solution method, $K_{BC}^{pot(I)}$ and by the mixed-solution method, $K_{BC}^{pot(II)}$, may be described by the equation

$$K_{BC}^{pot(I)} = K_{BC}^{pot(II)} + 1 - \frac{KD_B}{KD_B + D_C} \quad (13)$$

which follows from comparison of the equations given for case (B) in Table 1 (this being the general case of our considerations). These differences can be experimentally evaluated for systems where K is close to unity.

The detailed examination of the relationships may also indicate that the selectivity coefficient of the diffusion model is never greater than the ratio D_C/D_B or the equilibrium constant K.

EXPERIMENTAL

In the measurements the following ion-selective electrodes were used: Radelkis OP-Cl-711 (chloride) and OP-Br-711 (bromide); Orion 94-82 (lead) and 94-16 (silver).

A saturated calomel reference electrode was used, with a 1*M* potassium nitrate salt-bridge. The potentials were measured with a Radiometer pHM-64 pH-meter and Servograph REC 61 recorder. The potential readings were taken at 25°, when they were stable to ±0.1 mV. All measurements were obtained in solutions with ionic strength 1.0 (KNO_3).

Measurements were made on systems which may belong to all the cases discussed, according to the value of K. The selectivity coefficients experimentally determined by both methods were compared with data obtained by other authors. Table 2 gives the values of the coefficients calcu-

Table 1. Selectivity coefficient expressions for different methods of calculation, and various approximations according to the value of the equilibrium constant

Case	Method I, [B] = [C]	Method II, [B] = [C]
(A) ($K \gg 1$)	$10^{\pm(E_C - E_B)/59.2} = \frac{D_C}{D_B}$	$10^{\pm(E_{BC} - E_B)/59.2} - 1 = \frac{D_C}{D_B}$
(B) ($K \approx 1$)	$10^{\pm(E_C - E_B)/59.2} = \frac{KD_C}{KD_B + D_C}$	$10^{\pm(E_{BC} - E_B)/59.2} - \frac{KD_B}{KD_B + D_C} = \frac{KD_C}{KD_B + D_C}$
(C) ($K \ll 1$)	$10^{\pm(E_C - E_B)/59.2} = K$	$10^{\pm(E_{BC} - E_B)/59.2} - \frac{KD_B}{D_C} = K$
Calculated from empirical equations	$10^{\pm(E_C - E_B)/59.2} = K_{BC}^{pot(I)}$	$10^{\pm(E_{BC} - E_B)/59.2} - 1 = K_{BC}^{pot(II)}$

The signs + and − are used for cation- and anion-selective electrodes, respectively.

lated as the diffusion-coefficient ratio on the basis of the diffusion-layer model and also from the solubility product ratio. The constants used in these calculations are summarized in Table 3.

DISCUSSION OF RESULTS

The comparison of literature data and experimental results in this paper may serve as an illustration of the validity of the diffusion-layer model. Though the treatment is far from comprehensive, the good agreement of data indicates that the approach can be successfully applied in consideration of electrode selectivity.

For example, when the behaviour of the lead sulphide electrode in a solution containing lead and cadmium was studied, for both concentrations experimentally used and for the diffusion-layer model the difference [equation (13)] between the selectivity coefficients for methods I and II is practically the same.

Such good agreement has encouraged us to use the experimental selectivity coefficients (0.34 and 0.37, mean 0.355), the equilibrium constant and the diffusion coefficient of the bromide ion for calculation of the diffusion coefficient of the thiocyanate ion. The value $D_{SCN} = 2.5 \times 10^{-5}$ cm^2/sec is close to the value for the cyanide ion.

For case (A) the AgCl electrode in Cl^-, Br^- media is of special interest. For $10^{-3}M$ concentrations the experimental value is close to the theoretical and the discrepancy may be attributed to the fact that even in this case we do not have a pure diffusion-layer model. When the concentration is increased to $0.1M$, the selectivity coefficient comes close to the value described by the equilibrium constant. This indicates that the electrode surface is completely covered by silver bromide, and that a chloride electrode no longer exists. When the electrode is placed in a $10^{-2}M$ solution a change of potential may be observed, which corresponds to the change of selectivity coefficient due to coverage of the electrode surface with AgBr (Fig. 1). It is obvious that if the selectivity coefficients are determined in such conditions large differences in experimental values may be expected. This gives a practical hint about the choice of conditions for individual electrodes, and probably the significant variations in the literature data for this system may be explained in this way. Similar conclusions may be drawn for the bromide electrode in Br^-, Cl^- solution.

From these considerations it is possible to estimate for which values of equilibrium constant K the variability of selectivity coefficients of ion-selective electrodes, predicted theoretically, may also be experimentally verified. These correspond to the approximate range

$$3 \times 10^{-2} < K < 3 \times 10^{2}.$$

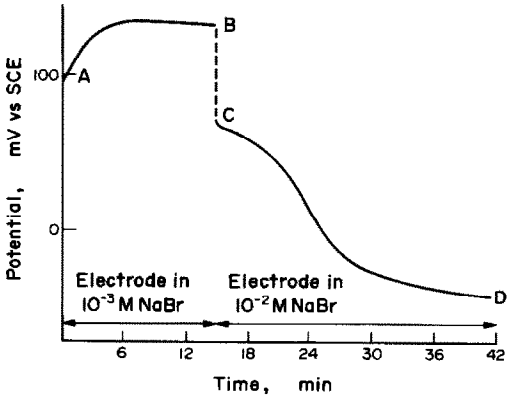

Fig. 1. The change of potential of an AgCl electrode placed in $10^{-2}M$ and $10^{-3}M$ NaBr. The points A, B, C correspond to $K_{Cl,Br} = 2$, point D corresponds to $K_{Cl,Br} = 3.3 \times 10^2$.

Table 2. Calculated, determined and literature data for selectivity coefficients of various systems

Case	Electrode system AB/B,C	$K_{BC}^{calc.}$ for diffusion-layer model	$K_{so(AB)}/K_{so(AC)}$	D_C/D_B	K_{BC}^{pot}			Literature data (Reference)
					$C_B' = C_C$	Method I	Method II	
$K \gg 1$	$PbS/Pb^{2+},Ag^+$	0.84*	4.0×10^{22}	0.84*	10^{-3}	1.6×10^{22}	—	
					10^{-1}	—	—	
	$AgCl/Cl^-,Br^-$	1.02	3.4×10^2	1.03	10^{-3}	2.1	2.7	1.2 (21); 40 (11) 3.3×10^2 (20)
					10^{-1}	3.3×10^2	3.1×10^2	1.2 (23); 2.0×10^2 (13) 3.3×10^2 (19) 2 (22); 3.0×10^2 (17) 15 (14); 3.0×10^2 (18)
$K \approx 1$	$AgBr/Br^-,SCN^-$	0.35	0.48	1.21	10^{-3}	0.34	0.62†	0.195 (4)
					10^{-1}	0.37	0.65†	0.65 (18)
	$PbS/Pb^{2+},Cd^{2+}$	0.22	0.32	0.74	10^{-3}	0.23	0.53†	0.3–0.8 (15)
					10^{-1}	0.22	0.50†	0.3 (method I) (16) 0.7 (method II) (16)
$K \ll 1$	$AgBr/Br^-,Cl^-$	3.0×10^{-3}	3.0×10^{-3}	0.97	10^{-3}	5.6×10^{-3}	—	1.8×10^{-3} (4) 3.3×10^{-3} (18)
					10^{-1}	2.9×10^{-3}	—	5.0×10^{-3} (22) 6.0×10^{-3} (22) 1.0×10^{-2} (14)
	$Ag_2S/Ag^+,Pb^{2+}$	2.5×10^{-23}	2.5×10^{-23}	1.68	10^{-3}	1.3×10^{-15}	—	1.6×10^{-22} (24)
					10^{-1}			4.0×10^{-14} (25) 1.0×10^{-12}–2.5×10^{-21} (26)

* $D_C/2D_B$ was taken instead of D_C/D_B.

† $K_{BC}^{pot} + 1$; before measurements in solution of B + C, the electrode was immersed for 3 min in 0.1*M* solution of C.

Table 3. The constants used in calculations of selectivity coefficients in the diffusion-layer model

Compound	pK_{so}	Ref.	Ion	D_x 10^{-5} cm^2/sec	Ref.
Ag_2S	49.20	27	I^-	2.05	30
AgI	16.08	27	Br^-	2.03	30
AgBr	12.30	27	Cl^-	2.08	30
AgCl	9.75	27	CN^-	2.50	31
AgSCN	11.97	27	SCN^-	2.52*	—
Cu_2S	47.60	28	Pb^{2+}	0.98	30
PbS	26.6	27	Cd^{2+}	0.72	30
CuS	35.20	28	Ag^+	1.65	30
CdS	26.1	27			
$Ag(CN)_2^-$	18.75†	29			

* Estimated from equation (13) on the basis of experimental selectivity coefficients.
† Log β_2.

When K is $>3 \times 10^2$ the electrode AB is rapidly and completely covered with AC. When K is $<3 \times 10^{-2}$ the interaction between the main ion B and the electrode covered with AC leads to dissolution of AC and restoration of the pure electrode surface. Within the indicated range of K a proper choice of the ratio [B]/[C] may provide fulfilment of the mixed-phase condition.

Summarizing the discussion, it can be stated that the well-known variability of selectivity coefficients of solid-state electrodes (*e.g.*, ref. 32) can be explained on the basis of the diffusion-layer model. The selectivity coefficients are influenced by phenomena occurring at and close to the electrode surface. The full description of these processes demands the knowledge of some non-thermodynamic parameters, such as the degree of surface coverage by the compound of the interfering ion, the rate of mixing, response time *etc.* At least some of them depend on the pretreatment of the electrode, surface area of the membrane, composition of the solution and procedure used for determination of selectivity coefficients.

APPENDIX—THE CYANIDE ELECTRODE

The case of the cyanide electrode based on silver iodide may be treated by the diffusion-layer model, as an intermediate example. For the reaction

$$AgI + 2\,CN^- \overset{K}{\rightleftharpoons} Ag(CN)_2^- + I^-$$

the value of K is $21.7^2 = 470.9$, but in this system no coverage of the electrode surface with a new compound occurs.

For this electrode Bound *et al.*[9] have assumed that $K \gg 1$ [case (A)] and consequently

$$[I^-]_0 = [I^-] + \frac{D_{CN^-}}{2D_{I^-}}[CN^-]$$

However, it seems more reasonable, on the basis of our discussion, to treat this system as case (B) and to present the electrode behaviour according to the equation

$$[I]_0 = \frac{2D_I K^{1/2}}{2D_I K^{1/2} + D_{CN}}[I] + \frac{D_{CN} K^{1/2}}{2D_I K^{1/2} + D_{CN}}[CN]$$

Treatment of the system according to case (B) should give values of $K_{I,CN} = 0.59$ irrespective of the method used. The values found by Bound *et al.* for $10^{-3}M$ solution, 0.60 and 0.57 for the separate- and mixed-solution methods, respectively, agree excellently with the predicted values for case (B). Other literature data cover a relatively broad range, *i.e.*, 1.0,[4] 0.59,[22] 0.42,[20] 0.40,[19] and 0.33.[21] It seems that in discussing such values of K, the formation of AgCN as well as $Ag(CN)_2^-$ should be taken into account.

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SHORT COMMUNICATIONS

CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—XXVI DETERMINATION OF CALCIUM IN THE PRESENCE OF LARGE AMOUNTS OF MAGNESIUM

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Summary—Two methods for the determination of calcium in the presence of very large amounts of magnesium are proposed. Both are based on back-titration of excess of EGTA, Thymolphthalexone being used as indicator. In the one method the titrant is a zinc solution, in the other a calcium solution is used, with a small amount of zinc present for end-point indication. Both titrations can be performed either visually or spectrophotometrically.

EGTA—ethyleneglycol-bis-(2-aminoethyl ether)tetra-acetic acid—has become a very attractive reagent for the titration of calcium in the presence of magnesium. The relatively large difference in stability between the calcium and magnesium EGTA complexes (log $K_{CaY} = 11.0$, log $K_{MgY} = 5.2$) offers the best possibility for direct titration of calcium. EGTA is unique amongst the complexans in this respect.

From the theoretical point of view the problem seems very simple: to titrate calcium directly with EGTA, with an indicator suitable only for calcium. As yet, however, there is no indicator for calcium which does not also respond to magnesium. This problem has, however, been solved in various ways, which have been recently reviewed.[1–3]

We cannot consider EGTA to be a good titrant for magnesium, or EDTA for successive titration of calcium and magnesium. Nevertheless, two papers have recently appeared describing attempts to use either EGTA or EDTA for such determinations. Wallén[4] titrates calcium at pH 9 with EGTA and then magnesium with EGTA after addition of 80% of alcohol. He follows both titrations potentiometrically with the Hg-electrode in solutions containing a small amount of Hg–EGTA complex. The method is said to be suitable for calcium up to 3.6 mg and for magnesium up to 2.3 mg. Christiansen *et al.*[3] describe successive EDTA titration of calcium and magnesium by potentiometric titration, using a calcium-selective electrode in solutions containing acetylacetone or 3,4-dihydroxybenzoic acid. Both compounds can form a more stable complex with magnesium than with calcium. As a result, the conditional stability constants of the calcium and magnesium EDTA complexes are both lowered a little but their difference is increased.

Nearly all published methods deal with the determination of calcium in the presence of reasonable amounts of magnesium (*e.g.*, at Ca:Mg ratios from 1:10 to 10:1). Many of them are reliable only under certain conditions which have to be maintained in the solution. These are often inconvenient for routine analysis. The problem of how to determine calcium when the ratio Mg:Ca is more than 100 is still open.

In the present work we have paid attention to the reaction of zinc ions with Thymolphthalexone. In alkaline medium, with alkaline earth metal cations this indicator forms intensely blue Me_2In^{2-} complexes. The corresponding zinc complex Zn_2In^{2-} is practically colourless and only slightly pink in high concentrations. We have found that in borax solution (pH 9–10) only magnesium forms a coloured complex with the indicator, provided that calcium (or strontium or barium) is bound as the EGTA-complex. Thus in the titration of EGTA with zinc solution, magnesium is displaced from its complex with the indicator at the end-point:

$$\underset{\text{blue}}{Mg_2In^{2-}} + 2\,Zn^{2+} = \underset{\text{colourless}}{Zn_2In^{2-}} + 2Mg^{2+} \qquad (1)$$

This reaction proceeds quantitatively even with very large amounts of magnesium (*e.g.*, 200 mg), which in borax solution is not precipitated as hydroxide. The course of the reaction is clear from Fig. 1, showing the spectra recorded during the titration of EGTA with zinc solution in the presence of a small amount of magnesium. At the end-point the blue solution becomes colourless. The colour change is also very sharp for visual titration. It should be mentioned that the magnesium must be present in at least $10^{-4}M$ concentration, because neither the Ca–EGTA complex nor free zinc gives a colour reaction with the indicator.

On this principle two methods for the determination of calcium in the presence of arbitrary amounts of magnesium were developed. The first is based on the titration of excess of EGTA with zinc solution, the second on the titration of excess of EGTA with calcium solution in the presence of a small amount of zinc ions. During the titration interesting colour changes take place, which will be further explained.

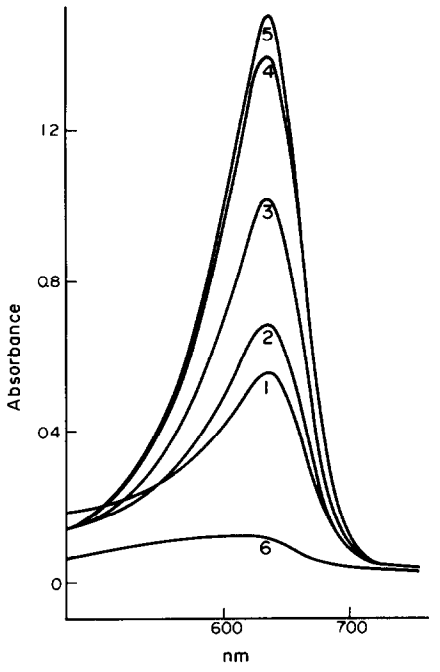

Fig. 1. Spectrophotometric titration of EGTA with zinc solution. Solution: 10 ml of 0.05*M* EGTA + 5 ml of 0.05*M* Mg + 1.5 ml of 0.1% freshly prepared solution of Thymolphthalexone + 10 ml of satd. borax solution. Final volume 60 ml. Cuvette 10 cm. Measured between 500 and 750 nm. Titration with 0.05*M* Zn. Fraction titrated, %: *1*—0; *2*—19.0; *3*—37.9; *4*—56.8; *5*—75.8; *6*—100.

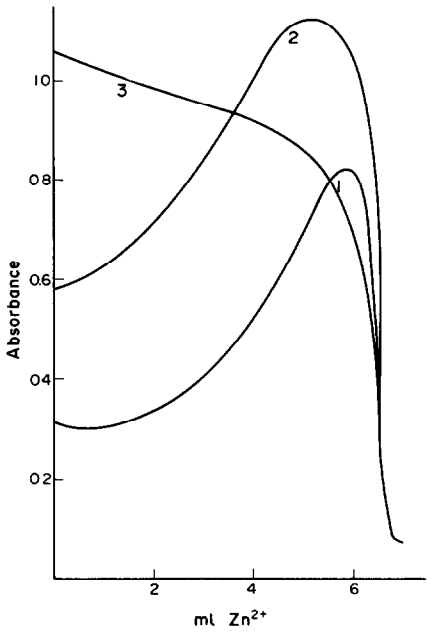

Fig. 2. Determination of 0.5 ml of 0.05*M* calcium by back-titration of excess of EGTA with zinc solution in the presence of various amounts of magnesium. Solution: 0.05*M* Ca + *x* ml of 0.05*M* Mg + 7 ml of 0.05*M* EGTA + 10 ml of satd. borax solution and 0.1 ml of 0.1% Thymolphthalexone solution. *1*—*x* = 1 ml of 0.05*M* Mg; *2*—*x* = 2 ml of 0.05*M* Mg; *3*—2 g of $MgSO_4 \cdot 7H_2O$.

EXPERIMENTAL

Reagents

EGTA, 0.05M.
EDTA, 0.05M.
Calcium chloride, 0.05M.
Magnesium chloride, 0.05M.
Zinc chloride, 0.05M.
Buffer solution. Saturated borax solution.
Indicator. Freshly prepared 0.1% solution of Thymolphthalexone. Colourless solutions are stable for several days. For visual titrations a solid mixture with potassium nitrate (1:100) can be used.

Spectrophotometric titration of calcium

A slightly acidic solution containing 0.5–10 mg of calcium and 1–200 mg of magnesium is pipetted into the cuvette, then 8–10 ml of 0.05*M* EGTA and 10 ml of saturated borax solution are added and the whole is diluted to about 60 ml; then 0.2 ml of 0.1% indicator solution is added. The titration is performed by making successive additions of 0.05*M* zinc solution and after each addition measuring the absorbance at 640 nm. The end-point is given by a sudden drop of the absorbance at 640 nm nearly to zero.

Remarks. The order of addition of reagents must be strictly adhered to, because calcium (not bound with EGTA) is precipitated in borax solutions. As already said, the titrations can be performed only in the presence of magnesium. Very low amounts of magnesium are also nearly all bound with EGTA and the initial solutions after the addition of indicator are coloured only very slightly or not at all. During the titration with zinc, magnesium is displaced from its EGTA complex and reacts with the indicator:

$$2MgY^{2-} + 2Zn^{2+} + H_2In^{4-} = 2ZnY^{2-} + Mg_2In^{2-} + 2H^+ \quad (2)$$
colourless blue

Therefore the blue colour becomes progressively deeper up to the end-point, and disappears suddenly when excess of zinc is present, according to equation (1). The spectrophotometric curves for small amounts of magnesium are somewhat deformed sinusoids (Fig. 2, curves 1 and 2). In the presence of large amounts of magnesium, only a relatively small part of it is bound with EGTA and the curves are normal in shape (Fig. 2, curve 3). From Fig. 2 we also see that the initial colour of the solution depends on the Mg:EGTA ratio and on the concentration of indicator. For a volume of 60–70 ml and a 10-cm cuvette, the most suitable volume of the indicator is 0.2 ml of freshly prepared 0.1% solution. A large excess of the indicator causes a very deep blue colour which cannot be measured spectrophotometrically, but its disappearance can be followed visually.

Table 1. Determination of calcium in the presence of magnesium

Taken			Back-titration,	
Ca, 0.05*M*, *ml*	Mg, 0.05*M*, *ml*	EGTA, 0.05*M*, *ml*	Zn, 0.05*M*, *ml*	Ca found, 0.05*M*, *ml*
3.03	10	9.65	6.63	3.02
	15		6.63	3.02
	20		6.63	3.02
	30		6.65	3.00
	50		6.64	3.01
	100		6.60	3.05
1.01	25	4.82	3.76	1.07
	50		3.76	1.07
9.10	1	9.65	0.51	9.14
	9		0.61	9.04

Table 2. Analysis of magnesites

Composition, %	Nominal CaO, %	Found, CaO, %
SiO_2 1.64, Fe_2O_3 4.22, Al_2O_3 0.21 MgO 41.30, CO_2 49.12	3.56	3.76, 3.70 3.77, 3.74
SiO_2 1.41, Fe_2O_3 3.72, Al_2O_3 0.48 CO_2 49.64, MgO 43.94	0.84	0.87, 0.90
SiO_2 0.56, TiO_2 0.01, Fe_2O_3 2.15 Al_2O_3 0.39, MnO 0.15, Na_2O 0.02 P_2O_5 0.05, CO_2 50.25, MgO 45.01	0.56	0.62, 0.64

By the method described we can determine as little as 1 mg of calcium in the presence of 2 g of $MgSO_4 \cdot 7H_2O$ (see Fig. 2, curve 3).

Visual titration of calcium

The sample solution is prepared in a 200–250-ml flask as for the spectrophotometric titration, and diluted to about 150 ml. Then a small amount of indicator mixture is added and the solution is titrated with 0.05*M* zinc until the solution is decolourized.

The solution must be thoroughly mixed after each addition of titrant. Typical results are summarized in Table 1.

Alternative spectrophotometric titration

The back-titration of excess of EGTA can be modified as follows. To the calcium–magnesium solution 0.1 ml of 0.05*M* zinc solution and enough 0.05*M* EGTA to complex the calcium and zinc are added. After addition of 10 ml of saturated borax solution and 0.2 ml of 0.1% indicator solution the mixture is titrated spectrophotometrically with 0.05*M* calcium, at 640 nm. First, that part of the magnesium bound with EGTA is displaced from the complex and reacts with the indicator. At the end-point zinc is also displaced and reacts with the Mg-indicator complex according to equation (1) and the absorbance drops nearly to zero. Visual titrations can be performed similarly but must be done a little more slowly in the vicinity of the end-point because the final displacement reaction Zn–EGTA + Ca^{2+} = Ca–EGTA + Zn^{2+} proceeds slowly (log K_{ZnEGTA} = 12.2; log K_{CaEGTA} = 11.0). The results obtained by this method are in good agreement with those obtained by the back-titration with zinc.

Interferences

The method described is applicable only to pure calcium–magnesium solutions. For the analysis of various geological materials it can be applied after separation of all interfering elements. First of all, iron and aluminium must not be present. Triethanolamine cannot be used for their masking, because it needs a very high pH (about 12), at which magnesium is precipitated as hydroxide. Precipitation with ammonia cannot be used either, because ammonium salts interfere in the titration of EGTA with zinc solution. It is very convenient, however, to use precipitation with hexamethylenetetramine (see below). Iron can be extracted with a 50% solution of acetylacetone in chloroform. Other elements such as nickel, manganese, copper, must also be removed before the calcium determination, or their sum with calcium determined and a correction applied for the amounts of them present.

PRACTICAL APPLICATIONS

We have applied this method to material having a very low calcium content. For this purpose we used three samples of standard magnesite and one sample of serpentinite.

Determination of calcium in magnesite

After precipitation of Fe, Al, Ti with hexamethylenetetramine. Dissolve 0.2–0.5 g of the sample in 2 ml of conc. hydrochloric acid and 10 ml of water and evaporate the solution to dryness. Add several drops of hydrochloric acid to the residue and dissolve it in hot water. Cool the solution, add 0.5 g of hexamethylene and boil for 5–10 min. Filter off the precipitated hydroxides. To the filtrate, in a titration flask, add 10–15 ml of 0.05*M* EGTA, 10–15 ml of saturated borax solution and a small amount of solid indicator, and titrate the diluted solution with 0.05*M* zinc from blue to colourless.

After extraction of iron and traces of aluminium with acetylacetone. Dissolve the sample as described above. Then adjust the pH of the solution to 1, and extract the iron with three 25-ml portions of a 50% solution of acetylacetone in chloroform. Separate the aqueous phase and boil off the dissolved acetylacetone (traces of which decolorize the Mg-indicator complex and must not be present). Neutralize the solution with sodium hydroxide and then continue as described for the precipitation method.

Analysis of serpentinite

Fuse the sample with sodium carbonate, dissolve the cooled melt in hydrochloric acid and evaporate the solution to dryness. Filter off the silica and evaporate the filtrate to dryness. Extract the iron and continue with the titration as described above.

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USE OF HYDROXYLAMINE HYDROCHLORIDE IN THE TITRIMETRIC DETERMINATION OF MANGANESE IN PYROLUSITE

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Summary—A procedure is described for the determination of total manganese in pyrolusite. The sample is decomposed with hydroxylamine hydrochloride solution. The residue left after filtration is fused with sodium carbonate and extracted again with hydroxylamine hydrochloride solution. A suitable aliquot is titrated with EDTA at pH 10, with Eriochrome Black T as indicator, after masking of interfering elements.

The determination of manganese in pyrolusite by existing methods such as Volhard's[1] and the bismuthate method[2] is long and somewhat tedious. It is the dissolution of the ore that makes these methods time-consuming: the finely powdered ore is first digested with hydrochloric acid and any unreacted residue is filtered off, then fused with alkali, the melt is extracted with acid to ensure complete dissolution, and finally the filtrates are fumed with sulphuric acid.

In the present method, hydroxylamine hydrochloride solution is used to dissolve the ore, attacking it vigorously even at room temperature, bringing into solution within a few minutes all the MnO_2 together with any MnO and Mn_2O_3 present. Only a small quantity of manganese (0.2–0.5%) is left in the residue, probably as silicate or other manganese compounds and is brought into solution by fusing the residue with sodium carbonate and subsequently extracting the melt with hydroxylamine hydrochloride solution.

In this dissolution process, all the manganese is in the bivalent state in the final solution. Another advantage of the method is that the other metallic elements present in the ore, *viz.* iron, aluminium, calcium, magnesium and barium, are not dissolved to any appreciable extent. The total manganese content is determined by titration with EDTA at pH 10, with Eriochrome Black T as indicator,[3] after masking of iron(II) with cyanide in the presence of ammonia,[4] aluminium with triethanolamine,[5] calcium with molybdate[6] and magnesium with fluoride.[7]

The accuracy and the precision of the method have been determined by analysing British Chemical Standards Manganese Ore No. 176 and Bureau of Analysed Samples Ltd. pyrolusite Mn-ore 18 and Mn-ore 18aG. Results for a few pyrolusite ores were also compared with those obtained by the bismuthate and Volhard methods.

EXPERIMENTAL

Reagents

Hydroxylamine hydrochloride solution, 20% *w/v*.

Sodium fluoride solution, 10% *w/v*.

Ammonium molybdate solution, 5% *w/v*.

Potassium cyanide solution, 5% *w/v*.

Ammonia solution. Dilute concentrated ammonia solution with an equal volume of distilled water.

Triethanolamine solution, 30% *v/v*.

Ammonium chloride-ammonia buffer. Add 284 g of concentrated ammonia solution to 35 g of ammonium chloride and dilute to 500 ml with distilled water.

Eriochrome Black T indicator. Dissolve 0.2 g of dye in 15 ml of triethanolamine and 5 ml of absolute alcohol.

EDTA solution, 0.01*M*.

Standard manganese solution, 1 *mg/ml*. To 0.5000 g of the pure electrolytic metal in a covered 250-ml beaker with a lid, slowly add 25 ml of 20% hydroxylamine hydrochloride solution. When the reaction has subsided and the metal is completely dissolved, rinse the lid and the sides of the beaker, transfer the solution into a 500-ml volumetric flask, and make up to volume with distilled water.

Dissolution of sample

Weigh 0.5 g of the finely powdered ore (about 100-mesh, dried at 110°) into a 250-ml beaker covered with a lid. Add 20 ml of 20% hydroxylamine hydrochloride solution gradually, with due precaution, since the reaction is very vigorous even at room temperature. After the reaction has subsided (about 15 min), wash down the lid and the sides of the beaker. Filter the solution into a 250-ml volumetric flask through a Whatman No. 42 paper or equivalent. Wash the residue several times with 10% hydroxylamine hydrochloride solution and finally with distilled water. Ignite the paper and residue in a platinum crucible, fuse the product with sodium carbonate, and extract the cooled melt with 10% hydroxylamine hydrochloride solution at room temperature. Filter the solution into the volumetric flask containing the original solution, and wash the paper first with a few ml of 10% hydroxylamine hydrochloride solution and then with distilled water. Make up to volume and mix.

Titration

The cyanide complex of manganese(II) reacts with Eriochrome Black T to form a red complex, but also reacts with EDTA, and the manganese can be determined in the presence of cyanide.[8]

Place a suitable aliquot of the sample solution in a 250-ml conical flask and dilute it to about 30 ml with distilled water. Heat the solution to 50–60° and add 5 ml of sodium fluoride solution and 10 ml of triethanolamine solution, (if necessary more hydroxylamine hydrochloride solution may be added to keep the manganese in the bivalent state and prevent its precipitation). Make the solution faintly ammoniacal with dilute ammonia solution and add 2 ml of potassium cyanide solution followed by 5 ml of ammonium molybdate solution. Heat the solution to 60–80° and then cool it to room temperature. The heating is necessary for efficient masking. Titrate with 0.01*M* EDTA after the addition of ammonium chloride–ammonia buffer (10 ml) and 3 or 4 drops of Eriochrome Black T indicator, till the colour changes from wine-red to blue or blueish green.

Standardize the EDTA similarly against a suitable aliquot of the standard manganese solution.

RESULTS AND DISCUSSION

The results obtained by the proposed method were in good agreement with those obtained by standard methods

Table 1

Sample	Manganese,* % Proposed method	Volhard method	Bismuthate method	Mean certified value, %
BCS 176	51.4 ± 0.2	51.4	51.4	51.3
BAS 18	51.1 ± 0.2	51.2	51.3	51.2
BAS 18aG	58.3 ± 0.2	58.4	58.5	58.3
PYR-1	36.5 ± 0.1	36.6	36.6	—
PYR-2	23.6 ± 0.1	23.7	23.8	—
PYR-3	42.7 ± 0.1	42.6	42.7	—
PYR-4	31.5 ± 0.1	31.5	31.5	—
PYR-5	55.2 ± 0.2	55.3	55.3	—

* Mean and range of 5 determinations.

Table 2

Sample	Ca, *ppm*	Mg, *ppm*	Fe, *ppm*	Al, *ppm*	Ba, *ppm*
BCS 176	1.84	0.92	1.09	3.04	0.56
BAS 18	1.87	1.42	2.07	0.87	0.79
BAS 18aG	1.95	1.48	1.22	4.18	0.67
PYR-1	0.62	0.24	2.01	2.04	0.92
PYR-2	0.59	0.25	2.64	3.20	0.32
PYR-3	1.17	0.52	2.73	1.47	0.54
PYR-4	0.78	0.36	3.22	2.11	0.62
PYR-5	1.32	0.62	0.73	1.11	0.46

and with the certified values for the standards, and are shown in Table 1.

The results obtained when the fusion of the residue from the first dissolution step was omitted were uniformly 0.3–0.5% lower than those in Table 1, and this amount of manganese was shown to be left in the residues (determined colorimetrically by periodate oxidation).

The major extractable interfering elements were determined in the solutions prepared by the recommended procedure, iron by the bypridyl method,[9] aluminium by 8-hydroxyquinoline,[9] and calcium, magnesium and barium by atomic absorption (with compensatory amounts of manganese added to the standards, and lanthanum as releasing agent when necessary). The results are given in Table 2 and clearly show the suitability of the method for the estimation of manganese in pyrolusite ores. The interfering elements are extracted in such minor amounts that they do not pose any problem in the titration of manganese by EDTA as they can be easily masked. The ease and the simplicity of the method add to its suitability.

Table 3

Sample	Manganese,* % Rapid method	Bismuthate method
BCS 176	50.9 ± 0.2	51.4
BAS 18	50.4 ± 0.2	51.3
BAS 18aG	57.8 ± 0.2	58.5
PYR-1	35.9 ± 0.1	36.6
PYR-2	23.0 ± 0.1	23.8
PYR-3	41.9 ± 0.2	42.7
PYR-4	30.9 ± 0.1	31.5
PYR-5	54.9 ± 0.2	55.3

* Means and range of 5 determinations.

Rapid estimation of the total manganese content in pyrolusite

Treat 0.1 g of finely powdered ore with 25 ml of 20% hydroxylamine hydrochloride solution in a 250-ml conical flask and dilute to about 30 ml with distilled water after the reaction has subsided. Titrate with EDTA at pH 10, after masking interfering elements, as already described. The end-point is not so stable, and lower values are obtained, but the method is useful for exploratory evaluation of ores in field operations and prospecting. Typical results are given in Table 3.

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ETUDE DE LA BASICITE DANS LE PHENOL AQUEUX: APPLICATION AU TITRAGE DE BASES ORGANIQUES

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Résumé—Les bases faibles peuvent être titrées par potentiométrie ou conductimétrie dans le phénol aqueux 90/10 (p/p). L'étude spectrophotométrique en présence de dinitro-2,4 phénol a permis d'établir une classification des bases organiques sensiblement superposable à celle observée dans d'autres solvants; la mesure de constante diélectrique confirme que le solvant est un hémihydrate. Les modalités de titrage et le domaine d'application à un grand nombre de bases organiques d'intérêt pharmaceutique sont décrits.

La protométrie dans les solvants non aqueux a fait l'objet de multiples applications et les analystes disposent d'une gamme très étendue de solvants qui leur permet de résoudre très aisément les problèmes de titrage des bases et acides organiques. L'étude fondamentale des couples acide–base est également très poussée avec le recours aux méthodes électrochimiques, spectrophotométriques et a donné lieu à de nombreux travaux tels que les ouvrages, mises au point ou mémoires de Kolthoff et Bruckenstein, Charlot, Trémillon et les revues générales bisannuelles d'*Analytical Chemistry*. La recherche de nouveaux solvants continue néanmoins de susciter de l'intérêt dans la mesure où ils sont commercialement accessibles dans un état de pureté convenable pour la pratique courante de l'analyse et permettent d'envisager de nouveaux types d'application ou d'améliorer des procédés classiques; tel est le cas du phénol aqueux (90/10; p/p) dont l'emploi est décrit dans le présent mémoire. Ce solvant se prête au dosage des bases organiques et de leurs sels selon des modalités et un domaine d'application superposables à ceux de l'acide acétique anhydre avec toutefois des différences de comportement.[1,2] L'étude a été envisagée sur le plan de l'application pratique au dosage des bases organiques à usage pharmaceutique. Les constantes d'équilibre acide-base et l'ordre de classement des bases organiques ont été établis dans le phénol aqueux par spectrophotométrie dans le visible, en utilisant le dinitro-2,4 phénol comme indicateur coloré de référence selon la méthode préconisée par Trémillon *et al.*[3,4]

PARTIE EXPERIMENTALE

Réactifs

Phénol aqueux. Phénol–eau 90/10 p/p.

Solutions de bases organiques 1.10^{-2} *à* 1.10^{-4} *M dans le phénol aqueux.*

Solution 0,1 *N d'acide perchlorique dans le phénol aqueux*, Obtenue par dilution de 10 ml de solution aqueuse d'acide perchlorique (d = 1,67 g/ml) dans le phénol aqueux pour obtenir 1000 ml. La solution est étalonnée au moyen du carbonate monopotassique par potentiométrie ou en présence d'hélianthine.

Solution aqueuse 0,5 *M d'acétate mercurique dans le phénol aqueux.*

Solution aqueuse 0,5 *M d'acétate de baryum.*

Solution $5{\cdot}10^{-5}$ *M de dinitro*-2,4 *phénol dans le phénol aqueux.*

Détermination de la basicité

Déterminer l'absorption à 410 nm de solutions dans le phénol aqueux renfermant la même quantité d'indicateurs ($5{\cdot}10^{-5}$ *M*) et des concentrations croissantes de base comprises entre 10^{-2} et 10^{-4} *M*.

Tracer la droite $1/D$ en fonction de $1/C_B$, D représentant l'absorption et C_B la concentration de la base.

Titrage potentiométrique des bases organiques et de leurs sels

Dissoudre une prise d'essai exactement connue voisine de 0,5 m*M* dans 50 ml de phénol aqueux. Adapter les électrodes, (verre–calomel), titrer au moyen de la solution 0,1 *N* d'acide perchlorique et déterminer le point d'équivalence.

Dans le cas des chlorures et des sulfates de bases organiques, ajouter avant le titrage, la quantité nécessaire respectivement d'acétate mercurique 0,5 *M* ou d'acétate de baryum 0,5 *M*; l'excès de l'un ou l'autre réactifs no doit pas dépasser 10%.[2]

Les titrages conductimétriques[2] peuvent être effectués dans les mêmes conditions.

RESULTATS

Constantes de basicité des couples acide–base

La forme acide du dinitro–2,4 phénol (HIn) n'absorbe pas à partir de 410 nm (Fig. 1, courbe 1); entre l'indicateur acide faible et la base B dont la concentration est supérieure à celle de la forme acide de l'indicateur, il s'établit un équilibre

$$B + HIn \rightleftharpoons BHIn$$

avec

$$K = \frac{[B][HIn]}{[BHIn]}$$

qui se traduit par une absorption 410 nm (Fig. 1, courbes 2 à 8). Les bases organiques en solution dans le phénol aqueux sont de force voisine; la méthode spectrophotométrique directe préconisée par Trémillon[3,4] est de ce fait applicable au calcul de la constante d'équilibre K.

L'expression $K = [B][HIn]/[BHIn]$ peut être mise sous la forme

$$\frac{1}{D} = \frac{1}{dc_1} + \frac{K_B}{dc_1} = \frac{1}{C_B}$$

dans laquelle

$$C_B = [B] + [BHIn]$$
$$C_1 = [HIn] + [BHIn]$$
$$[BHIn] = D/d$$

Les variations de $1/D$ en fonction de $1/C_B$ permettent d'obtenir une droite qui a pour ordonnée la valeur $1/dc_1$.

Tableau 1.

Classification des bases dans le phénol aqueux	$1/dc_1$	K_B/dc_1	K_B	pK_B
Ephédrine	0,75	$2{,}4\cdot10^{-3}$	$3{,}2\cdot10^{-3}$	2,49
Atropine	0,62	$9{,}0\cdot10^{-4}$	$1{,}46\cdot10^{-3}$	2,83
Quinine I	0,58	$2{,}61\cdot10^{-3}$	$4{,}5\cdot10^{-3}$	2,34
Quinidine I	0,68	$2{,}58\cdot10^{-3}$	$3{,}8\cdot10^{-3}$	2,42
Morpholine	0,80	$2{,}0\cdot10^{-3}$	$2{,}5\cdot10^{-3}$	2,60
Codéine	0,92	$4{,}87\cdot10^{-4}$	$5{,}3\cdot10^{-4}$	3,27
Papavérine	0,99	$7{,}42\cdot10^{-4}$	$7{,}5\cdot10^{-4}$	3,12
Pilocarpine	1,20	$1{,}20\cdot10^{-5}$	10^{-5}	5,0
Strychnine	1,47	$5{,}58\cdot10^{-5}$	$3{,}0\cdot10^{-5}$	4,52
Spartéine	1,71	$6{,}49\cdot10^{-5}$	$3{,}8\cdot10^{-5}$	4,42
Cinchonine	2,00	$9{,}0\cdot10^{-5}$	$4{,}5\cdot10^{-5}$	4,34

A partir de ces valeurs, le calcul des pK_B permet d'établir une classification expérimentale constituant l'échelle de basicité des bases organiques dans le phénol aqueux (Tableau 1).

La classification des bases d'après le calcul des pK_B à partir des mesures spectrophotométriques avec le dinitro-2,4 phénol est superposable à celle obtenue[2] à partir des mesures de conductivité en solution 0,01 M et correspond sensiblement à l'échelle de basicité dans l'eau.

Constante diélectrique du phénol aqueux

La constante diélectrique (ϵ) du phénol aqueux a été mesurée sur appareil Dipolmètre (W.I.W., Type D.M.O.$_1$); elle varie linéairement en fonction de la teneur en eau du mélange.[2]

Phénol, g	Eau, g	ϵ à 27°C
100	10	15,5
100	11,5	16,4
100	15	17,5
100	17,5	18,4
100	20	19,2
100	30	22,6

Ces valeurs sont plus faibles que celles obtenues par calcul; l'interprétation de ce fait réside en accord avec Rhodes et Markley[5] dans la formation d'un hémihydrate de phénol $2C_6H_5OH\cdot H_2O$ renfermant 8,25% d'eau. La teneur en eau du phénol aqueux 100/10 (p/p) employé comme solvant, est proche de cette valeur (8,74%). L'eau est d'ailleurs assez fortement liée ainsi que le montrent les résultats déficitaires de la détermination de la teneur en eau selon Karl Fischer ou les mesures physiques effectuées sur les mélanges phénol–eau.[6,7]

La constante diélectrique du phénol aqueux est voisine de celle des alcools benzylique (13,1) amylique (13,9), isoamylique (14,7), et de la méthyléthylcétone (18,4) et méthylisobutylcétone (13,1). Elle conduit à classer le phénol dans le groupe des solvants faiblement protiques. Les domaines d'application du phénol aqueux et de ces solvants, au titrage des bases organiques et de leurs sels ne sont pas strictement superposables. Ces solvants sont utilisables pour le titrage des bases organiques faibles avec une détection précise du point d'équivalence. Un prix de revient modique et un pouvoir solvant plus étendu jouent en faveur du phénol aqueux. De plus, la constante diélectrique du solvant n'est pas le seul facteur à prendre en considération; le titrage des composés dibasiques dissous dans les alcools ou les cétones révèle un seul point d'équivalence; dans le phénol aqueux, les deux fonctions basiques sont décelées; il présente aussi cet avantage par rapport à l'acide acétique anhydre dans lequel par suite de l'effet de nivellement les bases bifonctionnelles ne sont pas différenciées. Enfin, le domaine d'application est décelé vers une zone plus basique; le phénol aqueux autorise en effet le dosage de bases organiques faibles non titrables dans les alcools et les cétones.

Application au dosage des bases organiques

Le dosage des bases organiques ou de leurs sels (à l'exception des chlorures et sulfates) en solution dans le phénol aqueux ne présente aucune difficulté. Le point d'équivalence est décelé par potentiométrie ou conductimétrie. Dans le cas des molécules dibasiques (éthylénediamine, quinine...) deux inflexions sont observées; tel est à titre indicatif (Fig. 2) le cas du dosage potentiométrique de la quinine. Le procédé est directement applicable aux chlorures après complexation par l'acétate mercurique, par transposition du procédé de Pifer et Wollish,[8] Les sulfates sont précipités à l'état de sulfate de baryum par addition d'acétate de baryum avant le titrage. Ce procédé n'est pas applicable[9] dans l'acide acétique anhydre en raison de la solubilité notable du sulfate de baryum; la précipitation à l'état de sulfate de benzidine préconisée dans l'acide acétique anhydre n'a pas été reprise en raison de la toxicité de la benzidine et ses dérivés. Les procédés décrits dans la partie expérimentale ont permis de doser avec la précision habituelle des méthodes volumétriques les bases organiques appartenant aux diverses séries d'amines pri-

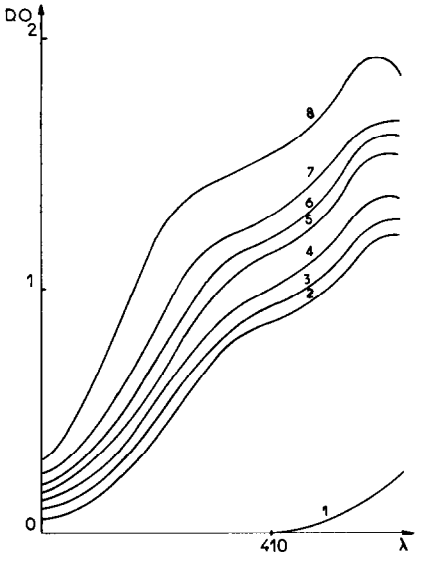

Fig. 1. Densité optique en fonction de la longueur d'onde. 1, Dinitro-2,4 phénol, $5\cdot10^{-5}$ M; 2–8, ephédrine (2; $4\cdot10^{-3}$ M: 3; $6\cdot10^{-3}$ M: 4; $8\cdot10^{-3}$ M: 5; 10^{-2} M: 6; $2{,}5\cdot10^{-2}$ M: 7; $4\cdot10^{-2}$ M: 8; $2{,}25\cdot10^{-1}$ M).

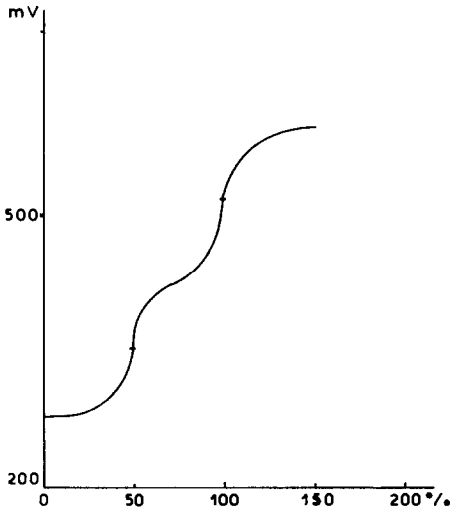

Fig. 2. Titrage potentiométrique de la quinine.

maires, secondaires, tertiaires aliphatiques et aromatiques et à des séries variées de bases organiques et leurs sels d'intérêt pharmaceutique: ammoniums quaternaires à longue chaine, dérivés de la phénothiazine, anesthésiques locaux, spasmolytiques, éphédrines, vitamines (thiamine, pyridoxine ...), alcaloïdes (atropine, quinine, quinidine, cocaïne, papavérine, pholcodine *etc.*), médicaments à noyau pyridique, pipéridinique, pyrazinique, imidazole, quinoléine, isoquinoléine *etc.* Le phénol aqueux constitue un bon solvant pour certaines matières plastiques; Basu,[10] a préconisé son emploi, le procédé décrit au dosage des fonctions basiques libres des polyamides 6–6 et 6–10, pour le titrage du nylon. Le procédé décrit est applicable au dosage des fonctions basiques libres dans les polyamides.

En conclusion, l'intérêt du phénol aqueux réside à la fois dans son pouvoir dissolvant et dans son large domaine d'applications au dosage des bases organiques. Les procédés sont faciles à mettre en oeuvre, les titrages sont rapides et atteignent la précision exigée des méthodes volumétriques.

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Summary—Weak bases can be titrated potentiometrically or conductimetrically in phenol–water mixture (90/10 w/w). A spectrophotometric study in presence of 2,4-dinitrophenol is used to establish a classification of organic bases that is superposable on that found for other solvents; measurement of the dielectric constant confirms that the solvent is a hemihydrate. The methods of titration and range of application to many organic bases of pharmaceutical interest are described.

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DETERMINATION OF LEAD AND ANTIMONY IN FIREARM DISCHARGE RESIDUES ON HANDS BY ANODIC STRIPPING VOLTAMMETRY

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(*Received* 19 *August* 1976. *Accepted* 13 *October* 1976)

Summary—When a person fires a gun, trace quantities of lead, antimony and barium are deposited on the hand. Detection of high levels of these trace metals on the hand of a suspect may therefore be significant evidence in an investigation. In this study conditions for the determination of lead and antimony in gunshot residues by anodic stripping voltammetry using a mercury-coated graphite electrode are established. A sample is collected by washing the hand in 1*M* hydrochloric acid. Lead is determined in a portion of this sample, with 1*M* hydrochloric acid as electrolyte. Antimony is determined in a second portion, with 4*M* hydrochloric acid as electrolyte. Prior separation or preconcentration steps are not required for either analysis. The procedure has been applied to samples obtained from five "normal" hands and five hands after they have fired a weapon.

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The amounts of lead, antimony and barium found on normal hands and hands after firing have been reported by Krishnan[3] on the basis of 12–30 samples. The ranges are summarized in Table 1. Since the amounts of residue

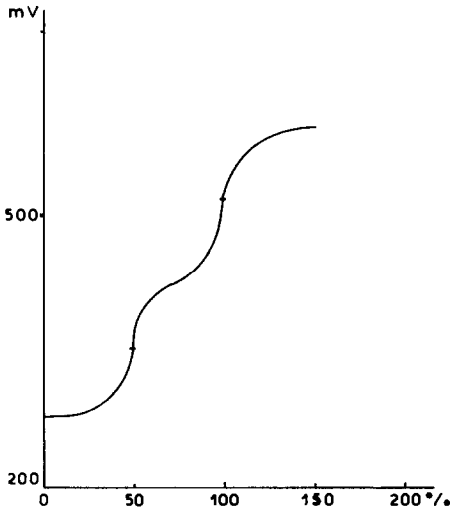

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Table 1. Ranges of amounts of trace metals found on hands[3] (μg)

	Lead	Antimony	Barium
Normal hands	<5–95	<0.003–0.94	0.07–0.27
After firing a .38 revolver	13–326	0.35–5.9	0.19–1.4

are in the microgram or submicrogram range, the method of analysis chosen should be very sensitive. Chemical spot-tests have been used but are relatively insensitive and not usually quantitative. Neutron-activation analysis was the first widely used instrumental approach and is still an important method. Antimony and barium may both be determined after drying, irradiation with thermal neutrons, chemical separation, and counting. Unfortunately this method requires access to a reactor or other neutron source and in any case cannot be used for the determination of lead. Recently a number of atomic-absorption procedures, both with flames[3,4] and without[5,6,7] have been reported. Difficulties with these techniques, in addition to those peculiar to any one element, include the need for preconcentration and/or separation before analysis[5] and the problems of calibration, which are especially severe for atomic absorption using a graphite furnace atomizer.[8]

Another method of trace analysis is anodic stripping voltammetry (ASV). Since ASV is applicable only when a metal can be readily reduced to the elemental state and reoxidized, it may be used for the determination of lead[9] and of antimony[10] but not of barium. ASV is sensitive, the instrumentation is not expensive and in most cases calibration procedures which take account of the matrix are straightforward.[11] Because the quantity of electricity indicated by the area of the stripping peak is proportional to the concentration of the element in solution (under specific conditions), there is a fundamental linear relationship between peak-area and concentration of analyte. In many instances this relationship extends over several orders of magnitude of concentration,[11] and calibration by the method of standard additions is possible. Measurements are often simplified by using peak-height (which is also proportional to concentration under ideal circumstances) instead of peak-area.

This paper describes procedures for the determination of lead and antimony in firearm discharge residues on hands, by use of anodic stripping voltammetry.

EXPERIMENTAL

Reagents

All chemicals used were of reagent grade. The water was redistilled from an all-glass apparatus. A 1000-ppm stock solution of lead was prepared by dissolving lead nitrate in 0.5% v/v nitric acid, and a 100-ppm working solution by dilution of the stock with 0.5% nitric acid. A 1000-ppm stock solution of antimony was prepared by adding just sufficient concentrated hydrochloric acid to antimony trioxide to dissolve it; the solution was then diluted to volume with 2*M* hydrochloric acid. A working solution (either 1 or 5 ppm) was prepared daily by appropriate dilution of the stock with 2*M* hydrochloric acid.

Apparatus

Anodic stripping voltammograms were run on a PAR Model 174A Polarographic Analyzer and the peaks recorded on a Hewlett Packard 7101BM Strip Chart Recorder. For the antimony determination a current compensation device was constructed similar to that described by Gilbert and Hume.[10] The cell was a PAR Model 9300 Electrolytic Cell containing two nitrogen inlet ports and three electrode ports. A saturated calomel electrode was used as the reference electrode, without an additional salt bridge. The counter-electrode was a piece of platinum wire in a compartment separated from the main cell by a fine fritted-glass disc. This compartment was filled with the same electrolyte as that used in the main cell, *i.e.*, 1*M* hydrochloric acid for lead determinations and 4*M* hydrochloric acid for antimony determinations. The working electrode was a mercury-coated graphite electrode (MCGE) prepared in the manner described by Gilbert and Hume,[10] except that acidified distilled water was used instead of sea-water. The cell was stirred magnetically with a small Teflon-covered stirrer rotating at 900 rpm. When not in use the cell was stored in 10% v/v nitric acid. The electrode was stored in distilled water acidified to pH 2.5 with nitric acid, under an applied potential of −0.10 V *vs.* SCE. Stored in this manner, the electrode could be used for at least four determinations each of lead and antimony and over a period of more than one week.

Standard additions were made with a Pipetman Model P200D micropipette.

Recommended analytical procedures

Sample collection. Polyethylene bags (Baggies Alligator™ Plastic Bags, 29 × 34 cm) and 100-ml polyethylene bottles are prewashed by soaking them in 10% v/v nitric acid and then carefully rinsed with water. Exactly 30 or 50 ml of 1*M* hydrochloric acid are carefully poured into the bag without touching the inside. The suspect's hand is inserted into the bag and shaken in the acid for about 30 sec, ensuring that all parts of the hand are wetted. The acid is then transferred into one of the bottles and kept for analysis.

Analysis for lead. One ml of the sample is pipetted into the electrolysis vessel and diluted to exactly 20 ml with 1*M* hydrochloric acid. The solution is deaerated for approximately 10 min and nitrogen is then passed over the solution for the duration of the analysis. The electrodes are placed in the assembly and a potential of −0.70 V is applied for 180 sec while the solution is stirred at 900 rpm. The stirring is stopped and electrolysis is continued for a further 20 sec. The anodic scan at 10 mV/sec is then begun and continued to −0.25 V with a current sensitivity of 0.5 mA for full-scale deflection. The lead peak occurs at −0.50 V and the copper peak at −0.29 V but the latter was not considered in the present application. The measurement procedure is repeated after adding successive spikes of 20 μl of 100-ppm lead solution, corresponding to added lead concentrations of 100 ppM (parts per milliard). Five such spikes are added and each measurement procedure is repeated to check the reproducibility.

For lower concentrations of lead, as in the case of a "blank" hand, 10 ml of sample solution may be used and made up to 20 ml with 1*M* hydrochloric acid.

The peak-height is plotted against concentration and the slope and intercept are calculated by the method of least squares. Peak-area may be used if desired, but results were found to be not significantly different from those obtained by using peak-height.

A typical set of scans is shown in Fig. 1 and results are given in Table 2.

Analysis for antimony. Fifteen ml of sample and 5 ml of concentrated hydrochloric acid are transferred to the electrolysis cell and deaerated as for the lead determination. A potential of −0.38 V is applied for 60 sec with stirring followed by 20 sec without stirring. At a current sensitivity of 20–50 μA and a scan-rate of 10 mV/sec the potential is scanned up to −0.16 V. The antimony peak occurs at −0.24 V. Because of the steeply rising current over the region of interest, due to hydrogen ion reduction, an appropriate current compensation is applied throughout the scan.

For solutions containing low concentrations of antimony the same sample size is used but a deposition time of 280 sec with stirring and 20 sec without stirring is used. The current sensitivity during the scan is 5 or 10 μA.

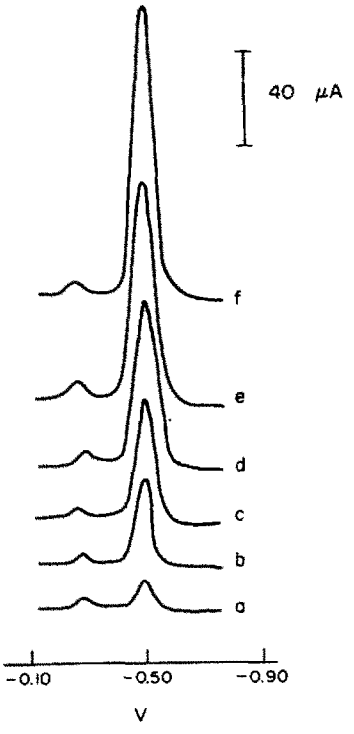

Fig. 1. Anodic stripping voltammograms for lead on hands after firing a gun. Curve a, sample; Curves b–f, sample plus 100-ppM incremental additions of lead. The small peak at −0.29 V is due to copper.

Five spikes of 20 μl of 1- or 5-ppm antimony solution corresponding to added antimony concentrations of 1 or 5 ppM are added and the measurement procedure is carried out twice after addition of each spike.

Peak-area is plotted against concentration and the amount of antimony in the original solution calculated in the same manner as for lead. Peak-height may also be used although a larger scatter of results was found on the least-squares plot, probably on account of the curved baseline.

A typical set of scans is shown in Fig. 2 and results are given in Table 2.

Sample 8 was analysed in triplicate for lead, and sample 9 for antimony, giving 87.6, 93.9 and 80.5 μg, and 731, 670 and 704 ng respectively.

RESULTS AND DISCUSSION

Electrolyte

The choice of electrolyte depends on two factors—the method of sample collection and the analytical procedure itself. Sample collection using paraffin wax,[12] cotton swabs moistened with dilute acids,[1] and an acid rinse have all been recommended for obtaining gunshot residues. However, a comparative study based on lead[2] has shown that a dilute nitric acid rinse is the most effective means of removing the residual metal. A dilute hydrochloric acid rinse was approximately 70% as effective in removing lead.

Nitric acid electrolyte. In 1*M* nitric acid, antimony showed multiple (two or three) stripping peaks with the main peak at −0.14 V. The behaviour observed was not reproducible from one run to the next, but for any one solution the peak-size did not change with time. This is in contrast to the claim of Lyungrin *et al.*[13] who reported a decrease with time in the height of the antimony peak from a vitreous carbon electrode. They attributed this decrease to the slow conversion of antimony(III) into electroinactive antimony(V).

Table 2. Amounts of lead and antimony found on hands

Hand blank (without firing)			Hand sample (after firing)*		
Sample	Lead, μg	Antimony, ng	Sample	Lead, μg	Antimony, ng
1.	16	43	6.	63	250
2.	11	16	7.	114	1310
3.	10	34	8.	87	341
4.	5.5	19	9.	115	731
5.	8.0	22	10.	85	270

* After single shots from a Smith and Wesson .357 Magnum Handgun.

In 1*M* nitric acid lead gave a small stripping peak at −0.55 V but it was difficult to measure because of the large cathodic wave due to hydrogen-ion reduction, which overlaps the beginning of the lead peak.

Because of these difficulties, nitric acid was not chosen as the electrolyte.

Hydrochloric acid electrolyte. In 1*M* hydrochloric acid, antimony gave a well-defined peak at −0.13 V. This conflicts with the claim of Gilbert and Hume[10] that antimony is not electroactive in this medium, but supports the data of Gornostaeva and Pronin[14] who reported good anodic stripping peaks for antimony. However, it was also found that 1 ppm of copper interferes when 10 ppM (parts per milliard) of antimony is determined, as the large copper peak at −0.28 V overlaps the smaller antimony peak at

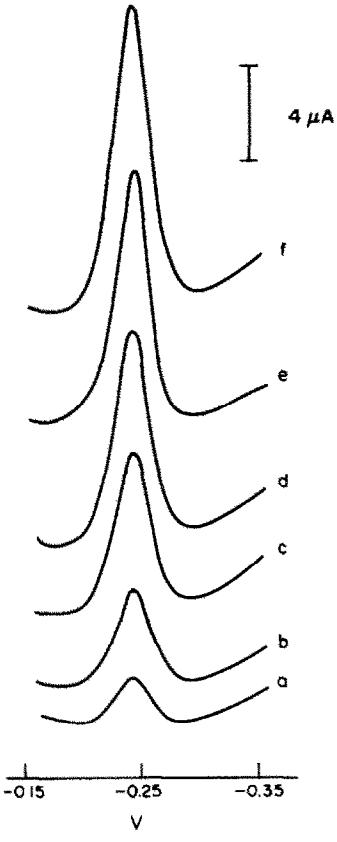

Fig. 2. Anodic stripping voltammograms for antimony on hands after firing a gun. Curve a, sample; Curves b–f, sample plus 10 ppM incremental additions of antimony.

−0.13 V. Since relatively large amounts of copper are often present in gunshot residues this electrolyte was not chosen for antimony determinations. For lead, 1*M* hydrochloric acid was found to give good peaks at −0.50 V and there were no serious interferences (*vide infra*).

A 4*M* hydrochloric acid electrolyte has been recommended for antimony.[10] In this medium the peak was found to occur at −0.24 V and there were no serious interferences (*vide infra*).

On the basis of these results, 1*M* hydrochloric acid was chosen for sample collection and the analysis was done in 1*M* and 4*M* hydrochloric acid for lead and antimony respectively.

Deposition potential and interferences

Interferences could be expected from those elements which may be present in gunshot residues or in the electrolyte and which will be stripped at potentials near that of the element of interest. In the case of antimony, potential interferences are copper and lead; and in the case of lead, cadmium (which is not likely to be present in residues but is known to be oxidized at a potential near that of lead) must be considered as well as copper. In addition, the hydrogen-ion reduction wave might interfere with the determination of either metal.

Lead. In 1*M* hydrochloric acid, cadmium was found to be oxidized with a peak potential of −0.77 V. Therefore any interference from cadmium may be avoided by deposition at a less negative potential. Furthermore, deposition potentials more negative than −0.70 V lead to considerable hydrogen-ion reduction currents. For these reasons a potential of −0.70 V was chosen for the electrolysis.

The copper stripping peak occurred at −0.29 V, which is sufficiently well separated from the lead peak to avoid overlap. It was found that a 100-ppM lead peak was unaffected by the presence of 2 ppm of copper in the solution.

Antimony. In 4*M* hydrochloric acid the copper stripping peak occurred at −0.43 V and lead was oxidized at a potential more negative than −0.50 V. These results indicate that a deposition potential of −0.38 V should prevent reduction of these two metals and thus allow the determination of antimony in their presence. A 10-ppM solution of antimony gave a peak which was not affected by the presence of 10 ppm of lead and 10 ppm of copper.

Analysis of orchard leaves

No suitable standard reference material is available, but the method was applied to a digested sample of orchard leaves (NBS SRM1571) in order to check the validity of the method for lead (there are no certificate values for antimony in this sample). Approximately 0.18 g of dried material was placed in a Teflon bomb along with 2 ml of nitric acid and 1 ml of 50% hydrogen peroxide. The bomb was sealed and kept in an oven at 50° for 2 hr and then at 120° overnight. After cooling, the bomb was opened and the liquid carefully evaporated just to dryness on a hot-plate. The residue was taken up in 1*M* hydrochloric acid, transferred to a 25-ml volumetric flask and made up to the mark with 1*M* hydrochloric acid. For analysis, 10 ml of sample and 10 ml of hydrochloric acid were transferred to the electrolysis cell. After deposition for 210 sec with stirring and 40 sec without stirring, the peak was recorded. Instrument settings, standard additions and calculations were done as already described. The results obtained on three samples were 43, 45 and 46 ppm of lead compared with a certificate value of 45 ± 3 ppm. Of note is the fact that a relatively high background current made accurate measurement of the lead peak more difficult than in the case of the handwash samples.

CONCLUSIONS

Anodic stripping voltammetry provides a rapid (<2 hr), simple and accurate means of determining antimony and lead in firearm discharge residues on hands. No separation or preconcentration steps are required, and there appear to be no interferences under normal conditions. The method of analysis for lead has been shown to be reliable by applying it to a standard reference sample.

There are two disadvantages, however. The method does not yield a result for barium, which is a third important metal in gunshot residues, and it requires the use of the somewhat less efficient hydrochloric acid rinse for obtaining samples. The use of nitric acid would have been marginally preferable.

Acknowledgements—Thanks are due to Dr. S. S. Krishnan for useful discussions concerning this work and to Mr. Glen Westenhaefer for providing samples for analysis.

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ASSAY OF *p*-AMINOBENZENESULPHONAMIDES WITH CHLORAMINE-T

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Summary—New spectrophotometric and titrimetric methods for the assay of *p*-aminobenzenesulphonamides with chloramine-T have been developed. They are simple, reproducible and accurate within the limits described (±3%) and are useful at high concentration levels. These methods are also applicable to the assay of *p*-aminobenzenesulphonamides in rat urine.

Several methods of assay for *p*-aminobenzenesulphonamides (p-H_2N-C_6H_4-SO_2NHR) are cited in the literature.[1–4] Among these, the method of Bratton and Marshall[2] is the one biologists and pharmacologists normally prefer, owing to its high sensitivity, but this method is reliable only for lower concentrations (*i.e.*, <100 μg/ml). For higher concentrations, this method requires multiple dilutions, which is inconvenient and may introduce some error. New spectrophotometric and titrimetric methods using chloramine-T (CAT) have recently been developed in our laboratory which are satisfactory for higher amounts of *p*-aminobenzenesulphonamides. Those reported here are quite suitable for purity assays in the pharmaceutical industry, because of the utility at higher concentrations. Preliminary experiments show that these methods have biological application in that *p*-aminobenzenesulphonamides in rat urine have been assayed successfully.

EXPERIMENTAL

Procedure

Spectrophotometric method. This method is based on the development of the yellow chromogen (absorption maximum at 525 nm) produced by the chlorination of the sulphonamide by CAT at pH 7.4 in phosphate buffer. The absorbance of the solution is directly proportional to the amount of the sulphonamide in the solution.

Different volumes containing different amounts of sulphonamide are pipetted out (the maximum volume should not exceed 4 ml) into different tubes. To each tube is added 1 ml of 8% CAT solution and the volume is made up to 5 ml with pH 7.4 phosphate buffer.[5] After 4 hr, the intensity of the yellow colour developed is measured at 525 nm against a blank containing 1 ml of CAT solution and 4 ml of phosphate buffer. At the maximum concentration for each of the sulphonamides studied, the absorbance reaches a steady value in 3–4 hr at room temperature and remains constant over a period of nearly 30 hr. If the temperature is increased to 50°, a steady absorbance is achieved in about 1 hr (Fig. 1) and only a small error will be introduced as a result of evaporation.

Titrimetric method. An aliquot of the sulphonamide solution is mixed with a known excess of CAT in a conical flask and the mixture kept for a period of 4 hr (for the largest amounts reported) at room temperature. The unreacted CAT is then allowed to react with potassium iodide solution and sulphuric acid. The iodine liberated is titrated with standard sodium thiosulphate solution, with starch as indicator. The amount of sulphonamide is calculated on the basis of the 1:2 stoichiometry ([p-H_2N-C_6H_4-SO_2NHR]:[CAT]).

Biological experiments

Sulphonamides were isolated from rat urine by the method of Cantelli Forti *et al.*[6–8] For the Bratton–Marshall method, the procedure reported in the literature[2,6–8] was followed. For the comparative chloramine-T methods, 3 ml of urine were pipetted out and the protein was precipitated with trichloroacetic acid (0.5 ml of 10% solution). Both spectrophotometric and titrimetric methods were employed for the assay. To the clear centrifuged solution, a few drops of concentrated sodium hydroxide solution were added to adjust the pH to 7.4, after which 1 ml of 8% CAT solution was added and the solution was made up to 5 ml. After 4 hr, the intensity of the colour was read at 525 nm, against a blank containing 3 ml of urine

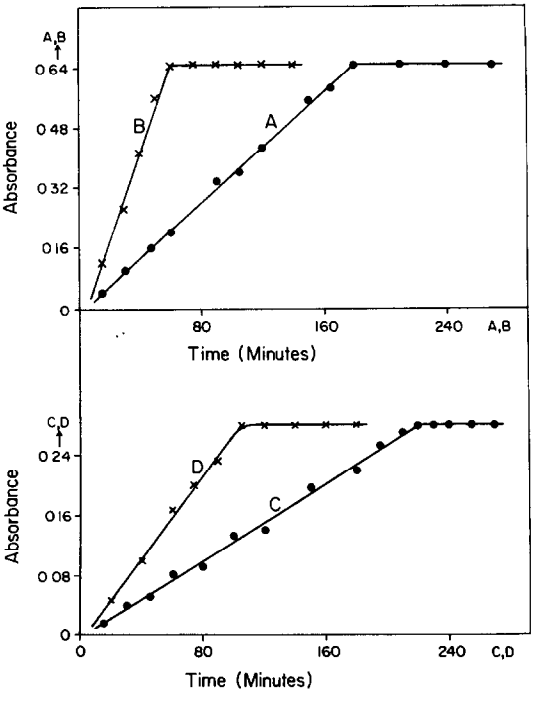

Fig. 1. Plots of absorbance vs. time at two different temperatures. Amount of sulphonamide = 8000 μg; pH 7.4. (A) sulphanilamide and (C) sulphacetamide at room temperature (26 ± 2°); (B) sulphanilamide and (D) sulphacetamide at 50°.

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Table 1. Titrimetric assay of sulphonamides, using excess of chloramine-T

Sulphonamide	Amount added, *mmole*	Amount found,* *mmole*
Sulphanilamide	0.058	0.059
	0.116	0.117
	0.233	0.227
	0.465	0.476
	0.698	0.695
	0.930	0.939
	1.163	1.134
Sulphacetamide	0.047	0.047
	0.093	0.095
	0.234	0.230
	0.467	0.461
	0.701	0.710
	0.935	0.928
Sulphisoxazole	0.035	0.035
	0.070	0.069
	0.176	0.173
	0.264	0.270
	0.352	0.343
	0.704	0.714
Sulphadiazine	0.020	0.021
	0.040	0.040
	0.101	0.103
	0.201	0.206
	0.302	0.306
	0.402	0.393
	0.805	0.795

* Values reproducible within the limits of experimental error, ±3%.

and 2 ml of water. It was also demonstrated titrimetrically that CAT does not react with rat urine containing no sulphonamide. The amount of free (unmetabolized) sulphonamide was calculated from the standard curve (plot of absorbance *vs.* amount of sulphonamide) for each compound, and was also found titrimetrically by adding a known excess of CAT to a known volume of urine after precipitation of protein and pH-adjustment as described above. To determine the total amount (unmetabolized + metabolized) of the sulphonamide present, the urine (3 ml) was hydrolysed by heating at 100° for 2 hr with 1 ml of 4*N* hydrochloric acid after the protein-precipitation step. Then 1 ml of 8% CAT solution was added and the final volume adjusted to 5 ml. The intensity of the colour was read after 2 hr. The total was also found titrimetrically.

Product

With sulphanilamide as model test sample, the product produced by oxidation with excess of CAT was analysed. The initial product (m.p. 100–102°) was identified from NMR, infrared and elemental analysis data as *N*,*N*-dichloro-*p*-aminobenzenesulphonamide.

RESULTS AND DISCUSSION

The standard curves (plot of absorbance *vs.* μg of sulphonamide) were linear up to 8000 μg of sulphanilamide and sulphacetamide, and 6000 μg of sulphadiazine and sulphisoxazole, the slope for sulphanilamide being over twice that for the other three compounds. Table 1 gives the results for the assay of sulphonamides by the titrimetric method, and Table 2 the results for the assay of some sulphonamides (both free and total) in rat urine. The values are comparable to those obtained by using the Bratton–Marshall[2] procedure. These methods have also been found to be suitable for various other *p*-aminobenzenesulphonamides. These were tested qualitatively under similar conditions and each gave the same colour with an absorption maximum at 525 nm. The method is therefore expected to be generally applicable. It is simpler than the Bratton–Marshall method and applicable to higher concentration levels, and would be useful for analysis of waste effluent in the pharmaceutical industry.

Mechanism

It is known that CAT can act as a chlorinating[9,10] or a two-electron oxidizing[11–17] agent giving *p*-toluenesulphonamide. The emf. of the CAT–*p*-toluenesulphonamide system is pH-dependent and decreases with increase in pH of the medium.[18] The disproportionation of *N*-chloro-*p*-toluenesulphonamide into dichloramine-T and *p*-toluenesulphonamide has been studied by Higuchi *et al.*,[19] who observed that the disproportionation does not occur at pH 7 and dichloramine-T does not exist under these conditions. Thus, at the pH used in our investigation (pH 7–8), *N*-chloro-*p*-toluenesulphonamide or its anion is the predominant chlorinating species derived from CAT.

The reaction between a sulphonamide and CAT can be expressed by the following equation.

$$\underset{\text{(}N\text{-chloro-}p\text{-toluenesulphonamide)}}{H_2N\text{–}C_6H_4\text{–}SO_2NHR} + 2\,H_3C\text{–}C_6H_4\text{–}SO_2NHCl \rightarrow \underset{\text{(}N,N\text{-dichloro-}p\text{-aminobenzenesulphonamide)}}{Cl_2N\text{–}C_6H_4\text{–}SO_2NHR} + 2\,H_3C\text{–}C_6H_4\text{–}SO_2NH_2$$

The detailed mechanism for this reaction will be reported elsewhere.

Table 2. Assay of some sulphonamides in rat urine–comparison with Bratton and Marshall method*

Sulphonamide	Bratton & Marshall method, *μg/ml*		Chloramine-T methods, *μg/ml*			
			Spectrophotometric method		Titrimetric method	
	Free†	Total‡	Free†	Total‡	Free†	Total‡
Sulphanilamide	240	420	255	433	242	420
	210	360	240	417	238	426
Sulphacetamide	1040	1600	1175	1620	1202	1620
	1200	1560	1140	1680	1184	1632
Sulphisoxazole	90	128	—	—	95	135
	88	140	—	—	93	138

* The same pooled sample was used for determination of each sulphonamide by the Bratton & Marshall and two chloramine-T assays. Experiments were conducted in duplicate.

† Free denotes unmetabolized sulphonamide.

‡ Total denotes unmetabolized + metabolized sulphonamide.

Acknowledgements—We are grateful to the Robert A. Welch Foundation, Houston, Texas (Grant H-416) and the Dow Chemical Co., Freeport, Texas, for supporting the present work. We also thank Professor Gian Luigi Biagi, Department of Pharmacology, University of Bologna, Italy for the generous supply of sulphonamides.

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DETERMINATION OF CERTAIN UNSATURATED HYDROCARBONS BY TITRATION WITH PERMANGANATE IN NON-AQUEOUS MEDIUM

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(*Received* 7 *May* 1976. *Revised* 17 *August* 1976. *Accepted* 13 *October* 1976)

Summary—Ion-association complexes of permanganate with tetrabutylammonium can be dissolved in chloro- or bromobenzene and used for photometric titration of certain unsaturated hydrocarbons at 45–50°. MnO_2 is precipitated and must be filtered off before the absorbance is measured.

Quaternary ammonium salts[1] as well as crown polyethers and cryptates[2] are used in organic synthesis for making inorganic salts soluble in solvents of low dielectric constant.

These compounds cause an increase in the solubility and reactivity of unsolvated anions in an ion-pair. By use of dicyclohexyl-18-crown-6 a 0.06*M* solution of potassium permanganate in benzene has been obtained.[3] Quaternary ammonium and phosphonium salts[4] also extract permanganate fully and rapidly from the aqueous phase into benzene, giving the latter a purple colour.

The aim of the work reported here is to make use of such permanganate solutions in photometric titration. The following unsaturated hydrocarbons have been determined by this method: styrene, α-methylstyrene, *trans*-stilbene and 1-dodecene. Titrimetric methods of determining hydrocarbons have been described in the literature.[5] This method was chosen because unsaturated hydrocarbons readily undergo oxidation. Permanganate was extracted from the aqueous into the organic phase by using a tetrabutylammonium salt Bu_4NX, where X = Cl, Br, I or OH. The organic solvents tested were benzene, toluene, chloroform, carbon tetrachloride, dioxan, chloro- and bromobenzene, but only the last two proved suitable. With benzene and toluene no clear solutions were obtained, as Bu_4NMnO_4 precipitates in the form of suspended matter. It is rather difficult to see the suspended matter in the coloured solution. However, its existence was easily established by filtration or centrifugation. The authors[4] who used the solution of permanganate in benzene for synthesis probably did not notice the suspended matter at all. Solutions in chloroform and dioxan are fairly unstable, and there is no extraction of permanganate into carbon tetrachloride.

EXPERIMENTAL

Reagents

A chloro- or bromobenzene solution of permanganate was prepared as follows: to a definite volume of 0.02*M* potassium permanganate the same volume of solvent was added, and a 1.5-fold excess of tetrabutylammonium salt in relation to the concentration of permanganate. Shaking the mixture for 1 min transferred the permanganate into the organic phase, colouring it violet. The solution of permanganate was standardized by titration of a weighed portion of *trans*-stilbene. Tetrabutylammonium chloride and tetrabutylammonium bromide were prepared as described in the literature.[6] Chlorobenzene solutions of hydrocarbons were prepared from weighed portions.

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Hydrocarbons were determined both by photometric titration and by use of a calibration curve.

Photometric titration. The concentration of the chlorobenzene solutions of hydrocarbons was 3 mg/ml. A known

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(*Received* 7 *May* 1976. *Revised* 17 *August* 1976. *Accepted* 13 *October* 1976)

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Procedure

Hydrocarbons were determined both by photometric titration and by use of a calibration curve.

Photometric titration. The concentration of the chlorobenzene solutions of hydrocarbons was 3 mg/ml. A known

Table 1. Determination of hydrocarbons

Styrene		α-Methylstyrene		*trans*-Stilbene		1-Dodecene	
Taken, *mg*	Found, *mg*	Taken, *mg*	Found, *mg*	Taken, *mg*	Found, *mg*	Taken, *mg*	Found, *mg*
4.0	3.9	4.7	4.8	3.0	3.1	3.7	3.8
8.0	7.8	9.2	9.0	7.6	7.5	7.4	7.1
20.0	19.3	14.1	13.5	12.0	11.8	13.5	13.3
		23.5	22.9	24.0	23.8		

volume of hydrocarbon solution was pipetted and made up to a volume of 60 ml with chlorobenzene. Titrant was added in 0.5-ml portions. After each addition the solution was heated in a water-bath at a temperature of 45–50° until a yellow colour appeared, then the solution was filtered through a G-5 crucible to separate MnO_2, and the absorbance was measured. The MnO_2 precipitate was not washed. The temperature range was set at 45–50° because at lower temperatures the oxidation rate is rather low and at higher temperatures the solvent is partly oxidized. The impurities in the chlorobenzene were oxidized by permanganate and probably caused the yellow colour. The results are tabulated in Table 1. In Fig. 1 the photometric titration curve for α-methylstyrene is shown.

Calibration curve method. The concentrations of hydrocarbon (styrene, α-methylstyrene, *trans*-stilbene and 1-dodecene) were 0.03 mg/ml. A definite volume of the stock solution was pipetted and 1 ml of 0.008*M* permanganate was added. Next the specimens were diluted with chlorobenzene to exactly 10 ml. The solution was heated in a water-bath at 45–50° for 5–10 min, then filtered through a G-5 crucible, and the absorption was measured. This method can be used for determining from 0.02 to 0.09 mg of hydrocarbons.

RESULTS AND DISCUSSION

The solution of permanganate in chlorobenzene or bromobenzene is fairly stable. During a week, at a temperature of 10°, the titre changes by 5%. The absorption spectrum has four maxima (at 510, 530, 550 and 575 nm) and resembles the spectrum of permanganate in aqueous solution.[7] The molar absorptivity at 530 nm is 1.85×10^3 l. $mole^{-1}$. cm. The signal δ-$CH_2N = 2.40$ ppm (8 H, m) occurs in the nmr spectrum, which suggests that the permanganate ion occurs in the form of an ion-pair $Bu_4N^+ MnO_4^-$. Bu_4NI was used as a standard. According to the literature data on the stoichiometry of the oxidation reaction of hydrocarbons in aqueous[8] and benzene solution[3] [equation (1)], 3 moles of hydrocarbon react with 8 moles of permanganate.

$$3RCH = CHR + 8KMnO_4 \rightleftharpoons 6RCO_2K + 8MnO_2 + 2KOH + 2H_2O \quad (1)$$

To confirm this stoichiometry the hydrocarbons were oxidized under the same conditions as for the photometric titration, and the oxidation products were separated.[4] Benzoic acid was obtained from *trans*-stilbene and styrene and partly from α-methylstyrene, and nonanoic acid was obtained from 1-dodecene. In the case of α-methylstyrene some deviations from the stoichiometry mentioned above were observed; from the photometric titration curves 1 mole of permanganate reacts with 1 mole of hydrocarbon, which suggests that at the end-point of the titration there may be oxidation products other than acids.

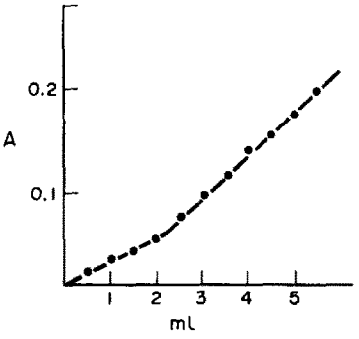

Fig. 1. Photometric titration curve of α-methylstyrene with tetrabutylammonium permanganate. Permanganate concentration = 0.02*M*, α-methylstyrene = 4.4 mg.

From the research done it is evident that chloro- and bromobenzene solutions of permanganate may be employed for quantitative determination of certain unsaturated hydrocarbons when these are present alone.

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INVESTIGATION OF PHASE-GROWTH KINETICS DURING INTERACTION OF SILICON SINGLE CRYSTALS AND MOLYBDENUM THIN FILMS

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Summary—Investigation of the phase-growth kinetics and identification of the phases formed as a result of reactive diffusion in the system of Si single crystals and Mo thin films, has been carried out by electrochemical anodic etching.

So far only fragmetrary results have been obtained on the growth kinetics of silicides during the interaction of silicon single crystals and molybdenum thin films. These were obtained by the back-scattering of 2-MeV $^4He^+$ ions, the temperature range being 1200°.[1] A linear law of $MoSi_2$ phase growth was established.

In our experiments an electrochemical technique was used to investigate both interaction kinetics in the Mo–Si system at temperatures of 525–600° and to identify the composition of the compound formed.[2]

EXPERIMENTAL

Samples were prepared by the sublimation of molybdenum onto polished wafers of *n*-type single-crystal silicon in a vacuum (3×10^{-6} mmHg) so that the thickness increased at a rate of 25 nm/min. The wafers were boiled in a 100:1 mixture of hydrogen peroxide and hydrochloric acid, etched in hydrofluoric acid and washed in demineralized water immediately before being placed in the vacuum system. Samples were isothermaly annealed in vacuum (3×10^{-6} mmHg).

An aqueous solution containing 3% KHF_2 + 1% NiF_2 was used for the anodic etching of the Mo–Si system. The value of the Mo electrochemical potential was more negative than that of the *n*-type Si potential for the electrolyte and conditions employed. As a result a stepwise etching occurred, Mo being etched first, followed by Si. There were two well-defined regions on the current–time curves, one characteristic of Mo etching (etching current 5×10^{-5} A), the other of Si etching (etching current 0.7×10^{-5} A). The etching of isothermally annealed samples gave current–time curves different from those obtained with non-annealed samples, showing that during annealing intermetallic compounds are formed. These curves did not contain clearly pronounced regions corresponding to Mo etching and the etching of the intermetallic compound and the resulting curves were difficult to correlate.

The absence of clearly pronounced regions is due to the fact that in the electrolyte employed the value of the electrochemical potential of the intermetallic compound (formed as a result of annealing) is more negative than that of the Mo electrochemical potential.

The etching of such a system when a top layer (which is in contact with an electrolyte) has a positive electrochemical potential compared with that of the lower material, occurs in a complicated way, depending on the values of the electrochemical potentials, current density, thickness and structure of the top layer. Both a simultaneous etching of the materials in question and etching of the lower layer through the top one can occur.

Procedure

The etching of the Mo–intermetallic compound–Si system was performed in two electrolytes: 3% KHF_2 + 1% NiF_2 and 8% KOH. The first step was Mo etching in the 8% KOH electrolyte (the electrolyte in question caused Mo etching but affected neither Si nor its compounds containing Mo under the conditions employed). The end of the Mo etching was indicated by a sharp drop in the etching current (Fig. 1). The sample was then washed with distilled water. The etching of the intermetallic compound and Si was performed in the 3% KHF_2 + 1% NiF electrolyte. The current–time curves for this process are shown in Fig. 2.

The film thickness was determined to within ± 30 nm with a standard MUU-4 interferometer.

RESULTS AND DISCUSSION

The etching area was constant and equal to 3.14×10^{-2} cm^2. The relationship between the quantity of electricity required for Mo and Si etching and thickness was linear. The slopes of the curves (or the proportionality constants) were 6.1 ± 0.2 nm/mC in 8% KOH and 6.5 ± 0.2 nm/mC in 3% KHF_2 + 1% NiF_2 for Mo. The corresponding value for Si was 22.9 ± 0.7 nm/mC in 3% KHF_2 + 1% NiF_2, and for $MoSi_2$ 12.6 ± 0.8 nm/mC in the same medium.

Figures 1 and 2 show the current–time curves for the process of anodic etching of Si–Mo samples before and after annealing in two different electrolytes. After annealing, the amount of unreacted Mo decreases (the area under

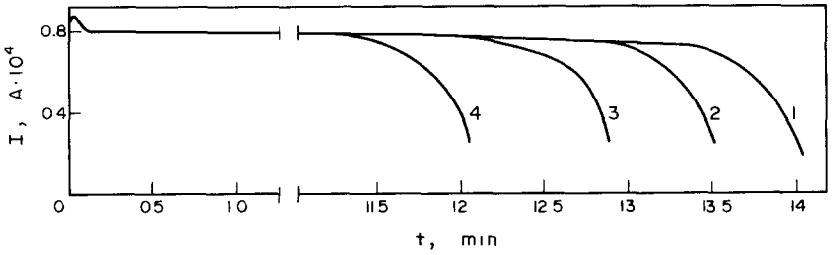

Fig. 1. Current–time curves for anodic etching of Mo thin films in 8% KOH solution, *1* before annealing, *2,3* and *4* after annealing at 525° for 25, 100 and 225 min respectively.

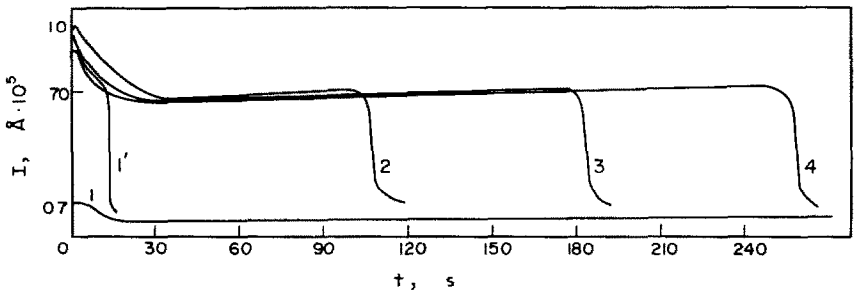

Fig. 2. Current–time curves for anodic etching of Si and $MoSi_2$ in the 3% KHF_2 + 1% NiF_2 electrolyte. *1* before annealing, Si etching; *1'* before annealing, $MoSi_2$ layer obtained by Mo deposition; *2,3,4*, after annealing at 525° for 25, 100 and 225 min respectively.

the *I–t* curves for Mo etching in 8% KOH decreases). Apart from the etching region of pure silicon (0.7×10^{-5} A, curve *1*) there appears a further region with an etching current of 0.7×10^{-4} A (in the 3% KHF_2 + 1% NiF_2 electrolyte, Fig. 2). The growth of this additional region with annealing time and the decrease in Mo amount are related to the growth of the intermetallic compound.

The layer of intermetallic compound can be obtained during the process of Mo deposition, *e.g.*, when producing films of considerable thickness, of the order of 300 nm (curve *1'*, Fig. 2). The proportionality coefficient α for the layer of the growing phase was experimentally determined for the samples annealed at various temperatures and times. It was found to be 12.6 nm/mC. A knowledge of the proportionality coefficient α for Mo, Si and the intermetallic compound permits the determination of the composition of the growing phase:

$$\alpha_i = \frac{\alpha_{Si}\alpha_{Mo}(a_i + 1)}{\alpha_{Mo} + a_i\alpha_{Si}} \qquad (1)$$

where α_i is the proportionality coefficient of phase *i*, and a_i is the ratio of the effective thicknesses of Mo and Si in phase *i*

$$a_i = \frac{d_{Mo}}{d_{Si}} = \frac{C_{Mo}\cdot\rho_{Si}\cdot A_{Mo}}{\rho_{Mo}\cdot A_{Si}(100 - C_{Mo})} \qquad (2)$$

where ρ and A are the density and atomic weight respectively and C_{Mo} is the concentration of Mo in phase *i*.[2]

The ratio [calculated from equation (1)] of the numbers of atoms of Si and Mo in the growing layer is 1.82, which is close to the ratio of the number of atoms of Si and Mo in $MoSi_2$. This ratio for other phases existing in the Mo–Si system is 0.66 for Mo_3Si_2 and 0.33 for Mo_3Si.

The composition of the growing phase can be determined from the ratio of the effective thicknesses of reacted Mo and of the phase formed. The effective thickness of the phase formed can be expressed in terms of the amount of Mo transformed into phase *i*,

$$d_{F_i} = d_{Mo} + d_{Si} = d_{Mo} + \frac{d_{Mo}}{a_i}$$

where d_{F_i} is the thickness of phase *i* so formed. It is assumed that the atomic packing of the Mo and Si remains unchanged.

Thus the ratios calculated for different phases were $d_{Mo_3Si_2} = 1.76d_{Mo}$, $d_{Mo_3Si} = 1.38d_{Mo}$ and $d_{MoSi_2} = 3.31d_{Mo}$.

Figures 3 and 4 show the amount of Mo transformed at 550°, calculated by using $d_{Mo} = \Delta Q \cdot d_{Mo}$ from the current–time curves of the anodic etching of Mo thin films in 8% KOH. The conversion of Mo corresponds to the reaction 2 Si + Mo = $MoSi_2$. The $MoSi_2$ phase growth with time at various temperatures of isothermal annealing is presented in Fig. 3. The $MoSi_2$ phase growth is governed by a parabolic law at annealing temperatures in the range 525–600°. This shows that the diffusion process of Mo and Si through the layer of the $MoSi_2$ phase is a limiting stage of the phase growth. This behaviour is unaffected by the initial formation of an intermetallic phase during the evap-

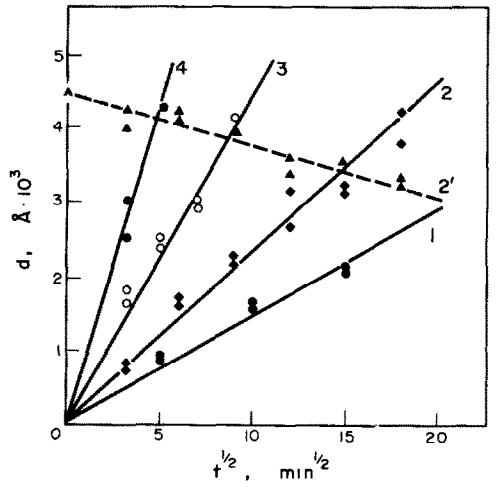

Fig. 3. Phase growth of $MoSi_2$ with time at 525, 550, 575 and 600°, (curves *1,2,3* and *4* respectively; *2'*, Mo conversion during annealing at 550°).

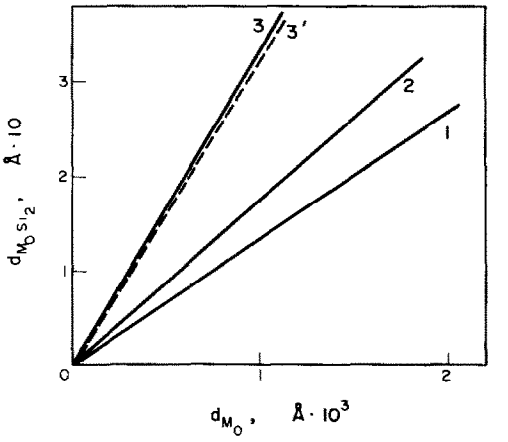

Fig. 4. Relation between effective thickness of Mo reacted and of that of the phase layer for the three possible reactions: *1*, 3Mo + Si = Mo_3Si; *2*, 3Mo + 2Si = Mo_3Si_2; *3*, Mo + 2Si = $MoSi_2$; *3'*, experimental data for annealing at 550°.

oration process. The values of the growth constants (K) of the $MoSi_2$ phase are as follows: 3.1×10^{-14}; 8.62×10^{-14}; 3.22×10^{-13}; 1.2×10^{-12} cm^2/sec at 525, 550, 575 and 600° respectively.

The temperature-dependence of the growth constants may be expressed in the form $K_{MoSi_2} = 7.95 \times 10^6 \exp(-3.2/kT)$ cm^2/sec.

CONCLUSIONS

1. The electrochemical etching technique has been developed to study interaction kinetics for cases when the value of the electrochemical potential of the intermetallic compound is more negative than that of the initial materials.

2. Of the three existing phases in the Mo–Si system only one phase was observed to grow at 525–600°. The phase growth is governed by a parabolic law.

3. The dependence of the growth constant of the $MoSi_2$ phase on temperature is given by the Arrhenius equation with the parameters $K_0 = 7.95 \times 10^6$ cm^2/sec and $E = 74$ kcal/mole.

Acknowledgement—The authors are greatly indebted to Prof. L. N. Aleksandrov for discussions when carrying out the work.

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TRACE ENRICHMENT WITH ACTIVATED CARBON AND DETERMINATION OF TRACE METALS IN HIGH-PURITY ZINC AND ZINC(II) NITRATE

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(*Received* 19 *August* 1976. *Accepted* 24 *September* 1976)

Summary—A method is described for the enrichment and determination of trace metals such as Ag, Bi, Cu, Co, Cd, In, Pb, Ni, Tl, Fe and Hg, present as impurities in high-purity zinc and zinc(II) nitrate. When the sample solution, after addition of potassium ethyl xanthate, is filtered through a small filter paper coated with 50 mg of activated carbon, the trace elements are quantitatively adsorbed on the carbon. The trace elements (with the exception of Hg) are dissolved off with nitric acid and determined by atomic-absorption or emission spectrometry. Mercury is evaporated at 650° and determined by flameless atomic-absorption. In 10 g of Zn oe 50 g of $Zn(NO_3)_2 \cdot 6H_2O$ the limit of detection is 0.1–60 ppM and the coefficient of variation was 2.7–20%.

Recently, Jackwerth *et al.*[1] devised a method for trace enrichment, using activated carbon as an adsorbent. In the presence of potassium ethyl xanthate (EtX) trace metals present are adsorbed on the activated carbon, but the matrix is not. In a previous study[2] it was shown that though several trace metals could be adsorbed from a manganese or chromium matrix under these conditions, zinc was scarcely adsorbed at all. This suggested the possibility that many trace metals could be extracted from a zinc matrix by adsorption of their complexes on activated carbon. The present paper describes a simple method for the determination of trace metals in zinc matrices which does not involve the use of buffer solutions or large amounts of complexing reagents.

EXPERIMENTAL

Reagents

High-purity zinc turnings (99.999%) and guaranteed-reagent grade (G.R.) zinc nitrate were used as the test samples.

Activated carbon (G.R.), potassium ethyl xanthate (G.R.) and nitric acid of super special grade (S.S.G., Wako Pure Chemicals Industries Ltd.) were used without further purification.

Preparation of standard solutions. A stock solution of indium(III) (2.5 mg/ml) was prepared by dissolving 0.6050 g of In_2O_3 (G.R.) in hot nitric acid and making up to 100 ml with 1M nitric acid. Stock solutions (250 ml containing 2.5 g of metal) were prepared by dissolving the calculated amounts of the nitrates of silver, thallium(I) and the bivalent metals in water and making up to volume. Bismuth and iron(III) nitrate solutions were similarly prepared in 1M nitric acid. The standard solution for calibration, containing 1–20 μg of these metals in 10 ml of 20% v/v nitric acid, was prepared from the stock solutions. The water used was prepared by distilling demineralized water containing dilute alkali and permanganate, in a glass still.

Preparation of sample solutions. $Zn(NO_3)_2 \cdot 6H_2O$ (50.00 g) was weighed out and dissolved in 300 ml of water and 5 ml of 0.2% EtX solution were added. The pH was 4.8 ± 0.1.

Zinc turnings (10.00 g) were weighed into a 100-ml beaker and dissolved by adding slowly 35.0 ml of concentrated nitric acid. The solution was heated on a hot-plate at about 200° for a few hr to remove excess of nitric acid and then transferred to a 300-ml beaker with water. If the solution became turbid because of hydrolysis a little nitric acid was added to give a final pH of 4.0–5.5 in a total volume of 300 ml: 5 ml of 0.2% EtX solution were then added.

Procedure

The 300 ml of sample solution (plus the given amount of potassium ethyl xanthate) were filtered through a 2-cm filter paper coated with 50 mg of activated carbon. The filter paper was dried at 60° for 30 min and the activated carbon was transferred to a 20-ml beaker The activated carbon was treated with 1 ml of hot nitric acid and the solution evaporated to dryness. Then 3 ml of 20% nitric acid were added and the suspension was transferred to

oration process. The values of the growth constants (K) of the $MoSi_2$ phase are as follows: 3.1×10^{-14}; 8.62×10^{-14}; 3.22×10^{-13}; 1.2×10^{-12} cm^2/sec at 525, 550, 575 and 600° respectively.

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Procedure

The 300 ml of sample solution (plus the given amount of potassium ethyl xanthate) were filtered through a 2-cm filter paper coated with 50 mg of activated carbon. The filter paper was dried at 60° for 30 min and the activated carbon was transferred to a 20-ml beaker The activated carbon was treated with 1 ml of hot nitric acid and the solution evaporated to dryness. Then 3 ml of 20% nitric acid were added and the suspension was transferred to

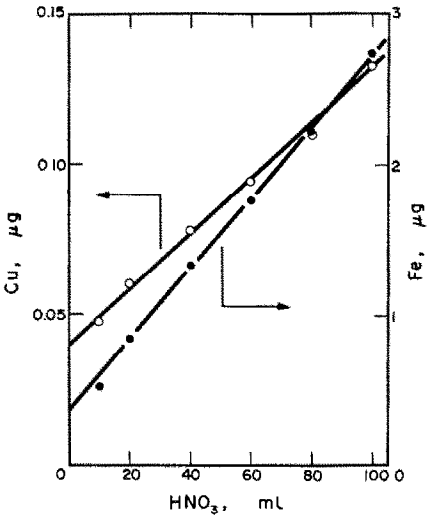

Fig. 1. Concentration of copper and iron as trace impurities in high-purity nitric acid (S.S.G.).

a 9-mm test-tube and centrifuged. The concentrations of the trace metals in the solution were measured on 100-μl subsamples with a Hitachi 518 Atomic Absorption Spectrometer.

Determination of mercury

The 300 ml of sample solution were filtered through a 2-cm filter paper coated with 50 mg of activated carbon. The carbon was then heated for 5 min at 650° in an Automatic Mercury Evaporator, model ANA-K801, Tokyo Photo-Electric Co. Ltd., and the mercury trapped on a silver wire, re-evaporated and measured with an Hg-Microgas Analyzer, model ANA-K80, Tokyo Photo-Electric Co. Ltd., with a 100-cm light path.

Determination of impurities in nitric acid

Separate 10, 20, 40, 60, 80 and 100-ml portions of the concentrated nitric acid (S.S.G.) were evaporated to dryness in 20-ml beakers. Then 3 ml of 20% nitric acid were added to each and the amounts of metal ions in the solution determined by atomic-absorption spectrometry. It was found that no Ag, Bi, Co, Cd, In, Pb, Ni and Tl could be detected, but appreciable amounts of iron and copper were present (Fig. 1). The non-zero intercepts are due to contamination from the beakers or the surrounding atmosphere. The 35 ml of nitric acid used to dissolve the 10-g Zn sample were shown to contain 0.074 μg of Cu and 1.20 μg of Fe and these values were subtracted from the results obtained.

RESULTS AND DISCUSSION

Enrichment and determination of Ag, Bi, Cu, Co, Cd, In and Pb

When 300 ml of a solution containing 10 mg of potassium ethyl xanthate and 10 g of zinc or 50 g of $Zn(NO_3)_2 \cdot 6H_2O$ were filtered through 50 mg of activated carbon, it was found that the seven trace elements were quantitatively retained. Plots of amount of metal recovered against the amount added were linear with slopes of unity

Table 1. Determination of trace metals in zinc and zinc nitrate*

Sample	Trace metal	Content, *ppm*	Recovery, %	C.V. ($N = 10$)‖ %	Limit of detection 3σ, *ppM* ($N = 10$)¶
Zn (10.00 g)	Ag	0.031	100	16.0	4.5
	Bi	0.11	>97	9.3	60
	Cu	0.156	100	10.3	6
	Cd	0.079	98	15.9	6
	Co	0.015	97	16.3	8
	Pb	0.99	100	15.2	30
	In	—	98	—	24
	Ni	0.20	97	8.8	30
	Tl	—	93	—	60
	Fe	1.13	98	2.7	30
$Zn(NO_3)_2 \cdot 6H_2O$ (50.00 g)	Ag	0.0389	100	5.9	0.6
	Bi	—	>97	—	10
	Cu	0.555	100	3.9	1
	Cd	0.235	99	7.5	1
	Co	0.262	98	3.6	2
	Pb	0.710	98	11.8	5
	In	—	97	—	5
	Ni	0.257	>95	4.7	3
	Tl	—	90 – 96	—	23
	Fe†	0.12	100	20	20
	Hg	0.0034		7.6	0.1
		0.0035§	>96	13§	0.05§
		0.0032†		25†	

* Measurements of metals other than In, Tl and Hg were made with a Hitachi 518 AAS with a C_2H_2–air flame; In and Tl were determined by emission spectrometry at 4511.3 and 5350.5 Å respectively, with the same apparatus. Hg was determined with an automatic mercury evaporator ANA-K801 and Hg-microanalyser ANA-K80, Tokyo Photoelectric Co., Ltd.

† 20 g of $Zn(NO_3)_2 \cdot 6H_2O$ were used.

§ 100 g of $Zn(NO_3)_2 \cdot 6H_2O$ were used.

‖ C.V. = coefficient of variation, N = number of replicates.

¶ σ = standard deviation, ppM = parts per milliard (10^9).

Table 2. Variation of enrichment of Ni and Tl with EtX concentration*

EtX, *mg*	Recovery, % Ni	Tl	Zr (adsorbed), *mg*
0	<5	0	0.2
10	50	45	1.0
15	65	60	1.3
40	80	70	3.0
60	>94	>80	3.9
80	>95	90–96	4.1
100	>95, 97†	90–97, 93‡	5.1

* 50 g of $Zn(NO_3)_2 \cdot 6H_2O$ as matrix.
† 10 g of Zn as matrix.

but with intercepts on the recovery axis, arising (presumably) from impurities in the activated carbon and representing analytical blanks which must be subtracted from the values obtained. These blank values were below the limit of detection for Bi and In, while those for Ag, Cu, Co, Cd, and Pb were 0.075, 0.60, 0.03, 0.10 and 1.00 μg respectively. The sample solutions of zinc and zinc nitrate were treated as described above and the amounts of the trace metals separated from the matrix were determined by atomic-absorption spectrometry. The results obtained are listed in Table 1.

Enrichment and determination of nickel and thallium

Table 2 gives the effect of the amount of EtX on the recovery of nickel and thallium(I).

It was found that 0.1 g of EtX was necessary to ensure complete retention of both metals on the carbon. A small proportion of the zinc matrix was also adsorbed, the amount increasing with increasing EtX concentration. With excess of zinc a soluble complex $Zn(EtX)^+$ may be formed[3] and it is possible that a zinc xanthate complex may be adsorbed on the activated carbon.

When 100 mg of EtX were used, the background values were 0.09 μg for Ni and less than the limit of detection for Tl.

Enrichment and determination of iron

In preliminary experiments it was found that the proportion of the iron adsorbed was not altered by increasing the EtX concentration but was dependent on the pH of the sample solution. Iron was quantitatively adsorbed in the pH range 5.8–6.2 without the use of additional reagent. The pH of the sample solution was adjusted by addition of 5 ml of 1*M* sodium acetate. The background for iron was 13.0 μg, which was assumed to come mainly from the activated carbon.

Enrichment and determination of mercury

It was found that mercury(II) nitrate was quantitatively adsorbed from zinc nitrate in the pH range 2.0–5.1 without addition of a complexing reagent such as ethyl xanthate. When 20, 50, and 100 g of $Zn(NO_3)_2 \cdot 6H_2O$ were dissolved in 300 ml of water, the pH values were 5.1, 4.8 and 4.2 respectively. These are in the correct range and the results of enrichment studies on these solutions are given in Table 1. Metallic zinc was not used as a matrix in enrichment studies of mercury because of the high mercury content of the nitric acid used to dissolve the sample and the possibility that some mercury could be volatilized during the dissolution.

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A STATISTICAL APPROACH BY SERIAL CORRELATION TO ASSESSMENT OF STABILITY OF ANALYTICAL SYSTEMS

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Summary—The functional instability of infrared spectrometers can result in serious errors of analysis. This work shows that the stability can be tested by means of the serial correlation method, and the various causes of unstable conditions and equipment faults identified. Drift and large oscillations present separately or together can be detected by new statistics developed from the serial correlation method.

The functional instability of any analytical system can result in serious errors of analysis. Consequently, it is necessary to verify the stability of the parameters of the calibration equation $y = f(c)$. This was done by Hooton and Parsons[1] application of the method of mean squares of successive differences.[2] This test is particularly sensitive to long-term trends or to highly rapid oscillations in a series of results.

Another statistical test that could be used (and is equally efficient) is that of serial correlation.[3] This paper shows its application to testing the stability of an infrared spectrometer.

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A STATISTICAL APPROACH BY SERIAL CORRELATION TO ASSESSMENT OF STABILITY OF ANALYTICAL SYSTEMS

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Summary—The functional instability of infrared spectrometers can result in serious errors of analysis. This work shows that the stability can be tested by means of the serial correlation method, and the various causes of unstable conditions and equipment faults identified. Drift and large oscillations present separately or together can be detected by new statistics developed from the serial correlation method.

The functional instability of any analytical system can result in serious errors of analysis. Consequently, it is necessary to verify the stability of the parameters of the calibration equation $y = f(c)$. This was done by Hooton and Parsons[1] application of the method of mean squares of successive differences.[2] This test is particularly sensitive to long-term trends or to highly rapid oscillations in a series of results.

Another statistical test that could be used (and is equally efficient) is that of serial correlation.[3] This paper shows its application to testing the stability of an infrared spectrometer.

For a stable analytical system, the stability coefficient obtained from a set of data has a random variation of certain statistical parameters. Instability can arise from drift of some periodic fluctuations or discontinuities, separately or simultaneously. Serial correlation,[3] in other words the correlation between pairs of equally spaced observations from a set of experimental data, has a high sensitivity to periodic effects in series of observations. For a series of observations $y_1, y_2, \ldots, y_n$, a serial correlation would be the correlation between the pairs y_i and y_{i+h} where h is called the lag. For $(i + h) > n$, the serial correlation is "circular", with $y_{i+h} = y_{i+h-n}$. Thus for the series of values 4.80, 4.76, 4.24, 4.57, 4.63, 4.65, 4.25, 4.77, 4.69, 4.82, 4.78, with $n = 11$, for $h = 1$ the value paired with $y_{11} = 4.76$ would be $y_{11+1-11} = y_1 = 4.80$, or for $h = 4$ the value paired with $y_9 = 4.69$ would be $y_{9+4-11} = y_2 = 4.76$.

The serial correlation coefficient, R_h, which is the stability variable, is calculated from

$$R_h = \frac{\sum_{i=1}^{n} y_i y_{i+h} - \left(\sum_{i=1}^{n} y_i\right)^2 \Big/ n}{\sum_{i=1}^{n} y_i^2 - \left(\sum_{i=1}^{n} y_i\right)^2 \Big/ n} \qquad (1)$$

If $h = 0$ or n, the value paired with every y_i would be itself, so that $R_h = 1$; thus there are $n - 1$ serial correlations possible for each set of n samples, representing lags from 1 to $n - 1$. As with the usual correlation coefficient, R_h must lie between $+1$ and -1.

For the series of data in the above-mentioned example, $R_1 = 0.001$, $R_2 = -0.029$, $R_3 = -0.151$, and so on.

For a large number of normally distributed values of y, R_1 is approximately normally distributed[4] with:

$$\text{ave}(R_1) \frac{-1}{n-1} \qquad (2)$$

$$\text{var}(R_1) \frac{n-2}{(n-1)^2} \qquad (3)$$

Hence for larger values of n, the Student variable t can be computed as

$$t_{1(\text{exp})} = \frac{R_1 - \text{ave}(R_1)}{\sigma_{R_1}} \qquad (4)$$

and then compared with the percentage points for a standard normal deviate. This approximation is allowed because the approximate percentage points are somewhat larger in absolute value than the exact ones.

It must be mentioned that if h and n have no common factors, then the sampling distributions of R_h and R_1 are identical. In particular, if n is a prime number, all the $n - 1$ serial correlations have identical normal distributions. In practical situations, it is generally simpler to drop enough observations to obtain one of these two conditions and then the serial correlations with any lag can be tested, by using the approximation for R_1.

In Table 1 are given the one-sided upper and lower percentage points of R_1 and t, for the 0.05 and 0.01 significance levels and for various values of n.

Generally, the serial correlation coefficients are computed for small values of h, since this gives better information about the state of the analytical system.

The presence of a drift, or other variations, on the correlogram [a plot of $R_h = f(h)$], may indicate instability even when the individual R_h values are not individually statistically significant.

For detecting drift, it is preferable to use the "non-circular" serial correlation, omitting the pairs $y_{i+h} = y_{i+h-n}$ for $(i + h) > n$.

To estimate the stability of an analytical system, the normally distributed experimental R_1 values are compared with tabulated values, in the same way as a χ^2 variable.[1]

Table 1. The one-sided upper and lower percentage points of R_1 and t, for 0.05 and 0.01 significance levels

	R_1			
	Lower percentage points		Upper percentage points	
n	0.995	0.975	0.025	0.005
10	−0.705	−0.564	0.360	0.525
20	−0.524	−0.399	0.299	0.432
30	−0.433	−0.325	0.257	0.370
	t (Student)			
	Lower percentage points		Upper percentage points	
n	0.995	0.975	0.025	0.005
25	−2.787	−2.059	2.059	2.787
28	−2.763	−2.048	2.048	2.763
30	−2.750	−2.042	2.042	2.750

(*a*) If $R_{1(0.975)} < R_{1(\text{exp})} < R_{1(0.025)}$, then the serial correlation is not statistically significant (the analytical system is stable).

(*b*) If $R_{1(0.975)} > R_{1(\text{exp})} > R_{1(0.995)}$ or $R_{1(0.025)} < R_{1(\text{exp})} < R_{1(0.005)}$, then the serial correlation is statistically significant (system stability is doubtful).

(*c*) If $R_{1(\text{exp})} < R_{1(0.995)}$ or $R_{1(\text{exp})} > R_{1(0.005)}$, then the serial correlation is highly statistically significant (the analytical system is unstable).

Similarly, the experimental values of variable t_1 will be compared with the tabulated values for $n - 1$ degrees of freedom.

EXPERIMENTAL

Apparatus

A Zeiss UR-10 spectrophotometer with recorder, to which an integrating digital system was coupled, was used with slit 4, amplification 6, recorder sensitivity 2, bandwidth 2, with retarder, counting time 12 sec. These normal working conditions were sometimes modified, to create new conditions giving some instability to the system, *e.g.*, slit 2 or 8, amplification 7, bandwidth 3, recorder sensitivity 5. The recording conditions are given in Table 2. The measurements were carried out at certain fixed frequencies, with different compounds and solvents.

RESULTS

The results of the measurements for three cases of analytical system stability are tabulated in Table 2 and are represented in Fig. 1.

Equipment stable

The values of R_h for different lags, obtained from the data for acetonitrile given in Table 2, column 1, are tabulated in Table 3, column 2 and are represented in Fig. 2, curve 1.

The values of R_h will have identical distributions because $n = 29$ is a prime number.

The condition $R_{1(0.975)} = -0.325 < R_{h(\text{exp})} < 0.257 = R_{1(0.025)}$ is fulfilled for all values of R_h so the serial correlation is not statistically significant, and the analytical system is therefore stable. The same conclusion may be reached both from the individual fluctuations of the analytical signal with time (Fig. 1, curve 1) and from the correlogram (Fig. 2, curve 1).

The experimental t_h values for different lags, obtained from the data for acetonitrile given in Table 3, are tabulated in Table 4.

One can observe that for all values of t, the condition $t_{0.975} = -2.05 < t_{h(\text{exp})} < 2.05 = t_{0.025}$ is fulfilled and thus the serial correlation is not statistically significant and the analytical system is stable.

Table 2.

Fixed frequency, cm^{-1}		2252 (1)	550 (2)	805 (3)
Compound		Acetonitrile	Benzene	CCl_4
Solvent		CCl_4	CCl_4	CCl_4
Counting time, *sec*		12	12	12
Observation No.	1	2144	2185	3271
	2	2234	2230	3249
	3	2244	2144	3277
	4	2196	2140	3274
	5	2285	2233	3274
	6	2255	2187	3287
	7	2166	2159	3288
	8	2068	2307	3262
	9	2183	2151	3268
	10	2166	2237	3269
	11	2119	2349	3297
	12	2121	2311	3243
	13	2251	2218	3316
	14	2217	2347	3246
	15	2220	2194	3246
	16	2146	2273	3265
	17	2109	2308	3240
	18	2208	2329	3285
	19	2188	2363	3267
	20	2164	2326	3224
	21	2226	2304	3127
	22	2198	2230	3083
	23	2196	2202	3071
	24	2179	2291	3105
	25	2179	2272	3119
	26	2286	2315	3088
	27	2225	2343	3135
	28	2210	2379	3144
	29	2175	2328	3149

Equipment with doubtful stability

The values of R_h for different lags, based on the data for benzene from Table 2, are given in Table 3 and are represented in Fig. 2, curve 2.

Because $R_{1(0.025)} = 0.257 < R_{1(exp)} = 0.356 < 0.370 = R_{1(0.005)}$ the serial correlation is statistically significant and the stability of the analytical system is doubtful. This conclusion may also be reached from the drift of the individual fluctuations of analytical signal with time. This is why the other R_h values ($h = 2,\ldots,6$) do not fulfil either of the two criteria of doubtful stability.

Table 3. The values of the R_h serial correlation coefficient for the data from Table 2

Lag, h	R_h Acetonitrile	Benzene	CCl_4
1	0.247	0.356	0.830
2	−0.172	0.245	0.720
3	−0.078	0.207	0.540
4	−0.042	−0.208	0.350
5	−0.107	−0.231	0.230
6	−0.150	0.063	0.057
Conclusions	Stability	Doubtful stability (drift)	Instability (long-term oscillation)

Table 4. The values of the variable t for the data from Table 3

Lag, h	Acetonitrile	Benzene	CCl_4
1	1.528	2.115	4.680
2	−0.737	1.517	4.081
3	−0.229	1.312	3.131
4	−0.036	−0.931	2.100
5	−0.769	−1.055	1.424
6	−1.007	0.533	0.501
Conclusion	Stability	Doubtful stability (drift)	Instability (long-term oscillation)

That the stability is questionable may be observed very well from the correlogram (Fig. 2, curve 2), because of the six values of R_h the first five continuously decrease but with a marked fluctuation.

From the t values for different lags, based on the data for benzene given in Table 3 and tabulated in Table 4, it can be seen that $t_{0\,025} = 2.05 < t_{1(exp)} = 2.11 < 2.76 = t_{0.005}$.

The value of t indicates a statistically significant serial correlation and a doubtful stability of the analytical sys-

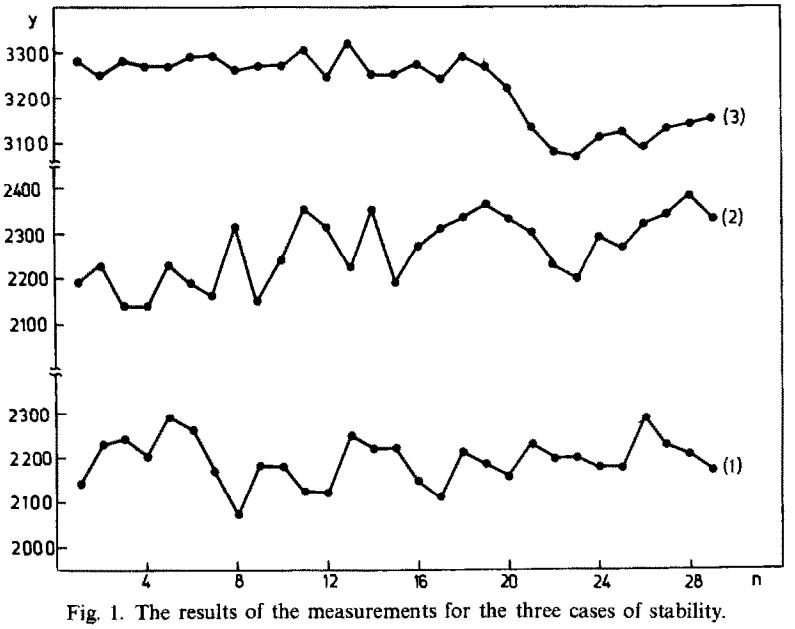

Fig. 1. The results of the measurements for the three cases of stability.

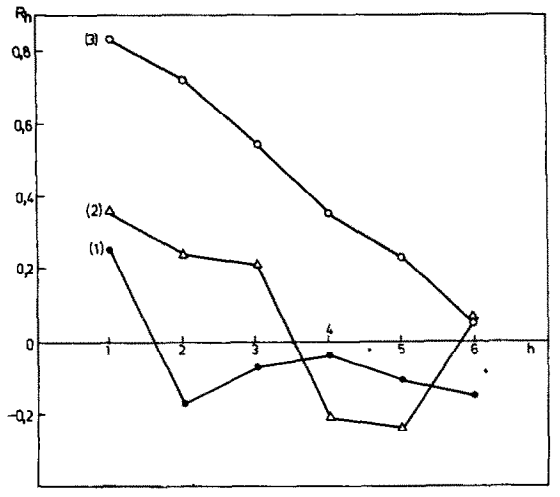

Fig. 2. The values of the R_h coefficient for different lags, based on the data from Table 2.

tem. The other values of t are not statistically significant and have a similar variation with R_h values.

Equipment unstable

The values of R_h for different lags, based on the data for carbon tetrachloride from Table 2, are tabulated in Table 3 and represented in Fig. 2, curve 3.

Because $R_{1(exp)} = 0.830 > 0.370 = R_{1(0.005)}$ the serial correlation is highly statistically significant, thus the analytical system is unstable. The same conclusion can be reached from the fluctuations of the analytical signal, as there appears to be an oscillation with a long-term periodicity. The correlogram (Fig. 2, curve 3), shows the instability clearly, as evidenced by the almost linear decrease in R_h as a function of h.

The values of t for different lags, based on the data for carbon tetrachloride from Table 3, are tabulated in Table 4. Because $t_{1(exp)} = 4.68 > 2.76 = t_{0.005}$, the serial correlation is again highly significant, and thus the analytical system is unstable. The continuous decrease in the values of t also indicate the instability.

CONCLUSIONS

The processing of these three sets of experimental data, with n chosen so that $n - 1$ values of R_h would have identical distributions, shows that a stability of the analytical system can be assessed from the R_1 value, since for stable systems all the R_h values lead to the same conclusion.

If the R_1 value indicates a doubtful stability, the other R_h values must be examined. A continuous but markedly fluctuating decrease in the R_h values indicates that the stability is questionable, but a continuous and almost linear decrease indicates that the equipment definitely has instability. The correlogram makes it easier to judge the trends. Alternatively, the values of t may be used, as they have a variation similar to that of R_h and lead to the same conclusions.

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RAPID DETERMINATION OF NITRATE NITROGEN IN SOILS

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(*Received* 20 *July* 1976. *Accepted* 24 *October* 1976)

Summary—A simple but effective method for pretreatment of soil samples is suggested. The application of an electrodynamic vibrator or ultrasonic device eliminates the necessity for continuous stirring in direct potentiometric determination of nitrate nitrogen. It also makes the extraction process faster, and the apparatus could easily be used in automatic systems for continuous soil control.

The nitrate nitrogen content is an important characteristic of soil. Titrimetry, colorimetry, spectroscopy, and polarography are widely used to determine the nitrate concentration in soil extracts.[1–7] Recently, direct potentiometry with ion-selective electrodes has made this determination faster, more accurate and precise,[8–14] but the pretreatment of the soil samples (extraction, shaking, filtration) still takes a long time, often several hours, so automation of the analysis is essentially prevented. The need for constant stirring of the solution or soil suspension during the direct potentiometric determination of nitrate nitrogen is another limitation on the construction of automatic systems.

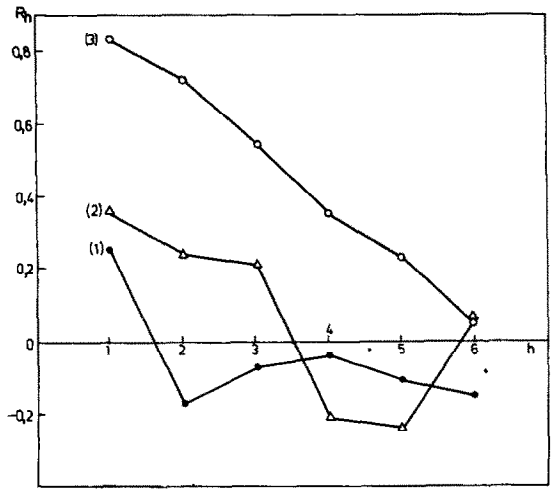
The aim of the present paper is to suggest a simple but effective method for pretreatment of the soil samples. The application of ultrasonic or electrodynamic mixing makes the extraction process faster and eliminates the necessity for continuous use of a magnetic stirrer during the potentiometric determination. Both ultrasonic and electrodynamic vibrators can be simply connected into an automatic system for continuous soil analysis.

EXPERIMENTAL

Reagents and apparatus

An Orion model 92-07 nitrate ion-selective electrode was used in conjunction with an Orion model 90-01 reference electrode to measure nitrate ion concentration. The emf was recorded to 0.1 mV with an Orion model 801 digital pH/mV-meter, used in conjunction with an Orion model 751 printer. Calibrating emf measurements were made as appropriate on fresh solutions prepared by serial dilution of 0.1*M* potassium nitrate with demineralized water. Since the nitrate concentration was the object of investigation, no inert electrolyte or buffer was added to the calibration solutions.

A low-frequency electrodynamic vibrator was used to mix the solutions. It is shown schematically in Fig. 1. This



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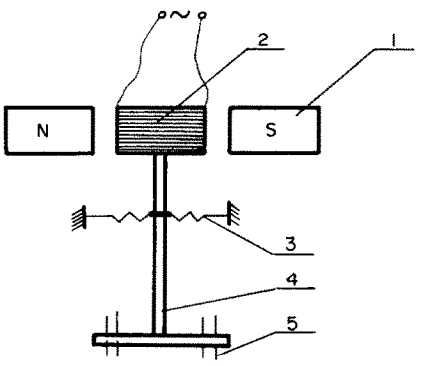

Fig. 1. Electrodynamic vibrator 1—d.c. magnet; 2—magnetic coil; 3—elastic element; 4—lever; 5—vibrating disc.

vibrating system consists of a d.c. magnet (1) and a magnetic coil (2) connected to an elastic element (3). The lever (4) holds the vibrating disc (5). Figure 2 shows the form of the openings on the disc, which ensure the intensive mixing of the soil suspension or solution investigated. Experiments have shown that a short pretreatment (30–60 sec) makes the constant stirring during the measurements completely unnecessary.

The slope of the calibration graph is almost Nernstian (54–56 mV per decade) between pNO_3 1 and 4, followed by a non-linear region down to pNO_3 5. The well-known drift of this nitrate electrode,[14] (20–25 mV per month in our investigation) was simply compensated, but in any case the electrode response remained close to Nernstian even at higher drifts of the electrode potential. The response time for the region investigated was less than 20 sec.

Procedure

The soil samples were prepared by mixing 10 g of air-dried and milled soil with 50 ml of demineralized water. The electrodynamic vibrator was applied for three 20-sec periods to the suspension thus obtained. Then the nitrate and reference electrodes were dipped into the suspension and the emf recorded. The pNO_3 values were determined from the calibration graph.

The soil suspension can be similarly pretreated with an ultrasonic device (high-frequency generator with magnetostriction concentrator) for the same time.

To check the results obtained, measurements were performed after filtration of the soil extracts. The solutions thus obtained were also treated before the determination of nitrate concentration.

RESULTS AND DISCUSSION

Eight Bulgarian soils were examined. For each sample 10 runs were performed and standard deviations and confidence intervals (confidence level 95%) of the mean and of a single determination were calculated. To assess the accuracy of the accelerated pNO_3 determination, the same soil samples were analysed spectrophotometrically by a routine method.[15]

Table 1 shows the mean values of pNO_3 obtained for the suspension after sonic pretreatment and for the filtrate

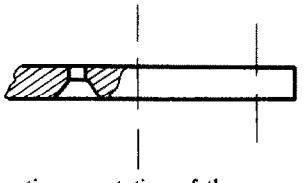

Fig. 2. Schematic presentation of the cross-section of the vibrating disc, showing the form of the openings.

Table 1. Comparison between pNO_3 values obtained by different mixing methods for suspension and filtrate

	Suspension						
No.	edv	us	ms	edv	us	ms	Filtrate spectrophotometry
1	3.21	3.21	3.20	3.22	3.22	3.23	3.22
2	3.69	3.69	3.69	3.69	3.69	3.70	3.71
3	3.80	3.80	3.82	3.81	3.79	3.83	3.75
4	3.55	3.55	3.54	3.55	3.57	3.55	3.59
5	3.43	3.43	3.43	3.45	3.45	3.47	3.41
6	3.27	3.26	3.26	3.25	3.27	3.27	3.20
7	3.85	3.85	3.88	3.85	3.84	3.81	3.80
8	3.91	3.92	3.90	3.89	3.90	3.91	3.94

edv = electrodynamic vibrator; us = ultrasound; ms = magnetic stirrer.

with standard magnetic stirring, and also those for the standard spectrophotometric determination.

The relative standard deviations for pNO_3 determination are between 1 and 2%, the confidence intervals of the mean between $\pm$ 0.04 and $\pm$ 0.02, and the confidence intervals for a single determination between $\pm$ 0.16 and $\pm$ 0.07. The correlation coefficient, comparing the direct potentiometric and spectrophotometric methods, is $r = 0.97$.

As seen, the application of electrodynamic or sonic pretreatment of the soil samples can replace completely the continuous stirring of the soil suspension or solution during the direct potentiometric determination of nitrate nitrogen. It also allows an easier automatation of the analytical procedure. Since no difference was found between the results of either the electrodynamic or the ultrasonic pretreatment, the electrodynamic vibrator is preferred because of its simplicity, cheapness and portability.

This method of pretreatment of soil samples also eliminates the lengthy shaking procedure that is routinely used in agricultural chemistry.

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PRELIMINARY COMMUNICATION

ACETALDEHYDE AS AN END-POINT INDICATOR IN THE CATALYTIC THERMOMETRIC TITRATION OF WEAK ACIDS

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In their original paper on the technique of catalytic thermometric titrimetry, Vaughan and Swithenbank[1] observed that while acetone was an efficient thermometric indicator for the non-aqueous titration of weak acids, acetaldehyde was not. When they used the latter as the sample solvent, an immediate and significant temperature rise occurred on addition of the alkali titrant, i.e., before the acid sample could be titrated, whereas with acetone as the solvent the temperature rise indicating the end-point occurred after the acid was neutralized.

This difference in the behaviour of the two carbonyl compounds was attributed to differences in the kinetics of their alkali-catalysed self-condensations. It was pointed out that, according to Sykes,[2] the condensation step in the dimerization of acetone is slow, while the corresponding step with acetaldehyde is fast, and it was concluded that the dimerization of acetaldehyde occurs before the acid sample can undergo reaction with the titrant. However, in a re-investigation of the use of acetaldehyde as a thermometric indicator, we find that satisfactory end-points can be achieved in the titration of solutions of acids in acetaldehyde, when either alcoholic or aqueous 0.5M potassium hydroxide is used as the titrant. End-point sharpness can be improved by using mixtures of acetaldehyde and water as the solvent instead of acetaldehyde alone. This improvement can be seen in Figs. 1 and 2, which show the titration curves obtained when 0.5M solutions of potassium hydroxide in propan-2-ol and water, respectively, are used as the titrants for the determination of benzoic acid and for blank, i.e., solvent, titrations. The thermometric titration curve for benzoic acid dissolved in dry acetone is included for comparison (Fig. 1h).

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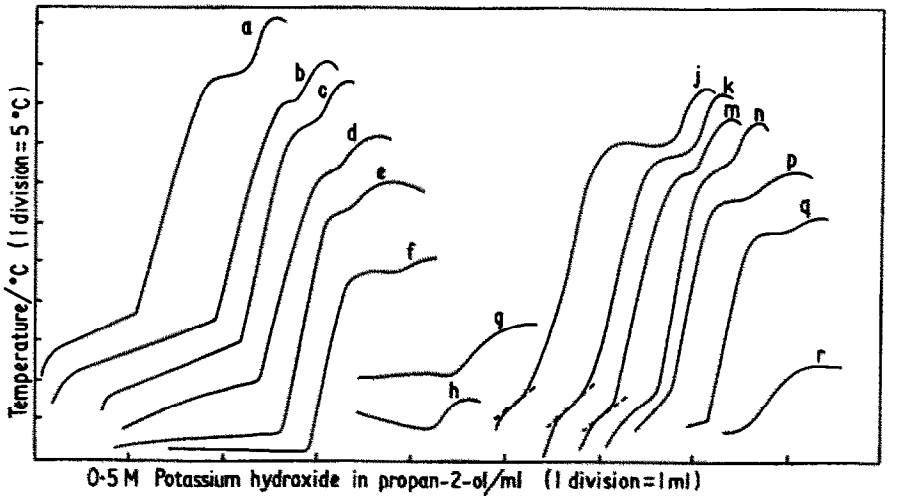

Fig. 1. The catalytic thermometric titration of benzoic acid in aqueous and non-aqueous acetaldehyde with 0.5M potassium hydroxide in propan-2-ol.

Benzoic acid/mg - acetaldehyde/ml - water/ml : a, 34.1:4:0; b, 67.0:4:0.1; c, 63.5:4:0.5; d, 60.0:4:1; e, 80.4:4:2; f, 64.6:3:3; g, 42.8:1:5; h, 44.1:4*:0. Curves j - r correspond to a - g, with the benzoic acid omitted. *Acetone solvent.

When the acetaldehyde solvent mixture contains not more than about 10% of water, the titration curves obtained by using the propanolic titrant show four distinct inflexions (Fig.1, a - c). The initial temperature rise of about 4°C (the one observed by Vaughan and Swithenbank) is independent of the amount of acid sample and occurs in both the blank and sample titrations. This sharp rise in temperature is followed by a more gradual one corresponding to the neutralization of the acid, and then by a second sharp rise of about 25°C marking the end-point of the titration. The solution boils at this stage but the linearity of the temperature rise appears to be unaffected by the loss of solvent. A third sharp rise in temperature, of about 4°C, occurs before the temperature finally decreases on the further addition of titrant. Because of the low b.p. of acetaldehyde (21°C) it is preferable to cool it initially to about 15°C.

The initial temperature rise, noted above, is hardly apparent when the water content of the solvent exceeds 20%, irrespective of the titrant solvent, and the final temperature rise is no longer sharp (Figs. 1, d - g; 2, c - e). The blank titration curves are similar to those for the acid titrations, but the end-point inflexions are harder to locate when the water content of the solvent is low. There is still a significant blank titration value even when there is little or no initial temperature rise (Figs. 1, q and r; 2, k and m). Although the rise in temperature after the final inflexion is relatively small, i.e., 1 - 2°C, in all determinations in which the aqueous titrant is used, the main temperature rise is of the same order as that obtained by using the non-aqueous titrant.

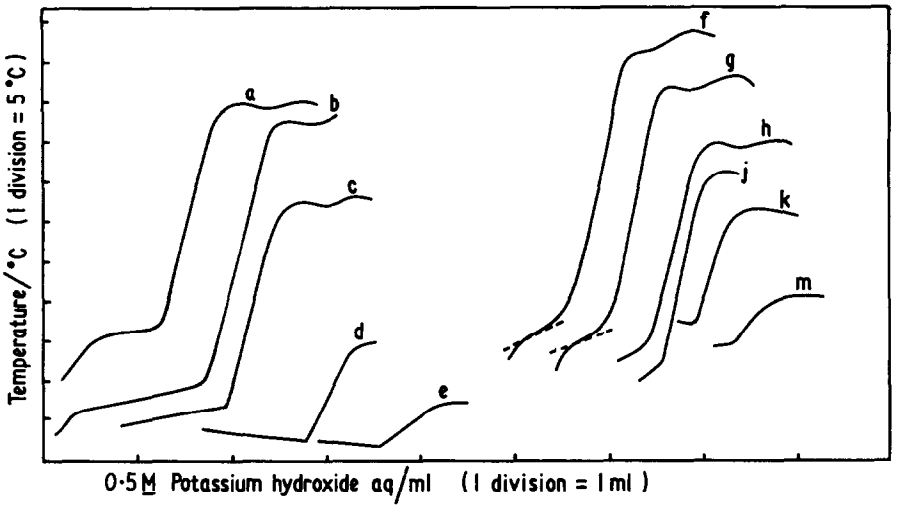

Fig. 2. The catalytic thermometric titration of benzoic acid in aqueous and non-aqueous acetaldehyde with 0.5M aqueous potassium hydroxide.

Benzoic acid/mg - acetaldehyde/ml - water/ml : a, 38.4:4:0; b, 57.8:4:0.1; c, 38.6:4:2; d, 46.2:2:4; e, 28.0:1:5. Curves f, g, h, k and m correspond to a - e, with the benzoic acid omitted; j is 0:3:2.

Even with solvent systems containing 80% of water, the temperature changes at the end-point are significantly greater than those possible with acetone as the thermometric indicator.

The acetaldehyde indicator has been evaluated for the determination of boric acid, phosphoric acid, 4-hydroxybenzoic acid, glycine, valine, histidine, tryptophan, 6-aminohexanoic acid, 3,5-dimethylphenol and 5,5-dimethyl-1,3-cyclohexanedione (Fig.3). Phosphoric acid and 4-hydroxybenzoic acid are titrated as dibasic acids, histidine shows a reaction stoichiometry of 1.3 and the other compounds, with the possible exception of 3,5-dimethyl phenol, are determined as monobasic acids. The result for histidine suggests that cyclic secondary amine, as well as carboxylic acid, is being determined. Titration curves for 3,5-dimethylphenol obtained under aqueous (Fig. 3d) and non-aqueous (Fig. 3c) conditions did not show sharp end-point inflexions, and the end-point in the titration of a mixture of 3,5-dimethylphenol and phosphoric acid in aqueous acetaldehyde corresponded to the acidity of the phosphoric acid only (Fig. 3f). This result suggests that the technique might be suitable for the determination of stronger acids in the presence of phenols.

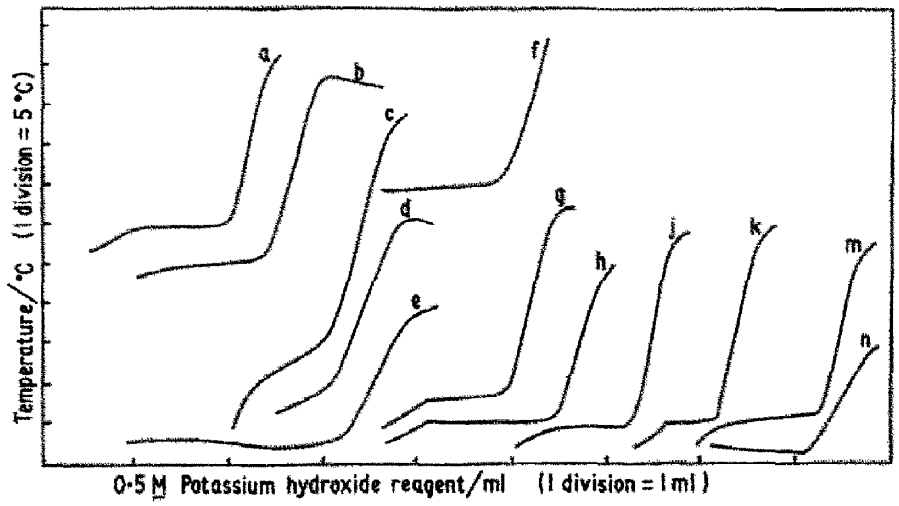

Fig. 3. The catalytic thermometric titration of acids in aqueous acetaldehyde with 0.5M aqueous potassium hydroxide.

Acid (mg) : a, boric acid (31.1); b, phosphoric acid (22.4); c, 3,5-dimethylphenol* (63.9); d, 3,5-dimethylphenol (58.6); e, 4-hydroxybenzoic acid (66.3); f, 3,5-dimethylphenol (61.0) + phosphoric acid (22.4); g, glycine (37.8); h, valine (71.4); j, histidine (45.8); k, tryptophan (62.2); m, 6-aminohexanoic acid (62.7); n, 5,5-dimethyl-1,3-cyclohexanedione (60.2). Solvent system: 3 ml acetaldehyde + 2ml water. Phosphoric acid is 90% H_3PO_4; the weight is corrected to 100%. *Solvent: 5 ml acetaldehyde; titrant: 0.5M KOH in propan-2-ol.

A pale yellow colour develops, after the acid sample is neutralized, in titrations in which the water content of the solution does not exceed about 50% at the end-point. When the alcoholic titrant is used the colour deepens to orange and finally to red; the colour changes appear to correspond approximately to inflexions in the titration curves.

We believe that the initial rise in temperature in these titrations is caused not by the aldol reaction but by the hydration of acetaldehyde, or by hemiacetal formation when an alcoholic titrant is used. The other steps in the titration curve may correspond to stages of the aldol condensation and the subsequent dehydration to unsaturated resins. This possibility and the relevance of the colour changes are being investigated.

Professor H. J. V. Tyrrell is thanked for helpful discussions.

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TALANTA REVIEW*

DETECTION AND MEASUREMENT OF VOLATILE HYDROCARBONS AT AMBIENT CONCENTRATIONS IN THE ATMOSPHERE

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Summary—Modern techniques for the sampling and analysis of volatile hydrocarbons present at ppm–ppM levels in air are reviewed. Emphasis is placed on methods designed to detect and determine individual hydrocarbons of particular interest. Advances in instrumentation and automation are discussed with particular reference to systems combining gas chromatography, mass spectrometry and computerized data-analysis.

In recent years considerable interest has arisen, and research efforts have been invested, in studies of the effects of air-pollution on man and his environment. A major proportion of this activity has been directed towards the estimation of hydrocarbon levels in the atmosphere. Still more recently, interest in this general field has been concentrated on investigations into the identification and measurement of levels for groups of compounds or even individual pollutants. This review is concerned with the determination of volatile hydrocarbons in the atmosphere, primarily alkanes or lower alkenes and aromatics as a group of unsaturated hydrocarbons. Primary sources quoted have been extracted from the literature from 1970 until the early months of 1976—we consider that work before this period has been adequately reviewed elsewhere.[1] No techniques of sampling and analysis of general applicability to various environments and the wide range of potential pollutants have as yet been reported. In this review sampling and analytical procedures are considered separately; it should be remembered, however, that the validity of results will depend on the efficiencies of both procedures, and on their compatibility.

Methane, which is the only hydrocarbon found naturally occurring worldwide, has a background concentration in the atmosphere of 1.3–1.4 ppm. Other hydrocarbons found in air are derived from a wide variety of sources, the most significant of which include oil and petroleum refineries and storage depots; chemical production and oil-burning industries; commercial and geological gas-leaks; biological processes;[2] agricultural and forest-burning programmes.[3] In certain forest areas terpenes are emitted by the living trees.[4,5]

At the ppM (parts per milliard) concentrations in which they are normally encountered in the atmosphere the hydrocarbons are relatively harmless to mammals. It has been shown,[6] however, that ethylene at concentrations as low as 0.01 ppm, and to a lesser extent other hydrocarbons, can have deleterious effects on various species of plant. A more serious problem is the so-called photochemical smog,[7–9] which is produced under certain meteorological conditions by the reactions of nitrogen oxides with other air-pollutants, including hydrocarbons, leading to the formation of compounds such as ozone, aldehydes, peroxyacyl nitrates and alkyl nitrates. These reaction products can cause severe irritation of the eyes and mucous membrane. Visibility may also be reduced by the formation of aerosols of polymer molecules originating from photochemical reactions of hydrocarbons.

Specific hydrocarbons derived from different sources will have varying degrees of impact on the environment. Thus ideally it would be desirable to determine levels of individual hydrocarbons in the atmosphere. Many surveys, however, have measured only total hydrocarbon levels, *e.g.*, at St Louis,[10] and in a comparison of Paris with other cities.[11]

A more significant survey measured total hydrocarbons and calculated non-methane hydrocarbon levels in the U.S.A.,[12] using an empirical relationship derived from previous measurements. Thus measurements of non-methane hydrocarbon levels are to be preferred to those of total hydrocarbon levels. More information may be obtained by monitoring specific compounds, and a study of diurnal patterns for several aliphatic and aromatic hydrocarbons has resulted in their occurrence being attributed to automobile exhaust.[13] A similar range of compounds has been investigated by evaluating vehicular emissions,[14] which involved measurements in New York and New

*For reprints of this Review see Publisher's announcement near the end of this issue, TALR 58.

Jersey and included calculations to demonstrate the effect of wind direction on hydrocarbon levels. A study in Los Angeles[15] has attempted to correlate measured hydrocarbon levels with possible sources of such species, and the relative significance of sources was quoted as: automobile exhausts 47%, evaporative losses of gasoline 31%, geological gas-leaks 14%, and leaks in commercial natural-gas supply systems 8%. An attempt has been made[16] to produce a distribution profile for individual hydrocarbons (benzene and toluene) over a large area (Toronto) by sampling at 12 sites simultaneously. Overall average concentrations were 13 and 30 ppM respectively but the levels could vary between individual sites by a factor of up to 40. The toluene:benzene ratio has been suggested as an indication of the proportion of atmospheric hydrocarbon pollution produced by automobiles. Other workers[17,18] have found similar ratios to those recorded in Toronto. In Zürich, however, a far lower toluene:benzene ratio has been found.[19] Benzene and toluene have been measured[20] at levels of 23 and 11 ppm respectively in the vicinity of a chemical reclamation plant.

A three-month survey of a rural community in Eastern Pennsylvania showed that EPA limits for hydrocarbons[21] were not exceeded.[22] Other measurements have been reported covering several molecular-weight ranges and include: C_1–C_5 by an automatic method;[23] C_1–C_5 amongst other gases associated with peat and coal;[24] C_8–C_{18} in Paris air;[25] C_6–C_{20} in Zürich,[19] C_9–C_{20} in Italy;[26] C_6–C_{10} in the Netherlands.[27]

SAMPLING

Principles of sampling procedures

The accuracy and precision of a sampling technique are of the utmost importance and such a technique must allow ready relation of the values measured to those present in the environment. These requirements are of course true of all analyses and in this application inert materials such as glass, polytetrafluoroethylene (PTFE) and stainless steel should be used to reduce the adsorption effects on the walls of containers and transfer lines. Particular attention should be given to the cleaning of all apparatus and to the selection and application of any sealing or lubricating materials, in order to avoid contamination.

Both the duration of sampling and the time at which samples are taken should be related to the purpose of a particular investigation. Studies on short-duration pollution incidents require rapid sampling techniques, whereas in investigations into ambient levels of pollutants time-averaged results over as long a period as is practicable are desirable. German States developing legislation in respect of smog incidence are specifying half-hour sampling periods and in the U.S.A. a three-hour mean sample is prescribed.[28]

Apparatus and methods for gas sampling

At the ambient levels normally encountered, preconcentration (of the volatile components from a highly diluted sample) before analysis is usually required; however, some methods in which a gas-sample is analysed directly have been reported.[13,23] The high volatility of the low molecular-weight hydrocarbons requires the use of cryogenic trapping techniques to ensure 100% retention, whereas for the higher molecular-weight compounds ($\geq C_6$) adsorption onto solid adsorbents is the preferred technique.[29–32]

Gas–tight syringes,[16,32] glass aspirators and PTFE bags[16,23,33,34] have all been used as sample containers. Ambient gas has been sampled by using a modified gas-pipette with "Teflon"-coated rubber seals and GC/MS (gas chromatography–mass spectrometry) analysis gave a reported detection limit of 5 $\mu g/m^3$.[35] The use of "Saran" bags for the sampling of industrial atmospheres contaminated at the 200–1000 ppm level has been reported[33] and losses (after three hours) of 15% and 40% for benzene and toluene respectively were recorded. A remote sequential sampler has been described,[36] in which spring-loaded syringes are activated by a timer; the samples can be stored for 18 hours without leakage. A small lightweight gas-sampler for time-integrated samples has been described.[37] An evacuated container equipped with an orifice of specific size is used to collect the sample, and the sampling period is dictated by the area of the orifice and the volume of the container. The system has been evaluated for efficiency in sampling of methane, ethane, benzene and hexane.

Cryogenic systems

A battery-operated system for sampling in remote areas has been reported.[38] It requires approximately three litres of liquid nitrogen, and has been shown to have variable freeze-out efficiency and require constant attention. A portable cryocondenser has been shown[39] to give a high enrichment when used for large air volumes and, when connected to a gas chromatograph operated at low temperature and fitted with a flame-ionization detector, to give a detection limit at sub-ppM level. A similar system has been used for the sampling of industrial air pollutants at various altitudes.[40] A more elaborate application of a freeze-out technique to ultratrace analysis has been described,[41] in which a temperature gradient is applied to a tube packed with a GLC stationary phase on an appropriate support. The main problem with freeze-out techniques is the presence of water vapour in the air. The use of drying agents before the condensation has reduced this problem and systems based on this principle have been described.[42] The contents of cryogenic traps have been separated by sequential increase in temperature[43] or by a preparative gas chromatographic technique,[42] before analysis by mass spectrometry.

Although cryogenic sampling is the only technique at present available which produces directly a true sample composition in the low molecular-weight range of air pollutants, procedures involving sorption on solid adsorbents or in liquids coated on inert supports and acting as stationary phases, are simpler and more convenient for field-sampling. Adsorption techniques suffer from high losses of volatile compounds. The chemical nature of a solid adsorbent has a considerable influence on the adsorption/desorption characteristics for specific compounds, and losses due to irreversible adsorption are common, particularly when thermal desorption is used.

Adsorption on activated carbon, silica gel, support-bonded stationary phases or porous polymers

Activated carbon is particularly likely to adsorb certain organic species irreversibly. Recovery of the adsorbed material by solvent extraction is more complete but is also a more time-consuming and complex process. This material has, however, been used widely as an adsorbent, followed by either thermal desorption[25] or by various methods for solvent extraction[19,26,44] of the adsorbed species. Carbon disulphide has been shown to be an effective solvent for the purpose.[19]

The usefulness of silica gel as an absorbent for sampling of environmental samples is greatly reduced by its affinity for water and the consequent influence of relative humidity on the adsorption curves for hydrocarbons. Sampling onto silica gel followed by thermal desorption of the adsorbed species, their oxidation to carbon dioxide and determination by acidimetric and coulometric measurements has recently been reported.[45] The procedure is limited by the number of adsorption/desorption cycles that can be carried out, by inadequate desorption temperatures and by variations in retention volumes for specific organic species.

The use of support-bonded chromatographic stationary phases for sampling has been investigated[46] and it has been shown that high concentrations of stationary phases are required in order to maximize the retention of organic species. This method is limited to atmospheric pollutants of relatively low volatility but may be improved by operation at low temperature.

Porous polymers with high capacities for the sampling of organic compounds and low affinities for water are extremely useful adsorbents and have been extensively investigated,[2,41,47–54] both thermal desorption and solvent extraction being used. An evaluation of various organic adsorbents and their relative dynamic capacities for certain classes of compounds has been reported.[29] Chromatographic packing materials studied were "Poropak P" (a porous polymer of styrene and divinylbenzene), "Carbosieve", prepared by thermally cracking poly(vinylidene chloride), and "Tenax GC", a porous polymer of 2,6-diphenyl-*p*-phenylene oxide. In this as in other recent publications[48,54,55] "Tenax GC" has been shown to be superior as a general adsorbent, having excellent stability up to 380° and proving easy to handle. In these studies relative humidity, ubiquitous background levels, repetitive use, transportation and storage were all considered. Mieure and Dietrich[52] classified the adsorption/desorption characteristics of various column packings.

ANALYSIS

There is a need for high specificity in measuring the components of an environmental sample, but it is also desirable that the analysis can be performed routinely, rapidly and with precision. The apparatus should be simple if it is required for use in a mobile laboratory. GLC is the only really useful system for the analysis of complex environmental air-samples, and a flame–ionization detector is most commonly used. Conventional packed columns are adequate for many applications, but in order to achieve the required separation of the broad range of components detectable and accurate measurement of retention times, capillary columns are increasingly used. There are no accepted standard methods for the analysis of hydrocarbons, and it is difficult to envisage their establishment in the near future because of the large variation in the analytical requirements of various applications.

Several GLC systems have been described and compared;[56] it was concluded that there is a need for better chromatographic methods designed to resolve the 50–100 or more readily measurable hydrocarbons in urban atmospheres. The authors added that methods should be developed, standardized and more generally used so that comparative and collaborative studies would be more meaningful. There is also a need to reduce experimental error in identification and estimation of individual compounds, especially in the correlation of the photochemical reactivity of specific hydrocarbons with the resulting oxidant formation.

Rasmussen *et al.*[56] described "some of the present-best GC-column methods used in this laboratory". They preferred a packed capillary column for the analysis of light hydrocarbons, having compared its performance with that of 1/8-in. o.d. packed columns and support-coated open tubular (SCOT) columns. The column used was 20 ft long, 1/16-in. o.d., 0.03-in. i.d., packed with "Durapak" (n-octane, Porasil C). Sub-ambient temperature programming was found to give excellent separation of the C_2–C_6 hydrocarbon fraction. The construction of a suitable cryogenic GC oven has been described.[57] When considering methods for the analysis of hydrocarbons it is convenient to treat the compounds in groups specified by a range of molecular weights. Thus Rasmussen *et al.*[56] considered intermediate hydrocarbons aromatic and aliphatic (C_6–C_{12}) compounds, and discussed their comparative chromatographic character-

istics on several types of column, *viz.* open tubular columns of relatively large diameter, capable of accepting high sample loadings [300 ft, 0.06-in. o.d., *m*-bis-(*m*-phenoxyphenoxy)benzene]; a system of three packed 1/8-in. o.d. columns in series; and small diameter (0.01 in. i.d.) open tubular columns in conjunction with temperature programming designed to produce optimum resolution. They found a 0.02-in. i.d., 200-ft OV-101 SCOT column to be the most satisfactory.

Low molecular-weight hydrocarbons (C_1–C_5)

Jeltes and Burghardt[23,58] have reviewed methods available for the analysis of the C_1–C_5 hydrocarbon fraction present in air and described an automatic GC method, claiming it to be "a relatively simple, direct and inexpensive method for sensitive and quick measurement". Having considered both the spectroscopic and chromatographic methods available, they chose to develop an automatic system for measurement of hydrocarbons, with the intention of providing (1) maximum information: separate measurement of individual hydrocarbons, measurement of ethylene (phytotoxic), "fingerprinting" of hydrocarbon fraction (source identification); (2) relatively convenient automated mode; (3) equipment as inexpensive as possible; (4) simplicity of the whole set-up; (5) quick sampling and analysis; (6) quick results for guarding and "alarms"; (7) specificity; (8) sensitivity. The merits of methods involving preconcentration, as opposed to direct analysis, for the two distinct hydrocarbon fractions (C_1–C_5) and (C_5–C_9) were also discussed. A 2 m × 4 mm i.d. column packed with 80–100 mesh alumina (type F1) was employed for the analysis, with air as carrier-gas. The detection limits at a signal-to-noise ratio of 2 were 2–5 ppM for C_1–C_3 hydrocarbons and 7–20 ppM for the C_4–C_5 fraction. An "AQUASORB" filter was used to remove water from the air-samples. The cycle-time for this system was 45 min, including n-C_5 compounds. An automatic system for C_1–C_5, total C_6 and benzene, working on a 30-min cycle, has also been described.[59]

The problems associated with the condensation of water vapour are even more severe in cryogenic sampling systems. To minimize such difficulties samples have been passed through a desiccant before freeze-out; potassium carbonate has been reported[42,60] to be extremely effective for this purpose owing to its very low affinity for organic compounds. It has been used in a cryogenic U-tube containing glass beads,[42] and the sensitivity was quoted as 0.2 ppM for organic compounds concentrated from 20 litres of air, the efficiency being 100%. A range of desiccants has been examined,[60] including anhydrous salts such as potassium carbonate, calcium sulphate and sodium sulphate, and adsorbents such as "Sephadex" (G-100) or Linde molecular sieve 3A. The same authors considered the removal of water by its conversion into acetylene and hydrogen by calcium carbide and calcium hydride.

A cryogenic sampling system incorporating a freeze-trap containing stainless-steel gauze and employing potassium carbonate as desiccant has been reported[31] to give complete recovery of all hydrocarbons boiling above −90°, with a detection limit of 0.1 ppM; 50–100-litre air-samples were taken and liquid oxygen was used as coolant. The transfer of the concentrate from the trap was a two-stage process: initially into evacuated containers by pressure equalization and secondly by use of Töpler pumps to give a residual pressure of less than 1 mmHg in the trap. Subsequent analysis was by GC, by using retention data from several columns, or with suitable samples by GC coupled with infrared spectroscopy.

Light hydrocarbons have been measured[13] directly on a 5-ml sample, and C_2–C_5 aliphatic hydrocarbons (excluding C_4 alkenes) have been investigated[14] by a more elaborate technique involving a silica gel column at liquid nitrogen temperature. The latter analysis employed an 8 ft × 1/8-in. stainless-steel column packed with the same silica gel stationary phase and operated at 30°. The same workers have measured C_4–C_8 aliphatic hydrocarbons and C_6–C_{10} aromatic hydrocarbons, using different trapping and analytical columns for each group. The C_4–C_8 aliphatic hydrocarbons were trapped on a 1 ft × 1/8 in. stainless-steel column packed with 10% "Carbowax 1540" on 60–80 mesh "Gas Chrom Z," and separated at 0° on a 300 ft × 0.06 in. i.d. open tubular column coated with dibutyl maleate. The C_6–C_{10} aromatic hydrocarbons were trapped on a 1 ft × 1/8 in. stainless-steel column packed with 60–80 mesh glass beads, and analysed at 70° on a 300 ft × 0.06 in. i.d. open tubular column coated with *m*-bis(*m*-phenoxyphenoxy)benzene. Carbon monoxide and methane were separated at 70° on an 8 ft × 1/8 in. stainless-steel column packed with 60–80 mesh 13X molecular sieve (Wilken Instrument Co.). The three gas chromatographic procedures produced 52 measurable hydrocarbon peaks representing the C_1–C_{10} hydrocarbons. The higher molecular-weight hydrocarbons (C_{11}, C_{12}) were observed on occasion but at very low concentration levels. Some peaks contained unresolved shoulders. The overlap of alkane and alkene species was not a significant problem. There were interferences between benzene and some of the C_7 and C_8 alkanes, particularly methylcyclohexane. A direct comparison has been made of the resolution obtained for similar ambient air samples on a 2 m × 1/8 in. packed analytical column and on a 100 ft × 0.02 in. SCOT column; the latter proved far superior.[52]

Benzene and toluene have been determined along with other compounds[16] by trapping on an 8 × 1/8 in. stainless-steel column packed with 20% Dow-Corning "SF 20" on 60–80 mesh "Columpak" at "dry ice"/acetone temperature, followed by analysis at 50° on a 6 ft × 1/8 in. stainless-steel column packed with 8% "SF 96" on 60–80 mesh "Chromosorb" W.

Higher molecular-weight hydrocarbons (C_6–C_{20})

Grob and Grob,[19] in agreeing with a previous worker[61] that high molecular-weight hydrocarbons in the atmosphere represent a complex mixture of hundreds of compounds, considered the analysis of such mixtures required three separate operations, namely high-resolution trace analysis on capillary columns as a necessary prerequisite; appropriate sampling of volatile organic compounds for qualitative and/or quantitative analysis; GC/MS with the full separation power of a high-resolution column and working in the nanogram range. They emphasized[19] that the key to the possibility of injecting very dilute solutions into capillary columns is the avoidance of stream-splitting.[62] They also showed that direct sampling would not work for any but the most abundant species, as the majority of components were present in the 0.1–10 ppM range and 0.1 ng of an individual compound was required for positive identification. Altogether, 108 volatile organic substances were identified in the C_6–C_{20} range, the majority being aliphatic or aromatic hydrocarbons. The samples were trapped at ambient temperature in a glass tube containing 25 mg of wood charcoal, as used for cigarette filters, with an average particle size of 0.08 mm. The filters were extracted with carbon disulphide. The analyses were carried out on two GC columns, a 120 m × 0.33 mm "Ucon HB 5100" for the full spectrum (C_6–C_{20}) and an 80 m × 0.33 mm "Ucon LB550" for the volatile fraction (from benzene to C_3-substituted benzenes) with temperature programming from ambient to 190° and 120° respectively. A more recent application of this type of technique (carbon adsorption) allied to semiautomatic sampling and chromatography on highly polar columns has been reported[63] for the analysis of C_6–C_{20} fractions.

By using a similar approach, but substituting a thermal desorption step for liquid extraction of the sampling trap, Bertsch *et al.*[48] have found several hundred substances in the C_5–C_{16} range and identified almost 100. The sampling traps used were 110 × 8 mm i.d. stainless-steel tubes containing "Tenax GC" and the GLC was carried out on 100 m × 0.5 mm i.d. nickel open tubular columns coated, as described elsewhere,[64] with "Emulphor" ON 870.

"Tenax GC" has been used as an adsorbent[51] with the subsequent desorption step achieved by the passage of current through a heating tape attached to the sampling tube. The tube was heated to 260° for 5 min, the desorbed components being retained at the front of the analytical capillary column at ambient temperature, before temperature-programmed elution.

Raymond and Guiochon have discussed the merits of graphitized carbon black as an absorbent for a wide range of organic compounds[65] and subsequently described[25] its use as the sampling component of a GC/MS system, with which they identified more than 70 components in Paris air. These compounds were in the C_8–C_{18} range and predominantly aliphatic or aromatic hydrocarbons. Sampling was carried out at ambient temperature with tubes 5 cm × 4 mm i.d. packed with 0.25–0.40 g of 200–250 μm sieved graphitized carbon black. Desorption was achieved by heating the trap to 400° within 15 sec with an electric wire ("Thermocoax") soldered around it. The analytical column was maintained at ambient temperature so that the compounds eluted from the sampling tube were retained at the column inlet; desorption usually took approximately 5 min. The analytical column used was 100 m × 0.4 mm i.d. coated with "OV 101", and was operated with temperature-programming from ambient to 230°.

A "timed elution" technique has been described,[18,47] involving adsorption on a solid adsorbent followed by thermal desorption and analysis by GC/MS. The technique is given its name because of the method of eluting the adsorbed species from the sample tube, which, after sampling, is placed in an oven and connected to the analytical column by a valve system. After sufficient time for thermal equilibrium to be established in the sample tube, a known amount of carrier gas is passed, calculated to flow for the precise time required to displace the equilibrated gas phase from the sample tube into the gas chromatograph. The sample tubes were made of stainless steel, 4 × 1/4 in. o.d., packed with 0.3 g of "Chromosorb 102", and desorbed at 130° onto the analytical column, which was stainless steel, 12 ft × 1/8 in. o.d., packed with 5% "Carbowax 20m" on "Chromosorb W AW-DMCS" and operated at 90°. Individual hydrocarbons were identified at the 20 ng level. Application of discontinuous carrier-gas flow for the elution of adsorbed species from sample tubes is at present under study.[66]

A rather complex two-stage extraction/injection system has been described,[49] which was designed to overcome problems of water condensation from the air sampled. The air-sample is first concentrated on "Chromosorb 102" at ambient temperature; the subsequent "thermal" desorption step is somewhat unusual in that the sampling tube is warmed only slightly above ambient temperature but the collecting vessel (part of the injection port) is cooled to liquid-nitrogen temperature. After condensation of the organic compounds the injection port is rapidly heated and analysis carried out on a 100 ft support-coated "Carbowax 20M" column, temperature-programmed between 60° and 180°.

Several reports[52,67] have appeared describing the connection of the sample-collection tube directly to the analytical column. An interesting extension of this approach was presented by Mieure and Dietrich,[52] who designed their sample-tube so that it could be incorporated into the injection-port of their chromatograph. This design has considerable potential for chromatography of less volatile hydrocarbons as it allows independent and rapid heating of sample-tubes to higher temperatures than those required for analytical columns.

Mass spectrometry

Use of mass spectrometry is almost mandatory if definitive identification of organic compounds in environmental samples is required. Even with this powerful technique it is often difficult to differentiate between the many similar compounds which may be present, and thus considerable effort is currently being directed towards improvement of MS techniques in this application.

GC/MS systems, many of which are interfaced to computerized data-handling systems, are now in widespread use.[43,44,47,48,68–72] A high-resolution mass spectrometer coupled to a computer has been used for the analysis of multi-component air-samples.[73]

Experiments have been conducted[74] with a photoionization instrument, irradiating at specific wavelengths selected to produce ionization of trace gases and to avoid activation of major air-components. Measured sensitivities and calculated detection limits are disappointing and require improvement, however.

A technique[75] which has found application in the estimation of refinery pollutant dispersion and in air quality-control utilizes a mass spectrometer modified by the incorporation of a static condensation system and gives results for hydrocarbons quantitative within $\pm 10\%$ at the 5-ppm level and $\pm 20\%$ at 1 ppm.

A technique has been described by which it is claimed that micropollutants present in air at concentrations of 10^{-4}–$10^{-8}\%$ v/v may be separated and identified routinely on commercial equipment.[76] Enrichment is carried out on a microgradient tube followed by separation on a glass thin-film open tubular column by linearly programmed low-temperature gas chromatography and identification by mass spectrometry. The authors reported that significant MS data were obtained for concentrations down to 0.02 ppM.

A portable MS-based vapour-detection system with complete digital control has recently been described,[77] which is reported to give detection limits in the ppM range with a reproducibility of approximately 5% when used with a compatible GC system.

Cryogenic preconcentration of volatile trace components in air-samples has recently been exploited[78] in chemical-ionization mass spectrometry by using the condensed water as a secondary chemical-ionization reagent gas. Further refinements in the cryogenic trap and heater system should produce lower detection limits.

ROUTINE INSTRUMENTAL METHODS

Gas chromatography

Several commercial instruments equipped with flame-ionization detectors (FIDs) are available for the continuous measurement of hydrocarbons at ambient levels. The FID is capable of providing a continuous response, which for hydrocarbons is approximately linear over a wide range of concentrations. Carbon atoms bonded to other atoms (such as oxygen, nitrogen or halogen) give a decreased FID response, and measurements of total hydrocarbon levels can be distorted by the presence of organic compounds which are not purely hydrocarbons. Comparative evaluations of the available instruments have been reported[79,80] and their sensitivity, accuracy, portability and ease of operation discussed. Calibration techniques for such instruments have also been reported,[81] which use standard calibration gases from cylinders and diffusion or permeation tubes.

FID instruments have been operated under reduced pressure[82,83] with the sample passing through the column and detector before entering the pump. This method has been applied to corrosive or unstable compounds. As previously noted, non-methane hydrocarbon measurements are of greater significance than methane measurements as methane contributes little to photo-chemical reactions.

There are now many commercial non-methane hydrocarbon monitors available, the majority of which operate by producing a value for the difference between total hydrocarbon and methane levels.[84] Methane and non-methane hydrocarbon levels may be monitored continuously and simultaneously with a dual-flame instrument.[85] A system has been described[86] which measures methane and/or total hydrocarbons by selective combustion. Selective combustion has also been used, with the incorporation of a water-sorption detector, to measure hydrogen, methane and reactive and non-reactive hydrocarbons. The air is first dried and then passed into a flame, the reactive hydrocarbons being distinguished from the non-reactive species by the relative ease of their combustion. In this context the term reactive refers to the ease with which a particular hydrocarbon will undergo photochemical reaction with nitric oxide or ozone. All hydrocarbons appear to be capable of taking part in such processes, but the reaction rates are extremely dependent on molecular structure.[87] Methane is the least reactive and its residence time in the atmosphere is estimated to be up to sixteen years,[88] thus in terms of urban air quality it may be considered as photochemically inert. The most reactive of such species probably have residence times of only hours in ambient air and strong sunlight.[89] A total hydrocarbon analyser modified to facilitate simultaneous monitoring of ambient air for reactive hydrocarbons has recently been reported.[90]

Instruments have been described[91–93] for the measurement of carbon monoxide and methane, in which the carbon monoxide is first reduced to methane and subsequently detected by an FID; detection limits of a few ppM have been quoted.[94]

Interference-free measurements of carbon monoxide, methane and total hydrocarbons in the range 0–1 ppm have been obtained automatically with a cycle time of 5 min;[95] similarly an automatic timing device has been incorporated into a total hydro-

carbon analyser to enable repetitive measurements to be made of methane, total hydrocarbons and reactive hydrocarbons.[96] An automatic gas chromatographic system, which measured carbon monoxide, methane and non-methane hydrocarbons in a single sample, has recently been described.[97]

Instruments are also available for the measurement of methane, ethylene, acetylene, carbon monoxide and total hydrocarbons[98–101] with detection limits in the region of 200 ppM for total hydrocarbons and 1 ppm or better for individual components. An air-quality chromatograph (AQC) system has been reported[102] and evaluated for the measurement of methane, ethylene, acetylene, propene, propane, isobutane and n-butane. Methane has been separated from the other hydrocarbons in air by use of a cryogenic trap.[103] The device traps more than 95% of all non-methane hydrocarbons and when used in conjunction with a total hydrocarbon analyser makes possible the continuous determination of methane.

Spectroscopic methods

Reactive hydrocarbons can be estimated by utilizing the chemiluminescent reaction of oxygen atoms with unsaturated hydrocarbons at pressures of ~ 1 mbar, which produces intense emission in the 700–900 nm region.[104] Owing to the high background level of methane, techniques for the determination of total hydrocarbons in air do not require exceptional sensitivity (merely a capability for precise operation at the ppm level). Although only of barely adequate sensitivity for ambient-concentration measurements, non-dispersive infrared spectroscopy[105] has been a popular technique. The sensitivity and selectivity of the method have been improved by refinements in instrument design.[106]

High-resolution infrared spectroscopy has been used to monitor methane in the Pyrenees.[107] A problem in using it for the measurement of trace levels of organic compounds has been its limited sensitivity. The sensitivity has been improved[108] by using a scanning Michelson interferometer, cooled solid-state detectors, a fast minicomputer and multiple-pass long path-length cells. The spectra are analysed by the computer, which minimizes the interference from water and carbon monoxide and makes it possible to measure organic compounds at ppM levels.

Laser Raman spectroscopic techniques have been employed for the remote sensing of organic compounds[109] and in particular for methane,[110,111] ethylene[112] and acetylene and ethane.[113] The detection limits for hydrocarbons by laser Raman methods have been quoted as 1–7 ppm.[114] Direct-current discharge emission spectra have been reported for selected organic compounds.[115] An advanced theoretical treatment of remote air-pollution measurement has been published,[116] in which several techniques made possible by the advent of high-energy tunable laser sources are discussed and compared.

METHODS FOR SPECIFIC COMPOUNDS

Ethylene.[117] Air is passed through 200 ml of 0.1% methanolic solution of mercuric acetate at 500 ml/min. The solution is evaporated down to 10 ml and a 1-ml aliquot is applied to a TLC plate. After separation the ethylene band is removed and reacted with sodium borohydride, releasing mercury, which is detected by atomic absorption and is directly related to the ethylene level, for which, it is claimed, the detection limit is 0.1 ppm.

Benzene. It has been claimed[118] that benzene may be determined by using a tube containing silica gel impregnated with paraformaldehyde and sulphuric acid. A critical appraisal[119] of another tube system showed that none of the tubes tested gave a result correct within 25% in the 20–160 ppm range.

Several other "chemical" methods in use for many years before the advances in GC techniques have been reported[28] and may still be of value when instrumental methods are not practicable. These methods deal mainly with alkenes and aromatic species.

CALIBRATION

The types of analytical method described in this review do not determine the absolute amount of compound present but do measure a property of that compound which may be related to its concentration by an appropriate calibration procedure. Gas chromatographic techniques require particular care in calibration as the response of the many components of a complex mixture may vary non-linearly with relatively slight changes in operating parameters.

Gas mixtures containing very low but accurately known levels of organic compounds are extremely difficult to prepare. The techniques which are available for the generation of such standard gas mixtures fall into two categories, static and dynamic procedures. Static procedures are usually necessary in the preparation of multicomponent systems while dynamic methods are applied to the introduction of trace levels of single species into carrier or diluting gas streams.

A major problem in preparing very dilute mixtures is adsorption of trace components onto the walls of cylinders and tubing; this effect may be reduced by rigorous cleaning and careful choice of materials. Mixtures of saturated hydrocarbons in clean glass or metal containers are relatively stable. Unsaturated compounds, however, especially acetylene and butadiene, are slowly decomposed, particularly in the presence of water vapour and oxygen.

Static procedures

Mixtures may be prepared in glass containers or purchased as "standard gases" in cylinders; it is often unwise to place too much reliance on commercially available standards without first checking them against their specification. Mixtures for less rigorous work can be prepared in plastic bags but must be

used within a short time to avoid excessive diffusion losses.

Dynamic procedures

Gas-mixing pumps are available and the use of a two-stage apparatus has made it possible to produce standards at concentration levels down to 1 ppm. Another system, suitable for work not demanding the highest accuracy, employs motor-driven syringes.

Permeation and diffusion tubes

A more accurate dynamic procedure employs permeation tubes, in which the component of interest (in either the liquid or the gas phase) is enclosed in a cylindrical ampoule made of plastic (often PTFE). After a certain induction period the material permeates slowly through the plastic at a uniform rate by a diffusion-controlled process. An apparatus based on this principle requires precise and stable control of two physical parameters, temperature and dilution-gas flow-rate. These parameters are readily controlled to within 1% and thus the overall precision of the system is high. The absolute amount of a compound released has been determined in several ways; for liquid hydrocarbons gravimetric methods are accurate and simple to perform. Such techniques allow the confident production of standards at the ppM level. Diffusion tubes may also be used to produce mixtures at similar concentration levels. The principles of operation of permeation and diffusion tube devices have been extensively discussed,[120–124] though not with specific reference to their application to hydrocarbons.

Capillary-restricted flow

In this method the calibration component to be diluted is measured into a carrier-gas stream through a restricting capillary. The concentration is calculated in accordance with the Hagen–Poiseuille flow-laws. As the 4th power of the capillary radius enters these calculations, the radius must be known precisely. This procedure produces absolute standards with an error of 1–2%.[125]

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SPURENANALYSE IN WOLFRAM: EISEN
EIN KRITISCHER VERGLEICH STANDARDISIERTER ANALYSENVERFAHREN

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Zusammenfassung—Drei Methoden zur Erfassung von Eisenspuren in Wolfram werden aufgrund entsprechender statistischer Kenndaten sowie anhand von Ablaufschematas kritisch miteinander verglichen. Es handelt sich um folgende Verfahren: ein lösungsabsorptionsphotometrisches Verfahren mit α,α'-Dipyridyl als Farbreagens; ein röntgenfluoreszenzanalytisches Verfahren mit vorheriger Spuren–Matrix-Trennung durch Spurenfällung mit 1-(2-Pyridylazo)-2-naphthol; ein atomabsorptionsspektrometrisches Verfahren ohne Spuren–Matrix-Trennung in der Graphitrohrküvette, welches mit nur 50 mg Probenmenge auskommt. Alle drei Methoden wurden nach einem kürzlich von Gottschalk vorgeschlagenen Schema standardisiert. Die Auswahl der hier angewandten Methoden aus einer Vielzahl von Möglichkeiten wird begründet. Die Bedeutung der Durchschnittsspurenanalyse zur chemischen Charakterisierung von Metallen trotz der heutigen Möglichkeiten der topochemischen Mikro- und Spurenanalyse wird diskutiert.

Hier soll über Arbeiten berichtet werden, die der 1971 ins Leben gerufene und 1975 in den Chemikerausschuß der Gesellschaft Deutscher Metallhütten- und Bergleute eingegliederte Arbeitskreis "Analytik hochschmelzender Metalle", im folgenden als AHM-Kreis bezeichnet, durchgeführt hat.* In den ersten Veröffentlichungen dieses Arbeitskreises werden Verfahren der Durchschnittsspurenanalyse in der Matrix Wolfram behandelt. Als vordringlichste Aufgabe wurde ein kritischer Vergleich moderner und in den einzelnen Laboratorien des Arbeitskreises routinemäßig erprobter Spurenanalysenmethoden für die technologisch bedeutsamsten Spurenverunreinigungen bzw. absichtlich zur Erreichung bestimmter Eigenschaften zudotierter Spurenkomponenten wie Kalium, Aluminium und Silizium ins Auge gefaßt.

In der Literatur findet sich eine erstaunlich große Zahl verschiedenster Spurenanalysenmethoden für die Refraktärmetalle, insbesondere für Molybdän und Wolfram.[1–6] Viele dieser Methoden entbehren jedoch wichtiger Kennzahlen wie der Standardabweichung bei verschiedenen Konzentrationsniveaus oder einer exakt angegebenen Nachweis- bzw. Bestimmungsgrenze. Ein kritischer Vergleich solcher Methoden auf der Basis einheitlich festgelegter und vergleichbarer Kenngrößen und Vorgehensweisen steht überhaupt aus. Sämtliche im AHM-Kreis bearbeiteten Analysenverfahren wurden hingegen nach der kürzlich veröffentlichten Standardisierungsmethode von Gottschalk[7] getestet, um statistisch einwandfreie Kriterien zum Vergleich der Methoden in der Hand zu haben.

Wie beinahe überall in der metallurgischen Technologie stellen Eisenspuren auch in den Roh-, Zwischen- und Endprodukten der pulvermetallurgischen Wolframproduktion eine der wichtigsten Spurenverunreinigungen dar. Besonders problematisch ist dabei die Tatsache, daß das Eisen nicht homogen über die oft pulverförmige Matrix verteilt ist—Wolfram wird ja ausschließlich auf pulvermetallurgischem Weg hergestellt—sondern in Form von Rost- oder Abriebpartikeln bisweilen extrem inhomogen das Material durchsetzt. Über die analytische Erfassung solcher heterogener Verunreinigungen in den Ausgangs- und Zwischenprodukten der pulvermetallurgischen Wolframerzeugung sowie über ihre Auswirkungen auf das Endprodukt wurde bereits berichtet.[8–11] Trotzdem bleibt die Durchschnittsspurenanalyse, die ja auch heterogen verteilte Verunreinigungen möglichst vollständig miterfassen soll, Ausgangs- und Bezugspunkt für jede weitere chemische Charakterisierung von reinen Feststoffen. Dies ist schon deshalb der Fall, weil viele moderne topochemische und mikroanalytische Verfahren wie z.B. die Sekundärionenmassenspektrometrie oder die Rasteraugerelektronenspektrometrie auf die Eichung ihrer Signale mittels Durchschnittsspurenanalyse angewiesen sind. Weiters basieren sämtliche Materialspezifikationen

*An den Arbeiten über Eisen in Wolfram waren beteiligt: Metallwerk Plansee: H. M. Ortner; Osram München: G. Gottschalk und V. Scherer; Radium Wipperfürth: F. Schröder; H. C. Starck Goslar: O. Hilmer.

für Wolfram auch weiterhin auf Werten der Durchschnittsspurenanalyse.

AUSWAHL DER ZU STANDARDISIERENDEN ANALYSENVERFAHREN

Zur Erfassung von Eisenspuren in Wolfram wurden folgende drei Verfahren aus einer Vielzahl von Möglichkeiten ausgewählt.

1. *Die lösungsabsorptionsphotometrische (LAS) Eisenbestimmung mit α,α'-Dipyridyl*

Diese Methode ist aufgrund des geringen apparativen Aufwands, der hohen erreichbaren Präzision und der Stabilität sowie ausgezeichneten Reproduzierbarkeit der Analysenfunktion als Schiedsverfahren prädestiniert. Nicht nur in unserem Arbeitskreis, sondern auch in internationalen Gremien der Standardisierung von Analysenverfahren wie z.B. der International Standards Organization (ISO) ist man bemüht, für alle zu bearbeitenden Analysenprobleme eine Methode mit möglichst geringem apparativem Aufwand und hoher Präzision sowie guter Richtigkeit mitzustandardisieren. Meist handelt es sich dabei um sogenannte klassische Analysenverfahren, zu denen ja auch die LAS zu zählen ist. In der analytischen Routine werden dagegen heute meist Schnellverfahren, womöglich der simultanen Multielementanalyse mit hohem instrumentellem Aufwand und eventuell auch geringerer Reproduzierbarkeit vorgezogen. So stellt auch die LAS-Bestimmung von Eisenspuren in Wolfram mittels α,α'-Dipyridyl eine Methode mit im Vergleich zu den anderen hier standardisierten Verfahren bester Reproduzierbarkeit, jedoch mit erheblichem Zeitaufwand dar.

Andere photometrische Eisenbestimmungsverfahren in Wolfram wie die mittels 1,10-Phenanthrolin, Bathophenanthrolin, Thiocyanat, Ferron u.a.[1,12,13] sind dem hier standardisierten Verfahren prinzipiell gleichwertig, jedoch wurden die Querempfindlichkeiten für eine Vielzahl möglicher Störionen am hier beschriebenen System von Osram München am sorgfältigsten untersucht.

2. *Die röntgenfluoreszenzspektrometrische (RFA) Eisenbestimmung nach einer Spuren–Matrix-Trennung mit 1-(2-Pyridylazo)-2-naphthol (PAN)*

RFA-Spurenbestimmungsmethoden haben sich in der Analytik hochschmelzender Metalle sehr bewährt.[14,15] Zur Spurenanalyse bis in den Bereich von 1 ppm ist allerdings eine Abtrennung der für Röntgenstrahlung stark absorbierend wirkenden Wolframmatrix erforderlich. Die Spurenfällung mit PAN ist dabei besonders vorteilhaft. Bei richtig durchgeführter PAN-Fällung entstehen nämlich sehr kompakte, gut manipulierbare Niederschläge, die sich für RFA-Messungen bestens eignen. Dabei wirkt PAN einerseits als Gruppenkomplexierungsmittel für Spuren der Elemente Mangan, Eisen, Kobalt, Nickel, Kupfer und Zink, andererseits fungiert der PAN-Überschuß gleichzeitig als Fällungsmittel zur Erzeugung eines voluminösen und gut filtrierbaren Niederschlags, sodaß sich die Zugabe eines weiteren Spurenfängers erübrigt. Auf diese Weise können Spuren der Elemente Mangan bis Zink gemeinsam erfaßt werden. Diese Methode wird im Metallwerk Plansee routinemäßig angewandt.

3. *Die Eisenbestimmung mittels Atomabsorptionsspektrophotometrie (AAS) in der Graphitrohrküvette ohne Spuren–Matrix-Trennung*

AAS-Methoden in der Graphitrohrküvette gehören heute zu den nachweisstärksten Spurenanalysenmethoden überhaupt. Die Eisenbestimmung mittels AAS gelingt in Wolfram ohne vorherige Spuren–Matrix-Trennung. Diese Methode hat den Vorteil, mit sehr geringen Probemengen bis herab zu 0,1 mg auszukommen und wird von Osram München u.a. zur Überprüfung der Eisenverteilung in Wolframfeindrähten herangezogen. Für Durchschnittsspurenanalysen werden im allgemeinen Probemengen von 50 mg verwendet. Diese Methode stellt damit ein wichtiges Zwischenglied zwischen Durchschnittsspurenanalyse und topochemischer Mikroanalyse mit hohem instrumentellem Aufwand dar.

Die Emissionsspektralanalyse wird von keinem der Laboratorien des AHM-Kreises zur routinemäßigen quantitativen Erfassung von Spuren in hochschmelzenden Metallen angewandt. Die überaus linienreichen Spektren der Refraktärmetalle erlauben eine einigermaßen verläßliche Spurenanalyse nur unter Verwendung höchstauflösender Gitterspektrographen bei Matrixemissionsunterdrückung durch Karbidbildung sowie bei Spurenverflüchtigung mit Hilfe eines Carriers wie Silberchlorid.[2,3] Dadurch bleibt nach unseren Erfahrungen die Reproduzierbarkeit emissionsspektrographischer Verfahren weit hinter der der hier beschriebenen Methoden zurück. Im allgemeinen sind mit der Emissionsspektralanalyse in Wolfram für den Einser- und Zehner-ppm-Bereich lediglich Richtwertverfahren möglich. Als solche sind Verfahren mit einer relativen Standardabweichung von > 25% zu verstehen. Auch erste Versuche der Durchschnittsspurenanalyse mittels Emissionsspektrometrie mit induktiv gekoppeltem Plasma verliefen nicht zufriedenstellend. Hier ist eine Matrixemissionsunterdrückung prinzipiell nicht möglich und dies dürfte der Grund für die schlechte Nachweisempfindlichkeit in der Matrix Wolfram dieses sonst vielversprechenden Verfahrens sein.

Aktivierungsanalytische Analysenverfahren zur Spurenanalyse in Wolfram sind zwar bekannt,[1,16] jedoch macht die starke Matrixaktivierung eine Spuren–Matrix-Trennung vor der Gammaaktivitätsmessung erforderlich. Dies wiederum bedingt einen beträchtlichen apparativen Aufwand aufgrund der relativ hohen Strahlendosis neutronenaktivierten Wolframs. Als Routinemethoden scheiden aktivierungsanalytische Verfahren schon meist wegen der

Entfernung der Produktionsstätten zum nächsten Reaktor und aufgrund des hohen apparativen und personellen Aufwands aus.

Auch die Funkenmassenspektrometrie dürfte infolge des enormen apparativen Aufwands und derzeit auch noch wegen des Fehlens von Eichfaktoren für die meisten Refraktärmetalle in nächster Zeit kein spurenanalytisches Betriebsverfahren werden. Problematisch ist hier das extrem kleine, erfaßbare Probenvolumen, welches aufgrund häufiger Mikroinhomogenität der Spurenverteilung eine verläßliche Durchschnittsspurenanalyse erschwert.

Rasteraugerelektronenspektroskopie, dynamische Sekundärionenmassenspektrometrie, Rasterelektronenmikroskopie mit energie- und/oder wellenlängendispersivem Analysatorzusatz stellen heute faszinierende Möglichkeiten zur topochemischen Mikro- und teilweise auch Spurenanalyse dar. Alle diese Verfahren eignen sich jedoch nicht—einige zumindest derzeit noch nicht—zur verläßlichen quantitativen Durchschnittsspurenanalyse. Auch für diese Geräte bedingt ihr enormer Preis und der hohe personelle Aufwand, daß ihre industrielle Anwendung zunächst auf die Zusammenarbeit mit entsprechenden Forschungs- und Hochschulinstituten beschränkt bleibt. Immerhin wurden auf diese Weise bereits überaus interessante Ergebnisse auf dem Gebiet der topochemischen Mikroanalyse für Molybdän und Wolfram erzielt.[17–19]

VERGLEICH DES ABLAUFS VON ANALYSENVERFAHREN DURCH IDEOGRAPHISCHE SYMBOLE

Für einen kritischen Vergleich des Ablaufs von Analysenverfahren hat sich die Ablaufdarstellung in Form ideographischer Symbole bestens bewährt. Nur so ist nach unserer Meinung eine schnelle und objektive vergleichende Abschätzung des experimentellen Schwierigkeitsgrades mehrerer zur Auswahl stehender Analysenverfahren möglich. Darüber hinaus erleichtern derartige Ablaufschemata nach den in den Laboratorien des AHM-Kreises gesammelten Erfahrungen die praktische Einarbeitung bei Verwendung eines neuen Verfahrens sehr.

Ideographische Ablaufschemata wurden erstmals von Malissa und Jellinek vorgeschlagen.[20] Diese Symbole wurden nach unseren Erfordernissen modifiziert und ergänzt. Abbildung 1 zeigt die vom AHM-Kreis verwendeten Symbole für Analysengeräte, Analysenoperationen und Endbestimmungsverfahren. In Abb. 2 sind die Ablaufschemata der drei hier beschriebenen Analysenverfahren zur Erfassung von Eisenspuren in Wolfram vergleichend dargestellt.

ARBEITSVORSCHRIFTEN UND MERKMALMATRIZES FÜR DIE DREI STANDARDISIERTEN VERFAHREN ZUR EISENSPURENBESTIMMUNG IN WOLFRAM

Nachfolgend beschriebene Analysenverfahren wurden in jeweils 24 Testuntersuchungen für einen

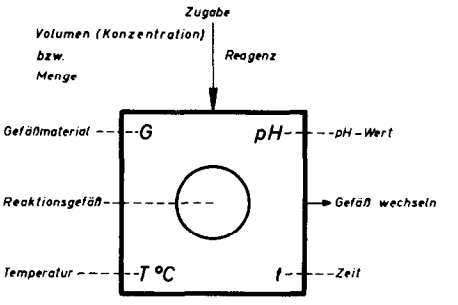

Abb. 1*a*. Erläuterung der in Ablaufplänen verwendeten Symbole. Die einzelnen Analysenschritte werden in Form von Quadratflächen symbolisiert. Das Schema der näheren Angaben für diese Schritte ist hier dargestellt. Vorgänge, die in demselben Gefäß unmittelbar hintereinander stattfinden, werden durch aneinandergrenzende Quadratflächen symbolisiert. Abkürzungen der verwendeten Gefäßmaterialien: Pt = Platin; PÄ = Polyäthylen; PP = Polypropylen; T = Teflon; keine diesbezügliche Angabe: Glasgefäß. Sämtliche Volumen sind in ml angegeben, alle Mengen in mg. Tr = Tropfen.

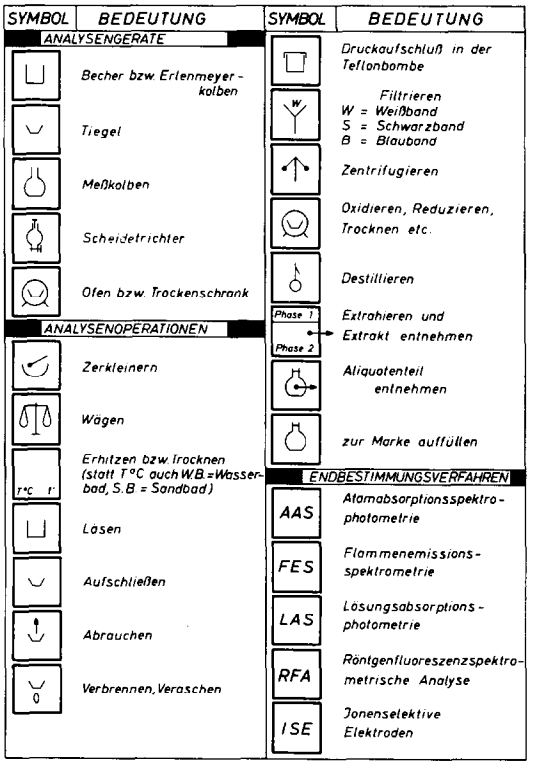

Abb. 1*b*. Erläuterungen der in Ablaufplänen verwendeten Symbole. Darstellung der Symbole für Analysengeräte, Analysenoperationen und Endbestimmungsverfahren.

Zehnerpotenz-Arbeitsbereich standardisiert.[7] In den Tabellen 1 bis 3 sind die einzelnen Verfahren nach einem einheitlichen Schema, welches ebenfalls vom AHM-Kreis erarbeitet wurde, detailliert beschrieben. In Tabelle 4 sind die Verfahrenskenndaten aller drei Verfahren einander gegenübergestellt. Größen, Sym-

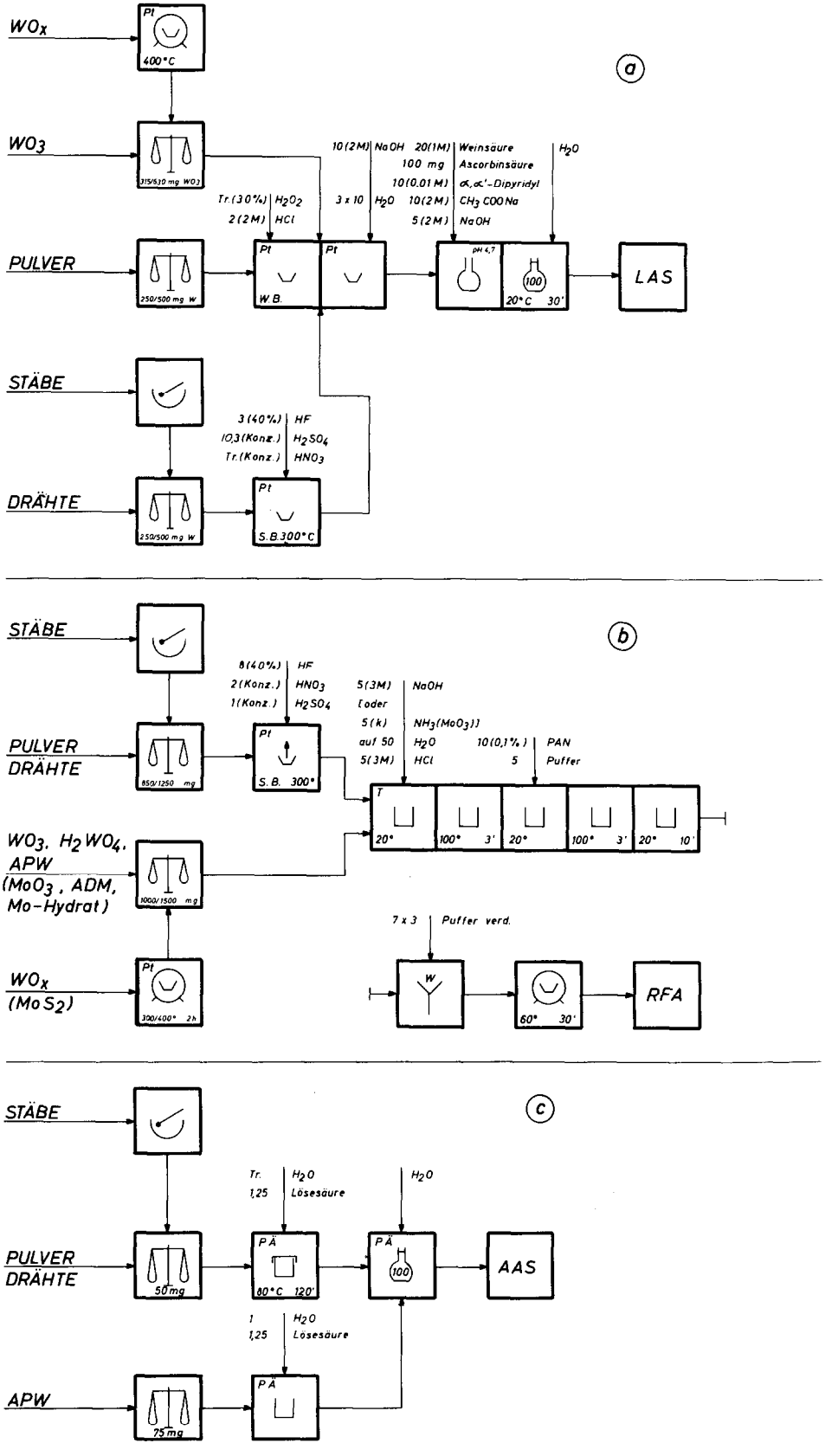

Abb. 2. Vergleich des Analysenablaufs für die drei standardisierten Verfahren der Eisenspurenbestimmung in Wolfram. (*a*) LAS-Verfahren, (*b*) RFA-Verfahren, (*c*) AAS-Verfahren.

Tabelle 1. Arbeitsvorschrift zur LAS-Bestimmung von Eisenspuren in Wolfram:

1. VERFAHRENSPARAMETER

Meßkolbenvolumen:	100,0 ml
Meßwellenlänge:	546 nm (Hg); Minimum 420 nm, Maximum 520 nm, steiler Abfall ab 530 nm
Schichtdicke:	4,00 cm
Meßgerät:	Eppendorf-Linienspektralphotometer, Photozelle 90B und Filter 546 nm (Hg)

2. ARBEITSVORAUSSETZUNGEN

Arbeitsgeräte:	Quarzkasserolle (*ca.* 50 ml); Pt-Tiegel (hohe Form); eventuell Pt-Schale. Eichfähige Vollpipetten (5, 10, 20 ml); 100 ml Meßkolben (eichfähig, gepreßtes Stopfenbett, Kunststoffstopfen!).	
		Reinheitsgrad entsprechend Merck-Nr.:
Reagenzien:	H_2O_2, 30%, z.A.	7209
	HF, min. 40%, suprapur	335
	HNO_3, min. 65%, suprapur	441
	H_2SO_4, min. 96%, suprapur	714
	NaOH, 2*M*, Ansatz aus NaOH suprapur	5589
	HCl, 2*M*, Ansatz aus HCl, min. 30%, suprapur	318
	Weinsäure, 1*M*: 150 g $C_4H_6O_6$ z.A. mit H_2O auf 1000 ml	804
	Natriumacetat, 2*M*: 164 g CH_3COONa z.A. mit H_2O auf 1000 ml	6268
	Ascorbinsäure, z.A.	127
	Farbreagenz:	
	0,01*M* α,α'-Dipyridyl, z.A.	3098
	(farblos!): 1,56 g Dipyridyl z.A. in 1000 ml Meßkolben mit 700 ml H_2O versetzen; bis zur vollständigen Auflösung schütteln. Mit H_2O auf 1000 ml auffüllen. Aufbewahrung in Plastikflaschen.	

3. DURCHFÜHRUNG

Vorbehandlung:

PULVER:

Probe (250 bzw. 500 ± 5 mg W) in Quarzkasserolle durch tropfenweisen Zusatz von 30% igem H_2O_2 lösen. Zusatz von 2 ml 2*M* HCl. Auf Wasserbad bis zur Trockene eindampfen. Rückstand in 10,0 ml 2*M* NaOH klar lösen.

STÄBE, DRÄHTE:

In Hartmetallmörser zerkleinern. Probe (250 bzw. 500 ± 5 mg W) in Pt-Tiegel mit 3 ml konz. HF und 0,3 ml konz. H_2SO_4 versetzen und durch tropfenweise Zugabe von konz. HNO_3 lösen. Eindampfen zur Trockene und auf Sand- bzw. Luftbad abrauchen. Rückstand in 5,0 ml 2*M* NaOH lösen.

OXIDE, WO_x:

Bei $x < 3$ (blaue, braune, schwarze Pulver) vor der Einwaage ausreichende Probemenge in Pt-Tiegel oder Pt-Schale im Muffelofen (400°C, unter Sauerstoff-Strom) zu gelbem Oxid oxidieren. Probe (315 ± 5 mg WO_3 bzw. 630 ± 5 mg WO_3) in 10,0 ml 2*M* NaOH lösen.

AMMONIUMPARAWOLFRAMAT:

Vor der Einwaage ausreichende Probemenge in Pt-Schale zu WO_3 verglühen (Bunsenbrenner) und weiterbehandeln wie Oxide.

Arbeitstechnik:

Die vorbehandelte Probelösung mit 3mal 10 ml H_2O in 100 ml Meßkolben überführen.
+20,0 ml 1*M* Weinsäure, umschwenken, bis Lösung klar ist
+Spatelspitze Ascorbinsäure (*ca.* 100 mg)
+10,0 ml 0,01*M* α,α'-Dipyridyl, gut durchmischen
+10,0 ml 2*M* CH_3COONa
+5,0 ml 2*M* NaOH, gut durchmischen
Kontrolle pH = 4,7 ± 0,2; Lösung auf 20 ± 0,2°C temperieren; mit Wasser zur 100 ml Marke auffüllen und gut durchmischen.
Zur Bestimmung des Blindwertes: Aufschlußlösungen eindampfen, 10,0 ml 2*M* NaOH zugeben und weiterbehandeln entsprechend obiger Arbeitstechnik.
Bei Serienbestimmungen reichen im allgemeinen jeweils 2 Leerwerte vor und nach der Serie aus, die zu $\bar{E}_B$ gemittelt werden. Bedingung hiefür ist $\bar{E}_B \leq 0{,}03$.

Messung:

Innerhalb von 10–30 min. E_x bzw. E_B bei 20 ± 0,2°C in gleicher Küvette d = 4,00 cm bei λ = 546 nm (Hg) gegen Nullstandard Wasser messen. Man bildet: $E = E_x - \bar{E}_B$

Auswertung:

ppm Fe = $256{,}1 \times 10^3 \times E/m_P$
m_P = Einwaage in mg W,
m'_P = Einwaage in mg WO_3 ($m_P = 0{,}7929 \times m'_P$)

Tabelle 1. *(fortführung)*

4. STÖRUNGEN
Bei Blindwerten $\bar{E}_B > 0{,}03$ sind die Bestimmungen mit sauberen Reagenzien oder einwandfreien Arbeitsgeräten zu wiederholen. Trübe Lösungen und solche mit Tyndalleffekten sind zu verwerfen. Merkliche Störungen zu erwarten bei $m_P = 250$ mg W für Ni > 0,48; Cr > 2,08; Co > 0,76%.

Tabelle 2. Arbeitsvorschrift zur RFA-Bestimmung von Eisenspuren in Wolfram

1. VERFAHRENSPARAMETER	
Meßgerät:	Röntgenfluoreszenzspektrometer Philips PW 1220/C (Sequenzspektrometer)
Meßparameter:	Messung der rotierenden Probe unter Vakuum; Bedeckung mit Goldstempel; Meßzeit 20 s; Küvettenfenster: 6 µm Mylarfolie; Goldröhre, Anregung: 60 kV, 40 mA; Zähler: Proportional- und Szintillationszähler in Serie; Kollimator: fein (160 µm Lamellenabstand); Messung der Fe$K_{\alpha 1,2}$-Linie in 1. Ordnung mit LiF (200)-Kristall; automatische Impulshöhendiskriminierung durch Kristallabschwächer für LiF (200) und mit festem Fenster.

2. ARBEITSVORAUSSETZUNGEN		
Arbeitsgeräte:	Muffel bzw. Simon-Müller-Ofen Pt-Tiegel (hohe Form) Teflonbecher (200 ml) Filternutsche (z.B. Glasfiltrationsgerät SM 163 06–25 mm ϕ von Heraeus) Mikropipettiersystem 100, 200, 500 µl	
		Reinheitsgrad entsprechend Merck-Nr
Reagenzien:	HF, min. 40%, suprapur	335
	HNO_3, min. 65%, suprapur	441
	H_2SO_4, min. 96%, suprapur	714
	HCl, 3*M*, Ansatz aus HCl, min. 30%, suprapur	318
	NaOH 3*M*, Ansatz aus NaOH, min. 30%, suprapur	5589
	PAN-Lösung in Äthanol, 0,1% Ansatz aus 1-(2-Pyridylazo)-2-naphthol und Äthanol	7531 972
	NH_3-NH_4Cl-Puffer, pH 10: 70 g NH_4Cl werden in *ca.* 300 ml Wasser gelöst, 570 ml konz. NH_3 werden zugegeben. Dann wird auf 1000 ml aufgefüllt. Ansatz aus:	
	Ammoniaklösung, min. 25%, suprapur	5428
	Ammoniumchlorid, suprapur	1143
	NH_3–NH_4Cl-Puffer, pH 10, wie oben, jedoch 1:10 verdünnt Eisen, durch Reduktion hergestellt, z.A.	3819
Spezielle Vorbereitung:	Herstellung von Bezugstandards: Diese enthalten 10 µg Mn, je 20 µg Co, Ni, Cu, Zn; 50 µg Fe. Die Standards werden etwa einmal monatlich fünffach hergestellt. Die drei am besten mit den Mittelwerten aller sechs Metalle übereinstimmenden Präparate werden als Bezugsstandards verwendet. Zur Herstellung von Bezugsstandards wird von 1*M* salzsauren Stammlösungen ausgegangen, die jeweils 100 mg/l der einzelnen Elemente Mn bis Zn enthalten. Halbjährliche Neuherstellung ist ausreichend. Von diesen Stammlösungen werden für die Standardherstellung 100 µl (Mn), je 200 µl (Co, Ni, Cu, Zn) bzw. 500 µl (Fe) pipettiert und mit etwa 50 ml Wasser versetzt. Dann werden 5 ml Pufferlösung zugesetzt und es wird weiter wie unter PAN-Fällung angegeben verfahren.	

3. DURCHFÜHRUNG	
Vorbehandlung:	METALLPULVER, DRÄHTE: 1000 mg in Pt-Tiegel mit 8 ml 40% HF und 1 ml konz. H_2SO_4 versetzen. Durch tropfenweise Zugabe von 2 ml konz. HNO_3 lösen. Vorsichtig erwärmen bis alles gelöst ist, dann auf Sandbad zur Trockene eindampfen. KOMPAKTE STÜCKE: Mit Trennscheibe schneiden. Wolfram zwischen Mo-Platten zerschlagen. Metallproben 1 min. mit HF–HNO_3 (10:1) abbeizen, mit Wasser und dann mit Äthanol p.a. waschen und trocknen. Weiterbehandlung wie Metallpulver.

Tabelle 2. *(fortführung)*

	OXIDE, OXIDHYDRATE, AMMONIUMWOLFRAMATE (AUCH AMMONIUMMOLYBDATE):
	Ohne Vorbehandlung einwiegen.
	$WO_x (x < 3)$, (MoS_2): Vor der Einwaage ausreichende Probemenge im Pt-Tiegel bei 300–400°C zu VI-wertigem Oxid oxidieren (2 Stunden).
	$(MoO_2$: Probe in Pt-Tiegel dreimal mit 5 ml konz. HNO_3 versetzen, zunächst vorsichtig, dann stärker erhitzen. Knollen ev. mit Glasstab zerdrücken. Dann 2 Stunden bei 400°C belassen.)
Arbeitstechnik:	PAN-Fällung: Probe in 5 ml 3*M* NaOH lösen (bei Molybdän in 5 ml konz. NH_3; Teflonbecher). Gegebenenfalls etwas erhitzen bis zur klaren Lösung. Wasser auf *ca.* 50 ml sowie 5 ml 3*M* HCl zugeben. 3 min. aufkochen, abkühlen, 10 ml 0,1%ige PAN-Lösung sowie 5 ml NH_3–NH_4Cl Puffer zugeben und nochmals 3 min. aufkochen. Abkühlen lassen, Niederschlag in Filternutsche auf Weißbandfilter abfiltrieren und mit 7mal 3 ml verdünnter Pufferlösung waschen. Filterscheibchen mit PAN-Niederschlägen bei 60°C *ca.* 1/2 Std. trocknen.
Messung:	Messung mit den unter 1. angegebenen Parametern, vollautomatisch nach einer modifizierten X-ray 10 Methode[15] (Vakuumverzögerung 40 sec).
Auswertung:	Die gemessenen Impulsraten sind jeweils auf den Mittelwert von mindestens 3 mitgemessenen, repräsentativen Standard- bzw. Blindwertproben zu beziehen. Bei manueller Messung erfolgt die Berechnung nach: $$\text{ppm Fe} = \frac{\text{Impulsr. Pr.} - \text{Mittelw. Blindpr.}}{\text{Mittelw. Standardpr.} - \text{Mittelw. Blindpr.}} \cdot \frac{\text{ppm Standard}}{m_P}$$ m_P = Probemenge für W in g $m'_P = 0{,}682 \times m_P$ für APW $= 0{,}793 \times m_P$ für WO_3

4. STÖRUNGEN

Ausreißer werden meist durch heterogene Verunreinigungen im Probengut (vor allem in Rohstoffen) verursacht.[8] In solchen Fällen ist eine Rückstandsanalyse nach WO_3-Auflösung in NaOH aufschlußreich (Einwaagen über 10 g).
Die Impulsraten der jeweils mitgemessenen Blind-und Standardproben werden aufgelistet. Dies erleichtert die Fehlersuche bei krassen Abweichungen durch Kontamination oder instrumentelle Schwierigkeiten. Bei Metallmengen über 500 µg im PAN-Niederschlag treten Abweichungen von der Eichgeraden ein.

Tabelle 3. Arbeitsvorschrift zur AAS-Bestimmung (flammenlos) von Eisenspuren in Wolfram

1. VERFAHRENSPARAMETER

Meßkolbenvolumen:	100 ml		
Einspritzvolumen:	25 µl		
Meßgerät:	Beckman Atomabsorptionsspektrometer Modell 495 mit Massmann-Küvette, Power Supply Beckman GRM 1268 und 10-in. Recorder.		
Meßparameter:	Messung an der Eisenresonanzlinie bei 248,3 nm mit Einzelelement-Hohlkathodenlampe für Eisen, Lampenstromstärke 30 mA; spektrale Bandbreite 0,20 nm; Photomultiplier: 620 V; Einstellzeit: Resp. Time 2; Spreizung für E_R = 0,55; Span 50,0; Unterdrückung für E_B = <0,10: Suppr. 0,0; Schreiber: 100 mV; 1,0 in./min.		
	Massmann-Küvette		
	Gasspülung:	Argon 1,0 kg/cm²	
	Trocknung:	Stufe 2 25 sec	(100°C)
	Veraschung:	Stufe 2/10 18 sec	(700°C)
	Atomisierung:	Stufe 3/10 9 sec	(3080°C)
	Ausheizung:	Stufe 3 6 sec	(>3300°C)

Tabelle 3. *(fortführung)*

2. ARBEITSVORAUSSETZUNGEN

Arbeitsgeräte:

Hartmetallmörser
Polyäthylenmeßpipetten 10 ml
Polyäthylenmeßkolben 100 ml
Sieb, 200 mesh
Polyäthylenbecher, 5 ml
Trockenschrank

Reagenzien:

	Reinheitsgrad entsprechend Merck-Nr.:
Flußsäure, 40%, suprapur	335
Salpetersäure, 65%, suprapur	441
Fe-Stammlösung: 1,000 g Fe/1000 ml (Titrisol)	9972
Wolframpulver (Fe-freies Material, Fe < 5 ppm)	

Spez. Lösungen:

LÖSUNGSSÄURE, hergestellt aus: 400 ml Flußsäure, 40%, 530 ml H_2O; 70 ml Salpetersäure, 65%. 0,00001 *M* EISEN-STANDARD-LÖSUNG (0,56 μg Fe/ml):
Die Fe-Stammlösung wird verdünnt wie folgt: 5,0 ml Fe-Titrisollösung werden in einen 500-ml Meßkolben pipettiert und mit Wasser zur Marke aufgefüllt ($\hat{=}$ Verd. 1:100 oder 10 μg Fe/ml). Hiervon werden 5,6 ml in einen 100 ml Meßkolben pipettiert und mit Wasser aufgefüllt ($\hat{=}$ 0,56 μg Fe/ml).

LEERWERT-NORMIERUNGS-LÖSUNG

Wolfram-Standard (50 mg W-Pulver) lösen entsprechend Probenvorbehandlung bzw. weiterbehandeln entsprechend Arbeitstechnik.

REFERENZ-NORMIERUNGS-LÖSUNG

Wolfram-Standard (50 mg W-Pulver) lösen entsprechend Probenvorbehandlung, 10,0 ml Eisen Standard-Lösung zufügen und weiterbehandeln entsprechend Arbeitstechnik.

3. DURCHFÜHRUNG

Vorbehandlung:

PULVER, DRÄHTE:
Probe (m_P = 50 mg) im 5 ml PÄ-Becher (mit Deckel) mit einigen Tropfen H_2O anfeuchten und mit 1,25 ml Lösungssäure versetzen. Die zunächst meist einsetzende heftige Reaktion abwarten. Löst sich die Probe bei Raumtemperatur nicht, dann 1–2 h bei 80°C (z.B. Wasserbad) unter gelegentlichem Umschwenken behandeln.

STÄBE:

Im Hartmetallmörser zerschlagen, sieben, Fraktion größer, 0,15 mm ϕ nochmals zerkleinern, dann wie Pulver behandeln.

AMMONIUMPARAWOLFRAMAT:

Probe (m'_P = 75 mg) in Meßkolben einwiegen, mit *ca.* 1 ml H_2O aufschlämmen und durch Zugabe von 1,25 ml Lösungssäure auflösen. Erwärmen ist im allgemeinen nicht erforderlich.

Arbeitstechnik:

Die saure Probelösung in 100-ml PÄ-Meßkolben überspülen und mit Wasser von 20 ± 0,2°C zur Marke auffüllen.

Anmerkung:
Trübe oder opaleszierende Lösungen ergeben Unterbefunde und sind zu verwerfen.

Messung:

1.—Einstellung der Signal- und Arbeitsparameter entsprechend Geräteeinstellung.
—Je Analyse werden mindestens 2 Probelösungen angesetzt. Mit jeder Probelösung werden 2 Meßreihen mit je E_R, E_B und E_x durchgeführt.

2. Referenzlösung:
—Einstellung von E_R auf 0,50 bis 0,60 (mit Knopf Span justieren) durch Einspritzen von jeweils 25 μl Referenz-Normierungs-Lösung.
—Einspritzen von 25 μl Referenzlösung:
Messung von E_R

3. Leerwertlösung:
Einspritzen von 25 μl Leerwert-Normierungs-Lösung: Messung von E_B. Sofern $E_B \geq 0{,}10$, Untersuchung abbrechen und mit neu angesetzten Referenz- bzw. Leerwert-Normierungs-Lösungen wiederholen.

4. Probelösung:
Einspritzen von 25 μl Probelösung:
Messung von E_x
Die Werte E_R, E_B, E_x werden als Peakhöhen vom Schreiberbild abgelesen.

Tabelle 3. *(fortführung)*

Auswertung:	Man bildet aus den Werten einer Meßreihe (E_R, E_B, E_x) den Informationswert $I = (E_x - E_B)/(E_R - E_B)$, anschließend $\bar{I}$ für die 2 Probelösungen. Der Gehalt, stets auf W bezogen, ergibt sich zu: ppm Fe = $5{,}58 \times 10^3 \times \bar{I}/m_P$ m_P = Probemenge W in mg m'_P = $0{,}682 \times m_P$ (gilt für Ammoniumparawolframat)

4. STÖRUNGEN

Keine Störungen bis 500 ppm für folgende Elemente: K, Al, Ca. Bei Gehalt > 500 ppm können geringfügige Unterbefunde auftreten.[21]

Tabelle 4. Vergleichende Übersicht der Merkmalsmatrizes für die standardisierten Verfahren der Eisenspurenbestimmung in Wolfram

Fe	LAS	RFA	AAS
1. Anwendungsbereiche			
Arbeitsbereiche	1000 bis 100 nmole 56 bis 6 µg	1700 bis 170 nmole 100 bis 10 µg	100 bis 10 nmole 5,6 bis 0,6 µg
Probemengen	große Gehalte: 250 ± 5 mg W kleine Gehalte: 500 ± 5 mg W	1000 mg ± 10 mg W	50 mg ± 0,5 mg W
Gehaltsbereiche	225 bis 22,4 ppm bzw. 112 bis 11,2 ppm	100 bis 10 ppm	112 bis 11,2 ppm
2. Verfahrens-Kenndaten			
Standardabweichung	16 nmole ≙ 0,86 µg ≙ 1,5 ppm bzw. 32 nmole ≙ 1,72 µg ≙ 3 ppm	26,5 nmole ≙ 1,56 µg ≙ 1,56 ppm	1,5 nmole ≙ 0,08 µg ≙ 1,5 ppm
Variationskoeffizient	1,5–15%	1,6–16%	1,5–15%
Bestimmungsgrenze	64 nmole ≙ 3,4 µg ≙ 6,0 ppm	122,2 nmole ≙ 7,2 µg ≙ 7,2 ppm	6,0 nmole ≙ 0,3 µg ≙ 6,0 ppm
Empfindlichkeit	$= 5{,}45 \pm 0{,}06$ cm²/µmole	88 Ips/µg	0,035 E/ng
Leerwerte	$E_B \leq 0{,}03$	$I_0 \leq 1100$ Ips	$E_B \leq 0{,}10$
Zeitbedarf			
f. Einzelbestimmung	1,5 h	1 h	2 h
f. Zehnerserie	4 h	4 h (bei Mitmessung von Mn, Co, Ni, Cu, Zn)	8 h

bole und Darstellungsarten entsprechen nationalen und internationalen Normen (DIN, ISO).

DISKUSSION DER STANDARDISIERTEN ANALYSENVERFAHREN

Vergleicht man die verschiedenen Kenndaten der Merkmalsmatrizes in Tabelle 4 für die drei Eisenspurenbestimmungsverfahren in Wolfram, so läßt sich folgendes feststellen.

Arbeitsbereiche; Gehaltsbereiche; Verfahrensstandardabweichungen; Bestimmungsgrenzen

Trotz durchaus verschiedener Arbeitsbereiche sind die Gehaltsbereiche für die drei Verfahren vergleichbar. Die Bestimmungsgrenzen liegen zunächst überraschend einheitlich bei 6–7 ppm Eisen und die Verfahrensstandardabweichungen bei 1,5 ppm. Dies weist darauf hin, daß für Eisenspuren die Umwelt- und Reagenzienkontamination den limitierenden und die Nachweisgrenze bestimmenden Faktor darstellt.

Sowohl für das RFA-Verfahren, als auch für das AAS-Verfahren könnte man von der Nachweisstärke der Verfahren her Bestimmungsgrenzen erwarten, die etwa eine Zehnerpotenz niedriger liegen. Die sich aus der Zählstatistik für das RFA-Verfahren ergebende Nachweisgrenze liegt bei 1,1 ppm Eisen. Dabei verändert sich sowohl die Untergrundzählrate, als auch die Empfindlichkeit mit zunehmendem Alter der verwendeten Röntgenfluoreszenzanlage durch Anodenaufrauhung, Kristallalterung, Zähldrahtverschmutzung des Proportionalzählers und für Eisen wohl auch durch steigende Apparatekontamination mit Eisen. Zu einem früheren Zeitpunkt wurde eine Empfindlichkeit von 120 Impulsen. sec^{-1}. μg^{-1} bei einem Untergrund von 725 Impulsen/sec bei gleichen Apparateeinstellungen gemessen.[15] Daraus ergab sich eine zählstatistische Nachweisgrenze von 0,7 ppm Eisen. Auch für das AAS-Verfahren ergibt sich mit einer Bestimmungsgrenze von 6 ppm unter den gegebenen Bedingungen ein Wert von 75 pg absolut, der eine gute Zehnerpotenz über den üblichen erreichbaren

Nachweisgrenzen für Eisen in reinen Lösungen liegt. Letztere werden meist mit etwa 1–10 pg angegeben.[22] Die hohe bei dem hier standardisierten Verfahren verwendete Matrixverdünnung (50 mg Probe auf 100 ml) macht einen massiven Matrixeffekt unwahrscheinlich. Auch Deuteriumkompensation ist dadurch nicht erforderlich. Der Vorteil der AAS-Methode liegt vor allem—wie schon erwähnt—in der geringen erforderlichen Probemenge von 50 mg.

Analysenfunktionen

Diese sind für alle drei Verfahren Gerade, die für die Nettowerte durch Null gehen. Dabei ist nur die Analysenfunktion für die LAS-Methode von allgemeiner Gültigkeit. Sowohl für die RFA, als auch für die AAS ist die Analysenfunktion für jedes Gerät neu zu erstellen, da sie von sehr vielen speziellen Geräteparametern abhängt. Auch kann sie sich für ein und dasselbe Gerät mit der Zeit ändern.

Zeitbedarf und Arbeitsaufwand; Einzel- und Multielementverfahren; Simultanbestimmungsverfahren

Aus Abb. 2 geht hervor, daß der Arbeitsaufwand für die LAS und RFA-Methode vergleichbar sind. Der geringe Arbeitsaufwand der AAS-Methode ist wohl kaum mehr zu überbieten. Der etwas höhere Zeitbedarf der AAS-Methode ist vorwiegend durch die Aufschlußdauer von 2 Stunden bedingt. Ferner fällt hier auch die etwas längere Meß- und Auswertungszeit ins Gewicht.

Die LAS-Methode ist natürlich wie die meisten photometrischen Verfahren eine Einzelbestimmungsmethode, wohingegen sowohl die RFA- als auch die AAS-Methode als Multielementbestimmungsverfahren konzipiert sind.

Mit der PAN–RFA-Methode sind Mangan-, Eisen-, Kobalt-, Nickel-, Kupfer- und Zink-Spuren in einem erfaßbar. Ein weiterer Vorteil dieser Methode ist ihre Anwendbarkeit auch auf Molybdän als Matrixelement. Dies ist auch aus dem entsprechenden Analysenablaufschema der Abb. 2 ersichtlich. Für Molybdän als Matrix wird lediglich zur Auflösung der oxidierten Proben Ammoniak anstelle von Natronlauge verwendet.

Die Endbestimmung erfolgt im Metallwerk Plansee mit dem Philips Sequenzspektrometer PW 1220/C mit angeschlossenem 8-K Computer vollautomatisch mit Hilfe des für die Spurenanalyse eigens modifizierten Software-Paketes "X-ray 10" von Philips.[15] Die Meßdauer beträgt für die Erfassung der Elemente Mangan bis Zink für je 4 Proben etwa 20 min. Bei Verwendung eines Simultanspektrometers kommt man mit 40 sec Meßzeit pro Probe aus. Die Röntgenfluoreszenzspektrometrie bietet demnach prinzipiell die Möglichkeit einer Simultanendbestimmung von bis zu 30 Elementen, während dies für die AAS zumindest derzeit nicht realisierbar ist.

Die hier beschriebene Probenvorbereitung zur AAS-Eisenspurenbestimmung erlaubt die Erfassung von Natrium-, Kalium-, Calcium-, Magnesium-, Chrom-, Mangan-, Kobalt- und Nickel-Spuren aus derselben Probenlösung. Die AAS-Methode ist also wie die RFA-Methode als Multielementverfahren anzusprechen. Die Probenmenge kann für das AAS-Verfahren noch weiter reduziert werden, wenn man auf die Möglichkeit der Bestimmung anderer Spurenkomponenten aus derselben Lösung verzichtet. Bei Osram München wurden durch direkte Auflösung von Probenmengen bis herab zu 0,1 mg in der Spitze einer Mikroliterpipette Eisenspuren bis herab zu 10 ppm in 0,1 mg-Proben erfaßt. Die etwas höhere Bestimmungsgrenze ist bedingt durch die leicht erhöhte Verfahrensstandardabweichung für dieses Mikroverfahren. Über die Möglichkeit der topochemischen Mikroanalyse an Wolfram mittels flammenloser AAS wird demnächst gesondert berichtet werden.

Selbstverständlich ist die Eisenspurenbestimmung in Wolfram auch mittels FAAS (AAS in der Flamme) möglich, sofern man keine Geräte mit Brennerköpfen aus Edelstahl sondern aus Titan zur Analyse verwendet. Dazu werden 1 g Proben unter Zugabe von je 5 ml Flußsäure (40%) und Salpetersäure (65%) gelöst und mit je 10 ml 1*M* Zitronensäure und 0,1*M* Cäsiumchlorid-Lösung versetzt. Dann wird mit Ammoniak auf pH 3,0 gebracht und mit Wasser auf 100 ml aufgefüllt. Auf diese Weise können Ag, Bi, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Sb, Sn und Zn-Spuren in Wolfram aus derselben Probelösung erfaßt werden. Die Bestimmungsgrenze für die Erfassung von Eisenspuren in der Luft–Azetylenflamme (Dreischlitzbrennerkopf, Spalt 0,7 Å) liegt bei 10 ppm bei einer Empfindlichkeit von 0,05 Extinktionseinheiten . ml^{-1} . μg^{-1}. Da dieses Verfahren keine wesentlichen Vorteile gegenüber den hier detailliert beschriebenen RFA- und AAS-Verfahren aufweist, wurde es bislang noch nicht standardisiert.

RINGUNTERSUCHUNG

Schließlich wurde im Rahmen einer Ringuntersuchung die Richtigkeit der standardisierten Verfahren

Tabelle 5. Ringanalysenergebnisse für die Eisenspurenbestimmung in Wolfram

Probe	Osram-München LAS	Osram-München AAS	Radium-W. LAS	H. C. Starck LAS	Metallwerk Plansee LAS	Metallwerk Plansee RFA	Metallwerk Plansee FAAS
P 1	16,0 ±0,7	18,0 ±1,0	17,1 ±0,6	18,3 ±0,8	17,4 ±0,9	16,0 ±0,8	19,2 ±1,7
R 2	88,0 ±1,1	82,0 ±1,3	86,0 ±1,4	87,6 ±1,6	88,5 ±2,3	80,0 ±3,6	86,5 ±3,2

überprüft. Es wurden zwei sorgfältig homogenisierte Wolframpulver analysiert. Die Ergebnisse sind in Tab. 5 zusammengefaßt. Die tabellierten Analysenmittelwerte und zugehörigen Standardabweichungen wurden aus jeweils vier Parallelbestimmungen ermittelt. Die Übereinstimmung der Werte ist zufriedenstellend. Für die Probe P-1 beträgt der Gesamtmittelwert 17,4 ppm, die zugehörige Standardabweichung 1.2 ppm. Für die Probe R-2 liegt der Gesamtmittelwent bei 85,5 ppm, die entsprechende Standardabweichung bei $3{,}2_5$ ppm. Systematische Fehler sind daher bei keinem der angewandten Analysenverfahren feststellbar. Auch die Reproduzierbarkeit liegt für alle Verfahren ähnlich, obwohl man erkennt, daß die LAS die Methode mit der besten Reproduzierbarkeit darstellt. Beschränkte Mengen der hier untersuchten Wolframpulver sind als Standardmaterial für eventuelle weitere Vergleichsuntersuchungen verfügbar. Muster derselben Wolframpulver wurden auch an ein einschlägiges Laboratorium zur emissionsspektralanalytischen Untersuchung auf Eisenpuren verschickt. Da die Ergebnisse sowohl was die Richtigkeit anbelangt als auch in bezug auf die Reproduzierbarkeit nicht entsprachen, wurden sie nicht in Tab. 5 mitaufgenommen.

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Summary—Three methods for the determination of traces of iron in tungsten are compared critically on the basis of characteristic data found by standardization according to a recently published scheme. The methods are: a photometric procedure with α,α'-bipyridyl as colorimetric reagent; an X-ray fluorescence spectroscopic procedure with prior trace–matrix separation with 1-(2-pyridylazo)-2-naphthol as trace-precipitating agent; an atomic-absorption spectrophotometric procedure using a graphite cell without separation of the matrix, which needs only 50 mg of sample. The importance of bulk trace analysis for the chemical characterization of metals in spite of modern possibilities of topochemical trace- and microanalysis is discussed. The reasons for the choice of the methods discussed here are also explained.

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EVALUATION OF A PULSED EIMAC SOURCE FOR ATOMIC-FLUORESCENCE SPECTROMETRY*

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Summary—An EIMAC xenon arc continuum source operated in the pulsed mode has been evaluated for potential use as a source of excitation in atomic-fluorescence spectrometry. The results were compared with those obtained with a similar lamp operated in the continuous-wave mode; little or no improvement was evident from this comparison. The lamp was found to be unstable in the pulsed mode, requiring the use of a rather large residual d.c. current in conjunction with a relatively low amplitude power-pulse in order to sustain the arc. Moreover, the pulsed source yielded a large background signal because of scattering of source-radiation in the flame; the background spectrum (with source "on") contained numerous large peaks due to fluorescence of molecular species in the flame and to irregularities in the spectral distribution of the pulsed lamp output transmitted to the signal detector by scatter.

For the analysis of a multielement mixture by atomic-fluorescence spectrometry, a potentially attractive alternative to the use of conventional line-sources of excitation is the possibility of simultaneous excitation of many elements with a single continuum source. Available continuum sources offer good stability, long useful life and simplicity of operation in comparison to many line sources, particularly the electrodeless discharge lamp. However, numerous studies[1–3] have indicated that an important limitation associated with the application of continuum sources to analytical atomic-fluorescence spectrometry is the low output intensity relative to that of atomic line-sources, especially in the short wavelength region (180–260 nm); as a result, limits of detection for elements with resonance lines in this region are typically one or two orders of magnitude worse than those obtainable with line-sources. Interference from source-light scattered in the flame, although considerably greater when a continuum source is used, because the scatter signal is then dependent on the square of the spectral bandpass of the monochromator, can be minimized by choice of flame and flame conditions and can be compensated for by wavelength scanning in the vicinity of the fluorescence line.[2]

The useful photon flux reaching the atomic vapour from a continuum excitation source can be increased by increasing the input power to the source, by improving the efficiency of light-gathering by the source-optics, and/or by pulsing the source while synchronously gating the signal-detection system. Unfortunately, at present there is only limited room for improvement in signal-to-noise ratio to be obtained by use of sources with higher input powers, because the output stability of many available sources deteriorates rapidly with an increase in operating current. Moreover, lamp-life is generally significantly reduced, and operational difficulties may be encountered. The light-gathering efficiency of the source-optics, often severely limited by the geometry of the lamp itself, seems also to have reached a practical limit for currently available sources with the design of the EIMAC lamp. Therefore, pulsing of an EIMAC continuum source (with synchronous gating of the detector) appears to offer the greatest potential for increasing the usable exciting flux at the atomic vapour.

A probable fringe benefit expected to result from the pulsing of continuum sources is enhanced radiant output in the ultraviolet.[4] Such enhancement would depend upon the ability of a power-pulse to increase significantly the colour temperature of the source during the lifetime of the pulse.

A pulsed flash-tube continuum source for application to atomic-fluorescence spectrometry was evaluated by Johnson *et al.*, but their work was considerably hampered by experimental difficulties. The high-voltage pulses needed to start the xenon-arc flash-tube generated a great deal of radiofrequency interference, and the noise level observed was strongly dependent upon the orientation of the output cables from the pulsed power-supply. Furthermore, the radiative efficiency of the long capillary flash-tube, *i.e.*, the light-gathering efficiency of the optical system, was relatively low. The results indicated that detection limits with the flash-lamp source were approximately an order of magnitude poorer than those obtained with the 150-W EIMAC xenon-arc lamp operated in the continuous-wave mode.

The work described here attempts to circumvent these experimental limitations through operation of an EIMAC continuum source in the pulsed mode

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with the pulse superimposed upon a constant d.c. level. Efficiency of radiative transfer from source to flame is very high with this source, and it can be pulsed without the use of a high-voltage pulse to initiate the discharge if a residual d.c. current is permitted to flow through it between pulses. A stoichiometric argon-separated air/acetylene flame was used for all elements studied, in order to facilitate comparison of results with those of other atomic-fluorescence studies utilizing the EIMAC lamp (operated in the continuous-wave mode) and other excitation sources.[1-3,5,6] Other experimental parameters, such as the monochromator slit-width and the observation height in the flame, were also chosen with this purpose in view.

EXPERIMENTAL

Apparatus (*see Table* 1)

A block diagram of the system used is shown in Fig. 1. Light from a pulsed EIMAC xenon-arc continuum source was focused by a single lens into the centre of an argon-separated air/acetylene flame at a fixed height above the burner top. The diameter of the focused beam at the centre of the flame was approximately 8 mm. The nebulizer, burner, monochromator, detector (with housing), photon-counting system, mirror, light-trap and entrance-optics employed have already been described.[1]

A 300-W EIMAC xenon-arc continuum source enclosed in a fan-cooled housing was used for excitation of atomic fluorescence. The lamp contains a built-in parabolic aluminium-coated reflector which reflects most of the emitted radiation through a 2.5-cm diameter sapphire window. Power supplied to this source consisted of periodic pulses superimposed upon a constant d.c. level. Power-pulses were supplied from a Velonex High Power Pulse Generator with a plug-in output unit (V-1766) designed to deliver up to ± 120 V at high current-levels. A conventional series-controlled, constant-current d.c. power-supply was employed to keep a constant residual d.c. current flowing through the lamp while it was being pulsed.

The outputs of these two power-supplies were wired in parallel as shown in Fig. 1. Switch S1 protects diode D1 from the 15-kV pulse. Switch S2 isolates the d.c. power supply from the pulse-generator and is left open while the lamp is being started. S1 is opened as soon as the lamp is started, and S2 is closed immediately before the pulse-generator is switched on. The purpose of the diodes is to prevent reverse current-surges.

The pulsed output of the high-power pulse-generator was synchronized with the photon-counter data-sampling gate by simultaneously triggering both instruments from a function-generator, which was set to provide a 300-Hz square-wave trigger-signal. A gate-triggering delay-control on the photon-counter permitted the gate to be finely tuned to coincide with the lamp output-pulse. A gate-width or sampling-period of 20 μsec was applied to both scalers of the photon-counter, and the pulse-width of the lamp input-pulses was fixed at approximately 15 μsec. Further reduction in the photon-counter gate-width would have proportionately decreased its dynamic range, already sharply restricted in the pulsed mode (as compared to operation in the continuous-wave mode; refer to Results and Discussion).

Procedure and experimental conditions

The experimental conditions used throughout this study are summarized in Table 2. All components of the experimental system were operated according to the directions given in the manufacturers' manuals, except where otherwise noted. The monochromator slit-width, the observation height in the flame, and the argon–fuel–air ratios for the flame were established initially at values intended to represent a signal-to-noise compromise for all the elements, and were held constant throughout the study.

The chemicals used in the preparation of stock solutions were all reagent grade. All standard solutions employed in this work were obtained by serial dilution of the stock solutions.

The analytical calibration-curve data presented in this work are based on ten 10-sec measurements while the precision data (relative standard deviations) are based on ten 1-sec measurements (use of ten 10-sec measurements improved the precision by a factor of $\sim 1/\sqrt{10}$).

The detection-limits were obtained from the ten 1-sec measurements and converted into the limits corresponding

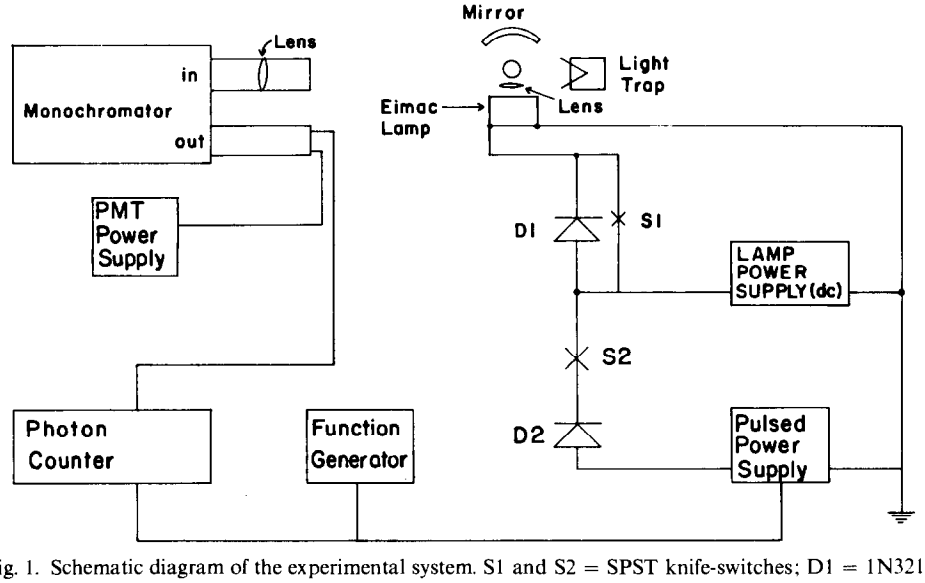

Fig. 1. Schematic diagram of the experimental system. S1 and S2 = SPST knife-switches; D1 = 1N3212 (with heat sink); D2 = 1N4722.

Table 1. Experimental components and manufacturers

Item	Type	Source
Monochromator	218	GCA/McPherson, Acton, MA 01720
Photomultiplier	EMI 6256S	Gencom Div., Plainview, NY 11803
Photomultiplier housing	1151	SSR Instruments Santa Monica, CA 90404 (now Princeton Applied Research, Princeton, NJ 08540)
Amplifier/discriminator	1120	SSR Instruments Santa Monica, CA 90404
Digital synchronous computer	1110	SSR Instruments Santa Monica, CA 90404
Nebulizer	303–0110	Perkin-Elmer Norwalk, CT 06852
Capillary burner	—	Laboratory constructed[7]
Xenon-arc lamp	VIX 300 UV	EIMAC, Div. of Varian, San Carlos, CA 94070
Lamp power-supply (d.c.)	PI50S-71	EIMAC, Div. of Varian, San Carlos, CA 94070
Pulsed power-supply	350	Velonex, Div. of Pulse Engineering, Inc., Santa Clara, CA 95050
Function generator	110	Wavetek, Inc., San Diego, CA 92123

Table 2. Experimental conditions for atomic-fluorescence studies

Monochromator	0.3 m, Czerny-Turner, $f/5.3$, 600 mm^{-1} grating blazed at 300 nm
slit-width	75 μm
slit-height	1 cm
band-pass	0.4 nm
Lamp-current	6.5 A
Pulsed power-supply	
amplitude setting	$\sim\frac{1}{2}$ full-scale
pulse-width	$\sim$15 μsec
repetition rate	300 Hz
Flame conditions	
Air	9.7 l./min
C_2H_2	1.3 l./min
Ar	10 l./min
Observation height in flame, 2.5 cm above burner top	
Photomultiplier voltage, 1115 V	
Photon-counter gate-width, 20 μsec	

to 10-sec counting times; these values were obtained with solutions with concentrations about 100 times the detection limit for each element, and were estimated by extrapolation to a signal equal to twice the noise of the blank signal.

RESULTS AND DISCUSSION

In Table 3, atomic-fluorescence detection-limits are given for 16 elements, along with values for comparison purposes obtained in a previous study[2] with a 500-W EIMAC continuum source employed in the continuous-wave mode. When a photon-counting detection-system is used and the major noise is shot-noise, the root-mean-square background noise (source-induced scatter and fluorescence of flame-gas species and flame-emission) can be estimated with sufficient accuracy by taking the square root of the background signal obtained when distilled water is aspirated into the flame. (The background shot-noise must exceed ξ times the background, where ξ is the "back-

Table 3. Limits of detection obtained for several elements in the argon-separated air/acetylene flame by atomic-fluorescence spectrometry with a pulsed continuum source

Element	Wavelength, *nm*	Detection limit, *μg/ml*	
		Pulsed continuum source (this work)	500-W continuum source*[2]
Se	196.0	1	—
Zn	213.9	0.009	0.015
Cd	228.8	0.0014	0.006
Ni	232.0	0.02	0.025
Co	240.7	—†	0.015
Fe	248.3	—†	0.01
Au	267.5	0.2	0.15
Mn	279.5	0.003	0.002
Mg	285.2	0.0004	0.0001
Sn	303.4	1	0.5
Cu	324.7	0.004	0.0015
Ag	328.1	0.003	0.001
Pd	340.1	0.03	0.1
Cr	357.9	0.004	0.0015
Tl	377.6	0.01	0.006
Pb	405.8	0.03	0.05
In	451.1	0.01	0.025
Sr	460.7	0.003	0.0009

* Values for comparison purposes from Table 4, Reference 2. Experimental conditions are identical for each element.

† Noise due to background fluorescence resulted in analytically useless detection limits.

Table 4. Precision of analytical determinations of several elements by atomic-fluorescence spectrometry with a pulsed continuum source

Element*	Average background signal *cps*	Relative standard deviation of background %	Relative standard deviation of analyte fluorescence signal %
Se	42	17.7	17.1
Zn	195	18.4	2.3
Cd	1233	3.7	7.2
Ni	626	6.4	7.9
Au	1126	5.0	2.8
Mn	465	6.0	1.9
Mg	1014	4.4	1.8
Sn	322	10.9	1.6
Cu	1294	3.4	2.1
Ag	1124	6.7	2.2
Pd	418	7.5	4.0
Cr	335	11.9	5.9
Tl	442	7.3	4.6
Pb	358	7.6	2.2
In	383	7.5	2.2
Sr	528	7.5	3.0

* Wavelengths of lines used are listed in Table 3. Analyte concentrations were ~100 times the detection limit for each element.

ground" flicker-factor. Thus if the "background" flicker-factor is ~0.003, typical for the EIMAC induced-scatter background, the total noise is predominantly "background" shot-noise as long as the background count is below $\sim 3 \times 10^4$ counts.) The analytical calibration-curves shown in Fig. 2 and the relative standard deviations listed in Table 4 lend support to the general validity of this estimate.

The analytical calibration-curves in Fig. 2 reflect an important instrumental limitation associated with the utilization of a photon-counter with a small duty-factor. Since the maximum usable count-rate is eventually limited by the pulse-pair resolution of the photon-counter, a restriction is imposed upon the total number of counts that can be recorded in a given measurement (time) interval without incurring an intolerably large counting error due to pulse overlap. If the actual photon-counting system "on" time is very much smaller than the measurement interval (*i.e.* small duty-factor), the restriction above is proportionately more stringent. The duty-factor for our system, as operated by us, was 0.006 (that is, 20 μsec times 300 gate-intervals per second), and the instrumental pulse-pair resolution was 12 nsec. From these parameters, the practical upper limit on the total number of counts per 10-sec measurement was estimated to be 10^5 counts. Therefore, none of the analytical calibration curves in Fig. 2 was extended beyond this level, even though the linearity limit due to self-absorption was not reached for any of the elements, except possibly zinc. The linearity limit imposed by the photon-counters can be increased by means of neutral filters placed in the optical path to reduce the photon-flux reaching the detector.

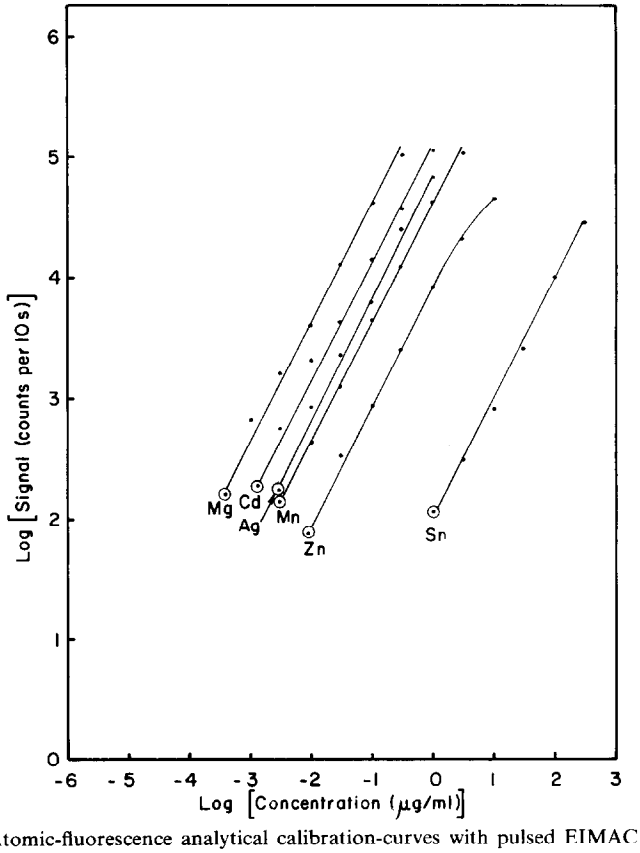

Fig. 2. Atomic-fluorescence analytical calibration-curves with pulsed EIMAC source.

From Table 3, it is apparent that the limits of detection obtained with this pulsed system are roughly comparable to those obtained with the 500-W EIMAC continuum source operated in the continuous-wave mode. That the expected improvement largely failed to materialize is due partly to the inherent instability of the EIMAC lamp when operated in the pulsed mode, and to the high level of background scatter-radiation (and thus noise) observed during the "on" time of the pulse. A rather high residual d.c. current (6.5 A) was required to sustain the arc, even at moderate pulsing amplitudes. The total signal (including atomic fluorescence) generated by the flame and the source *during* a 20-μsec interval between pulses, was electronically *subtracted* from the same signal produced *within* the duration of the pulse. Moreover, the background signal occurring between pulses was *added* to the background signal associated with the pulses in order to determine the noise of the background. Thus, the signal-to-noise ratio also depended upon the residual d.c. current flowing through the lamp between pulses. Visible fluctuations in the lamp-output intensity were observed at all but the lowest of pulse power-settings, but the precision data in Table 4 suggest that the noise amplitude in many cases was not significantly greater than that which is expected from a measurement system limited by the shot-noise; consequently, these source-fluctuations may not have contributed significantly to the total noise at the signal levels used to determine the precision-data. The background-scatter-signals obtained with the present pulsed system were substantially larger than those observed in previous continuous-wave mode studies. We consider this to be the most important limitation (with respect to signal-to-noise ratio) encountered in the present study.

The reasons for the large background signal are not yet well understood. However, there is little doubt that, at any given wavelength, scattering of the incident source-radiation from molecules in the flame (Rayleigh scattering) accounted for a significant proportion of the total background-signal. It should be noted that several previous studies[1,2,5] of atomic fluorescence excited by a continuum source have reported little or no evidence of scatter when the argon-separated air/acetylene flame was used.

The phenomenon of light-scatter is not sufficient, however, to explain the substantial irregularity observed in the spectral distribution of the background-radiation. Scattering of source-radiation might be expected to produce some contour in the background spectrum if the spectral distribution of the source-radiation contained prominent emission lines and bands superimposed upon the emitted continuum. Preliminary studies of the spectral output of the pulsed EIMAC lamp have indicated that a structured spectrum of this type is indeed emitted. Nevertheless, many of the most prominent anomalous features in the background-spectrum are known or suspected to have resulted from the fluorescence of molecular species in the flame.[5,6] The molecular-fluorescence bands of phosphorus monoxide (PO) between 230 and 270 nm interfered so extensively with the Co atomic line at 240.7 nm and the Fe line at 248.3 nm that useful detection-limits for these elements could not be determined at those wavelengths. Another PO fluorescence band not previously reported by the authors and lying between 323 and 330 nm, interfered significantly with the Cu 324.8-nm line, adversely affecting the detection-limit for that element. Similar molecular-fluorescence band interferences are believed to have occurred elsewhere in the spectrum. The observed background irregularities due to source-scatter and molecular fluorescence were of sufficient magnitude and number to cause widespread error if background correction by means of measurement at neighbouring wavelengths were attempted in multielement analysis as described in reference 2. A more detailed study of these effects is currently in progress.

Observations of the spectral radiant intensity of the EIMAC lamp indicated a shift in the source-output toward the ultraviolet, as a result of the pulsing of the lamp. However, the background-interferences discussed above were most apparent in the short-wavelength region of the spectrum, and these appeared to nullify any improvement which might otherwise have been expected in the detection-limits of those elements with resonance lines at short wavelengths. Operation of the EIMAC source in the pulsed mode did not seriously decrease the useful lifetime of the source (the lamp used has been operated for more than 200 hr with no apparent loss in light-output), and no radiofrequency or ground-loop type interference was experienced with the system as employed in this work.

In summary, the pulsed EIMAC xenon-arc continuum source at present offers little improvement over the same lamp operated in the continuous-wave mode, as a source of excitation in atomic-fluorescence spectrometry. A lamp especially suited to pulsed operation is needed, along with a way to reduce or eliminate the particularly severe background interference from molecular fluorescence associated with the operation of the pulsed-continuum source, such as removal of the interfering species from the fuel if possible and/or by adjustment of flame conditions.

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APPLICATIONS OF THE ZEEMAN EFFECT TO ANALYTICAL ATOMIC SPECTROSCOPY—IV

CAPACITIVELY-COUPLED RADIOFREQUENCY SPECTRAL SOURCES

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Summary—A magnetically-stable spectral source is described in which a radiofrequency plasma is generated within a single hollow-cathode electrode. Power is coupled to the plasma by placing metal electrodes at the radiofrequency supply potential, around the outside of the lamp-casing. The sources are simple to build, and the capacitive power-coupling technique is convenient for generating a plasma at any desired point within the envelope. The performance of the sources is compared with that of the corresponding commercial hollow-cathode lamps driven from a direct current supply.

Generation of frequency-shifted components of an atomic line by the Zeeman effect has proved to be a powerful technique for background correction in analytical atomic-absorption spectroscopy (AAS).[1–5] However, the method cannot yet be said to be generally applicable, owing to constraints on spectrometer design imposed by the required application of an intense magnetic field across either the analyte atom cloud or the source. The first approach permits use of conventional spectroscopic-line sources, but restricts the physical dimensions of the atomizer to those of, for example, a carbon rod such as that described by Dawson,[6] unless magnets of extreme size and power are available. The second approach permits use of any atomizer, but requires use of magnetically-stable spectral sources, such as EDLs operating at either radio or microwave frequencies,[6–9] radiofrequency-powered vapour-discharge lamps,[10] or d.c.-driven plasmas of specialized design.[11] In this application, EDLs show some variability of performance, demonstrated specifically for strontium tubes by Jansen *et al.*;[12] vapour-discharge lamps behave well, but are available for a strictly limited number of elements, and d.c. sources require a complex assembly procedure before their performance becomes satisfactory.[13]

The exclusion of hollow-cathode lamps (HCLs) from the list of useful magnetically-stable sources has undoubtedly limited any widespread adoption of Zeeman background correction, since HCLs are still the most readily available and widely used sources for most of the elements routinely determined by AAS. However, by analogy with the studies of Ioli *et al.*[10] on the operation of vapour-discharge lamps in magnetic fields, it appears reasonable that a hollow-cathode electrode configuration in fact could be used as a Zeeman-modulated source provided it was driven by a radiofrequency (RF) rather than a d.c. power supply.

The present work was carried out to examine the behaviour of a hollow cathode subject to an RF discharge within magnetic fields of up to 16 kG. The hollow-cathode sources used were specifically designed to operate under these conditions, and in addition were constructed to fit into a 6-mm magnet gap to permit high field strengths to be obtained without requiring an excessively large and powerful magnet. The magnet used was the 200-W unit described elsewhere.[11] The criteria above lead to the following design features for the source. First the lamp-case around the hollow cathode was reduced to a 6-mm diameter tube, into which the cathode fitted exactly. The lamp-case thus also served as an insulator to confine the discharge. Secondly, since RF excitation was to be used, there was no need for a direct electrical connection between the power supply and the plasma (the coupling used was capacitive, and is described in more detail below). Thus only one electrode was used within the lamp: the hollow cathode itself (the name is retained for convenience, though it has no electrical connotation) within which sputtering and excitation occurred. No direct connection was made to the cathode, thereby simplifying construction by the elimination of all glass–metal seals. Thus in general the sources described here lie somewhere between a conventional HCL and an EDL, since a stable vapour-phase atom-cloud is maintained by sputtering from a solid electrode, but power is transmitted through the uninterrupted insulating lamp envelope. (These sources can of course be operated without an internal electrode, by introduction of a trace of metal or salt as with an EDL, but the lifetime and stability suffer severely in consequence.)

A power-supply frequency of 2 MHz was chosen, since a large quantity of data is available on the behaviour of vapour-discharge lamps operated at around this frequency.[10] Higher frequencies were avoided, since 100-MHz plasmas, for example, do not

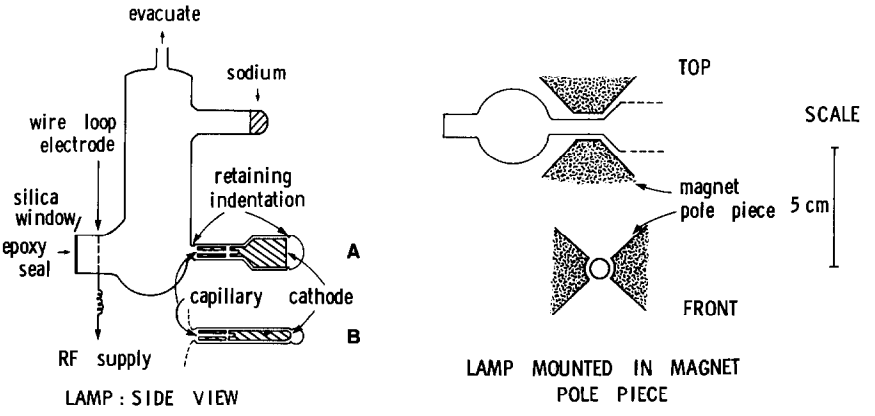

Fig. 1. Electrodes and lamp-envelope. The envelope is constructed of Pyrex except where stated. A: enlarged electrodes used for Ca, Cu, Zn. B: Cr, Ni electrode.

appear to cause sputtering.[14] In addition the generation and shielding of high power-levels become technically easier at lower frequencies.

EXPERIMENTAL

The spectrometer used in the present work was that described in detail elsewhere.[3] Measurements were all made on the d.c. signals from the pre-amplifier output of the π optical channel.

Lamp construction

Figure 1 shows the design of the electrodes and lamp-casings used. The elements for which sources were built were Cr, Ni (Fisher "Stainless"), Cu (pure metal), Zn (brass), Ca ($CaCl_2$). These elements were selected as showing a wide range of variation in their properties of sputtering, excitation, volatility and chemical reactivity.

All cathodes were made with a cavity 1.5 mm in diameter and 2 mm deep drilled in a rod of the material to be excited, machined at the front to fit within the 6-mm o.d. Pyrex tube forming the portion of the lamp-case within the magnet gap. Other cathode dimensions are shown in Fig. 1. The greater size of the Ca, Cu and Zn cathodes was not essential, but gave greater heat dissipation at higher power-levels.

Owing to the chemical reactivity of calcium metal, it was found to be more convenient to prepare this cathode from fused calcium chloride. This was done by preparing a Cu cathode as described above, with a cavity enlarged to 2 mm in diameter and 4 mm in depth. Calcium chloride was fused within this cavity until the bottom 2 mm was filled with the salt, while the top 2 mm received a surface coating (due to surface tension).

The capillary shown in front of the cathode in Fig. 1 served two purposes. First, even at a maximum lamp current of 30 mA, spectroscopic examination perpendicular to the capillary axis showed atomic emission only at the extreme end where the discharge entered the cathode. This examination was made for Cd, Cu and Zn, by using silica lamp-cases, and indicates that the pinched plasma within the capillary acted as a barrier, reducing atomic diffusion away from the cathode. Thus self-absorption in these sources should be slight, a conclusion supported by the 1% absorption sensitivities in Table 1 below. The second function of the capillary was to protect the outer case from chemical attack by deposited metal sputtered from the electrode. This deposit built up in the absence of the capillary, and the more active metals (Ca and Zn in particular) reacted with eventual release of elemental Si, to cause weakening and cracking of the case.

Power supply

Lamps were driven from a 2-MHz fixed-frequency supply with a maximum output of 90 mA at 2.8 kV. The circuit diagram of the output stage is given in Fig. 2. Lamps were all capacitively coupled by placing metal electrodes against the outside of the lamp-case at points where plasma generation was required. In the present work two such electrodes were used (Fig. 1). The magnet pole-piece around the cathode provided the ground electrode. It also provided a more effective heat sink than is available to conventional HCLs. The high-voltage electrode was formed by wrapping a single turn of 28-gauge copper wire round the front of the lamp-case. This arrangement gave a maximum lamp-current of 20–30 mA, although this could be increased by increasing the electrode areas. To operate the lamp the oscillator was tuned for maximum RF output at the 807 anode, and the oscillator voltage increased until the desired lamp-current (monitored at the 33-Ω ground return shown in Fig. 2) was reached. Lamps struck automatically without initiation by a Tesla discharge, *etc.*

One advantage of this type of plasma generation is

Table 1. Performance comparison between RF sources and commercial HCLs

Element	Line, Å	Lamp current, mA	Slit-width μm	Intensity ratio HCL:RF	RF source line:background ratio	1% Absorption sensitivity RF	1% Absorption sensitivity HCL	HCL manufacturer
Ca	4227	12	33	0.65	100:1	0.1	0.1	Perkin-Elmer
Cr	3579	18	28	4.1	10:1	0.2	0.07	Varian
Cu	3248	10	33	1.7	100:1	0.03	0.03	Perkin-Elmer
Ni	3415	18	28	9.0	20:1	0.2	0.3	Corning
	3462	18	28	10	20:1	—	—	Corning
	3525	18	28	14	20:1	—	—	Corning
Zn	2139	15	45	0.22	80:1	0.01	0.008	Varian

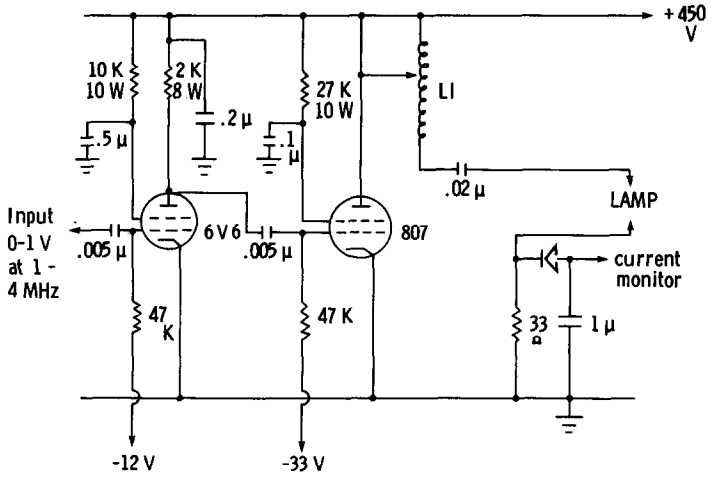

Fig. 2. Circuit diagram of RF output stage. L1: 70 μH, 90 pf; 200 turns of 22-gauge magnet wire wound on 1.8-cm diameter air-cored glass former. Variable tapping to give from 10:1 to 1:1 step-up.

the automatic current-stabilization achieved, provided the coupling capacitance is sufficiently low to drop the maximum lamp-current significantly in comparison to the maximum supply-current available. The coupling impedance then exceeds the plasma impedance sufficiently to buffer current changes due to variations in the latter. This type of stabilization is more feasible with the present sources than with their d.c. counterparts, owing to the zero power-dissipation within a capacitive power-coupling.

Conditioning procedure

Sources were evacuated, with a liquid-nitrogen trap in the line, the cases degassed with an oxy-propane flame, and sodium melted into the side-arm as described elsewhere.[11] The sodium was heated to its melting point, but not strongly enough for a sodium film to develop on the inside of the case. Argon was introduced and the emission-intensity of the required line monitored at a lamp-current of 20 mA. The source was evacuated and refilled at ap-

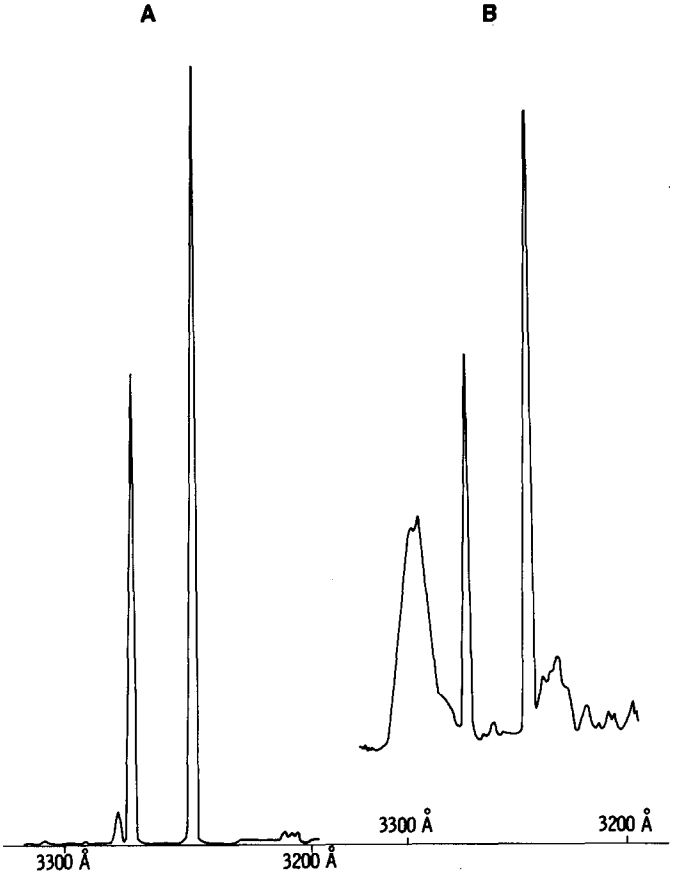

Fig. 3. Copper spectra (A) after and (B) before Na vapour discharge. Scanned at constant amplification; lamp-current of 14 mA, 33-μm monochromator slit.

proximately 5-min intervals as the cathode became degassed. Once a constant emission-intensity was reached, the lamp was filled to its optimum pressure and sealed. Interestingly, all the lamps built showed an optimum pressure of about 3 mmHg. This is thought to represent the optimum pressure for coupling RF power to a localized plasma confined within the cathode and capillary pinch, and minimizing diffuse plasma formation due to the self-capacitance of the envelope beyond this region.

After sealing of the lamp, two electrodes, each about 5 cm^2 in area, were wrapped round the side-arm containing the sodium, and round the body of the lamp just below this side-arm. These electrodes were then connected to the RF supply at its maximum output. Over the course of some 10–15 min the discharge current rose to its maximum value of 90 mA, by which time an intense sodium-vapour discharge was observed in the side-arm. The discharge was allowed to run at full current for about 5 min. This procedure served to clean the filler-gas: its efficacy in improving line intensities and line-to-background ratios is illustrated for the Cu source by the spectra in Fig. 3.

RESULTS

Comparison of RF and HCL sources

The results reported below were obtained to determine whether any marked differences in spectroscopic performance existed between the RF lamps described here, and commercial HCLs run from a d.c. supply. One immediate difficulty found in making the comparison was that of measurement of lamp power-dissipation when using the RF supply. This arose because the only voltage available for measurement was the 2.8-kV supply output, which gave no direct information regarding either the magnitude of the plasma driving voltage or of the voltage–current phase relation. Measurement of the power input to the 807 was an equally uncertain technique, since the loose coupling used permitted considerable stray power losses by radiation, eddy-current generation, *etc.* The approach taken was to assume a constant plasma driving voltage irrespective of whether the voltage was d.c. or RF, and then to match d.c. and root-mean-square (RMS) RF current levels. Thus all current values reported refer either to d.c. or RMS readings, as appropriate. In reality this assumption is probably reasonable in view of the high voltage-stability of a low-pressure discharge, together with the

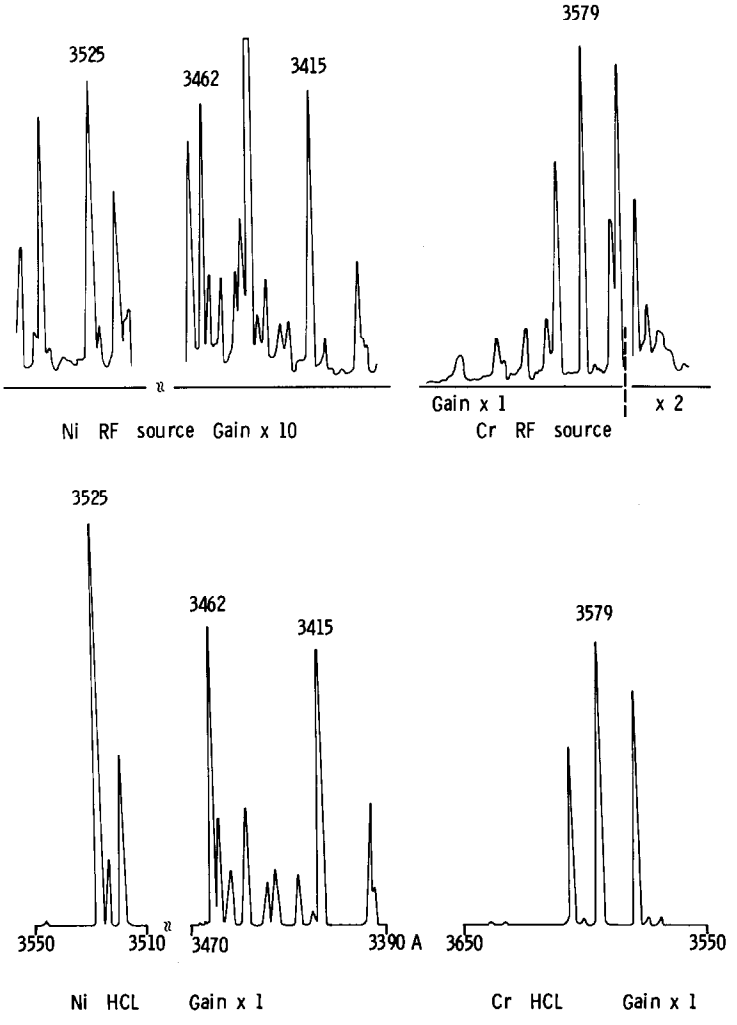

Fig. 4. RF source and HCL spectra for Cr and Ni; 28-μm monochromator slit, lamp-current 18 mA.

high voltage-swing available from the RF supply, and it is supported by the consistency in fact observed between the d.c. and RF figures.

The spectra of the Ca, Cu and Zn lamps showed no unusual features, and the appropriate resonance lines were well isolated from the nearest argon lines. Their line-to-background ratios and intensities relative to those of the corresponding HCLs are given in Table 1. The Cr and Ni lamps gave more complex spectra, attributed to the use of argon as filler-gas. These spectra are shown in Figure 4. In view of the difficulty of RF power measurement, as well as variations in lamp design and operation due to differences in cathode geometry and composition, plasma density, *etc.*, it is considered that intensity differences between RF and HCL sources can only be considered significant if they exceed an order of magnitude. The necessity for such a wide margin is further indicated by the lack of any apparent trend in the departures of the relative RF/HCL intensities in Table 1 from unity.

The most extreme intensity variations are seen for nickel and zinc. The reason for a low nickel-intensity from the RF source almost certainly lies in the low nickel concentration of the alloy used. However, the reason for a high RF source zinc-intensity is less clear, especially since the electrode was made of brass and not the pure metal and this would be expected to reduce the intensity.[15] The reason does not appear to lie in the HCL (a new Varian lamp), the performance of which was quite satisfactory when compared to that of other HCLs available.

Values of 1% absorption sensitivities for the RF and HCL sources are given in Table 1. Performance differences here for the two types of source appear marginal.

Figure 5 shows the dependence of % absorption for a 0.1-ppm zinc solution and of relative output intensity on lamp-current for the RF and HCL zinc sources. Zinc was used for comparison since its high volatility and low resonance-line wavelength were expected to emphasize any differences between the two sources. The main feature of the data in Fig. 5 is that the absorption curve for the RF source shows significantly less variation than that of the HCL, suggesting a reduced level of self-absorption for the former. This accords with the behaviour of the capillary plasma pinch, mentioned above. The RF intensity curve in Fig. 5 shows a slight convexity which contrasts with the typical, approximately exponential, curve of the HCL. Virtually identical curves were also found for the other RF lamps. The reason for this shape may lie in an increasing fraction of RF power dissipated to the lamp-envelope because of the self-capacitance of the glass. The effect is convenient since lamp-stability is not as critically dependent on current-stability as with an HCL.

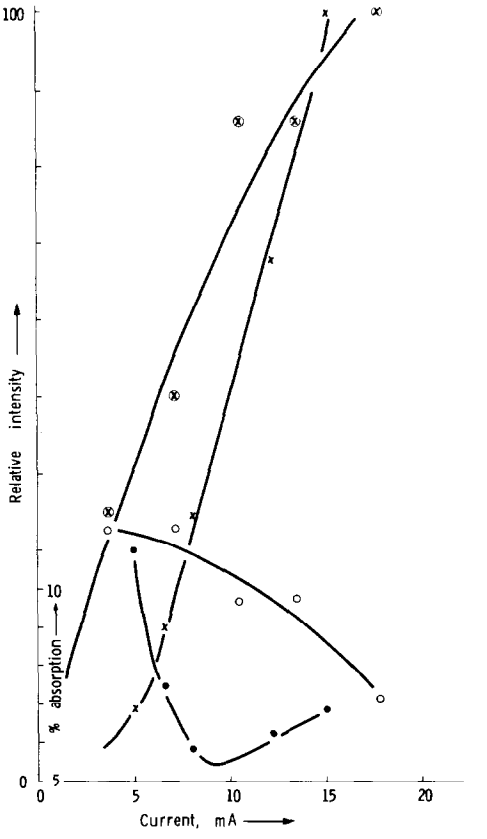

Fig. 5. Relative intensity and % absorption (0.1 ppm solution) plots for Zn RF and HCL sources. ⊗: RF intensity, ×: HCL intensity, ○: RF % absorption, ●: HCL % absorption.

Stability

Figure 6 shows three 5-hr stability plots obtained for the RF Cu source on three successive days. The plots are quite typical of those given by the other sources. The stability is thought to be quite satisfactory for a Zeeman-modulated source, or indeed even for a single-beam AAS source. However, the plots are characterized by abrupt jumps of 5–10%, which are not typical of a normal HCL output. The reason for this appears to lie in slight random variations in plasma density around the cathode, again thought to be caused by grounding of the plasma by the self-capacitance of the lamp envelope.

Some magnetic-stability plots for the RF Cu source are shown in Fig. 7. These plots were found to be rather non-reproducible in form, apparently because the balance between the current conducted by the lamp-envelope and by the cathode could fluctuate as the operational parameters (magnetic field strength at fixed lamp-current, or current at fixed field-strength) changed. The curves in Fig. 7 were obtained at 3 different lamp-currents, but similar behaviour occurred on successively increasing the magnetic field-strength with a varying current. Similar behaviour was also observed for the other sources.

CONCLUSIONS

Although developed specifically for examination of the behaviour of hollow-cathode electrodes driven at

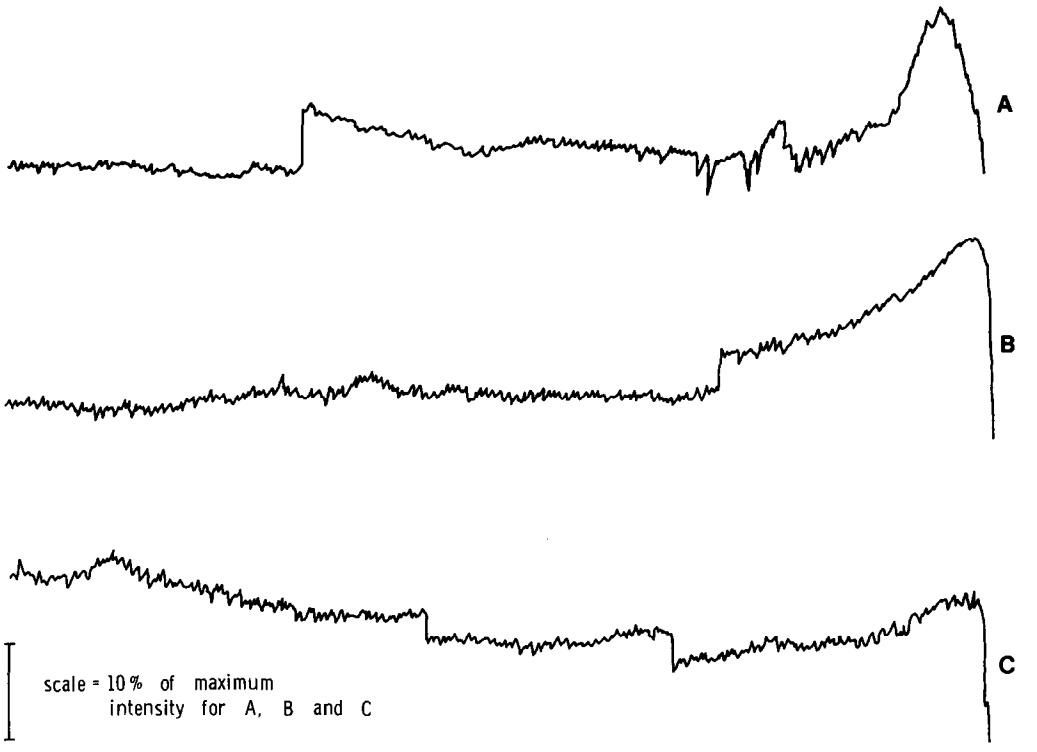

Fig. 6. Stability plots for Cu; lamp-current 8 mA, amplifier time-constant 0.3 sec. A, B, C represent chronological order. Plots shown are offset. Initial intensities for A, B and C were initially equal within ±30 V at a photomultiplier voltage of 1100 V.

radiofrequencies within a magnetic field, the present devices may also be of more general interest in their demonstration of the technical convenience of capacitive plasma coupling. The work has shown the hollow-cathode electrode configuration to be suitable for operation under these conditions, and hence to offer a useful Zeeman-modulated source.

The results shows some similarity between the RF and d.c. driven HCL sources in performance in a zero magnetic field. Therefore it seems possible that the resemblance may also extend to operation in a magnetic field, and that commercial HCLs may merit examination as sources in Zeeman background-corrected spectrometers.

Acknowledgement—The author is indebted to the National Research Council of Canada for support of this work.

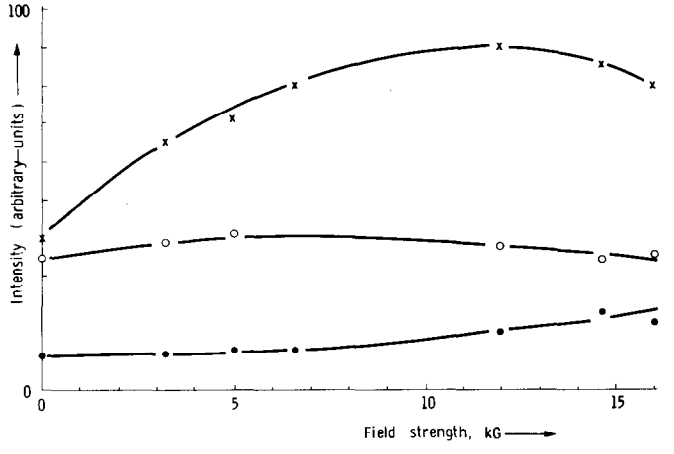

Fig. 7. Magnetic-stability plots for Cu scanned from high to low field-strengths. ×: 15 mA; ○: 8 mA; ●: 4 mA.

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THE USE OF A CHELATING RESIN COLUMN FOR PRECONCENTRATION OF TRACE ELEMENTS FROM SEA-WATER IN THEIR DETERMINATION BY NEUTRON-ACTIVATION ANALYSIS

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Summary—A Chelex-100 resin column has been employed for the preliminary concentration of trace elements in water samples before their determination by neutron-activation analysis. The column, filled with a 1:1 mixture of the resin (50–100 mesh) and Pyrex glass powder of the same mesh-size, is shown to maintain a constant flow-rate and give reproducible results. By a combination of preconcentration and neutron-activation analysis it is possible to determine Ba, Ca, Cd, Ce, Co, Cr, Cu, Fe, La, Mg, Mn, Sc, U, V and Zn in sea-water and/or fresh water simultaneously at the parts per milliard level.

Because of the extremely low concentration of trace elements in fresh water and sea-water, a preliminary concentration step is usually required for their determination. There have been a number of references to the preconcentration method employing a Chelex-100 resin column,[1–4] followed by determination by either atomic-absorption spectrophotometry[1] or X-ray spectrometry.[3] However, there are few reports on preconcentration with Chelex resin, followed by determination by neutron activation.

Initially we employed the chelating resin column for preconcentration in the manner described by Riley and Taylor.[1] In this method, sea-water is passed through a column of Chelex-100 resin and the trace elements sorbed are eluted with nitric acid. However, it was found that swelling and contraction of the resin occurred, making it difficult to maintain a constant flow-rate through the column. When a large volume of sea-water was passed through it, the resin gradually became so rigid that the ion-exchange capacity could not be predicted.

This difficulty was greatly reduced by employing a column prepared with a mixture of the resin and Pyrex glass powder. The present paper describes an investigation of the efficiency with which various trace elements can be concentrated from sea-water by means of such a resin column, and the subsequent determination of a number of them by neutron-activation analysis.

EXPERIMENTAL

Reagents

Ion-exchange column and its operation. Chelex-100 resin (50–100 mesh) in the hydrogen form was mixed with an equal amount of Pyrex glass powder of the same particle size. The mixture, slurried in water, was poured into a glass tube (12 mm diameter) to give a column length of 14 cm. A sufficient volume of sea-water or fresh water (2 litres) was passed through the resin column at its natural pH (7.7–8.2) at a flow-rate of about 3.5 ml/min. After the passage of the sample, the trace elements sorbed were eluted with various concentrations of nitric acid. The flow-rate in this column could be maintained at 3.5 ml/min during operation.

Solvents. Distilled water, nitric acid and ammonia solution were redistilled in a Pyrex still.

Mixed standard solution. Approximately 100 mg of each metal or metal oxide, (Johnson and Matthey "SpecPure") were accurately weighed, dissolved in about 2 ml of hot concentrated nitric acid and finally diluted to 100 ml with distilled water. Mixed standard solutions containing 0.1–10 μg of each metal in 10 ml were prepared from these solutions.

Apparatus

Gamma-ray spectrometry. Gamma-counting was done with a coaxial lithium-drifted germanium detector and a 4000-channel analyser. System resolution was better than 2.8 keV (FWHM at 1.33 MeV), with a peak-to-Compton ratio of 19:1.

Punched paper tape output from the multichannel analyser was fed to a CDC Cyber computer. The Sampo program used was that due to Routti and Prussin[5,6] and by Carder and Filmore,[7] which has been developed further by an IAEA expert at this laboratory. This program found the peaks in a gamma-ray spectrum, determined the shape and area of each peak, and also carried out energy calibrations. The decay-corrected peak-areas were then used to determine the trace elements in the sample solutions by comparison with the mixed standard solutions as described below.

Separation of trace elements from interfering activation products

Water samples were collected in polyethylene containers, acidified to pH 1 with nitric acid and stored. After filtering through a 0.5-μm Millipore paper, an aliquot (1–4 litres) was spiked with appropriate activities of ^{24}Na, ^{82}Br, ^{42}K, ^{115m}Cd, ^{64}Cu, ^{56}Mn and ^{65}Zn. The sample solution was adjusted to pH 8.0 with dilute ammonia solution. An aliquot (1 litre) of filtered solution was passed through the

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Table 1. Separation of interfering elements from trace elements, % recovery

Isotopes	From effluent (2 litres)	From successive 20-ml portions of 0.01*M* HNO_3					From successive 10-ml portions of 4*M* HNO_3					Total
		1	2	3	4	5	1	2	3	4	5	
^{24}Na	95.1	3.9	0.5	0.3	0.1	0	0	0	0	0	0	99.9
^{82}Br	98.2	1.3	0.4	0.1	0	0	0	0	0	0	0	100.0
^{42}K	96.3	3.0	0.5	0.4	0.1	0	0	0	0	0	0	100.3
^{38}Cl	97.0	2.4	0.6	0.2	0	0	0	0	0	0	0	100.2
^{115m}Cd	0	0	0	0	0	0	18.1	37.0	38.4	6.2	0.3	100.0
^{64}Cu	0	0	0	0	0	1.4	31.2	43.1	21.7	2.5	0	99.9
^{56}Mn	0	0	0	0	0	0	21.8	33.0	32.7	10.3	1.9	99.7
^{64}Zn	0	0	0	0	0	0	19.9	38.1	39.9	2.2	0.1	100.2

Chelex resin column and the flow-rate was adjusted to *ca.* 3.5 ml/min. Then the column was washed with 100 ml of 0.01*M* nitric acid and subsequently with 50 ml of 4*M* nitric acid. Successive 10-ml portions of the eluate were analysed by counting with a 3 × 3 in. NaI(Tl) detector coupled with a 400-channel analyser or with a Ge(Li) detector coupled with the 4000-channel analyser. The photo-peak areas of the tracers were evaluated and compared with corresponding areas from the total spiked amounts of tracers. The results, which are shown in Table 1, indicate that the interfering activities of ^{24}Na, ^{82}Br, ^{42}K and ^{38}Cl were eliminated completely by elution with 100 ml of 0.01*M* nitric acid, ^{115m}Cd, ^{64}Cu, ^{56}Mn and ^{65}Zn being quantitatively eluted with the subsequent 50 ml of 4*M* nitric acid.

Proposed procedure. On the basis of the results obtained from the preliminary experiment, a procedure was proposed as follows.

Water samples, treated as above, were passed through the resin column, and eluted with 100 ml of 0.01*M* nitric acid and the eluate was discarded. Trace elements were collected from the column by eluting with 50 ml of 4*M* nitric acid. The eluate was heated to reduce its volume, transferred to a volumetric flask and diluted to 10 ml.

A 3.5-ml portion in a 4-ml polyethylene vial was irradiated for 5 min. Another portion, 3.0 ml, in a 3.5-ml silica vial, was irradiated for 3 days. The short irradiation was carried out with the pneumatic transfer system of TRIGA Mark III reactor, and the rotary specimen rack of the reactor was used for the long irradiation. After the short irradiation, 3 ml of the irradiated solution were transferred into an activity-free vial and submitted to gamma-ray spectrometry with a Ge(Li) detector coupled with the 4000-channel analyser. After the long irradiation the sample was allowed to cool for 3 days, then the surface of the silica ampoule was cleaned with dilute nitric acid, and the sealed ampoule was placed in the counter (the background activity of the ampoule was negligible). Gamma-ray energy and peak-areas were calculated by the Cyber computer as described above. In order to determine the half-lives of the nuclides produced, the counting was repeated at appropriate intervals. The gamma-ray spectra obtained from sea and river waters after short irradiation are given in Figs. 1 and 2 respectively. The spectra obtained similarly after long irradiation are given in Figs. 3 and 4. As seen in the figures, it was possible to identify good photo-peaks of some activation products from sea and/or river waters.

Recovery of trace elements from water samples

To find the feasibility of the method for determination of the trace elements with peaks shown in these spectra, the recovery ratios were determined.

Trace elements were stripped by passing 1 litre of the filtered fresh or sea water (at pH 8) through the column. The eluate from the column was spiked with known amounts of the mixed standard solution containing Ba, Ca, Ce, Co, Cr, Cu, Fe, La, Mg, Mn, Sb, Sc, U, V and Zn. The solution thus prepared was adjusted to pH 8.0 and passed through the column. The column was eluted with 100 ml of 0.01*M* nitric acid and the eluate was discarded. The column was further eluted with 50 ml of 4*M* nitric acid. The eluate was evaporated and diluted to 10 ml. The appropriate volume of this solution was irradiated together with a flux monitor[10] and the gamma-ray spectra were obtained for both short- and long-lived nuclides, as described above under *Proposed procedure.* Portions of the mixed standard solution were taken in polyethylene vial

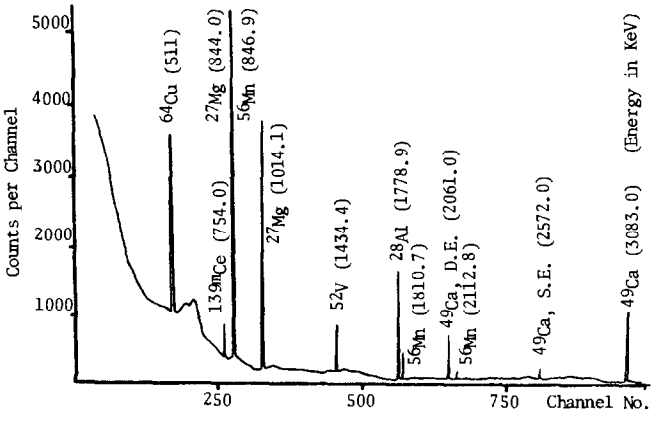

Fig. 1. Gamma-ray spectrum of preconcentrated sea-water after short irradiation. Irradiation time 5 min; thermal-neutron flux 1×10^{13} n.cm^{-2}.sec^{-1} decay period 3 min; counting time 100 sec.

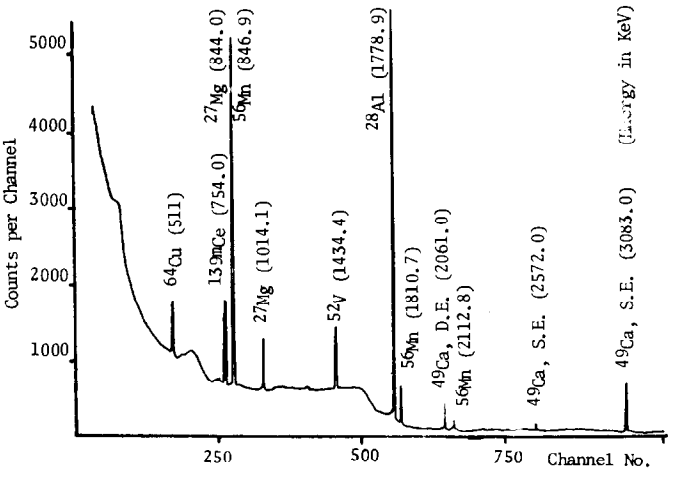

Fig. 2. Gamma-ray spectrum of preconcentrated river water after short irradiation. Irradation time 5 min; thermal-neutron flux 1×10^{13} n.cm^{-2}.sec^{-1} decay time 3 min; counting time 100 sec.

and/or silica ampoules and irradiated in similar manner, and their gamma-ray spectra obtained as reference. Their decay-corrected peak-areas were compared with those obtained for the eluate, to determine the recovery ratios. The results are shown in Table 2.

RESULTS AND DISCUSSION

As shown in Table 1 and Figs. 1–4, the major interfering elements such as sodium, potassium and bromine and chlorine were completely removed from the column with 100 ml of 0.01*M* nitric acid, whereas many trace elements were quantitatively retained. These elements were eluted with the succeeding 50 ml of 4*M* nitric acid.

The recovery ratios shown in Tables 1 and 2 indicate that the added traces of Cd, Ce, Cu, La, Mn, Sc and Zn are quantitatively recovered. These results are generally in agreement with those obtained by Riley and Taylor.[1] The recoveries of Ba, Co, Cr, Fe, U and V were also satisfactory, in contrast to the results obtained by these authors.[1] This might be attributable to the differences between the two sets of experimental conditions as follows. Riley and Taylor loaded sea-water on the column after filtering it

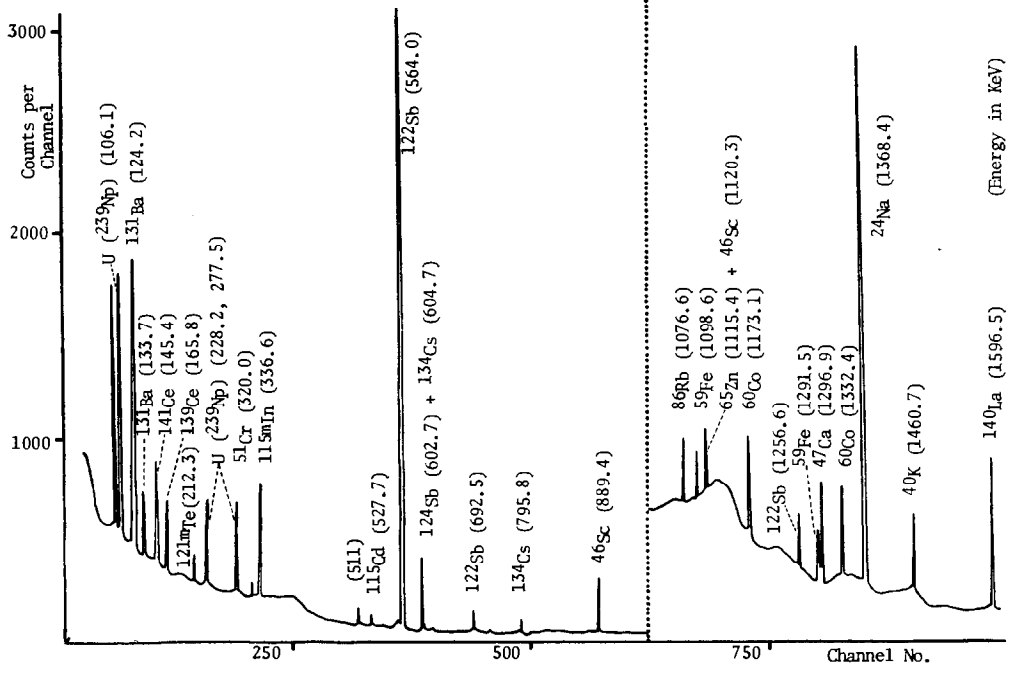

Fig. 3. Gamma-ray spectrum of preconcentrated sea-water after long irradiation. Irradiation time 3 days; thermal-neutron flux 1×10^{13} n.cm^{-2}.sec^{-1}; decay time 3 days; counting time 1000 sec.

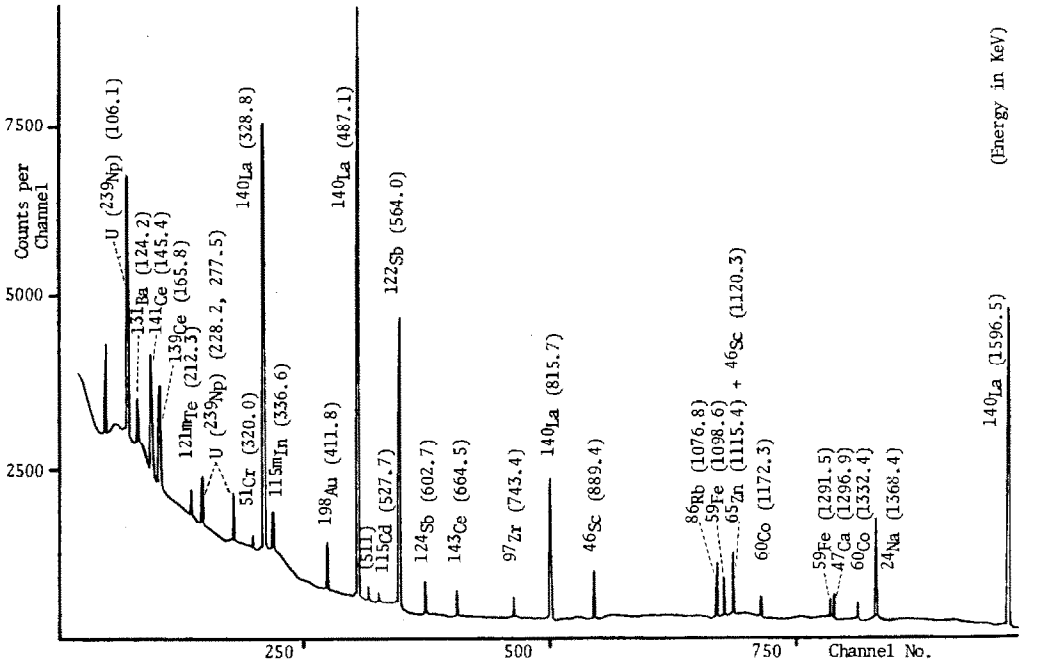

Fig. 4. Gamma-ray spectrum of preconcentrated river water after long irradiation. Irradiation time 3 days; thermal-neutron flux 1×10^{13} n.cm^{-2}.sec^{-1}; decay period 3 days; counting time 1000 sec.

through the membrane, whereas in the present work, the water samples were stored at pH 1 for several days as recommended elsewhere.[8,9] Before loading on the column, our water samples were adjusted to a pH value of *ca.* 8 with ammonia and allowed to pass through the column at a suitable flow-rate. Moreover, in the present work, 50 ml of 4*M* nitric acid were used for the collection of trace elements from the column as compared to 25 ml of 2*M* nitric acid employed by Riley and Taylor.[1] These changes might cause differences in hydrolysis and recovery of some of the trace elements.

As shown in Table 2, the recoveries of Ca and Mg were satisfactory in the case of river water but very poor for sea-water. The reasons for this were not investigated, but may be connected with matrix effects.

Recently, Florence and Batley[2] reported that the bound metals, or bound forms of trace elements such as Cd, Cu, Pb and Zn in sea-water were poorly retained by Chelex resin, whereas labile metals were almost completely retained at about pH 7. In agreement with their results, we found complete recovery of Cd, Cu and Zn from sea-water as shown in Table 2. This was further confirmed by triplicate analyses

Table 2. Recovery of trace elements from spiked samples of stripped waters

	Sea-water			River water		
Element	Added, μg	Found, μg	Yield, %	Added, μg	Found, μg	Yield, %
Ba	1.44	1.48	103	1.44	1.44	100
Ca	—	—	—	4770	4690	98.3
Cd	30.0	27.6	90.0	30.0	29.8	99.3
Ce	1.48	1.45	98.0	1.48	1.47	99.3
Co	1.50	1.49	99.3	6.23	6.30	101
Cr	230	230	100	230	227	98.7
Cu	189	187	98.9	189	193	102
Fe	615	615	100	72.0	70.0	97.2
La	0.830	0.832	100	0.830	0.829	100
Mg	—	—	—	3290	3210	97.6
Sb	—	—	—	46.0	4.10	8.90
Sc	0.140	0.142	101	0.140	0.136	97.1
U	0.160	0.157	98.1	—	—	—
V	27.0	27.0	100	27.0	25.3	93.7
Zn	401	397	99.0	45.0	45.0	100

Table 3. Results of replicate analysis for trace elements in waters taken from the Kwangyang Bay and the Nakdong River, South Korea

Element	Results, *ppM**	
	Sea-water	River water
Ba	4.8 ± 0.8	18.6 ± 0.6
Ca	—	57600 ± 750
Cd	0.20 ± 0.05	—
Ce	16.7 ± 0.7	5.96 ± 0.09
Co	—	0.38 ± 0.01
Cr	2.33 ± 0.20	
Cu	1.1 ± 0.07	63.6 ± 0.9
Fe	250 ± 10	940 ± 15
La	0.72 ± 0.04	3.94 ± 0.09
Mg	—	4480 ± 200
Mn	1.50 ± 0.04	51.0 ± 0.2
Sc	0.098 ± 0.004	0.11 ± 0.02
U	1.86 ± 0.1	—
V	2.14 ± 0.05	3.77 ± 0.09
Zn	45.9 ± 1.4	60.1 ± 2.5

* Parts per milliard (10^9).

of the total metals (bound metal + labile metal) in sea-water which was stored at pH 1 as above and then heated to boiling for 10 min before loading onto the column. Triplicate analyses were also made, without the boiling, of the sea-water which was stored at pH 1, as described in the proposed method. The two sets of results agreed within *ca.* 10% relative for Fe, La, Sc and Zn, *ca.* 20% for Cd, Ce, Co and Cr, and *ca.* 40% for Ba. The complete recoveries obtained suggest that the relatively high acidity used for storage of the water samples might have converted the bound metals[2] into labile forms.

In the present work, sea-water samples were stored at pH 1 for several days and adjusted to pH 8 with ammonia before loading. Therefore, the resin, which was originally in the H^+-form, may have finished up mainly in the Na^+-form. During the final stage of the present work, it was reported by Florence and Batley[2] that in order to obtain better retention of heavy metals the resin should originally be in the Na^+- or NH_4^+-form before sea-water is loaded onto the column. However, the use of the resin in these two forms was not attempted in the present investigation. After the elution with 4*M* nitric acid, the column was washed with water until acid-free, and was then ready for reuse. However, it was found that after some 4 or 5 runs the column became brownish, and it was then discarded and a new one prepared.

In order to evaluate the precision of the method, replicate analyses were carried out by the proposed procedure, for trace elements in a sea-water sample taken from the Kwangyang Bay and river water from the Nakdong River. The results in Table 3 show satisfactory precision. The results for zinc show a rather higher value than that reported by others.[11] Such a large difference cannot be accounted for at present, though it may be attributable to local contamination.

It seems that the Pyrex glass powder used in the present work may be replaced by other inert material such as silica gel, *etc.*

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THE SOLUBILITY PRODUCTS OF SOME SLIGHTLY SOLUBLE LEAD SALTS AND THE POTENTIOMETRIC TITRATION OF MOLYBDATE, TUNGSTATE, PERRHENATE AND FLUORIDE WITH USE OF A LEAD ION-SELECTIVE ELECTRODE

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Summary—The conditional solubility products of lead molybdate, lead tungstate and lead perrhenate were found to be $1.2 \pm 0.3 \times 10^{-13}$, $8.4 \pm 0.1 \times 10^{-11}$ and $6.9 \pm 0.8 \times 10^{-9}$, respectively. In the case of lead perrhenate, the conditional stepwise formation constants for $PbReO_4^+$ and $Pb(ReO_4)_2$ were found to be $1.2 \pm 0.1 \times 10^5$ and $1.2 \pm 0.2 \times 10^3$, respectively. Conditions for the potentiometric titration of molybdate, tungstate, perrhenate and fluoride with lead were established. The precipitates obtained during the titration of molybdate, perrhenate and fluoride mixtures have been proved to be physical mixtures of lead molybdate, perrhenate, fluoride and hydroxide, by infrared spectrometry. The pK_{sp}-values of the lead salts of chromate, molybdate and tungstate are shown to increase linearly with increasing atomic number or electronegativity of the Group VI metal ion.

Precipitation titrations have been reviewed by Püschel and Lassner.[1] A simple precipitation titration of molybdate, tungstate, perrhenate and fluoride with lead has been developed by Cheng and Goydish.[2] In their method, PAR [4-(2-pyridylazo)resorcinol] was used as indicator; mixed precipitates of $PbMoO_4 \cdot Pb(ReO_4)F$ were also reported. In the present study, the lead ion-selective electrode was used instead of PAR as indicator.

At the present time, few chemical methods are available for the determination of rhenium, especially in the milligram range. Rhenium has a variety of oxidation states which permit several disproportionation reactions; therefore, there was a need to develop a potentiometric titration method for the determination of rhenium, not based on its redox reactions.

The precipitation of lead molybdate was used to determine both lead and molybdate. The solid solution of lead molybdate and tungstate was used to determine the tungstate, and the formation of a lead molybdate, tungstate, perrhenate and fluoride solid solution was used to determine perrhenate and fluoride. Owing to the higher solubility of lead perrhenate and lead fluoride, perrhenate and fluoride were each determined in the presence of excess of the other, and 50% of methanol was also added to suppress the solubility.

The solubility of each compound at pH 6 was studied by various methods. Owing to the low solubility of lead molybdate, the extended Debye-Hückel equation[3] was employed to calculate the activity coefficients. The higher solubility of lead tungstate and lead perrhenate made possible the direct determination of their conditional solubility products.

The infrared spectra of the solid solutions obtained in the titrations were compared with those of synthetically prepared mixtures of lead molybdate, lead perrhenate, lead fluoride and lead hydroxide. They suggest that the solid solution of lead molybdate, perrhenate, fluoride and hydroxide is primarily a physical mixture.

EXPERIMENTAL

Reagents

Standard lead solutions were prepared by dissolving 99.999% pure lead metal in nitric acid. Other solutions were prepared from reagent grade chemicals and standardized against a standard lead solution. A 0.02% PAR solution was prepared by dissolution of the solid in 5 ml of methanol and dilution to volume with distilled water. Hexamethylenetetramine (hexamine) was used as a pH-6 buffer reagent. Reagent grade chemicals were used without further purification.

Lead molybdate, lead tungstate and lead perrhenate were prepared at pH 6. After being washed with distilled water more than 10 times, the precipitates were boiled in distilled water for 3 min; after filtration, they were dried in an oven at 100°. Lead molybdate was separated by centrifugation.

Apparatus

The emf measurements were made with a Corning model 10 pH-meter, with expanded scale, a lead ion-selective electrode (Orion model 94-82) and a double-junction reference electrode (Orion model 90-02). A Corning glass electrode and a calomel reference electrode were used for pH-measurements.

A Perkin-Elmer model 337 grating infrared spectrophotometer was used.

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Procedure

Titrations of lead, molybdate and tungstate. Solutions containing lead or molybdate, adjusted to pH 6 with hexamine, were titrated with molybdate or lead, respectively. For the titration of a mixture of molybdate and tungstate or of tungstate alone, a known amount of molybdate was added, so that the amount of molybdate present was greater than that of the amount of tungstate.[2] After adjustment of the pH to 6, the solution was titrated with a lead solution. The end-point was located from the potentiometric titration curve (lead ion-selective electrode).

Titration of perrhenate. Known amounts of molybdate were added to solutions containing perrhenate, the ratio of molybdate to perrhenate was adjusted to >3, the total volume was raised to 50 ml with distilled water and 5 drops of 48% hydrofluoric acid were added. The pH was adjusted to 8 with dilute ammonia solution and 50 ml of methanol were added. The solution was titrated with a lead solution, the lead ion-selective electrode being used as indicating electrode.

Titration of fluoride. Known amounts of molybdate (0.5 mmole) and approximately 0.25 mmole of perrhenate were added to five fluoride solutions of different concentrations containing 0.1–2 mmole of fluoride. The total volume was raised to 50 ml with distilled water, the pH was adjusted to 8 with ammonia solution and 50 ml of methanol were added. With the lead ion-selective electrode as indicator electrode, the solutions were titrated with a standard lead solution. The fluoride calibration curve was constructed by plotting the amount of fluoride present *vs.* the excess of lead used for fluoride. The fluoride content of an unknown sample was found from the calibration curve.

RESULTS AND DISCUSSION

There are many methods for the determination of cations, such as EDTA titration, but few for directly determining anions such as tungstate and fluoride. Since the solid solution of lead molybdate, tungstate, perrhenate and fluoride can be used to determine the perrhenate and fluoride, it would be interesting to explore their potentials in chemical analysis. The conditional solubility products of these individual precipitates were studied at pH 6.

Determination of conditional solubility product (K'_{sp}) *of lead molybdate*

The lead-ion concentration in a saturated lead molybdate solution was too low to be determined by either potentiometric or direct visual titration. However, at higher ionic strength, the solubility of lead molybdate was greatly increased and this made the determination feasible.

From the extended Debye-Hückel equation, equation (1) was derived for an aqueous medium at 25°:

$$\mathrm{pPb} = \frac{2.04\sqrt{\mu}}{1+\sqrt{\mu}} + \tfrac{1}{2}\mathrm{p}K'_{sp} \qquad (1)$$

where μ is the ionic strength; a plot of pPb *vs.* $\sqrt{\mu}/(1+\sqrt{\mu})$ will result in a straight line. By extrapolation, $\frac{1}{2}\mathrm{p}K'_{sp}$ may be found. Aliquots of saturated lead molybdate solutions at different ionic strengths were titrated with a standard EDTA solution at pH 6, PAR being used as indicator.[4] The pPb-values were then calculated and plotted *vs.* $\sqrt{\mu}/(1+\sqrt{\mu})$. The K'_{sp} of lead molybdate at pH 6 was found to be $1.2 \pm 0.3 \times 10^{-13}$, which agrees with the reported value of 1×10^{-13} estimated by the calorimetric method.[5] This is the conditional constant, but it should be very close to the thermodynamic K_{sp} because any deviations caused by pH effects and isopolymolybdic acids are insignificant at pH 6.

Determination of K'_{sp} *of lead tungstate*

Because of the higher solubility of lead tungstate, the direct determination of its K'_{sp} was possible. Aliquots of saturated lead tungstate solution were titrated with a standard EDTA solution, with PAR as indicator. The K'_{sp} of lead tungstate at pH 6 was found to be $8.4 \pm 0.1 \times 10^{-11}$. K_{sp} values for $PbWO_4$ are not available in the literature.

Determination of K'_{sp} *and conditional stepwise formation constants of lead perrhenate*

The activity of the lead ion in a filtered solution previously saturated with lead perrhenate was measured with a lead ion-selective electrode. The K'_{sp} of lead perrhenate was found to be $6.9 \pm 0.8 \times 10^{-9}$ at pH 8.0. Since lead and perrhenate are not in one-to-one ratio in lead perrhenate and the solubility is high, it was thought possible that the conditional stepwise formation constants of lead perrhenate could be determined. The reactions are:

$$Pb^{2+} + ReO_4^- \rightleftharpoons PbReO_4^+$$

$$k'_1 = \frac{[PbReO_4^+]}{[Pb^{2+}][ReO_4^-]} \qquad (2)$$

$$PbReO_4^+ + ReO_4^- \rightleftharpoons Pb(ReO_4)_2$$

$$k'_2 = \frac{1}{K'_{sp}k'_1} = \frac{1}{[PbReO_4^+][ReO_4^-]} \qquad (3)$$

Taking logarithms of equation (2) gives

$$\mathrm{p}k'_1 = -\mathrm{pPb} + \log\frac{[ReO_4^-]}{[PbReO_4^+]} \qquad (4)$$

and when $[ReO_4^-]$ is equal to $[PbReO_4^+]$, then $\mathrm{p}k'_1$ is equal to $-\mathrm{pPb}$. The value of $\mathrm{p}k'_1$ may be found graphically from a potentiometric titration curve, at 25% titration of perrhenate with lead.

The value of k'_2 was then calculated from potentiometric measurements on a solution with a 1:2 ratio of lead to perrhenate in the absence of any $Pb(ReO_4)_2$ precipitate. From the lead-ion concentration calibration curve, k'_1 and k'_2 were found to be $1.2 \pm 0.1 \times 10^5$ and $1.2 \pm 0.2 \times 10^3$, respectively.

Determination of lead, molybdate and tungstate

Either lead or molybdate may serve as a titrant to determine the other (Table 1). Tungstate alone cannot be quantitatively precipitated with lead unless a sufficient amount of molybdate is present, thus co-precipitation helps the completion of tungstate precipitation (Table 2).

Table 1. Precipitation titration of molybdate and lead, with lead ion-selective electrode as indicator electrode, at pH 6 and 25°, final volume 100 ml

Molybdate present, *mmole*	Lead present, *mmole*	Molybdate found, *mmole*	Lead found, *mmole*	Error, %
1.451×10^{-1}		1.439×10^{-1}		0.82
7.257×10^{-3}		7.269×10^{-3}		0.16
1.451×10^{-3}		1.471×10^{-3}		1.37
5.985×10^{-1}		6.045×10^{-1}		1.00
	1.015×10^{-1}		1.014×10^{-1}	0.09
	1.015×10^{-2}		1.016×10^{-2}	0.09
	1.015×10^{-3}		1.009×10^{-3}	0.59
	2.030×10^{-4}		1.981×10^{-4}	2.41

Table 2. Precipitation titration of tungstate with lead, using a lead ion-selective electrode as indicator electrode, in presence of known amounts of molybdate, at pH 6 and 25°, final volume 100 ml

Molybdate added, *mmole*	Tungstate present, *mmole*	Lead used, *mmole*	Tungstate found, *mmole*	Error %
0.5985	0.2426	0.8401	0.2416	0.41
0.5985	0.2426	0.8412	0.2427	0.04
0.5985	0.1456	0.7461	0.1476	1.37
0.0726	0.0467	0.1223	0.0497	6.42

Table 3. Precipitation titration of perrhenate with lead, using a lead ion-selective electrode as indicator electrode, in presence of molybdate, tungstate and excess of fluoride at pH 8 and 25° in 50% methanol

Molybdate added, *mmole*	Tungstate added, *mmole*	Perrhenate present, *mmole*	Lead used, *mmole*	Perrhenate found, *mmole*	Error %
0.1197	—	0.0205	0.1387	0.0190	−6.8
0.0599	—	0.0082	0.0680	0.0081	−1.2
0.0599	0.0242	0.0205	0.1061	0.0220	+6.8
0.0599	0.0242	0.0328	0.1165	0.0324	−1.2
1.1970	—	0.2386	1.4420	0.2450	+2.7
1.1970	0.0242	0.2050	1.4242	0.2030	−1.0

Determination of perrhenate and fluoride

Perrhenate is quantatively precipitated at pH 8 in the presence of a sufficient amount of molybdate, an excess of fluoride, and 50% methanol (Table 3). The ratio of lead to perrhenate was found to be 1:1 in the presence of excess of fluoride, indicating a precipitate with composition 1:1:1 Pb:Re:F. The linear relationship of the fluoride ion content in the titration solution and the excess of lead consumed is shown in Fig. 1 and Table 4. The ratio of fluoride to lead in the lead perrhenate fluoride precipitates varies according to the ratio of molybdate and perrhenate present; when this ratio becomes larger, the fluoride to lead ratio in the precipitate becomes smaller. More fluoride is co-precipitated with increase in the amount of molybdate present, but the fluoride is never completely co-precipitated. The lead used in the titration is that for the whole of the molybdate and part of the perrhenate, hydroxide and fluoride. Therefore, in the determination of fluoride, an empirical calibration curve is proposed.

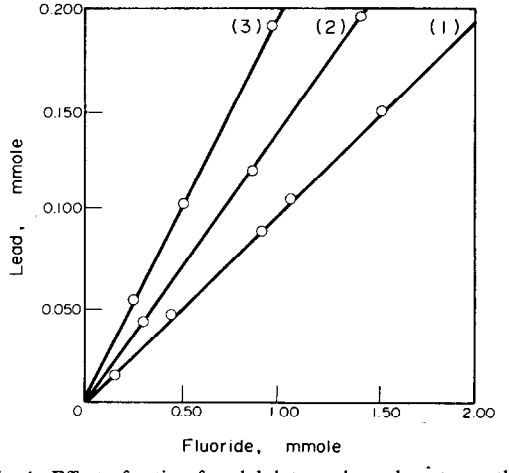

Fig. 1. Effect of ratio of molybdate and perrhenate on the ratio of fluoride and lead. For details see Table 4.

Infrared spectrum of the mixed precipitate (excess of fluoride present)

The precipitates obtained in titrations were filtered off and washed with 50% aqueous methanol. Fresh precipitates of PbF_2 and $Pb(OH)_2$ were also prepared for comparison of the infrared spectra. The spectrum of the precipitate obtained at pH 8 shows strong

Table 4. Precipitation titration of fluoride with lead, in 50% methanol, at pH 8 and 25°, in presence of added molybdate and perrhenate (see also Fig. 1)

Molybdate added, *mmole*	Perrhenate added, *mmole*	Fluoride present, *mmole*	Lead used, *mmole*	Lead used for fluoride, *mmole*
(1) 0.599	0.220	0.000	0.598	0.000
0.599	0.220	0.167	0.614	0.015
0.599	0.220	0.450	0.642	0.043
0.599	0.220	0.880	0.682	0.083
0.599	0.220	1.043	0.697	0.098
0.599	0.220	1.521	0.747	0.148
(2) 1.197	0.330	0.309	1.239	0.042
1.197	0.330	0.821	1.313	0.116
1.197	0.330	1.419	1.389	0.192
(3) 0.599	0.110	0.283	0.649	0.050
0.599	0.110	0.500	0.695	0.096
0.599	0.110	0.950	0.784	0.185

absorption bands for metal hydroxide and fluoride at 10 and 14.3 μm, respectively, whereas the spectra for those obtained at pH 6 and 7 show only a slight absorption, if any, at these wavelengths. The increase in fluoride content of the precipitate when the pH of precipitation is raised from 6 to 8 can be seen from the increase in absorption at 14.3 μm. The spectra of mixtures of PbF_2, $Pb(OH)_2$ and the pH-6 precipitate matched well with those of the pH-8 precipitates. This not only demonstrates that the pH-8 precipitate is a physical mixture of lead molybdate, perrhenate, fluoride and hydroxide, but also indicates the optimum pH for the precipitation.

Similar amounts of lead are required to start the precipitation of solutions of $10^{-2}M$ perrhenate and fluoride at pH 8. The K_{sp}-values for lead perrhenate, lead fluoride and lead hydroxide are $6.9 \pm 0.8 \times 10^{-9}$, 2.69×10^{-8} and $10^{-15.7}$, respectively.[6] It is not surprising that these compounds can be co-precipitated. The composition of the precipitate may be written as:

$$x\mathrm{PbMoO_4} \cdot y\mathrm{Pb(ReO_4)_2} \cdot z\mathrm{PbF_2} \cdot t\mathrm{Pb(OH)_2}$$

or

$$x\mathrm{PbMoO_4} \cdot y\mathrm{PbReO_4(F,OH)}$$

when excess of fluoride is present, because the lead then reacts with perrhenate in 1:1 ratio. The precipitates obtained at pH 8 were found to be soluble in $1M$ sodium hydroxide. An electro-deposition method was used to determine the amount of lead in them. The PbO_2 deposited on the anode was dissolved in dilute nitric acid, then titrated with EDTA solution; 99% or more of the lead added was recovered, indicating that the lead added during the titration was quantitatively precipitated. It is believed that under controlled conditions a definite proportion of the fluoride was precipitated. There was free fluoride present in the solution throughout the precipitation; in other words, a fluoride calibration curve is necessary for the determination of fluoride. The mechanism by which fluoride reacts to form the precipitate is not yet known, however.

Obviously, it is unsatisfactory to estimate the solubility of each component of a solid solution according to the K_{sp}-values. It may be necessary to consider the solid solution as a whole because co-precipitation decreases the solubility of each individual component. The study of the solubility of solid solutions offers an interesting problem.

It is interesting to note that a linear relationship is obtained by plotting the pK_{sp}-values for $PbCrO_4$ (12.6), $PbMoO_4$ (11.0), and $PbWO_4$ (8.2) *vs.* the atomic numbers. This may be related to the electronegativities (Pauling scale) of these elements. In this case, the solubility of the lead salts increases with increasing atomic number or electronegativity of the Group VI metal ion.

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OXIDATION OF SULPHIDE MINERALS—I

DETERMINATION OF FERROUS AND FERRIC IRON IN SAMPLES OF PYRRHOTITE, PYRITE AND CHALCOPYRITE*

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Summary—A method has been developed for determining small amounts of both ferrous and ferric iron in oxidized samples of pyrrhotite, pyrite and chalcopyrite. The oxidized iron is selectively dissolved in 10*M* phosphoric acid under reflux and can be determined with the accuracy generally accepted in chemical phase analysis.

As part of a general study to establish the "shelf-life" or stability of certified reference ores and concentrates,[1] it is desirable to understand more fully the air-oxidation of sulphide minerals. In order to do so for pyrrhotite, $Fe_{12}S_{13}$, pyrite, FeS_2, and chalcopyrite, $FeCuS_2$, it is necessary to be able to determine the ferrous and ferric iron in the oxidation products† in these minerals. For brevity, the expressions "ferrous and ferric iron from pyrrhotite, *etc.*" and "oxidized iron" will be used hereafter to describe the iron in the oxidation products and do not refer to the pure sulphide minerals.

In general, the determination of ferrous and ferric iron in ores and minerals is subject to appreciable error if even a small amount of sulphide is present, because the H_2S evolved on dissolution of these sulphides readily reduces ferric to ferrous iron.[2,3] It is evident, therefore, that the determination of small amounts of oxidized iron in pyrrhotite, pyrite or chalcopyrite samples could be very troublesome. Moreover, for samples of these minerals, a determination of the total oxidized iron can give high results because the H_2S consumed in the reduction of ferric to ferrous iron is lost, so that a true correction for the amount of iron derived from dissolved sulphide mineral cannot be applied to the total oxidized iron.

Because pyrite and chalcopyrite are relatively inert to non-oxidizing acids of moderate strength,[4,5] the selective dissolution and subsequent determination of oxidized iron presents only minor difficulty. Pyrrhotite, however, is readily attacked by such acids and the selective dissolution of oxidized iron without some dissolution of the pyrrhotite is difficult. Of a series of non-oxidizing acids, both organic and inorganic, that were tested, 10*M* phosphoric acid was found to permit the determination of oxidized iron associated with pyrrhotite and, of course, also with pyrite and chalcopyrite. This paper describes the conditions for such a determination.

EXPERIMENTAL

Pretreatment of mineral samples

Lumps of high-purity monoclinic pyrrhotite, pyrite and chalcopyrite (Wards Scientific) were crushed mechanically and the −200–325 mesh fraction (Tyler), *i.e.*, 44–74 μm, was collected for subsequent study. The non-sulphide impurities were removed from this fraction by density separation with di-iodomethane (s.g. 3.3). In order to remove as much as possible of the oxidation products formed during crushing, approximately 20 g of each sulphide mineral were shaken for 2 hr with 100 ml of ammonium sulphide solution[6] freshly prepared by saturation of 400 ml of water and 14 ml of concentrated ammonia solution with H_2S gas. The minerals were then filtered off, washed with deaerated water, anhydrous methanol and ethyl acetate, and dried under suction. The minerals were stored in vials (previously flushed with nitrogen) in a desiccator.

Controlled oxidation of mineral samples

For each mineral, ~1.5-g samples were weighed into each of five 30-ml crystallization dishes, which were then placed in a controlled temperature and humidity chamber set at 52° and 70% relative humidity (RH). The samples were removed from this chamber at various preselected times, dried in a desiccator for 18–24 hr and weighed to determine Δw, the change in weight due to oxidation, before analysis for oxidized iron. Two additional samples of pyrrhotite (~2.5 g) were treated in this way for 1 and 2 weeks. An X-ray diffraction analysis of these latter samples of pyrrhotite indicated the presence of goethite, FeO(OH), and elemental sulphur.

Determination of oxidized iron

All chemicals used were analytical grade. The reagents were 10*M* phosphoric acid (680 ml of concentrated acid diluted to 1 litre), ammoniacal cadmium chloride solution (23.7 g of $CdCl_2 \cdot 2\frac{1}{2}H_2O$ dissolved in water, followed by addition of 200 ml of concentrated ammonia and dilution to 2 litres), sulphuric acid (1 + 3), iodate–iodide solution (2.44 g of KIO_3, 100 g of KI and 2 g of NaOH dissolved

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† The oxidation products are iron oxide, hydroxide, carbonate, sulphate, thiosulphate, *etc.* and both ferrous and ferric iron can be present.

in water and diluted to 2 litres), and thiosulphate solution (22.7 g of $Na_2S_2O_3 \cdot 5H_2O$ and 0.2 g of Na_2CO_3 dissolved and diluted to 2 litres with deaerated water.

Recommended procedure

A portion (0.3–0.5 g) of each sample is transferred to a 100-ml two-neck round-bottom flask equipped with a reflux condenser and a nitrogen inlet tube that extends to near the bottom of the flask. Then 25 ml of 10*M* phosphoric acid are added and the contents refluxed for 3.5 min. After cooling in ice-water for 5 min, the contents are transferred to a 200-ml volumetric flask, diluted to the mark and filtered through a Whatman No. 42 paper. The nitrogen used to purge the flask during both heating and cooling is passed through 60 ml of ammoniacal cadmium chloride solution in a 100-ml Erlenmeyer flask to collect any H_2S evolved due to dissolution of the sulphide mineral.

The H_2S evolved is determined iodometrically. After the addition of 10.00 ml of iodate–iodide solution to the ammoniacal cadmium chloride solution, 25 ml of sulphuric acid (1 + 3) are added and the excess of iodine is back-titrated with thiosulphate. The titration was performed in this laboratory with a Mettler Automatic Titrator equipped with a Radiometer PP1311 twin platinum wire dead-stop electrode. The quantity of iron arising from the dissolution of the sulphide mineral is readily calculated from the amount of H_2S evolved. This iron must be subtracted from both the ferrous and total oxidized iron derived from oxidation products of the sulphide mineral or other iron-bearing materials in the sample.

The ferrous iron in the filtrate is determined spectrophotometrically as its 1,10-phenanthroline complex.[7] After the determination of total oxidized iron, the ferric iron can be calculated by difference. In this study, the total oxidized iron was determined with a Techtron AA6 spectrophotometer, with standard solutions having a phosphoric acid content very similar to that of the oxidized iron samples.

RESULTS AND DISCUSSION

Some products such as iron sulphate, thiosulphate, *etc.* formed by oxidation of the iron sulphide minerals are, in general, soluble in water. Others, *e.g.*, goethite, the major product from pyrrhotite, and probably formed to some extent from pyrite and chalcopyrite, require acidic dissolution media. In fact, the goethite formed from pyrrhotite in this investigation seemed to be soluble only in acid that is more concentrated than 0.5*M* and heated under reflux. This material was, however, shown to be readily attacked by phosphoric acid.

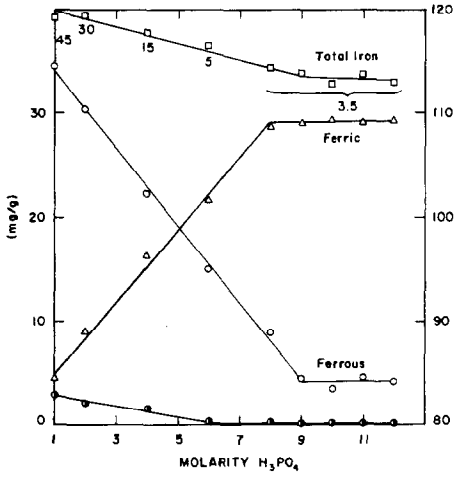

Fig. 1. The effect of phosphoric acid concentration on the determination of ferrous and ferric iron in pyrrhotite. ◑—Ferrous iron calculated from H_2S evolved. ○—Ferrous iron. □—Ferric iron. △—Total iron.

Effect of phosphoric acid concentration

Figure 1 shows the effect of phosphoric acid concentration in the determination of oxidized iron in a sample of pyrrhotite that was maintained at 52° and 70% RH for 1 week. The numbers below the points for total iron give the reflux time (min) required for complete dissolution of the goethite (visual observation) plus 1 min extra. Also depicted is the quantity of ferrous iron that can be attributed to the dissolution of pyrrhotite; this has been subtracted from the results for ferrous and total iron.

Figure 1 illustrates that for a phosphoric acid concentration less than 9*M* the amount of pyrrhotite dissolved which can be accounted for from the H_2S evolved is accompanied by a greater amount from which the H_2S is not evolved but reduces ferric to ferrous iron. Moreover this additional dissolution of pyrrhotite causes high values for total iron. At a phosphoric acid concentration greater than 9*M*, no dissolution of pyrrhotite (as detected by the evolution of H_2S) is observed and both the ferrous and total iron values appear to be constant within experimental error. The reason for this is probably the shorter time available for dissolution of any goethite. A phosphoric acid concentration of 10*M* was chosen for the procedure because it lies in the region of acidity where a constant value of ferrous and total iron is obtained but still permits the determination of ferrous iron.[7] The use of a higher concentration would require partial neutralization before ferrous iron could be determined, and addition of base to the phosphoric acid filtrate containing the ferrous iron causes rapid oxidation of the ferrous iron to ferric.

Effect of 10M phosphoric acid on ferrous iron

Because ferric iron has a strong affinity for phosphate, the oxidation of ferrous iron proceeds readily in phosphate medium. The possibility of oxidation of ferrous iron during the refluxing with 10*M* phosphoric acid, dilution to 200 ml or filtration was investigated and oxidation shown to occur. The calibration curves for the ferrous 1,10-phenanthroline complex formed (*a*) from solutions of ferrous ammonium sulphate in water and (*b*) from equivalent solutions added to 25 ml of 10*M* phosphoric acid refluxed under nitrogen for 3.5 min, diluted and filtered, are parallel but whereas that for (*a*) is linear and passes through the origin, (*b*) gives an intercept on the iron-concentration axis. This possibility of oxidation is also present in the determination of ferrous iron in iron sulphide samples and it is therefore imperative that a calibration curve of type (*b*) be used for mineral analysis. It is also important to note that 0.25 mg of

Table 1. Determination of known quantities of Fe(II) and Fe(III) in pyrrhotite

Fe(II), *mg*			Fe(III), *mg*		
Added	Found	Found, minus pyrrhotite	Added	Found	Found, minus pyrrhotite
0	0.7	—	0	16.3	—
1.1	1.7	1.0	5.6	22.0	5.7
2.0	2.6	1.9	3.7	20.1	3.8
3.6	4.1	3.4	2.2	18.7	2.4
5.6	6.2	5.5	1.2	17.6	1.3

ferrous iron is the minimum that can be detected. Consequently a zero ferrous iron content obtained for a particular sample weight of mineral should be verified by another determination on an appreciably larger sample weight.

Accuracy and reproducibility of recommended method

The accuracy or even the applicability of the recommended method in determination of oxidized iron in iron sulphide minerals cannot be verified by comparison with results obtained by another existing analytical method. This must be done by the determination of known amounts of ferrous and ferric iron added to iron sulphide samples. Table 1 gives the results for a series of known additions of $Fe(NH_4)_2(SO_4)_2 \cdot 7H_2O$ and Fe_2O_3 to 0.1800 ± 0.0005-g samples of the pyrrhotite treated at 52° and 70% RH for 1 week. It is evident that both the added ferrous and ferric iron can be determined with acceptable accuracy.

Figure 2 shows the ferrous and ferric iron in the samples of pyrrhotite, pyrite and chalcopyrite as a function of the change of weight observed in one oxidation run. The good linear relationship between ferric iron and Δw again suggests that the recommended method is well suited to the determination of oxidized iron in iron sulphide minerals.

The constancy of the ferrous iron content with increasing oxidation was unexpected and it was considered necessary to determine whether the 10*M* phosphoric acid exerted a levelling effect on the ferrous iron. The ferrous iron in the pyrrhotite treated

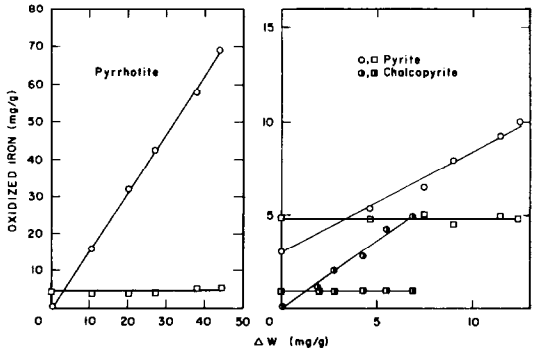

Fig. 2. Ferrous and ferric iron in pyrrhotite, pyrite and chalcopyrite. Circles—ferric iron. Squares—ferrous iron.

Table 2. Effect of sample weight on Fe(II) results for pyrrhotite

Sample weight, *g*	Fe(II) found, *mg*	Fe(II), *mg/g*
0.1007	0.5	4.9
0.3028	1.4	4.6
0.6013	3.0	5.1
1.0009	5.0	5.0

for 2 weeks was determined on 4 different sample weights. The results are summarized in Table 2. The good agreement for results from such a wide range of sample weights clearly shows the absence of any levelling effect. It can therefore be concluded that the quantity of ferrous iron is not increased under the conditions used in this study. The nature of this ferrous iron will be discussed in a future study of the oxidation process of iron sulphide minerals.

The results in Table 2 suggest that the reproducibility of the recommended method is ± 0.03 mg for 4.9 mg of Fe(II) per g of pyrrhotite. If, however, the ferrous iron values are compared for samples of sulphide minerals within any one oxidation run, the reproducibility is ± 0.5 mg for 3–5 mg/g for 27 samples of pyrrhotite in 5 different runs, ± 0.3 mg for 3–5 mg/g for 12 samples of pyrite in 2 runs, and ± 0.2 mg for 1–1.5 mg/g for 12 samples of chalcopyrite in 2 runs. That is to say, there is an uncertainty of 10–20% in the ferrous iron content. This uncertainty is high but still remains acceptable in chemical phase analysis, particularly for small amounts of the phase concerned.[2,3]

The reproducibility for ferric iron can, of course, be no better than that for ferrous iron because the former is given by the difference between total iron and ferrous iron. On the assumption that the determination of the total iron can be done with greater reproducibility than the phase separation, it seems reasonable that the overall reproducibility for the total iron might be similar to that for ferrous iron. Accordingly, the reproducibility for ferric iron should be approximately twice that for ferrous iron. Because the amount of ferric iron varies with the extent of oxidation, the uncertainty will decrease with increasing oxidation. For example, a reproducibility for Fe(III) of ~0.6 mg/g leads to an uncertainty of 20% at the 3 mg/g level but only 6% at 10 mg/g.

Effect of dissolution of sulphide minerals

The 10*M* phosphoric acid used is not a completely selective solvent for oxidized iron species in sulphide minerals. Occasionally some attack on the sulphide mineral is observed (as evolution of H_2S), particularly for pyrrhotite. Such attack was not noted in 12 tests with chalcopyrite and only twice in 12 tests on pyrite, performed for this and subsequent oxidation studies. In both instances for pyrite, the ferrous iron derived from dissolution of the pyrite was 0.25 mg/g, which is only 5% of the total ferrous iron determined (5

mg/g). It should be noted that this dissolution of pyrite is not accompanied by the undeterminable dissolution in which the H_2S formed reduces ferric iron to ferrous (see Fig. 1) (the ferrous iron content for these two pyrite samples was the same as that of the other samples in the same oxidation run.

Attack on pyrrhotite occurred in 8 of 27 experiments performed in this or subsequent studies. It was concluded that the extent of attack on pyrrhotite decreases with increasing extent of oxidation and, in fact, only one sample of pyrrhotite, treated for longer than 4 days at 52° and 70% RH, has thus far been found susceptible to attack by 10*M* phosphoric acid. The ferrous iron content of the pyrrhotite samples which were attacked by the acid was the same within the estimated reproducibility as that of samples of the same oxidation run not undergoing attack. This again suggests that ferric iron in 10*M* phosphoric acid is stable towards reduction by the small amounts of H_2S arising from dissolution of the iron sulphide.

Pyrrhotite that has been freshly treated with ammonium sulphide is very readily attacked by 10*M* phosphoric acid. Consequently, it was necessary to reduce the reflux time to 0.5 min, but even with this change the ferrous iron from the dissolution of pyrrhotite was several times greater than that due to oxidation. The latter was, however, the same within the estimated reproducibility of the recommended method as that for the pyrrhotite samples where no dissolution was observed. There is no danger of reducing ferric to ferrous because, in fact, ferric iron has, as yet, not been detected in 5 samples of pyrrhotite freshly treated with ammonium sulphide. The attack by 10*M* phosphoric acid on a freshly prepared sample of pyrrhotite and samples oxidized for short periods can probably be attributed to the relatively clean unoxidized surfaces of these samples.

CONCLUSION

A method has been developed for determining ferrous and ferric iron in the oxidation products of pyrrhotite, pyrite and chalcopyrite. Although this method was applied only to an oxidation study of samples of these minerals which had undergone a special "cleaning up", it can also be used for naturally-occurring samples of these minerals to determine their extent of oxidation, *i.e.*, weathering. Moreover, there is some doubt about the safety of marine transport of chalcopyrite concentrate, and use of the described method for analysing this copper concentrate before and after transport could give a measure of the extent of oxidation undergone during transport.

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SHORT COMMUNICATIONS

QUANTITATIVE REFLECTOMETRY—IV, DETERMINATION OF COPPER IN NICKEL-PLATING SOLUTIONS

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Summary—The determination of copper in nickel-plating solutions with commercial test-strips has been investigated. The rate of colour development, which is normally slow in the presence of high concentrations of foreign ions, has been speeded up by flushing sample solutions over the strips, rather than by immersion. Relative precision is 2.7–12% over the concentration range 2–25 ppm of copper. The accuracy of the reflectance method compares favourably with that of atomic-absorption spectrophotometry and is better than that of a visual colorimetric procedure involving dithizone.

Electroplated and electroformed nickel surfaces are required in a number of industrial processes, including the manufacture of gramophone records and decorative plating. The presence of copper as an impurity in a nickel-plating solution may adversely affect the electro-deposit formed. Concentrations as low as 10 ppm can discolour the plated surface[1] and electron micrographs have revealed that low levels of copper lead to modifications in the growth mechanism of the deposit.[2] Various analytical methods are available for the determination of copper in nickel-plating solutions but they are either time-consuming or involve relatively expensive instrumentation. The most widely used methods are colorimetry, involving a chromogenic reagent such as in 2,2′-biquinolyl or dithizone, and atomic-absorption spectrophotometry. In the present work, a rapid and inexpensive method for the determination of copper by means of commercially available test-strips has been investigated. Such strips are now made for a number of metal ions and other species in solution and are designed for semi-quantitative determinations in the ppm range by visual comparison with colour charts. It is, however, possible to obtain reliable quantitative data by instrumental means and the principles and application of reflectance measurements have been reported in earlier papers.[3,4] The test-strips for copper are similar to those described for nickel.[3] The purple colour developed when the test-strip is immersed in solutions of copper ions is comparable to that produced when 2,2′-biquinolyl reacts with Cu(I) in weakly acid solution. As Cu(II) does not react with 2,2′-biquinolyl it is necessary to reduce it to Cu(I) by adding hydroxylamine hydrochloride before the reagent or along with it. The commercial strips respond to both Cu(II) and Cu(I) ions and it is presumed that a reducing agent has been incorporated into the test area. Reflectance measurements have been made with the diffuse reflectance attachment of a Unicam SP 8000 spectrophotometer as reported previously.[3–5] In addition, the performance of a portable and inexpensive reflectance meter has been assessed and a method for the determination of copper in nickel-plating solutions is described.

EXPERIMENTAL

Reagents

Standard copper solution, 2000 ppm. Pure copper foil was degreased, briefly dipped in nitric acid (1 + 1) and rinsed in distilled water. The clean foil (0.5000 g) was dissolved in 30 ml of nitric acid (1 + 1) and the solution diluted to 250 ml. Further standards were prepared by dilution as required, the pH of each being adjusted to 3.0 with sodium acetate.

Nickel sulphamate plating solution. High-purity plating concentrate (equivalent to 453 g of nickel sulphamate), nickel chloride (19 g) and boric acid (25 g) were dissolved in 1 litre of distilled water.

Copper test-strips. "Merckoquant", E. Merck.

Visible reflectance spectrum of the copper complex

Six test-strips were immersed together in a 100-ppm copper solution for 1 min (± 1 sec), rinsed briefly with distilled water and dried with a hot-air blower at 35–40° for 4 min. The strips were trimmed to facilitate mounting on a 68 × 76 mm white card. The visible reflectance spectrum of the copper complex was recorded on an SP8000 spectrophotometer with freshly prepared magnesium oxide as a

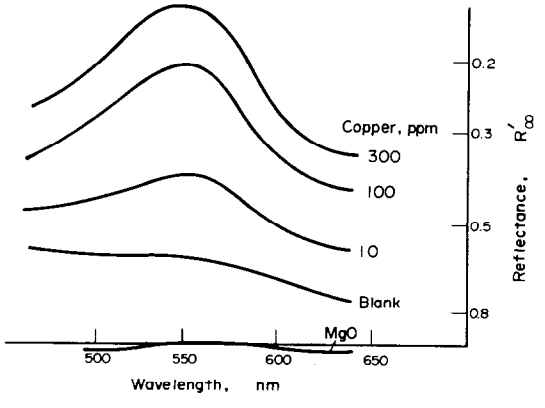

Fig. 1. Reflectance spectra of copper test-strips (reference MgO).

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Table 1. Statistical evaluation of reflectance measurements with the Eyetone portable reflectance meter (copper in water).

Copper, *ppm*	Meter reading (mean of 6 replicates)	Standard deviation	Relative precision, %
0	9.7	1.0	10.7
50	113	2.1	1.9
75	141	1.0	0.7
100	161	2.3	1.4
200	236	4.0	1.7
300	283	3.7	1.3

reference standard[3] (Fig. 1). This procedure was repeated for a series of copper concentrations between 5 and 300 ppm and the data used to prepare Kubelka–Munk and Ringbom curves. A statistical assessment (Table 1) of these strips was also made, after measurement of the reflectance of each with an Eyetone portable reflectance meter (Ames Company).

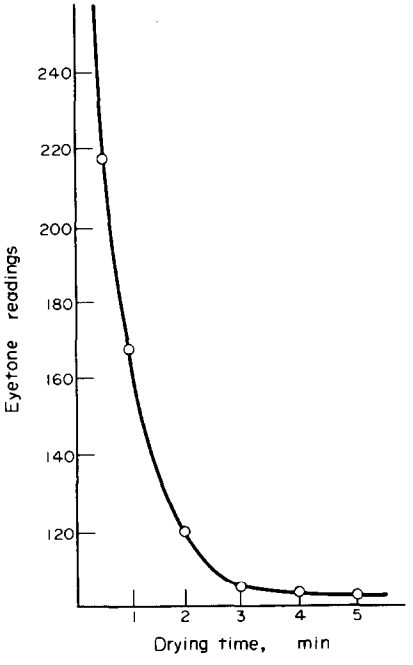

Fig. 2. Reflectance of copper test-strips as a function of drying time. Measurements made with the Eyetone portable reflectance meter.

Immersion and drying times

From preliminary observations the immersion time was set at 1 min ± 1 sec. The reflectances of single test-strips were measured with the Eyetone reflectance meter, a layer of thick plastic being fixed at the back of the sample holder to ensure reproducible location of successive strips. A series of individual strips was immersed in 50-ppm copper solutions for 1 min (± 1 sec), rinsed with distilled water and dried for 0.5–5 min with a hot-air blower. The reflectance of each strip was measured with the Eyetone reflectance meter (Fig. 2). Care was required in loading incompletely dried strips into the sample holder.

Determination of copper in nickel plating solutions

Two additional methods of colour development were investigated for the determination of copper in a simulated nickel-plating solution. Suitable aliquots of the standard copper solution were diluted with the plating solution to give copper concentrations in the range 2–300 ppm. The pH of each was adjusted to 3.0 with sodium acetate.

Method (i). Six test-strips were immersed in plating solutions containing 50–300 ppm of copper for 1 min (±1 sec), rinsed briefly with distilled water and dried for 4 min as before. Meter readings and statistical data are given in Table 2.

Method (ii). Sets of six strips were immersed in plating solutions containing 2–25 ppm of copper for 15 min with continuous stirring. The strips were rinsed and dried as before. Meter readings and statistical data are given in Table 3.

Method (*iii*). Volumes of 100 ml of plating solution containing 2–300 ppm of copper were flushed over the reagent areas of test-strips either by means of a plastic wash-bottle or a glass extraction-funnel with the end of the stem cut square. The jet was removed from the outlet tube of the wash-bottle, leaving a 3-mm orifice; gentle pressure was applied so that the 100 ml of sample solution were flushed over the strip in 15–18 sec. The extraction funnel was allowed to empty the 100 ml of sample solution over the strip by gravity alone (about 20 sec). All strips were rinsed and dried as before. Meter readings and statistical data

Table 2. Statistical evaluation of reflectance measurements obtained with the Eyetone portable reflectance meter. (copper in a simulated nickel plating solution, (method i))

Copper, *ppm*	Meter reading (mean of 6 replicates)	Standard deviation	Relative precision, %
0	16.4	2.1	12.6
50	190	11.7	6.2
75	201	12.5	6.2
100	239	22.5	9.4
200	265	11.2	4.2
300	291	18.2	6.2

Table 3. Statistical evaluation of reflectance measurements obtained with the Eyetone portable reflectance meter. (copper in a simulated nickel plating solution, (method ii))

Copper, *ppm*	Reflectance (mean of 6 replicates)	Standard deviation	Relative precision, %
0	15.8	0.8	5.3
2	68.4	7.8	11.4
5	206	11.9	5.8
10	295	15.8	5.4
15	336	15.2	4.5
25	354	18.2	5.1

Table 4. Statistical evaluation of reflectance measurements obtained with the Eyetone portable reflectance meter. (copper in a simulated nickel plating solution, (method iii))

Copper, *ppm*	Reflectance (mean of 6 replicates)	Standard deviation	Relative precision, %
Strips developed by flushing from a wash-bottle			
0	17.0	1.8	10.9
10	54.0	1.8	3.3
50	108	4.4	4.1
100	158	10.8	6.9
200	221	29.7	11.2
300	305	18.6	6.1
Strips developed by flushing from an extraction funnel			
0	16.0	0.7	4.4
2	39.0	4.6	12.0
5	94.0	11.3	12.0
10	127	5.5	4.3
15	163	6.3	3.8
25	185	5.0	2.7

are given in Table 4 (the scale readings differ between the two methods because the scale expansion was increased for the lower concentration range).

Comparison of reflectometry, colorimetry and atomic-absorption spectrophotometry for the determination of copper in a nickel-plating solution

Replicate samples of a used nickel-plating solution were analysed for copper by the extraction-funnel technique for colour development (method iii). Additional samples were analysed by a dithizone colorimetric procedure involving visual comparison of samples and freshly prepared standards. To suitable aliquots of copper standards and samples (0.2–5 ml) were added aqueous hydroxylamine hydrochloride solution (1 ml, 20% w/v), dilute hydrochloric acid (5 ml, pH 1.5) and dithizone in carbon tetrachloride (3 ml, 0.005% w/v) and the mixtures were vigorously shaken for 30 sec. The colours of the carbon tetrachloride layers of samples and standards were then compared. A calibration curve for the atomic-absorption method was prepared, the copper 324.8-nm line and an air/acetylene flame being used. Standards were prepared to cover the range 0–100 ppm copper and their gross composition was matched to that of the nickel-plating solution. The composition of replicate samples was determined from the linear calibration curve. Results for all three methods are compared in Table 5.

RESULTS AND DISCUSSION

The visible reflectance spectrum of the copper complex shows a broad maximum at 547 nm which undergoes a slight shift towards 549 nm as the concentration increases over the range 0–300 ppm (Fig. 1). Adherence of the system to the Kubelka–Munk equation is observed up to 150 ppm and a slight curvature at higher concentrations can be attributed to an increasing contribution from regular reflectance.[3] A Ringbom plot confirms that 150 ppm represents the upper limit of the optimum working range for a 1-min immersion time. The curve is linear down to 5 ppm or even less and the range could be extended by increasing the immersion time or modifying the development procedure. Strips should be dried for at least 4 min to ensure the best precision (Fig. 2).

The precision of measurements made with the Eyetone reflectance meter was assessed for copper in distilled water and also for each of the three methods of colour development studied in the determination of copper in a simulated nickel-plating solution. Precision was improved by careful selection of test-strips before use, and discard of those showing (by surface discoloration) signs of deterioration

Table 5. Comparison of methods for the determination of copper in a used nickel plating solution

Analytical method	Copper, *ppm*
Atomic absorption spectrophotometry	19
Colorimetry (dithizone)	12–16
Reflectometry	19

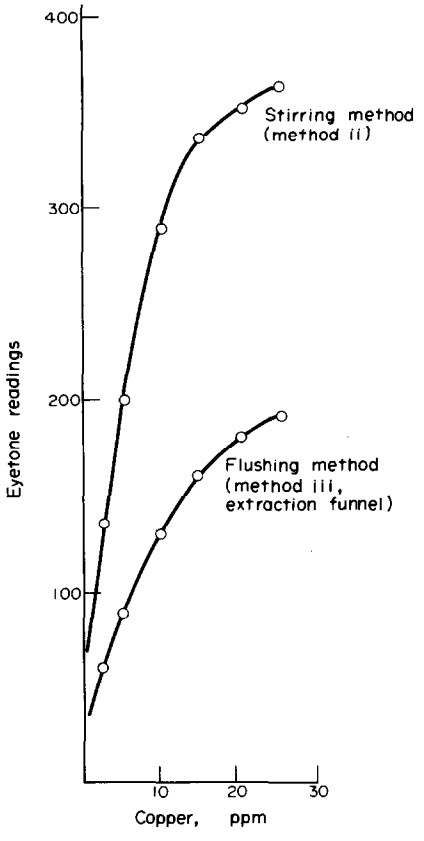

Fig. 3. Calibration curves for the Eyetone portable reflectance meter and alternative methods of colour development.

during storage. Approximately 5% of strips were eliminated in this way. When strips from a box of 100 were compared visually, they were of the same shade of extremely pale brown, although slight differences in reflectance measurements were observed. When compared on a box-to-box basis some variation in degree of discoloration was noted. New strips exposed to the air turned slightly darker after 4–5 days, an effect due perhaps to oxidation or to an increase in the moisture content of the paper. Table 1 shows the mean meter readings, estimated standard deviations and relative precisions for copper in distilled water over the range 2–300 ppm, with an immersion time of 1 min. The relative precision is comparable to that found for nickel test-strips[4] and is between 0.7 and 1.9%. Colour development for copper in the simulated nickel-plating solution was found to be fairly rapid at concentrations above 50 ppm, but at lower levels the reaction was considerably slower. This effect is probably caused by reduced rates of diffusion to the surface of the strip, owing to the formation of an electrical double-layer at the solid–liquid interface.[4] The precision of these measurements (Table 2) is not as good as that for the determination of copper in distilled water, but the range 4.2–9.4% is not significantly worse than measurements on nickel test-strips in the presence of a high concentration of foreign ions.[4] As it was of importance to obtain quantitative data at low copper levels, various methods of increasing the rate of colour development were investigated, *viz.* lowering the surface tension by adding a wetting agent, increasing the temperature of the test solution, stirring and flushing the test solution over the strip. The last two methods produced the most significant reduction in development time and sufficient data for statistical analysis were collected for each of them over the range 2–300 ppm. Results are given in Tables 3 and 4. In method 2, it was necessary to keep the rate of stirring constant throughout the 15-min immersion period to obtain relative precisions of 4.5–11.4%. Both variations of the flushing method could be accomplished in 20 sec or less and the relative precision of each (Table 4) was 2.7–12%. Because of the far faster rate of colour development and comparable precision for the flushing methods, either is considered superior to a 15-min immersion with stirring, for copper levels below 100 ppm in nickel-plating solutions.

The scale of the Eyetone reflectance meter is not calibrated directly in reflectance (R_∞) or the Kubelka–Munk function $F(R_\infty)$, as it was designed to measure blood-glucose levels by use of appropriate test-strips. For this reason a linear relation between meter reading and copper concentration could not be found. Typical calibration curves for the stirring and flushing methods are shown in Fig. 3. The much higher readings for the stirring method arise from the longer development times. As the system has been shown to follow the Kubelka-Munk equation, the non-linear response of the meter is unimportant although it imposes the need for a calibration curve rather than a conversion factor. It is desirable to run a daily check on at least one point on the calibration curve.

Results for the analysis of a used nickel-plating solution (Table 5) by the proposed reflectance method are in excellent agreement with those of the atomic-absorption method, whilst those of the visual colorimetric procedure, used hitherto in the laboratories of one of the authors, appear to have a negative bias. The precision of the reflectance method is not as high as that of atomic absorption but is more than adequate for this type of application.

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POLAROGRAPHIC DETERMINATION OF SOME METAL DIETHYLDITHIOCARBAMATES

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Summary—The polarographic behaviour of Cu, Pb, Zn, Mn, Cd, Ni and Bi diethyldithiocarbamates in benzene–methanol media was examined. A separation method was developed which allowed polarographic determination of all of these complexes without mutual interferences. Good precision and accuracy were obtained in the analysis of artificial mixtures and standard samples.

The dithiocarbamate ion forms insoluble compounds in aqueous media with cations such as Cu(II), Pb(II), Zn(II), Mn(II), Cd(II), Ni(II), Bi(III), *etc.* These are usually coloured and soluble in solvents with low dielectric constant, *e.g.*, chloroform, benzene, ethyl acetate, methyl isobutyl ketone. Many analytical applications have been found for the diethyldithiocarbamates,[1–6] the most commonly used methods including ultraviolet,[7] visible,[8] infrared[9] and atomic-absorption spectrophotometry,[10] gravimetry[11] and titrimetry.[12] Polarographic determination of Bi, Cu, Tl, Pb and Hg diethyldithiocarbamates in a ternary mixture of chloroform–methyl cellosolve–water was carried out by Fujinaga *et al.*[13,14] Budnikov *et al.*[15,16] studied the polarography of the nickel and cobalt complexes of dithiocarbamic acid derivatives and the effect of the adsorption of a depolarizer on the polarographic reduction of some metal dithiocarbamates in organic solvents.

In the work described in this paper, the polarographic behaviour of the diethyldithiocarbamates of Cu(II), Pb(II), Zn(II), Mn(II), Cd(II), Ni(II) and Bi(III) in benzene–methanol media and in the presence of lithium perchlorate or chloride as supporting electrolyte, has been examined. A method of separating these compounds by selective extraction with benzene, which permits the polarographic determination of all of them without mutal interference, was also investigated. Good precision and accuracy were obtained by using this method for determining some elements in artificial mixtures and in standard samples.

EXPERIMENTAL

Reagents

Sodium diethyldithiocarbamate solution, 0.05*M*.

Lithium chloride and perchlorate solutions in methanol, 1*M*.

Standard 0.05*M solutions of Ni, Bi, Pb, Zn, Mn, Cd, and Cu*. Prepared by dissolution of the nitrates, and standardized by EDTA titration.

Triton X-100. A 0.02% methanolic solution.

Demineralized water and analytical-grade reagents were used throughout.

Apparatus

An MECI 123 polarograph was employed, equipped with a conventional cell, a dropping mercury electrode and calomel (S.C.E.) reference electrode, connected through an agar-potassium chloride plug. Unless otherwise stated, the best operating conditions were potential sweep 3 mV/sec, height of mercury reservoir 35 cm, mercury flow-rate 1.5 mg/sec, temperature 20 ± 0.1°, damping 2 and sensitivity 15 μA full-scale deflection.

Procedures

Polarographic behaviour of diethyldithiocarbamates of Cu, Pb, Mn, Ni, Cd, Zn, and Bi. The solid complexes (0.25–2.5 × 10^{-3} mole), previously obtained by precipitation at 60%, filtration and recrystallization from benzene, were dissolved in 12.5 ml of benzene and adjusted to 25 ml with lithium chloride or perchlorate solution; 5 ml of this solution were introduced into the polarographic cell and 0.1 ml of Triton X-100 solution was added. Oxygen was removed by passage of argon saturated with benzene and methanol vapour for 5 min at a moderate flow-rate. The argon flow was maintained over the solution during the polarographic sweep. Identical results were obtained for the compounds prepared individually or extracted selectively with benzene as described below. The results are summarized in Table 1.

Extraction. The selective extraction procedure is illustrated in Fig. 1. The initial volume of aqueous solution containing the mixture of the elements was 25 ml and the concentration was in the range of 0.2–2m*M*. The volume of the benzene solution for each separation was 25 ml and 2.5 ml of this solution were adjusted to 5 ml with lithium chloride or perchlorate solution and polarographed as above.

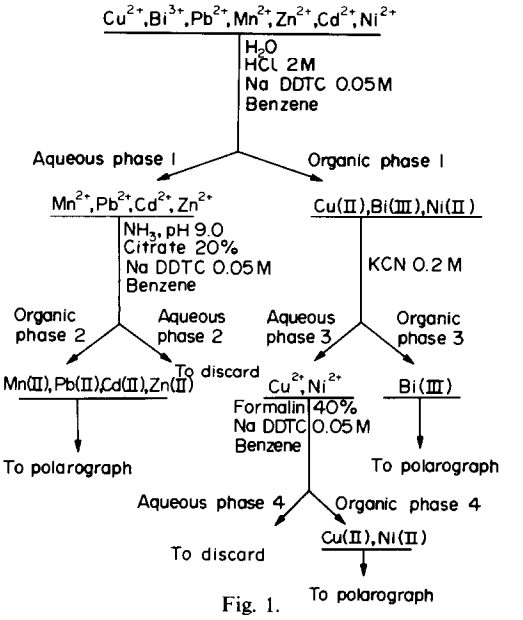

Fig. 1.

Table 1. Polarographic behaviour of metallic diethyldithiocarbamates

Supporting electrolyte	*M*	$E_{1/2}$ *vs.* S.C.E. *V* Ni	Pb	Bi	Cd	Mn	Zn	Cu
LiCl	0.1	elongated wave	−0.81	−0.59	−0.94	−0.58†	elongated waves	−0.54 −0.82*
	0.3	elongated wave	−0.80	−0.58	−0.90	−0.54	elongated waves	−0.53 −0.80
	0.5	elongated wave	−0.80	−0.59	−0.90	−0.54	elongated waves	−0.54 −0.85
$LiClO_4$	0.1	−1.46	−0.81*	−0.58	−0.90	elongated wave	−1.56	−0.58 −0.80*
	0.3	−1.45	−0.79*	−0.58	−0.90	−0.56	−1.54	−0.58 −0.83*
	0.5	−1.45	−0.80*	−0.56	−0.90	−0.56	−1.54	−0.58 −0.83*
Recommended supporting electrolyte		$LiClO_4$ 0.5*M*	LiCl 0.5*M*	$LiClO_4$ 0.5*M*	$LiClO_4$ 0.5*M*	$LiClO_4$ 0.5*M*	$LiClO_4$ 0.5*M*	LiCl 0.5*M*

* With maximum at −0.90 v.
† With maximum at −0.70 v.

Both procedures were applied to the analysis of an artificial mixture containing all these elements and to the analysis of standard samples that contained some of them. The results obtained are shown in Table 2. The partial decomposition of the sodium diethyldithiocarbamate in 2*M* hydrochloric acid was without effect.

RESULTS AND DISCUSSION

The metal diethyldithiocarbamates are soluble in several solvents. Initially we looked for solvents that would give a convenient solubility and a wide range of potential in the presence of a suitable supporting electrolyte. In this way, a greater number of the complexes can be determined. The following solvents were tested: benzene, carbon tetrachloride, ethyl acetate, toluene and methyl isobutyl ketone. all mixed with 0.5*M* lithium chloride or perchlorate in methanol.

The best results were obtained in benzene–methanol media (1:1 v/v), which gave a potential range from 0.2 to −1.9 V *vs.* S.C.E., the range being limited by oxidation of mercury and reduction of the supporting electrolyte. This range of potential is much greater than that of the other mixtures tried. Toluene is not recommended because the solubility of some of the complexes is limited and an emulsion is formed with the methanolic solution of supporting electrolyte.

The concentration of supporting electrolyte was varied from 0.1 to 0.5*M*. The most satisfactory results were obtained with 0.5*M* lithium perchlorate except for the determination of the lead and copper complexes, for which 0.5*M* lithium chloride is recommended. Lithium chloride cannot be used when the zinc complex is determined, because a series of three polarographic waves is obtained, because of the chloro-complex(es) of zinc.

All the reductions were found to be diffusion-controlled, and the diffusion currents varied linearly with the concentration of the complexes in the range from 0.1 to 1.0 m*M*. The general characteristics of the polarographic waves studied are shown in Table 1. Some of the $E_{1/2}$ values are too close for all the complexes to be determined sequentially in the same solution, but these interferences are eliminated by means of the selective extraction according to the scheme in Fig. 1. In all cases three portions of benzene gave quantitative extraction.

Finally, as seen from Table 2, the methods were applied satisfactorily to the analysis of artificial mixtures and standard samples. The calibration graphs were obtained according to the general procedure already described. For the analysis of the B.C.S. Steel No. 261/1, Aluminium Alloy No. 300 and Magnesium Alloy No. 307, the prior separation of the base metal was not necessary. The error was generally ± 0.8% and the precision ± 0.5%, except for copper, for which the error was +5% and the precision ± 1%.

Table 2. Polarographic determinations of some metallic elements

Sample	Element	Taken, *mg/ml*	Found,* *mg/ml*	Certified, %	Found,* %
Artificial	Ni	0.172	0.172	—	—
	Bi	0.0504	0.0503	—	—
	Mn	0.0288	0.0287	—	—
	Cd	0.281	0.282	—	—
	Cu	0.0922	0.0964	—	—
	Zn	0.197	0.197	—	—
	Pb	0.516	0.518	—	—
B.C.S./S.S. No. 261/1	Ni	—	—	13.1	13.0
(Nb—stabilized stainless steel)	Mn	—	—	0.83	0.83
B.C.S. No. 300 (Aluminium alloy)	Zn	—	—	5.98	5.97
B.C.S. No. 307 (Ce-Zn-Zr-Mg alloy)	Zn	—	—	2.08	2.08

* Averages of 3 determinations.

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CHROMAZUROL S ION-SELECTIVE ELECTRODE FOR CHELATOMETRIC TITRATION

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Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Japan

(*Received* 13 *July* 1976. *Accepted* 28 *October* 1976)

Summary—A liquid membrane type Chromazurol S ion-selective electrode has been constructed and applied to chelatometric titrations. In aqueous medium, zephiramine (benzyldimethyltetradecylammonium chloride) forms with the anion of Chromazurol S an ion-pair which is easily extracted into nitrobenzene. The extract is used as the liquid ion-exchanger for the Chromazurol S ion-selective electrode. The most suitable ion-pair concentration in the liquid ion-exchanger membrane is $10^{-4}M$. The linear Nernstian-response range of the Chromazurol S anion in aqueous solution is 10^{-2}–$10^{-6}M$. The electrode has been successfully applied to the chelatometric titration of Cu(II), Ni(II), Fe(III) and Pb(II) with EDTA.

Chromazurol S is one of the most useful metallochromic indicators for chelatometric titrations,[1–3] and is also a reagent for the colorimetric determination[4–5] of metals. This tetrabasic acid forms chelates with many metal ions such as Al(III), Cu(II), Ni(II), Fe(II), Fe(III) and the alkaline earth metal ions. Ishida[6] reported the dissociation constants of Chromazurol S, the three pK values of which were 2.45, 4.85 and 11.57, respectively. The sulphonic acid group of the reagent is completely dissociated even in strongly acidic solution.

In a previous paper,[7] we reported on chelatometric titration by means of an Eriochrome Black T ion-selective electrode. In the present investigation, an ion-selective electrode sensitive to Chromazurol S was constructed and applied to some chelatometric titrations.

EXPERIMENTAL

Reagent

Chromazurol S was obtained from Wako Pure Chemicals Co., and used without further purification. The reagent was standardized by the mole-ratio method against thorium nitrate, which forms a stable chelate $Th(H_2ChS)_2$, and the purity was found to be about 82.5%. The stock solution, which was 0.01M in Chromazurol S, was prepared by dissolving 0.5944 g of the reagent in 100 ml of demineralized water and was stored in the dark. Other chemicals used were all of analytical reagent grade.

Preparation of ion-exchange membrane

The liquid ion-exchange membrane was prepared as follows. To a 3-ml portion of freshly prepared $10^{-3}M$ Chromazurol S solution in a 100-ml separatory funnel were added 2 ml of $10^{-3}M$ zephiramine (benzyldimethyltetradecylammonium chloride), 2 ml of 0.2M acetate buffer solution (pH 3.5), 13 ml of water and 10 ml of nitrobenzene (NB) and the mixture was shaken for 15 min. The organic phase was separated and dehydrated by addition of anhydrous sodium sulphate. The cell composition including the ion-selective electrode is shown as follows.

Ag|AgCl	Aqueous reference solution. $10^{-3}M$ NaH_3ChS. pH = 3.5	Liquid ion-exchanger. $10^{-4}M$ $(Z^+)_2(H_2ChS^{2-})$ in NB	Aqueous test solution containing Chromazurol S	Saturated KNO_3 solution	SCE

Ion-selective electrode

The cell assembly was similar to that described previously.[8,9] The tapering bottom of the glass tube, where the wick of the so-called "sign pen" was plugged, was filled with the liquid ion-exchanger. The organic phase was poured in, followed by the aqueous reference Chromazurol S solution (previously saturated with silver chloride) and the silver–silver chloride internal reference electrode was then inserted.

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The cell assembly was similar to that described previously.[8,9] The tapering bottom of the glass tube, where the wick of the so-called "sign pen" was plugged, was filled with the liquid ion-exchanger. The organic phase was poured in, followed by the aqueous reference Chromazurol S solution (previously saturated with silver chloride) and the silver–silver chloride internal reference electrode was then inserted.

RESULTS AND DISCUSSION

Selection of ion-pair concentration in membrane

Calibration curves of the electrode for aqueous test solutions, buffered at pH 3.5 with acetate buffer, are shown in Fig. 1. The linear response range becomes narrower with increasing ion-pair concentration in the membrane phase. This may be caused by leakage of Chromazurol S ion from the surface of the membrane. The membrane with $5 \times 10^{-5}M$ ion-pair concentration is not really suitable, because it takes a long time to give a stable potential, perhaps because of increasing electrical resistance of the membrane phase. The membrane with $10^{-4}M$ ion-pair concentration is the most suitable.

The composition of the ion-pair extracted from the aqueous phase (at pH 3.5) was examined by the continuous variation method. As shown in Fig. 2, the absorption due to Chromazurol S remaining in the aqueous phase increased abruptly when the ratio $[Z^+]/([Z^+] + [H_2ChS^{2-}])$ became higher than 0.66. The composition of the extracted ion-pair is thus $(Z^+)_2(H_2ChS^{2-})$.

Selection of the internal reference electrode

Silver–silver chloride, platinum and platinized platinum electrodes were prepared and tested as internal reference electrodes, the results being shown in Fig. 3. Only the silver–silver chloride electrode gave linear response, the slope of which was about 60 mV per decade. If the extracted ion-pair had the composition $(Z^+)_2(H_2ChS^{2-})$, the slope would be about 30 mV per decade. The reason for this discrepancy is not clear but may be due to impurities in the reagent.

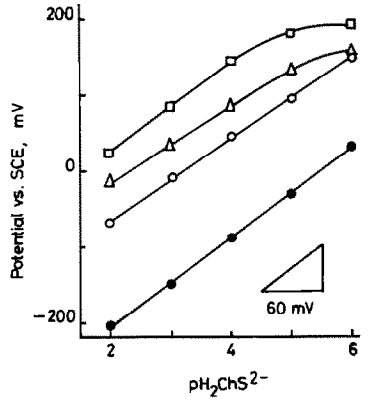

Fig. 1. Variation in measured potential with pH_2ChS^{2-} $(Z^+)_2(H_2ChS^{2-})$ ion-pair concentrations in the organic ion-exchanger: —□—, $5 \times 10^{-4}M$; —△—, $2.5 \times 10^{-4}M$; —○—, $10^{-4}M$; —●—, $5 \times 10^{-5}M$. pH 3.5. Temperature 20.2°. The triangle shows a slope of 60 mV/decade.

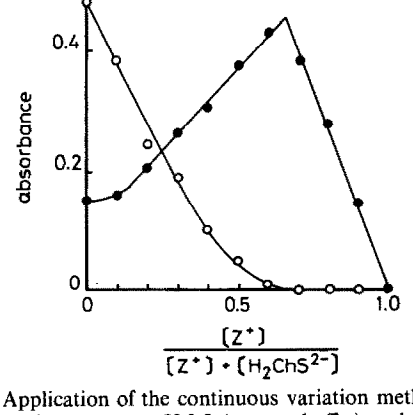

Fig. 2. Application of the continuous variation method to the extraction system. pH 3.5 (acetate buffer), volume of aqueous phase: 22 ml; volume of organic phase: 10 ml. $[H_2ChS^{2-}]_w + [Z^+]_w = 10^{-6}M$. —○—, absorbance of aqueous phase at 490 nm; —●—, absorbance of organic phase at 601 nm.

Selectivity coefficient

The effect of diverse ions on the electrode potential is given by the selectivity coefficient $K^{Pot}_{(ChS)B}$ and the Nikolsky–Eisenman equation:[10]

$$E = E^0 + \frac{2.303\,RT}{nF} \log[a_{ChS} + K^{Pot}_{(ChS)B} a_B^{n/z_B}]$$

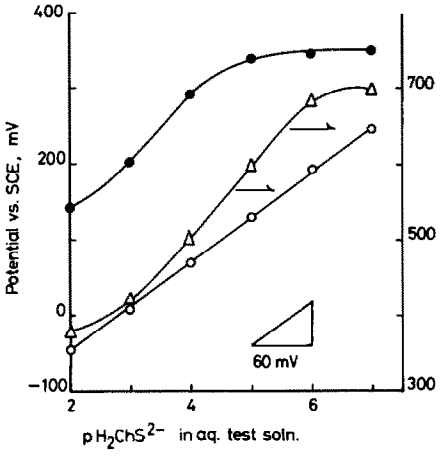

Fig. 3. Selection of internal reference electrode: —●—, Pt; —△—, Pt–Pt; —○—, Ag|AgCl electrode. Temperature 20.0°.

Table 1. Selectivity coefficients $K^{Pot}_{(ChS)B}$ of the Chromazurol S ion-selective electrode

Anion	$-\log K^{Pot}_{(ChS)B}$
NO_3^-	2.83
Cl^-	2.88
SO_4^{2-}	3.07
CH_3COO^-	3.29
$EDTA^{2-}$	4.18

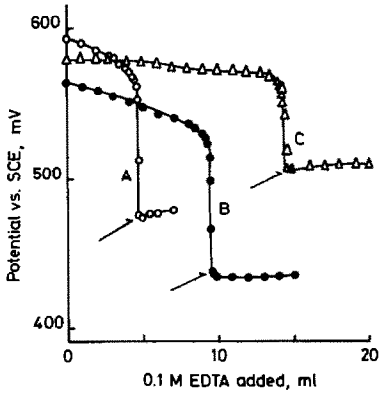

Fig. 4. Chelatometric titration of iron(III) at pH 2.0 with EDTA, using Chromazurol S ion-selective electrode. Volume of $9.64 \times 10^{-2}M$ Fe(III) taken: A, 5; B, 10; C, 15 ml.

Table 2. Comparison of potentiometric and visual methods

Solution titrated*	0.1*M* EDTA required (mean), *ml*			
	Potentiometric	Visual	F_0†	t_0§
$Cu(NO_3)_2$	9.62	9.58	6.73	2.30
$FeCl_3$	9.66	9.58	1.12	2.30

* Five separate 10-ml portions of *ca.* 0.1*M* solution were titrated by each method.

† $F_{(4,4,0.025)} = 9.60$.

§ $t_{(8,0.05)} = 2.31$.

where a_{ChS} and a_B are the activities of the Chromazurol S anion and the ion B, n and z_B are the absolute values of the charges on the Chromazurol S ion and the ion B, respectively. Selectivity coefficients for several anions were evaluated by using the graphical method of Rechnitz,[11] that is by measuring the potential while varying the concentration of Chromazurol S from $2 \times 10^{-5}M$ to $2 \times 10^{-6}M$ at a high, constant concentration of interfering ion. The ion activity-coefficient table of Kielland[12] was used for the conversion of ionic concentration into activity. The selectivity coefficients for some anions were calculated from the slope of the plot of the two exponential functions (Table 1). These anions do not interfere with the measurement of the Chromazurol S activity in chelatometric titration.

Electrode response as a function of pH

The potential of $10^{-3}M$ Chromazurol S was measured at various pH values. The potential is almost constant over the pH range 2–4.8, but becomes more positive as the pH increases. The break point agrees with the reported value[6] of $pK_3 = 4.85$.

Chelatometric titrations

Although the function of the electrode is not clearly understood, it can be used in potentiometric titration, the procedure being as follows.

To a known amount of solution in a 100-ml beaker, 2 ml of Britton–Robinson buffer and 1 ml of $10^{-3}M$ Chromazurol S solution were added. Water was added to a final volume of 50 ml and the solution titrated with EDTA. Before the equivalence point, EDTA forms a complex with the free metal ion. When all the free metal ions are consumed, the EDTA liberates the Chromazurol S anion. Thus, at the equivalence point, a sudden potential change is observed.

Figure 4 shows the titration curves of 0.1*M* iron(III), the colour change of the indicator being shown by arrows. Al(III), Cu(II) and Pb(II) were also successfully titrated in the same way. The potentiometric methods of determining Cu(II) and Fe(III) were compared statistically with the normal visual method, and the results are tabulated in Table 2. There is no significant difference between the means and the variances obtained by the two methods.

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INFLUENCE OF AROMATIC COMPOUNDS IN SUGAR CHROMATOGRAPHY ON ANION-EXCHANGE RESINS

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Summary—In sugar separations by partition chromatography on anion-exchange resins in aqueous ethanol, phenolic compounds are eluted within the same range as sugars and interfere when non-specific detectors are used. The simultaneous application of the orcinol method for sugars and an ultraviolet-detector for the aromatic compounds makes it possible to determine both types of compounds in the same chromatographic run.

Partition chromatography of sugars on anion-exchangers in the sulphate form is a useful method both for analytical and preparative purposes.[1–3] There is no interference from other solutes, for instance, in analyses of sulphite spent liquor when the eluate is analysed automatically by the orcinol method.[4] Plug-flow cannot be approached in an analytical system of this type, which means that a broadening of the elution peaks occurs. When a refractive-index detector is used, which also eliminates handling of the reagent solution, the broadening is less. On the other hand, this method has the disadvantage of being non-selective.

In most sugar separations it is convenient to choose the elution conditions so that the sugars exhibit volume distribution coefficients (D_v) within the range 1–30. The results reported in Table 1 show that phenolic compounds are eluted within this range. Hence, serious errors in sugar analyses can be obtained in the presence of phenols unless specific analytical methods are applied.

On the other hand, aromatic solutes which lack phenolic hydroxyl groups and carboxylic acid groups are only slightly retarded. Hence benzene, benzaldehyde, 4-methoxybenzaldehyde, benzyl alcohol, and 3-phenylpropan-1-ol exhibit D_v values within the range 0.27–0.52. This means that the concentration of these solutes is lower in the resin phase than in the mobile phase. Evidently non-polar interactions, which in water contribute significantly to the D_v of these solutes, and interactions with the π-electrons, are of little importance in aqueous ethanol.

A major factor responsible for the retention of sugars is their higher solubility in the water-rich resin phase than in the ethanol-rich mobile phase.[5] The observation that chlorophenols are retained more strongly than phenol and that an increasing number of substituent chlorine atoms (increasing hydrophobicity) leads to higher D_v values, shows that other factors must be responsible for the retention of these solutes. Chlorinated compounds lacking hydroxyl groups, such as 2,3-dichloromethoxybenzene ($D_v = 0.44$) and 2,6-dichloromethoxybenzene ($D_v = 0.35$), are only slightly retarded and exhibit D_v values close to those of non-chlorinated compounds (methoxybenzene, 0.34 and 1,3,5-trimethoxybenzene 0.28). The enrichment of this type of solute in the mobile phase can be ascribed to their higher solubility in the ethanol-rich phase.

The dissociation constants of the phenols under the conditions applied are not known. Investigations by Drahonovský and Vacek[6] show that in methanol the order of the pK_a values of most chlorinated phenols is the same as in water. Table 1 shows that with few exceptions the chlorinated phenols are eluted in order of decreasing pK_a (at 25° in water) and that this elution order was also obtained for the nitrophenols. Similarly, 4-hydroxybenzaldehyde, which is a much stronger acid than its isomers, is held more strongly than the isomers, and 4-hydroxy-3-methoxybenzaldehyde more strongly than 3-hydroxy-4-methoxybenzaldehyde. These results suggest that the sorption of these solutes is mainly due to either ion-exchange

Table 1. Volume distribution coefficients (D_v) of aromatic compounds in 85% w/w ethanol at 75° on the sulphate form of a strongly basic anion-exchange resin (Dowex 1-X8, 13 20 μm).

Phenol	1.18	(0.59)*	Benzoic acid	>50	(0.33)
1,2-Dihydroxybenzene	8.2	(1.15)	3,4,5-Trihydroxybenzoic acid	>50	(5.9)
1,3-Dihydroxybenzene	9.2	(3.2)	2-Chlorophenol	2.3	(0.76)
1,4-Dihydroxybenzene	4.7	(1.43)	3-Chlorophenol	1.84	
1,2,3-Trihydroxybenzene	>50	(2.8)	4-Chlorophenol	2.0	
1,3,5-Trihydroxybenzene	>50	(7.2)	2,3-Dichlorophenol	5.2	
2-Methoxyphenol	0.82		2,4-Dichlorophenol	4.5	
3-Methoxyphenol	1.42		2,5-Dichlorophenol	4.7	
4-Methoxyphenol	1.15		2,6-Dichlorophenol	9.1	
2,6-Dimethoxyphenol	0.52		2,4,5-Trichlorophenol	18.9	
2-Methoxy-4-allylphenol	0.43		2,4,6-Trichlorophenol	>50	
2-Hydroxybenzaldehyde	1.43		3,4,5-Trichlorophenol	9.0	(0.76)
3-Hydroxybenzaldehyde	1.87		2,3,4,5-Tetrachlorophenol	>50	
4-Hydroxybenzaldehyde	4.4		Pentachlorophenol	>50	
3,4-Dihydroxybenzaldehyde	>50		2-Nitrophenol	20	
4-Hydroxy-3-methoxybenzaldehyde	3.8		3-Nitrophenol	4.1	
3-Methoxy-4-hydroxybenzaldehyde	0.96		4-Nitrophenol	53	(1.34)

* Values in parenthesis refer to elution with 0.005*M* sulphuric acid in 85% ethanol.

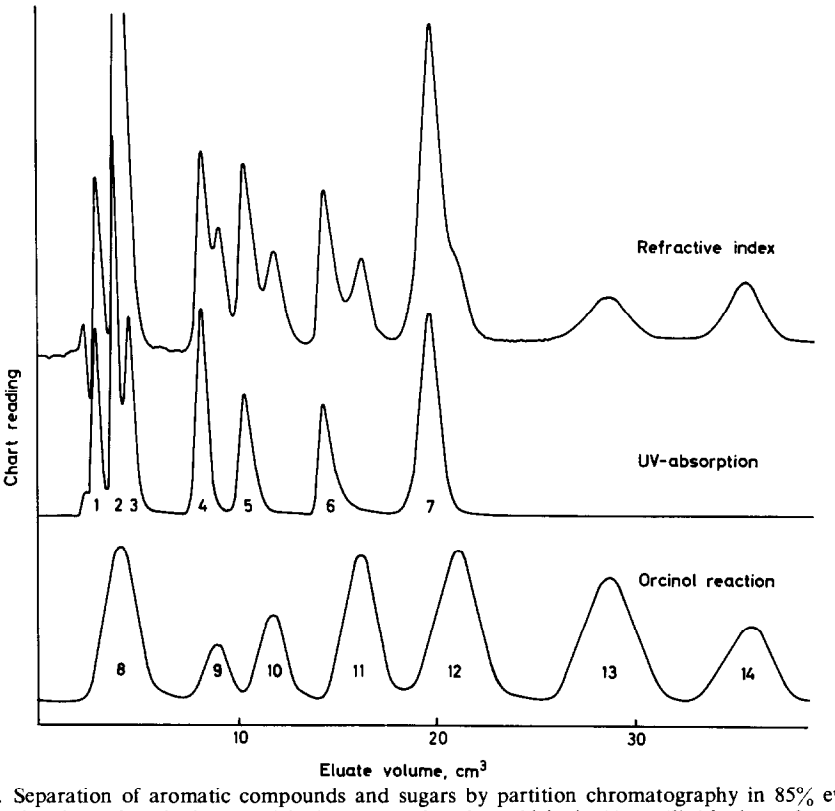

Fig. 1. Separation of aromatic compounds and sugars by partition chromatography in 85% ethanol. (1) 2,6-Dimethoxyphenol, 29 μg; (2) 3-hydroxy-4-methoxybenzaldehyde, 11 μg; (3) 4-hydroxy-3-methoxybenzaldehyde, 9 μg; (4) 3,4,5-trichlorophenol, 50 μg; (5) 1,2-dihydroxybenzene, 52 μg; (6) 2,4,5-trichlorophenol, 50 μg; (7) 1,3-dihydroxybenzene, 100 μg; (8) ethyl-α-D-arabinopyranoside, 100 μg; (9) methyl-α-D-glucopyranoside, 100 μg; (10) rhamnose, 100 μg; (11) ribose, 100 μg; (12) lyxose, 100 μg; (13) xylose, 125 μg; (14) mannose, 150 μg. Column: 2.8 × 600 mm; Technicon T5C, SO_4^{2-}, 14–17 μm. Nominal linear flow (calculated for an empty column): 5.1 cm/min.

or hydrogen-bonding of the phenolic proton to some proton-accepting groups.

In systems where hydrogen-bonding predominates, 2,6-substituted phenols are retained less strongly than their isomers.[7] On the sulphate resin 2,6-dichlorophenol and 2,4,6-trichlorophenol, which are stronger acids than their isomers, are held more strongly than the latter. The hydrogen-bonding mechanism should therefore not predominate.

In aqueous solution strong acids (HA) are retained by an anion-exchanger in the sulphate form, by conversion of the resin into the hydrogen sulphate form:[8]

$$R_2SO_4^{2-} + H^+ + A^- \rightleftharpoons RHSO_4^- + RA^-.$$

Weak acids are slightly retarded, and phenol is retained by a non-ionic sorption mechanism.[9] Washing the resin with water displaces the equilibrium to the left. It is noteworthy that the hydrogen sulphate form of the resin is much more stable in ethanol than in water.[10] If, in aqueous ethanol, this ion-exchange mechanism is mainly responsible for the sorption of the strongly acidic phenols and the carboxylic acids, their D_v values should decrease drastically if sulphuric acid is present in the eluent to depress the ionization of the solutes. This is confirmed by the results (Table 1) obtained with 0.005*M* sulphuric acid in aqueous ethanol.

From a practical point of view it is evident that the pH of the sample solution and the method for converting the resin into the sulphate form will affect the peak positions in chromatography of the strongly acidic phenols. It is worth mentioning that during a period of three weeks when a column had been used continuously in separations of phenolic compounds and aromatic acids, the D_v value of the marker (4-hydroxy-3-methoxybenzaldehyde) varied within ±3%. This is about twice the variation observed for sugars under comparable conditions. A variation in the amount added (9–50 μg) had no significant effect on the D_v value.

Interestingly, the most hydrophilic compounds, containing two or three phenolic hydroxyl groups, exhibit the highest D_v values in acidified aqueous ethanol. These results indicate that for these solutes the sorption mechanism for sugars referred to above contributes markedly to the D_v value of these compounds.

A chromatogram recorded for a complex mixture of sugars and phenolic compounds is given in Fig. 1. It is seen that phenolic compounds are eluted at positions very similar to those of several sugars and that it is impossible to use refractive-index determinations for analysis of this mixture, while a satisfactory resolution is obtained by recording the phenolic compounds by ultraviolet spectrophotometry and the sugars by the orcinol method. The retention time for the last compound (mannose) is 2 hr under the conditions applied. The results show that in favourable conditions it is possible to determine sugars and phenolic compounds in the same chromatographic run on an anion-exchange resin in the sulphate form. No interference of phenolic compounds was observed in the sugar determinations or of sugars in the determination of phenols.

EXPERIMENTAL

All experiments were made in 85% w/w ethanol in water at 75° in jacketed columns packed with the sulphate form of a strongly basic anion-exchange resin under conditions similar to those applied in previous reports on sugar separ-

ations.[1–4] The volume distribution coefficient, D_v, was calculated from the peak elution volume ($\overline{V}$) by the equation $D_v = \overline{V}/X - \epsilon$, where X is the bed volume and ϵ the interstitial fraction.

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EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF URANIUM WITH MALACHITE GREEN

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(*Received* 24 *August* 1976. *Accepted* 29 *October* 1976)

Summary—A sensitive spectrophotometric method based on the extraction of a uranium–benzoate–Malachite Green complex by chlorobenzene is described. The absorption maximum is at 635 nm and the molar absorptivity is 8.3×10^4 l.mole^{-1}.cm^{-1}. A preliminary separation of uranium by extraction with methyl isobutyl ketone from acid-deficient aluminium nitrate solution is used to avoid interferences. An aliquot of the extract is then diluted with chlorobenzene and shaken with benzoate buffer containing Malachite Green (MG). The method has been applied for the determination of uranium in a synthetic leach solution. The complex extracted is probably $[UO_2(C_6H_5COO)_3^-][MG^+]$.

Various inorganic and organic reagents have been reported for the spectrophotometric determination of uranium(VI).[1–4] However, few reagents form uranyl complexes with a molar absorptivity (ϵ) greater than 2×10^4 l.mole^{-1}.cm^{-1}, *e.g.*, 4-(2-pyridylazo)resorcinol,[5] $\epsilon = 3.87 \times 10^4$ 4-(2-thiazolylazo)resorcinol,[6] $\epsilon = 3.3 \times 10^4$; Arsenazo III,[7] $\epsilon = 5.3 \times 10^4$ and Eriochrome Black-T,[8] $\epsilon = 3.0 \times 10^4$.

Basic dyes of the triphenylmethane, xanthene and thiozine groups are highly coloured and have been used for the extractive spectrophotometric determination of a number of cations and anions, and have been reviewed.[9–12] Rhodamine B,[13–15] Methylene Blue[16,17] and Azure B[16] have been used as reagents for uranium.

We have studied the use of Malachite Green, a triphenylmethane dye, for the determination of uranium. By incorporation of an extraction procedure the method has been made selective. The combined extraction–spectrophotometric method tolerates much larger quantities of other ions and thus has definite advantages over some of the methods employing basic dyes for the determination of uranium.[14–17]

EXPERIMENTAL

Reagents

Standard uranium solution, 1.0 mg/ml. Dissolve pure U_3O_8 in the minimum quantity of nitric acid, evaporate to near dryness on a water-bath and dilute with distilled water. Dilute further as required.

Benzoate buffer. Dissolve 12 g of benzoic acid in about 75 ml of 1.0*M* sodium hydroxide, dilute to about 950 ml and adjust to pH 6 with sodium hydroxide solution and dilute to 1 litre. Filter and store in a polythene container.

Malachite Green solution, 0.2%.

Acid-deficient aluminium nitrate solution. Prepare according to the procedure recommended by Nietzel and De Sesa.[18]

Recommended procedure

To not more than 3 ml of solution containing up to 20 μg of uranium add 5 ml of benzoate buffer, 1.5 ml of Malachite Green solution and water to make up to 10 ml, and shake with 10 ml of chlorobenzene for 5 min. Let the layers separate, then collect the organic extract and centrifuge it. Measure its absorbance at 635 nm against a reagent blank. Prepare a calibration graph similarly.

Procedure when solution contains interfering ions

Add not more than 3.0 ml of the sample solution to 15 ml of acid-deficient aluminium nitrate solution and extract with 20 ml of MIBK. Separate the layers, and transfer to another separating funnel 0.5–2 ml of the organic phase and enough chlorobenzene to make the total volume 10 ml. Add a mixture of 5 ml of benzoate buffer, 1.5 ml of Malachite Green solution and 3.5 ml of water, shake the funnel for 5 min, separate the phases, collect and centrifuge the organic layer and measure its absorbance at 635 nm against a blank prepared in the same way.

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Table 1. Effect of foreign ions on absorbance of 0.200 mg of uranium(VI)

Ion	Added as	Amount, *mg*	Absorbance	Deviation of absorbance from that of U(VI)
Ca(II)	Nitrate	0.50	0.350	nil
Fe(III)	Ferric ammonium sulphate	50	0.355	+0.005
Co(II)	Sulphate	50	0.355	+0.005
Ni(II)	Sulphate	50	0.360	+0.010
Cu(II)	Sulphate	50	0.360	+0.010
La(III)	Nitrate	50	0.365	+0.015
Th(IV)	Nitrate	50	0.700	+0.350
Th(IV)*	Nitrate	50	0.360	+0.010
Mo(VI)	Molybdate	10	0.355	+0.005
V(V)	Vanadate	10	0.325	−0.025
Cr(III)	Sulphate	10	0.345	−0.005
Zr(IV)	Oxychloride	10	0.350	nil
Cl^-	Sodium salt	50	0.350	nil
SO_4^{2-}	Sodium salt	50	0.345	−0.005
PO_4^{3-}	Dihydrogen phosphate	50	0.340	−0.010

* EDTA (0.5 mg) was added at the time of colour development.

RESULTS AND DISCUSSION

Interferences

It was found that many metal ions cause positive interference and that addition of EDTA as masking agent does not give very satisfactory results. However, methyl isobutyl ketone (MIBK) has been used as a simple and efficient method for separation of uranium from a wide variety of cations and anions,[18] and it was found that when the MIBK extract was mixed with chlorobenzene in 1:4 v/v ratio and this mixed-solvent phase was shaken with an aqueous solution of benzoate and Malachite Green, the ion-association complex was formed in the organic phase. Table 1 shows that the interference of several metal ions can be prevented in this way.

Application of the method

The method was tested with a synthetic solution (pH 1.5) having the composition (concentrations in mg/ml): U(VI) 0.2, Fe(III) 4.0, Al(III) 1.0, Ni(II) 0.2, Cu(II) 1.0, Mn(II) 2.5, Ca(II) 0.7, Mg(II) 1.0, PO_4^{3-} 1.2, SO_4^{2-} 30. This composition resembles that of a sulphuric acid leach solution obtained from a low-grade uranium ore. The mean of 11 replicate analyses for uranium on 1.0-ml aliquots was 203 μg/ml with a standard deviation of 4 μg/ml.

Properties of the complex

The molar absorptivity of Malachite Green (MG) in chlorobenzene is about 1×10^5 l.mole^{-1}.cm^{-1}. Since Job's method shows that the U:MG ratio in the extracted species is 1:1, a molar absorptivity of about the same order is expected for the complex, but a value of only 8.3×10^4 l.mole^{-1}.cm^{-1} was found. This is due to incomplete extraction of the uranium (85% extraction was observed, with ^{233}U tracer). Extraction can be improved by using a higher concentration of the dye or repeating the extraction, but the blank also increases. Hence for analysis a single extraction under the recommended conditions is preferred, but it is necessary to use exactly the same volumes of the two phases every time.

As MG gives a univalent cation it is presumed that the species extracted is an ion-association complex $[UO_2(C_6H_5COO)_3^-][MG^+]$.

The method is not only selective for uranium but also very sensitive.

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OXIDATION OF SULPHIDE MINERALS—II

DETERMINATION OF METAL IN THE OXIDATION PRODUCTS OF GALENA, SPHALERITE AND CHALCOCITE*

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Summary—A 15% ammonium acetate and 3% acetic acid solution has been shown to be useful in the determination of the principal metal in small amounts of the oxidation products of galena, sphalerite and chalcocite. Its use in the determination of the extent of oxidation in concentrates or complex ores of these minerals is implied.

For the investigation of the air-oxidation of the common sulphide minerals, currently being pursued in this laboratory,[1] it was necessary to develop a method to determine ferrous and ferric iron in the oxidation products of pyrrhotite, pyrite and chalcopyrite.[2] Similarly, a method to determine the lead, zinc and copper in small amounts of the oxidation products of galena, sphalerite, and chalcocite (Cu_2S) was needed, and is described here.

The selective separation of lead minerals such as anglesite, $PbSO_4$, and cerussite, $PbCO_3$, from galena can be accomplished by means of a solution containing 15% ammonium acetate and 3% acetic acid[3,4] (hereafter denoted by 15N, 3 H). Only approximately 0.05% of the galena dissolves.[4] This minor amount of dissolution presents no problem in the determination of small amounts of lead provided that the H_2S evolved is determined and the appropriate correction made to the lead value. For highest accuracy, however, the amount of lead from dissolution of galena should not greatly exceed that from the oxidation products.

Several methods for determining the metal in the oxidation products of zinc and copper sulphides are available.[5–8] A 30% ammonium acetate solution selectively dissolves zinc oxide and sulphate from sphalerite.[5] "Oxidized" or "acid-soluble" copper in copper sulphides is in general determined by using 5% sulphuric acid saturated with sulphur dioxide,[6] 6% thiourea solution[7] or 1% unithiol solution.[8] This paper describes the use of 15N, 3 H to determine the metal in small amounts of the oxidation products of sphalerite and chalcocite (as well as galena) and discusses the advantage of this reagent over those hitherto employed for zinc and copper sulphides.

EXPERIMENTAL

Pretreatment of mineral samples

Lumps of high-purity galena, sphalerite and chalcocite (Wards Scientific) were crushed mechanically and the 200–325 mesh (Tyler) fraction was collected for subsequent study. The non-sulphide impurities were removed from this fraction by density separation with di-iodomethane (s.g. 3.3). In order to obtain portions of these minerals containing as little as possible of the oxidation products formed during crushing, approximately 10 g of each mineral were boiled in 100 ml of 15N, 3 H for 5 min, washed with water and acetone and air-dried.

Determination of metal in oxidation products

All chemicals were analytical grade. The 15N, 3 H solution was prepared by dissolving 150 g of ammonium acetate and 30 ml of glacial acetic acid in 400 ml of water and diluting to 1 litre. Ammoniacal cadmium chloride solution, sulphuric acid, iodate–iodide solution and thiosulphate solution were prepared as in Part I.[2]

Recommended procedure

A portion (0.3–0.5 g) of each sample is transferred to a 100-ml two-neck round-bottom flask equipped with a reflux condenser and a nitrogen inlet tube that extends to near the bottom of the flask, 25 ml of 15N, 3 H are added and the contents are refluxed for 5 min. After cooling in ice-water for 5 min, the contents are transferred to a 200-ml volumetric flask, diluted to the mark and filtered through a Whatman No. 42 paper. The nitrogen used to purge the flask during both heating and cooling is passed through 60 ml of ammoniacal cadmium chloride in a 100-ml Erlenmeyer flask to collect any H_2S evolved during dissolution of the sulphide mineral. The H_2S is determined iodometrically as in Part I.[2] The quantity of metal obtained from the dissolution of the sulphide mineral is readily calculated from the amount of H_2S evolved and must be subtracted from the total metal determined, to give the true amount of metal in the oxidation products. It must be noted that in all the determinations performed in this investigation no dissolution of the sulphide minerals was observed.

The metal in the oxidation products is determined by atomic absorption, with standard solutions having an ammonium acetate and acetic acid content very similar to that of the sample solutions.

RESULTS AND DISCUSSION

Solubility of possible oxidation products in 15N, 3 H

The ability of 15N, 3 H, heated under reflux for 5 min, to dissolve possible oxidation products of galena, sphalerite and chalcocite was evaluated. All compounds of lead, zinc and copper tested were analytical grade except for Cu_2O and CuO which were prepared according to known procedures.[9,10] It was assumed that solubility of a metal oxide in 15N, 3 H indicated similar behaviour for the corresponding metal hydroxide. It was found that 25 ml of 15N, 3 H readily dissolved 100 mg of PbO, $PbCO_3$ and $PbSO_4$; ZnO, $ZnCO_3$ and $ZnSO_4$; CuO, $CuCO_3$ and $CuSO_4$; 76 mg of Pb_3O_4 but only ~35 mg of Cu_2O. This relatively low solubility of Cu_2O should present no problem, because Cu_2O is rarely encountered in appreciable quantities in ores.[6]

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Table 1. Effect of reflux time on recovery of metal in oxidation products

Reflux time, min	Metal, *mg/g* Pb*	Zn	Cu*
5	23.0, 0.33	0.24	14.9, 0.73
10	23.0, 0.31	0.27	14.2, 0.71
30	22.7, 0.35	0.28	15.2, 0.74
60	22.8, 0.31	0.24	14.5, 0.74

* Two separate specimens.

Table 2. Effect of sample weight on recovery of metal in oxidation products

Sample weight, *g*	Metal, *mg/g* Zn	Cu*
0.25	0.28	22.0, 0.71
0.30	0.24	22.1, 0.73
0.50	0.24	22.4, 0.70
1.00	0.24	21.8, 0.75

* Two separate samples.

Table 3. Recovery of additions of $PbSO_4$, ZnO and CuO to sulphide minerals

Mineral, *g*	Compound added, *mg*	Metal added, *mg*	Metal found, *mg* Total	Corrected
Galena	$PbSO_4$	Pb		
0.30055	0.0	0.0	0.10	0.0
0.30236	1.68	1.15	1.18	1.08
0.30131	2.89	1.97	2.02	1.92
0.30181	5.91	4.04	4.00	3.90
0.30172	7.45	5.09	5.16	5.06
Sphalerite	ZnO	Zn		
0.30191	0.0	0.0	0.07	0.0
0.30153	0.65	0.52	0.60	0.53
0.30251	1.17	0.94	1.02	0.95
0.30014	2.52	2.02	2.09	2.02
0.30001	3.96	3.18	3.22	3.15
Chalcocite	CuO	Cu		
0.30276	0.0	0.0	0.22	0.0
0.30479	1.53	1.22	1.46	1.24
0.30041	2.60	2.07	2.34	2.12
0.30251	4.94	3.95	4.00	3.78
0.30135	6.18	4.94	5.20	4.98

Effect of reflux time

Table 1 illustrates the effect of the reflux period on the recovery of metal from the oxidation products of galena, sphalerite and chalcocite. Approximately 0.3 g of mineral was used in each determination. The lower lead and copper values refer to those samples of galena and chalcocite which had been previously treated with 15N, 3 H. The oxidation products thus removed had been formed during the grinding and crushing of these minerals. The results in Table 1 clearly indicate that a 5-min reflux period is sufficient to recover the metal in the oxidation products.

Recovery and accuracy

Table 2 summarizes the recovery of zinc and copper for various weights of sphalerite and chalcocite, respectively. This test was not performed for galena because 15N, 3 H is the accepted selective solvent for the oxidation products of this mineral.[3,4] The constant values of zinc and copper irrespective of sample weight indicate the usefulness of 15N, 3 H in determining these metals in the oxidation products of sphalerite and galena, at least for the amounts of oxidation products encountered in this study.

The recovery of known amounts of $PbSO_4$ added to galena, ZnO to sphalerite and CuO to chalcocite was also determined and as Table 3 shows, satisfactory results were obtained, provided of course, that the metal determination is reproducible.

The results in Tables 1 and 2 can be used to calculate the reproducibility. The average value and deviation from the mean are 21.9 ± 0.1 and 0.33 ± 0.02 mg/g for lead from galena (4 determinations for each sample), 0.26 ± 0.02 mg/g for zinc from sphalerite (7 determinations) and 14.7 ± 0.5 and 0.73 ± 0.03 mg/g for copper from chalcocite (7 determinations for each sample). The relative deviation, therefore, varies with the extent of oxidation, but even at low levels of metal is within the 10% frequently encountered (and accepted) in chemical phase analysis.[11]

The ability of the recommended procedure to yield accurate results for galena can be assumed.[3,4] The corresponding ability for sphalerite and chalcocite, however, was determined by comparison with results for the same samples obtained with 30% ammonium acetate solution (shaking at ambient temperature for 1 hr) for sphalerite[5] and 5% sulphuric acid saturated with sulphur dioxide for chalcocite.[6] For sphalerite, samples of 0.25, 0.50 and 1.0 g gave 0.28, 0.24 and 0.24 mg/g for zinc by the recommended procedure and 0.22, 0.21 and 0.19 mg/g with 30% ammonium acetate solution. For chalcocite, the recommended procedure gave 14.7 and 0.73 mg/g for copper and the comparison method yielded 15.0 and 1.4 mg/g. These results are in reasonable agreement when it is noted that the sulphuric acid system generally slightly dissolves the sulphide minerals.[6]

CONCLUSIONS

A 15% ammonium acetate and 3% acetic acid solution can be employed successfully to determine lead, zinc and copper in the oxidation products of galena, sphalerite and chalcocite, respectively, with the limits of reproducibility and accuracy accepted in chemical phase analysis. The recommended procedure is less time-consuming than the available methods for sphalerite and chalcocite; the dissolution period is reduced from ~1 hr to 15 min. In all determinations performed to date, no dissolution of the sulphide mineral has been observed. If, however, such dissolution were to occur, the metal values determined could be easily corrected to take it into account. No such correction is possible in the existing methods for zinc and copper sulphides. The recommended procedure, therefore, is capable of yielding more accurate results for very small amounts of oxidation products, particularly if dissolution of the sulphides is a possibility.

The effectiveness of 15N, 3 H permits the determination of metal in the oxidation products of galena, sphalerite and chalcocite by a single procedure. Moreover, the use of 15N, 3 H allows the simultaneous determination of lead, zinc and copper in the oxidation products of a complex ore containing these sulphide minerals. Indeed, 15N, 3 H has already been so used to compare the extent of oxidation of several samples of MP-1, a certified reference material prepared in this laboratory,[12] to ascertain its long-term stability.

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USE OF A PERIODATE-SENSITIVE PERCHLORATE ION-SELECTIVE ELECTRODE IN THE KINETIC ULTRAMICRODETERMINATION OF MANGANESE(II) BY MEANS OF ITS CATALYTIC EFFECT ON THE PERIODATE–ACETYLACETONE REACTION

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Summary—A kinetic method for the ultramicrodetermination of maganese, based on its catalytic effect on the periodate–acetylacetone reaction, is described. A perchlorate electrode is used as a periodate sensor to monitor the reaction. The time required for the potential to change by a preselected amount (10 mV) is measured automatically and related directly to the manganese concentration. Amounts of manganese in the range 40–240 ng were determined with relative errors of about 2–4%.

Recently we reported that a perchlorate ion-selective electrode responds quantitatively to periodate and described the application of the electrode to the potentiometric determination of vicinal glycols.[1] We have now extended the work to include the application of the perchlorate electrode to monitor other periodate reactions.

A mixture of sodium periodate and potassium permanganate has been used as a mild, specific reagent for the oxidation of various classes of organic compounds.[2] The action of the reagent on various functional groups has been examined to define its specificity.[3] We have studied the periodate–acetylacetone reaction and found that trace amounts of manganese catalyse this reaction. In this communication we describe a kinetic potentiometric method for the ultramicrodetermination of manganese, based on its catalytic effect on the periodate–acetylacetone reaction. The reaction is monitored with a perchlorate electrode acting as a periodate sensor, and the time required for the potential to change by a preselected amount (10 mV) is measured automatically with a solid-state "double-switching" network and related directly to the manganese concentration. Amounts of manganese in the range 40–240 ng were determined with relative errors of about 2–3% and measurement times of only about 15–50 sec.

EXPERIMENTAL

Apparatus

Electrodes and reaction cell. These were the same as previously described.[1] The perchlorate electrode should be conditioned by storing it overnight in a composite 0.01*M* $NaClO_4$–0.02*M* acetylacetone–0.016*M* phosphate pH-6.60 buffer solution.

Recording and measurement system. A pH/pIon electrometer (Heath-Schlumberger Model EU-200-30) is inserted between the electrodes and the recorder as a follower amplifier for impedance matching. A potentiometric recorder (Heath-Schlumberger Model EU-205B) is used to monitor the output from the electrometer and record the reaction curve. A connection in parallel to the recorder input drives a small portion of the current to the double-switching network, which is adjusted to measure the time required for the potential of the electrode to change by 10 mV. A Heath/Malmstadt-Enke EU-805A Universal Digital Instrument (U.D.I) in the "events counter mode" is coupled with the switching network and thus the time is measured automatically as the recorder-pen crosses two preselected positions.[4]

Reagents

All solutions are prepared in demineralized doubly distilled water and from reagent-grade materials.

Acetylacetone (0.40M)–phosphoric acid (0.001M) stock solution. Dissolve 20.0 g of recently distilled acetylacetone in 400 ml of water, add 1.00 ml of 0.50*M* orthophosphoric acid, and dilute with water to 500 ml (in the presence of phosphoric acid the solution is more stable). Store the solution in an amber bottle in a refrigerator.

Phosphate buffer, 0.300M, pH 6.60. Dissolve 10.2 g of $NaH_2PO_4 \cdot H_2O$ in 200 ml of water, adjust to pH 6.60 with 5*M* sodium hydroxide and dilute with water to 250 ml.

Composite 9.3×10^{-4}*M periodate–0.040M acetylacetone work solution.* Pipette into a 500-ml volumetric flask 1.00 ml of 0.050*M* phosphoric acid, 50 ml of acetylacetone stock solution and 9.3 ml of 0.050*M* sodium periodate and dilute with water to the mark. This solution has a pH of about 4 (at this pH practically no reaction takes place between periodate and acetylacetone). Prepare this solution fresh when needed and keep it in an amber bottle.

Manganese stock solution, 2000 ppm. Dissolve manganese metal (> 99.9% pure) in dilute hydrochloric acid or use any manganese(II) salt of known purity. Prepare standards containing 10–60 ppM (part per milliard) of manganese from the stock solution by dilution.

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USE OF A PERIODATE-SENSITIVE PERCHLORATE ION-SELECTIVE ELECTRODE IN THE KINETIC ULTRAMICRODETERMINATION OF MANGANESE(II) BY MEANS OF ITS CATALYTIC EFFECT ON THE PERIODATE–ACETYLACETONE REACTION

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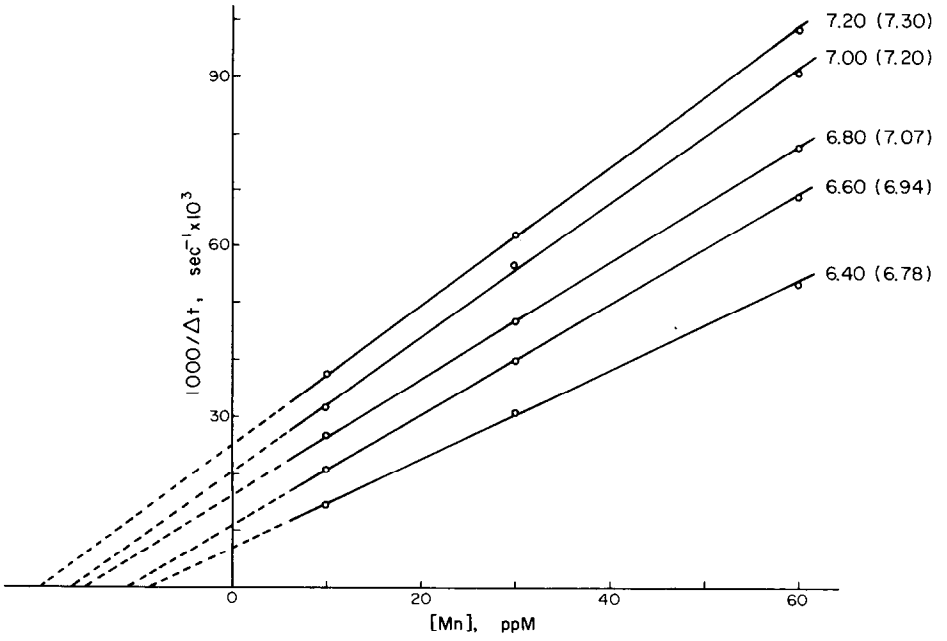

Fig. 1. Working curves for the determination at various pH-values (numbers in parentheses refer to the final pH).

Procedure

Into the reaction cell, kept at 25°, pipette 15.00 ml of composite periodate–acetylacetone solution and 4.00 ml of manganese standard or sample solution. Immerse the electrodes in the solution, start the stirrer and adjust the recorder pen to the right-hand side of the chart with the "offset" control. Press the "Start" button of the U.D.I. and start the reaction by quickly injecting 1.00 ml of phosphate buffer solution with a 1-ml syringe. The time, Δt, needed for the recorder-pen to cross the chart positions indicating a 10-mV change is measured automatically. Empty the cell by suction, rinse the electrodes and cell with water and dry by suction. Repeat the procedure for each analysis.

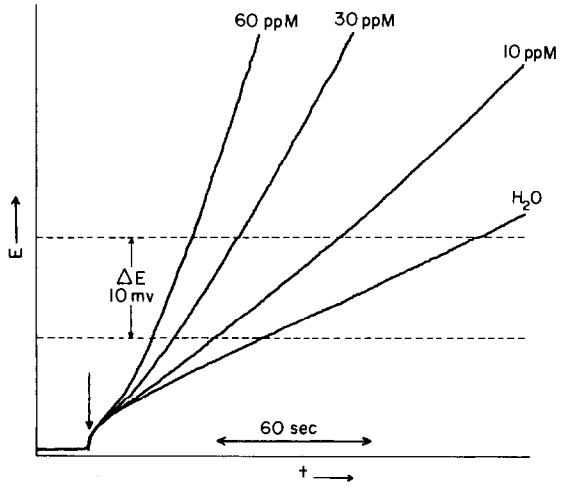

Fig. 2. Recorded curves of cell voltage *vs.* time for periodate–acetylacetone reaction in the presence of Mn(II). Initial concentrations: $NaIO_4$, $7.0 \times 10^{-4}M$; acetylacetone, $0.030M$; Mn, 1.8×10^{-6}–$1.09 \times 10^{-5}M$ (10–60 ppM). Final pH 6.94; total phosphate $0.016M$; ↓: buffer injection.

Calculations

Working curves reading in ppM of manganese(II) are made by plotting $1000/\Delta t$ *vs.* manganese concentration of the standards.

RESULTS AND DISCUSSION

Various ways of starting the manganese-catalysed periodate–acetylacetone reaction were tried. Periodate should be present before starting the reaction, to stabilize the electrode. The precision was poor when the reaction was started with concentrated acetylacetone solution. It is not practical to start the reaction with the manganese solution because at a pH of about 7 the uncatalysed reaction proceeds rather rapidly, thus making the adjustment of the recorder-pen impossible. More accurate and precise results were obtained if the catalysed reaction was started by rapidly increasing the pH with concentrated buffer solution. Since the rate of the catalysed reaction depends greatly on pH the manganese samples should be neutral (sodium hydroxide or hydrochloric acid can be used to bring the pH to about 7), so that the final pH after buffer injection is constant within ± 0.03 pH unit.

Figure 1 shows working curves obtained with phosphate buffers of various pH values. As the pH increases, the

Table 1. Results for the determination of Mn(II) in aqueous solutions

Mn(II), *ng*/4.00 *ml sample*			
	Found*		
Taken	A	B	C
40.0	38	40	40
72.0	73	74	74
120.0	123	122	124
180.0	176	187	190
240.0	244	253	254

* Measurements taken: A, immediately; B, 2 hr and C, 5 hr after the construction of the working curve.

Table 2. Effect of diverse ions on manganese determination at a concentration of $4.55 \times 10^{-7} M$ (25 ppM)

Ion*	Molar ratio to Mn	Sign of error	Ion*	Molar ratio to Mn	Sign of error
Cr^{3+} (NO_3^-)	30	+	Cu^{2+}(SO_4^{2-})	750	−
Co^{2+}(SO_4^{2-})	30	−	Zn^{2+}(SO_4^{2-})	750	+
Fe^{3+}(NO_3^-)	40	+	Cd^{2+}(SO_4^{2-})	750	+
Al^{3+}(SO_4^{2-})	250	+	Ca^{2+}(Cl^-)	800	+
Ni^{2+}(SO_4^{2-})	300	+	Pb^{2+}(NO_3^-)	1000	−
Mg^{2+}(SO_4^{2-})	500	+			

* These ions, when present in the stated ratio, caused a relative error of less than 5%.

measurement-times decrease but the blank increases. A buffer of pH 6.60 was chosen, as giving the best compromise between the reaction-rate and blank effects.

Figure 2 shows typical recorded curves. The corresponding working curve is shown in Fig. 1 (initial pH 6.60). There is good linearity between reaction rate and manganese concentration in the range 10–60 ppM. The working curve should be rechecked every 2–3 hr.

Analysis of aqueous manganese solutions of known concentrations at various times after the construction of the working curve gave the results shown in Table 1. The data indicate that submicrogram amounts of manganese in the range of 40–240 ng in a total volume of 20 ml and be determined with relative errors of 2–4%.

Ten replicate determinations were made with 15- and 45-ppM manganese smaples. The average Δt values were 40.62 sec (range = 1.04 sec) and 19.56 sec (range = 0.72 sec) and the relative standard deviations were 0.9% and 1.3% respectively.

The effect of diverse cations on the determination of manganese by the proposed method is shown in Table 2.

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ANALYTICAL DATA

LUMINESCENCE CHARACTERISTICS OF SEVERAL CLASSES OF DRUGS AFFECTING THE CENTRAL NERVOUS SYSTEM

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Summary—The excitation, fluorescence and phosphorescence characteristics of 29 compounds of psychopharmacological interest have been studied in ethanol at 77 K. Phosphorescence lifetimes are reported and the low-temperature luminescence spectra discussed. Luminescence characteristics of several important 1,4-benzodiazepines in acidic, basic and neutral solution are reported.

It has become clear that several important drugs used in psychiatry exert their clinical effects by affecting the synaptic action of the catecholamines in the brain. It is therefore important to understand the events at the noradrenergic synapses and to obtain further information on how the amines are released and subsequently inactivated. At present such information can only be obtained indirectly by *in vitro* studies or studies at peripheral receptor sites; in either case one of the major limiting factors is the estimation of extremely low levels of these drugs and the so-called transmitter substances.

Phosphorimetry has become an accepted analytical tool for the study and determination of compounds of clinical interest[1] and the purpose of the present work[2] was to determine the phosphorescence characteristics of some catecholamines and of several classes of psychotropic drugs which affect catecholamine metabolism. The luminescence of these drugs has so far been little studied. Spann *et al.*[3] described the phosphorescence of a number of catecholamine metabolites in a mixed methanol–water solvent. Miles and Schenk[4] listed the excitation, fluorescence and phosphorescence wavelengths and fluorescence:phosphorescence ratios of amphetamine and several related compounds, and a recent publication by de Silva *et al.*[5] describes the phosphorescence of some benzodiazepines in strongly acidified ethanol. The luminescence properties of the phenothiazines have already been described in detail by the present workers.[6]

EXPERIMENTAL

A Baird Atomic SF 100E spectrofluorimeter fitted with a 150-W Xenon source was used. Excitation and emission slits were fixed to provide a spectral bandpass of 6 nm. Phosphorescence measurements at 77 K were made with a rotating cylinder phosphoroscope and Spectrosil sample tubes (1-mm wall, 2-mm bore). A Bryans 26000 x–y recorder was used to record excitation and emission spectra and a Bryans 27000 x–t strip recorder was used to determine lifetimes >0.2 sec. Lifetimes shorter than 0.2 sec were recorded on a Remscope SOI storage oscilloscope.

Stock solutions of the drugs (100 μg/ml) in ethanol were prepared. The effect of pH on the characteristics of the 1,4-benzodiazepines was tested by making the stock solution 1*M* in hydrochloric acid or sodium hydroxide.

Most of the samples were generous gifts from various drug companies.

RESULTS AND DISCUSSION

The excitation, fluorescence and phosphorescence wavelength maxima and phosphorescence lifetimes of 29 compounds for which data are desirable in the study of central nervous system action are given in Table 1.

The phosphorescence properties of the catecholamines (compounds 1–4) in ethanol solution are similar to those obtained by Spann *et al.*[3] in a largely aqueous solvent. Another biogenic amine, 5-hydroxytryptamine, has quite different properties, its phosphorescence spectrum being similar to that of tryptophan, albeit with a shorter lifetime.

Drugs derived from thioxanthene are closely related in structure and metabolism to the phenothiazines, and the luminescence properties of thioxanthene itself and of chlorprothixene are fairly similar to those of most of the phenothiazines.[6] Thiothixene, on the other hand, exhibits fluorescence and not phosphorescence, a sharp contrast to the most closely related phenothiazine thioproperazine, which is only very feebly fluorescent.

Of the dibenzazepine tricyclic antidepressants (compounds 9–17) only desimipramine, chlorimipramine and trimipramine are phosphorescent: preliminary studies indicate that they can be detected at levels of approximately 1 μg/ml. As with the phenothiazines, this phosphorescence may derive from an n–π^* triplet state, involving the electron pair of the bridging nitrogen atom. Iprindole and dibenzepin are also phosphorescent, the properties of iprindole being similar to those of indole itself. Of the remaining tricyclic antidepressants, opiprimol and protriptyline are fluorescent but not phosphorescent, and amitriptyline, nortriptyline, doxepin and prothiaden are non-luminescent.

The amphetamines and a number of monoamine oxidase (MAO) inhibitors (compounds 20–26) contain benzene rings with ethylamine, piperidine, morpholine and alkyl hydrazine side-chains. All these compounds exhibit phosphorescence, with very long lifetimes characteristic of π–π^* transitions. In studies of a group of amphetamines Miles and Schenk[4] showed that these molecules exhibit fluorescence in acidic solutions and that they could be analysed at the 1 μg/ml level. The structurally-distinct MAO inhibi-

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Table 1. Luminescence characteristics of psychotropic drugs in ethanol at 77 K

No.	Compound	Excitation maxima, *nm*	Fluorescence maxima, *nm*	Phosphorescence maxima, *nm*	Phosphorescence lifetime, *sec*
	Catecholamines				
1	L-epinephrine	(255)* 295	—	435	0.5
2	DL-3,4-dihydroxymandelic acid	(255) 295	—	420	0.8
3	vanillylmandelic acid	(255) 290	—	430	0.6
4	normetanephrine	275	—	440	0.6
5	5-hydroxytryptamine	(235) 290 315	—	(430) 450	4.4
	Thioxanthenes				
6	thioxanthene	280	—	460	<0.2
7	chlorprothixene	(260) (310) 385	—	470	<0.2
8	thiothixene	335	385	—	—
	Tricyclic antidepressants				
9	desimipramine	300	—	455	0.95
10	chlorimipramine	305	—	450–470	0.12
11	trimipramine	300	—	450–470	0.70
12	opiprimol	(300) 365	520	—	—
13	amitriptyline	—	—	—	—
14	nortriptyline	—	—	—	—
15	protriptyline	320	355–375	—	—
16	doxepin	—	—	—	—
17	prothiaden	—	—	—	—
18	dibenzepin	330	—	470	0.09
19	iprindole	310	340–350	(425) 450 (485)	5.3
	CNS stimulants				
20	amphetamine	270 (355)	—	385	10.6
21	dexedrine	270 (355)	—	385	10.4
22	pipradol	(235) 265	—	395	6.1
23	phenmetrazine	265	—	385	7.4
	MAO inhibitors				
24	phenelzine	265	—	400	10.5
25	tranylcypromine	285	—	415	7.0
26	mebanazine	270 (285) 370	—	430	9.0
27	nialamide	320	—	470	<0.2
28	iproniazid	300 (370)	—	440	<0.2
29	isocarboxazid	320 (355)	—	410–435	<0.2

* Figures in brackets indicate subsidiary maxima in the spectra.

Table 2. Luminescence characteristics of some 1,4-benzodiazepines at 77 K

Compound	Conditions	Excitation, *nm*	Fluorescence, *nm*	Phosphorescence, *nm*	Phosphorescence lifetime, *msec*
Chlordiazepoxide	Acid	(295)* 365	—	485	102
	Base	310 (320)	—	(450)* 470	164
	Neutral	360	435	—	—
Medazepam	Acid	(318) 364	390–490	520	102
	Base	(280) 370	450	(450) 495 (530)	142
	Neutral	385	450	(450) 495 (530)	140
Oxazepam	Acid	(270) (312) 370	—	490	88
	Base	(285) 370	—	490	126
	Neutral	(295) 335	—	(445) 475 (510)	76
Diazepam	Acid	(360) 380	—	480	94
	Base	(290) 325	—	(445) 475 (512)	62
	Neutral	335	—	(440) 470 (510)	70
Flurazepam	Acid	(320) 370	—	475	80
	Base	(280) 330 (370)	—	(450) 475 (510)	172
	Neutral	(290) 325	370	(435) 470 (500)	56
Nitrazepam	Acid	378	—	(525) 555	310
	Base	395	—	(515) 535	320
	Neutral	363	435	—	—

* Figures in brackets indicate subsidiary maxima in the spectra.

tors nialamide, iproniazid and isocarboxazid exhibit very feeble phosphorescence which is not likely to be of analytical value.

The luminescence characteristics of some 1,4-benzodiazepines in neutral, acid (0.1*N* sulphuric acid), and basic (0.1*N* sodium hydroxide) solutions are shown in Table 2. Comparison of the results obtained in acid solution with those of de Silva *et al.*[5] (who used a more strongly acidic medium) reveals close agreement of the wavelength maxima in most cases. The phosphorescence lifetimes of the benzodiazepines, reported here for the first time, all fall in the range 60–320 msec, indicating the existence of an n–π^* transition. In many cases, preliminary data show the feasibility of determining benzodiazepines at the submicrogram level. The effects of pH on their luminescence spectra are complex, and will be discussed comprehensively in a forthcoming publication (L. A. Gifford, L. A. King and J. N. Miller, in preparation).

These findings indicate that phosphorimetric analysis could often be used to obtain information concerning the mechanism of psychotropic drug interactions not previously obtainable because of insensitive analytical methods. The lifetime data presented will facilitate the resolution of mixtures by time-resolved phosphorimetry,[7] and complex samples can also be studied by thin-layer phosphorimetry,[8] in which the sensitivity of luminescence spectroscopy is combined with the selectivity of thin-layer chromatography.

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DIRECT ATOMIC-ABSORPTION SPECTROMETRIC ANALYSIS OF GEOLOGICAL MATERIALS—A REVIEW

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Summary—A review is given of the problems likely to be encountered in the atomization of solid samples of geological materials, and of the applications of this technique.

Atomic-absorption spectrometry (AAS) based on atomization in flames is now a well-established and universally employed technique for simple, rapid and—above all—inexpensive determination of a large number of major, minor and trace elements in a variety of materials, including those of importance to geology and the mining and metallurgical industries.

During recent years much work has been devoted to the problem of replacing the conventional method of atomization in flames by more sensitive and convenient methods. Among the new techniques, atomization in non-flame cells has been found particularly promising. Compared with flame atomization, the non-flame cells have the advantages of requiring smaller amounts of sample, having lower limits of determination, and being well suited for direct atomization of minor and trace elements from solid samples.

The principle of analysing geological materials by atomizing the components directly from the solid state offers some definite advantages: the time-consuming decomposition step can be omitted, and the analysis can be done without addition of reagents and without any separation and/or concentration steps; the risks of introducing contamination and of losing the element to be determined are thus considerably reduced.

The disadvantages of direct AAS analysis of solid geological materials are that the method is destructive, normally only one element can be determined at a time, the use of small samples may introduce serious sampling errors, and the non-specific absorption of radiation during atomization may exceed the maximum compensating capacity of the background corrector.

The present paper gives a survey of the equipment and methods of the direct-atomization technique and its applications to the analysis of geological materials. The spectroscopic principles of the method and the construction of the AAS instruments will not be treated, discussion of these aspects being confined to pointing out the demands which the present technique makes on the instrumentation.

In most direct analysis of geological materials solid or liquid matrix particles and matrix molecules cause considerable background absorption which may introduce serious systematic positive errors. It is therefore imperative that the instrument is equipped with a device which compensates for this interference. Today most commercial AAS instruments are equipped with a background corrector, the correction for non-specific absorption of radiation being based on measurement of atomic absorption plus background, and of the background alone.

It should be noted that the arc-source deuterium lamps normally employed for background corrections only cover the wavelength range 180–350 nm. Some manufacturers offer instruments equipped with two background correctors, the second being a tungsten lamp containing some iodine. This lamp compensates for non-specific absorption in the wavelength range 300–700 nm. It is recommended to use the tungsten lamp for background corrections down to about 300 nm; in this way the lifetime of the much more expensive deuterium lamp may be considerably prolonged.

It should further be noted that the background correctors are only capable of compensating for a certain amount of non-specific absorption. Specifications from instrument manufacturers indicate maximum correction capacities ranging from about 65% absorption (absorbance 0.46) to approximately 99% absorption (absorbance 2.0).

The capacity of background correctors may be measured by inserting sieves of varying mesh-size in the light-path of the instrument.

Some authors and producers of commercial AAS instruments recommend basing the analysis on peak-heights. For high rates of atomization and sharp peaks to be obtained the sample must be heated rapidly to high temperatures. However, even at high atomization temperatures, the form of the peak varies with the composition of the matrix; the combination of high atomization temperatures and high rates of atomization may also produce non-atomic absorbing species in such quantities that the compensating capacity of the background corrector is exceeded; under these conditions the cell-life will also be reduced.

It is now generally accepted that analysis should be based on peak-areas instead of peak-heights; this technique allows the use of lower atomization temperatures and rates of atomization.

The atomization cell should be equipped with a power supply which permits ramp heating, *i.e.*, a gradual heating of the cell. A low rate of heating between the drying, ashing and atomization steps reduces the risks of violent reactions and sputtering.

A fast-response read-out system is essential in order to record the rapid transient absorption signals obtained during the atomization step.

The atomization cells which have been employed in the direct AAS analysis of geological materials may be classified in the following groups.

1. Flame cells

Devices have been constructed for introducing pulverized geological materials, such as silicate rocks, into flames;[1] however, most of these devices were made for flame emission work. Equipment for AAS determination of some of the alkali metals and of lead in silicate rocks is described by Govindaraju *et al.*[2] In some laboratories this type of cell is used in routine analysis of silicate rocks.

Experiments on the possibility of AAS analysis of soils, rocks and minerals by introduction of the powdered materials into flames by means of a standard nebulizer–spray chamber–burner system have been reported by Willis.[3] However, the accuracy obtained by this technique was less satisfactory.

2. Tube cells, crucible cells, or combinations of these cells

Devices in the form of a tube, a crucible, or a combination of these forms are the most common type of atomization cell. Figure 1 shows schematically the construction of these three main types of cells.

Tube furnaces for recording or comparing atomic-absorption lines or spectra were constructed by King[4] in 1908 and by Müller[5] in 1927.

Pioneer work on the construction, theory and application of electrothermal atomization cells for analytical purposes was started by L'vov[6] in 1959; in a series of papers he and his co-authors have laid the foundation for later developments in this field.

A survey of the literature shows that more than 30 papers deal with the construction of cells of this type (for a more comprehensive survey of non-flame cells, see the review by Kirkbright[7]); a selection of these cells is also commercially available.

The cells are normally made of high-purity graphite of the quality used for emission spectrography. To reduce the porosity of the graphite and prolong the life of the cell, the interior surface of the cell may be coated with a layer of pyrolytic graphite,[8] or a metal carbide,[9] *e.g.* of tantalum or niobium. It is also possible to make cells of glassy carbon, which is more dense than the normal or pyrolytically coated graphite. Some tube cells are also made of metal, *e.g.* tungsten; however, there seems to be a tendency to prefer graphite as the material for making atomization cells.

The cells are normally heated by resistance or induction circuits.

The disadvantages of many of these cells are that they require a considerable amount of electric power (up to 15 kW), that some of them exhibit memory effects when metal or matrix materials condense on and are later re-evaporated from the cooler parts of the tube, and that the price of the equipment is high.

Some general conclusions may be drawn about the applicability of this group of atomization cells to the direct analysis of geological materials. The most suitable tube cells are those which have an inner diameter larger than about 6 mm; it is difficult to introduce solid samples into tubes of smaller diameter, and the sample is also likely to interfere with the beam from the radiation source.

Most crucible cells, as well as the combination of crucible and tube cells, can be expected to be suited for direct analysis of geological materials.

3. Other atomization cells

In addition to the types of cells described above, some special cells have been found applicable to the direct analysis of solid geological samples.

It is not unexpected that the d.c.-arc has been utilized as an atomization cell. Belyaev *et al.*[10] describe the use of this equipment for AAS determination of cadmium and silver in nepheline syenites.

As demonstrated by Vul'fson *et al.*[11] atomic vapour may also be produced by laser radiation. This technique was used for the determination of silver, copper, manganese and zinc in silicate minerals and rocks.

Atomization cells consisting of an electrically heated carbon rod placed horizontally in a flame are described by various authors; the pulverized solid

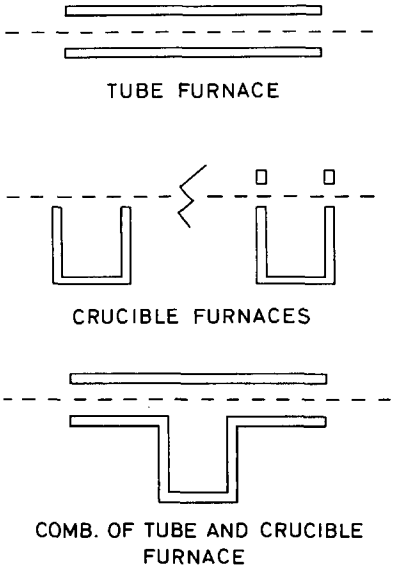

Fig. 1. Types of furnace.

samples are placed by Borzov *et al.*[12] in an open crater in the rod, and by Katskov *et al.*[13] in an axial hole in the rod (the hole then being closed with graphite powder). It is interesting to note that the latter construction prevents sputtering during heating, and that the measurements are based upon diffusion of atomic vapour through the porous graphite walls of the rod.

It has been shown by Gatehouse and Walsh[14] that cathodic sputtering is an efficient technique for producing atomic vapours from metals and alloys. The technique is also applicable to the analysis of non-conductive materials, such as rocks and ores, but it is then necessary to mix the sample with metal powder, *e.g.*, copper, to make it conductive.

The solid-propellent technique, based upon mixing a solid pulverized sample with a propellent powder, pressing the mixture to form a tablet and burning it below the light-path of an atomic-absorption spectrometer, is a simple and interesting method,[15] but does not seem to be used to any great extent.

In this survey of atomization cells the strip-cells—made of carbon or metal—have not been mentioned. These cells have some attractive advantages, but—to the best of the author's knowledge—they do not seem to have been applied to direct analysis of geological materials.

The reactions of geological materials during heating in atomization cells are complicated by the non-equilibrium conditions which may prevail during many atomization processes, and the high temperatures and correspondingly high rates of reaction. However, some of the reactions that have been studied and some that are likely to occur when geological materials are heated in carbon atomization cells and in an inert atmosphere will be discussed shortly.

Atomization cells are normally equipped with manually or automatically controlled power-supplies which allow heating in four stages, *viz.* the drying, ashing, atomization and cleaning steps.

During the drying at about 100° the main reaction is the removal of hygroscopic water. However, some highly volatile elements, such as mercury, may be lost during this operation.

The main purpose of the ashing step (heating at 400–500°) is to destroy organic matter; however, as many geological materials do not contain appreciable amounts of organic matter, the ashing step may be omitted.

When the samples contain hydroxides, carbonates, sulphates, nitrates, *etc.*, it is recommended that before atomization the salts should be converted into the corresponding oxides by heating at 800–1000°.

Atomizations are made at temperatures ranging from below 1000° up to about 3000°; in most analyses atomizations are made in the range 1500–2500°.

On heating, most silicate minerals and rocks behave like weakly associated aggregates of simpler oxide groups; at temperatures above 1000°, the silicate lattices break down and a melt is obtained.

The most likely reaction to occur when metal oxides are heated in contact with carbon is the reduction of the oxide to gaseous metal atoms and the formation of carbon monoxide. On calculating the temperature at which this reduction is thermodynamically feasible, and measuring the temperatures at which the first absorption signals were detected when metal oxides were heated in a graphite atomization cell, Campbell and Ottaway[15] found, for 22 of the 27 elements tested, that the agreement between the temperatures supported this theory. However, agreement with theory appeared to be poor for tin, potassium, antimony, calcium and magnesium; of these the metal vapour of the former three metals appeared at higher temperatures than predicted. A possible explanation for this is that although the reduction of the oxides is thermodynamically feasible, the rate of reduction may be too slow to produce a substantial population of free atoms until much higher temperatures are reached. These authors also pointed out the fact that at high temperatures potassium and antimony exist in associated forms. However, they could give no plausible explanation for calcium and magnesium signals appearing at temperatures much lower than predicted.

Similar calculations and experiments with graphite and tantalum atomization cells were made by Aggett and Sprott,[17] who concluded that carbon does not act as a reducing agent for aluminium, cadmium, calcium, magnesium, manganese and zinc, though it is active as a reducing agent for cobalt, nickel, iron and tin. A third group consists of the elements bismuth, chromium, copper and lead; despite favourable free energies for the reduction of the oxides by carbon, the metal vapours appear at higher temperatures than expected. The authors assume that in these systems the rate of the reduction of the oxides is slow relative to their thermal dissociation.

It should be pointed out that the two papers do not agree as to the behaviour of the various oxides in the graphite furnace and that for a number of systems the temperatures of the appearance of measurable amounts of metal vapour differ considerably.

As pointed out by Fuller,[18] these treatments do not take into consideration the formation of thermodynamically stable carbides of aluminium, calcium, chromium, molybdenum, titanium and vanadium. The formation of these carbides may take place at or below the temperatures at which ΔG° for the reduction of the oxides with carbon is zero.

For a number of elements, such as iron, copper, nickel, cobalt, tin, lead and bismuth, reduction of the oxides by carbon to the solid metal is thermodynamically feasible at relatively low temperatures. However, at these reduction temperatures no absorption signals may be observed, either because the rate of reaction is too low, or because the vapour pressure of the metals is not sufficiently high.

The only kinetic approach to atomization processes in a graphite cell was made by Fuller.[18] He studied

the behaviour of copper in the temperature range 1450–1950° and derived a rate-equation describing the variation of the amount of copper atoms with time. It was shown that the most probable reaction mechanism is a slow first-order reaction involving reduction of copper oxide by carbon, followed by a rapid volatilization of copper.

So far the present discussion has been limited to the reactions of oxides, or materials transformed into oxides by heating. No systematic studies seem to have been made of the behaviour of other geological materials, such as the industrially important sulphides, in carbon atomization cells.

When sulphide minerals and ores are heated in graphite furnaces to temperatures in the range 500–1000°, di- and polysulphides give off sulphur; in the author's laboratory it was found that at around 1500° the monosulphides produced either decompose or react with carbon. Iron-containing materials, such as pyrites, leave a residue—probably of iron carbide—in the furnace.

From the literature on the reactions in carbon atomization cells, it appears that many of the reactions are not yet fully understood and that further studies are required.

A survey of the literature on the application of the technique showed that the amounts of sample taken for analysis may vary from less than 1 mg up to about 500 mg; in most procedures amounts ranging from 5 to 20 mg were atomized. A convenient sample-manipulation technique for tube furnaces is to weight out a series of samples in small tantalum scoops. A sample is placed in the middle of the furnace by fastening the scoop to the end of an adjustable inserting device, moving the device into a preselected position, and emptying the scoop by turning it. (The scoops and the insertion device are produced by Perkin-Elmer.)

The determination of minor and trace elements in small samples raises a number of problems relating to sampling errors. In geological materials the minor and trace elements may be considered either to be evenly distributed in one or more of the major minerals, or to be present as discrete particles disseminated throughout the sample; as would be expected, the former case gives smaller sampling errors.

To demonstrate the order of magnitude of the sampling error under the conditions of the less favourable distribution, the method of Wilson[19] was applied by Solberg[20] to estimate the sampling error for mercury(II) sulphide distributed in a matrix of iron(II) sulphide. In Table 1 the relative standard deviation of the mercury content is given for various particle sizes and for 5-mg samples containing 1, 3, 10 or 30 ppm of mercury. From the table it appears that the sampling errors may be serious under combinations of unfavourable conditions.

It should, however, be mentioned that under favourable conditions the solid-sample technique may give satisfactory precision; in the author's laboratory relative standard deviations of 1% were obtained in the determination of about 100 ppm of rubidium in silicate rocks.

Some analysts have advised against the use of the technique on the grounds that the use of small samples introduces too-large sampling errors. However, in most analyses the amounts atomized correspond to the masses arced or sparked in atomic emission spectrographs, so the sampling errors of the two methods can be expected to be the same. It is surprising that the critics of the direct-atomization technique do not seem to have similar objections to the use of atomic emission.

In order to reduce the sampling errors to a minimum, samples of geological materials should be ground to a very fine state of subdivision. Most geological materials are relatively easily ground, *e.g.*, with an agate mortar and pestle, to pass a 270-mesh (53-μm) sieve, but further grinding, *e.g.*, to 400 mesh (31-μm) may take considerable time; with certain materials, *e.g.*, mica, there may be difficulty in grinding them to pass even a 270-mesh sieve. It should be noted that certain elements, such as mercury, may be lost during grinding of geological materials.

In some analyses sharper signals are obtained when the samples are mixed with graphite. The addition of graphite, *e.g.*, to samples of silicate rocks, prevents the sample from forming a molten globule, thus promoting the reduction and atomization processes; during the atomization of other materials, such as apatite, the matrix attacks the graphite severely; in these instances the addition of graphite to the sample prolongs the life of the furnace.

As pointed out by L'vov,[21] AAS analysis can be done without standards, *i.e.*, an "absolute" analysis is possible; however, this principle does not seem to

Table 1.

Particle diameter, μm	ASTM mesh number	Approx. number of particles per 5 mg of sample	Relative standard deviation of the Hg content, %			
			1 ppm	3 ppm	10 ppm	30 ppm
105	140	1.6×10^3	232	134	73	42
53	270	1.3×10^4	81	47	26	15
37	400	3.8×10^4	48	27	15	9
20	—	2.4×10^5	19	11	6	3.5
10	—	1.9×10^6	6.7	3.9	2.1	1.2

Table 2. Direct AAS analysis of geological materials—applications

Materials analysed	Elements determined	References
Aluminium oxide	Cu	12
Aluminium oxide	Cu, Mg, Fe	13, 23
Barium carbonate	Co, Cu, Fe	13
Bauxite	Ga, In	23
Chromium oxide	Cu	11
Clay	Ga, In	23
Copper ores	Cu	15
Gold ores	Au	24
Gold ores tailings	Au	24
Iron ores	Fe	15
Iron oxide	Cu	12
Laterite	In	23
Lead ores	Pb	15
Magnesium oxide	Cu	12
Manganese ore	Co	13
Mercury ores	Hg	15
Phosphate rock concentrates	Ag, Bi, Cd, In, Pb, Tl, Zn	25
Quartz	Au	24
Quartz (amorphous)	Au	13
Silica	Cu	13
Sulphide ores	Ag, Bi, Cd	26
Sulphide ores	In	23
Sulphide ore concentrates	In	23
Silicate minerals and rocks	Ag	27
	Ag, Cd, Pb, Tl, Zn	28
	Ag, Cu, Mn, Zn	11
	Cd	29,30
	Co, Cu, Sn, Tl	13
	Co	13
	Cs	32
	Cs, Rb	33
	Cu	34
	Hg	35
	Li	36
	Pb	37
	Rb	2
	Tl	38
Zinc oxide	Cu	12
Zirconium dioxide	Sb	13

have been employed in any direct analyses of geological materials.

The analysis of geological materials by the technique is based on one or more of the following four standardization techniques:

(*a*) measurements against standard solutions; (*b*) measurements against natural solid reference materials; (*c*) measurements against synthetic solid reference materials; (*d*) measurements according to the standard addition technique.

In a few cases, such as in the determination of cadmium in silicate rocks, it has been found possible to analyse solid samples by measurements against a series of standard solutions prepared from high-purity metals or compounds (preferably dissolved in nitric or sulphuric acid). In these instances the sample and the standards have a different matrix composition and the absorption signals are also likely to be different. It is recommended to base these measurements on addition of equal volumes of standard solutions, and measurement of peak-areas instead of peak-heights. It should be noted that in this solid-sample/liquid-standard technique the atomization mechanisms are different, because the standards will be present as very much thinner layers of oxide and/or carbide after the ashing stage.

When reliable solid reference materials are available with matrixes corresponding to those of the samples, measurements against such materials are to be preferred. However, as most analysts will know, the selection of reliable solid reference samples of geological materials with certified or recommended contents of minor or trace elements is rather limited.*

When reference materials are employed for calibration purposes, the reference value should always be given; if this value is changed, the analytical data based on it can also be corrected.

The content of an element in a reference material, or any other material having a suitable matrix composition, can of course also be established by analysis. Trace element contents can often be determined by decomposing the sample and determining the contents by the conventional AAS flame methods, or by

* Lists of suppliers of standard reference materials are published.[22]

atomizing the sample solution in a graphite furnace, or by any other suitable method. These important determinations should be made by at least two different methods.

When no suitable natural solid reference materials are available, it is possible to use synthetic solid reference samples. Such samples are produced commercially with a graphite or silica matrix; they may also be prepared from pure substances and with a matrix resembling that of the sample. However, the preparation of such samples is tedious and time-consuming.

Finally, it is possible to apply the standard addition technique by adding standard solutions to a series of solid samples which have been weighed accurately and have approximately the same mass. It is again recommended to add a constant volume of the standard solutions, to let the standard solution soak into the sample, and to employ the method of least squares for establishing the standard addition curve. The calculations are conveniently made with a computer, which may be programmed to give not only the intercept on the abscissa, which indicates the mean value, but also the standard deviation.

In a few laboratories geological materials are analysed on a routine basis by the solid-sample technique, but the application is still rather limited. Table 2 gives a survey of the applications of the technique to the analysis of geological materials.

From the table it appears that the method has been applied to the determination of about 20 elements in a variety of geological materials; the elements were present in concentrations varying from about 100 ppm to less than 1 ppM (part per milliard).

The accuracy of the present technique depends upon the systematic errors from the equipment, methods and standards, so no data can be given. However, this method of analysis can be expected to result in accuracies at least as good, or better than those obtained by conventional methods of trace analysis.

As to the precision of the direct atomization methods, relative standard deviations of 5–10% can be expected at the 1-ppm level; similarly, at the 1-ppM level, values ranging from 20 to 30% have to be considered as normal.

The developments during the past 5–6 years have demonstrated that direct AAS analysis for minor and trace elements in geological materials offers some definite advantages, which have not yet been utilized by analysts working in geology and in the mining and metallurgical industries. From the literature on this technique it appears that practically all analyses have been performed with home-made atomization cells; it is now up to the manufacturers of atomic-absorption instruments to construct and offer suitable equipment for routine work. When commercial instruments are available, the method can be expected to be universally applied to many more elements and materials.

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SPEKTRALPHOTOMETRISCHE CHARAKTERISIERUNG VON TERNÄREN KOMPLEXEN IN LÖSUNG DURCH INDIREKTE ANALYSE MIT HILFE LINEARER TRANSFORMATIONEN

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Zusammenfassung—Zur spektralphotometrischen Charakterisierung einkerniger ternärer Komplexe in der Lösung werden lineare Transformationen angegeben, die eine indirekte graphische Analyse der experimentell ermittelten Funktionen $E = f(\text{Ligandenkonzentration})$ sowie $E = f(\text{pH})$ gestatten. Neben Molarkoeffizienten und Protonenbilanzen erhält man dabei auch die Werte von Reaktionskonstanten und Extinktionskoeffizienten. Berücksichtigung finden neben einfachen Gleichgewichten auch Substitutionsgleichgewichte zwischen binären und ternären Komplextypen, wobei im untersuchten Bereich ein einheitliches Gleichgewicht vorliegen muß. Es werden Hinweise zur praktischen Durchführung der Auswertung gegeben und die zu beachtenden Bedingungen bei der Anwendung der Transformationen mitgeteilt.

Ternäre Komplexe gewinnen in der chemischen Analytik immer mehr an Bedeutung, und wegen der hohen Selektivität sind sie auch schon praktische angewendet worden.[1–3] Noch mehr als bei binären Systemen muß man aber für den Einsatz Bildungsbedingungen und andere komplexchemische Fakten kennen. Untersuchungen von Systemen M, L, L in Lösung unter Berücksichtigung ternärer Komplextypen sind erst in letzter Zeit in den Vordergrund getreten.[4]

Obwohl die Untersuchung gegenüber binären Systemen naturgemäß komplizierter ist, sind die experimentellen Methoden sowie die Verfahren der Auswertung zur Untersuchung von ternären Komplexgleichgewichten denen für binäre Systeme weitgehend äquivalent. Häufig werden potentiometrische sowie spektralphotometrische Verfahren[5] herangezogen, aber auch polarographische- und Extraktionsverfahren haben eine gewisse Bedeutung erlangt.[6] Die spektralphotometrischen Methoden gestatten in den meisten Fällen für die Reaktion

$$M^v + mH_aL^w + nH_bL'^y \rightleftharpoons (MH_jL_mL'_n)^z + xH^+$$

neben den Umsatzvariablen m und n—wie bei binären Typen[7]—nur die Ermittlung einer scheinbaren Stabilitätskonstante, weil Kenntnisse zur Protonisierung der Liganden im Komplex fehlen. Sind die Größen ϵ, m, n, bekannt, dann kann man die scheinbare Stabilitätskonstante in vielen Fällen bestimmen.[8] Es ergeben sich jedoch oft Schwierigkeiten, weil der zur Auswertung benötigte Wert des Extinktionskoeffizienten von $ML_mL'_n$ nicht bekannt ist bzw. sich nicht einfach ermitteln läßt, da selbst unter optimalen Bedingungen keine vollständige Komplexbildung vorliegt.

In der vorliegenden Arbeit werden für die wichtigsten Reaktionsmöglichkeiten (einkernige Komplexe) im System M, L, L′ ganz allgemein gültige Gleichungen abgeleitet, welche die mathematische Analyse der experimentell ermittelten Funktionen $E = f(\text{Ligandenkonzentration})$ und $E = f(\text{pH})$ ermöglichen. Neben dem Molarkoeffizienten und der Protonenbilanz erhält man auf dem angegebenem Wege auch unmittelbar den Wert des Extinktionskoeffizienten und der Reaktionskonstanten, wenn auf Grund experimenteller Voraussetzungen nur ein spezieller Reaktionsmechanismus vorliegt. Ähnliche Transformationen haben sich bei komplizierten binären Komplexgleichgewichten bewährt, wie Arbeiten von Sommer,[9,10] z.B. zeigen. Die Geradenmethode nach Asmus[11] zur Untersuchung einfacher Komplexe ist als Sonderfall der von Sommer angegebenen Transformationen unter vereinfachten Bedingungen anzusehen.

Aus der allgemeinen Form von Transformationen für mehrkernige Komplexe[12] lassen sich unter bestimmten Randbedingungen Gleichungen herleiten, mit denen man einige Gleichgewichte unter Beteiligung ternären Teilchen interpretieren kann.

Auch das Verfahren von Newman und Hume[13] gestattet die spektralphotometrische Untersuchung von Systemen M, L, L′ mit Hilfe linearer, logarithmischer Transformationen, die aber keine Aussagen über die Protonenbilanz der Reaktionen gestatten.

Verwendete Symbole

C_M	Gesamtkonzentration an Metallionen in mol/l.
C_L	Gesamtkonzentration des Liganden L in mol/l.
$C_{L'}$	Gesamtkonzentration des Liganden L′ in mol/l.
$[\bar{M}]$	freie Metallionenkonzentration in mol/l.

$$[\bar{M}] = [M(OH)_z] + [M(OH)_{z-1}] + \cdots [M] = \sum_{i=z}^{0} [M(OH)_i]$$

$[\bar{L}]$ freie Ligandenkonzentration L in mol/l.

$$[\bar{L}] = [H_aL] + [H_{a-1}L] + \cdots [L] = \sum_{i=a}^{0} [H_iL]$$

$[\bar{L}']$ freie Ligandenkonzentration L' in mol/l.

$$[\bar{L}'] = [H_bL'] + [H_{b-1}L'] + \cdots [L'] = \sum_{i=b}^{0} [H_iL']$$

E Extinktion $E = \log(I_0/I)$

d Schichtdicke in cm

ϵ molarer dekadischer Extinktionskoeffizient in l. mol^{-1}. cm^{-1}

μ Ionenstärke $\mu = \frac{1}{2}\sum_i z_i^2 c_i$

$[\ ]$ Gleichgewichtskonzentration in mol/l. bei μ = konst.

m, n, r, r' Molarkoeffizienten

x Protonenbilanz einer Reaktion

K' scheinbare Gleichgewichtskonstante für μ = konst.

K Gleichgewichtskonstante für μ = konst.

$K_{sL}, K_{sL'}$ Dissoziationskonstante von H_aL bzw. H_bL' für μ = konst.

$$K_{sL} = [H_{a-1}L][H^+]/[H_aL]$$

$$K_{sL'} = [H_{b-1}L'][H^+]/[H_bL']$$

a Anstieg einer Geraden $y = ax + b$; $a = \tan\alpha$

b Ordinatenabschnitt der Geraden $y = ax + b$ für $x = 0$

ALLGEMEINE VORAUSSETZUNGEN

Im System M, L, L' bestehen je nach den Bedingungen eine Vielzahl von Reaktionsmöglichkeiten, welche zurückgeführt werden können auf:

1. Bildung binärer Komplexe
2. Bildung ternärer Komplexe
3. Bildung von Teilchen, die durch Konkurrenzreaktionen des Metallions mit OH^- bzw. der Liganden mit H^+ entstehen.

Unter Vernachlässigung mehrkerniger Hydrolyseprodukte und Voraussetzung einkerniger Komplexe kann man schreiben:*

$$C_M = [\bar{M}] + \sum_{j=0}\sum_{m=0}\sum_{n=0}\sum_{k=0} [MH_jL_mL'_n(OH)_k] \quad (1)$$

$$C_L = [\bar{L}] + \sum_{j=0}\sum_{m=0}\sum_{n=0}\sum_{k=0} m[MH_jL_mL'_n(OH)_k] \quad (2)$$

$$C_{L'} = [\bar{L}'] + \sum_{j=0}\sum_{m=0}\sum_{n=0}\sum_{k=0} n[MH_jL_mL'_n(OH)_k], \quad (3)$$

wobei die Summation über alle möglichen Wertepaare (m, n, j, k) erfolgt. Unabhängig von j und k muß bei $m = 0$ $(n = 0)$ $n > 0$ $(m > 0)$ sein, denn bei (m, n) gleichzeitig null findet keine Komplexbildung statt.

Für den Fall, daß hohe Ligandenüberschüsse vorliegen, d.h.

$$C_L \gg C_M \quad C_{L'} \gg C_M \quad (4)$$

kann man die Konzentrationen der in den Komplexindividuen gebundenen Liganden vernachlässigen. Es gelten dann in guter Näherung wegen (2) und (3) die Beziehungen

$$C_L \approx [\bar{L}] \quad C_{L'} \approx [\bar{L}'] \quad (5)$$

* Exakt können natürlich die einzelnen Komplexe noch hydrolysiert und/oder protonisiert vorliegen.

bzw. für die durch Ligandensubstitution entstehende Konzentrationsänderung $\Delta[\bar{L}]$ und $\Delta[\bar{L}']$.

$$\Delta[\bar{L}] \ll C_L \qquad \Delta[\bar{L}'] \ll C_L \quad (6)$$

Bei Gültigkeit des Bouguer–Lambert–Beerschen Gesetzes ist bei $(\epsilon_L, \epsilon_L) \to 0$ vereinfacht†

$$E = \sum E_i = \sum_{m=0}\sum_{n=0} d\epsilon_i[ML_mL'_n] \quad (i = 0, 1, 2, \ldots) \quad (7)$$

Die Beziehung (1) vereinfacht sich unter experimentellen Bedingungen oftmals, d.h. es liegen nur wenige Komplexindividuen vor. Für $(m, n) > 0$ und $(j, m, n, k) =$ konst.$([\text{binäre Komplexe}] \to 0)$ gilt

$$C_M = [\bar{M}] + [\text{ternärer Komplex}]. \quad (8)$$

Es ist denkbar, daß unter bestimmten Voraussetzungen alle Metallionen komplex gebunden sein können $([\bar{M}] \to 0)$. Für den Fall, daß ein binärer und ein ternärer Komplex existiert ergibt sich aus (1)

$$C_M = [\text{binärer Komplex}] + [\text{ternärer Komplex}]. \quad (9)$$

Wenn $[\bar{M}] \to 0$ und $[\text{binärer Komplex}] \to 0$ kann wegen (1) auch der seltene Fall eintreten, daß

$$C_M = [\text{ternärer Komplex (I)}] + [\text{ternärer Komplex (II)}] \quad (10)$$

ist, d.h. es können zwei ternäre Komplexe nebeneinander vorliegen und es bildet sich kein binärer Komplex.

Gleichung (7) vereinfacht sich bei Gültigkeit von (8), (9) und (10) zu

$$E_0 = d(\epsilon_0[M] + \epsilon_1[\text{ternärer Komplex}]) \quad (11)$$

$$E_1 = d(\epsilon_2[\text{binärer Komplex}] + \epsilon_1[\text{ternärer Komplex}]) \quad (12)$$

$$E_2 = d(\epsilon_1[\text{ternärer Komplex (I)}] + \epsilon'_1[\text{ternärer Komplex (II)}]). \quad (13)$$

Nun darf man (8) mit (11), (9) mit (12) und (10) mit (13) kombinieren, da sie jeweils für ein System Gültigkeit haben. Die resultierenden Gleichungssysteme enthalten mehrere Variable, und man kann sie nach den vorliegenden Teilchenkonzentrationen auflösen. Es ergeben sich dabei Ausdrücke der Art

$$[ML_\alpha L'_\beta] = f_{\alpha,\beta}(E, d, C_M, \epsilon_i), \quad (14)$$

wobei $\alpha = 0$, $m - r$, m, $m + r$ und $\beta = 0$, $n - r'$, n, $n + r'$ sein kann.

Wenn man in einem Medium hoher und konstanter Ionenstärke arbeitet (μ = konst.), lassen sich folgende Ausdrücke für Bildungsreaktionen formulieren:

$$K'_i = \frac{[ML_mL'_n][\bar{L}]^\eta}{[ML_\alpha L'_\beta][\bar{L}]^\gamma[\bar{L}']^\delta} \quad (15)$$

für die Reaktion

$$ML_\alpha L'_\beta + \gamma\bar{L} + \delta\bar{L}' \rightleftharpoons ML_mL'_n + \eta\bar{L} \quad (16)$$

mit den Wertepaaren

$$(\alpha, \beta, \eta) = 0,\ \gamma = m,\ \delta = n$$

$$(\beta, \gamma, \eta) = 0,\ \alpha = m,\ \delta = n$$

$$(\beta, \gamma) = 0,\ \alpha = m + r,\ \delta = n,\ \eta = r$$

$$(\beta, \eta) = 0,\ \alpha = (m - r),\ \gamma = r,\ \delta = n$$

$$\eta = 0,\ \alpha = (m - r),\ \beta = (n - r'),\ \gamma = r,\ \delta = r'$$

$$(\gamma, \eta) = 0,\ \alpha = m,\ \beta = (n - r'),\ \delta = r'$$

$$\gamma = 0,\ \alpha = m + r,\ \beta = (n - r'),\ \delta = r',\ \eta = r.$$

Die Größe K_i' ist dabei eine scheinbare Reaktionskonstante für pH = konst.
Weiterhin ist

$$K_i = \frac{[ML_mL_n'][H_aL]^{\eta}[H^+]^{x_i}}{[ML_xL_\beta'][H_aL]^{\gamma}[H_bL']^{\delta}} \tag{17}$$

für die Reaktion

$$ML_xL_\beta' + \gamma H_aL + \delta H_bL' \rightleftharpoons ML_mL_n' + \eta H_aL + x_iH^+ \tag{18}$$

Im Gegensatz zu K_i' stellt K_i eine echte Gleichgewichtskonstante dar.

Gleichung (15) kann man wegen (5) bzw. (6) [Gültigkeit von Kriterium (4)] zu

$$K_i'[ML_xL_\beta'] C_L^{\gamma} C_{L'}^{\delta} = [ML_mL_n'] C_L^{\eta} \tag{19}$$

schreiben. Weiterhin lassen sich die entsprechenden Funktionen von (14) in (19) einführen und man kann die so erhaltenen Funktionen in die Form

$$y = ax + b \tag{20}$$

bringen.

Bei der Behandlung von Protonenbilanzen ist zu beachten, daß Gleichung (18) nur eine Vereinfachung darstellt, da die Liganden nur selten in einer einheitlichen Form vorliegen. Vielfach hat man mit stufenweiser Protonisierung zu rechnen, für die Gleichgewichte

$$H_aL \rightleftharpoons H_{a-1}L + H^+ \qquad (K_{sL}) \tag{21}$$

$$H_bL' \rightleftharpoons H_{b-1}L' + H^+ \qquad (K_{sL'}) \tag{22}$$

ist dann wegen (5)

$$C_L = [H_aL] + [H_{a-1}L] = [H_aL]\left(1 + \frac{K_{sL}}{[H^+]}\right) \tag{23}$$

$$C_{L'} = [H_bL'] + [H_{b-1}L'] = [H_bL]\left(1 + \frac{K_{sL'}}{[H^+]}\right) \tag{24}$$

Mit Hilfe der Beziehungen (23) und (24) läßt sich auf $[H_aL]$ und $[H_bL']$ normieren, Gleichung (17) gibt so

$$K_i[ML_xL_\beta'] C_L^{\gamma} C_{L'}^{\delta} \left(1 + \frac{K_{sL}}{[H^+]}\right)^{\eta}$$

$$= [ML_mL_n'][H^+]^{x_i} C_L^{\eta} \left(1 + \frac{K_{sL}}{[H^+]}\right)^{\gamma} \left(1 + \frac{K_{sL'}}{[H^+]}\right)^{\delta}. \tag{25}$$

Nunmehr lassen sich die Größen $[ML_xL_\beta']$ und $[ML_mL_n']$ mit (14) eliminieren und auch lineare Funktionen der Art (20) herleiten.

TRANSFORMATIONEN ZUR ANALYSE VON FUNKTIONEN $E = f$(LIGANDENKONZENTRATION)

Für experimentell ermittelte Funktionen $E = f$(Ligandenkonzentration) hat Gleichung (15) Gültigkeit, und mit den angegebenen Randbedingungen erhält man aus (16) folgende Gleichgewichten, die hier auf Grund der gewählten Versuchsbedingungen vorliegend betrachtet werden. Die Möglichkeit, daß mehrere Teilchenarten nebeneinander vorliegen können, soll hier der Einfachheit halber ausgeschlossen werden.

$$M + mL + nL' \rightleftharpoons ML_mL_n' \tag{Ia}$$

$$ML_m + nL' \rightleftharpoons ML_mL_n' \tag{IIa}$$

$$ML_{m+r} + nL' \rightleftharpoons ML_mL_n' + rL \tag{IIIa}$$

$$ML_{m-r} + rL + nL' \rightleftharpoons ML_mL_n' \tag{IVa}$$

$$ML_{m-r}L_{n-r'}' + rL + r'L' \rightleftharpoons ML_mL_n' \tag{Va}$$

$$ML_mL_{n-r'}' + r'L' \rightleftharpoons ML_mL_n' \tag{VIa}$$

$$ML_{m+r}L_{n-r'}' + r'L' \rightleftharpoons ML_mL_n' + rL \tag{VIIa}$$

Außerdem ist die Zersetzungsreaktion

$$ML_mL_n' + rL \rightleftharpoons ML_{m+r} + nL' \tag{VIIIa}$$

von Bedeutung. Wenn eine dieser Gleichungen für bestimmte experimentelle Bedingungen (pH, C_L, $C_{L'}$, C_M) volle Gültigkeit besitzt, d.h. die Konzentrationen aller anderen möglichen Teilchen gegen Null geht, sind die im Abschnitt "Allgemeine Voraussetzungen" gemachten Forderungen einzuhalten. Im einzelnen lassen sich dafür die Transformationen ableiten:

Zu (Ia)

ϵ_0 (M), ϵ_1 (ML_mL_n')

$$\frac{C_M}{Ed^{-1} - \epsilon_0 C_M} = \frac{1}{K_1'(\epsilon_1 - \epsilon_0)} \cdot \frac{1}{C_L^m C_{L'}^n} + \frac{1}{\epsilon_1 - \epsilon_0}$$

$$\epsilon_1 = 1/b + \epsilon_0,\ K_1' = 1/a(\epsilon_1 - \epsilon_0)$$

$$\frac{C_M}{Ed^{-1}} = \frac{1}{K_1'\epsilon_1} \cdot \frac{1}{C_L^m C_{L'}^n} + \frac{1}{\epsilon_1} \qquad (\epsilon_0 = 0)$$

$$\epsilon_1 = 1/b,\ K_1' = 1/a\epsilon_1$$

Zu (IIa)

ϵ_1 (ML_mL_n'), ϵ_2 (ML_m)

$$\frac{C_M}{Ed^{-1} - \epsilon_2 C_M} = \frac{1}{K_2'(\epsilon_1 - \epsilon_2)} \cdot \frac{1}{C_{L'}^n} + \frac{1}{\epsilon_1 - \epsilon_2}$$

$$\epsilon_1 = 1/b + \epsilon_2,\ K_2' = 1/a(\epsilon_1 - \epsilon_2)$$

$$\frac{C_M}{Ed^{-1}} = \frac{1}{K_2'\epsilon_1} \cdot \frac{1}{C_{L'}^n} + \frac{1}{\epsilon_1} \qquad (\epsilon_2 = 0)$$

$$\epsilon_1 = 1/b,\ K_2' = 1/a\epsilon_1$$

Zu (IIIa)

ϵ_1 (ML_mL_n'), ϵ_3 (ML_{m+r})

$$\frac{C_M}{Ed^{-1} - \epsilon_3 C_M} = \frac{C_L^r}{K_3'(\epsilon_1 - \epsilon_3)} \cdot \frac{1}{C_{L'}^n} + \frac{1}{\epsilon_1 - \epsilon_3}$$

$$\epsilon_1 = 1/b + \epsilon_3,\ K_3' = C_L^r/a(\epsilon_1 - \epsilon_3)$$

$$\frac{C_M}{Ed^{-1}} = \frac{C_L^r}{K_3'\epsilon_1} \cdot \frac{1}{C_{L'}^n} + \frac{1}{\epsilon_1} \qquad (\epsilon_3 = 0)$$

$$\epsilon_1 = 1/b,\ K_3' = C_L^r/a\epsilon_1$$

Zu (IVa)

$$\epsilon_1\,(ML_mL'_n),\ \epsilon_4\,(ML_{m-r})$$

$$\frac{C_M}{Ed^{-1}-\epsilon_4 C_M}=\frac{1}{K'_4(\epsilon_1-\epsilon_4)}\cdot\frac{1}{C_L^r C_{L'}^n}+\frac{1}{\epsilon_1-\epsilon_4}$$

$$\epsilon_1 = 1/b+\epsilon_4,\ K'_4 = 1/a(\epsilon_1-\epsilon_4)$$

$$\frac{C_M}{Ed^{-1}}=\frac{1}{K'_4\epsilon_1}\cdot\frac{1}{C_L^r C_{L'}^n}+\frac{1}{\epsilon_1}\qquad(\epsilon_4=0)$$

$$\epsilon_1 = 1/b,\ K'_4 = 1/a\epsilon_1$$

Zu (Va)

$$\epsilon_1\,(ML_mL'_n),\ \epsilon_5\,(ML_{m-r}L'_{n-r'})$$

$$\frac{C_M}{Ed^{-1}-\epsilon_5 C_M}=\frac{1}{K'_5(\epsilon_1-\epsilon_5)}\cdot\frac{1}{C_L^r C_{L'}^{r'}}+\frac{1}{\epsilon_1-\epsilon_5}$$

$$\epsilon_1 = 1/b+\epsilon_5,\ K'_5 = 1/a(\epsilon_1-\epsilon_5)$$

$$\frac{C_M}{Ed^{-1}}=\frac{1}{K'_5\epsilon_1}\cdot\frac{1}{C_L^r C_{L'}^{r'}}+\frac{1}{\epsilon_1}\qquad(\epsilon_5=0)$$

$$\epsilon_1 = 1/b,\ K'_5 = 1/a\epsilon_1$$

Zu (VIa)

$$\epsilon_1\,(ML_mL'_n),\ \epsilon_6\,(ML_mL'_{n-r'})$$

$$\frac{C_M}{Ed^{-1}-\epsilon_6 C_M}=\frac{1}{K'_6(\epsilon_1-\epsilon_6)}\cdot\frac{1}{C_{L'}^{r'}}+\frac{1}{\epsilon_1-\epsilon_6}$$

$$\epsilon_1 = 1/b+\epsilon_6,\ K'_6 = 1/a(\epsilon_1-\epsilon_6)$$

$$\frac{C_M}{Ed^{-1}}=\frac{1}{K'_6\epsilon_1}\cdot\frac{1}{C_{L'}^{r'}}+\frac{1}{\epsilon_1}\qquad(\epsilon_6=0)$$

$$\epsilon_1 = 1/b,\ K'_6 = 1/a\epsilon_1$$

Zu (VIIa)

$$\epsilon_1\,(ML_mL'_n),\ \epsilon_7\,(ML_{m+r}L'_{n-r'})$$

$$\frac{C_M}{Ed^{-1}-\epsilon_7 C_M}=\frac{C_L^r}{K'_7(\epsilon_1-\epsilon_7)}\cdot\frac{1}{C_{L'}^{r'}}+\frac{1}{\epsilon_1-\epsilon_7}$$

$$\epsilon_1 = 1/b+\epsilon_7,\ K'_7 = C_L^r/a(\epsilon_1-\epsilon_7)$$

$$\frac{C_M}{Ed^{-1}}=\frac{C_L^r}{K'_7\epsilon_1}\cdot\frac{1}{C_{L'}^{r'}}+\frac{1}{\epsilon_1}\qquad(\epsilon_7=0)$$

$$\epsilon_1 = 1/b,\ K'_7 = C_L^r/a\epsilon_1$$

Zu (VIIIa)

$$\epsilon_1\,(ML_mL'_n),\ \epsilon_3\,(ML_{m+r})$$

$$\frac{C_M}{Ed^{-1}-\epsilon_3 C_M}=\frac{K'_8}{(\epsilon_1-\epsilon_3)C_{L'}^n}\cdot C_L^r+\frac{1}{\epsilon_1-\epsilon_3}$$

$$\epsilon_1 = 1/b+\epsilon_3,\ K'_8 = a(\epsilon_1-\epsilon_3)C_{L'}^n$$

$$\frac{C_M}{Ed^{-1}}=\frac{K'_8}{\epsilon_1 C_{L'}^n}\cdot C_L^r+\frac{1}{\epsilon_1}\qquad(\epsilon_3=0)$$

$$\epsilon_1 = 1/b,\ K'_8 = a\epsilon_1 C_{L'}^n.$$

* Der Fall (C_L und/oder $C_{L'}$) = 0 hat keine physikalische Bedeutung und ist somit uninteressant.

Auf die Angabe von Ladungen der einzelnen Teilchen außer bei den H^+-Ionen soll wegen der Übersichtlichkeit verzichtet werden. Bei den Formulierungen ist die mögliche Koordination von H_2O nicht berücksichtigt.

Die für einige wichtige Reaktionsgleichgewichte abgeleiteten Transformationen gehen aus dem Massenwirkungsgesetz hervor, und sie erhalten somit Gleichgewichtskonstanten K'_i. Die Werte für K'_i sind aber nur dann konstant, wenn das MWG Gültigkeit hat, d.h. die entsprechenden Molarkoeffizienten des (der) variierten Liganden richtig sind. Für diesen Fall nehmen alle Transformationen lineare Form an. Aus den experimentell gemessenen Daten*

$$E = f_1(C_L, C_{L'}) \qquad (pH, \mu, C_M) = \text{konst.}$$

$$E = f_2(C_{L'}) \qquad (pH, \mu, C_M, C_L) = \text{konst.}$$

$$E = f_3(C_L) \qquad (pH, \mu, C_M, C_{L'}) = \text{konst.}$$

berechnet man nun für verschiedene Werte der Molarkoeffizienten (1, 2, 3, ...) die Werte für x and y und trägt sie gegeneinander auf. Nur für richtige Molarkoeffizienten ergibt sich eine Gerade, so daß somit Umsatzvariable indirekt ermittelt werden können. In den meisten Fällen ist nur ein Koeffizient, bei den Gleichgewichten (Ia), (IVa) und (Va) sind zwei zu variieren. Für Gleichgewicht (Ia) ergeben sich z.B. mit $(m, n) = 1, 2, 3$ folgende Möglichkeiten:

$$\frac{m=1}{n=1,2,3}\quad\frac{m=2}{n=1,2,3}\quad\frac{m=3}{n=1,2,3}$$

Ist (m bzw. n) = 0, so geht (Ia) mit den zugehörigen Transformationen in ein binäres Gleichgewicht über.

Aus den für die richtigen Werte der Molarkoeffizienten erhaltenen Geraden lassen sich durch Extrapolation ($x = 0$) die Größen b bestimmen und weiter nach den angegebenen Beziehungen die Extinktionskoeffizienten berechnen. Aus der Steigung $a = \Delta y/\Delta x$ kann man wie angegeben K'_i ermitteln. Die Konstanten K'_i sind dann in stöchiometrische Konstanten K_c umzurechnen.[14,15]

TRANSFORMATIONEN ZUR ANALYSE VON FUNKTIONEN $E = f(pH)$

Zur Interpretation der gemessenen Werte von $E = f(pH)$ lassen sich wie angegeben Transformationen ableiten. Aus (18) ergeben sich mit den aufgeführten Wertepaaren folgende wichtige Reaktionsmöglichkeiten:

Bildungsreaktionen

$$M + mH_aL + nH_bL' \rightleftharpoons ML_mL'_n + xH^+ \qquad \text{(Ib)}$$

$$ML_m + nH_bL' \rightleftharpoons ML_mL'_n + xH^+ \qquad \text{(IIb)}$$

$$ML_{m+r} + nH_bL' \rightleftharpoons ML_mL'_n + rH_aL + xH^+ \qquad \text{(IIIb)}$$

$$ML_{m-r} + rH_aL + nH_bL' \rightleftharpoons ML_mL'_n + xH^+ \qquad \text{(IVb)}$$

$$ML_{m-r}L'_{n-r'} + rH_aL + r'H_bL' \rightleftharpoons ML_mL'_n + xH^+ \qquad \text{(Vb)}$$

$$ML_mL'_{n-r'} + r'H_bL' \rightleftharpoons ML_mL'_n + xH^+ \qquad \text{(VIb)}$$

$$ML_{m+r}L'_{n-r'} + r'H_bL' \rightleftharpoons ML_mL'_n + rH_aL + xH^+ \quad \text{(VIIb)}$$

Zersetzungsreaktionen

$$ML_mL'_n + rH_aL \rightleftharpoons ML_{m+r} + nH_bL' + xH^+ \quad \text{(VIIIb)}$$

$$ML_mL'_n + zH_2O \rightleftharpoons M(OH)_z + mH_aL + nH_bL' + xH^+ \quad \text{(IXb)}$$

$$ML_mL'_n + zH_2O \rightleftharpoons ML_m(OH)_z + nH_bL' + xH^+ \quad \text{(Xb)}$$

Für die einzelnen Gleichgewichte ergeben sich dann unter den entsprechenden Voraussetzungen die zur Analyse von Funktionen $E = f(\mathrm{pH})$ wichtigen Transformationen.

Zu (Ib)

$$\epsilon_0\,(M),\ \epsilon_1\,(ML_mL'_n)$$

$$\frac{C_M}{Ed^{-1} - \epsilon_0 C_M} = \frac{1}{K_1(\epsilon_1 - \epsilon_0)C_L^m C_{L'}^n} \times [H^+]^x\left(1 + \frac{K_{sL}}{[H^+]}\right)^m\left(1 + \frac{K_{sL'}}{[H^+]}\right)^n + \frac{1}{\epsilon_1 - \epsilon_0}$$

$$\epsilon_1 = 1/b + \epsilon_0,\ K_1 = 1/a(\epsilon_1 - \epsilon_0)C_L^m C_{L'}^n$$

$$\frac{C_M}{Ed^{-1}} = \frac{1}{K_1\epsilon_1 C_L^m C_{L'}^n} \cdot [H^+]^x\left(1 + \frac{K_{sL}}{[H^+]}\right)^m \times \left(1 + \frac{K_{sL'}}{[H^+]}\right)^n + \frac{1}{\epsilon_1} \qquad (\epsilon_0 = 0)$$

$$\epsilon_1 = 1/b,\ K_1 = 1/a\epsilon_1 C_L^m C_{L'}^n$$

Zu (IIb)

$$\epsilon_1\,(ML_mL'_n),\ \epsilon_2\,(ML_m)$$

$$\frac{C_M}{Ed^{-1} - \epsilon_2 C_M} = \frac{1}{K_2(\epsilon_1 - \epsilon_2)C_{L'}^n} \times [H^+]^x\left(1 + \frac{K_{sL'}}{[H^+]}\right)^n + \frac{1}{\epsilon_1 - \epsilon_2}$$

$$\epsilon_1 = 1/b + \epsilon_2,\ K_2 = 1/a(\epsilon_1 - \epsilon_2)C_{L'}^n$$

$$\frac{C_M}{Ed^{-1}} = \frac{1}{K_2\epsilon_1 C_{L'}^n} \cdot [H^+]^x\left(1 + \frac{K_{sL'}}{[H^+]}\right)^n + \frac{1}{\epsilon_1} \qquad (\epsilon_2 = 0)$$

$$\epsilon_1 = 1/b,\ K_2 = 1/a\epsilon_1 C_{L'}^n$$

Zu (IIIb)

$$\epsilon_1\,(ML_mL'_n),\ \epsilon_3\,(ML_{m+r})$$

$$\frac{C_M}{Ed^{-1} - \epsilon_3 C_M} = \frac{C_L^r}{K_3(\epsilon_1 - \epsilon_3)C_{L'}^n} \times [H^+]^x \cdot \frac{\left(1 + \frac{K_{sL'}}{[H^+]}\right)^n}{\left(1 + \frac{K_{sL}}{[H^+]}\right)^r} + \frac{1}{\epsilon_1 - \epsilon_3}$$

$$\epsilon_1 = 1/b + \epsilon_3,\ K_3 = C_L^r/a(\epsilon_1 - \epsilon_3)C_{L'}^n$$

$$\frac{C_M}{Ed^{-1}} = \frac{C_L^r}{K_3\epsilon_1 C_{L'}^n} \cdot [H^+]^x \quad \frac{\left(1 + \frac{K_{sL'}}{[H^+]}\right)^n}{\left(1 + \frac{K_{sL}}{[H^+]}\right)^r} + \frac{1}{\epsilon_1} \qquad (\epsilon_3 = 0)$$

$$\epsilon_1 = 1/b,\ K_3 = C_L^r/a\epsilon_1 C_{L'}^n$$

Zu (IVb)

$$\epsilon_1\,(ML_mL'_n),\ \epsilon_4\,(ML_{m-r})$$

$$\frac{C_M}{Ed^{-1} - \epsilon_4 C_M} = \frac{1}{K_4(\epsilon_1 - \epsilon_4)C_L^r C_{L'}^n} \cdot [H^+]^x \times \left(1 + \frac{K_{sL}}{[H^+]}\right)^r\left(1 + \frac{K_{sL'}}{[H^+]}\right)^n + \frac{1}{\epsilon_1 - \epsilon_4}$$

$$\epsilon_1 = 1/b + \epsilon_4,\ K_4 = 1/a(\epsilon_1 - \epsilon_4)C_L^r C_{L'}^n$$

$$\frac{C_M}{Ed^{-1}} = \frac{1}{K_4\epsilon_1 C_L^r C_{L'}^n} \cdot [H^+]^x\left(1 + \frac{K_{sL}}{[H^+]}\right)^r \times \left(1 + \frac{K_{sL'}}{[H^+]}\right)^n + \frac{1}{\epsilon_1} \qquad (\epsilon_4 = 0)$$

$$\epsilon_1 = 1/b,\ K_4 = 1/a\epsilon_1 C_L^r C_{L'}^n$$

Zu (Vb)

$$\epsilon_1\,(ML_mL'_n),\ \epsilon_5\,(ML_{m-r}L'_{n-r'})$$

$$\frac{C_M}{Ed^{-1} - \epsilon_5 C_M} = \frac{1}{K_5(\epsilon_1 - \epsilon_5)C_L^r C_{L'}^{r'}} \times [H^+]^x\left(1 + \frac{K_{sL}}{[H^+]}\right)^r \times \left(1 + \frac{K_{sL'}}{[H^+]}\right)^{r'} + \frac{1}{\epsilon_1 + \epsilon_5}$$

$$\epsilon_1 = 1/b + \epsilon_5,\ K_5 = 1/a(\epsilon_1 - \epsilon_5)C_L^r C_{L'}^{r'}$$

$$\frac{C_M}{Ed^{-1}} = \frac{1}{K_5\epsilon_1 C_L^r C_{L'}^{r'}} \cdot [H^+]^x\left(1 + \frac{K_{sL}}{[H^+]}\right)^r \times \left(1 + \frac{K_{sL'}}{[H^+]}\right)^{r'} + \frac{1}{\epsilon_1} \qquad (\epsilon_5 = 0)$$

$$\epsilon_1 = 1/b,\ K_5 = 1/a\epsilon_1 C_L^r C_{L'}^{r'}$$

Zu (VIb)

$$\epsilon_1\,(ML_mL'_n),\ \epsilon_6\,(ML_mL'_{n-r'})$$

$$\frac{C_M}{Ed^{-1} - \epsilon_6 C_M} = \frac{1}{K_6(\epsilon_1 - \epsilon_6)C_{L'}^{r'}} \times [H^+]^x\left(1 + \frac{K_{sL'}}{[H^+]}\right)^{r'} + \frac{1}{\epsilon_1 - \epsilon_6}$$

$$\epsilon_1 = 1/b + \epsilon_6,\ K_6 = 1/a(\epsilon_1 - \epsilon_6)C_{L'}^{r'}$$

$$\frac{C_M}{Ed^{-1}} = \frac{1}{K_6\epsilon_1 C_{L'}^{r'}} \cdot [H^+]^x \left(1 + \frac{K_{sL'}}{[H^+]}\right)^{r'} + \frac{1}{\epsilon_1} \qquad (\epsilon_6 = 0)$$

$$\epsilon_1 = 1/b,\ K_6 = 1/a\epsilon_1 C_{L'}^{r'}$$

Zu (VIIb)

$$\epsilon_1\,(ML_mL'_n),\ \epsilon_7\,(ML_{m+r}L'_{n-r'})$$

$$\frac{C_M}{Ed^{-1} - \epsilon_7 C_M} = \frac{C_L^r}{K_7(\epsilon_1 - \epsilon_7)C_{L'}^{r'}} \times [H^+]^x \frac{\left(1 + \frac{K_{sL'}}{[H^+]}\right)^{r'}}{\left(1 + \frac{K_{sL}}{[H^+]}\right)^{r}} + \frac{1}{\epsilon_1 - \epsilon_7}$$

$$\epsilon_1 = 1/b + \epsilon_7,\ K_7 = C_L^r/a(\epsilon_1 - \epsilon_7)C_{L'}^{r'}$$

$$\frac{C_M}{Ed^{-1}} = \frac{C_L^r}{K_7\epsilon_1 C_{L'}^{r'}} \cdot [H^+]^x \frac{\left(1 + \frac{K_{sL'}}{[H^+]}\right)^{r'}}{\left(1 + \frac{K_{sL}}{[H^+]}\right)^{r}} + \frac{1}{\epsilon_1} \qquad (\epsilon_7 = 0)$$

$$\epsilon_1 = 1/b,\ K_7 = C_L^r/a\epsilon_1 C_{L'}^{r'}$$

Zu (VIIIb)

$$\epsilon_1\,(ML_mL'_n),\ \epsilon_3\,(ML_{m+r})$$

$$\frac{C_M}{Ed^{-1} - \epsilon_3 C_M} = \frac{K_8 C_L^r}{(\epsilon_1 - \epsilon_3)C_{L'}^{n}} \times \frac{1}{[H^+]^x} \frac{\left(1 + \frac{K_{sL'}}{[H^+]}\right)^{n}}{\left(1 + \frac{K_{sL}}{[H^+]}\right)^{r}} + \frac{1}{\epsilon_1 - \epsilon_3}$$

$$\epsilon_1 = 1/b + \epsilon_3,\ K_8 = a(\epsilon_1 - \epsilon_3)C_{L'}^{n}/C_L^r$$

$$\frac{C_M}{Ed^{-1}} = \frac{K_8 C_L^r}{\epsilon_1 C_{L'}^{n}} \cdot \frac{1}{[H^+]^x} \frac{\left(1 + \frac{K_{sL'}}{[H^+]}\right)^{n}}{\left(1 + \frac{K_{sL}}{[H^+]}\right)^{r}} + \frac{1}{\epsilon_1} \qquad (\epsilon_3 = 0)$$

$$\epsilon_1 = 1/b,\ K_8 = a\epsilon_1 C_{L'}^{n}/C_L^r$$

Zu (IXb)

$$\epsilon_1\,(ML_mL'_n),\ \epsilon_8\,(M(OH)_z)$$

$$\frac{C_M}{Ed^{-1}} = \frac{K_9}{\epsilon_1 C_L^m C_{L'}^{n}} \cdot \frac{1}{[H^+]^x} \left(1 + \frac{K_{sL}}{[H^+]}\right)^{m} \times \left(1 + \frac{K_{sL'}}{[H^+]}\right)^{n} + \frac{1}{\epsilon_1} \qquad (\epsilon_8 = 0)$$

$$\epsilon_1 = 1/b,\ K_9 = a\epsilon_1 C_L^m C_{L'}^{n}$$

Zu (Xb)

$$\epsilon_1\,(ML_mL'_n),\ \epsilon_9\,(ML_m(OH)_z)$$

$$\frac{C_M}{Ed^{-1}} = \frac{K_{10}}{\epsilon_1 C_{L'}^{n}} \cdot \frac{1}{[H^+]^x} \left(1 + \frac{K_{sL'}}{[H^+]}\right)^{n} + \frac{1}{\epsilon_1} \qquad (\epsilon_9 = 0)$$

$$\epsilon_1 = 1/b,\ K_{10} = a\epsilon_1 C_{L'}^{n}.$$

Auch die zur Analyse von Funktionen $E = f(\mathrm{pH})$ angegebenen Transformationen haben nur dann die Form $y = ax + b$, wenn a konstant ist. Dazu muß aber K_i eine Konstante mit richtiger Protonenbilanz sein. Sind bestimmte Umsatzvariable gleich null, so gehen die Transformationen sowie die dazugehörigen Gleichgewichte in binäre Formen über.

Zur Ermittlung der Protonenbilanz x variiert man x in den Transformationen und trägt nach Berechnung die entsprechenden Wertepaare gegeneinander auf. Die Größe x kann dabei die Werte $\pm 1, \pm 2, \ldots$ annehmen, $x = 0$ sind protonenfreie Gleichgewichte und $-x$-Werte treten bei protonverbrauchenden Gleichgewichten auf. Dabei gehen in die eine Variable alle die Terme ein, in denen $[H^+]$ enthalten ist. Die in den Ausdrücken auftretenden Umsatzvariablen müssen entweder bekannt sein oder gemeinsam mit x variiert werden. Bei diesem Vorgehen fallen neben x noch Molarkoeffizienten an; alle variierten Größen sind richtig gewählt, wenn bei der graphischen Darstellung eine Gerade resultiert.

Die in den Transformationen stehenden Klammerausdrücke mit K_{sL} bzw. $K_{sL'}$ vereinfachen sich oftmals, folgende praktisch interessante Grenzfälle existieren:

Ligand L ($i = m, r$)

$$[H^+] = K_{sL}: \quad \left(1 + \frac{K_{sL}}{[H^+]}\right)^{i} = 2^i \qquad (27)$$

$$[H^+] \gg K_{sL}: \quad \left(1 + \frac{K_{sL}}{[H^+]}\right)^{i} = 1 \qquad (28)$$

$$[H^+] \ll K_{sL}: \quad \left(1 + \frac{K_{sL}}{[H^+]}\right)^{i} = \left(\frac{K_{sL}}{[H^+]}\right)^{i} \qquad (29)$$

Ligand L' ($j = n, r'$)

$$[H^+] = K_{sL'}: \quad \left(1 + \frac{K_{sL'}}{[H^+]}\right)^{j} = 2^j \qquad (30)$$

$$[H^+] \gg K_{sL'}: \quad \left(1 + \frac{K_{sL'}}{[H^+]}\right)^{j} = 1 \qquad (31)$$

$$[H^+] \ll K_{sL'}: \quad \left(1 + \frac{K_{sL'}}{[H^+]}\right)^{j} = \left(\frac{K_{sL'}}{[H^+]}\right)^{j}. \qquad (32)$$

Eine Berechnung der Ausdrücke von (27) bis (32) erfolgt mit den Säuerekonstanten $K_{sL}(H_aL/H_{a-1}L)$ und $K_{sL'}(H_bL'/H_{b-1}L')$, wobei $a \neq b$ sowie $a = b$ sein kann. Es sei bemerkt, daß $H_aL(H_bL')$ nicht unbedingt neutral sein muß, sondern jede beliebige Ladung tragen kann. Im untersuchten pH-Gebiet dürfen maximal zwei Formen der im Säure-Base-Gleichgewicht befindlichen Liganden vorliegen. Ist das nicht erfüllt, d.h. ist im untersuchten pH-Bereich H_iL ($i = 0, 1, \ldots, a$) bzw. H_iL' ($i = 0, 1, \ldots, b$), so darf man nur den Teil der Funktion $E = f(\mathrm{pH})$ interpretieren, wo zwei Formen der jeweiligen Liganden vorhanden sind. Die dazu wichtigen Konzentrationsverhältnisse der möglichen Ligandenformen sind mit Hilfe der Säurekonstanten zu berechnen bzw. abzuschätzen.

Zur Berechnung der Transformationen geht man von Funktionen

$$E = f(\text{pH}) \quad (C_M, C_L, C_{L'}, \mu) = \text{konst.} \qquad (33)$$

aus, welche experimentell ermittelt werden. Bei den Gleichgewichten (IXb) und (Xb) ist $[H_2O]$ in den entsprechenden Transformationen vernachlässigt, die Anwendung dieser Gleichungen ist somit nur in verdünnten wäßrigen Lösungen gestattet. Wie bei der Analyse der Funktionen $E = f$(Ligandenkonzentration) beschrieben, kann auch hier nach Extrapolation die Größe b ermittelt und daraus ϵ_1 berechnet werden. Die Reaktionskonstanten K_i lassen sich aus der Steigung a der Geraden mit Hilfe der angegebenen Beziehungen finden.

ZUR ANWENDUNG DER TRANSFORMATIONEN

Die angegebenen Transformationen für Systeme mit ternärer Komplexbildung gestatten spektralphotometrisch ermittelte Funktionen $E = f$(Ligandenkonzentration) und $E = f$(pH) zu analysieren und somit Informationen über die Bildungsreaktionen zu erhalten. Am Anfang solcher Untersuchungen sollte zunächst Klarheit darüber bestehen, ob im zu untersuchenden System ternäre Komplexe auftreten. Eine solche Entscheidung ist nicht immer einfach,[16] eine sorgfältige Prüfung ist jedoch erforderlich, weil im Falle von nur binärer Komplexbildung einfachere Untersuchungsmethoden herangezogen werden können. Die Reaktionsbedingungen, unter welchen die Komplexbildung charakterisiert werden soll, richten sich nach der vorgegebenen Fragestellung oder werden durch die Eigenschaften von M, L und L (Hydrolysebeständigkeit, Löslichkeit, Oxydationsempfindlichkeit usw.) festgelegt. Überhaupt läßt sich zur komplexchemischen Untersuchung eines Systems M, L, L' kein allgemeingültiges Rezept angeben, man muß vielmehr die Art und Weise des Vorgehens den Besonderheiten des jeweiligen Systems anpassen.

Bei der Charakterisierung von ternären Systemen sollte man möglichst die Komplexchemie der binären Systeme M, L und M, L' kennen, da sich dann die Untersuchung entscheidend vereinfacht. Von besonderer Wichtigkeit ist dabei die Kenntnis der ϵ-Werte binärer Teilchen, weil sie in vielen Fällen in den Transformationen enthalten sind. Ist nun der Extinktionskoeffizient für eine bestimmte Wellenlänge bekannt, so läßt sich ϵ für eine andere Wellenlänge leicht bestimmen. In einem binären System ist

$$E_\lambda = \epsilon_\lambda C_\lambda d_\lambda; \quad E_{\lambda'} = \epsilon_{\lambda'} C_{\lambda'} d_{\lambda'} \qquad (34)$$

mit $d_\lambda = d_{\lambda'}$ und $C_\lambda = C_{\lambda'}$. Beziehungen (34) ergeben somit

$$\epsilon_\lambda = \frac{E_\lambda}{E_{\lambda'}} \epsilon_{\lambda'} \qquad (35)$$

Die zur Berechnung benötigten Größen E_λ und $E_{\lambda'}$ werden dabei einem experimentell ermittelten Spektrum des interessierenden binären Komplexes entnommen oder bei λ und λ' direkt gemessen. Von Vorteil ist, daß eine vollständige Bildung des binären Komplexes nicht erforderlich ist und die Größe $[ML_m]$ in die Rechnung nicht mit eingeht. Neben ML_m dürfen bei der Bestimmung von E_λ und $E_{\lambda'}$ unter den jeweiligen experimentellen Bedingungen keine weiteren Komplexindividuen vorliegen, weiterhin muß $\epsilon_{\lambda',\lambda}(M, L) \to 0$ erfüllt sein. Bei der experimentellen Ermittlung der Funktionen $E = f$(Ligandenkonzentration) und $E = f$(pH) sind einige Punkte zu beachten, auf die im folgenden kurz eingegangen werden soll. In den zu messenden Lösungen muß die Ionenstärke μ in bekannter Weise durch Zusatz eines Neutralsalzes konstant gehalten werden, da nur so die abgeleiteten Transformationen Gültigkeit haben. Auf die Verwendung von Pufferlösungen sollte möglichst verzichtet werden, um Konkurrenzreaktionen mit den Pufferionen auszuschalten. Besondere Aufmerksamkeit ist der Kinetik bei den Untersuchungen zu schenken. Es ist dabei nötig Funktionen der Art $E = f(t)$ aufzunehmen und daraus Folgerungen zur Gleichgewichtseinstellung zu ziehen. Eine Verfolgung der Gleichgewichtseinstellung mit Hilfe von pH(t) ist oft nicht möglich, da im System vorliegende Liganden als Puffersysteme wirken können.

Eine Anwendung der Transformationen setzt die Gültigkeit des Bouguer-Lambert-Beerschen Gesetzes voraus. In den zu messenden Lösungen dürfen deshalb keine Niederschläge sowie Kolloide, wie sie unter bestimmten Reaktionsbedingungen auch in Gegenwart von Liganden als Hydrolyseprodukte des Metallions auftreten, vorliegen.

Die spektralphotometrischen Messungen sollten in der Regel bei verschiedenen Wellenlängen erfolgen, weil die optischen Eigenschaften eines Systems am Anfang der Untersuchungen noch wenig bekannt sind. Zur Messung wird man—soweit diese Wellenlänge bekannt ist—bevorzugt λ_{max} des ternären Komplexes heranziehen, um dann unmittelbar ϵ_{max} für $ML_mL'_n$ durch graphische Analyse zu erhalten. Ligandenabsorption darf bei den Meßwellenlängen nicht auftreten, d.h. es muß $(\epsilon_L, \epsilon_{L'}) \to 0$ sein. In manchen Fällen gibt es jedoch kein Spektralbereich, wo das erfüllt ist. Es ist dann bei der Auswahl der zur Messung benötigten λ-Werte darauf zu achten, daß $(\epsilon_L, \epsilon_{L'}) \ll \epsilon_i$ gilt, wo die Extinktionswerte der in den Komplexen enthaltenen Liganden zu vernachlässigen sind. Die Messungen der entsprechenden Systeme erfolgen für diesen Fall gegen Vergleichsproben mit C_L und/oder $C_{L'}$. Je nach der Größe von ϵ_L bzw. $\epsilon_{L'}$ sind exakte Werte für Gleichgewichtskonstanten und Extinktionskoeffizienten nur durch Approximation zu erhalten.

Wichtig ist weiterhin, daß in den zu messenden Proben die Ligandenkonzentration viel größer ist als die vorliegende Metallionenkonzentration. Die genannten Bedingungen lassen sich aber nur dann einhalten, wenn in äquimolaren Systemen noch keine merkliche Komplexbildung eintritt, d.h. daß es sich um eine schwache Komplexbildung handelt. Bei

wenig dissoziierten, starken Komplexen hat man die Reaktionsbedingungen mit Hilfe der Wasserstoffionenkonzentration so festzulegen, daß zur Bildung von $ML_mL'_n$ hohe Ligandenüberschüsse erforderlich sind.

Eine Auswertung des experimentellen Materials mit den angegebenen Transformationen ist nur gerechtfertigt, wenn keine stufenweise Komplexbildung auftritt oder aber die einzelnen Stufen sich durch experimentelle Parameter abgrenzen lassen. Das gleiche trifft für Effekte der Metallionen- und Komplexhydrolyse zu. Auch hier müssen bei der Analyse von Funktionen $E = f(\text{pH})$ im untersuchten pH-Bereich einheitliche Formen der entsprechenden Hydrolyseprodukte vorliegen.

Läßt sich ein angenommener Reaktionsmechanismus durch den linearen Verlauf der entsprechenden Transformation bestätigen, so sind alle anderen denkbaren Reaktionen—auch die unter Beteiligung mehrkerniger Komplextypen—ausgeschlossen. Aus den aufgeführten Reaktionsmöglichkeiten und dazu gehörigen Transformationen erhält man leicht die äquivalenten Gleichungen durch Vertauschen von L mit L', m mit n und r mit r'. Um nun den richtigen Reaktionsmechanismus herauszufinden, ist es meistens nicht nötig, alle angegebenen Reaktionsvarianten durchzurechnen. Vielfach lassen sich einige wenige Reaktionsmechanismen wahrscheinlich machen, welche dann mit den dazugehörigen Transformationen bestätigt werden. Die nachstehende Reihenfolge zeigt, wie man bei der Untersuchung eines Systems M, L, L' vorzugehen hat.

1. Experimentelle Ermittlung von $E = f(\lambda)$ unter Variation von C_L, $C_{L'}$ und pH
2. Festlegung der Meßwellenlänge (n) $\lambda_1, \lambda_2, \ldots$
3. Experimentelle Ermittlung von $E = f(t)$ unter verschiedenen Bedingungen
4. Festlegung experimenteller Einzelheiten
5. Experimentelle Ermittlung von $E = f(\text{pH})$ unter Variation von C_L, $C_{L'}$ evt. C_M
6. Festlegung interessanter pH-Werte zur weiteren Untersuchung
7. Experimentelle Ermittlung von $E = f(\text{Ligandenkonzentration})$
8. Ermittlung von Molarkoeffizienten, ϵ und K'
9. Ermittlung von Protonenbilanzen, ϵ und K aus $E = f(\text{pH})$

Prinzipiell kann man Molarkoeffizienten sowie die Protonenbilanz durch Variation dieser gesuchten Größen in den Transformationen für $E = f(\text{pH})$ auf einmal ermitteln. Der hier angegebene Weg ist im allgemeinen vorzuziehen, weil die Zahl der Variationsmöglichkeiten und somit der Rechenaufwand geringer ist.

Mit Hilfe der Molarkoeffizienten und der Protonenbilanz lassen sich nun Angaben zur Komplexzusammensetzung machen und daraus Reaktionsgleichgewichte qualitativ und quantitativ formulieren. Es ist dazu nötig, zu wissen, wie sich die Liganden L und L' in $ML_mL'_n$ komplexchemisch verhalten, da die Protonenbilanz nur die Summe verschiedener Effekte darstellt. Vielfach lassen sich solche Informationen aus den entsprechenden binären Typen ziehen.

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Summary—Mathematical transformations are presented which enable one to characterize mononuclear ternary complexes in solution from experimental measurements of the absorbance as a function of the ligand concentration or the pH. In addition to getting the molar ratios and the proton balance, one can also find values for the formation constants and the molar absorption coefficients. Both simple equilibria and substitution equilibria between binary and ternary complexes are considered, with the proviso that only one equilibrium system is involved over the concentration range covered. Suggestions are given as to how the evaluation may be carried out in practice, and factors to be considered when using the transformations are pointed out.

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HAEMS AS POTENTIAL REAGENTS FOR CARBON MONOXIDE

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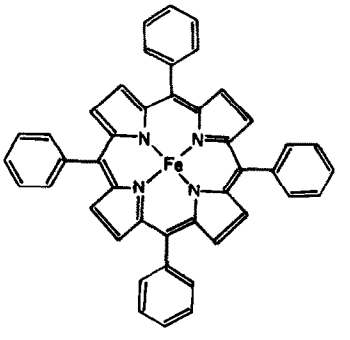
Summary—A study of the potential of a myoglobin model system based on dipiperidyltetraphenylporphinatoiron(II) for the spectrophotometric determination of carbon monoxide is reported. At room temperature, oxygen does not bind strongly at the iron centre and does not interfere. Nitric oxide, hydrogen sulphide and carbon dioxide interfere and must be removed before the determination if present in significant amounts. The main disadvantage of this novel method is the low sensitivity (about 300 ppm CO). Possible means of modifying the system to enhance the sensitivity and to further reduce the number of interfering species are discussed.

The haem group in haemoproteins shows a high degree of selectivity in reacting with gaseous ligands. Stable complexes are formed only with molecular oxygen, nitric oxide and carbon monoxide.[1] Haem compounds might thus serve as selective probes for these gases, especially for carbon monoxide. Although such a possibility had been recognized earlier by Adler *et al.*,[2] there is no evidence in the literature that serious attempts have been made in this direction. Because of their high affinity for oxygen, the haemoproteins themselves are unsuitable for the determination of carbon monoxide in oxygen-bearing atmospheres. A better understanding of the binding of gaseous ligands to haems has been made possible through recent studies on a variety of myoglobin model systems.[3–8] Of special interest are the models based on the dipiperidine complex of *meso*-tetraphenylporphinatoiron(II), Fe(II)TPP(pip)$_2$,[3,7,8] and on the monopyridylpropanol ester of mesohaem.[9] Both classes of model not only exhibit a much lower affinity for oxygen than the haemoproteins but bind carbon monoxide more strongly than oxygen. In the present study, an evaluation of the first model as an analytical reagent for carbon monoxide is reported. Although the second model system appeared to have even more desirable characteristics for this purpose, experimental work on it was terminated because of the high expense and difficulty in the synthesis of the compound in high purity.

The structure of *meso*-tetraphenylporphinatoiron(II), Fe(II)TPP, is shown at the top of the next column. The reaction of its dipiperidine complex, Fe(II)TPP(pip)$_2$, with carbon monoxide involves the displacement of one of the axial piperidine ligands:

$$\text{Fe(II)TPP(pip)}_2 + \text{CO} \rightleftharpoons \text{Fe(II)TPP(pip)(CO)} + \text{pip} \quad (1)$$

Nitric oxide and oxygen can also bind at the iron centre. As shown later, interference by oxygen is eliminated under the experimental conditions but not that of nitric oxide. More serious interferences, however, result from carbon dioxide and hydrogen sulphide which interact not by simple co-ordination at the haem centre but in a more complex manner. This interaction necessitates the prior removal of such gases in samples. In the absence of interfering gases, the haem reagent can be used to determine carbon monoxide in air-samples in the range 0.03% (300 ppm)–4% (v/v) with an error of ±5%. Although the sensitivity is inadequate for most analytical purposes, the potential does exist for improvement of the sensitivity of haem systems towards carbon monoxide, as discussed below.



EXPERIMENTAL

Reagents

Solvents. Toluene was distilled over sodium and stored over Linde 4A molecular sieve. The solvent was saturated with dry nitrogen before use. Piperidine was distilled over sodium hydroxide and the fraction boiling at 105–106° was collected and used immediately, or stored over Linde or Davison 4A molecular sieve in tightly capped bottles, which enhanced the stability of the reagent for up to two days.

TPP and Fe(III)TPPCl. *Meso*-tetraphenylporphine (TPP) was prepared and purified by the method of Adler

et al.[10] Fe(III)TPPCl was prepared by refluxing ferrous chloride with TPP in dimethylformamide as suggested by Adler *et al.*[11] Solutions of this compound in chloroform showed little or no fluorescence, indicating the absence of any appreciable contamination by free TPP. It is useful to note that both TPP and Fe(III)TPPCl are available commercially from various sources.

Standard stock solutions. Standard stock solutions of Fe(III)TPPCl ($3–5 \times 10^{-5} M$) in toluene were prepared. Since some porphyrins are photosensitive, the stock solutions were wrapped in aluminium foil to protect them from light and were found to be stable indefinitely.

Apparatus

Spectrophotometric measurements were made on a Bausch and Lomb Spectronic 600 double-beam instrument.

Gas-line assembly. A gas-rack assembly was constructed to incorporate two 2-litre gas-mixing bulbs with side septum ports to sample the gas mixtures for testing of the method. The gas-line also incorporated a conventional open-ended mercury manometer and a silicone-oil (Dow Corning 200 Fluid, 100 cs; density 0.93 ± 0.01 g/ml at 23°) manometer. The more sensitive oil manometer was used to monitor the addition of small amounts of carbon monoxide to the gas-line (10.0 mm of oil pressure corresponded to 0.682 ± 0.004 mmHg). Oil levels were measured with a cathetometer. Test mixtures of known amounts of carbon monoxide in air were prepared by introducing the carbon monoxide into the evacuated line and then diluting slowly with air passed through a tube of "Ascarite" to remove carbon dioxide, until the final pressure in the bulbs was one atmosphere. Samples were withdrawn from the bulbs by means of a 10-ml gas-tight syringe (Hamilton).

Procedure

The following procedure was used to obtain calibration curves and the equilibrium constant, K, for reaction (1). To a 10-ml volumetric flask were added 1.00 ml of the Fe(III)TPPCl stock solution and 1.00 ml of piperidine and the mixture was diluted to the mark with toluene. The solution was set aside for 15 min to allow complete reduction of the Fe(III) by the piperidine. Next, 3 ml of this solution were drawn into a 10-ml gas-tight syringe. The gas-sample was then drawn into the same syringe (so that it bubbled through the solution) to a total volume (solution plus gas) of 10 ml. The syringe was shaken for 1 min and set aside for 9 min to allow equilibrium between the gas and solution phases to be reached. A 1-cm cell (fused silica) was then completely filled with the solution and quickly stoppered, and the absorbance measured at 420 nm. The solution remaining in the volumetric flask served as the reference.

This procedure was also used for the determination of carbon monoxide in sample unknowns. For those samples at atmospheric pressure and containing normal concentrations of carbon dioxide (about 0.033% by volume) and similar or lower amounts of hydrogen sulphide, the sampling technique involved simply opening the evacuated 2-litre sampling flask, fitted at the neck with an "Ascarite" scrubber, to the atmosphere. The prior removal of small amounts of the interfering gases does not materially affect the concentration of carbon monoxide. If appreciable amounts of the interfering gases are present, these must be removed inside the 2-litre sampling flask, by exposure to "Ascarite" or a dilute solution of sodium hydroxide at the bottom of the flask. The amount of carbon monoxide lost to the "Ascarite" or the solution is negligible. A volume correction should be made if the "Ascarite" or solution exceeds 2% of the flask volume.

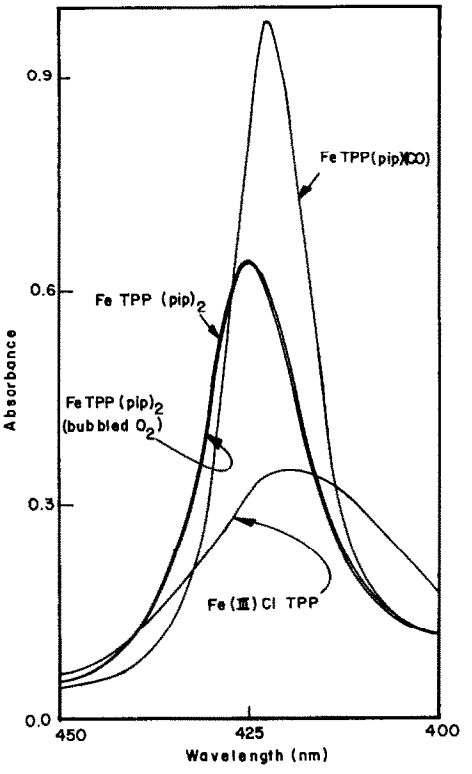


Fig. 1. Spectra of various iron–TPP species and effect of O_2 on the spectrum of Fe(II)TPP(pip)$_2$.

RESULTS AND DISCUSSION

The compounds Fe(III)TPPCl, Fe(II)TPP(pip)$_2$ and Fe(II)TPP(pip)(CO) exhibit absorption maxima at 417, 424 and 422 nm, respectively (Fig. 1). The difference spectrum of Fe(II)TPP(pip)$_2$ and the CO complex shows an absorption maximum at 420 nm and all measurements were made at this wavelength.

The formation of Fe(II)TPP(pip)$_2$

The basic requirements for the binding of gaseous ligands to iron porphyrins are that the iron should be in the ferrous state and a base co-ordinated at one of the axial positions on the iron. The gaseous ligand then binds at the other axial site. Piperidine conveniently serves to reduce Fe(III)TPPCl to Fe(II)TPP and to co-ordinate at the axial positions of the reduced species. Reaction with carbon monoxide then proceeds similarly to reaction (2). Prior reduction of the iron is necessary if other bases such as pyridine are to be used. We found that the reduction of iron done in the usual fashion with sodium dithionite[9] or calcium hydride[12] resulted in substantial losses of the haem either in the solvent interface or though adsorption on the solid material.

The rate of reduction of Fe(III)TPPCl by piperidine depends upon the concentration of the latter. Under the conditions described in this work, the reduction was complete within 15 min. Prior dilution of the

piperidine, lower concentrations of it or the use of impure piperidine resulted in a reduced rate of reduction or incomplete reduction. Reproducible results were obtained only if the piperidine was purified and used as described above. A final piperidine concentration of 1*M* was found to be most satisfactory in yielding a reasonable rate of reduction and retarding the rate of aerial oxidation (*vide infra*) without greatly lowering the effective stability of the carbon monoxide complex. The mechanism of the reduction is not known, although free radical species are thought to be involved.[13]

Stability of the reagent towards oxidation

Solutions of Fe(II)TPP(pip)$_2$ are irreversibly oxidized in air to form the μ-oxo-dimer (**IV**) via the oxygen complex (**III**). Kinetic studies[7,8] have led to the postulation of the following mechanism for the oxidation:

$$\underset{\mathbf{I}}{\text{Fe(II)TPP(pip)}_2} \rightleftharpoons \text{pip} + \underset{\mathbf{II}}{\text{Fe(II)TPP(pip)}} \overset{O_2}{\rightleftharpoons} \underset{\mathbf{III}}{\text{Fe(II)TPP(pip)(O}_2\text{)}} \xrightarrow{\text{fast}} \underset{\mathbf{IV}}{\text{TPPFe(III)–O–Fe(III)TPP}} \qquad (2)$$

The pentaco-ordinate species (**II**) can also react with carbon monoxide or nitric oxide. Binding of oxygen and oxidation to compound **IV** presents a potentially serious problem in the determination of carbon monoxide in air. However, although Basolo *et al.*[7] have shown that Fe(II)TPP(pip)(O$_2$) is readily formed at $-79°$, we found that at room temperature the compound is considerably destabilized, particularly in the presence of 1*M* piperidine. The CO complex remains stable under these conditions. Thus, bubbling oxygen through a solution of the reagent does not cause immediate formation of the oxygen complex (**III**) and its oxidation product (**IV**) (Fig. 1). A slow oxidation does occur but toluene solutions of compound **I** that are 1*M* in piperidine are stable in air for more than 90 min.

Selectivity of the reagent

The ideal haem compound for application to the determination of carbon monoxide would be one that binds no gaseous ligands but carbon monoxide at the iron centre. However, no haem compounds, natural or synthetic, are known that bind only carbon monoxide. Most form stable complexes with nitric oxide, carbon monoxide and oxygen, the stabilities decreasing in that order. As shown above, with Fe(II)TPP(pip)$_2$, the interference by oxygen is effectively eliminated at room temperature. Nitric oxide, however, was found to bind strongly and, as expected, caused a low recovery of carbon monoxide (Table 1). Since nitric oxide is rapidly oxidized to nitrogen dioxide, its background level in air is only 0.0002–0.002 ppm[14] and is not a serious problem in the determination of carbon monoxide.

The presence of hydrogen sulphide caused very erratic behaviour, however, leading to both high and low recoveries of carbon monoxide (Table 1). Initially, in the presence of carbon monoxide, there is an increase in the absorbance at 420 nm to above the expected value, followed quickly by a decrease to below that value. Hence unless the measurement is taken at a precise time, the reproducibility is poor. Although the manner in which hydrogen sulphide interferes is not known, it may well involve interaction between the iron centre and sulphide. Recently, Chang and Dolphin[15] reported evidence for mercaptide (RS^-) co-ordination at the iron centre when reduced haem, thiol, carbon monoxide and a strong base are mixed together.

In view of the fact that sulphur dioxide does not interfere, the interference by carbon dioxide (Table 1) is surprising. The spectrum of Fe(II) TPP(pip)$_2$ is unaffected when the reagent solution is saturated with carbon dioxide, suggesting that a complex at the iron centre is not formed. Nevertheless, when carbon monoxide is determined in the presence of carbon dioxide, the absorbance at 420 nm is lower than expected, although no band shifts or new spectral structure are observed. The ultimate source of the interference may involve reaction of carbon dioxide with the piperidine, in a manner similar to the reaction of carbonyl sulphide with piperidine to produce piperidine oxythiocarbamate.[16]

Evaluation of the equilibrium constant

The equilibrium constant for reaction (1) is expressed as the dimensionless quantity:

$$K = \frac{[\text{Fe(II)TPP(pip)(CO)}][\text{pip}]}{[\text{Fe(II)TPP(pip)}_2][\text{CO}]} \qquad (3)$$

If the concentration of carbon monoxide in solution is expressed through Henry's law as the partial pressure (P_{CO}), then a conditional constant, K', can be defined as

$$K' = \frac{SK}{[\text{pip}]} = \frac{[\text{Fe(II)TPP(pip)(CO)}]}{[\text{Fe(II)TPP(pip)}_2]P_{CO}} \qquad (4)$$

where S is the solubility of carbon monoxide in mole.l^{-1}. mmHg^{-1}. At 23°, for toluene as solvent, $S = 8.6 \times 10^{-6}$ mole.l^{-1}.mmHg^{-1}.[17] Under the experimental conditions, the initial concentration of piperidine is large (1*M*), so that [pip] is effectively constant (1*M*).

Evaluation of K' requires knowledge of ϵ_C, the molar absorptivity of the CO complex. Both ϵ_C and

Table 1. Determination of carbon monoxide in air-samples in the presence of other gases

Gas	P_{gas}, *mmHg*	P_{CO} taken, *mmHg*	P_{CO} found, *mmHg*	Recovery, %
SO_2	3.42	3.95	3.96	100
	3.96	4.09	4.05	99.0
CO_2	3.64	4.06	3.74	82.1
	4.37	5.43	4.25	78.3
H_2S	3.81	3.36	2.51	74.6
	4.95	4.06	4.56	112
NO*	4.82	4.09	3.22	78.7

* Experiments carried out in a nitrogen atmosphere.

K' were evaluated by the method of Gans and Irving.[18] The method is based on a computerized search technique and requires no constraints on the relative concentration of the reactants. For $\Delta\epsilon = \epsilon_C - \epsilon_O$, where ϵ_O is the molar absorptivity of Fe(II)TPP(pip)$_2$, a value of 1.25×10^5 l.mole^{-1}.cm^{-1} was obtained. The average value of K' was 0.071 mmHg^{-1}, with a standard deviation of 0.003. The value of K was calculated to be 8300.

Calibration curves

The lowest value of P_{CO} taken in this study corresponds to a concentration of carbon monoxide (in the solution) that is already higher than that of the reagent, Fe(II)TPP(pip)$_2$, and a calibration curve expressed as ΔA versus P_{CO} shows curvature with increasing P_{CO}. However, since the solubility of carbon monoxide in toluene is low, the partial pressure P_{CO} in the gas mixture remains constant to a good approximation and on this basis, the following linear expressions can be derived to serve as calibration curves:

$$\Delta A = A - A_0 = K'\Delta\epsilon C_0 \frac{P_{CO}}{1 + K'P_{CO}} \quad (5)$$

and

$$P_{CO} = \frac{1}{K'} \frac{\Delta A}{\Delta A_{max} - \Delta A} \quad (6)$$

where $\Delta A_{max} = \Delta\epsilon C_0$, A_0 is the absorbance of the reagent alone, A is the absorbance of the reagent in the presence of carbon monoxide and C_0 is the initial concentration of the reagent. The first expression relates ΔA to a function of P_{CO} and the second relates P_{CO} to a function of ΔA. In both cases, the x-scale is compressed at the higher end, leading to inaccuracies at high levels ($P_{CO} > 76$ mmHg) of carbon monoxide. A set of twenty data points was used to evaluate the calibration curves. Slopes of 0.031 ± 0.002 and 14.1 ± 0.9 were found for equations (5) and (6) respectively, with $C_0 = 3.51 \times 10^{-6} M$. The scatter in the data is indicated in Fig. 2, the calibration curve based on equation (5).

Accuracy, precision and sensitivity

The accuracy and precision were tested with nine air-samples containing carbon monoxide in the range 0.2–4% (v/v). The results are presented in Table 2. The average error and mean relative deviation are

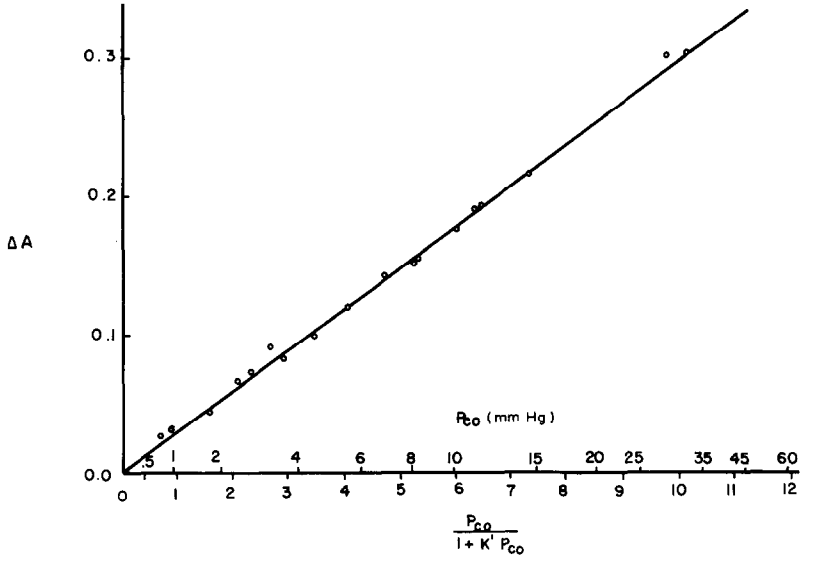


Fig. 2. Calibration curve for the determination of carbon monoxide (absorbance measured at 420 nm, $C_0 = 3.51 \times 10^{-6} M$).

Table 2. Determination of carbon monoxide in air-samples at 1 atmosphere pressure

Taken		Found*			
P_{CO}, *mmHg*	%, *v/v*	P_{CO}, *mmHg*	%, *v/v*	Error, %	Precision,† %
1.43	0.188	1.50	0.197	4.9	11.2
1.83	0.241	1.76	0.226	5.9	0
3.67	0.482	3.53	0.464	3.6	4.6
3.98	0.524	4.32	0.568	8.5	2.3
7.58	0.997	7.37	0.970	2.8	0
9.34	1.23	9.00	1.18	2.7	6.3
14.65	1.93	14.71	1.94	0.4	5.1
21.06	2.77	19.66	2.59	6.7	3.9
28.78	3.79	26.78	3.52	7.0	0

* Average of two determinations.
† Relative average deviation.

each 5% over this range. Although not exhaustive, the results show that the model haem systems have the potential to yield results of sufficient accuracy and precision for analytical purposes. In addition to the interferences, the other serious shortcoming of the method is the lack of sensitivity. For example, with $C_0 = 5 \times 10^{-6} M$ and the remaining experimental conditions as specified, if $\Delta A_{limit} = 0.01$, then the limit of sensitivity as calculated by equation (5) or (6) is 0.23 mmHg of carbon monoxide. For a gas-sample at one atmosphere pressure, this corresponds to 0.03% (300 ppm). This sensitivity is far too poor for use in the determination of carbon monoxide in cities, where the median annual concentrations lie in the range 3–13 ppm.[19]

Possible modifications to the reagent system

To be acceptable as an analytical procedure and competitive with other methods, for example, the method of Lambert and Wiens,[20] the sensitivity must be improved by a factor of 1000. Two ways by which this may be brought about are: (*a*) to improve the spectral resolution or (*b*) to increase the value of *K*. First, a more favourable separation of the Soret bands of the carbonylated and the uncarbonylated species than that shown in Fig. 1 will enhance the sensitivity. This resolution may be brought about by co-ordination of sterically-hindered bases (*e.g.*, α-picoline or 2,6-lutidine) to the axial positions of the iron(II) to keep the iron in a predominantly pentaco-ordinate high-spin state, thus shifting the Soret-band position from that of the hexaco-ordinate low-spin carbon monoxide complex.[21] Preliminary studies on such a system, however, indicate that it will be difficult to stabilize the system with respect to aerial oxidation. Second, in the search for haem systems with larger *K* values, it should be noted that natural or related haems such as haematohaem have higher binding constants for carbon monoxide than Fe(II)TPP but are much more susceptible to aerial oxidation and thus are unsuitable for analytical purposes. The pyridine–mesohaem model system reported by Chang and Traylor,[9] however, has a high affinity for carbon monoxide and a surprisingly low affinity for oxygen and would seem to be ideal for analytical exploitation. Unfortunately, the synthesis of monopyridine-mesohaem in high purity is both difficult and expensive and thus not practical. An easily and inexpensively synthesized compound is the dipyridine complex of Fe(II)TPP. This compound appears to have a greater affinity for carbon monoxide and a lower affinity for oxygen than the dipiperidine complex.[7] Further, the use of pyridine instead of piperidine might eliminate the interference caused by carbon dioxide. The potential of the dipyridine complex as a reagent for carbon monoxide is now being investigated.

CONCLUSION

The present study represents an initial attempt to demonstrate the suitability of a model compound for a biological process as an analytical reagent. Although solutions of Fe(II)TPP(pip)$_2$ can be used for the determination of carbon monoxide, the analytical system described lacks sufficient sensitivity. Also, interference by carbon dioxide and hydrogen sulphide causes a decrease in selectivity. Modifications involving the use of different axial ligands could well increase the sensitivity to useful levels and improve the selectivity.

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ANALYTICAL STUDIES USING IODINE–LUMINOL CHEMILUMINESCENCE

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Summary—Trace amounts of substances have been related to iodine consumption monitored by chemiluminescence from the iodine–luminol system. Iodine titrations of sulphite and arsenic(III) have been carried out at levels of 1.0×10^{-7} and $5.0 \times 10^{-8} M$ with a precision and error of better than 1% on a day-to-day basis. A calibrated standard of 1.8 ppm SO_2 in air was analysed with a precision of ±1.2% and an error of 0.9%. A rate method has been developed based on the reaction between iodine and penicillin G; a linear range from 10^{-8} to 10^{-7} *M* was found, the precision being ±9%.

Halogens are known to react with luminol (5-amino-2,3-dihydrophthalazine-1,4-dione) in basic aqueous solution to produce intense chemiluminescence (CL). Halogen-induced CL of luminol has been used to determine chlorine in water[1,2] and has shown potential for indirect determination of species that can be titrated with iodine.[3] An extensive study of the hypochlorite–luminol system has been reported by Seitz.[4]

Babko *et al.* were the first to investigate the iodine CL reaction.[5] Subsequently, Seitz and Hercules[6] studied CL of the iodine–luminol reaction in basic aqueous solution. They observed that in the presence of excess of luminol, the CL intensity was proportional to $[I_2]$, $[I_2]^2$ and/or $[I_2]^3$. This was explained in terms of a mechanism involving an azaquinone intermediate as shown in Fig. 1. They observed that at pH-values above 11.5 CL was directly proportional

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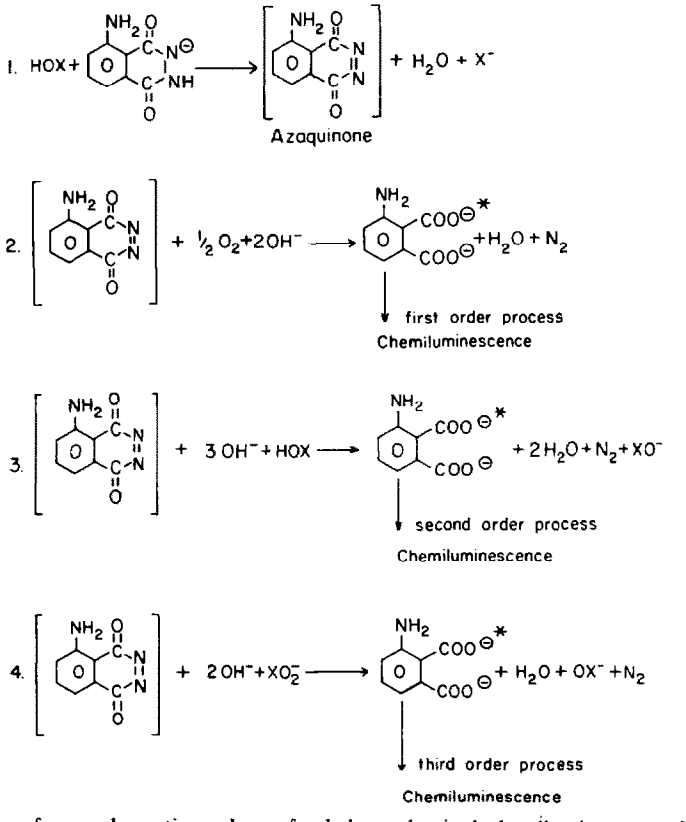

Fig. 1. Diagram of general reaction scheme for halogen–luminol chemiluminescence. X = Cl, Br, I; reaction 4 occurs only for bromine and iodine.

to iodine concentration, from a detection limit of approximately $10^{-9}M$ up to $3 \times 10^{-7}M$ I_2. Above $3 \times 10^{-7}M$ I_2, the response is complicated by higher order processes.

A substance that can be titrated conventionally with iodine can be titrated at much lower concentrations by a CL titration. Such a titration can be compared to a photometric titration of a non-absorbing sample with an absorbing titrant. No CL response is detected above the background level before the end-point is reached, since all the I_2 is reduced to I^-. After the end-point, added increments of iodine produce CL and the end-point is determined by extrapolation. The feasibility of such a titration has been described in a preliminary publication.[3]

In the present study we have titrated sulphite and arsenic(III) with a precision and error of better than 1% on a day-to-day basis. The reaction between sulphite and iodine has also been applied to determination of SO_2 in air with a precision of 1.2% and an error of 0.9%. A rate method for penicillin G has been developed, which has a linear response over a range of at least one order of magnitude, at a precision of ±9%.

EXPERIMENTAL

Apparatus

Chemiluminescence intensity was measured with the apparatus shown diagrammatically in Fig. 2. The system used two 100-ml glass syringes; one contained luminol dissolved in $0.1M$ H_3BO_3–KOH buffer and the other a background solution of $0.1M$ $H_2PO_4^-$–HPO_4^{2-} buffer. The syringes were driven by a Harvard Model 600-2-200 infusion pump.

Samples were introduced into the background-buffer flow-line by a Chromatronix SV-8031 sample-injection valve. The valve has two positions; in one position $0.01M$ phosphate buffer flows to the CL cell, in the second position sample solution contained in the sample loop is pushed by the pump to the CL cell. The cell was fabricated from a 9-mm o.d. Pyrex tube and had a volume of 1.2 ml. The base of the cell was constructed to allow the independent entry of the liminol solution, background-buffer–sample solution and the compressed air used to mix the two solutions. "Teflon" tubing, 1/32-in. bore, was fitted into two of the nipples and extended into the centre of the cell. This was to ensure that the reagents mixed in the centre of the cell; it also reduced the possibility of solution back-up into the tubing. The tubing for compressed air was 1/64-in. bore to produce small bubbles for efficient mixing. The top of the cell was constricted to a single exit for the reaction products to pass to a waste receptacle.

Increments of iodine titrant were added with a Syringe Microburet model 582 (Micro-Metric Instrument Co.) with a precision of 0.1% when dispensing 20-μl portions. Samples to be titrated were added from a 5-ml burette graduated in 0.01-ml divisions.

CL was detected with an RCA 1P21 photomultiplier attached to the face of the cell. The signal was amplified by a Princeton Applied Research (PAR) model 270 d.c. photometer–preamplifier in conjunction with a PAR model 280 power supply. The response was recorded on a Hewlett-Packard model 7101B potentiometric recorder.

A 2-Hz low-pass electronic filter (8-pole, Butterworth; Burr-Brown) was used in experiments with small sampling volumes (*ca.* 0.75 ml) to determine more precisely the steady-state CL.

A 1-litre gas syringe (Hamilton) was used to dispense a 1.8-ppm Matheson SO_2-in-air gas standard.

Chemicals and materials

Luminol was converted into the sodium salt with sodium hydroxide. Some luminol used in this study was purified by dissolving it in potassium hydroxide solution, adding "Norit", filtering, and then precipitating the luminol with concentrated hydrochloric acid. A $1.5 \times 10^{-3}M$ luminol solution was prepared by dissolving 0.300 g of the luminol sodium salt or 0.265 g of luminol, 61.8 g of boric acid, and 56.1 g of potassium hydroxide in one litre of water.

Stock iodine solutions were prepared by dissolving analytical-reagent grade iodine in 4% w/v potassium iodide solution. Iodine solutions prepared in this way were found not to change titre over a period of six months. Primary standard arsenious oxide was dissolved in 20 ml of $1M$ sodium hydroxide and neutralized with $1M$ hydrochloric acid. The iodine stock solutions, which were either 1.250 or $2.500 \times 10^{-2}M$, were then titrated with the standard arsenious oxide solution, using the starch end-point method described by Kolthoff and Sandell.[8]

Sulphite solutions were prepared by bubbling nitrogen for 15 min through $1.0M$ potassium dihydrogen phosphate before dissolving the anhydrous sodium sulphite used. The sodium sulphite solutions were usually $4.0 \times 10^{-3}M$.

Penicillin G solutions were prepared by dissolving 25–35 mg in sufficient $0.01M$, pH-9, HPO_4^{2-} buffer to make 25 ml.

Two litres of $1.0M$ pH-6.9 buffer were prepared from 138 g of disodium hydrogen phosphate, and 268 g of sodium dihydrogen phosphate. A $10^{-2}M$ solution of this

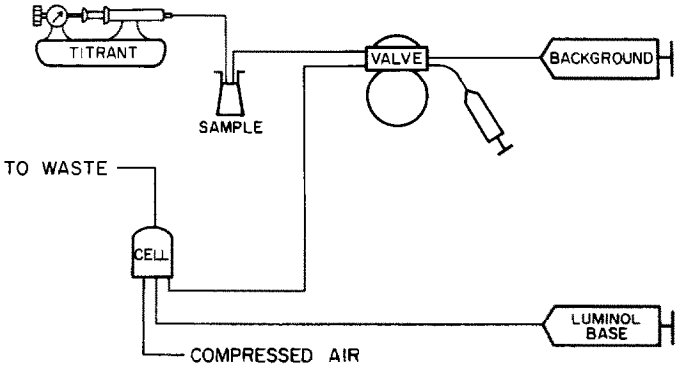

Fig. 2. Diagram of the flow system for chemiluminescence titrations.

buffer, for use as the background solution, was prepared by diluting 20 ml to 2.0 litres.

All the reagents were prepared with demineralized water.

Procedures

The sample to be titrated was placed in the 0.01*M* phosphate buffer and baseline chemiluminescence was established by withdrawing several increments before the equivalence point and allowing them to react with liminol. Successive equal increments of iodine were added and CL measured at each point. A significant increase in CL occurred with each addition after the equivalence point had been passed.

A sample of raw CL titration data is shown in Fig. 3. The CL intensity is determined by subtracting the background from the CL steady-state value. The CL intensities are then plotted *vs.* volume of titrant and analysed by a linear least-squares method as shown in Fig. 4.

For the experiments with 25 ml of sample, 0.75-ml portions of titration solution were withdrawn for each measurement. This was done by drawing solution into the sample loop of the sampling value up to a precalibrated mark and then removing the sampling tube from the sample.

Volume corrections are necessary in CL titrations because a finite volume must be removed from the titration solution in order to make a CL measurement. If the sample volume is large (*ca.* 500 ml) compared to the volume necessary for the CL measurement (*ca.* 2.5 ml) then no correction need be made for the decrease in sample volume. However, when dealing with small sample volumes (*ca.* 25 ml), a correction is necessary because the increase in iodine concentration in titration solution is not a linear function of the volume of iodine solution added. As an experimental convenience, because of the high precision

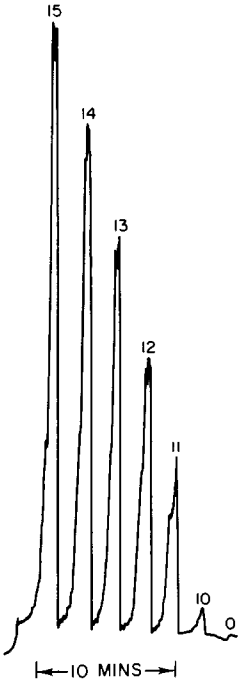

Fig. 3. Data obtained for the chemiluminescence titration of 25.00 nmole of As(III) with 5.00-nmole increments of iodine. The numbers over the peaks indicate the total nember of 5.00-nmole increments of iodine added before measurement. Sample volume 500 ml; 2.50-ml sampling "slug"; titrant concentration $2.500 \times 10^{-4}M$ iodine; 20-μl increments of titrant used; CL cell pH 11.5–12.0.

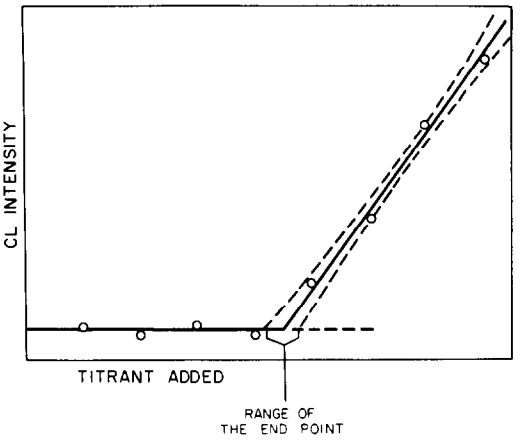

Fig. 4. Confidence limit around the linear portion of a chemiluminescence titration curve. O–CL data points. (–)–Linear least-squares line. (---)–Confidence limits around least-squares line.

and accuracy of the microburette used, the titrant (iodine) increment size was adjusted to keep the increase in iodine concentration in the titration solution the same for each addition. For example, if the sample volume was reduced by 3% to make a CL measurement, then the volume of the next increment of iodine solution was reduced by 3%.

It was necessary for the coarse glass frits used to bubble the 1.8-ppm SO_2 gas sample to be treated overnight with a 6:1 v/v mixture of acetone and "Sigmacote" (hydrophobic agent, Sigma) to prevent an abnormally high background produced when the sample was bubbled through an untreated frit. The frits were then dried and used to bubble the sample gas through a 0.01*M* sodium dihydrogen phosphate solution which had been deaerated for *ca.* 30 min by passage of nitrogen.

The rate of consumption of iodine by penicillin was measured at room temperature (*ca.* 21°). A sample of penicillin in pH-6.0 phosphate buffer was added to a sample bottle containing $5.0 \times 10^{-8}M$ iodine in 0.01*M* pH-6.9 phosphate buffer. The decrease in iodine signal strength was measured *vs.* time. The concentration of penicillin was proportional to the initial iodine concentration measured by extrapolation. The CL readings were taken at intervals of 45–120 sec for a period of 6–7 min.

The sensitivity (towards iodine) of different $1.0 \times 10^{-4}M$ luminol solutions (at the same pH), that have been prepared from the same $1.0 \times 10^{-3}M$ luminol stock solution, can vary by a factor of as much as three. The sensitivity of the same $1.0 \times 10^{-2}M$ solution of luminol can also vary to the same degree over a period of months. Therefore, it was necessary when making rate measurements to run a control with $5 \times 10^{-8}M$ iodine before each rate measurement, to correct for any change in sensitivity of the luminol, and all rate data used to make the penicillin calibration curve were run with the same luminol solution.

RESULTS AND DISCUSSION

Arsenic titrations

Arsenic(III)–iodine CL titrations were studied because iodine solutions are normally standardized with As_2O_3 as a primary standard,[8] and should give an indication of the best precision and accuracy possible for iodine CL titrations.

Stock $2.50 \times 10^{-2}M$ iodine solutions were titrated with a $1.250 \times 10^{-2}M$ arsenic(III) solution; the arsenic(III) stock solution was then diluted and a CL

titration performed. When 25.0 nmole of As(III) (calculated from sample volume of diluted $1.250 \times 10^{-2}M$ stock solution) were titrated with 5.0-nmole increments of $2.50 \times 10^{-4}M$ iodine stock solution an average of 24.8 nmole of iodine was consumed. The coefficient of variation for 8 titrations was 0.8% and there was a 0.8% difference between the 25.0 nmole of As(III) taken and the 24.8 nmole found in the CL titration with iodine.

These data indicate quite clearly that it is possible to titrate low concentrations of substances, classically titrated with iodine, with both good precision (0.8%) and good accuracy (0.8% error).

Sulphur dioxide titrations

Replicate samples of stock sulphite solutions were diluted and analysed by iodine CL titration. Typical results obtained with a 500-ml sample bottle and a sampling volume of 2.5 ml gave a precision of 0.8% for 11 titrations but a 4% difference from the sulphite concentration determined by macrotitration of the more concentrated sulphite solution. That difference was attributed to loss of iodine or sulphite in a dilution process. Loss of iodine by volatilization was eliminated by addition of iodide and use of fewer dilution steps. Loss of sulphite was due to oxidation by dissolved oxygen. When all solutions coming into contact with sulphite were deaerated by passage of nitrogen (for *ca.* 8 min) a 2% difference between macro and CL titration values was found. With more extensive and careful deaeration (*ca.* 15–20 min) the difference was reduced to 0.5%.

Experiments were also conducted with smaller volumes of titration solution and CL samples. A CL titration of 1.15 nmole of sulphite with increments of iodine nominally equivalent to 0.107 nmole (see above for explanation of successive reductions in volumes added) gave a coefficient of variation of ±6% (10 results). The decrease in precision was attributed to increased uncertainty in measurements of the steady-state CL intensity, because of the decreased size of the CL sample. A 2-Hz low-pass filter was used to filter out high-frequency noise on top of the peak, so that the steady state could be measured more precisely. By use of the 2-Hz electronic filter the coefficient of variation was decreased to ±1%.

Iodine titrations were then applied to the determination of SO_2 in air. Other workers had measured SO_2 concentrations in air by iodine titration,[9] but their method involved a very large air sample (*ca.* 200 ft^3). The present method requires a sample as small as 300 ml.

Analyses were performed on a standard 1.8-ppm SO_2-in-air sample obtained from Matheson Gas Products. The results for these analyses are presented in Table 1, and indicate that varying amounts of SO_2 may be bubbled through a collecting solution and determined with good accuracy (error *ca.* 1%).

Based on a 25-ml solution volume and a 500-ml air sample, a detection limit of lower than 0.01 ppm of SO_2 in air should be possible by the CL titration method. This compares with the detection limit for the standard West–Gaeke referee method for SO_2, which is 0.005 ppm based on a 10.0-ml collecting solution and a 33.2-litre air sample.[10] Therefore, it is possible, using comparatively inexpensive instrumentation, simple sample preparation, and small air samples, to determine SO_2 in air to a high degree of precision and accuracy by CL titrations.

Table 1. Triplicate chemiluminescence titrations of different volumes of a 1.8-ppm standard sample of sulphur dioxide in air

Sample volume, *ml*	Coefficient of variation, %	Difference from nominal value, %
900	0.9	−2.3
600	1.2	−0.9
500	3.0	0.0
300	7.0	+5.0

In order to compare the chemiluminescence method with the standard West–Gaeke method, samples of air were analysed by each method in the range from 0.5 to 2 ppm SO_2. The correlation between the two sets of results was excellent. Therefore, the CL method offers a useful alternative to collecting the large air samples needed for use in the West–Gaeke method.

Rate method for penicillin G

The penicillins can be assayed by treatment with base and reaction with an excess of iodine. Alicino studied a number of natural and synthetic penicillins and reported the following iodine equivalents:[11] benzylpenicillin (penicillin G) 9.0; α-phenoxyethyl penicillin acid, 9.0; 6-aminopenicillanic acid, 8.0; phenoxyethylpenicillin, 9.0; cephalosporin C, 4.0.

In an attempt to titrate penicillin G with iodine by CL we studied the reaction between $1 \times 10^{-7}M$ iodine and $2.1 \times 10^{-8}M$ penicillin. This reaction required more than 2 hr to go to completion. To shorten the analysis time we have developed a method based on the rate of reaction between iodine and penicillin.

The reaction between $5 \times 10^{-8}M$ iodine and a range of penicillin concentrations from 2.1×10^{-8} to $2.1 \times 10^{-7}M$ in a 500-ml sample volume was followed by measuring the decrease in CL intensity produced by the iodine, as a function of time. As shown in Fig. 5, the initial rate appears to increase with increasing penicillin concentration and then becomes constant after about 1 min. If the linear portion of the plot is extrapolated to zero time and the relative iodine CL intensity at zero time is plotted *vs.* log of the penicillin concentration, a linear relationship is obtained.

From the kinetic curves it appears that two reactions are occurring: the first appears to be the formation of an intermediate by the reaction of iodine and penicillin, the second presumably involves the inter-

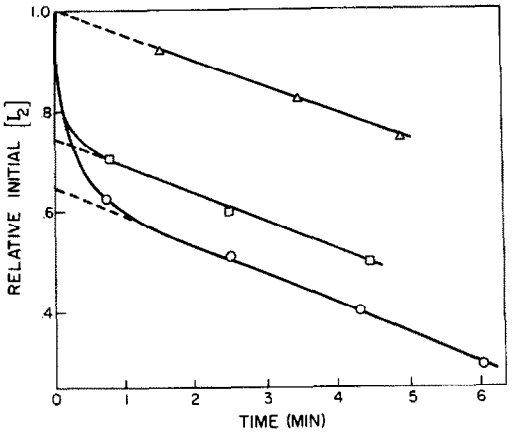

Fig. 5. Analysis of rate data showing the decrease in iodine chemiluminescence intensity (initial relative concentration = 1.0) after addition of penicillin. Initial iodine concentration $5 \times 10^{-8}M$ (500 ml of solution); $2.1 \times 10^{-8}M$ penicillin (△); $5.3 \times 10^{-8}M$ penicillin (□); $1.07 \times 10^{-7}M$ penicillin (○).

mediate and a molecule of iodine. The rate of the first reaction is proportional to the log of the penicillin concentration, while the rate of the second reaction does not appear to depend on the concentration of either iodine or penicillin but is constant. Extrapolation to zero time in the plots shown in Fig. 5 gives an estimate of the amount of iodine consumed in the first reaction.

To test the validity of the calibration curve (which gave excellent linearity) it was necessary to prepare and analyse a solution of penicillin independently. A stock penicillin solution (35 mg/25 ml) was treated with base and analysed by addition of excess of iodine and titration of the unreacted iodine with standard As(III) solution.[11] The stock solution of penicillin was then diluted and assayed by the CL rate method. The penicillin concentration values obtained and corrected for the dilution factor are compared in Table 2.

Because of the change in CL sensitivity of luminol to iodine on different days, a slope correction had to be made to the rate data used to obtain Table 2. The data were fitted to the linear equation.

$$[I_2]_e = [I_2]_i - m_a t_i \qquad (6)$$

where $[I_2]_i$ and t_i are the iodine peak-heights and time, respectively, for each pair of rate measurements; m_a is the average of all constant slopes of the rate data used to obtain the calibration curve. A value of $[I_2]_e$ (relative extrapolated $[I_2]$) was calculated for each data point and all values were then averaged to obtain the penicillin concentration.

The detection limit for the penicillin CL rate method was found to be 2.0×10^{-8} mole of penicillin in a 500-ml sample. If the sample volume is lowered to 25 ml it should be possible to detect 5.0×10^{-10} mole of penicillin.

CONCLUSIONS

We have demonstrated that the iodine-luminol chemiluminescence system may be used for trace analysis of arsenic(III) and sulphite in solution, SO_2 in air, and as a rate method for penicillin G. The advantages are that analyses may be performed at low substrate concentrations with good precision and accuracy. It should be possible to extend the utility of the iodine–luminol CL system to any species that may be titrated with iodine.

The flow system used for our titrations has many analytical advantages, including the possibility of automation, though a major difficulty for this would be the problem of point-by-point titrations. This problem could be eliminated by developing a continuous titration apparatus. In such an apparatus the sample and standard iodine solutions would be placed in syringes and mixed before entering the chemiluminescence cell. The luminol base solution would flow independently into the cell and there mix with the reactants. The flow-rate of the standard iodine solution could be varied (probably in a linear fashion) as a function of time so that at some flow-rate an excess of iodine would be present in the cell and produce a chemiluminescence response signalling the end-point. This "end-point" flow-rate could be related to the concentration of the unknown sample by means of the equation:

$$C_{\text{unknown}} = C_{I_2} \times \frac{(\text{flow-rate})_{\text{iodine}}}{(\text{flow-rate})_{\text{unknown}}}$$

where the two flow-rates and the iodine concentration at the end-point are known. The continuous titration apparatus would overcome the problem of the volume correction for small samples.

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Table 2. Results for penicillin G samples analysed by chemiluminescence rate method

Penicillin concentration, $10^{-8}M$		
I_2/As(III) method[11]	CL method	Difference, %
4.2	3.6	14
8.4	8.9	9
12.7	13.8	9
16.9	17.8	5

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ON THE ACCURACY OF ACID-BASE DETERMINATIONS FROM POTENTIOMETRIC TITRATIONS USING ONLY A FEW POINTS FROM THE TITRATION CURVE

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Summary—There are several procedures which use only a few points on the titration curve for the calculation of equivalence volumes in acid–base titrations. The accuracy of such determinations will depend on the positions of the points on the titration curve. The effects of errors in the stability constants and in the pH measurements on the accuracy of the analysis have been considered, and the results are used to establish the conditions under which these errors are minimized.

The equation of the titration curve for an acid–base titration suggests that equivalence volumes can be calculated from a limited number of measurements of corresponding values of pH and V, where V is the volume of titrant added. When the equilibrium constants are known, the minimum number of pH, V pairs required is equal to the number of acids present in the sample. Although Auerbach and Smolczyk[1] obtained good results by using only a limited number of points from the titration curve to calculate the equivalence volume, their procedure appears to have been comparatively little used. Recently Ivaska [2,3] has made an extensive investigation of the method.

The success of the method will, of course, depend on the accuracy of the values of the stability constants and the pH measurements. The errors in the equivalence volumes caused by errors in these quantities will depend on the pH, V pairs selected for the calculations. It is the aim of this paper to illustrate this dependence and to determine the optimum pH-ranges.

THEORY AND RESULTS

The theory will be presented for titrations of acids with strong base, *i.e.*, OH^-. The hydroxide ion is assumed to be generated coulometrically or added from a microburette. Dilution effects can then be neglected. Activity coefficients are assumed to be held constant by addition of inert salt.

The following notation will be used: U = amount of hydroxide ion added, divided by the sample volume; $U_e = U$ at the equivalence point; $[Z]_0$ = initial or total concentration of Z; [Z] = concentration of species Z at equilibrium. Charges will be omitted for convenience.

The stepwise stability constants of the acid H_nX are defined by $K_{H_nX} = [H_nX]/[H][H_{n-1}X]$. The hydrogen-ion concentration, [H], is determined by emf measurements with electrodes standardized in a solution of known [H] in the titration medium. It is then unnecessary to introduce the hydrogen-ion activity into the equations. pH will be understood to refer here to $-\log[H]$ rather than $-\log a_H$. K_W is the ionic product of water.

Case 1. Weak monoprotic acid, HX

The proton condition yields

$$[X] = U + [H] - [OH] \tag{1}$$

Measurement of U and [H] can thus be regarded as determination of [X]. The total concentration of HX is found by multiplying [X] by $([HX]_0/[X]) = (1 + [H]K_{HX})$. After rearrangement

$$U_e - U = U[H]K_{HX} + ([H] - [OH]) \times (1 + [H]K_{HX}) \tag{2}$$

is obtained. (Note that $U_e = [HX]_0$.) Equation (2) is the Ingman and Still relation.[4] When K_{HX} is known it can be used to find U_e from a single measurement of U and [H].

Errors in U_e caused by the errors in [H], K_{HX} and U will vary with U. The effect of these errors on U_e can be estimated from the partial derivatives of $U_e = f(U, [H], K_W, K_{HX})$:

$$\left(\frac{\delta U_e}{\delta U}\right) = 1 + [H]K_{HX} \tag{3a}$$

$$\left(\frac{\delta U_e}{\delta [H]}\right) = UK_{HX} + ([H] - K_W/[H])K_{HX} + (1 + [H]K_{HX})(1 + K_W/[H]^2) \tag{3b}$$

$$\left(\frac{\delta U_e}{\delta K_{HX}}\right) = U[H] + [H]^2 - K_W \tag{3c}$$

$$\left(\frac{\delta U_e}{\delta K_W}\right) = K_{HX} - 1/[H] \tag{3d}$$

The error is expressed as a percentage, $F = 100 \times \Delta U_e/U_e$, and presented as a function of (U/U_e), the

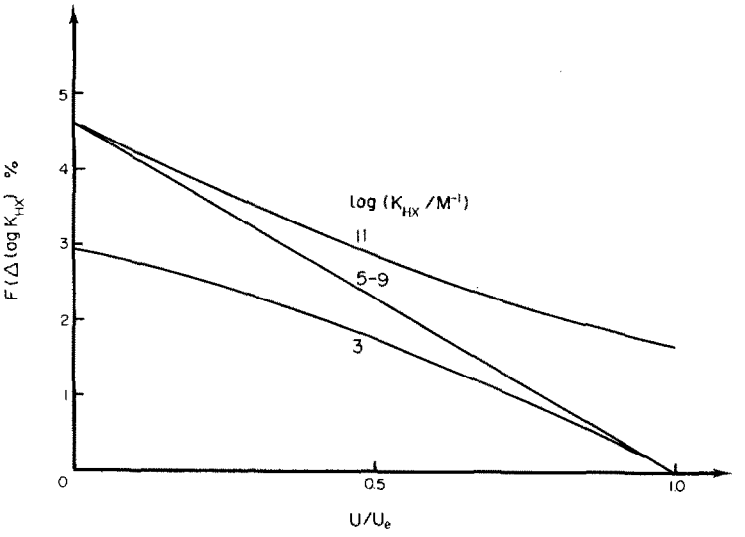

Fig. 1. $F(\Delta \log K_{HX})$ as a function of U/U_e for some values of K_{HX}. The curves have been calculated with $\Delta \log K_{HX} = 0.02$ and $U_e = 0.005M$.

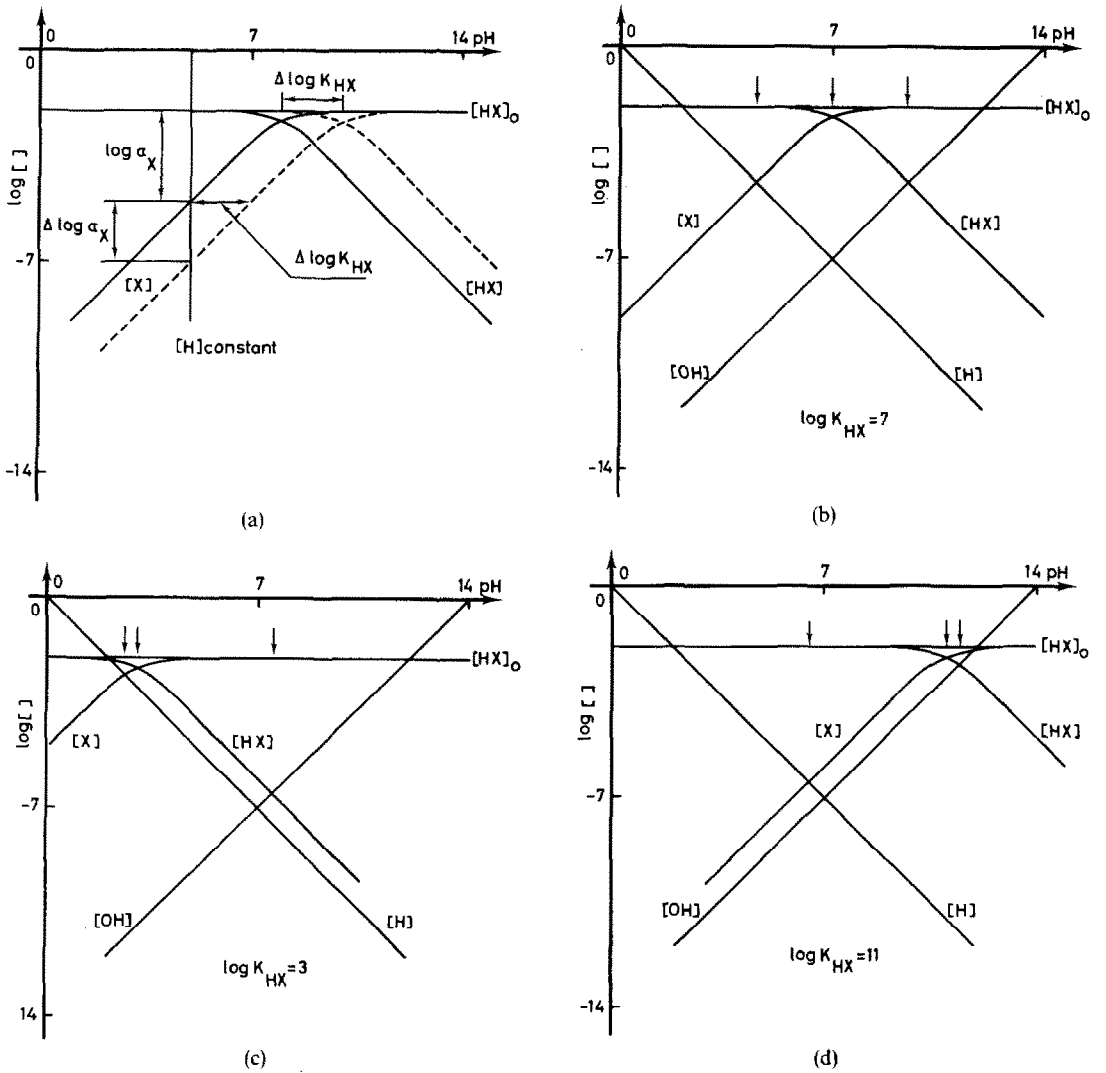

Fig. 2. Logarithmic diagrams for $0.01M$ monoprotic acids. The arrows show the pH-values for $U/U_e = 0$, 0.5 and 1 respectively.

degree of titration. The error in a quantity A is denoted by ΔA and the corresponding function of A is denoted by $F(\Delta A)$. The functions were:

$$F(\Delta A) = 100 \times (\delta U_e/\delta A)\Delta A/U_e$$

$$F(\Delta \log A) = 100 \times \ln 10 \times A(\delta U_e/\delta A)\Delta \log A/U_e$$

In Fig. 1, $F(\Delta \log K_{HX})$ calculated from (3c) is shown for various values of K_{HX}. The error in the constant, $\Delta \log K_{HX}$, was taken as 0.02 and U_e was 0.005M. A single curve has been drawn for log K_{HX} = 5, 7 and 9 since the differences between the separate curves are small. For these log K_{HX} values $F \approx 100 \times \ln 10 \times (1 - U/U_e)\Delta \log K_{HX}$, *i.e.*, there is a linear relationship between F and U/U_e. In all cases the error decreases towards the equivalence point. If the titration is stopped well before this point, K_{HX} must be very accurately known. Since F is approximately proportional to $\Delta \log K_{HX}$, Fig. 1 can be used to find the error for other values of $\Delta \log K_{HX}$ as well.

The shapes of the error curves in Fig. 1 can be qualitatively understood from logarithmic diagrams. As already mentioned, an experimental point basically yields [X]. $U_e = [HX]_0$ is found by dividing [X] by α_x, where $\alpha_x = [X]/[HX]_0$, *i.e.*, the fraction of the HX–X$^-$ system present as X$^-$. In Fig. 2a log α_x is shown as well as the error in log α_x caused by an error in log K_{HX} at constant [H]. Since the slope of log [X] = f(pH) gradually increases from 0 at pH $\approx$ log K_{HX} + 2 to 1 at pH $\approx$ log K_{HX} − 2, the effect of an error in K_{HX} on α_x will be greater as the pH-value of the chosen experimental point is decreased.

For log K_{HX} values in the range 5–9 (Fig. 2b) the pH at the start of the titration is in the most error-sensitive region, so the error is largest at the start of the titration. It then steadily decreases and approaches 0 at the equivalence point since there α_x is almost unaffected by a change in K_{HX}. For log $K_{HX} \lesssim 3.5$ (Fig. 2c) the pH at the start of the titration is quite close to pH = log K_{HX}. Hence F will always be smaller than in the previous case. For log $K_{HX} \gtrsim 9.5$ (Fig. 2d) F is large at the start of the titration, and it remains so, since the equivalence point pH is in the vicinity of pH = log K_{HX}.

Figure 3 shows results from equation (3b) with $\Delta \log [H] = 0.005$, which corresponds to an uncertainty of about 0.3 mV in the emf measured at 25°. For log K_{HX} values in the range 5–9, F approaches the straight line $F = 100 \times \ln 10 \times (1 - U/U_e)\Delta \log [H]$ as U/U_e increases. An error in pH and log K_{HX} will thus affect U_e to the same extent. This can be inferred from equation (2), since U_e depends on [H] and K_{HX} in the same way when the second term can be neglected. The greater errors found with small and large K_{HX} values arise largely from this second term in (2).

An error in K_W will be negligible unless K_{HX} is large. The error from uncertainties in U is given by $F = 100 \times (1 + K_{HX}U)\Delta U/U_e \approx 100 \times \Delta U/U$ and needs no further comment.

The effect of the errors discussed above on the finally determined value of the equivalence volume indicate that the pH, U pair should be chosen close to the equivalence point. If this is not feasible, very accurate values of K_{HX} and [H] are needed.

Case 2. One diprotic acid, H_2X

For a diprotic acid, H_2X, with stability constants K_{H_2X} and K_{HX}, the equations are:

$$[HX] + 2[X] = U + [H] - [OH] \quad (4)$$

$$U_e = (U + [H] - [OH]) \times (1 + K_{HX}[H] + K_{H_2X}K_{HX}[H]^2)/(2 + K_{HX}[H]) \quad (5)$$

U_e can thus be found by using only one pH, U pair if the equilibrium constants are known. Only the effect of uncertainties in these constants on U_e will be discussed, since in general the values of [H] and U will be more precisely known than K_{H_2X} and K_{HX}.

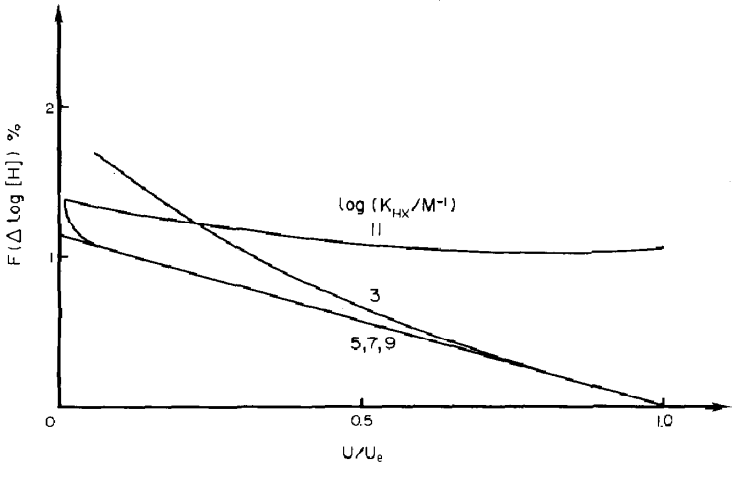

Fig. 3. $F(\Delta \log [H])$ as a function of U/U_e for some values of K_{HX}. The curves have been calculated with $\Delta \log [H] = 0.005$ and $U_e = 0.005M$.

Table 1. Values of F (%) for a diprotic acid, calculated with $\Delta\log K = 0.05$ and $U_e = 0.005M$. Each subtable refers to a particular combination of K_{H_2X} and K_{HX}. The figures in the four rows of a subtable are the values of $F(K_{H_2X})$ and $F(K_{HX})$ at $U/U_e = 0.5$, 1, 1.5 and 1.75. For $U/U_e = 2$ the errors are negligible

K_{H_2X} =	10^1		10^2		10^3		10^4	
$\log(K_{HX}/K_{H_2X})$	$F(H_2X)$	$F(HX)$	$F(H_2X)$	$F(HX)$	$F(H_2X)$	$F(HX)$	$F(H_2X)$	$F(HX)$
1	0.2	1.7	2.0	2.3	4.8	1.6	6.0	1.2
	0.1	1.4	0.9	2.3	1.9	2.3	2.2	2.2
	0.0	0.8	0.2	1.8	0.4	2.0	0.4	2.0
	0.0	0.4	0.1	1.1	0.1	1.3	0.1	1.2
2	0.3	1.7	1.8	0.6	4.4	0.2	5.6	0.2
	0.1	2.0	0.5	1.4	0.9	1.0	1.0	1.0
	0.0	1.7	0.0	1.9	0.1	1.9	0.1	0.9
	0.0	1.0	0.0	1.2	0.0	1.2	0.0	1.2
3	0.3	0.4	1.7	0.1	4.4	0.0	5.6	0.0
	0.1	1.2	0.2	0.6	0.3	0.4	0.3	0.4
	0.0	1.9	0.0	1.9	0.0	1.9	0.0	1.9
	0.0	1.2	0.0	1.2	0.0	1.2	0.0	1.2
4	0.2	0.1	1.7	0.0	4.4	0.0	5.6	0.0
	0.0	0.5	0.1	0.2	0.1	0.1	0.2	0.1
	0.0	1.9	0.0	1.9	0.0	1.9	0.0	1.9
	0.0	1.2	0.0	1.2	0.0	1.2	0.0	1.2

The calculation of F is based on the partial derivatives

$$\left(\frac{\delta U_e}{\delta K_{H_2X}}\right) = K_{HX}[H]^2\,(U + [H] - [OH])/(2 + K_{HX}[H]) \quad (6a)$$

$$\left(\frac{\delta U_e}{\delta K_{HX}}\right) = [H]\,(U + [H] - [OH]) \times (1 + 2K_{H_2X}[H])/(2 + K_{HX}[H])^2 \quad (6b)$$

Results for $U_e = 0.005M$ and $\Delta\log K = 0.05$ are given in Table 1. The errors have deliberately been made rather large in order to emphasize their influence on F.

The dependence of F on U/U_e will vary with K_{H_2X} and with the quotient K_{HX}/K_{H_2X}. F will, however, generally tend to 0 as U/U_e approaches 2. Thus, the pH, U pair should preferably be chosen close to the second equivalence point.

Certain trends in F are evident from Table 1. These can be understood from logarithmic diagrams from which the variation of the sum $[HX] + 2[X] = A$ with changes in the stability constants at constant pH can be estimated—the greater this variation, the greater the error in F.

An error in K_{H_2X} will affect A mainly by its effect on [HX]. From Fig. 4 it is seen that the variation will be greatest for pH < log K_{H_2X}. Hence the pH, U pair should be chosen so that $U/U_e > 0.5$. This recommendation applies also to moderately strong acids, since, though $F(\Delta\log K_{H_2X})$ is small, the error from ΔpH will be appreciable.

As can be expected from Fig. 4 and as the figures in Table 1 verify, $F(\Delta\log K_{HX})$ shows a maximum at $U/U_e \approx 1.5$. It can be shown from equation (6b) that the position of the maximum will approach $U/U_e = \sqrt{2}$ as $\log(K_{HX}/K_{H_2X})$ increases. Titrating to $U/U_e \approx 1.5$ should thus be avoided. Other trends in the errors given in Table 1 will not be discussed, as they are shown in Fig. 4.

In summary the best results can be expected if the pH, U pair is chosen close to the second equivalence point. The two buffer regions should be avoided. For acids with large values of K_{HX}/K_{H_2X}, pH values in the vicinity of the first equivalence point ($U/U_e = 1$) are also useful.

Case 3. Two monoprotic acids; sum known

When two monoprotic acids HX and HY have total concentrations $[HX]_0 = U_e^X$ and $[HY]_0 = U_e^Y$, respectively,

$$U + [H] - [OH] = [X] + [Y] = U_e^X/(1 + K_{HX}[H]) + U_e^Y/(1 + K_{HY}[H]) \quad (7)$$

and

$$U_e = U_e^X + U_e^Y \quad (8)$$

Elimination of U_e^Y between equations (7) and (8) yields

$$U_e^X = \frac{1 + K_{HX}[H]}{[H](K_{HY} - K_{HX})}\{(U + [H] - [OH]) \times (1 + K_{HY}[H]) - U_e\} \quad (9)$$

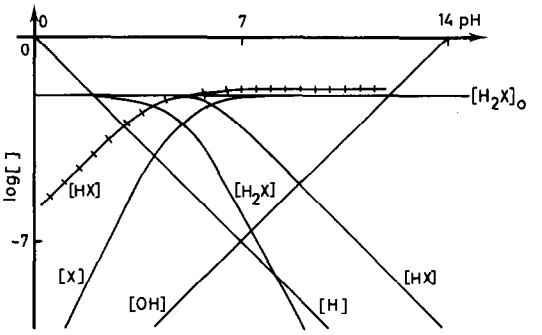

Fig. 4. Logarithmic diagram for a diprotic acid. $A = [HX] + 2[X]$ as a function of pH is indicated with short dashes. At constant pH, A is most sensitive to changes in K_{H_2X} and K_{HX} in the regions pH < logK_{H_2X} and pH ≈ logK_{HX}.

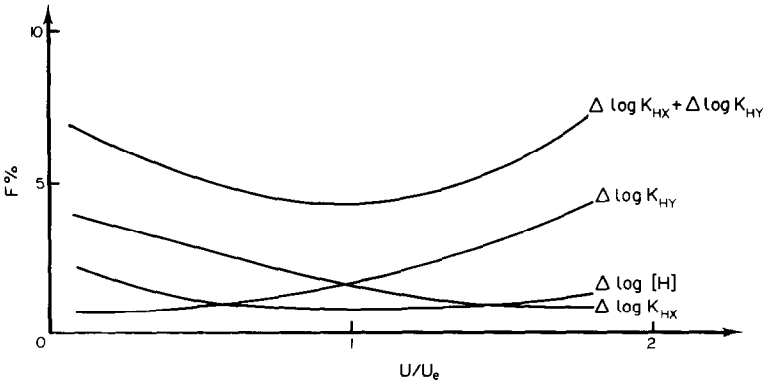

Fig. 5. F as a function of U/U_e for a mixture of two monoprotic acids. The curves have been calculated with $U_e^X = U_e^Y = 0.005M$; $\log K_{HX} = 3.5$; $\log K_{HY} = 4.5$; $\Delta\log[H] = 0.005$; $\Delta\log K_{HX} = \Delta\log K_{HY} = 0.02$. The type of error is indicated on each curve.

If their sum is known, the two equivalence volumes can be obtained from a single point on the titration curve before the equivalence point. This technique has been used by Johansson,[5] and by Frisque and Meloche.[6] The latter authors discuss the influence of an error in the pH measurements on U_e^X and U_e^Y.

Equation (9) shows that the general level of the F-values will increase as the difference between K_{HY} and K_{HX} diminishes. F can be estimated from the partial derivatives of equation (9). Note that $dU_e^X = -dU_e^Y$ since U_e is considered to be known exactly. Since rather lengthy expressions are obtained for the derivatives they will not be reproduced here. Instead a typical result of such a calculation is shown in Fig. 5.

$F(\Delta\log[H])$ and $F(\Delta\log K_{HX}) + F(\Delta\log K_{HY})$ exhibit minima. Assuming equal errors in the stability constants, it can be shown that for both types of error the minimum will occur in the vicinity of the pH at which [HX] = [Y], *i.e.*, at the first equivalence point. Frisque and Meloche[6] recommend titration to $pH = 0.5(\log K_{HX} + \log K_{HY})$, which for all practical purposes corresponds to the recommendations given here.

Case 4. Two monoprotic acids; sum not known

In this case equation (7) applies, and it may conveniently be rewritten as

$$y = xU_e^Y + U_e^X \qquad (10)$$

where

$$x = (1 + K_{HX}[H])/(1 + K_{HY}[H])$$

and

$$y = (U + [H] - [OH])(1 + K_{HX}[H]);$$

x and y can be calculated for each experimental point (U, [H]) if the stability constants are known. U_e^X and U_e^Y can thus be found by using two pH, U pairs and solving the resulting simultaneous equations.

Systematic errors in the equilibrium constants, random and systemic errors in U and [H] and the choice of pH regions will affect the accuracy of the equivalence volumes. Guidance on the sizes of these effects can be obtained from computer-simulated titrations. These can be conveniently performed as follows. First values of U are calculated from equation (9) with the "true" values of U_e^X, U_e^Y, K_{HX} and K_{HY} for a number of preselected pH-values. The (U, pH) values thus obtained would be those found in a titration if no experimental errors were present. Then x and y are calculated with $K_{HX} + \Delta K_{HX}$, $K_{HY} + \Delta K_{HY}$, $U + \Delta U$ and pH + ΔpH. All the pairs of equation (10) are then solved for U_e^X and U_e^Y. In conjunction with the "true" values these are then used to calculate the errors in the equivalence volumes. Since ΔU and ΔpH often represent random errors it may be appropriate to include them in only one of the two simultaneous equations used for computing U_e^X and U_e^Y.

It is not possible to formulate simple rules of general validity for selecting preset pH values, but useful guidance can be obtained from computer-simulated titrations. Some trends may be mentioned, however. An error in K_{HX} will always affect the result when $U/U_e < 1$. (In case 4 U/U_e is defined as $U/U_e = U/U_e^X$ for $U < U_e^X$ and as $1 + (U - U_e^X)/U_e^Y$ for $U > U_e^X$.) As K_{HY}/K_{HX} increases, K_{HX} will affect U_e^X and U_e^Y less and less as U/U_e tends towards 2. If an error mainly in K_{HX} is suspected, the pH-values should be chosen in the region $1 < U/U_e < 2$ and preferably in the upper part of this region.

An error in K_{HY} will have a minimal effect on U_e^X when U/U_e is small, unless K_{HY} and K_{HX} are close. Choosing two points at low U/U_e will then give an accurate value of U_e^X (unless K_{HX} is in error), but U_e^Y will be subject to a large error. To find U_e^Y one of the points must have $U/U_e > 1$. The error in U_e^Y as a function of the selected U/U_e often goes through a minimum, but the pH corresponding to this minimum is a rather complicated function of the parameters.

Simulated titrations clearly demonstrate the importance of accurate values of the stability constants. For $\log(K_{HY}/K_{HX}) < 1$ the logarithms of constants must be correct to within ± 0.01 if results with an error <1–2% are required. Hence a separate determination

of these constants under the actual experimental conditions used is almost a necessity for success.

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DETERMINATION OF GOLD IN TISSUE BY CARBON-FURNACE ATOMIC-ABSORPTION SPECTROMETRY

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Summary—A sensitive and reproducible technique is reported for the determination of gold in tissue by carbon-furnace atomic-absorption spectrometry. Results are compared with those obtained by using a flame-atomization procedure and by neutron-activation analysis. The method is used to analyse samples of kidney, liver, spleen, nails and hair from human subjects. A possible correlation between gold levels in nails and plasma is suggested.

Drugs containing gold are among the few, other than standard anti-inflammatories and steroids, that are effective in the treatment of rheumatoid arthritis. Their effectiveness was originally noted in the 1930s during clinical studies on tuberculosis[1] and was confirmed later by double "blind" trials.[2,3] The use of these drugs is often criticised, mainly on the grounds of toxicity,[4] yet neither the therapeutic nor the toxic action is understood. It is not, therefore, possible to decide whether more effective or less toxic gold drugs or regimes can be devised.

One of the major problems in studying the action of gold drugs is finding a simple, sensitive and reliable method of analysis which will allow clinical and animal model studies to be carried out in sufficient detail. For example, clinical studies have concentrated mainly on measuring gold levels in plasma,[5,6] although most investigators[7] but not all,[8] believe that this measurement does not give an accurate indication of the therapeutic response. Recently, a new atomic-absorption method was proposed for the determination of gold in blood by using carbon-furnace atomization.[9] With this method it was possible, for the first time, to analyse various blood-fractions. Approximately 4% of the blood-gold was found in the white cells, and it is possible that this intracellular-gold level may give a better correlation with therapeutic response.

A full understanding of the action of gold drugs requires an understanding of the tissue-gold distribution as well as that of the levels in blood, faeces and urine, but remarkably few results have been reported. Neutron-activation analysis was used to make a post mortem study of a wide variety of tissue-gold levels in a patient who had been receiving gold therapy[10] and in another study atomic absorption with flame atomization was used to investigate the levels in synovial fluid, muscle, bone and fat.[11] There are also several brief reports on human subjects and extensive animal studies.[16–20] This paper reports a study of the problem of determining gold in tissues. Results obtained by neutron-activation analysis and by atomic absorption with flame atomization are compared with a new atomic-absorption method for gold, with carbon-furnace atomization. The new method appears to have significant advantages over those used previously.

EXPERIMENTAL

Apparatus

The instrument used for all determinations using carbon-furnace atomization was a Perkin-Elmer model 306 atomic-absorption spectrometer equipped with an HGA72 heated graphite-tube atomizer and deuterium-arc background-corrector, and coupled to a Servoscribe RE511 strip-chart recorder. A Perkin-Elmer hollow-cathode lamp was used as the source. The design and operation of the HGA72 are described in detail elsewhere.[21] Samples were atomized in a graphite tube, 5.3 cm long and 1 cm in diameter, under an argon atmosphere. They were transferred to the centre of the tube with either a 10- or a 50-μl Oxford micropipette. The instrument has variable time and temperature selectors for sequential drying, ashing and atomization of the samples and, this sequence of operations once set, proceeds automatically. Signals are measured on the recorder which, for analysis purposes, is switched on only during the atomization stage.

A Shandon Southern A3417, 12-cm single-slot air–acetylene burner mounted on an A3400 atomic-absorption spectrometer was used for all determinations using flame atomization. A Pye-Unicam hollow-cathode lamp was used as the source. Sample signals were measured on a Servoscribe RE511 strip-chart recorder.

For the activation analysis, the reactor at the Scottish Universities Reactor Centre, East Kilbride, was used for the irradiation. Samples were prepared in the same way as for the atomic-absorption analysis, but were not dissolved. The solid samples were irradiated with a thermal neutron flux of 3.6×10^{12} n·cm^{-2}·sec^{-1} for 6 hr and allowed to decay for 48 hr to reduce the activity of 15.0-hr ^{24}Na before counting. The detector was a 25- or 40-cm^3 Ge(Li) detector with a resolution of 2.3 keV at 1.332 MeV. Each sample was counted for 10 or 30 min, as required, and the results were calculated with reference to the 412-keV photopeak of 2.7-day ^{198}Au.

Reagents

Use demineralized water in the preparation of all solutions.

Gold(I) stock solution (Au250 μg/ml). Dissolve the contents of one ampoule of the drug myocrysin (May and Baker) in 100 ml of water and standardize as already described.[9]

"Aristar" sulphuric and nitric acids (or equivalent).

Sulphuric acid/gold standards. Dilute 2 ml of 250-μg/ml gold stock solution to 100 ml with water and transfer 0, 1, 2, 3, 4, 5 and 6 ml of this solution to 100-ml graduated flasks. Add about 50 ml of water and 5 ml of concentrated sulphuric acid to each flask, cool, and dilute to the mark with water. These solutions contain 0, 0.05, 0.1, 0.15, 0.20, 0.25 and 0.30 μg of gold per ml in 5% v/v sulphuric acid.

Preparation of sample solutions

It is usual to express the heavy metal-ion concentration in tissue in terms of the dry weight of the tissue. Before the solutions are prepared the samples are treated as follows.

For liver, kidney and spleen samples, select a suitable portion of the sample and wash it thoroughly with water and physiological saline solution to remove any residual blood. Dry the sample for 6 hr at 120°, grind, and mix carefully to achieve homogeneity. For finger nail and hair samples, use the same procedure but without the washing.

Sample dissolution procedure.[23] Weigh accurately about 100 mg of the dried sample and transfer it to a PTFE beaker. Add 5 ml of concentrated sulphuric acid and place the beaker on a hot-plate at 70°. After 5 min, add nitric acid dropwise until all visible reaction has ceased and continue heating for a further 5 min. Remove from the hot-plate, cool, add about 25 ml of water, cool, transfer to a 100-ml calibrated flask and dilute to the mark with water. This provides a sample solution with the same sulphuric acid concentration as the standards.

Procedure for carbon-tube method

Inject 10-μl aliquots of standard and sample solutions into the graphite tube and atomize under the following conditions:

wavelength	242.8 nm
lamp current	10 mA
spectral band-width	0.7 nm
drying	40 sec at 130°
ashing	35 sec at 480°
atomization	5 sec at 2200°
argon flow-rate	1.5 l./min at 40 psig

Match the deuterium-arc background-corrector to the hollow-cathode light-beam. With low gold concentrations, as in the case of finger nails and hair, inject 50-μl aliquots of standard and sample solutions instead of 10 μl. The maximum-temperature button should be pressed to clear the tube after every sample and standard. Inject three different standards before injection of the samples. Inject other standards at intervals during analysis of the samples and finally the original three standards again to check for overall drift. Drift was never found to be significant and the standards may be injected in any order in terms of concentration. Find the gold concentration from the calibration graph.

Procedure for flame-atomization method

Prepare the sample solutions as already described, but from 1 g of dried sample instead of 100 mg. Prepare standard solutions as described, but covering the range 1–5 μg/ml.

Adjust the flame until the incandescence due to carbon species in the secondary reaction zone just disappears. Use the following operating conditions:

wavelength	242.8 nm
slit-width	0.10 mm
band-pass	0.6 nm
burner height	18 mm (position 4)
air flowmeter reading	7.5 (12 l./min at 30 psig)
acetylene flowmeter reading	2.5 (2.5 l./min at 8 psig)

Aspirate the solutions and determine the gold concentration from the calibration graph.

RESULTS AND DISCUSSION

It is usually necessary to destroy the organic matter in tissue before determining metal-ion concentrations by atomic-absorption spectrometry. The method used must release all the metal ion in question from the tissue and not affect the analysis. The two methods commonly used are (*i*) dry-ashing followed by dissolution in various acids, and sometimes subsequent extraction with methyl isobutyl ketone (MIBK) or ammonium pyrrolidinedithiocarbamate (APDC), and (*ii*) wet-ashing with either acid or alkaline media. Method (*i*) has the disadvantage of greater risk of loss of metal ions and in general larger samples are used. We therefore considered two wet-ashing procedures, one using acid digestion and the other tetraethylammonium hydroxide.

Many authors favour a hydrochloric acid–nitric acid mixture to digest the tissue because sulphuric acid causes interference in flame-atomization procedures.[22] However, this mixture does not break down fat-lipid fractions efficiently,[22] so a sulphuric acid–nitric acid mixture was used with the carbon-furnace atomization method.[23] Nitric or sulphuric acid is an ideal medium for carbon-furnace atomization.[24,25]

Most metal salts are broken down into oxides which are atomized at the appropriate carbon-reduction temperature.[25] Atomization is reproducible under these conditions for many types of sample, with no matrix interference. In the case of gold, however, the oxides are volatile and unstable at high temperatures so that some loss of gold is possible before atomization. Under the conditions used here, no loss of gold was found, presumably because the oxides decomposed before any appreciable amount of volatilization had occurred. The tissue was completely and easily solubilized in a very short time and there was no precipitation at any dilution. It is unlikely that the tissues were completely digested during this rapid procedure but they were completely solubilized and the solutions were homogeneous.[23] This is entirely satisfactory for carbon-furnace atomization as the ashing procedure (35 sec at 480°) is used to complete the destruction of the organic matrix *in situ* after the sample has been injected into the furnace. The major advantage is that the small amount of sample required is rapidly dissolved and the procedure is made much faster than conventional procedures requiring total chemical destruction of the matrix.

Direct insertion of tissue samples into the furnace, followed by ashing *in situ*, was not attempted. The

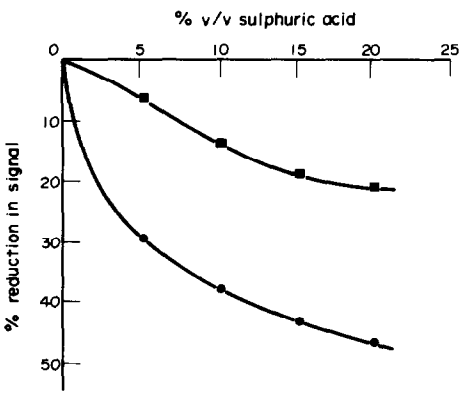

Fig. 1. The effect of increasing sulphuric acid and tetraethylammonium hydroxide concentrations. Peak-height measurements during atomization: (■) sulphuric acid (●) TEAH.

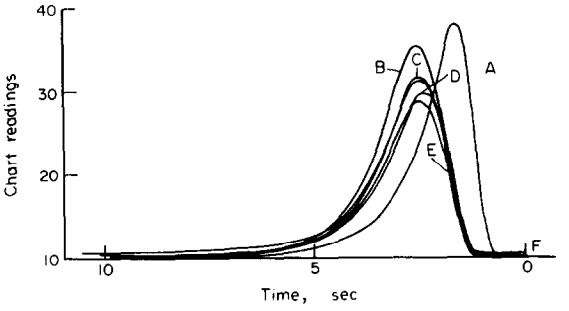

Fig. 2. Carbon-furnace atomic-absorption signals during atomization of 10 μl of 0.05 μg/ml gold solution at 2200°. (*A*) aqueous standard, (*B*) 5% v/v sulphuric acid (*C*) 10% v/v sulphuric acid (*D*) 15% v/v sulphuric acid (*E*) 20% v/v sulphuric acid. In each case, atomization starts at *F*.

small sample-size would have increased the effect of inhomogeneity in the sample, and the procedure developed was convenient, rapid and of adequate precision.

It is essential that all the forms of gold likely to be found in the tissues should be dissolved. We have satisfied ourselves that our procedure will dissolve gold compounds, colloidal gold and finely dispersed precipitates of gold metal completely. Gold wire was only partially dissolved, but massive gold is extremely unlikely to occur in tissue.

The carbon-furnace results were of acceptable precision and were in close agreement with those obtained by flame atomic-absorption spectrometry and neutron-activation analysis. Since the three procedures are substantially different and the neutron-activation method utilizes the sample in solid form, there appears to be no appreciable matrix interference in the carbon-furnace method and the results confirm that all the gold is dissolved. Slightly lower results were obtained by the flame atomic-absorption procedure for the analysis of spleen and it is suspected that dissolution of the large amount of sample required is incomplete in this case. This does not occur for any type of sample with the carbon-furnace method, where only 0.1 g of dried material is required.

Sulphuric acid causes a depression of the atomic-absorption signal for gold when carbon-furnace atomization is used, and also causes a change in the time, and hence temperature, of atomization (Figs. 1 and 2). The depressive effect is due to the change in surface tension of the solution, which causes a change in distribution of sample along the carbon tube, but no definite explanation can yet be offered for the change in atomization time.

It is for these reasons that the sulphuric acid concentration for samples and standards is made the same. When the background-corrector is used and correctly aligned, no atomization signal is obtained for blank samples from patients not treated with gold. A small, non-specific signal is, however, obtained during the ashing step, even with the background-corrector in operation, but has no effect on the analysis.

Tetraethylammonium hydroxide (TEAH) has been used as a rapid dissolution medium for tissue samples.[26,27] However, we found that low results were obtained, particularly at high TEAH concentrations, and the signals from standards were considerably depressed (Fig. 1). It was found that, despite its low concentration, the gold had precipitated. The precipitate could not be seen but could be recovered from the bottom and sides of the dissolution flask. This solvent medium, therefore, appears to be unsatisfactory for the determination of gold.

The advantages of carbon-furnace over carbon-filament atomization for biological samples containing gold have been discussed previously[9] and the carbon-furnace technique is preferred. A major advantage of carbon-furnace atomization over flame atomization is its sensitivity. The results in Table 2 lie close to or below the sensitivity limit for flame-atomization techniques but there is good agreement between the carbon-furnace and neutron-activation results. Typical relative standard deviations for the carbon-furnace technique are 1.6% for nails and 1.7% for hair (9 analyses from one sample solution of each). Hence

Table 1. A comparison of the gold levels found in human tissue samples by neutron-activation and atomic-absorption methods

Sample	Carbon-furnace results, μg/g	Flame-atomization results, μg/g	Neutron activation, μg/g
Liver	106, 105, 103(±1.6%*)	107, 104, 104(±8.4%*)	105.2 ± 0.5
Kidney	113, 113, 111(±1.6%*)	110, 115, 106(±8.5%*)	107.0 ± 0.8
Spleen	58, 58, 57(±2.5%*)	51, 53, 51(±8.4%*)	57.3 ± 0.4

* Relative standard deviation (9 replicates from 1 sample).

Table 2. A comparison of the gold level found in hair and nail samples from human subjects, by neutron-activation and carbon-furnace atomic-absorption methods. Serum gold determinations were by direct injection after dilution[9]

Patient	Gold in serum,[9] μg/ml	Gold in hair		Gold in nails	
		Carbon-furnace atomic absorption, μg/g	neutron activation, μg/g	Carbon-furnace atomic absorption, μg/g	neutron activation, μg/g
1	1.52	0.12	0.22	2.61	2.50
2	1.86	0.68	0.63	3.42	3.46
3	2.12	0.70	0.68	4.12	4.31
4	1.78	0.64	0.60	3.66	4.02
5	1.46	0.21	0.18	2.41	2.31

Table 3. Recovery of gold added to a human liver sample containing 106 μg/g

Dried liver sample taken, g	Gold added, μg	Total gold found, μg	Added gold recovered	
			μg	%
0.115	5	17.0	4.8	96
0.100	10	20.8	10.2	102
0.084	10	18.6	9.7	97
0.063	15	21.2	14.5	97
0.046	20	25.4	20.5	103

we consider that carbon-furnace atomization is the preferred atomic-absorption technique for the determination of gold in tissues. The results for this method agree well with those obtained by neutron-activation analysis (Tables 1 and 2), and the carbon-furnace technique has significant advantages in cost, simplicity, availability of apparatus, and speed. The recovery of various amounts of gold added to various amounts of a human liver sample was between 96 and 103% (Table 3), which confirms the accuracy of the procedure.

The liver, spleen and kidney samples were taken at autopsy from a patient who died 378 days after chrysotherapy was discontinued and their possible significance has been discussed elsewhere.[28] Hair and nail samples were taken from patients who had been under gold therapy for some time, to see whether there was any correlation between the gold levels and therapeutic response. The level in nails is higher than in hair and there appears to be a correlation between the levels in the nails and in the serum (Fig. 3), but study of many more samples will be required to substantiate this. However, the present work clearly shows that it is now relatively simple to obtain quick and accurate analyses for gold at low concentrations and in small tissue sections, by using a rapid dissolution procedure and carbon-furnace atomic-absorption spectrometry.

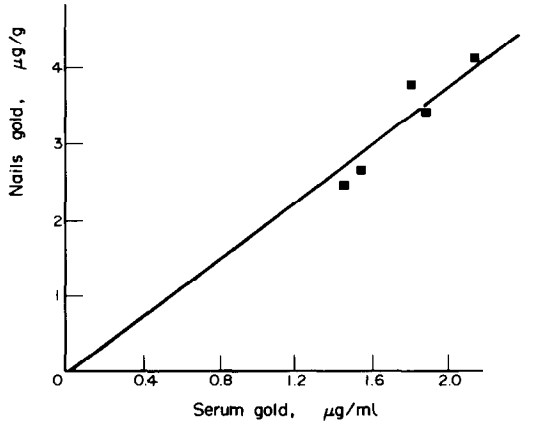

Fig. 3. A plot of the correlation between the gold level found in nails and serum gold levels for human subjects, all of whom had been receiving gold treatment for some months.

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AEROSOL DEPOSITION IN FURNACE ATOMIZATION*

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Summary—A novel approach to sample deposition in furnace atomization is suggested, which obviates the need for skilled application of microvolumes by syringe. The analyte in aerosol form is deposited under controlled conditions on the internal surface areas of graphite furnaces. Precision approaching that of flame atomization systems is achieved and at the same time, concentrational sensitivity may be increased simply by extending the deposition time. The amount of analyte deposited in the furnace is restricted only by the sample volume available and the matrix concentration. A single standard can be used to construct a calibration curve by simply varying the aerosol deposition time.

Introduction of sample in the form of an aerosol into the graphite furnaces used in atomic spectroscopy has so far been limited to continuously operated systems.[1] Dry sample aerosol in argon as carrier-gas is introduced into a vertical furnace maintained at constant temperature. As in flame atomization, a steady atom population is generated and consequently this type of furnace suffers from a serious loss of sensitivity when compared with the now conventional pulse-operated furnaces. This is because the efficiency of the nebulizer determines the rate at which atoms can be delivered into the furnace.

The smallest pulse-operated graphite furnace[2] [named rather incorrectly by the manufacturer as a carbon *rod* atomizer (CRA 63)], exhibits the best absolute sensitivities in comparison with its larger counterparts. When sufficient volume of sample is available, however, the small furnace is somewhat handicapped by its inability to accept samples in excess of 5 μl (in the tube version) without resort to use of multiple aliquots with drying between additions or application of larger volumes by syringe, with continuous drying on contact with the furnace.[3]

The concentrational sensitivity of any pulse-operated furnace can be considerably improved by depositing the analyte in aerosol form on the internal surface areas of the furnace under controlled conditions.[4] This approach also obviates the need for skilled application of microvolumes of analyte in solution, as used in existing systems. Existing procedures require stringent control to achieve high precision for volume measurement and for reproducible sample placement. Aerosol deposition, requiring a minimum number of operations and skills, readily provides higher precisions than those obtained by experienced operators using existing systems.

EXPERIMENTAL

Apparatus

Measurements were performed with a Varian Techtron model 63 CRA furnace mounted in a Varian Techtron AA-5 atomic-absorption spectrometer. Furnaces coated with pyrolytic graphite, with the coating removed from the exterior, were used. This modification was found to result in highly reproducible furnace operation since the contacts between the furnace and the supporting electrodes were maintained in perfect order throughout the lifetime of the furnace.

Hollow-cathode lamps by the same manufacturer were used for all elements investigated and were operated at the manufacturer's recommended currents. Peak-heights were recorded with a Mace FBQ 100 chart-recorder. Drying temperatures were monitored with a chromel–alumel thermocouple inserted inside the furnace to make contact with the inside wall. The hot-junction was made very fine in order to reduce the time constant.

The aerosol generation system, shown schematically in Fig. 1, was constructed by coupling a standard nebulizer–spray chamber system from a Perkin-Elmer 460 atomic-absorption spectrometer to a droplet separator and thence to a suitable tapered delivery tube. The variable nebulizer is operated by air supplied through a solenoid valve controlled by a timer.

The stream of sample aerosol enters the tubular furnace through the sampling orifice, which is only 1.5 mm in diameter. If a delivery tube of comparable diameter were used, the pressure inside the system would be excessive. In order to keep the pressure within 5 mmHg above atmospheric pressure, a diameter of 2.5 mm was selected for the delivery-tube and the air flow-rate was maintained at 9 l./min. With this arrangement a reproducible portion of the sample aerosol was deposited on the outside of the furnace as well as the inside. When atomized, the material from the outside furnace surface is swept upwards by the protective nitrogen sheath and therefore does not contribute to the measured atomic-absorption signal. Reduced sensitivities were obtained when the aerosol stream was divided between two delivery tubes with one matching the diameter of the sampling orifice and the other vented, the total cross-sectional area of the delivery tubes being selected so that the pressure inside the system was again not more than 5 mmHg above the atmospheric pressure.

When the cup version of the furnace was used, the delivery tube was positioned so that the aerosol entered through the top opening. With a range of delivery tubes of 1.5–2.5 mm diameter, the total volume of the aerosol entered the cup.

Procedure

With the graphite tube clamped between supporting electrodes, the delivery tube is mounted approximately

* Presented in part at the FACSS-CSI conference, 17 November 1977.

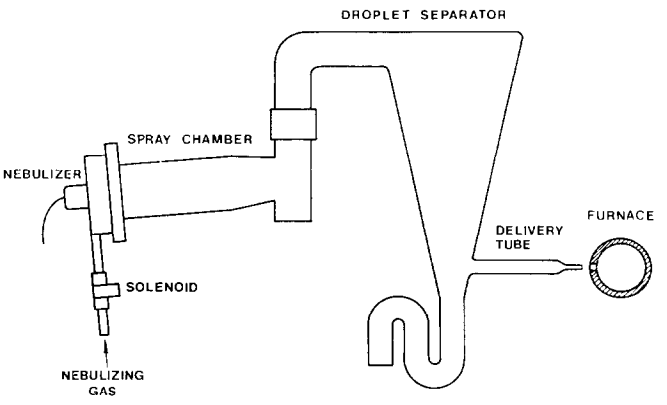

Fig. 1. Aerosol generation system.

5 mm from the sampling orifice or the cup opening. It is positioned centrally with respect to the sampling orifice so that the wet aerosol stream enters the furnace and collides with the opposite wall and is then deposited over a proportion of the internal areas. The quantity of analyte accumulated in the furnace is accurately controlled by timing the aerosol production by means of the solenoid valve. Alternatively, measured volumes of the analyte solution can be nebulized.

If the deposition process takes place with no heating applied to the furnace, liquid accumulates so rapidly that within a few seconds it fills the furnace and is forced out of the ends by the air stream. When, on the other hand, the furnace is maintained at a suitable elevated temperature while the aerosol is being deposited, the wet aerosol is dried on contact with the furnace wall and the range of amounts of analyte deposited can be varied from ultra-trace to macro levels.

Ideally, the furnace temperature should remain constant while the aerosol is being deposited. Since the furnace control system used in this study is not able to keep the furnace at a preset constant temperature, some time has to be allowed, after the initiation of the heating sequence, for the furnace to reach the operating temperature suitable for aerosol deposition.

Measurements with a chromel–alumel thermocouple indicated that 15 sec is sufficient time for the furnace to reach a nearly constant temperature. For example, when the heating is applied for a further 5 sec, the temperature rises by only approximately 10%.

Typically, the preheating period of 15 sec is followed by aerosol deposition lasting usually between 5 and 20 sec. With air used as nebulizing gas, 5–10 sec are allowed between the end of deposition and the start of ashing or atomization so that air and water vapour are removed from the furnace by the purging gas. The atomization voltage is then applied for 3 sec. Consequently the typical cycle time is 20–50 sec.

RESULTS AND DISCUSSION

Drying temperature

The effect of drying temperature (average values) on the lead atomic-absorption signal measured with the cup version of the furnace is shown in Fig. 2. At drying temperatures below 70° the deposited aerosol was not completely dried and additional drying had to be applied before proceeding to the atomization stage. From Fig. 2 it can be seen that the efficiency of aerosol deposition rapidly declines at temperatures above 200° and at approximately 350° practically no aerosol is retained on the furnace wall. The same behaviour is observed for the tubular furnace.

The decline in the efficiency of aerosol capture can probably be explained in terms of the progressive drying of the aerosol during its passage through the furnace. As the furnace temperature increases, a larger proportion of the dry aerosol is formed and when the aerosol is dried completely before it reaches the inside wall of the furnace, none of it is retained.

Delivery-tube position and solution uptake-rate

Figure 3 illustrates the variation in the lead atomic-absorption signal measured in the tubular furnace as a function of the delivery-tube position and solution uptake-rate. The optimum position of the delivery tube for maximum deposition is at 5 mm from the furnace. The delivery tube is not affected by the heat radiated when atomization takes place.

The effect of the solution uptake-rate on the analytical signal is similar to the behaviour of flame systems. The efficiency of aerosol production decreases as the solution uptake-rate increases and consequently only a modest improvement in sensitivity is realized by increasing the uptake rate from 2 ml/min to 4 ml/min, and there is practically no further effect on sensitivity at rates above 4 ml/min.

Precision

Relative standard deviations for series of 20 measurements for lead, copper and cadmium aqueous solutions at 0.01–0.2 ppm levels and 5-sec deposition times, ranged between 0.6 and 1.4% for the tubular furnace and between 2.5 and 4.0% for the cup furnace.

The result for the tubular furnace suggests that it is indeed possible for furnace atomizers to approach the precision of flame atomization systems once the error inherent in the syringe application of small volumes has been eliminated. It is also clear that the actual process of atom production in the furnace system studied is inherently reproducible. During the experimental work, however, it was observed that strong air movement, such as that caused by extractor hoods, may affect the atom population inside the furnace because of the open construction of this system.

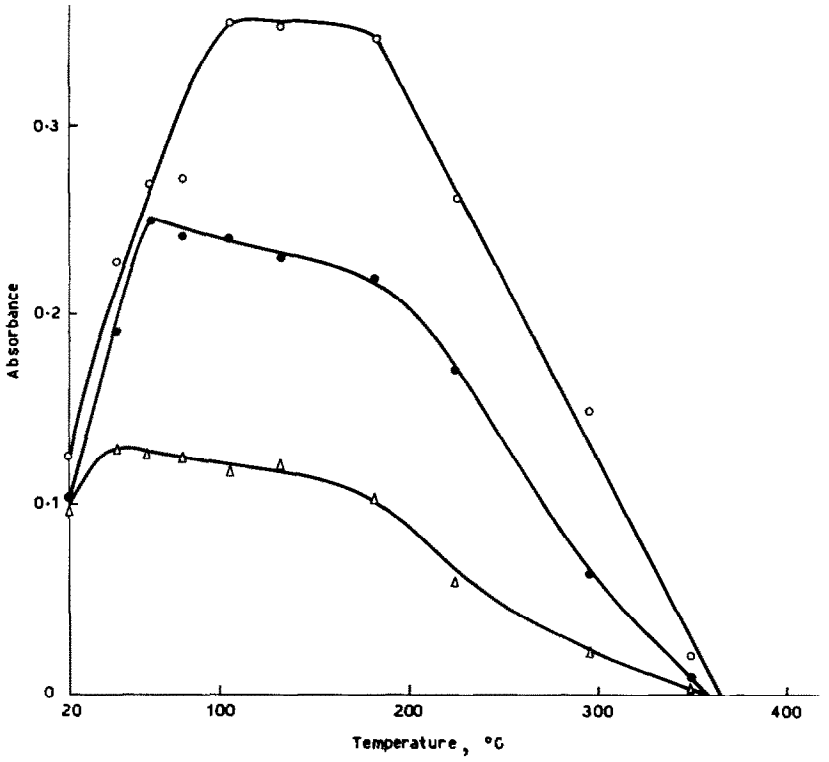

Fig. 2. The effect of drying temperature on lead absorbance at 283.3 nm, with the cup furnace and delivery tubes 1.5 (—△—), 2.0 (—●—) and 2.5 mm (—○—) in diameter.

Once the furnace was located in a relatively draught-free position, the problem was eliminated.

The high precision of the tubular furnace operation may also be partly ascribed to the deposition of the aerosol in the form of a thin uniform layer rather than as a single large droplet. As matrix residues confined to limited areas can lead to reduced sensitivity,[5] aerosol deposition should prove beneficial for work with complex matrices.

To account for the lower precision observed with the cup furnace, it has to be realized that the wet aerosol collides with the furnace wall at a velocity of approximately 30 m/sec. In the tubular furnace, the portion of the aerosol which is not deposited can leave through the ends of the tube without any obstruction and is then swept upwards by the nitrogen stream. The construction of the cup version of the furnace does not allow free expansion of the

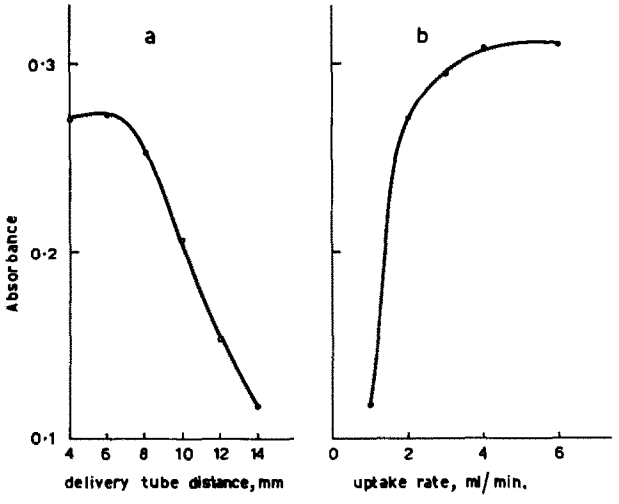

Fig. 3. The effect of (a) delivery-tube position (distance of orifice from furnace wall) and (b) solution uptake-rate, on lead absorbance at 283.3 nm, measured in the tubular furnace with 1.5 mm diameter delivery tube.

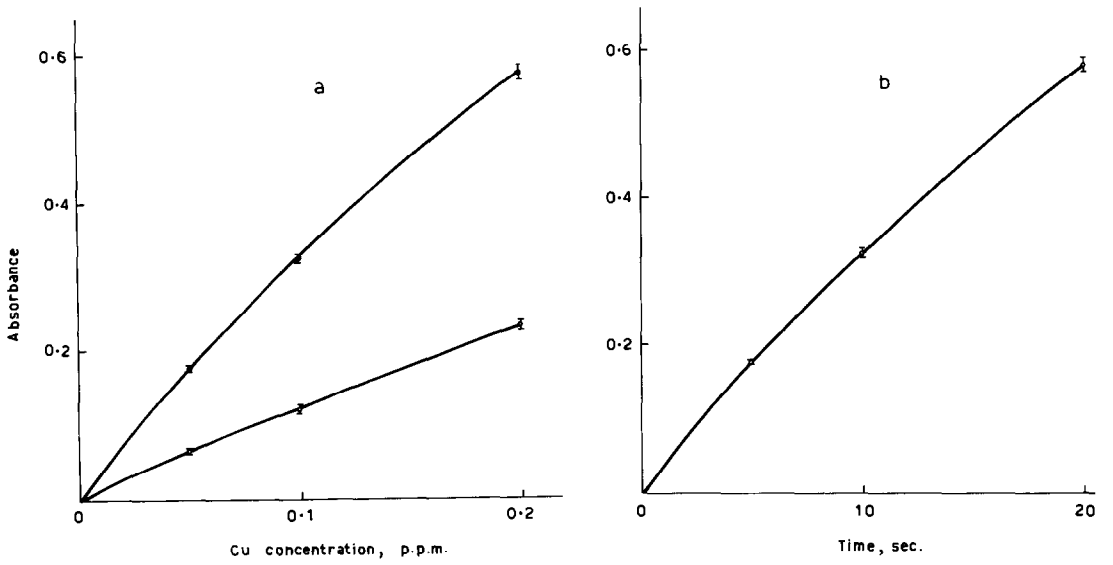

Fig. 4. Calibration curves for copper measured at 324.8 nm in the tubular furnace. (a) Syringe application of 2-μl volume (—○—) and aerosol deposition time of 5 sec (—●—); (b) 0.05-ppm copper solution deposited for times shown.

aerosol stream and this is mainly responsible for the lower precision.

The efficiency of aerosol deposition

To establish the proportion of the nebulized analyte solution which is deposited in the furnace, 5 ml of 1000-ppm copper solution were nebulized and delivered *via* a 2.5 mm diameter delivery tube. The material deposited on the furnace under the previously mentioned conditions was then dissolved in distilled water and the solution analysed by flame atomic-absorption. For the tubular furnace, 4.0% of the nebulized solution was retained on both the inside and outside of the furnace. From comparison of the copper atomic-absorption signals for the syringe and aerosol deposition of dilute solutions, the proportion of the nebulized solution deposited inside the furnace was estimated to be between 1.9 and 2.6%. These values correspond to a solution deposition rate of approximately 1 μl/sec.

Experiments with a larger diameter delivery tube confirmed that the essential requirement for efficient deposition is that the aerosol should strike the furnace wall at high velocity. For example, increasing the cross-sectional area of the delivery tube by a factor of 5.8 (*i.e.*, increasing the diameter from 2.5 to 6 mm) reduces the aerosol velocity from 30.5 to 5.3 m/sec. At the same time, the sensitivity is reduced by a factor of 47. Even when a correction is introduced for the larger proportion of aerosol deposited on the outside of the furnace with the wider delivery tube, the reduced aerosol velocity still results in reduction in the efficiency of deposition by a factor of 8.

Sensitivity

As mentioned above, only a limited volume of analyte solution can be deposited in the furnace. Consequently, the high absolute sensitivity values which can be obtained are not reflected in the corresponding concentrational sensitivities. Also, if the volume of the analyte solution is increased within the optimum range, the increase in sensitivity is not directly proportional to the volume applied,[3] even in the low concentration range.

Table 1. Sensitivities* for syringe and aerosol deposition

Element	Line, *nm*	Absolute sensitivity, *pg*	Concentrational sensitivity (2-μl volume), *ppM*†	Concentrational sensitivity (20-sec deposition), *ppM*
Cd	228.8	0.3	0.2	0.02
Cu	324.8	6	3	0.4
Pb	217.0	2	1	0.2
Pb	283.3	8	4	0.4

* For 1% absorption.
† Parts per milliard (10^9).

Figure 4a shows a comparison of calibration curves obtained by use of both syringe and aerosol deposition for solutions of variable concentration. Sensitivities for these two techniques are compared in Table 1. When the experimental values shown here for syringe-deposition are compared with those for 20-sec aerosol deposition (equivalent to a volume of 20 μl), it is obvious that the increase in sensitivity is virtually linearly related to the volume of sample deposited.

Figure 4b demonstrates the possibility of using a single standard to construct a calibration curve by varying the aerosol deposition time. The amount of the analyte deposited in the furnace from the aerosol and therefore the improvement in concentrational sensitivity, is restricted only by the sample volume available and the matrix concentration.

CONCLUSIONS

Even though aerosol deposition was studied only for copper, lead and cadmium, the results have general validity for dilute solutions. For low analyte concentrations, the efficiency of the deposition process for a given system and conditions depends only on the properties of the solvent used.

Aerosol deposition is now being used to determine lead in whole blood. Blood samples are diluted with distilled water to overcome the viscosity effect and then deposited for correspondingly extended periods. The standard addition method is applied by adding a lead standard *in situ* to deposited blood samples. Only a single standard is used and the deposition time is varied to obtain the required concentration range.

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SHORT COMMUNICATIONS

AMPEROMETRIC COMPLEX-FORMATION TITRATIONS AT A DROPPING MERCURY ELECTRODE, EMPLOYING NORMAL PULSE POLAROGRAPHY

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Summary—Selective determinations of several metal ions by means of amperometric complex-formation titrations employing normal pulse polarography with a DME appear to be possible. Concentrations down to $3 \times 10^{-7} M$ have been determined with adequate accuracy. In alkaline medium deaeration is necessary; in acidic medium it can be omitted.

Amperometric complex-formation titrations of metal ions with indication of the end-point by following the anodic wave of the excess of ligand have been described, and sensitivity was increased by using a rotating instead of a dropping mercury electrode as the indicator electrode.[1-4] The preparation of these rotating mercury electrodes demands some skill and experience,[5,6] however; furthermore the electrode generally shows a gradually decreasing sensitivity. Although this sensitivity can be restored by immersion in mercury, after a few months the platinum wire is so affected that the electrode can no longer be used.

A similar or even better sensitivity can be obtained with the more familiar and reproducible DME by using either normal or differential pulse techniques. Any problem with the preparation of the electrodes can thus be avoided. Myers and Osteryoung[7] decribe for instance the amperometric titration of copper(II) with EDTA, and use differential pulse polarography to follow the cathodic diffusion current of the free copper(II) ion.

The present communication deals with the application of normal pulse polarography with a DME to amperometric titrations by following the anodic dissolution wave of mercury in the presence of an excess of ligand. By means of an appropriate choice of pH and titrant, selective determinations of several metal ions at low concentration levels appear to be possible.

Another advantage of the application of normal pulse polarography is the fact that the potentials can be chosen in such a way that the anodic reaction occurs only during the very short interval of the pulse (in our case 56.7 msec). The amount of mercury(II) produced in this way is so small that the systematic error arising from the consumption of ligand by mercury(II) ions remains negligible.

In order to illustrate the potentialities of the method, direct titrations of thorium(IV), copper(II) and calcium(II) were carried out as well as a back-titration of zinc(II) with thorium(IV) as the back-titrant.

EXPERIMENTAL

Apparatus and chemicals

Apart from the replacement of the glassy carbon electrode by a dropping mercury electrode, the equipment was the same as that described previously.[8] Titrations were carried out by adding the titrant solution from a 1-ml syringe microburette. The titration vessel was of glass and previously silanized.[8]

All solutions were prepared from analytical grade chemicals and redistilled water. EDTA was used as the titrant, a $10^{-4} M$ solution being freshly prepared each week by dilution of a $10^{-3} M$ stock solution.

Selection of the potential

A potential has to be selected for the indicator electrode such that the current due to dissolution of the mercury is limited by the ligand concentration. As low concentrations of the ligand produce ill-developed waves, it is best to select on the basis of polarograms of solutions of higher concentration (about $10^{-5} M$). It is also possible, however, to record polarograms in the absence of ligand, but under otherwise identical conditions and select a potential at the foot of the dissolution wave of mercury. The latter method demands somewhat more experience.

Procedure

The PAR 174 polarographic analyser was used in the normal pulse mode (drop-time 0.5 sec; initial potential about 200 mV more negative than the selected indication potential). The sample was put in the titration cell and had to be deaerated if it was alkaline; in acidic medium the deaeration could be omitted. A scan in the positive direction was made until the desired indication potential was reached; at that point the "hold" button was pressed. The current was recorded after 7 drops in order to ensure the charging of the memory circuits.

After each addition of titrant, the solution was mixed (and deaerated, if necessary) by bubbling nitrogen through the solution. This procedure was continued until 100% excess of titrant had been added.

RESULTS AND DISCUSSION

A survey of the results obtained with the proposed method is presented in Table 1. EDTA is used as the titrant in the case of direct titrations; in the case of Zn(II), thorium is used as the back-titrant.

The following observations have been made on the influence of oxygen. In acidic medium no deaeration is necessary. Polarograms show that at a potential about 200 mV more negative than the indication potential no significant reduction of oxygen occurs. Therefore the initial potential, which is also the rest-potential in the interval between two successive pulses, is set to this value. In alkaline medium no suitable titration curves can be obtained

Table 1. Titrations with EDTA

Metal ion	Taken, μg/15 ml	Found μg/15 ml	Error, %	Relative std. devn., % [no. of detns.]	Medium	Indication potential vs. SCE, V
Th(IV)	3.48	3.48	—	2.7 [4]	pH 2; $HClO_4$	+0.25
	1.74	1.81	+4.0	5.6 [4]	pH 2; $HClO_4$	+0.25
	1.04	1.10	+6.0	8.0 [4]	pH 2; $HClO_4$	+0.25
Zn(II)*	0.980	1.03	+4.7	1.6 [4]	pH 4.8; acetate buffer	+0.30
Cu(II)	0.641	0.635	−1.0	6.6 [4]	pH 4.8; acetate buffer	+0.24
	0.321	0.321	—	11.0 [4]	pH 4.8; acetate buffer	+0.24
Ca(II)	0.442	0.455	+3.0	5.7 [4]	pH 10; ammonia buffer	+0.03

* Back-titration of the excess of EDTA with Th(IV).

if oxygen is not removed. Polarograms recorded in this medium show an almost complete overlap of the anodic dissolution wave of mercury with the cathodic wave corresponding to the reduction of oxygen. This implies that at the rest-potential a large cathodic current will occur and the solution around the drop will be strongly affected; moreover, it is impossible to find a suitable indication potential if oxygen is present in the solution.

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AQUEOUS ACETIC ACID AS A MEDIUM FOR THE FACILE USE OF FERROIN AS REDOX INDICATOR IN THE PRESENCE OF PERCHLORIC ACID

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Summary—Ferroin cannot be used as an indicator in perchloric acid medium because of precipitation of ferroin perchlorate. There is no precipitation, however, if the solution contains 30% (v/v) of acetic acid.

Although tris(1,10-phenanthroline)iron(II) (ferroin) is a good redox indicator, it suffers from the disadvantage that it cannot be used for titration in perchloric acid medium,[1–5] because it gives a scarlet precipitate.[6, 7] The solubility is about 10^{-3} *M* in water and 0.5×10^{-4} *M* in 0.01 *M* perchloric acid.[7] Evidently the solubility would be much less ($\sim 10^{-9}$ *M*) in the 1–2*M* perchloric acid commonly encountered in titrations.

We have made the interesting observation that ferroin perchlorate is soluble in 30% v/v aqueous acetic acid, even when the perchloric acid concentration is in the range 1–2*M*. We have determined the transition potentials by the method of Knop.[8] They are 1.11 and 1.08 V respectively for 1 and 2*M* perchloric acid, in 30% aqueous acetic acid medium.

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AQUEOUS ACETIC ACID AS A MEDIUM FOR THE FACILE USE OF FERROIN AS REDOX INDICATOR IN THE PRESENCE OF PERCHLORIC ACID

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SOME TRIPHENYLMETHANE DYES AS REDOX INDICATORS IN THE TITRATION OF ANTIMONY(III) WITH CERIUM(IV) SULPHATE

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Summary—Erioglaucine A, Eriogreen B, Patent Blue and Xylene Cyanol FF work satisfactorily for the titration of Sb(III) with Ce(IV) in 1–2*N* sulphuric acid medium with iodine as catalyst. In hydrochloric acid medium the colour of the oxidized dye is very evanescent but is very much improved in intensity and stability by the addition of manganese(II) sulphate; no catalyst is needed.

Rathsburg[1] was the first to titrate antimony(III) with cerium(IV) sulphate; he used Methyl Red, Methyl Orange, Congo Red and Methylene Blue as (irreversible) indicators and this was followed by the investigations of Furman,[2] Swift,[3] Přibil[4] and Petzold.[5] Přibil[4] reported that the procedure proposed by Willard and Young[6] using ferroin as a reversible indicator is unworkable. Hammock, Brown and Swift[7] stated that even the extractive iodine monochloride end-point procedure does not work satisfactorily and preferred the Andrews iodate procedure. Smith and Wilcox,[8] however, found that the iodate method is not suitable for the determination of antimony in tartrate solutions because of the failure of carbon tetrachloride or chloroform to develop a violet colour during the titration. The use of potassium bromate for the determination of antimony(III) was comprehensively investigated by Bishop, Ottaway and Short.[9] A high acid concentration leads to incomplete oxidation of antimony(III), while at low acid concentrations there is an induced oxidation of antimony(III) by dissolved oxygen. Bishop and Jennings[10] stated that an accurate determination of antimony(III) with chloramine-T is possible with the addition of iodine monochloride and Amaranth as indicator, but the acid concentration is critical. The presence of tartaric acid again leads to positive errors. Other indicators are subject to errors and defects. The defects of the permanganate procedure for antimony(III) have been summarized by Kolthoff and Belcher[11] and by Swift.[12] The British Pharmacopoeia procedure for the assay of tartar emetic with iodine has been the subject of criticism by Pathak and Uppadhyaya.[13] We have investigated some triphenylmethane dyes (TPM) as reversible indicators for the determination of antimony(III) with cerium(IV) sulphate. These indicators have been used before in cerate oxidimetry[14,15] but not in titration of antimony(III). We have observed that iodine accelerates the reaction between antimony(III) and cerium(IV) sulphate in sulphuric acid medium and also the slow reaction between the oxidized dye and antimony(III), sufficiently to make the titration practicable. Although the reaction of antimony(III) with cerium(IV) sulphate in 1–2*M* hydrochloric acid and that of the oxidized TPM dyes with antimony(III) are fast enough for titration, the oxidized TPM dye decomposes too rapidly in this medium for the titration to be practicable. However, addition of a small amount of manganese(II) sulphate overcomes this problem.

EXPERIMENTAL

Reagents

Antimony(III) solution, 0.05*N*. Prepared by dissolving antimony(III) oxide in 3*M* hydrochloric acid and standardizing with potassium bromate.[16]

Potassium antimonyl tartrate solution, 0.05*N*. Standardized by the method of Rao, Viswanath and Gandikota.[17]

Cerium (IV) sulphate, 0.05*M in* 1.0*N sulphuric acid*. Prepared and standardized as described by Gandikota and Rao.[18]

Iodine catalyst solution, 0.01*N*. Prepared by mixing 20.8 ml of 0.1*M* potassium iodide and 4.16 ml of 0.1*M* potassium iodate and diluting to 250 ml.

Indicator solutions, 0.1%.

Titration in sulphuric acid medium

To 5–10 ml of 0.05*N* antimony(III) solution, add sufficient 10*N* sulphuric acid to make the acid concentration 1–2*N* when diluted to 50 ml, and 1 ml of catalyst solution. Titrate with cerium(IV) sulphate. Towards the end of the titration a light yellow colour, due to iodine, appears and disappears, giving a warning of the approach of the end-point. When the yellow colour persists for a little while the end-point is very near; add 0.2 ml of indicator and titrate dropwise with a wait of 8–10 sec between drops. The yellow colour of the iodine disappears only slowly just before the end-point because of the large decrease in the concentration of antimony(III) at this stage. It is recommended that an extra 0.02 ml of cerium(IV) sulphate is added after the first appearance of the orange-red colour at the end-point, to secure a vivid colour change stable for at least 5 min, and to deduct 0.02 ml from the total volume used. The visual end-points then agree with those obtained potentiometrically. At sulphuric acid concentrations greater than 2*N* the rate of oxidation of indicator is too slow for practical use.

Titrations with 0.01*N* solutions are conducted in the same way, but with half the amount of catalyst, and indicator corrections are necessary [0.1 ml of 0.01*M* cerium (IV) sulphate for Patent Blue, and 0.04 ml for Erioglaucine A and Eriogreen B; Xylene Cyanol FF is not satisfactory].

Titrations in hydrochloric acid medium

The procedure is similar to that for sulphuric acid medium, except that 2–4 ml of 1.5% manganese(II) sulphate solution are added per 50 ml of the titration mixture, in place of the iodine catalyst.

RESULTS AND DISCUSSION

All four indicators tested (Erioglaucine A, Eriogreen B, Patent Blue and Xylene Cyanol FF) gave results correct to within ±0.3% for antimony titration by either method and also for antimony(III) in tartar emetic determined by

Table 1. Transition potentials of TPM dyes in antimony(III) titrations

Dye	Transition potentials *vs.* NHE, *V*			
	1*N* H_2SO_4	2*N* H_2SO_4	1*M* HCl	1*M* HCl
Erioglaucine A	0.90	0.92	1.07	1.12
Eriogreen B	0.89	0.90	1.06	1.09
Patent Blue	0.89	0.92	1.07	1.09
Xylene Cyanol FF	0.88	0.89	—	—

titration in sulphuric acid medium with Erioglaucine A as indicator.

Interferences

Sulphuric acid medium. Manganese(II) did not interfere at the 0.001*M* level, but somewhat reduced the intensity and stability of the transient colour of the oxidized dye.

If a mixture of iron(II) and antimony(III) is titrated in the absence of the iodine catalyst, the colour of the oxidized dye does not appear at the equivalence point for iron(II), but only after a slight excess of cerium(IV) sulphate is added. If the catalyst is present, the pink colour appears at the stoichiometric end-point corresponding to the total of iron(II) plus antimony(III).

Hydrochloric acid medium. Iron(II) interferes, because the yellow colour of iron(III) chloride masks the colour of the oxidized dye. This cannot be avoided by adding phosphoric acid as this precipitates the cerium(IV) and retards the oxidation of the indicator.

Since arsenic(III) is not rapidly oxidized by cerium(IV) in hydrochloric acid medium in the absence of a catalyst, it might be expected that antimony(III) could be titrated first without a catalyst, and then arsenic(III) after addition of iodine monochloride as catalyst, but this expectation is not realized, no end-point being obtained for antimony(III). If iodine monochloride is added at the start of the titration, the end-point corresponds to the sum of antimony(III) and arsenic(III). Iodine cannot replace iodine monochloride satisfactorily.

Mechanism

Various experiments led us to the qualitative conclusion that the TPM dyes act as reversible indicators through a free radical mechanism. The TPM dye is first oxidized by cerium(IV) to a pink transient free radical which is reduced by antimony(III) to the original dye under the experimental conditions detailed in this paper.

Transition potentials

These have been measured by Knop's method and are higher in hydrochloric acid than in sulphuric acid medium (Table 1).

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A DIRECT METHOD OF ESTIMATING CYANIDE ION IN METAL SALTS AND COMPLEXES BY MEANS OF CHLORAMINE-T, DICHLORAMINE-T AND LEAD TETRA-ACETATE

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Summary—A simple and rapid method of determining cyanide in metal salts and complexes with chloramine-T, dichloramine-T and lead tetra-acetate, in presence of KBr and acetic acid, has been developed.

Back-titration methods have been employed by the authors for estimating cyanide in metal salts and complexes, with organic haloamines.[1] The present communication reports a simple and rapid alternative involving titration of chloramine-T (CAT), dichloramine-T (DCT) or lead tetra-acetate (LTA), in presence of KBr, with the cyanide solution, visual or potentiometric point detection being used. The cyanide undergoes a two-electron change under these conditions.

EXPERIMENTAL

Reagents

Analytical grade potassium and sodium cyanides were used without further purification. CAT was purified by the method of Morris *et al.*[2] A 0.05*N* solution was standardized iodometrically. DCT was prepared and purified by the method of Jacob and Nair.[3] A 0.05*N* solution in glacial acetic acid (containing 10% acetic anhydride) was standardized iodometrically. Lead tetra-acetate was used without further purification. A 0.05 *N* solution in glacial acetic acid was standardized iodometrically and stored in an amber-coloured bottle. All other materials and reagents were of accepted grades of purity. A platinum indicator electrode and a reference calomel electrode were used for potentiometric titrations. Silver cyanide, zinc cyanide and the complexes $KAg(CN)_2$ and $K_2Zn(CN)_4$ were prepared by standard methods.

Titration of soluble cyanides

Take V ml of oxidant solution (of normality N) in a 100-ml conical flask. Add 10 ml of 1*N* potassium bromide and 1 ml of carbon tetrachloride (also 5 ml of 1*N* acetic acid for CAT, or 10 ml of 20% sodium acetate solution for LTA) and titrate with the cyanide solution with stirring till the disappearance of bromine from the organic layer. Alternatively, use potentiometric determination of the end-point for the titration done in the same way. The weight (mg) of cyanide (CN^-) in the volume of cyanide solution used for the titration is $13.0NV$.

Insoluble or complex cyanides

Convert insoluble cyanides into complex cyanides by dissolving them in *yM* potassium cyanide (0.04*M* is recommended and the solution must be standardized). Then treat as for soluble cyanides. Complex cyanides are titrated in the same way as soluble cyanides.

If a ml of cyanide mixture is required for V_1 ml of oxidant, the volume of oxidant (V_2 ml) required for a ml of yM potassium cyanide would be $V_2 = 2ya/N$, where N is the normality of the oxidant. Then $(V_1 - V_2)$ ml of the oxidant would have been used for oxidation of the insoluble cyanide. The weight (x mg) of insoluble cyanide in the sample solution is $x = EN(V_1 - V_2)$ where E is the equivalent weight of the insoluble cyanide (calculated on the basis of a two-electron oxidation of CN^-). For complex cyanides with equivalent weight E, ENV_1 gives the weight of complex (mg) in the volume used for the titration.

RESULTS AND DISCUSSION

The oxidation of CN^- in these reactions has two-electron stoichiometry and presumably bromine is the reaction intermediate formed from the potassium bromide by the oxidants:

$$MCN + Br_2 \rightarrow MBr + CNBr$$
$$K_2Zn(CN)_4 + Br_2 \rightarrow 4\,CNBr + 2\,KBr + ZnBr_2$$
$$KAg(CN)_2 + 2\,Br_2 \rightarrow 2\,CNBr + KBr + AgBr.$$

The cyanogen bromide formed could be quantitatively estimated by the iodometric method.[4]

Table 1 gives some typical results. It was found that common anions such as Cl^-, F^-, NO_3^-, ClO_4^-, SO_4^{2-} and PO_4^{3-} do not interfere, but N_2H_4, SCN^- and I^- are oxidized.

Table 1. Estimation of cyanide in metal salts and complexes

Compound	Range studied, *mg*	Range of error in recovery, % CAT I	CAT II	DCT I	DCT II	LTA I	LTA II
KCN	2–85	0.1–0.9	0.2–1.1	0.0–1.1	0.0–0.9	0.2–1.3	0.0–1.8
NaCN	1–80	0.0–1.6	0.0–1.6	0.0–0.5	0.0–0.8	0.0–0.9	0.0–0.9
AgCN	1–70	0.2–1.4	0.1–2.2	0.0–0.6	0.1–1.5	0.3–1.3	0.3–1.6
$Zn(CN)_2$	1–70	0.1–1.4	0.0–1.1	0.1–0.9	0.0–0.9	0.2–1.3	0.2–1.3
$KAg(CN)_2$	3–120	0.0–0.7	0.0–0.7	0.0–0.3	0.0–0.3	0.0–0.4	0.0–0.5
$K_2Zn(CN)_4$	2–105	0.0–0.8	0.0–0.7	0.0–0.6	0.2–1.2	0.1–1.4	0.1–1.4

I Visual end-point.
II Potentiometric end-point

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DETERMINATION OF URANIUM AND IMPURITIES IN PORTUGUESE YELLOW-CAKES

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(*Received* 13 *January* 1976. *Revised* 19 *November* 1976. *Accepted* 1 *December* 1976)

Summary—A method is described for separation of impurities in uranium yellow cakes from Urgeiriça (Portugal). The trace metals are separated and concentrated by solvent extraction from 6*M* nitric acid into 100% TBP. The raffinate is then analysed directly by flame spectrometry. Uranium is determined gravimetrically after stripping of the organic phase. The method is fast and economic, and the results are in good agreement with those obtained by specific methods for each element after prior separation of uranium by precipitation or solvent extraction with various solvents.

Uranium compounds used in various nuclear applications must meet rigid purity specifications. A large number of methods have been reported in the literature for the control of uranium and its impurities in such materials.[1–5]

The trace elements are often determined either colorimetrically or by emission spectroscopy. Colorimetric procedures are subject to elemental interferences, so separate determinations must be made for each element. Direct spectrographic determinations lack accuracy.[6] Lately atomic-absorption spectrophotometry has been used with good results for determination of impurities in various materials,[7,8] but as the direct determination of impurities in uranium solutions by atomic absorption gives poor sensitivity and spreads radioactive contamination, the matrix element must be separated either by ion-exchange or by solvent extraction.[6]

Direct determination of ppm amounts of vanadium in uranium solutions by atomic absorption gives low results, owing to the effect of the matrix element, which is more pronounced at low than at high concentration of vanadium.[9]

Strelow and Weinert studied a selective separation of uranium from other elements by cation-exchange chromatography in hydrobromic acid and hydrochloric acid–acetone mixtures.[10] Korkisch and Gross separated vanadium and molybdenum from samples of yellow-cakes and uranium-bearing minerals by anion-exchange from hydrochloric acid medium.[9]

Korkisch and Dimitriadis analysed 6*M* hydrochloric acid solutions of yellow-cake samples and uranium minerals for Fe, V, Mo and alkali and alkaline-earth metals, *etc.*, using Dowex 1 × 8 resin (Cl^- form) previously treated with 6*M* hydrochloric acid–tetrahydrofuran–2-methoxyethanol (1:5:4).[11] Ion-exchange separations, though more universal and adaptable for handling a large number of samples, are slower than separations by solvent extraction and usually require preliminary sample preparation to convert uranium into the ionic form required for sorption on the resin.[9,11,12] Furthermore, the chemistry of uranium makes the metal particularly adaptable to solvent-extraction separations.[12]

Walker, Vita and Sparks separated and concentrated antimony, iron and molybdenum from uranium compounds, by solvent extraction of these elements into n-amyl acetate from 8*M* hydrochloric acid,[13] and extracted copper, iron and nickel from uranium by means of the bathophenanthroline–methyl isobutyl ketone extraction system.[6]

The best known solvent-extraction systems for uranium use tri-iso-octylamine and tri-n-butyl phosphate. In the tri-iso-octylamine system, the uranium must be in chloride solution, which is not a usual dissolution medium in uranium technology.[12]

The TBP system was chosen as the simpler and more efficient, and as giving more reliable results, in the separation of uranium from trace metals. In this system, uranium is extracted from nitrate solution, which is more commonly used in the nuclear industry for the separation of uranium from impurities before production of high grade UO_2 and UO_3.[1,14,15]

The TBP is usually diluted with an inert solvent to prevent extraction of other elements, but the dilution decreases the extraction coefficient of uranium.[12]

Eschrich and co-workers simultaneously extracted nitric acid and macroquantities of uranyl nitrate with 100% TBP,[16] and also studied the distribution of uranyl nitrate in the system uranyl nitrate–nitric acid–100% TBP.[17] Distribution coefficients between nitric acid and TBP solutions of U(VI) and the impurities usually present in uranium ores and concentrates were compiled by the group at the Japanese Atomic Energy Research Institute and referred to by Marcus and Kertes[14] as being of the order of 10^2 for U(VI) and 10^{-2} for impurities, for a 6*M* nitric acid aqueous phase.

The present paper reports on the solvent extraction system 100% TBP–6*M* nitric acid for separation of uranium from its impurities in Urgeiriça yellow-cakes. After extraction of the aqueous phase with 100% TBP a second extraction is made with 20% TBP in carbon tetrachloride to improve the yield of extraction and allow better phase separation. Finally the aqueous phase is washed with carbon tetrachloride to remove any $UO_2(NO_3)_2 \cdot n$ TBP complexes

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Table 1. Extraction efficiency of separation of uranium from its impurities

Yellow cake (reference)	U in organic phase, %	U in aqueous phase, %	Extraction efficiency, %	U total ($U_{org} + U_{aq}$), %	U total,* %
1/73	77.51	0.062	99.9	77.57	77.45
2/73	77.08	0.080	99.9	77.16	77.25
3/73	77.61	0.076	99.9	77.69	77.55
4/73	77.91	0.055	99.9	77.97	77.72
5/73	76.99	0.065	99.9	77.06	76.92
10/73	76.91	0.053	99.9	76.96	76.96

* Determined by the gravimetric method of analysis used in this laboratory.

remaining in it.[1,7] Similar distribution coefficients for uranium are achieved with 100% TBP from 6*M* hydrochloric acid but the separation from the impurities is either poor or does not occur at all.

EXPERIMENTAL

Reagents

Use reagent grade chemicals. Demineralize the water and distil it twice.

Tri-n-butylphosphate. Wash the solvent twice, during 15 min, with an equal volume of water. Shake the washed TBP for 5 min with an equal volume of 6*M* nitric acid. Separate the phases and store the TBP in the dark at room temperature.

TBP in carbon tetrachloride, 20% solution. Dilute 20 ml of washed TBP to 100 ml with carbon tetrachloride and equilibrate for 3 min with an equal amount of 6*M* nitric acid. After the phases have separated, discard the aqueous phase.

Stripping solution. Ammonium acetate solution, 350 g/l.

Preparation of sample

Dry the sample in an oven for 48 hr at 140°. Then dissolve 5.0000 g of sample in 10 ml of conc. nitric acid in a 50-ml beaker. Heat the mixture and after dissolution is complete evaporate it to dryness. Treat the residue with 10 ml of 6*M* nitric acid pre-equilibrated with TBP.

Extraction

Transfer the sample solution to a separatory funnel, rinsing the beaker with 6*M* nitric acid pre-equilibrated with TBP. The final volume of sample should not exceed 40 ml. For each 1.0 g of uranium add 12.5 ml of washed TBP. Extract the uranium, shaking the separatory funnel vigorously for 5 min in a mechanical shaker. After the phases have separated, transfer the aqueous phase to a second separatory funnel. Wash the organic phase twice with about 25 ml of 6*M* nitric acid pre-equilibrated with TBP. Add the acidic wash solutions to the aqueous phase in the second separatory funnel. Wash the combined aqueous phase with 50 ml of 20% TBP in carbon tetrachloride. Transfer the organic phase to a 250-ml volumetric flask and wash the aqueous phase twice with 25-ml portions of carbon tetrachloride. Add the organic washes to the volumetric flask, and make up to volume with carbon tetrachloride. Transfer the aqueous phase either to a 150-ml volumetric flask or, after reducing the volume by evaporation, to a 25-ml volumetric flask.

Analytical procedures

Strip a suitable aliquot of the organic phase with ammonium acetate, then precipitate uranium as ammonium diuranate and determine it gravimetrically as U_3O_8. Analyse for the metal impurities in the raffinate

Table 2. Determination of impurities in the Portuguese yellow-cakes after separation of uranium by solvent extraction

Yellow-cake (sample reference)	Fe, %			Na, %		K, %		V, *ppm*		Mo, *ppm*		CaO, %		
	A	B*	B†	A	B§	A	B§	A	B†	A	B†	A	B†	B†¶
1/73	0.13	0.13	0.14	0.31	0.35	0.06	0.06	<5	n.d.	<10	<10	0.14	—	—
2/73	0.14	0.13	0.15	0.37	0.35	0.05	0.05	<5	<5	29	n.d.	0.15	—	—
3/73	0.12	0.12	0.14	0.32	0.33	0.06	0.06	<5	n.d.	26	<10	0.13	—	—
4/73	0.15	0.14	0.16	0.38	0.36	0.07	0.06	<5	n.d.	11	—	0.10	—	—
5/73	0.14	0.15	0.13	0.32	0.33	0.07	0.06	17	19	<10	<10	0.15	—	—
6/73	0.15	0.16	0.18	0.33	0.32	0.06	0.06	69	72	33	<10	0.14	0.16	0.16
7/73	0.21	0.21	0.23	—	0.26	—	0.06	76	85	<10	<10	0.17	—	0.18
8/73	0.22	0.23	0.26	—	0.24	—	0.06	112	115	13	<10	0.17	—	0.18
9/73	0.19	0.23	0.25	—	0.26	—	0.05	99	100	14	<10	0.14	—	0.20
10/73	0.13	0.13	0.15	—	0.32	—	0.04	51	58	n.d.	<10	0.16	0.20	—
11/73	0.13	0.12	0.14	—	0.27	—	0.04	19	20	<10	<10	0.16	0.21	—
12/73	0.17	0.12	0.20	—	0.27	—	0.04	10	9	<10	<10	—	0.22	—

A. Determined by classical methods.
B. In the raffinate.
* By 1,10-phenanthroline.
† By atomic absorption.
§ By flame photometry.

Spectrophotometric determination by the standard thiocyanate method after separation of molybdenum thiocyanate with isoamyl alcohol–carbon tetrachloride was not satisfactory. The results were often erratic, mainly because of the number of separations involved and the high readings of the reagent blank.

¶ Standard addition method.

either by atomic-absorption spectrometry (Ça, Fe, V, Mo), flame photometry (Na, K) or spectrophotometry (Fe).

Uranium can also be determined spectrophotometrically in the raffinate by the dibenzoylmethane method.

RESULTS

Table 1 shows some results for the extraction of uranium from Urgeiriça yellow-cakes. The efficiency of extraction was 99.9%. Uranium determinations proved to be poor when the solutions analysed were a week or more old. Separation of uranium from impurities was as good as expected from the results published in the literature.

Table 2 compares results obtained for the determination of impurities after separation of the matrix element by the technique described, and the results of specific methods for each element with previous separation of uranium by precipitation or solvent extraction.

The agreement is good. The procedure described in this paper is less time-consuming, permitting the simultaneous determination of uranium in the organic phase, and of impurities by atomic absorption or flame photometry, after preconcentration, in the aqueous phase. At the same time the method overcomes the problems arising from radioactive contamination and the matrix effects due to high salt concentration.

Acknowledgements—The authors thank their colleagues of the Analytical Group for some determinations of uranium and impurities.

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Summary—A spectrophotometric method for determining some penicillins has been developed. A known volume of the penicillin solution—in phosphate buffer of pH 6.8—is boiled with ammonium vanadate solution—in sulphuric acid medium—for 10 min and the absorbance of the colour formed is measured at 750 nm. The excess of vanadate can also be determined volumetrically. The method has been successfully applied for the determination of penicillin G sodium, phenoxymethyl penicillin, ampicillin sodium, phenethicillin potassium, cloxacillin sodium and methicillin sodium. The procedure is also used for analysing some pharmaceutical preparations of these drugs, *e.g.*, injections. The results obtained are in agreement with those of the B.P. 1973 methods.

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ing on the iodine consumption by penicilloic acid. Studies have indicated that the iodine consumption is dependent upon the pH and the concentration of iodide in the iodine solution.[6-9] The iodine consumption was found to be variable, and the exact equivalent was determined by using an authentic sample as a standard reference.

Penicillin has been recently determined with iodine monochloride as reagent.[10] This procedure utilized the iodine liberated—in highly acid medium—as a measure of the penicillin content.

Spectrophotometric methods have also been used for the quantitative analysis of penicillins. Herroit[11] and Stock[12] described a method which involves measurement of the increase in absorbance at 322 nm after acid degradation. The cleavage of the amide linkage by alkaline hydrolysis[13] has also been used for the determination of phenylacetic acid concentration at 257 or 263 nm after extraction with chloroform from acid medium. Methods based on hydroxamic acid,[14, 15] molybdenum blue[16] and methylene blue[17] have also been described.

EXPERIMENTAL

Reagents

Ammonium vanadate solution, 1*M*. Dissolve 29.25 g of ammonium vanadate in boiling 50% v/v sulphuric acid. Dilute to 250 ml with 50% v/v sulphuric acid. This solution is stable for 3 days.

Phosphate buffer pH 6.8. Dissolve 13.80 g of sodium dihydrogen phosphate and 35.80 g of disodium hydrogen phosphate in 1 litre of water.

Concentrated sulphuric acid (A.R.).

Penicillin solutions. Freshly made, containing 2 mg/ml in phosphate buffer pH 6.8. Laboratory reference standards were used for calibration.

General procedure

Transfer known volumes (<5 ml) of the different penicillin solutions, containing from 1.0 to 10.0 mg, to a 100-ml conical flask and dilute to 5.0 ml with the phosphate buffer. Add 10.0 ml of 1*M* ammonium vanadate, 10 ml of conc. sulphuric acid and boil gently for 10 min. Cool, transfer to a 50-ml measuring flask and dilute to volume with water. Cool thoroughly for 5 min, and then measure the absorbance at 750 nm against a blank treated similarly.

For injections. Weigh accurately 0.25 g of the vial content into a 250-ml standard flask, dissolve by shaking in the pH-6.8 phosphate buffer, then make up to volume with the same buffer. Transfer 5.0 ml of this freshly prepared solution into a 100-ml conical flask and complete the assay as described above.

RESULTS AND DISCUSSION

The method has been used for the determination of a variety of penicillins. The optimum conditions have been investigated thoroughly. The oxidation of the acid degradation products of penicillins by vanadate is best carried out in sulphuric acid medium (*ca.* 20*N*). The heating period has also been studied, and the resultant heating-time response curve indicates 10 min gentle boiling to be sufficient. The colour formed is measured 5 min after dilution and mixing and is stable for 3 hr. The excess of vanadate in solution can also be determined titrimetrically. The spectrophotometric and titrimetric methods give concordant results.

The blue colour developed is attributed to the reduction of vanadium(V) to vanadium(IV) by the acid degradation products of penicillins.

The method proposed is simple and sensitive. The results obtained are compared with those of the official methods (B.P. 1973) (Table 1) and found to be in agreement. Beer's law is obeyed for the penicillins investigated, in the range 1.0–10.0 mg. The proposed method has been used for the analysis of penicillin vials supplied by different factories and can be recommended for the routine analysis of these drugs either in pure form or in vials.

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Table 1. Results obtained by the proposed method and by B.P. 1973 (8 replicates)

Penicillins in pure and in injectable form		Ammonium vanadate method Recovery, %	B.P. 1973 Recovery, %
Penicillin G sodium powder	(1)	98.6 ± 2.1	100.2 ± 0.9
Penicillin G sodium injections	(2)	102.4 ± 1.6	101.4 ± 1.3
Penicillin G sodium injections	(3)	101.7 ± 2.1	102.5 ± 1.5
Phenoxymethyl penicillin acid	(1)	98.5 ± 1.6	98.3 ± 1.3
Ampicillin trihydrate powder	(4)	99.5 ± 1.3	99.6 ± 1.7
Ampicillin sodium powder	(3)	101.8 ± 1.0	100.3 ± 1.7
Ampicillin sodium injections (Penbritin)	(4)	100.6 ± 1.1	101.9 ± 1.1
Ampicillin sodium injections (Pentrexyl)	(5)	101.3 ± 0.9	98.9 ± 1.4
Ampicillin sodium injections	(3)	98.9 ± 1.5	99.8 ± 2.0
Phenethicillin potassium powder (Broxil)	(4)	101.3 ± 1.8	102.3 ± 0.9
Cloxacillin sodium powder (Orbenin)	(4)	101.3 ± 1.1	102.3 ± 1.1
Cloxacillin sodium injections (Orbenin)	(4)	100.9 ± 0.9	100.9 ± 1.5
Cloxacillin sodium injections (Prostaphlin A)	(5)	101.2 ± 0.8	100.6 ± 1.8
Methicillin sodium powder (Celbenin)	(4)	98.9 ± 0.9	98.3 ± 1.4
Methicillin sodium injections (Celbenin)	(4)	99.8 ± 1.1	98.0 ± 1.8
Methicillin sodium injections (Staphcillin)	(5)	98.4 ± 1.4	101.9 ± 2.0

Suppliers: (1) Biochemie (2) CID (3) MISR (4) Beecham (5) Bristol. % Results obtained are the average of 8 experiments.

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SELECTIVE DETERMINATION OF ANTIMONY(III) AND ANTIMONY(V) WITH AMMONIUM PYRROLIDINEDITHIOCARBAMATE, SODIUM DIETHYLDITHIOCARBAMATE AND DITHIZONE BY ATOMIC-ABSORPTION SPECTROMETRY WITH A CARBON-TUBE ATOMIZER

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(*Received* 2 *September* 1976. *Accepted* 24 *October* 1976)

Summary—The extraction behaviour of antimony(III) and antimony(V) with ammonium pyrrolidinedithiocarbamate, sodium diethyldithiocarbamate and dithizone in organic solvents has been investigated by means of flameless atomic-absorption spectrophotometry with a carbon-tube atomizer. The selective extraction of antimony(III) and differential determination of antimony(III) and antimony(V) have been developed. With ammonium pyrrolidinedithiocarbamate and methyl isobutyl ketone, when the aqueous phase/solvent volume ratio is 50 ml/10 ml and the injection volume in the carbon tube is 20 μl, the sensitivity for antimony is 0.2 ng/ml for 1% absorption. The relative standard deviations are *ca.* 2%. Interferences by many metal ions can be prevented by masking with EDTA. The proposed methods have been applied satisfactorily to determination of antimony(III) and antimony(V) in various types of water.

Increased emphasis on the analysis of natural waters and waste waters for trace metal pollution has created the need for more rapid, sensitive, and reliable analytic procedures. Moreover, the potential toxicity of arsenic, antimony, selenium, *etc.* is considered to depend on their oxidation state. There are few techniques for estimating differentially trace amounts of these elements in different oxidation states. However, we have reported the selective determination of arsenic(III) and arsenic(V) by atomic-absorption spectrophotometry with a carbon-tube atomizer.[1]

Atomic-absorption techniques for antimony determination in aqueous samples have recently been refined and improved in sensitivity,[2–5] and include a stibine method[6,7] and a carbon-tube method.[8–10] These methods will not differentiate between antimony(III) and antimony(V), however. In this paper, we extend to antimony determination the techniques we used successfully for arsenic,[1] namely selective extraction with ammonium pyrrolidinedithio-carbamate (APDC) and atomic-absorption determination with a carbon-tube atomizer.

EXPERIMENTAL

Reagents

All solutions were prepared from analytical-reagent grade chemicals and demineralized water, and stored in polyethylene bottles.

Standard antimony(III) solution, 1000 ppm. Prepared by dissolving 1.371 g of potassium antimony tartrate in water and diluting to 500 ml with water. Diluted with water to give a concentration of 0.2 ppm before use.

Standard antimony(V) solution, 10 ppm. Prepared by oxidizing the standard antimony(III) solution with permanganate, by taking 5 ml of the 1000-ppm antimony(III) solution, adding about 2 ml of sulphuric acid and 4 ml of 1% potassium permanganate solution and heating (*ca.* 80°) for half an hour, adding hydrogen peroxide to remove excess of permanganate and the manganese dioxide produced, and diluting to 500 ml with 4*M* hydrochloric acid. Diluted with water to give a concentration of 0.2 ppm before use.

Antimony(III)-124m solution. Prepared by reducing 1 mCi of antimony(V)-124m ($SbCl_5$ in a mixture of 6*M* hydrochloric acid and 6*N* nitric acid) with potassium iodide and sodium thiosulphate,[1] and diluting to a suitable concentration with addition of inactive antimony(III) solution as carrier.

APDC solution, 1% w/v aqueous.

DDTC solution, 1% w/v aqueous.

Dithizone solution, 0.03% w/v. Prepared by dissolving 75 mg of refined dithizone in 250 ml of organic solvent.

EDTA (disodium salt) solution, 5% w/v.

Buffer solution, pH 5.5. Prepared by mixing 1*M* acetic acid and 1*M* sodium acetate in suitable ratio.

Apparatus

The apparatus was that described before,[1] except for the light-source, a Hamamatsu TV antimony hollow-cathode lamp.

Recommended general procedure

Antimony(III) determination. Take an aliquot of a sample solution containing not more than 1 μg of antimony(III),

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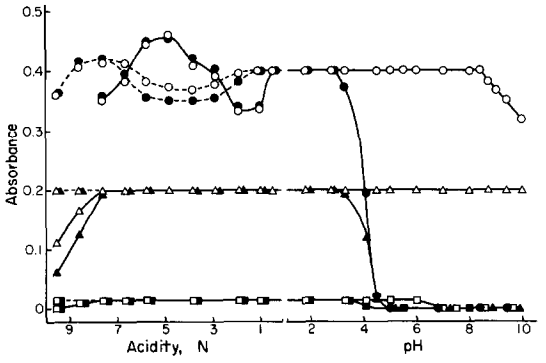

Fig. 1. Effect of acidity on the extraction of Sb(III) and Sb(V) with APDC. ○, Sb(III)–MIBK; ●, Sb(V)–MIBK; △, Sb(III)-NB; ▲, Sb(V)–NB; □, Sb(III)–CCl_4; ■, Sb(V)–CCl_4; (——), hydrochloric acid medium; (– – –), sulphuric acid medium; aqueous phase, 25 ml; organic phase, 10 ml; Sb(III) or Sb(V), 1 μg

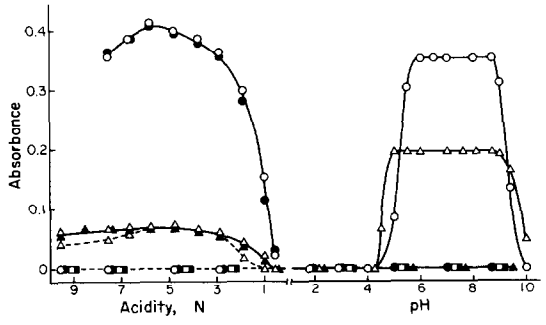

Fig. 2. Effect of acidity on the extraction of Sb(III) and Sb(V) with DDTC. Symbols and conditions as for Fig. 1.

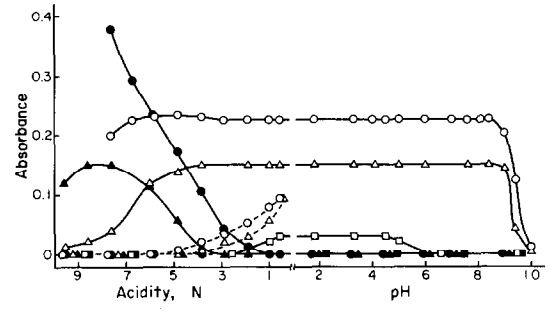

Fig. 3. Effect of acidity on the extraction of Sb(III) and Sb(V) with Dz. Symbols and conditions as for Fig. 1.

in a separatory funnel. Add 5 ml of the EDTA solution. Add 2 ml of the APDC solution and 5 ml of the acetate buffer solution. Dilute the mixture to 25 ml with water, the pH of the resulting solution being 5–6. Shake the funnel for 2–5 min with 10 ml of MIBK. Let stand for 20–30 min and separate the organic phase.

Inject 20 μl of the organic phase by micropipette into the carbon tube. Pass argon through the furnace at a flow-rate of 3 l./min, and then atomize the sample by the following heating sequence: drying for 30 sec at 20 A (*ca.* 200°), ashing for 120 sec at 60 A (*ca.* 900°), and atomization for 7 sec at 240 A (*ca.* 2500°). Record the absorption signal at 2176 Å. Run a reagent blank at the same instrumental settings and subtract it from the analytical value.

Total antimony determination. Take an aliquot of a sample solution containing not more than 1 μg of antimony, in a separatory funnel. Add 5 ml of the EDTA solution. Then addd 2 ml of the APDC solution and 2 ml of 1*M* hydrochloric acid or sulphuric acid. Dilute the mixture to 25 ml with water, the pH of the resulting solution being *ca.* 1. Do the extraction and measure the atomic absorption as for antimony(III).

The amount of antimony(V) is estimated from the difference between total antimony and antimony(III).

RESULTS AND DISCUSSION

Optimization of the atomization system

The heating conditions were examined in the same way as for arsenic and followed the same pattern, the useful limits being 20–30 A for 30 sec (200–300°) for drying, 50–70 A for 120 sec for ashing, and 230–260 A for 7 sec (2400–2800°) for atomization.

The shielding-gas flow-rates should be the same as for arsenic.[1]

Extraction

Extraction behaviour of Sb(III) and Sb(V). The extraction behaviour of antimony(III) and (V) with APDC, DDTC and dithizone in MIBK, nitrobenzene and carbon tetrachloride was investigated. The effect of acidity and the degree of extraction are shown in Figs. 1–3 and Table 1.

With APDC, at pH 5–8.5 (MIBK), 5–10 (NB), 5–6 (CCl_4), antimony(III) is extracted completely into MIBK, moderately into BN, very poorly into CCl_4, but antimony(V) not at all. The order of extraction efficiency of the solvents, CCl_4 < NB < MIBK, again holds for acidic medium, both antimony(III) and antimony(V) being extracted. The apparently higher degree of extraction from 5*M* hydrochloric acid (Fig. 1) is attributed to decrease in the volume of the organic phase because of the greater solubility of MIBK in such an acid solution. It is very difficult to account for the complicated differences in the extraction efficiency of the three solvents in neutral and acidic media.

The extracted species in the neutral medium should be $Sb(APDC)_3$, and this was confirmed by continuous variation plots. In a strongly acidic region, however, both antimony(III) and (V) are converted into chloro or sulphato complexes, which are also well extractable.

With the DDTC system, antimony(III) is extracted into MIBK or NB at pH 5.5–9, but less than with APDC. The order of extraction efficiency of the solvents is the same as for APDC. Antimony(V) is not appreciably extracted at pH 1–10.

Dithizone extracts antimony(III) over a wide range of pH, but the extractability is very poor compared to that with APDC or DDTC.

Table 1a. Degree of extraction

Reagent	Solvent	pH	Extraction, % Sb(III)	Sb(V)
APDC	MIBK	5.5	100	0
APDC	MIBK	1.0	100	100
APDC	NB	5.5	50	0
APDC	NB	1.0	50	50
APDC	CCl_4	5.5	3	0
APDC	CCl_4	1.0	3	3
DDTC	MIBK	6.5	88	0
DDTC	NB	6.5	49	0
DDTC	CCl_4	6.5	0	0
Dithizone	MIBK	4.0	57	0
Dithizone	NB	4.0	38	0
Dithizone	CCl_4	4.0	8	0

Table 1b. Degree of extraction in strongly acidic medium

Reagent	Solvent	Acid	Concn., *N*	Extraction, % Sb(III)	Sb(V)
APDC	MIBK	HCl	5	103	102
APDC	MIBK	H_2SO_4	5	93	88
APDC	NB	HCl	5	50	50
APDC	NB	H_2SO_4	5	50	50
APDC	CCl_4	HCl	5	3	3
APDC	CCl_4	H_2SO_4	5	3	3
DDTC	MIBK	HCl	6	92	91
DDTC	MIBK	H_2SO_4	6	0	0
DDTC	NB	HCl	6	18	17
DDTC	NB	H_2SO_4	6	18	17
DDTC	CCl_4	HCl	6	0	0
DDTC	CCl_4	H_2SO_4	6	0	0
Dithizone	MIBK	HCl	5	54	42
Dithizone	MIBK	H_2SO_4	5	2	0
Dithizone	NB	HCl	5	33	16
Dithizone	NB	H_2SO_4	5	0	0
Dithizone	CCl_4	HCl	5	0	0
Dithizone	CCl_4	H_2SO_4	5	0	0

Selective determination of Sb(III) and Sb(V). From these results it is concluded that APDC–MIBK extraction from neutral medium (pH 5–8) is best for the selective separation of antimony(III) and (V). Total antimony is separately determined by the extraction at pH 1–3. Recovery tests showed (Table 2) that the recommended procedure gave good results.

Effect of reagent concentration. To obtain maximum extraction, a minimum 700-fold w/w ratio (520-fold molar ratio) of APDC to antimony(III) is enough. Therefore, a reagent concentration of *ca.* 800 μg/ml is recommended when the antimony concentration is 0.04 μg/ml or less. A large excess of buffer or EDTA solution is without deleterious effect.

Effect of shaking time and stability of the extracts. Extraction is quantitative in 15 sec of shaking and continuing the shaking for up to 20 min produces no further change in absorption. The absorption signal of the extract remains almost constant for at least 6 hr after the extraction.

Effect of phase-volume ratio on sensitivity. Ten ml of MIBK were used for the extraction from various volumes of aqueous phase (pH 5.5), each containing 0.5 μg of antimony(III). A plot of relative absorption *vs.* phase-volume ratio was practically linear, the relative sensitivity increasing with increase in V_w/V_0 owing to the solubility of MIBK in water (*ca.* 2%). If an appropriate V_w/V_0 ratio is chosen according to the antimony content of the samples, it is possible to determine antimony over a wide concentration range from ng/ml to μg/ml levels.

Table 2. Recovery tests on antimony(III) and antimony(V)

Antimony added, *ng/ml* Sb(III)	Sb(V)	Antimony found, *ng/ml* Sb(total)	Sb(III)	Sb(V)
40	0	40	40	0
32	8	39	32	7
24	16	39	24	15
16	24	40	16	24
8	32	40	8	32
0	40	41	0	41

Calibration curve and precision

Calibration can be done with antimony(III) at pH 5.5 or with antimony(V) at pH 1. The linearity is good over the range 1–20 ng/ml with $V_w/V_0 = 5$. The sensitivity for 1% absorption was found to be 0.2 ng/ml. The relative standard deviation was *ca.* 2% for 40 ng/ml of antimony(III) (ten determinations, three injections each).

Interferences

The interference of large amounts of alkali and alkaline

Table 3. Permissible amount of foreign ions in determination of 1 μg of Sb per 25 ml (to give < 10% error)

Ion	Added as	Limit, [Ion]/[Sb]	
Fe^{3+}	Chloride	70	(350)
Co^{2+}	Chloride	70	(750)
Ni^{2+}	Chloride	700	(1000)
Ag^{+}	Sulphate	200	(380)
Hg^{2+}	Chloride	2.3	(5)
Cd^{2+}	Chloride	11	(11)
Sn^{2+}	Sulphate	300	(1000)
As^{3+}	Arsenious acid	15	(15)
Bi^{3+}	Nitrate	70	(90)
Se^{4+}	Selenious acid	150	(150)
Te^{4+}	Tellurous acid	140	(140)

The following are tolerable in 1000-fold ratio to Sb: NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Al^{3+}, Cr^{3+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, As^{5+}, Cl^-, Br^-, I^-, NO_3^-, CH_3COO^-, SO_4^{2-}, SiO_3^{2-}, PO_4^{3-}, CN^-, S^{2-}.

Values in parentheses apply when 1% EDTA is present.

Table 4. Analytical results on various samples

Sample	Sb(total), *ng/ml* added	found	Sb(III), *ng/ml* added	found	Sb(V), *ng/ml* added	found
River water	—	ND	—	ND		ND
River water	8.0	8.0	8.0	8.0	—	ND
River water	8.0	8.1	—	ND	8.0	8.1
Waste water 1	—	6.4	—	ND	—	6.4
Waste water 1	8.0	13.8	8.0	7.6	—	6.2
Waste water 1	8.0	14.4	—	ND	8.0	14.4
Waste water 2	—	8.0	—	ND	—	8.0
Waste water 2	8.0	15.6	8.0	7.8	—	7.8
Waste water 2	8.0	15.8	—	ND	8.0	15.8
Sea-water	-	ND	—	ND	—	ND
Sea-water	8.0	8.0	8.0	8.0	—	ND
Sea-water	8.0	8.2	—	ND	8.0	8.2
Sea-water	16.0	16.0	8.0	8.0	8.0	8.0

ND: not detected.

earth metals in the determination of antimony by direct injection[10] is avoided by extracting the antimony before the atomic-absorption analysis. However, large amounts of metal ions which react with APDC lower the degree of extraction of antimony(III). In many cases, such interferences can be reduced by masking with EDTA. Table 3 shows the effects of various ions; the data in parentheses were obtained with 1% of EDTA in the aqueous phase.

Application to water analysis

The results of the selective determination of antimony(III) and antimony(V) in various types of water are presented in Table 4 together with those of a recovery test run on the samples. All the samples used were acidified with hydrochloric acid to *ca.* pH 1 immediately after sampling. According to the method proposed here, ng/ml levels of antimony(III) and antimony(V) in waste water or seawater can be selectively determined. In the waste waters, antimony is found to be present in the quinquevalent state.

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METAVANADATE AS A REAGENT FOR THE COLORIMETRIC DETERMINATION OF ACIDS

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(*Received* 9 *April* 1976. *Revised* 15 *September* 1976. *Accepted* 15 *November* 1976)

Summary—Acids with $pK_a > 6$ can be determined colorimetrically by their reaction with metavanadate, provided they are not coloured and do not give complexation or redox reactions with the polyvanadate.

Continued addition of acid to a solution of orthovanadate results in a series of yellow condensed polyvanadates.[1–13] The colour at pH 2–6 has been used for determination of vanadium.[14, 15] In view of the importance of knowledge of the acidity for control of various technological processes, for example in the food and pharmaceutical industries, we decided to study the reaction of metavanadate with acids. We chose ammonium metavanadate because the pH of its solutions is about the same as the upper limit for polyvanadate formation (~ 6). The metavanadate solution has a feeble yellow colour initially, because of hydrolysis to form some decavanadate. We have found that the colour is intensified on addition of acid (Fig. 1).

When different mole-ratios of acid and metavanadate are taken, at constant total concentration of the two, it is found that the colour is maximal when the ratio $[H^+]/[\text{vanadate}]$ is 0.4 (Fig. 2). Further, if the metavanadate concentration is kept constant, the colour intensity is proportional to the hydrogen-ion concentration for $[H^+]/[V(V)]$ ratio < 0.4. The proportionality is lost when $[H^+]/[V(V)]$ is between 0.4 and 1, and at ratios > 1 the colour disappears because of decomposition of the polyvanadate. Examination of the kinetics shows that the reaction is complete in 20 min and that the colour is stable for at least an hour. Beer's law is obeyed at 400 nm by the system, for $[V(V)] = 0.004M$ and $[H^+] = 10^{-4}$–$10^{-3}M$.

However, the system is applicable only to acids which do not form complexes with vanadate. For example, tartaric acid initially gives the yellow colour, but this rapidly changes to the red of the vanadate—tartrate complex (which has been used for determination of tartrate).[16,17] The interfering reactions can be classified in two groups.[18]

(*a*) Reactions in which difficultly soluble or coloured complexes are formed, usually with carboxylic acids containing other functional groups such as hydroxyl.[19–22] In general these reactions take place at the same time as the formation of polyvanadate and thus interfere competitively.

(*b*) Reactions taking place in presence of a catalyst or a third reactant or on heating. They include those in which the acid is oxidized by vanadate (formic, oxalic acid *etc.*)[23, 24] or forms polyvanadate complexes (phosphoric,[25] malonic,[26] caprohydroxamic acid[27] *etc.*). Nevertheless, many of these acids can be determined if a sufficiently low concentration is used ($\sim 2 \times 10^{-4}M$).

In principle, all acids can be determined by this method, provided they are not themselves coloured, do not give competitive reactions with vanadate, and are not too weak. The lower limit for the acid dissociation constant seems to be about 10^{-6}. Both inorganic and organic acids can be determined. Typical results are shown in Table 1. The method is simple and rapid.

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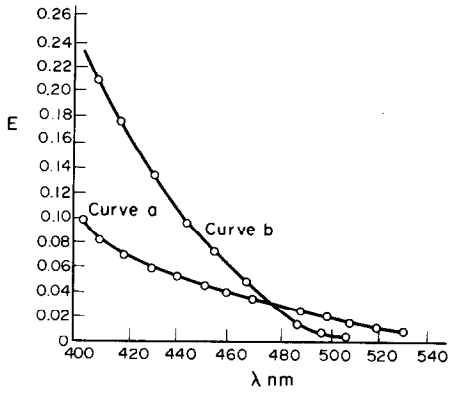

Fig. 1.

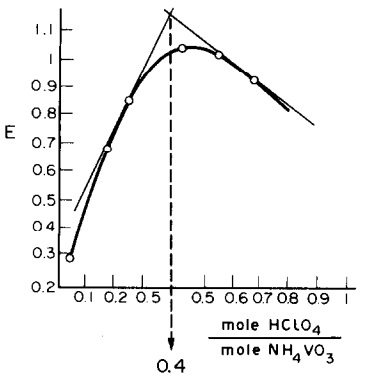

Fig. 2.

Table 1.

Acid	Weight taken, μg	Absorbance	Amount found μg	Amount found μeq
HCl	73	0.34	73	2.0
	164	0.78	164	4.5
H_2SO_4	50	0.17	49	1.0
	196	0.70	196	4.0
$HClO_4$	200	0.34	201	2.0
	300	0.52	300	3.0
Acetic	60	0.17	60	1.0
	300	0.86	300	5.0
Oxalic	50	0.14	51	0.8
	200	0.54	202	3.2
Succinic	150	0.47	150	2.5
	250	0.72	248	4.2
Quinoxalinic	100	0.16	98	0.9
	400	0.63	403	3.7

Procedure

To 1 ml of the 10^{-4}–$10^{-3}M$ acid add 1 ml of 0.02M ammonium metavanadate, dilute to 5 ml with distilled water and after 20 min read the absorbance at 400 nm, against a water blank. Construct a calibration curve with any convenient acid.

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PRELIMINARY COMMUNICATION

NON-VOLUMETRIC TITRATIONS

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During its existence of more than 150 years, the technique of titrimetry has remained essentially unchanged, the end-point being determined by means of a change in a physicochemical parameter of the titration mixture, and the quantity of determinand calculated from the volume of titrant required. This comparatively complex procedure is necessary because the quantity of determinand cannot be determined directly from the value of the measured parameter (e.g., pH). In the following, a special technique of titration is recommended, which dispenses with these limitations in a number of determinations and is in many respects simpler than conventional titration.

The underlying principle is the use of the buffer-addition method[1,2] and linear-response reagent compositions.[3–7] Mixed with the sample, the latter enter into successive reactions with the determinand and the pH of the mixture is directly proportional to the quantity of determinand. In this way, acids and bases can be determined by a single pH measurement instead of by titration.

This technique can be extended to the determination of components which liberate an acid or base when a suitable reagent is added. For example, EDTA reactions:

$$Me^{2+} + H_2Y^{2-} \rightleftharpoons MeY^{2-} + 2H^+ \quad (1)$$

$$Me^{2+} + HY^{3-} \rightleftharpoons MeY^{2-} + H^+ \quad (2)$$

On the basis of these reactions and the use of linear-response reagent compositions, various metal ions can be determined complexometrically without titration, through a single pH measurement.[8,9]

It is now found that the buffer-addition technique is suitable not only for direct determinations but also for end-point indication in complexometric titrations. The proposed technique can be applied throughout the entire field of complexometry. Since the parameter to be measured is the pH of the solution, the task is simple and suitable for automation. The technique is also applicable to other determinations such as that of mercaptans in non-aqueous solution.

EXPERIMENTAL

Instruments

A RADELKIS recording pH meter Type OP-207 was used for pH measurement and recording; the measuring electrode was a RADELKIS shock-resistant combination electrode Type OP-871. The titrant solution was delivered by a RADELKIS automatic burette Type OP-930. All titrations were performed at a constant rate; no end-point anticipation was applied.

Chemicals

Reagent type DH-B2,[5,7] of 0.1M concentration (diethylmalonic acid, citric acid, diethylbarbituric acid, m-chlorophenol, boric acid and phenol) was diluted tenfold, made 2M in potassium chloride to maintain constant ionic strength and diffusion potential in the pH-determinations, and finally adjusted to pH 8.00 by the addition of solid potassium hydroxide. The reagent composition (type DH-A2) thus obtained was used for the tests. For mercaptan determinations, the same reagent was diluted with methanol instead of water, and no potassium chloride was dissolved in it.

Roughly 0.1M EDTA (2M with respect to potassium chloride and adjusted to pH 8.00 with solid potassium hydroxide) was used as titrant. For mercaptan determination, the titrant was roughly 0.1M mercuric chloride solution in methanol. The components of the titrants were weighed approximately and the solutions were not standardized.

The metal salts tested were used as 0.1M aqueous solutions. The mercaptan was n-octanethiol, as a 1% solution in methanol.

All chemicals except the diethylmalonic acid were of analytical grade.

Complexometric determinations

Portions of sample solution (0.25 - 1.5 ml) were added to 10 ml of the DH-A2 reagent and titrated with the EDTA, changes in the pH being measured as a function of the volume of titrant added. On addition of titrant the pH was lowered, as a linear function of the quantity of titrant added. The curve then passed through a minimum and the pH rose again (Fig. 1). Similar curves were obtained with zinc, cadmium, manganese and even calcium and magnesium.

The assumption that the peak of the curves represents the equivalence point appeared to be self-evident. The relationship between the volume of titrant required up to the peak and the quantity of metal ion added was found to be linear in each case. A unique feature of the titration curves is that the position of the peak is shifted along the pH-axis as well as along the titrant volume axis, as a function of the amount of metal ion present, i.e., the change in pH during a titration is a function of the metal ion content. This suggests the possibility of using the maximum change in pH instead of the volume as a measure of metal ion concentration. This can best be seen by using a low chart speed: the titration curves are distorted to sharp peaks. If the metal ion concentration is increased in equal steps, and the starting points of the curves are shifted uniformly, a calibration curve of [metal ion] vs. pH will be obtained by connecting the peaks (Fig. 2).

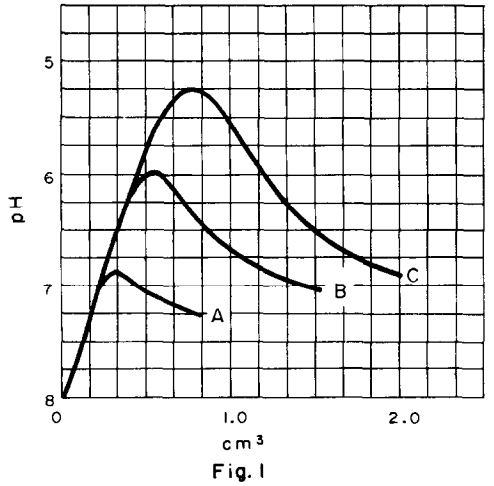

Fig. 1

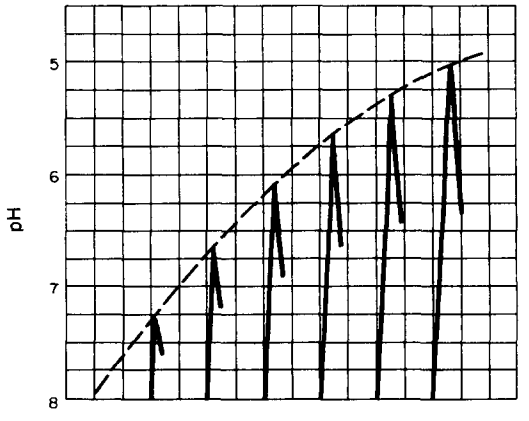

Fig. 2

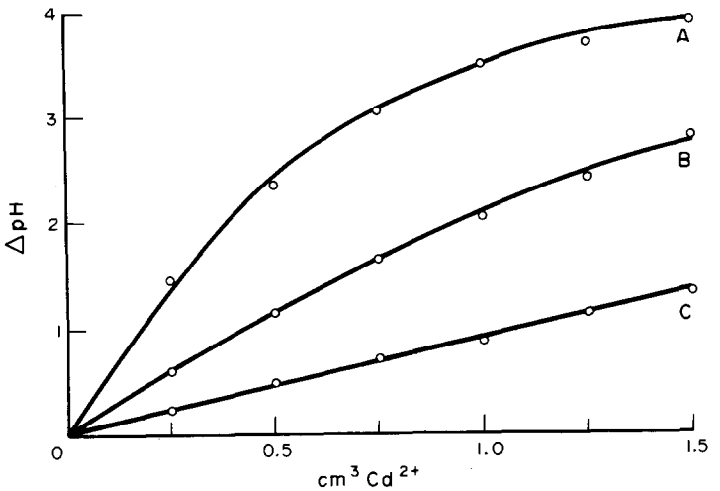

Fig.3

The character and extent of the change in pH can be influenced by varying the ratio of sample and DH reagent. The 10-fold diluted reagent gives a considerable change in pH ($\Delta pH = 4$) but the relationship is not linear (curve A in Fig. 3). At 5-fold dilution (curve B) the initial portion of the curve is linear, and at 2-fold dilution (curve C) the whole range is linear but ΔpH is smaller.

Parallel titrations of 0.0076M zinc sulphate with measurement of the pH and of the volume needed to reach the peak gave a relative standard deviation of 0.4% for the ΔpH method and 1.6% for the volume method.

Mercaptan determination

Another reaction accompanied by liberation of an acid is that[10,11] of a mercaptan with mercuric chloride:

$$R\text{-}SH + HgCl_2 = RSHgCl + HCl \qquad (3)$$

Portions (0.25, 0.50 and 0.75 ml) of 1% n-octanethiol solution were added to 10 ml of DH-A2 reagent diluted with methanol to 0.01M. The mixtures were titrated with 0.1M mercuric chloride in methanol, the pH changing linearly up to the end-point, and then remaining unchanged. Titration curves of this type are shown in Fig. 4. The relation between the quantity of mercaptan and change in pH is shown in Fig. 5.

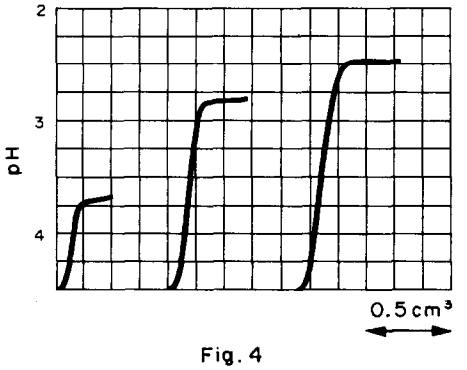

Fig. 4

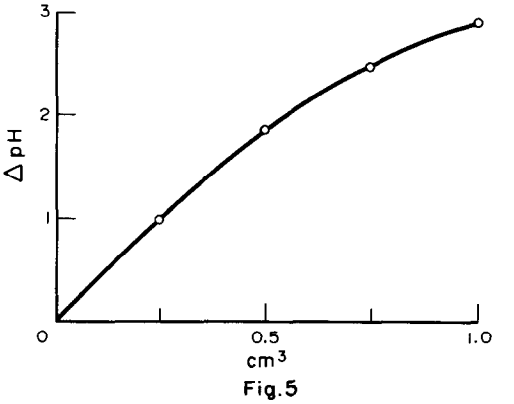

Fig.5

DISCUSSION

The shape of the titration curves may be explained as follows. In the initial stages, when the metal ions are present in excess, the acid liberated is equivalent to the quantity of EDTA added and because of the DH reagent, the pH of the solution varies linearly with this quantity of acid and hence with the quantity of EDTA added. After the end-point, no more hydrogen ions are liberated and the pH increases as a result of protonation of excess of EDTA.

It is self-evident that the technique can be applied to any reaction involving the liberation of an acid or a base. It represents a significant simplification in technique, dispensing with the need for standardization of titrant and their accurate delivery. Moreover, end-point detection is also eliminated, only the maximum change in pH being needed for a result.

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TALANTA MINI-REVIEW*

RECENT APPLICATIONS OF DIGITAL COMPUTERS IN ANALYTICAL CHEMISTRY

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Summary—Minicomputers are finding increasing use for the control and operation of analytical instruments. This role is likely to be shared in the near future with dedicated microcomputers. Applications of computers to electroanalytical chemistry, Fourier transform techniques, spectroscopy, rapid-reaction kinetics, equilibrium constants, studies of analytical methods and to literature searching, are also discussed.

Computer usage in analytical chemistry has increased markedly in the seven years since the earlier review,[1] both in extent and in sophistication, involving all types of analytical procedures and instrumentation. The diversity of the topic is illustrated by the use of a computer to classify archaeological artefacts by applying pattern recognition to their trace element composition.[2] Manual analytical methods have been made automatic, and new analytical techniques have been developed. Digital electronics and laboratory-scale digital computers are steadily moving towards a dominant position in the design of laboratory instruments and it is likely that they will become an indispensable part of much laboratory experimentation. Computers have also come into use for rapid data reduction during analysis.

However, relatively few new principles have emerged. For the present purpose it seems more appropriate to indicate recent changes and to point out new directions in which computer science may impinge on analytical chemistry.

Thus there have been significant advances in electronic circuitry and instrumental technology, with a large increase in the availability of computers, which now cover a much greater range of memory and capability, with an appreciable decrease in their cost. In particular, this period has marked the rise of the minicomputer and its use as a built-in (on-line) component of chemical instruments for real-time data acquisition, for system-control and for manipulation of data, thereby greatly increasing the applications of computers in analytical chemistry. At the same time, use of interpretative computer languages such as BASIC,[3] FOCAL[4] and LABTRAN[5] decreases the expertise necessary for their operation or for writing programs. The increased mathematical capability arising from the use of computers is typified by a general least-squares curve-fitting programme which finds the best values of n parameters in any given equation for any set of experimental data.[6] This program, modified to increase its speed, has been used for multiparametric curve-fitting in titrimetry to distinguish between polyfunctional and monofunctional acids and bases,[7] to locate the end-points in potentiometric titrations of weak bases with strong acids,[8] and to interpret titrations with unstandardized reagents.[9]

COMPUTER-CONTROLLED APPARATUS

A minicomputer may be shared by several instruments simultaneously. For example, Overton *et al.*[10] described a system in which eight instruments, comprising gas–liquid chromatographs, automatic analysers and pulse polarographs, were sampled at different data rates by a computer which also processed the stored data. Similarly, DeVoe *et al.* used a multiprogrammed minicomputer in a system supporting twenty instruments,[11] comprising spectrophotometers, electrochemical cells, mass spectrometer, electron-probe microanalysers, gamma-ray spectrometers, Mössbauer spectrometers and an electron spectrometer for chemical analysis. An on-line computerized system of elemental analysis for C, H, N and O, using four elemental analysers and two electronic microbalances, has been described.[12] Other examples of computer-based systems that provide for several instruments include those of Ziegler *et al.*[13] and Shapiro and Schultz.[14]

It is probably operationally more efficient if instruments with fast data-collecting rates (such as mass and nmr spectrometers) have their own (dedicated)

*For reprints of this Mini-Review, see Publisher's announcement near end of this issue TALMR 7.

computers whereas those with slow data-collecting rates (such as infrared and ultraviolet spectrophotometers, microcalorimeters and gas chromatographs) share a common central computer.[15] For instruments generating data at slow rates, processing is simplified by the use of an interpretative language such as BASIC[16] for data acquisition.

The name "minicomputer" may be somewhat deceptive. It is applied, for example, to a machine with 64000 bits of core memory, with 5 million bytes of disc storage, and carrying peripheral equipment such as line-printers and cathode ray tube (visual display) terminals. For many chemical purposes such a minicomputer is unnecessarily large. On the other hand, "hard-wired" (fixed automatic operation) scientific instruments leave little flexibility to the operator.

The gap between "hard-wired" control and the use of minicomputers has recently been filled by the development of integrated circuit microprocessors which are functionally similar to the central processing unit of a larger computer but are contained on a single silicon chip. They are already being used in programmable calculators and desk-top graphic display units. These calculators, in turn, can be used as system controllers. A microprocessor can be combined with integrated circuit memories, control circuitry and data input and output lines to comprise a microcomputer which can be built into instruments. Instrumentation-orientated microcomputers have been discussed by Woodward *et al.*[17]

Provided massive data-banks or programs exceeding, say, 3000 "words" are not required, such a combination can replace a dedicated laboratory computer interfaced to a normal instrument, with saving in cost and improvement in convenience to the user. Microcomputers should be considered where automation is primarily a control process, with only minor computation. Typical examples might include pulse polarography, automatic titration, data-correction in absorption spectroscopy and gas chromatography. Currently, there is considerable interest among manufacturers in the use of microprocessors, with the expectation that within several years microcomputer-based systems will displace most minicomputer-based systems except where the minicomputer services perhaps five or more instruments. Another possibility is to use microprocessors for each instrument, with a small backing memory, linked into a larger computer network. Microcomputers and their analytical applications have been reviewed.[18,19] Recently an automatic titrator incorporating a microprocessor for use in the sequential titration of adipic and boric acids has been described.[20]

Dessy and Titus[21] have described design considerations for interfacing analytical instrumentation with computers. Computer interfacing to chemical instruments, and the processing of the resulting data, have been discussed under the headings of data acquisition, analogue-to-digital conversion, digital preprocessing, procedural reduction, manipulation and transforma-

Table 1. Examples of computer-controlled analytical equipment

Apparatus	Ref.
Computer-controlled rapid-scan atomic-fluorescence spectrometer	23
Computer-controlled d.c. arc spectrometer	24
Computer-controlled flame emission spectrometer	25
Computer-controlled automatic titration apparatus with ion-selective electrodes	26
Computer-controlled automatic titrator	27
Computerized electroanalytical instrument	28
Computer-controlled electron spin resonance spectrometer	29
Programmable calculator interfaced to a gas chromatograph	30
System for automation of gas chromatography	31, 32
Gas chromatograph–mass spectrometer–computer systems	33, 34
Computerized fast-scanning gas chromatograph–mass spectrometer	35
Computerized infrared spectrometer using Fourier transform techniques	36
Computer-interactive system for stopped-flow kinetics with rapid scanning molecular-absorption spectrometer	37, 38
On-line computer control of a luminescence spectrometer	39
Continuous mass-spectrometer monitoring of liquid chromatography, by on-line computer	40
Computer-controlled microwave spectrometer	41
On-line qualitative gamma-spectrometer, with computerized data reduction	42
Computer-controlled triple-axis neutron spectrometer	43
Computerized system for sampled d.c. polarography	44
On-line, computer-controlled potentiometric analysis system	45
Computer system for automated Raman spectrometer	46
Automatic techniques for grating spectrometers in Raman spectrometry	47
Automated spectrofluorimeter with on-line minicomputer	48
Computer-controlled ultraviolet–visible region spectrophotometer	49
Computer-controlled double-beam absorption spectrophotometer for the ultraviolet, visible and near infrared	50
Multielement atomic spectrometer with a computerized vidicon detector	51
On-line computer-controlled spark-source mass-spectrometer	52

tion, and post-operative amalgamation and interpretation.[22] Where instruments are in limited use it is more economical to employ a general-purpose minicomputer data-acquisition and control system with appropriate interfaces for attachment to the various scientific instruments: the specifications of the computer system are governed by those of the individual instruments.

Some recent examples of computer-controlled equipment are given in Table 1. Such equipment is becoming commercially available. Thus, a commercial gas chromatograph has a built-in digital processor which operates the system throughout the analysis. It monitors the detector output, converts it into peak areas and times, calculates the results of the analysis and prints the report. Similarly a mass spectrometer linked to the output of a gas chromatograph and integrated with a small on-line laboratory computer takes less than one second for a mass scan, at the same time analysing and storing each peak: the combination makes a powerful tool for the qualitative and quantitative identification of unknown materials. A computer-controlled sequential multichannel automated continuous-flow analyser (SMAC) has been evaluated for clinical application.[53] It is capable of 40 simultaneous assays at a rate of 200 samples per hour, using less than 500 μl per sample.[54] The computer corrects for drift, noise, short samples, standardization and linearity; it also stores the colorimetric output data. Automatic off-line computer analysis of amino-acid chromatograms of protein hydrolysates allows separation and identification of bands, and the quantitative determination of components.[55–58]

ELECTROANALYTICAL CHEMISTRY

For most electrochemical measurements even modest minicomputer systems are more than adequate for experimental requirements of speed, accuracy and data-recording. In fact, computers make it possible to extract more information and to use more of the experimental measurements such as waveshapes. Conditions for the optimization of an analytical method can sometimes be achieved by an operator-interactive computer-assisted approach, provided the experimental variable-response characteristics can be defined, theoretically or empirically, and placed under computer control. The technique has been illustrated for anodic stripping voltammetry.[59] Curve-fitting techniques have been used to fit the experimental wave-forms of overlapping stationary-electrode polarographic curves.[60] Jagner[61] has discussed advantages of using computers in titrimetry.

FOURIER TRANSFORM TECHNIQUES

For some years, dedicated computers of averaged transients (CATs) have been used to improve signal-to-noise ratios, and hence to decrease the quantity of material required, for NMR spectra. However, disadvantages of this technique include base-line instability and long scanning time. An alternative approach which greatly increases the sensitivity of proton magnetic resonance measurements is to use a larger on-line computer and a pulse generator for the application of Fourier transform techniques.[67] Fourier transform spectrometers with small digital computers that are commercially available make it possible to study the NMR spectrum of ^{13}C at natural abundance levels. In such a spectrometer there may be computer control of the observing frequency transmitter, the decoupler frequency, pulse-widths, gating operation, data-acquisition display and plotting, receiver gain and T_1 sequences, with external memory devices and line-printers. The low cost and large storage capacity of magnetic tape cassette units makes them very useful for program and data storage.

Fourier-transform pulsed-wave NMR spectrometry depends on perturbing the sample with an intense, short-duration (fraction of a second) pulse of radiofrequency energy having a frequency range which extends over all resonance frequencies of the nucleus being studied. The resulting free induction signal from the nuclear spins in the sample is stored in the computer, and the process is repeated many times to improve the signal-to-noise ratio by averaging. Finally the signal is subjected to Fourier transformation[68] to give the usual form of NMR spectrum.

Fourier transformation techniques can also be used to improve spectra obtained by other methods, such as infrared,[69] circular dichroism,[70] ion cyclotron resonance spectroscopy[71] and electron spin resonance.[72] On-line fast Fourier transform procedures have applications in electrochemical relaxation measurements by making it feasible to study the kinetic-mechanistic status of an electrode reaction.[73] These procedures also lead to improvement in data quality by facilitating the mathematical processes of convolution and correlation and their inverse operations.

SPECTROSCOPY

Files of spectra are available for infrared,[74–77] ultraviolet,[75] proton NMR,[75,78–80] ^{13}C NMR[75,81] and mass spectrometry.[82,83] These include a file of over 92,000 infrared spectra collected by the American Society for Testing and Materials (ASTM).[77] Other sources have been listed by Gevantman.[84] Access to such collections has stimulated the development of computer programs for searching such files to identify unknown compounds. Procedures are well established for infrared,[85–88] mass[89–94], proton NMR[95,96] and ^{13}C NMR[97] spectra. A typical procedure is to select each reference spectrum in turn, compare it with the unknown spectrum, checking for peaks within specified tolerances, and then record the extent of matching of unknown and reference spectra. Some possible strategies for searching have been dis-

cussed.[86] An alternative approach is based on pattern recognition.[98,99]

Digitization of spectral data, followed by numerical data analysis, can make possible operations that would be difficult or impossible to do manually. Base-line corrections, conversion from wavelengths into wavenumbers, smoothing, line-sharpening, curve-fitting, time-averaging, area-determining, differentiating, peak-finding and resolution into component peaks are examples.

Curve-fitting methods are widely employed to determine areas or heights of bands in composite profiles such as those observed in ultraviolet–visible region and infrared spectrometry, and in iterative curve-fitting to chromatographic peaks.[100] Programs by Jones *et al.*[101–103] can be used to fit infrared data to suitable mathematical models for band-shapes but care is needed because more than one set of parameters can give a close fit to a given profile.[104,105]

Computers also make it possible to resolve spectra of mixtures by "spectrum stripping" in which known spectra of some of the components are successively subtracted from the spectrum of the mixture, characteristic peak-heights being used as measures of concentration. When only two or three species are present, partial fractionation of the sample enables the infrared spectrum of each species to be obtained from the spectra of the resulting mixtures by a matrix inversion technique.[106] Similarly, quantitative analysis of mixtures of compounds is possible from NMR spectra if the chemical shifts and coupling constants of the components are known, by computing the spectrum of each component and adjusting its assumed mole-fraction until the superimposed calculated spectra fit the experimental curve.[107]

Methods for searching mass-spectral data by computer have generally been based on the successive comparison of the unknown spectrum with each recorded spectrum to select the reference spectrum which reproduces the most features of the unknown. Adequate data storage may be a limitation, especially with minicomputers, but this may be partly overcome by using highly compressed spectral codes.[108] An alternative approach, "reverse searching", discussed by Abramson,[109] has advantages, especially when the unknown material is impure or is a mixture, because the data-base of the search becomes the library of spectra rather than the unknown species. The technique appears to have applications to other types of spectral searching.

REACTION KINETICS

Studies of the kinetics of fast reactions have been facilitated by coupling a computer to stopped-flow instruments.[110–114] Rapid-scanning ultraviolet–visible region spectrometers have been used in this way with scanning times of around 1 msec to acquire and process data.[114,115] A novel development has been the employment of a vidicon (television camera pick-up tube) spectrometer interfaced with a small general-purpose digital computer[116] with scan-times varying from 4 msec upwards and repetition rates varying between 250 and 0.1 per sec. Decay kinetics (in the msec range) of phosphorescence spectra have been studied with a computer-controlled laser phosphorimeter.[117] Experimental data for pseudo first-order growth or decay can be tested for fit by using a non-linear least-squares program.[118] Wiberg[119] has described methods of numerical integration of kinetic equations that can be applied to any sets of simultaneous reactions. Hogg[120] has compiled an annotated bibliography of computer programs for chemical kinetics from 1965 to 1972.

EQUILIBRIUM CONSTANTS

A significant recent development has been the publication of computer programs for calculating equilibrium constants from spectrophotometric data. Some of these[121–124] have been written on the basis of simplifying assumptions, such as the neglect of minor species, and are of limited usefulness. There have also been programs with more general application. A disadvantage of using absorbance measurements for this purpose is that at any wavelength there are $2n$ unknowns (the molar absorbtivity and the equilibrium constant for each of the n complexes), whereas in potentiometry there are only n. By taking measurements over a wide range of wavelengths advantage can be taken of matrix algebra for data reduction. Kankare[125] has used this approach in a set of programs for a small computer (16000 bytes of core) to obtain equilibrium constants from absorbance data.

A more general program, SQUAD,[126] derived from SCOGS,[127] allows evaluation of the best set of stability constants from absorbance measurements in systems containing up to two metal ions and two ligands, so long as the degree of complex formation is pH-dependent. It can yield pK_a values, metal-ion hydrolysis constants, and stability constants of simple, polynuclear, mixed-ligand and mixed-metal complexes. Kaden and Zuberbuhler[128] have published a general program which, by change of one or two subroutines, can process either potentiometric or absorbance data.

There has been less development of computer programs for potentiometric data. Feldberg *et al.*[129] simplified Sillén's twist matrix method[130] but the resulting program was very slow-running. LEAST[131] employs analytical expressions for calculating differential coefficients, instead of using the numerical differentiation of SCOGS and LETAGROP.[132] It gives better convergence properties but can be applied only to one-metal, one-ligand systems. The programme MINIQUAD[133] (including its improved version MINIQUAD 75[134]) is a generalization of LEAST and uses the Gauss–Newton[135] method of refinement (as in SCOGS). With a linear optimization of shifts, this method always leads to convergence of the esti-

mates of the equilibrium constants. PSEUDOPLOT[136] enables a computer to approach the normalized-curve method for selecting a set of formation constants to define a system of competing equilibria. It computes and plots titration curves which are compared, by superposition, with experimental ones. By varying the metal:ligand ratios and absolute concentrations it provides a searching check on the adequacy of the types of complex postulated.

THEORETICAL STUDIES OF ANALYTICAL METHODS

Insofar as many analytical methods depend on metal-complex and acid–base equilibria, and solubility or solvent extraction properties, it is possible to use suitable computer programs to make theoretical studies of the feasibility, precision and selectivity of a possible method and to suggest optimal experimental conditions. Programs such as COMICS[137] (including modifications by Cumme[138] and Ginzburg[139]), HALTAFALL[140] and EQUIL[141] have wide applicability for calculations of equilibrium concentrations of the various constituents of mixtures in ionic solutions. They can also be used for two-phase systems, including solvent–solvent mixtures and precipitates. Examples of the use of HALTAFALL in this way are given by Dyrssen *et al.*[142] COMICS has recently been the basis of a theoretical study of chelating agents for selectively eliminating toxic metal ions from blood plasma.[143] Simpler (MINICOMICS) programs have been developed for use on a small computer. Applications to analytical chemistry have included theoretical studies of the homogeneous precipitation of barium sulphate and the selective extraction of zinc by dithizone.[144] Similar studies have also been made of some masking reactions.[145] Compositions of pH-buffers can be computed from published programs.[146] A modified version of LETAGROP VRID[130] has been applied to evaluate chelatometric titrations with metallochromic indicators. This comprised a curve-fitting procedure, with five adjustable parameters (end-point, absorbance, concentration, equilibrium constants).[147] A different algorithm was used by Sato and Momoki[148] in a least-squares curve-fitting method for end-point detection.

Coupling an X–Y plotter such as a Hewlett-Packard model 7200A to the output of even a small computer enables curves to be obtained for pH–composition profiles or for the effect of a variable such as pH on conditional constants. It also facilitates the plotting of experimental results directly on to computed curves. For rapid visual examination of results, especially when they are provisional, it is often convenient to display them on a cathode ray tube (visual display screen).

LITERATURE SEARCHING

Since the previous review there has been a significant increase in computer-based aspects of information processing by the Chemical Abstracts Service (CAS), ranging from the alphabetical listing by name and phrase in each issue of Chemical Abstracts to the merging of computer-readable files which were used to organize and produce the semi-annual indexes and, in turn, to produce the Eighth Collective Index. This computerization facilitates literature searching, for example by using "CA Subject Index Alert" which is available as a fortnightly service giving details of relevant publications in an issue of Chemical Abstracts, or "CA Integrated Subject File" which is used for computer-based retrospective searching. Expensive equipment is required to process the computer-readable files from which the desired information is sought. To overcome this difficulty a number of organizations in various countries have been licensed to provide this service from CAS computer-readable files. An example is UKCIS (United Kingdom Chemical Information Service).[149] Veal[150] has discussed computer techniques for retrieval of information from the chemical literature. A recent review[151] illustrates an application of these facilities. Citations relevant to the subject of the review were selected by a computer search of "CA Condensates" (CAC) on magnetic tape. The computer program LISE (Literature Search and Edit) was used to generate the bibliography in computer-readable form on magnetic tape from the CAC data-base and in this form it was submitted for publication. A useful guide is the book by Ash and Hyde.[152]

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ANALYTICAL APPLICATIONS OF *o*-HYDROXYMERCURIBENZOIC ACID, DITHIOFLUORESCEIN AND MERCURATED FLUORESCEIN

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Summary—The application of the reagents mentioned in the title to titrimetric, photometric and fluorimetric analysis of several compounds of sulphur, nitrogen and mercury, including procedures for selective determinations, detection, location, identification and estimation in trace quantities, is reviewed.

Since their first use for the purposes[1–3] being reviewed the reagents have proved their worth for the analysis of a variety of organic compounds, but principally those containing sulphur, mercury or nitrogen.

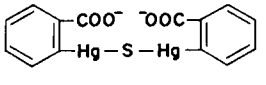
o-Hydroxymercuribenzoic acid (HMB) solution is made by dissolving the anhydride in alkaline medium. The anhydride can be obtained by the reaction between *o*-phthalic acid and mercuric acetate, which results in the replacement of one carboxyl group by the hydroxymercuric group.[4,5] A 0.05*M* (= 0.05*N*) solution of HMB is prepared by dissolving 16.035 g of the pure anhydride in either 100 ml of 1*M* sodium hydroxide or 100 ml of 20% v/v triethanolamine and diluting with water to 1 litre. Sometimes an HMB solution in 50% v/v propanol is used. Alkaline solutions of HMB are stable for at least one year.

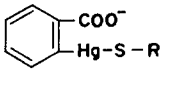
Dithiofluorescein (thiofluorescein), $C_{20}H_{12}O_3S_2$, m.w. = 364.2, is prepared according to Gattermann[6] by reaction of fluorescein dichloride with potassium hydrogen sulphide, which results in the introduction of two SH-groups in place of two OH-groups of the fluorescein. Alkaline solutions of dithiofluorescein are readily oxidized by air to form insoluble dithiofluorescein disulphide $C_{20}H_{10}O_3S_2$. The addition of EDTA has a marked stabilizing effect, particularly when the solution is protected from light.

Mercurated fluorescein is easily obtained by treatment of fluorescein with mercuric acetate,[7] to give either diacetoxymercurifluorescein (DMF) or tetraacetoxymercurifluorescein (TMF).

TITRATIONS WITH HMB

HMB in alkaline solution forms colourless soluble adducts with hydrogen sulphide and thiols





HMB is superior to other mercuric compounds as a reagent, for several reasons. It is very suitable for titration of hydrogen sulphide over a wide range of concentrations. It provides a reliable and convenient means of titrating thiols in the presence of certain other compounds whereas the titration with mercuric acetate may be erratic on account of formation of mixed adducts, *e.g.*, RS–Hg–I, RS–Hg–$S_2O_3^-$. It may be used for determination of so-called hydrolysable sulphur. It does not evolve any volatile toxic substances. It is more stable than *p*-chloromercuribenzoic acid in alkaline solution, its complexes are more soluble and it can be used for titration in acidic solution. Finally, the anhydride is very easy to synthesize.

HMB was first used for the titration of hydrogen sulphide with sodium nitroprusside as indicator,[1] but dithizone and dithiofluorescein are better indicators.[2,3] Dithizone is excellent for the titration of hydrogen sulphide and certain thiols such as cysteine, but gives a slightly premature end-point with thiols such as methanethiol or glutathione, and is completely unsuitable for aromatic thiols. On the other hand dithiofluorescein is suitable for titration of hydrogen sulphide and all thiols even in the presence of large amounts of halides and substances which interfere with several other mercurimetric indicators. Dithiofluorescein can be used in aqueous and alcoholic media, the optimal pH range being 9–11. Diphenylcarbazone is not very sensitive towards HMB, but can be used at pH 5 as indicator for titration of thiosulphate with HBM.[2] *p*-Dimethylaminobenzylidenerhodanine (DABR) can be used as indicator for titrations with HMB in strongly acidic aqueous alcoholic solutions.

Pure *o*-hydroxymercuribenzoic acid anhydride can be used directly as a working standard. If the product is not pure the solution can be standardized with diphenylthiourea[8] or antimony(III) sulphide[9] or by indirect comparison with a standard mercury(II) solution.[10] Another approach is to back-titrate an

excess of sulphide added to a mixture of HMB and mercury(II), *ca.* 1:1. As mercury(II) replaces the equivalent amount of HMB[11] the concentration of the latter can be calculated from the consumption of sulphide in two titrations, mercury(II) being added to one sample but not the other. Tri-tert-butoxysilanthiol has also been recommended for standardization of HMB.[12] Weighed samples are dissolved in propan-2-ol and titrated with HMB after addition of ammonia and dithiofluorescein.

HMB titrations with visual indicators can be divided into direct methods, direct methods with masking, and conversion methods. Hydrogen sulphide can be titrated in sodium hydroxide medium with 10^{-4}–0.05*M* HMB, the limit of determination being 0.2 μg of H_2S in a 2-ml sample. The method is applicable in the presence of large amounts of halides, sulphite and thiosulphate. In general the influence of other substances, except those that can be desulphurized, decreases with increasing pH. For example, in sodium hydroxide solution iodide does not interfere, in ammoniacal solution the interference by iodide is noticeable and in acidic solution iodide displaces thiols and sulphides from their adducts with HMB.

The sulphides of antimony(III) and tin(IV) can be titrated with HMB when dissolved in sodium hydroxide, whereas arsenic(III) sulphide must be heated with excess of HMB to remove all the sulphur as sulphide.[9] Dithiofluorescein can be used as indicator for titration of sulphide in black liquor.[13] Sulphide in dithionite can be titrated in presence of sodium hydroxide and formaldehyde.[14]

The titration of thiols with HMB in ammoniacal aqueous[15] or alcoholic solution[16] is satisfactory. Several thiols can be titrated in ammoniacal solution with dithiofluorescein as indicator and in sodium hydroxide with dithizone. The salts of zinc, cadmium and lead do not interfere when excess of EDTA is added. Aliphatic thiols (but not aromatic) can be titrated in sodium hydroxide solution with dithizone as indicator but both can be titrated in ammoniacal alcoholic medium with dithiofluorescein as indicator.[17] Thus aromatic thiols can be determined by difference. Organic disulphides and thio-ethers do not interfere. The interference from sulphur and carbon disulphide can be overcome by titration in an emulsion,[16] the thiols passing gradually from the hydrocarbon to the aqueous phase and combined with HMB, whilst sulphur and carbon disulphide remain in the hydrocarbon phase.

The titration with dithiofluorescein (DTF) as indicator has been successfully applied to the determination of thiomalic acid,[18] thioglucose and tetraacetylthioglucose,[19] and cysteine in foods.[20] Sulphur-containing organic tin compounds can be titrated with HMB in a toluene–ethanol–aqueous sodium hydroxide mixture with DTF as indicator.[21] Silanthiols of the type $(RO)_3SiSH$ can be titrated in propan-2-ol solution with HMB and DTF as indicator, producing 1:1 adducts.[12,22] The compound $(tert\text{-}BuO)_2Si(SH)_2$ consumes two moles of HMB per mole. On the other hand silanthiols containing aromatic constituents, *e.g.*, Ph_3SiSH, are readily hydrolysed to Ph_3SiOH and H_2S, which can then be titrated.

In alcoholic solution acidified with perchloric acid DABR can be used as indicator for determination of halides, thioureas, thioamides and thiols.[23] In acidic media aliphatic thiols consume two moles of HMB per mole of thiol, but in alkaline solution only 1:1 adducts have been observed. Although not as sensitive as tris-acetoxymercurianiline[24] as a titrant in acidic medium, HMB can conveniently be used for analysis of mixtures when only one component is titrated in alkaline medium and both in acidic medium, *e.g.*, determination of trialkylthioureas and dialkylarylthioureas in the presence of each other.[25]

Titration with HMB in alkaline medium has been widely applied to determination of thiols and hydrogen sulphide in gases, *e.g.*, in continuous titration of thiols separated by gas chromatography.[26] For the analysis of refinery gases, hydrogen sulphide can be selectively removed by cadmium chloride and the thiols titrated with HMB.[27] Hydrogen sulphide can be selectively retained by arsenic acid[28] or potassium antimonyl tartrate,[29] and thiols by a mixture of tributyltin chloride and triethanolamine.[29] The constituents retained can then be titrated with HMB in sodium hydroxide solution.

Water-soluble non-volatile thiols such as cysteine can be separated from each other by liquid–liquid extraction in the form of triethyl-lead mercaptides[30] or tributyltin mercaptides[31] and determined by titration with HMB. Several thiols can be separated from each other by using tributyltin chloride on polyamide as stationary phase and eluting with buffers of gradually increasing or decreasing pH.[31]

Titration of mixtures by use of masking agents

Co-titratable compounds may be determined in the presence of each other with the aid of two selective masking agents: formaldehyde and acrylonitrile. Formaldehyde converts cyanide[32] and aminothiols,[33] *e.g.*, cysteine, into compounds which do not react with HMB. Applications include determination of sulphide and thiols other than aminothiols in the presence of cyanide,[33] thioglycollic acid in the presence of cysteine,[33] and cysteine in the presence of its *N*-acid derivatives.[34] The sum of the two compounds is determined on one sample and then the masking reagent is applied to a second sample. Formaldehyde reacts with glutathione more slowly than with cysteine, and hence both compounds can be determined in the presence of each other.[35] Attempts have been made to follow the course of hydrolysis of the cystine-*N*-peptide bonds in keratin on the basis of the reaction with formaldehyde and titration with HMB.[36]

The rate of the reaction of sulphur compounds with acrylonitrile decreases in the sequence aliphatic thiols, aromatic thiols, sulphide and sulphite. Thiosulphate

does not react at all and the reaction with cyanide is very slow. Thiols and sulphides react to form thio-ethers, which do not react with HMB. Selective masking with acrylonitrile has been suggested for determination of sulphide and thiols in the presence of each other.[37] Only the thiols react rapidly at room temperature, leaving sulphide and cyanide unchanged. For the titration of thiols, cyanide can be removed either with formaldehyde or a stoichiometric amount of silver nitrate.[38]

Sulphide and sulphite react quantitatively with acrylonitrile if heated, leaving thiosulphate unchanged. Sulphide can be titrated with HMB, using dithizone as indicator. Thus by difference the three compounds—sulphide, sulphite and thiosulphate—can be readily determined in the presence of each other.[39] The same procedure has been applied to analysis of samples containing polysulphide and thiosulphate, after treatment with sodium sulphite.[39] The polysulphide number was calculated from the increase in thiosulphate content.

Acrylonitrile has also been used for analysis of mixtures of thioglycollic acid, sulphide, sulphite and thiosulphate;[40] cysteine, cystine and sulphide;[41] sulphide and dissolved keratin;[42] sulphide, cyanide, thiols and xanthate as obtained by absorption of tobacco smoke;[43] hydrogen sulphide, aliphatic thiols and aromatic thiols.[17]

Conversion into titratable compounds

Many compounds can be converted into hydrogen sulphide, thiols or thioureas. Excellent results have been obtained by decomposition of sulphur compounds with potassium followed by direct titration with HMB.[44] Any cyanide produced is removed with formaldehyde. Similarly, methods based on the thermal decomposition of the sample in a hydrogen atmosphere,[45] or desulphurization with Raney nickel[46] can be completed by HMB titration. Oxidation with bromine before the reaction with Raney nickel permits the determination of cystine and methionine in proteins,[47] lanthionine in alkali-treated wool,[48] and alkylating agents such as acrylonitrile.[49] Organic disulphides can be reduced to thiols by any method and the thiols titrated with HMB. When the sample is reduced with zinc, EDTA should be added in excess before the titration. Cystine can be reduced to cysteine by heating with hydriodic acid and potassium hypophosphite, and the cysteine titrated with HMB in sodium hydroxide solution.[50] The method has been used for the determination of cystine in wool.[51] It is essential to hydrolyse the wool before treatment with hydriodic acid, otherwise part of the cystine sulphur is reduced to hydrogen sulphide and low results are obtained. The thiol produced by the well-known reaction between some disulphides and sulphite

$$RSSR + HSO_3^- = RSH + RSSO_3^-$$

can be titrated with HMB (dithiofluorescein indicator) in a phosphate-buffered system at pH 8–9.[52] If sulphite is added after the titration of any thiol initially present, the thiol content and disulphide content can be determined separately.

Disulphides soluble in hydrocarbons can be split by reaction with butyl-lithium

$$RSSR + BuLi = RSBu + RSLi$$

and the thiol produced determined by titration with HMB.[53] Unfortunately the butyl-lithium is not quite inert toward thio-ethers and the reaction

$$BuLi + RSR = BuR + RSLi$$

may take place to some extent. Sulphur reacts with butyl-lithium to form butanthiol, which can be titrated with HMB.[54] Disulphides and sulphur in hydrocarbon solvents can be very conveniently reduced with sodium aluminium bis(2-methoxyethoxy)dihydride (SAMD) dissolved in benzene, to yield thiols and hydrogen sulphide respectively, and these may be titrated with HMB.[17]

Several groups of sulphur compounds can be determined by treatment with sodium hydroxide or dimethylamine to form hydrogen sulphide and thiols. *S*-Alkylthiouronium salts are rapidly decomposed by sodium hydroxide and can be titrated directly with HMB as the free thiols.[15] This titration has been proposed for the determination of the equivalent weight of organic acids, separated in the form of their *S*-benzylthiouronium salts.[55] The hydrolysis of carbonyl sulphide in sodium hydroxide solution, which is more rapid than that of carbon disulphide, has been used for the analysis of a mixture containing sulphide, trithiocarbonate, xanthate and *O*-alkylthiocarbonate.[56] Two samples are decomposed with acid in closed bottles to form H_2S, COS and CS_2. One sample is made alkaline with ammonia and the other with warm sodium hydroxide solution, and both samples are titrated with HMB. The carbonyl sulphide content is calculated by difference.

If an organic disulphide is decomposed in sodium hydroxide medium to form sulphinic acid, hydrogen sulphide and thiol, its concentration can be found from the equation[33,57]

$$[RSSR] = [H_2S] + \frac{[RSH] - [H_2S]}{1.5}.$$

Consequently, from independent determinations of H_2S and thiol, by use of acrylonitrile as selective masking agent, the concentration of disulphide can be calculated. If the ratio of hydrogen sulphide to thiol produced is constant, the disulphide content can be found from one titration with HMB. The method is applicable to the determination of dithioglycollic acid.[33,57] The analytical use of alkaline decomposition of disulphides is limited because many decompose too slowly. The disulphide bridge in keratin produces in addition a thio-ether bridge, so the formula given above cannot be used. If, however, the concentration of the disulphide is known, the determination of hydrogen sulphide and thiol can be used to follow

the course of formation of the thio-ether.[58] The presence of HMB increases the rate of decomposition of disulphides by sodium hydroxide.[59] The alkaline decomposition of penicillin to give penicillamine is also greatly accelerated by HMB,[60] and back-titration of the excess of HMB has been suggested for the determination of penicillin. Organic thiocyanates are readily decomposed by sodium hydroxide to form inorganic cyanates and thiols

$$RSCN + 2\ OH^- = RS^- + NCO^- + H_2O$$

which can be titrated with HMB.[25] Aromatic thiocyanates are in general readily hydrolysed and can be titrated directly with HMB, but aliphatic thiocyanates, being more resistant to hydrolysis, must be heated with an excess of HMB.

Another group of sulphur compounds, *e.g.*, isothiocyanates and thiol esters, can be converted into titratable form by reaction with ammonia or amines, especially dimethylamine.[25,61] Isothocyanates react to form trisubstituted thioureas which can be titrated in acid solution with HMB with DABR as indicator.[25] The thioureas obtained from aliphatic isothiocyanates are inert to HMB in sodium hydroxide solution, whereas those derived from aromatic isothiocyanates can be titrated like thiols in strongly alkaline solution. Thus aliphatic and aromatic isothiocyanates can be determined in the presence of each other.

Dimethylamine reacts readily with salts and esters of xanthic acids, producing sulphides or thiols:[61]

$$ROCSS^- + NH(CH_3)_2 = ROCSN(CH_3)_2 + HS^-$$

$$ROCSSR + NH(CH_3)_2 = ROCSN(CH_3)_2 + RSH.$$

The salts are dissolved in 40% w/v aqueous dimethylamine, heated, and titrated with HMB, with dithiofluorescein as indicator. The esters are more reactive than the salts. The estimation of the xanthate content of viscose involves the removal of sulphides and trithiocarbonates with Amberlite IRA-400, treatment of the cellulose xanthate with dimethylamine, and titration with HMB.[62] The same reaction can be used for the determination of esters of dithiocarboxylic acids[61] and thiocarboxylic acids:[63,64]

$$RCSSR + NH(CH_3)_2 = RCSN(CH_3)_2 + RSH$$

$$RCOSR + NH(CH_3)_2 = RCON(CH_3)_2 + RSH.$$

Some thiol esters, *e.g.*, acetates, can be titrated directly at room temperature, some, *e.g.*, glutarates and benzoates, in warm solution, and yet others must be heated with an excess of HMB. Free thiols can be titrated in the same sample before addition of the dimethylamine. The method is applicable to the determination of homocysteine and its thiolactone in the presence of each other.

The titration with HMB can be used for determination of alkylating agents after their conversion into thiols. One approach developed for acrylonitrile in water involves the reaction with sodium trisulphide, extraction, reduction with triphenylphosphine and titration with HMB.[65] A second approach is based on the reaction with thiourea to form *S*-alkylthiouronium salts which can be determined in the presence of an excess of thiourea by decomposition with sodium hydroxide and titration with HMB after addition of ammonium salts.[66] A method has also been developed for the determination of sulphonium salts which react with thiourea in dimethylformamide solution in the presence of iodide to form *S*-alkylthiouronium salts.[67]

Desulphurization

It has been observed that HMB accelerates the alkaline hydrolysis of sulphur compounds into sulphide and thiols, presumably because it enters into the reaction mechanism, combining with the final products.[68–70] For instance, thiourea is not hydrolysed at great speed when heated with sodium hydroxide, but on addition of HMB the decomposition takes place very rapidly. Some compounds are desulphurized so readily that they can be directly titrated with HMB in sodium hydroxide solution. This group includes mono- and dithiocarbamates derived from primary amines, and diphenylthiourea.[68–70] The titration of dithiocarbamates of the type $RNHCSS^-$ results in formation of hydrogen sulphide and isothiocyanate, which should be removed by adding an organic solvent to the aqueous sample.[70] Dithiocarbamate obtained from ethylenediamine can be titrated directly without interference because the isothiocyanate formed rearranges rapidly to give ethylenethiourea which is inert towards HMB.[70] The compounds more resistant to HMB can be titrated in warm solution or determined by back-titration after heating with an excess of HMB. Trisubstituted thioureas, cyclic thioureas, mercaptobenzothiazole, thiosulphate and inorganic thiocyanate are not desulphurized by HMB and do not interfere with determination of other substances in alkaline media. The substitution of one hydrogen atom in thioamides by an alkyl radical decreases the rate of desulphurization. Aryl derivatives of thioamides cannot be desulphurized but combine with HMB in 1:1 ratio in alkaline solution.[71]

This type of titration has been used for the determination of thiourea in inorganic thiocyanates,[72] for carbon disulphide and carbonyl sulphide in gases and hydrocarbons.[29,73,74] It has been observed that at pH 4 the carbonyl sulphide derivative of 1,3-diaminopropane is rapidly decomposed whereas that of carbon disulphide is relatively stable, and this difference allows both compounds to be determined.[29] Another application is the determination of total sulphur in viscose.[75]

Several determinations can be performed by adding a thiol and back-titrating with HMB. Hydrogen peroxide can be determined by reaction with thioglycollic acid in alkaline solution[8] and nitrite by reaction in acid solution.[76] By reaction of one aliquot in alka-

line medium and another in acid solution hydrogen peroxide and nitrite can be determined in the presence of each other. Unsaturated compounds which react readily with thiols can be determined in a similar way. Thus acrylonitrile in water has been determined after reaction with mercaptoethanol.[65]

Photometric procedures based on the HMB–DTF system

Dithiofluorescein and HMB form a colourless complex which on addition of thiols is decomposed with reappearance of the blue colour of the free dithiofluorescein. It is possible to determine a thiol by adding first HMB in excess and then DTF in excess, followed by measurement of the absorbance at 588 nm. The molar absorptivity of DTF in alkaline solution at 588 nm is *ca.* 3×10^4 l. mole^{-1}. cm^{-1}. The sensitivity corresponding to an absorbance of 0.01 is 0.02 μg of sulphur in H_2S or 0.05 μg in thiols, for a 5-ml sample and 1-cm cell. If 2 ml of $5 \times 10^{-5}M$ HMB and an excess of DTF are added to the sample followed by dilution to 5 ml, the concentration of thiol is given by:[77]

$$[\mathrm{RSH}] = 2 \times 10^{-5} + \frac{A}{\epsilon} - \left(2 \times 10^{-5} + \frac{A_0}{\epsilon}\right)\frac{V}{V_0}$$

where V and V_0 are the volumes of DTF taken in the sample and the blank, A and A_0 are the corresponding absorbances, and ϵ is the molar absorptivity of DTF. By this procedure it is possible to determine hydrogen sulphide,[28] thiols in serum,[77] and in wool.[78] The procedure has been further developed by use of selective masking agents. Formaldehyde decomposes the adducts of HMB and aminothiols and the displaced HMB decolorizes the equivalent amount of DTF.[77] The HMB–glutathione adduct is decomposed much more slowly than the HMB–cysteine adduct. Consequently, glutathione plus cysteine can be found from the consumption of HMB, and then the cysteine content from the absorbance after addition of formaldehyde. The method has been used for the determination of cysteine and protein thiol groups in serum in the presence of glutathione.[77] Treatment of serum with HMB and sulphite or dimethylamine permits the determination of disulphides and thiol esters respectively. The HMB–aminothiol adducts thus produced can be selectively determined kinetically by addition of formaldehyde in the presence of an excess of DTF.[79,80] Compounds that can be desulphurized can also be determined photometrically after being heated with sodium hydroxide and HMB, and finally adjusted to pH *ca.* 10. The method has been used for the determination of 0.01–0.05 μeq of phenylthiohydantoins[81] and *N*-substituted derivatives of thiourea.[82] The submicrodetermination of isothiocyanates can be performed by reaction with ammonia followed by desulphurizing and application of the photometric procedure.[82] Submicroamounts of xanthates and esters of xanthic acids can be determined photometrically after treatment with dimethylamine and HMB.[83]

DTF alone or with HMB and other reagents may be recommended as a very sensitive and selective spray for the location of several compounds on paper after electrophoretic or chromatographic separation.[84] An alkaline solution of DTF reveals mercury, silver and oxidizing agents, including some compounds with disulphide bonds such as thiuram disulphide, as white spots on the blue background. The HMB–DTF adduct in slightly alkaline solution reveals thiols as blue spots on a white background, and in strongly alkaline solution it gives blue spots for substances that can be desulphurized. An HMB–DTF–sulphite spray reveals disulphide, and one containing HMB–DTF–dimethylamine reacts with thiol esters. Subsequent treatment with formaldehyde removes the blue spots originating from aminothiols, whilst the other spots are not changed.

Miscellaneous applications of dithiofluorescein

DTF can be used as an indicator in the titration of thiols with different mercury compounds; in the absence of interfering ions such as iodide or thiosulphate mercuric acetate or nitrate can be used.[10,85,86] For thiol groups in reduced thiokol, phenylmercuriacetate is preferred on account of its solubility in organic solvents.[87]

DTF is also used as indicator for the titration of mercury compounds in ammoniacal solution with thiols such as thioglycollic acid, mercaptoethanol and cysteine. Sodium thioglycollate is recommended because it can be readily prepared by boiling pseudothiohydantoic acid with sodium hydroxide followed by dilution with sodium sulphite solution.[10] Mercury can be titrated in the presence of zinc, lead, nickel, manganese, and copper if an excess of EDTA is added. Crude phenylmercury acetate and other mercurials are analysed by direct titration or titration after decomposition with bromine.[88–91] The method can be applied to strongly coloured solutions.

The equivalent weight of thiols can be determined by addition of *p*-chloromercuribenzoic acid till the DTF end-point is reached, precipitation of the adduct by addition of acid, followed by determination of the mercury content of the dry product, after decomposition with bromine, by titration with sodium thioglycollate.[92]

Small amounts of mercury(II) and silver can be titrated with the solution of DTF to the first shade of blue.[10,93] Mercury(II) can be extracted from water with dodecanthiol in chloroform, the complex decomposed with bromine, and the mercury re-extracted into water and titrated with DTF.[94] Small quantities of mercury(II) can be titrated with a solution containing dispersed zinc sulphide, starch and sodium hydroxide after addition of EDTA to the sample.[95] The method has been applied to determination of thiosulphate and polysulphanedisulphonates

on paper electropherograms treated with mercuric chloride.[95]

DTF can be used as indicator for titration of cyanide in sodium hydroxide solution with silver nitrate[96] and *vice versa*.[97] The colourless silver–DTF adduct has been used for determination of hydrogen sulphide and hydrogen cyanide.[98] Both compounds induce the blue colour but the hydrogen cyanide can be masked with formaldehyde.

The compounds which react readily with mercuric nitrate to form organic mercury compounds, *e.g.*, styrene, allyl alcohol, thiophen, organic boron compounds,[85,99–101] can be determined by back-titration of excess of mercuric nitrate with sodium thioglycollate, DTF being used as indicator.

The bleaching of an alkaline solution of DTF by oxidizing agents may be used for determination of peroxides,[102,103] and the restoration of the colour by reducing agents for the determination of thiols.[104] The decolorization of DTF by cyanogen bromide has been used for determination of traces of inorganic thiocyanates,[105] and readily reducible disulphides, *e.g.*, thiuram disulphides.[106]

APPLICATION OF MERCURATED FLUORESCEIN

"Mercurated fluorescein" is a term applied to DMF or TMF indiscriminately, because the exact nature of the compound is immaterial, the properties of DMF and TMF as analytical reagents differing only slightly. In alkaline solution both compounds give a green fluorescence which is quenched by several sulphur and nitrogen compounds.[2,3] Alkaline solutions of mercurated fluorescein are stable when stored in darkness.

Mercurated fluorescein was first used for visual titration of hydrogen sulphide,[2,3] and later for levels down to 0.01 μg/ml. It may also be used for titration of some thiols and compounds which readily form hydrogen sulphide.[108] Its range can be extended by using non-aqueous solvents and/or a displacement titration.[28,109] The quenching of the indicator fluorescence varies widely for different compounds and depends on the solvent, pH and excitation wavelength. Unsubstituted thiols and dithiocarbamates form complexes having weak fluorescence in aqueous solution and strong fluorescence in organic solvents. Thiols containing hydrophilic substituents give compounds with strong fluorescence in aqueous solution and weak in organic solvents.[109] It is essential for titration that the complexes have very low fluorescence.

Displacement titrations are based on ligand exchange in mercurated fluorescein complexes with accompanying change in fluorescence. Thus, the fluorescence of TMF in alcoholic solution is quenched by oxine and restored by addition of unsubstituted thiols or dithiocarbamates, because these replace the oxine to form more stable complexes of strong fluorescence. The fluorimetric titration of such compounds with TMF in the presence of oxine gives a plot in the form of an inverted V.[109] The increase of fluorescence is due to formation of strongly fluorescent complexes, and the decrease to absorption of light by the red complexes of TMF and oxine.

The direct titration of hydrogen sulphide with TMF in aqueous solution has found wide application, *e.g.*, for the determination of atmospheric hydrogen sulphide after absorption as zinc sulphide,[28] sulphide in alkali metal hydroxides and halides,[110] and hydrogen sulphide in water after extraction as triethyl-lead sulphide.[111]

The displacement titration in organic solvents in the presence of oxine was suggested for the determination of atmospheric thiols separated as triethyl-lead mercaptides,[28] and of atmospheric carbon disulphide and carbonyl sulphide after trapping by diethylamine.[28] Brenner and Laufer[112] have applied the method to the determination of hydrogen sulphide and volatile thiols in beer. Free hydrogen sulphide and thiols are removed from beer by passage of a stream of nitrogen and absorbed in an alcoholic solution containing triethyl-lead chloride and triethylamine; one aliquot is used for titration of the thiols and another for titration of hydrogen sulphide. Addition of zinc ions prevents release of the hydrogen sulphide but has no effect on the release of thiols.

The fluorescence can also be measured directly and related to the concentration of substance by a calibration curve.[113] However, this approach, though at least as sensitive as the titrimetric procedure and more convenient for routine work, can give erratic results because of numerous interferences. On the other hand it can be successfully applied where the titrimetric method fails, *viz.* when the substance does not form a sufficiently strong complex to yield a distinct end-point, and when substances which are slow to desulphurize are determined.[113]

Andrew and Nichols[114] determined less than 0.01 ppm of hydrogen sulphide in air by recording the change in fluorescence of TMF on contact with the air sample. Axelrod *et al.*[115] suggested a method for atmospheric hydrogen sulphide, based on absorption in sodium hydroxide solution and a DMF-quenching calibration curve. The method appears to be of low reliability on account of ready oxidation of sulphide. Natusch *et al.*[116] described a method for measuring trace levels of hydrogen sulphide in the atmosphere, involving absorption on filter paper saturated with silver nitrate. Grünert *et al.*[117] investigated the determination of hydrogen sulphide in the range 1–10 ng/ml, using diphenylthiourea as calibration standard. Janyševa[118] used the quenching of TMF for determination of sulphur in phosphorus. Babko *et al.*[119] suggested a method based on separation of sulphur as mercuric sulphide, decomposition with hydrochloric acid and TMF-quenching. Several similar procedures have been described for determination of sulphur in high-purity reagents.[120]

The change of fluorescence on addition of sodium hydroxide to a neutral solution containing the substance and TMF can be used qualitatively, an increase of fluorescence indicating a substance that cannot be desulphurized, a strong decrease one that forms hydrogen sulphide, and a moderate increase or decrease (depending on the solvent) may indicate one which forms a thiol.[81,82]

Several nitrogen compounds such as proteins, amino-acids, purines, pyrimidines, uric acid, cyanuric acid, biuret, veronal, form complexes with mercurated fluorescein, usually of lower fluorescence than the parent substance.[121] Many of these complexes dissociate in sodium hydroxide solution, but not those produced with uric acid, cyanuric acid or guanine.

The principle of the displacement of ligands can be applied as a calibration-curve method as well. When thiosulphate or cyanide is added to a slightly alkaline solution containing TMF and biuret a fluorescence is induced,[122] which permits the determination of the added ion. Colovos *et al.*[123] determined thioglycollic acid and iodide. Cyanide can be determined by the increase of fluorescence in the presence of an excess of iodide.

The fluorescence of TMF–thiol complexes relative to TMF has characteristic values which can be used for identification of thiols in trace amounts.[124] It is best to use excitation wavelengths of 495 and 525 nm and pH 7–11. The thiols containing a carboxyl group can be easily recognized from the strong increase of relative fluorescence with increasing pH at excitation wavelength 525 nm. Under suitable conditions, different thiols, *e.g.*, cysteine, homocysteine and penicillamine, can be distinguished. The complexes of TMF with thiols are yellow in acidic solution and red to pinkish orange in alkaline solution. The pH at which the colour changes is characteristic of a given thiol.[124]

Cellulose powder impregnated with TMF can be used for preparation of detector tubes which indicate hydrogen sulphide in gases by a decay of fluorescence.[125] Impregnation with TMF–biuret complex gives tubes indicating hydrogen cyanide and thiols by the yellow fluoresence observed under filtered ultraviolet radiation. (An HMB–DTF filter tube has also been suggested for the estimation of H_2S.[125])

Mercurated fluorescein has proved a very sensitive spray reagent for detection and location of several compounds on paper chromatograms. Substances decreasing the fluorescence can be seen under filtered ultraviolet radiation, as dark spots on a fluorescent background. The sensitivity ranges from 0.01 $\mu g/cm^2$ for sulphide to 10 $\mu g/cm^2$ for nitrogen compounds forming weak complexes. The method has been applied to the location of phenylthiohydantoins,[81] thiourea and its derivatives,[82,126,127] nitrogen compounds,[121] *S*-derivatives of thiourea,[128] xanthydrazones,[129] cations in the form of sulphides,[130] *etc.*

Karush *et al.*[131] suggested an assay method for disulphide groups by fluorescence quenching of DMF in 1.5*M* sodium hydroxide. It should be realized, however, that the disulphide groups do not themselves quench the fluorescence, the effect being due to the thiols and sulphide formed by decomposition of the disulphide bond by sodium hydroxide. This decomposition is probably accelerated by mercurated fluorescein. The determination of disulphides as suggested by Karush *et al.*[131] cannot be regarded as reliable, for two reasons: first, the decomposition of disulphides by sodium hydroxide is a very complex reaction yielding different quantities of thiols and sulphide from different disulphides, and secondly, even in strongly alkaline solution the quenching by several nitrogen compounds such as uric acid cannot be neglected. In neutral medium there will be quenching by most of biologically occurring nitrogen compounds. Consequently, the methods recommended[131,132] for determination of thiols and disulphides in the presence of proteins must yield considerable disagreement with the true values.

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STRUCTURE AND BONDING IN THE METAL COMPLEXES OF ETHYLENEDIAMINETETRA-ACETIC ACID

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Summary—The metal-ion complexes of ethylenediaminetetra-acetic acid (EDTA) find widespread use not only in analysis, but also in foodstuffs, pharmacy, and medicine. A review of the structures of the solid complexes illustrates the considerable variation in co-ordination number of the metal-ion, and the possible denticities of EDTA. These data are relevant to the solid-state properties and also to the structures of the complexes in solution, which cannot be directly determined.

The disodium salt of ethylenediaminetetra-acetic acid (Na_2EDTA) (Fig. 1) was first produced in quantity in 1936 under the trade name "Trilon-B", and was marketed as a reagent capable of complexing metal ions.

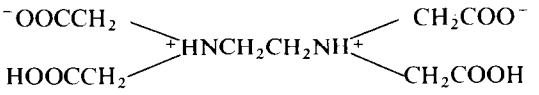

Fig. 1. Ethylenediaminetetra-acetic acid.

Some of the typical applications suggested included water-softening and the protection of metal-sensitive dyestuffs.[1–3] Although a number of EDTA–metal ion compounds were isolated[4] a proper understanding of the nature and function of EDTA was a direct result of the classic studies made by Schwarzenbach[5,6] who demonstrated that the complexes formed by multidentate ligands of the EDTA type involved the creation of multiple co-ordinated ring systems incorporating the metal ion. From experiment it was established that the optimum ring-size was five members, as is attained by EDTA, where an ethylenediamine chain forms the backbone of the complexing agent. The ease with which EDTA forms complexes, and an understanding of their nature, resulted in a plethora of applications involving metal ions, particularly in analysis. A number of these applications have been reviewed and reports are available on use of EDTA in industry,[7] foodstuffs[8] and pharmacy and medicine;[9] predominantly, however, the literature reflects the major use in analysis.[10,11] The cumulative number of publications on EDTA was by 1974 of the order of 8000. Despite this massive total, the number of chemical papers devoted to gaining an understanding of the nature of bonding in, and the structure of, EDTA–metal ion complexes is rather small.

For the solid state the potential configurations available for the ligand molecule are numerous, particularly since denticities for EDTA from two to ten have been established by X-ray structural analysis. Similarly, metal-ion co-ordination numbers ranging from four to ten have been established for EDTA–metal ion complexes, in which other ligands, particularly water, are often bonded. Because of this complexity, inferential physical techniques of structure determination, such as infrared and ultraviolet–visible spectroscopy or magnetochemistry, are not so valuable as direct structural methods, though the first method has been quite widely applied.[12] In contrast, for examination of solutions a wider range of techniques must of necessity be used, and ultraviolet–visible,[13] solution infrared, Raman[14,15] and NMR spectroscopy.[16,17] polarography,[18] and conductometry[19] have all been used. These methods suffer the disadvantage that none is a direct method of structure determination, and it is necessary to attempt to correlate the (often divergent) results from several methods, for a particular solution.

In general it appears that rather fewer co-ordination arrangements are present in solution than are known for the solid state. For the most part the complexes in solution apparently contain EDTA as a form with a denticity "statistically" intermediate between five and six, with essentially ionic bonds between the carboxylate groups and the metal ion, and with rather more covalent nitrogen metal ion bonds; in addition, one or more water molecules may also be incorporated into the co-ordination sphere.[16,17] The overall balance of lability and nature of bonding varies, however, with the radius and electronic charge of the metal ion. It is also inferred that in solution there are a few species which contain hydroxy groups[20] and amino groups.[21]

It is not readily possible to obtain a precise view of the stereochemistry of EDTA complexes in solution, but an initial approach includes examining the structures established for the solid state. Such a survey has the added advantage that in its course not only may the typical structures be observed, but also the many unusual and fascinating stereochemistries adopted by EDTA may be noted. That it is now possible to do this owes much to the structural determinations published by Hoard and by Kennard and their co-workers as well as those by the other crystallographers who are referred to in relevant parts of the

text. Recently, a classification for EDTA conformations has been proposed which appears to be particularly relevant to kinetic studies.[22] From the viewpoint of the inorganic chemist, however, such a classification is less useful than that based on the denticity of EDTA, with additional subdivision according to the co-ordination number of the metal ion. It is convenient to consider first the stereochemistry of the $[CoY]^-$ ion (abbreviated according to the convention $H_4EDTA = H_4Y$) which has the simplest possible stereochemistry for sexidentate EDTA. (We use the conventional nomenclature—protonated carboxyl group, ionic carboxylate group).

SEXIDENTATE EDTA

Co-ordination number 6

For EDTA with six available donor atoms the simplest possible stereochemistry is present in the rubidium and ammonium salts of the $[CoY]^-$ ion.[23] In these compounds, both nitrogen atoms and one of the oxygen atoms on each of the four carboxylate groups are bonded to Co(III); the stereochemistry is shown in Fig. 2, in which it may be seen that five ring systems are formed as a direct consequence of complexation. In addition, the donor atoms are present in pairs so that a two-fold axis passing through the metal ion also bisects the ethylene group bonding the two nitrogens. The rings thus formed can be classified into three types:

(*a*) an *E*-ring (*E*thylenediamine) containing Co(III) and two donor nitrogen atoms

(*b*) two *G*-rings (*G*irdle) each containing Co(III), one donor nitrogen atom and a co-planar donor oxygen atom

(*c*) two *R*-rings (*R*ight angle) each containing Co(III), one donor nitrogen atom, and a donor oxygen atom situated above or below the girdle plane.

The *R*-rings are virtually planar and nearly strain-free, but a consideration of the cumulative total of the internal bond angles shows that the puckered *G*-rings are more strained; as a result the *G*-rings are co-ordinated to the Co(III) through slightly longer Co–O bonds.

As in all EDTA and ethylenediamine complexes of metal ions, the *E*-ring is puckered and strained. The strain evident in the *E*- and *G*-rings illustrates the very basic difference between the complex of a sexidentate ligand, and co-ordination by six individual ligands: for the former there is an optimum metal-ion radius for maximum bonding stability, based upon additional geometrical considerations which need not be considered for the latter. With the rather small and polarizing Co(III) (ionic radius* = 0.63 Å) EDTA can virtually encircle the metal, forming six rather short bonds; with other ionic radii and electronic charges other patterns of bonding emerge.

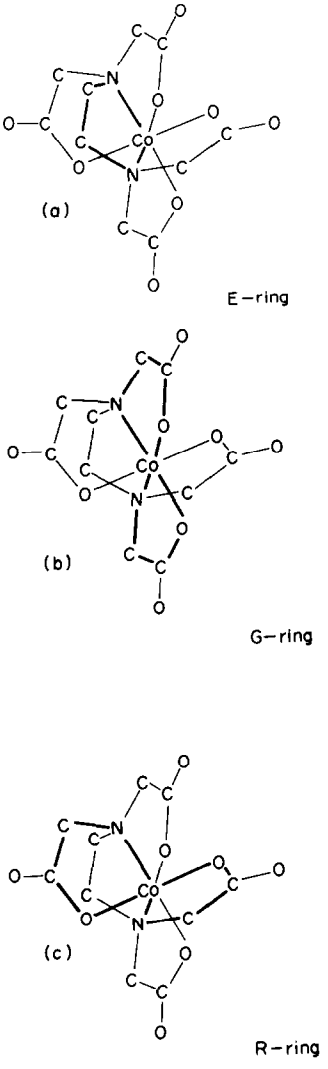

Fig. 2. CoY^- (from *J. Am. Chem. Soc.*, 1959, **81**, 549, by permission of the copyright holders, the American Chemical Society).

Co-ordination number 7 (*Fig.* 3)

In many EDTA–metal ion complexes, the co-ordination sphere is expanded to allow additional co-ordination of up to four water molecules. This increase results from two factors:

(*a*) an increase in the ionic radius of the metal ion beyond that of Co(III), and a corresponding decrease in the ability of the EDTA ligand to encircle the metal

Table 1. Structural features of CoEDTA

Cumulative bond-angles		Bond-lengths, Å	
E-ring	520.9°	Co–N	1.925
G-ring	523.5°	Co–O	1.915
R-ring	537.75°	Co–O	1.885
Strain-free ring	540.0°		

Adapted from Weakleim and Hoard[17]

* Pauling ionic radii are used throughout this discussion.

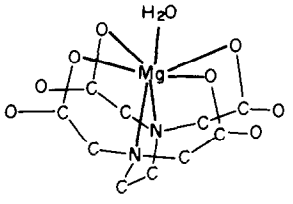

Fig. 3. H_2OMgY^{2-} (from *Inorg. Chem.*, 1973. **12**, 1749. by permission of the copyright holders. the American Chemical Society).

ion completely; co-ordination sites thus become available for additional small molecules, such as water; (*b*) a decrease in the strength of bonding between the metal ion and EDTA will also result in an expansion of the co-ordination sphere, with longer bonds and space for additional co-ordination.

It appears that for metals heavier than gallium the principal effect is that of increasing ionic radius, whereas, for those lighter than, and including, gallium both these effects play a part in determining the overall structures. The precise nature of the considerations involved has been discussed by Hoard for three heptaco-ordinate H_2OMY species[24] [M = Mg(II), Mn(II) and Fe(III), with radii of 0.65, 0.80 and 0.64 Å respectively]. The corresponding bond-lengths are given in Table 2, from which a most interesting comparison can be made, illustrating that for Mg(II) the smaller radius, but weaker bonding, allows a water molecule to enter into co-ordination, whereas for Mn(II) an increase in radius accomplishes the same end-result. Though the species concerned retain their two-fold symmetry (the water molecule occupies a position directly opposite the ethylene group) the distinction between *G*- and *R*-rings is less meaningful, and disappears with additional increase in radius.

Co-ordination number 10 (*Fig.* 4)

For lanthanum [La(III), ionic radius = 1.15 Å] the greater ionic radius renders EDTA completely incapable of encircling the tervalent ion, with the result that in $(H_2O)_4LaHY \cdot 3H_2O$ the metal is outwith rather than within the four co-ordinated EDTA oxygen atoms.[25] The "exposed" metal ion has four additional co-ordinated water molecules. In this complex three of the carboxylate metal ion bonds are slightly shorter than the fourth, reflecting protonation of one non-bonding oxygen atom.

Study of an EDTA zirconium complex[26] shows that a similar octaco-ordinate structure is involved, but with only two co-ordinated water molecules.

Table 2. Bond-lengths of heptaco-ordinate EDTA complexes, *Å*

	Mg(II)	Mn(II)	Fe(III)
M–N	2.38	2.38	2.32
M–O	2.08	2.23	1.98
N–O	2.27	2.25	2.10
$N–OH_2$	2.06	2.24	2.11

Adapted from Hoard *et al.*[18]

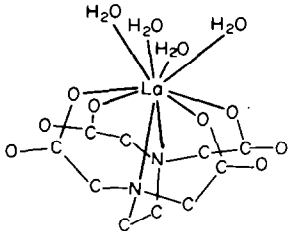

Fig. 4. $La(H_2O)_4HY$ (from *J. Am. Chem. Soc.*, 1965. **87**, 1611. by permission of the copyright holders. the American Chemical Society).

Co-ordination number 6 *plus an electron pair*

No mononuclear examples of this type of structure have been established, but the structure of the SnY^{2-} unit in binuclear $Sn_2Y \cdot 2H_2O$ [27] suggests the features to be expected for such structures. In the SnY^{2-} moiety, hexaco-ordination by the EDTA ligand results in ψ-heptaco-ordination of the Sn(II) ion, with the electron pair occupying the seventh co-ordination site. In contrast to other EDTA complexes, for SnY^{2-} the average Sn–N bond-length is shorter than the average Sn–O bond-length, possibly as a result of repulsion between the electron pair and the co-ordinated oxygen atoms. Thus in complexes of Pb(II) and Bi(III), where electron pairs are also present, similar structural features might be expected.

QUINQUEDENTATE EDTA

Co-ordination number 6 (*Fig.* 5)

There is definite evidence for the protonation and detachment of the carboxylate groups of EDTA metal complexes in acidic solutions.[14] A number of corresponding acid complexes have been isolated, and of these $H(H_2OFeY)$ is one of the more interesting since its structure[28] may readily be compared with that of the heptaco-ordinate H_2OFeY^- ion. For the protonated species a detached carboxyl group leaves a vacant *G*-ring site for a water molecule, which completes an almost regular octahedral arrangement. With the decrease in co-ordination number, and relaxation of the girdle-ring constraint, the Fe–N bonds and the remaining Fe–O bond are shortened slightly. The change from co-ordination number seven to six is interesting, for co-ordinated carboxyl groups are known and retention of heptaco-ordination is a possible alternative. The balance between the two

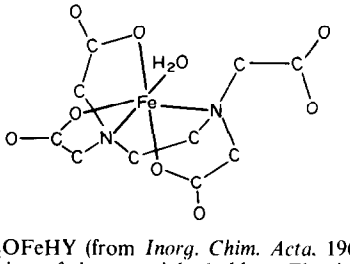

Fig. 5. H_2OFeHY (from *Inorg. Chim. Acta*, 1967, **1**, 347. by permission of the copyright holders. Elsevier-Sequoia, Lausanne).

alternatives may well be determined in the solid state by lattice-energy stabilization, arising from strong hydrogen-bond interconnections, which are a normal feature of the structures of EDTA complexes.

As a result of increased protonation, structures with greater distortion occur: for $H_2(H_2ONiY)$, and the isomorphous Cu(II) complex, a structure involving lengthened axial bonds, with consequent tetragonal distortion, has been established.[29] The co-ordination sphere includes two carboxylate oxygen atoms, a normal nitrogen–metal ion bond, and a longer nitrogen–metal ion bond opposite a long-bonded carboxylate oxygen atom. Water completes the hexaco-ordination, and the second carboxyl group is non-bonded. The Ni(II) is at the centre of a square plane (Ni–N = 2.08; Ni–O = 2.03, 2.04; Ni–OH = 2.08 Å) with the longer bonds above and below the plane (Ni–O = 2.16, Ni–N = 2.09 Å). The structure reaffirms the well-established lower stability of the *G*-rings. For the Cu(II) complex the greater axial distortion results in a structure which is virtually a square-based pyramid.[30]

Very few examples of species of the type MYX, where X is a donor molecule other than water, have been reported. One known series for which, however, no solid-state structures have been established, includes $K_2[HCoYCl]$.[31] Rather surprisingly, ^{13}C NMR indicates that in solution the substituent occupies an *R*-ring position.[32]

Additional investigation of this type of complex would be of interest not only for stereochemical reasons, but also because of the selectivity which could perhaps be built into a "tailor-made" EDTA complex.

QUADRIDENTATE EDTA

Co-ordination number 4 (*Fig.* 6)

Examples of EDTA exhibiting a denticity of less than five are rather rare; quadridentate EDTA is found, however, in $H_2NH_4VO_2Y \cdot 3H_2O$, where only four co-ordination sites are available on the VO_2 group.[33] The preference of the oxo-atoms of VO_2 for a *cis*-configuration ensures *R*-ring co-ordination. However, the strong *trans*-effect of the oxo-atoms, coupled with a low affinity of VO_2 for amino nitrogen-atoms results in long V–N bonds, and the introduction of some strain into the *R*-rings.

Co-ordination number 4 *plus an electron pair*

As with hexaco-ordination plus an electron pair, the only known example is that of an Sn(II) complex, H_2SnY,[34] in which the structure is markedly influenced by the presence of the electron pair. In terms of normal Sn–O bond-lengths (Sn = 2.13 and 2.40 Å) EDTA acts as a quadridentate ligand, but there are weak though definite additional Sn–O interactions (2.64 and 3.06 Å), involving the protonated carboxyl groups. The major difference between H_2SnY and the SnY^{2-} moiety in $Sn_2Y \cdot 2H_2O$ is a rotation of the

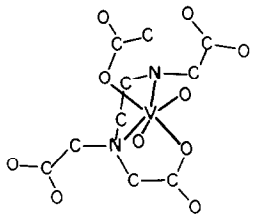

Fig. 6. $VO_2H_2Y^-$ (from *J. Am. Chem. Soc.*, 1971, **93**, 3873, by permission of the copyright holders, the American Chemical Society).

acetate groups about the nitrogen atoms, to the extent that in H_2SnY the groups are virtually equivalent. It is surmised[28] that in solution a quadridentate EDTA complex is formed, but that in the solid state the free acetate groups are attracted by the available orbitals of the metal ion to form weak links, thus causing rotation of the acetate groups.

BIDENTATE EDTA

Co-ordination number 4 (*Fig.* 7)

The complexes H_4PdYCl_2 and H_4PtYCl_2 have been shown to have EDTA bonded to the metal ion solely through the two nitrogen atoms, with two halogen atoms completing a square planar stereochemistry.[35] The four protonated carboxyl groups do not approach the metal and are held by hydrogen-bonds which form a three-dimensional network.

It has not yet been established whether complexes exist in which Pd(II) or Pt(II) approach square planarity with two additional Pd–O bonds. Such an arrangement seems unlikely in view of the strain which would be imposed on the *G*-rings by the rather large radius of the two bivalent metal ions, which would ensure that the complex did not have the 90° angles for which Pd(II) in particular shows a marked preference in its complexes.[36]

UNCO-ORDINATED EDTA

Though with some bivalent metal ions the H_2Y^{2-} species is co-ordinated through nitrogen metal ion bonds and has protonated carboxyl groups, non-co-ordinated configurations are found when the nitrogen–metal ion bond-strength is expected to be low. Two examples are the potassium and rubidium salts

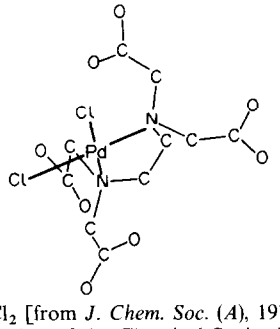

Fig. 7. PdH_4YCl_2 [from *J. Chem. Soc.* (*A*), 1970, 1008, by permission of the Chemical Society].

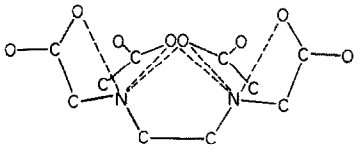

Fig. 8. H_2Y^{2-} ion in $Rb_2H_2Y \cdot 2H_2O$ (from *Acta Cryst.*, 1970. **B26**, 1152. by permission).

$M_2H_2Y \cdot H_2O$, which have very different structures. Each has protonated nitrogen atoms but the hydrogen-bond arrangement results in a difference in configuration. The potassium salt[37] (Fig. 8) has the EDTA skeleton in a contracted configuration such that each of two equivalent protons occupies a position between the oxygen atoms of three carboxylate groups; two of these belong to the carboxylate groups of the nitrogen atom to which the hydrogen atom is attached, the third is that of the other nitrogen atom. The two hydrogen-bonds of this latter type hold the ion in its folded configuration. In contrast, in $Rb_2H_2Y \cdot 2H_2O$ (Fig. 9) the EDTA skeleton is extended,[38] with two different types of nitrogen atom. The proton bonded to N(1) is hydrogen-bonded to two of the carboxylate oxygen atoms of N(1), and to a carboxylate oxygen atom of an adjacent H_2Y^{2-}. The proton on N(2) is similarly bonded to two carboxylate oxygen atoms of N(2) but in addition to a water molecule occupying a bridging position.[39]

The two configurations can differ but little in stability, and point to the wide range of configurations possible for EDTA in solution. It is evident that small variations in protonation may well result in dramatic changes of configuration, with consequent marked changes in spectroscopic and other physical properties as a function of pH.

The extent to which protonation of nitrogen is favoured is made apparent in the compound $H_2MgY \cdot 6H_2O$, which can be isolated from slightly acidic solution. In this interesting compound there are discrete hexa-aquated Mg(II) ions and non-co-ordinated H_2Y^{2-} ions which adopt a fully extended configuration.[40] It will be recalled that in contrast $Na_2MgY \cdot H_2O$ is heptaco-ordinate. with sexidentate EDTA.[24]

The parent acid H_4Y is now known[39] to be protonated at two nitrogen atoms and two carboxylate oxygen atoms. The carboxylate hydrogen atoms occupy very strongly hydrogen-bonded positions linking adjacent molecules; protons on the nitrogen atoms are intramolecularly hydrogen-bonded to three carboxylate oxygen atoms and hold the molecule in a configuration midway between those adopted in the rubidium and potassium salts of H_4Y. It is considered[39] that the very strong intermolecular hydrogen-bonding is responsible for the insolubility of H_4Y.

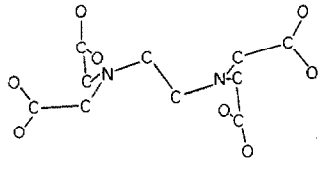

Fig. 9. H_2Y^{2-} ion in $K_2H_2Y \cdot 2H_2O$ (from *Acta Cryst.*, 1970. **B26**, 1152. by permission.

BRIDGING CARBOXYLATE GROUPS

Many binuclear EDTA complexes have been isolated, though rather few have been subjected to structural study. One group,[41] which includes several examples ($MgZnY \cdot 6H_2O$, $Co_2Y \cdot 6H_2O$ and $Zn_2Y \cdot 6H_2O$), has sexidentate EDTA forming a distorted hexaco-ordinate arrangement around one bivalent metal ion, with two carboxylate groups forming bridges to the second bivalent metal, which is also tetra-aquated.

In contrast to the rather weak bridge-bonds in $MgZnY \cdot 6H_2O$, the structure of $Sn_2Y \cdot 2H_2O$ shows[27] that for Sn(II) an increase in co-ordination is possible. The environment of the Sn(II) which is directly chelated by EDTA has already been described above (hexaco-ordination plus an electron pair); in addition, each of the carboxylate groups bridges to a second type of Sn(II) which is ψ-octaco-ordinate, though with rather irregular Sn–O distances.

Binuclear $Mn_2Y \cdot 9H_2O$ shows very little distortion of the MnY^{2-} co-ordination sphere even though bridges are formed to the second Mn(II).[42] The unusual complex $Mn_3(HY)_2 \cdot 10H_2O$. however. has two Mn(II) ions heptaco-ordinated by sexidentate EDTA and an additional water molecule.[43] The protons form strong hydrogen-bonds linking H_2OMnY^{2-} units in extended chains, while the third, unique, tetra-aquated Mn(II) ion reinforces this tendency by occupying a position bridging H_2OMnY^{2-} units parallel to the direction of chain formation.

Ethylenediamine bridging

The structure of the binuclear complex $Na_4(MoO_3)_2Y \cdot 8H_2O$ (Fig. 10) shows the use of the ethylenediamine backbone of EDTA as a bridging unit between the complexed MoO_3 moieties which have one nitrogen atom and two carboxylate oxygen atoms completing the hexaco-ordination of each Mo(VI) atom.[44]

A somewhat similar arrangement for EDTA is present[45] in $K[Mo_2(OH)_2(O_2CCH_3)Y]$ in which the

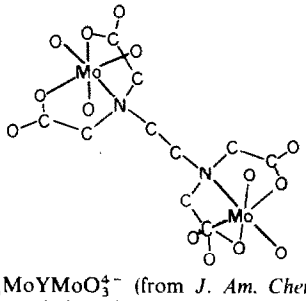

Fig. 10. $O_3MoYMoO_3^{4-}$ (from *J. Am. Chem. Soc.*, 1969, **91**, 301. by permission of the copyright holders. the American Chemical Society).

bridging ability of the ethylenediamine is coupled with that of two bridging hydroxy groups, and an acetate bridge. Each Mo(III) is, as a result, in a plane of four oxygen atoms (two hydroxy bridges, and two carboxylate oxygen atoms) with an acetate oxygen atom above the plane, and an ethylenediamine nitrogen atom below it.

Because the larger radius allows higher co-ordination numbers it is to be expected that in the future other novel arrangements will be identified for second- and third-row transition elements.

Complexes of copper, which often differ in structure from other first-row transition-element complexes with the same formulae, include the unusual structure which has been determined for $Cu_2Y \cdot 4H_2O$.[46] Again ethylenediamine bridges are formed between two Cu(II) ions which are each in a square plane, with one Cu–N bond, two Cu–O (carboxylate) bonds and one Cu–OH bond. A long bond in the axial position of each Cu(II) is occupied by a non-co-ordinating oxygen atom of another Cu_2Y unit.

Though at first sight the structural arrangements available to the EDTA ligand appear to be rather limited by geometry it is apparent that considered even in elementary terms of denticity and co-ordination number, the range of possibilities is very wide. Thus many of the arrangements discussed have possible optical or other isomers. In addition, we note that virtually all the complexes we discuss were made in aqueous solution. Complexes of the H_4PdYCl_2 type are soluble in organic solvents, as no doubt are many other EDTA complexes, and there appears to be potential for non-aqueous synthesis, which may well yield examples of new and unusual stereochemistries.

In a future article we shall attempt to correlate the structural features of some of the EDTA complexes we have discussed, with their established solution properties.

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THERMAL DECOMPOSITION OF ANALYTICALLY IMPORTANT THIOCYANATOBISMUTHATES(III)

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Summary—The thermal stability of Cs $[Bi(SCN)_4]$ and Cs_2Na $[Bi(SCN)_6]$ has been examined. The mechanism of the thermal decomposition of these compounds has been established. A simple procedure for analysis of the sinters has been developed and this procedure can be applied to other complex salts of bismuth.

Thiocyanatobismuthates(III) form the largest group of thiocyanate complex salts but few of them have found analytical application. The most sparingly soluble, caesium tetrathiocyanatobismuthate, has been used for the gravimetric, complexometric[1] and spectrophotometric[2] determination of caesium in the presence of potassium, ammonium, alkaline earth cations and aluminium. The complexometric method is characterized by a very distinct change of colour at the end-point. Cacsium sodium hexathiocyanatobismuthate(III) has been used in the gravimetric[1] determination and detection of sodium[1] (one of the most sensitive reactions for sodium with a limit of detection of 0.05 μg) at a dilution of 1 in 2×10^4. The formation of caesium tetrathiocyanatobismuthate by the decomposition of caesium sodium hexathiocyanatobismuthate can be applied in the detection of caesium in the presence of rubidium.[1]

The subject of the present paper is the thermal decomposition of these two thiocyanatobismuthates Cs $[Bi(SCN)_4]$ and Cs_2Na $[Bi(SCN)_6]$. For comparison purposes the behaviour of $Rb[Bi(SCN)_4]$ was also studied. Only three tetrathiocyanatobismuthates, *viz.* those of rubidium, caesium[3] and thallium[4] have been described. These compounds are formed only by cations of large ionic radii and thus in the alkali metal group, lithium, sodium and potassium form only hexathiocyanatobismuthates, rubidium forms both the tetra and hexathiocyanatobismuthate, while caesium forms only tetrathiocyanatobismuthate.[3]

EXPERIMENTAL

Apparatus

The thermal decomposition studies were made with derivatographs (MOM OD 102/1500° and OD 102/1200°) with α-Al_2O_3 as the inert substance. Other operating conditions were T_{max} 1000°; heating-rate 5°/min (type OD 102/1500°) and 3.95°/min. (OD 102/1200°); DTA sensitivity 1–20 (weight of sample 250 mg) and 1/15 (60-mg samples); TG sensitivity 200 or 100 mg; DTG sensitivity 1/15.

The X-ray analysis of sinters was done with a DRON-1 X-ray analyser with copper radiation and a nickel filter. The intensity of the reflections was measured with a scintillation counter. Diffractograms were recorded with an automatic recorder for 2θ angles from 2° to 70°.

The infrared spectra were obtained by means of a Zeiss IR-10 infrared spectrophotometer with sodium chloride and potassium bromide prisms. The KBr disk method and the Nujol mull technique were employed to obtain the spectra over the range 2300–1900 and 700–400 cm^{-1}.

Study of sinters

Caesium and rubidium tetrathiocyanatobismuthates and caesium sodium hexathiocyanatobismuthate were obtained by the methods described earlier.[3]

In order to examine the course of the reactions, sinters of the compounds studied were prepared, under conditions similar to those of the derivatographic examination. Weighed samples of the salt (250 mg) were heated, at a rate of 5°/min, up to the temperatures determined from the TG curve in the derivatogram. Sinters of $Cs_2Na[Bi(SCN)_6]$ were obtained at temperatures of 280°, 420°, 500°, 600° and 800°. The first loss in mass is associated with the exothermic peak at 280° (Fig. 1), and the second is associated with the DTA peaks at 480°. At 800°, after the mass of the sinter has increased over the range 500–700°, there is no further change in mass. Sinters of Cs $[Bi(SCN)_4]$ were obtained at 250°, 420°, 470°, 600° and 800°. The loss in mass of each sinter was checked.

Chemical analysis

It was found possible to separate the sinters into water-soluble and insoluble fractions by leaching with boiling water for several hr. In the course of leaching, alkali metal thiocyanates and sulphates pass quantitatively into solution. The soluble fraction of the total mass and the anion are determined (alkali metals need not be determined). Table 1 shows the results of analyses of the fractions and theoretical values calculated on the basis of appropriate equations.

In the soluble fraction, thiocyanate was determined argentometrically and sulphate as barium sulphate. The insoluble fractions of the sinters obtained at 280° and 500° were dissolved in a mixture of 9 ml of concentrated nitric acid, 3 ml of concentrated hydrochloric acid and 1 ml of bromine. The mixture was evaporated, the residue dissolved, and bismuth precipitated from the hot solution with a solution of ammonia and ammonium carbonate (800 ml of concentrated ammonia and 20 g of ammonium carbonate, diluted to 1 litre). The precipitate was dissolved in hydrochloric acid (1 + 1) and bismuth was determined as sulphide by precipitation with thioacetamide,[5] alternatively the precipitate was dissolved in nitric acid (1 + 1) and bismuth was determined by titration with EDTA in

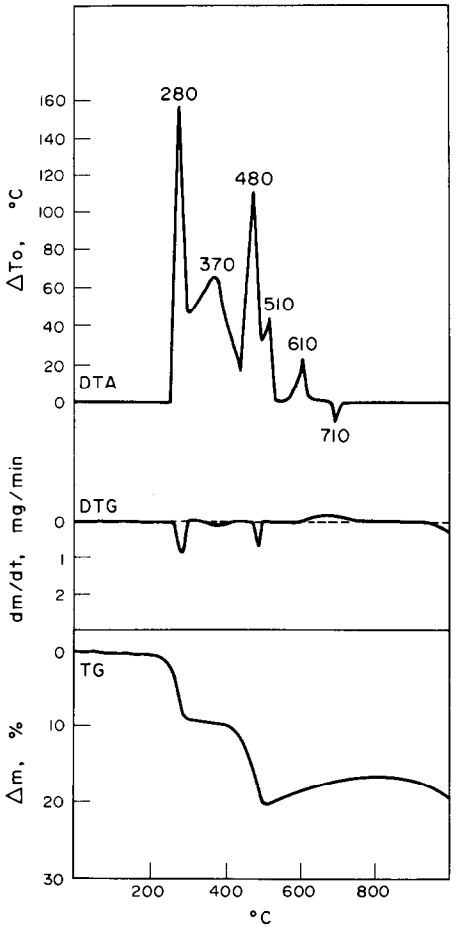

Fig. 1. Thermal analysis curves of caesium sodium hexathiocyanatobismuthate.

the presence of Catechol Violet. After precipitation of bismuth the sulphur in the filtrate was determined as barium sulphate. Sulphur in the sinters was also determined by fusion with sodium peroxide and sodium carbonate. Sulphate was determined after dissolving the sinters in hot hydrochloric acid (1 + 5) by precipitating as barium sulphate. The insoluble fractions of the sinters obtained at 800° were dissolved in hot hydrochloric acid (1 + 5) and the bismuth and sulphate determined as above. Carbon in the sinters was determined by combustion in a stream of oxygen at 1050° and by a gravimetric method; nitrogen was determined by the Dumas method, after decomposition of the substance in a carbon dioxide atmosphere.

The composition of the gaseous products obtained at 470° (for $Cs[Bi(SCN)_4]$) and at 500° (for $Cs_2Na[Bi(SCN)_6]$) was also determined. Sulphur dioxide was absorbed in 0.1*M* $HgCl_4^{2-}$ solution and the resulting hydrochloric acid was titrated with sodium hydroxide solution (sulphur trioxide was not formed). Carbon dioxide was determined gravimetrically (absorbed in "Ascarite") after sulphur dioxide had been adsorbed by silver wool. Nitrogen was determined by the Dumas method, Körbl's[6] preparation being used as auxiliary oxidant.

RESULTS

Figures 1–3 show the derivatograms of $Cs_2Na[Bi(SCN)_6]$. $Cs[Bi(SCN)_4]$ and $Rb[Bi(SCN)_4]$, respectively.

Table 1 presents the analyses of the sinters and Table 2 those of the gaseous products. Table 3 gives the results of the diffractometric analysis of the sinters of $Cs_2Na[Bi(SCN)_6]$ obtained at 280°. The sinter was shown to contain Bi_2S_3, NaNCS and CsNCS.

Figure 4 shows diffractograms of $Cs[Bi(SCN)_4]$ (1) and of its sinters obtained at 240° (2), 470° (3) (3*a* is a diffractogram of the sinter, 3*b* is a diffractogram of the insoluble fraction of the sinter) and at 800° (4).

The $Cs[Bi(SCN)_4]$ sinter obtained at 240° contained Bi_2S_3 and CsNCS, and that obtained at 470°, Cs_2SO_4, Bi_2S_3 and Bi. Since a number of the identification lines of Cs_2SO_4 coincide with those of Bi or Bi_2S_3, an additional diffractogram of the insoluble fraction of the sinter obtained at 470° was recorded. The sinter obtained at 800° contained $(BiO)_2SO_4$ and Bi_2O_3. Table 4 gives the frequencies of the fundamental vibrations of $Cs_2Na[Bi(SCN)_6]$, $Rb[Bi(SCN)_4]$ and $Cs[Bi(SCN)_4]$ and for comparison, CsNCS RbNCS and NaNCS.

DISCUSSION

The TG curves of the derivatograms show that caesium tetrathiocyanatobismuthate loses no mass up to 140°, and caesium sodium hexathiocyanatobis-

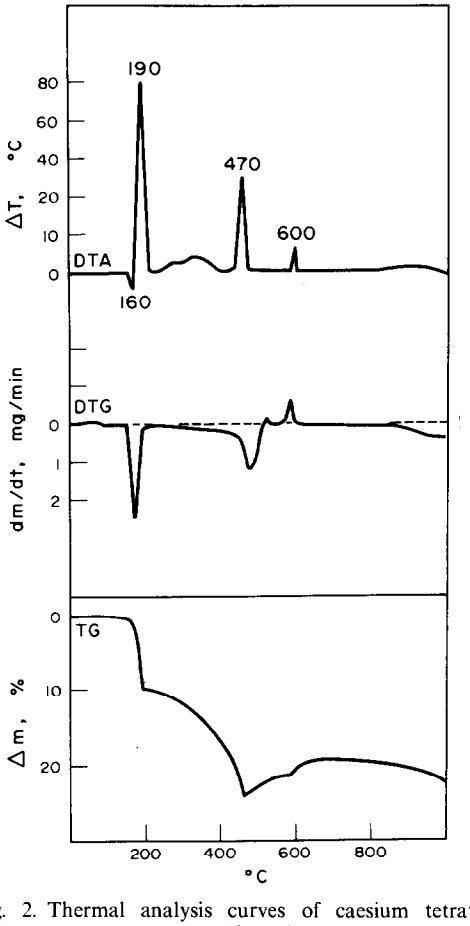

Fig. 2. Thermal analysis curves of caesium tetrathiocyanatobismuthate.

Table 1. Results of chemical analysis of sinters of caesium tetrathiocyanatobismuthate and caesium sodium hexathiocyanatobismuthate

Compound	Temperature, °C	Determined, % Soluble fraction	Determined, % Insoluble fraction	Calculated, % Soluble fraction	Calculated, % Insoluble fraction
$Cs[Bi(SCN)_4]$	250	9.85 SCN 0.95 SO_4	40.79 Bi 10.61 S 4.22 C 6.64 N	11.39 SCN [equation (3)]	
		37.05*	62.95*	37.45*	62.55*
	470	0.00 SCN 11.12 SO_4	5.09 S 2.93 SO_4 49.42 Bi	11.38 SO_4 [equation (6)]	7.60 S 49.52 Bi [equation (6)]
		42.50*	57.50*	42.88*	57.12*
	800	10.31 SO_4	7.16 SO_4 47.44 Bi	10.90 SO_4	7.27 SO_4 47.43 Si
		41.24*	58.76*	41.07*	58.93*
$Cs_2Na[Bi(SCN)_6]$	280	15.52 SCN 5.76 SO_4	25.84 Bi 6.17 S 3.22 C 4.58 N	14.99 SCN 6.20 SO_4 [equation (4)]	
		59.60*	40.40*	58.45*	41.55*
	500	0.00 SCN 21.40 SO_4	3.51 S 0.89 SO_4 31.24 Bi	21.38 SO_4 [equation (7)]	4.76 S 31.01 Bi
		64.30*	35.70*	64.23*	35.77*
	800	21.83 SO_4	4.30 SO_4 29.95 Bi	20.81 SO_4	4.61 SO_4 30.17 Bi [equation (8)]
		63.02*	36.98*	62.51*	37.49*

* Fraction of total mass.

muthate none up to 200°. Thus, for gravimetric determination the compounds may be safely dried at 100° though $Cs[Bi(SCN)_4]$ changes its colour on drying. On the basis of the derivatograms the compounds under study can be identified. The endothermic peak (Figs. 2 and 3) is connected with the heats of melting of the tetrathiocyanatobismuthates (caesium salt at 160°, rubidium salt at 150°). Immediately after melting there is a rapid decomposition of the compound, so the endothermic peak gives the temperature of the onset of the decomposition. The caesium salt is more stable than the rubidium salt, which is in agreement with the higher resistance of the former to hydrolytic decomposition. The peak in the TG curve at 605° is characteristic of $Rb[Bi(SCN)_4]$. Unlike most thiocyanatobismuthates, caesium sodium hexathiocyanatobismuthate does not melt before decomposing. By means of this property, and the weak endothermic peak at 710° which corresponds to the transition of Cs_2SO_4 from the orthorhombic to the hexagonal form,[7] it can be identified unambiguously. The configuration of the three exothermic peaks in the DTA curve of this compound is characteristic of thiocyanatobismuthates containing sodium.

Mechanism of the thermal decomposition

The thermal decomposition of the thiocyanatobismuthates may be divided into two main stages, the dissociation of the complex salt into thiocyanates and the decomposition of the resulting compounds. The

Table 2. Analysis of the gaseous products

Compound	Temperature°	Determined % SO_2	Determined % CO_2	Determined % N_2	Calculated %* SO_2	Calculated %* CO_2	Calculated %* N_2
$Cs[Bi(SCN)_4]$	470	26.15	29.58	8.98	27.89	30.66 [equation (6)]	9.76
$Cs_2Na[Bi(SCN)_6]$	500	25.64	30.43	8.86	26.50	31.20 [equation (7)]	9.93

* Yield on basis of equations quoted.

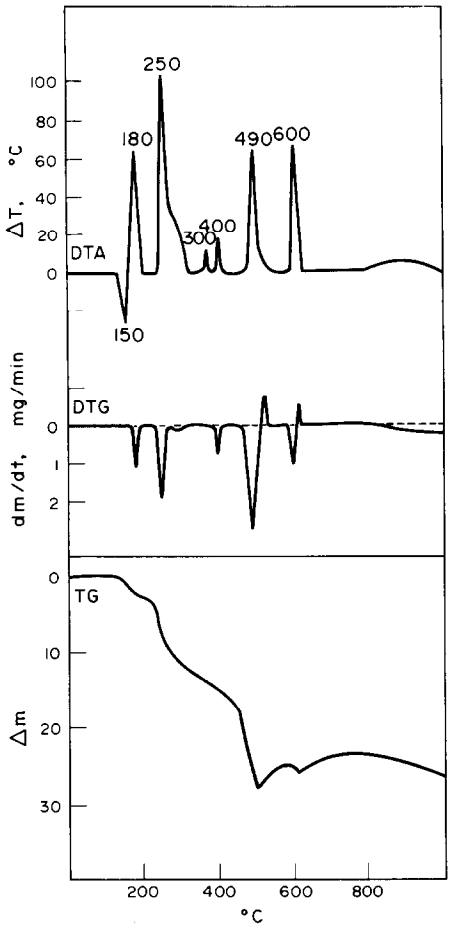

Fig. 3. Thermal analysis curves of rubidium tetrathiocyanatobismuthate.

dissociation proceeds in accordance with the equations:

$$M[Bi(SCN)_4] = MCNS + Bi(SCN)_3 \quad (1)$$

(where M = Rb, Cs)

$$Cs_2Na[Bi(SCN)_6] = 2\,CsNCS + NaNCS + Bi(SCN)_3 \quad (2)$$

The dissociation is indicated by the presence of alkali metal thiocyanates in the sinters obtained at temperatures of 240° and 280°, as established analytically, diffractometrically and spectrophotometrically. It is evident from Table 3 that for the sinters there is an increase in ν(CS) and a decrease in ν(CN) in relation to the frequencies in the thiocyanatobismuthates. Earlier infrared studies[8] showed that bismuth was coordinated to the SCN group through the sulphur atom, bringing about a decrease in ν(CS) in relation to that in isothiocyanate complexes and alkali metal thiocyanates. Thus, from the increase in ν(CS) in the sinters in relation to the original compounds, it follows that the Bi–SCN bond in thiocyanatobismuthates is ruptured and alkali metal thiocyanates are formed. This is confirmed by comparing the vibration frequency in the sinters with that in M–NCS (Table 4). The rupture of the Bi–SCN bond and the formation of M–NCS during the heating of tetrathiocyanatobismuthates is also indicated by the occurrence of only one ν(CN) band in the sinters of these compounds (Table 4). In tetrathiocyanatobismuthates several ν(CN) and ν(CS) bands occur. This probably results from the presence of two structurally different SCN groups which differ from each other in distances between the sulphur and bismuth atoms and distances between the atoms in the thiocyanate group. The occurrence of such groups has been demonstrated by structural studies on tetrathiocyanatobismuthates.[9]

The formation of $Bi(SCN)_3$ during the thermal dissociation is indicated by a study of the thermal decomposition of this compound.[10] However, this thiocyanate immediately decomposes because its decomposition temperature is lower than that of the onset of the decomposition of the thiocyanatobismuthates. That is why this thermal dissociation reaction is irreversible, because it proceeds with simultaneous decomposition of $Bi(SCN)_3$ and generation of gaseous products. The formation of alkali metal

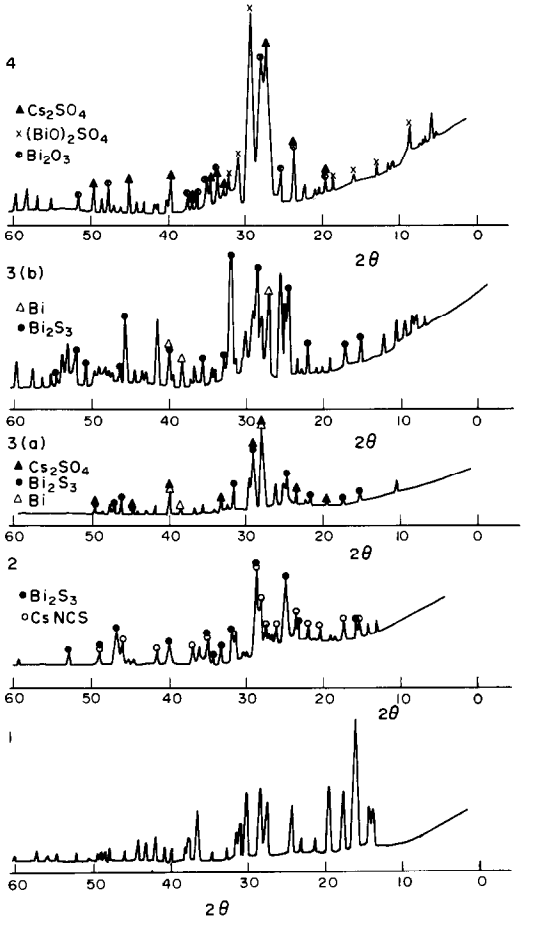

Fig. 4. X-Ray analysis of caesium tetrathiocyanatobismuthate: *1*, before sintering, *2*, after sintering at 240°, *3*, after sintering at 470° (*3a*, sinter, *3b*, the water-insoluble fraction), *4*, after sintering at 800°.

Table 3. X-ray identification of $Cs_2Na[Bi(SCN)_6]$ sinter (prepared at 280°)

Data from X-ray pattern of the sinter		Literature data: interplanar distances (*d*) formula and relative intensity of lines (%)
$2\theta°$	d/n Å	
8.15	10.86	unidentified
10.45	8.47	unidentified
17.55	5.05	5.07 CsNCS (9)
18.70	4.75	unidentified
20.30	4.37	unidentified
20.80	4.27	4.29 CsNCS (17)
22.30	3.99	4.01 CsNCS (12)
24.10	3.69	3.71 CsNCS (20)
25.00	3.57	3.56 Bi_2S_3 (94)
25.20	3.53	3.53 Bi_2S_3 (60)
25.60	3.48	3.49 NaNCS (53)
26.40	3.39	3.39 CsNCS (14)
28.1	3.18	3.20 NaNCS (100); 3.21 CsNCS (13)
28.3	3.15	3.16 CsNCS (100)
28.6	3.12	3.12 Bi_2S_3 (100); 3.14 CsNCS (100)
30.05	2.97	2.96 NaNCS (53)
32.0	2.80	2.81 Bi_2S_3 (63); 2.78 Na_2SO_4 (100); 2.80 CsNCS (4)
34.2	2.62	2.65 Na_2SO_4 (48)
35.3	2.55	2.56 CsNCS (12)
37.50	2.40	2.41 CsNCS (10)
39.50	2.28	2.29 CsNCS (2)
40.50	2.25	2.25 Bi_2S_3 (36)
42.80	2.11	2.12 CsNCS (8)
45.55	1.99	2.04 NaNCS (53)
46.80	1.94	1.95 Bi_2S_3 (55)
49.30	1.85	1.85 CsNCS (4); 1.86 Na_2SO_4 (31)
52.8	1.73	unidentified

thiocyanates during the thermal dissociation can be accounted for by the increase (as the temperature rises) of the vibrational amplitude of the SCN dipoles. At a certain temperature the interactions between the SCN ions and the central ion and the cations of the outer sphere become equal and a proportion of the SCN-ions passes from bismuth to the cations in the outer sphere.

The decomposition following dissociation can be divided into three stages. In the first stage only bismuth thiocyanate (exothermic peak) decomposes and bismuth sulphide is formed together with a (transient) intermediate which contains bismuth, sulphur, carbon and nitrogen. No free sulphur was found in the sinter. The results correspond to the reaction

$$6\,Cs[Bi(SCN)_4] \rightarrow 6\,CsNCS + Bi_2S_3 + 4\,Bis_{1.79}C_{2.70}N_{3.65} \quad (3)$$

The loss in mass calculated on the basis of equation (3) is 11.19%, while that determined from the derivatogram is 9.50% and that of the sinters is 9.15%.

The quantity of thiocyanate found in the soluble fraction of the sinter obtained at 250° is lower than the quantity calculated (Table 1). If, however, the quantity of thiocyanate which was oxidized to sulphate is taken into account, the value obtained 11.01%, agrees with the value calculated (11.38%). The decomposition of $Rb[Bi(SCN)_4]$ proceeds in the same way, but the empirical formula of the transient decomposition product is $BiS_{1.74}C_{2.43}N_{3.39}$. The transient products can have various compositions depending on the original compound and the conditions of decomposition.

The temperature at the onset of the decomposition of $Cs_2Na[Bi(SCN)_6]$ is higher and the proportion of thiocyanate oxidized to sulphate is higher than that for $Cs[Bi(SCN)_4]$. The quantity of sulphate formed is approximately 6%, which corresponds to about 3 moles of M_2SO_4 (from 6 moles of $Cs_2Na[Bi(SCN)_6]$). Since both sodium and caesium thiocyanates are subject to oxidation, the equation (gaseous products excluded) is as follows.

$$6\,Cs_2Na[Bi(SCN)_6] \rightarrow (12 - x)CsNCS + (6 - y)NaNCS + 3(Cs_{x/6}, Na_{y/6})_2SO_4 + Bi_2S_3 + 4\,BiS_{1.59}C_{3.26}N_{3.96} \quad (4)$$

where x is the number of moles of CsNCS oxidized to sulphate, y is the number of moles of NaNCS oxidized to sulphate, and $x + y = 6$. The loss in mass calculated according to this equation is 8.41%, that determined from the derivatograms is 8.10%, while that determined from the mass of the sinter is 8.23%.

In the second stage of decomposition in the temperature range 250–420° (for $Cs[Bi(SCN)_4]$), and 280–430° (for $Cs_2Na[Bi(SCN)_6]$), the main process is decomposition of thiocyanates, which decrease in the sinters from 9.85% to 2.50% for $Cs[Bi(SCN)_4]$, and

Table 4. Frequencies of the fundamental valence vibrations

Compound	ν(CS) cm^{-1}	ν(CN) cm^{-1}
$Cs_2Na[Bi(SCN)_6]$	2080	728
sinter—280°	2063	812, 752
CsNCS	2062	752
NaNCS	2080	758
$Cs[Bi(SCN)_4]$	2112, 2097, 2055	740, 725, 740
sinter—250°	2063	742
$Rb[Bi(SCN)_4]$	2115, 2090, 2052	740, 725, 710
sinter—250°	2055	750
RbNCS	2057	749

from 15.52% to 3.52% (for $Cs_2Na[Bi(SCN)_6]$), the main product being sulphate.

In the third stage (exothermic peak at 470°) the transient product decomposes with the formation of bismuth sulphide and bismuth. This is indicated by a decrease in sulphur content and an increase in bismuth content in the insoluble fraction of the sinter, as in equation (5).

$$4BiS_{1.79}C_{2.70}N_{3.65} \rightarrow Bi_2S_3 + 2\,Bi \qquad (5)$$

The reaction scheme expressing the decomposition of caesium tetrathiocyanatobismuthate at 470° is as follows;

$$6Cs[Bi(SCN)_4] + 45\,O_2 = 3Cs_2SO_4 + 2\,Bi_2S_3 + 2Bi + 15\,SO_2 + 24\,CO_2 + 12\,N_2 \qquad (6)$$

In sinters obtained at this temperature (the TG curve has the characteristic minimum) the presence of bismuth sulphide, bismuth and caesium sulphate was confimed by diffractometry. The caesium sulphate content calculated according to equation (6) agrees with that found in the soluble fraction of the sinter (Table 1). The lower sulphide content of the sinter compared to the theoretical is due to oxidation of part of the bismuth sulphide to bismuthyl sulphate[2] as indicated by the presence of sulphate in the sinters. If the amount of bismuthyl sulphate formed is calculated as the equivalent amount of bismuth sulphide, the initial sulphide found in the insoluble fraction is 8.02% and that calulated from equation (6) is 7.60%. The loss in mass calculated according to equation (6) is 26.51%, that determined from the derivatograms 24.60% and that determined from the sinter mass 25.10%. The loss is smaller (than that calculated) because of oxidation of the decomposition products of $Bi(SCN)_3$. The data in Table 2 indicate that sulphur dioxide, carbon dioxide and nitrogen are the main gaseous products at about 500°. The reaction scheme for rubidium tetrathiocyanatobismuthate is analogous, and that for caesium sodium hexathiocyanatobismuthate is

$$6\,Cs_2Na[Bi(SCN)_6] + 75\,O_2 = 6\,Cs_2SO_4 + 3\,Na_2SO_4 + 2\,Bi_2S_3 + 2\,Bi + 21\,SO_2 + 36\,CO_2 + 18\,N_2 \qquad (7)$$

The loss in mass calculated according to equation (7) is 20.36%, that determined from the derivatograms 20.20% and that determined from the sinter mass 20.60%. The gain in mass which occurs above 480° is associated with the oxidation of bismuth sulphide to bismuthyl sulphate and the oxidation of bismuth to oxide. Other products of oxidation of bismuth sulphide have been reported earlier.[11,12] That the reaction proceeds according to equation (8) is supported by the analyses of the insoluble fraction of the sinters formed at 800°.

$$2\,Bi_2S_3 + 2\,Bi + \tfrac{23}{2}O_2 = 2(BiO)_2SO_4 + Bi_2O_3 + 4\,SO_2 \qquad (8)$$

Initially the oxidation of bismuth sulphide proceeds slowly, but at 600° it becomes rapid. There is an exothermic peak on the DTA curve (and a peak on the TG curve) of the tetrathiocyanatobismuthates, in particular of $Rb[Bi(SCN)_4]$, which corresponds to this reaction. The occurrence of a peak on the TG curve indicates the oxidation reaction of Bi_2S_3 (Fig. 3), because there is an initial rapid loss in mass due to burning of part of the sulphur. Subsequently there is a rapid gain in mass due to the formation of bismuthyl sulphate. In sinters obtained at 600° only a negligible amount of sulphide was found. The mass loss which occurs above 900° is due to the decomposition[13] of $(BiO)_2SO_4$.

Conclusions

The paper has the following analytical significance:

(*a*) on the basis of the thermal curves analytically important thiocyanatobismuthates can be identified;

(*b*) on the basis of the thermal curves the safe temperature ranges for drying the compounds used for gravimetric purposes, can be determined;

(*c*) the analysis of the thermal decomposition reaction is needed for developing thermal methods of determination (*e.g.* a method of caesium determination, based on determination of the sulphur dioxide formed during thermal decomposition of $Cs[Bi(SCN)_4]$ is being developed);

(*d*) the analytical procedure developed can be applied to sinters of other complexes of bismuth containing sulphur. A significant achievement lies in the proof that sinters can be divided quantitatively into water-soluble and water-insoluble fractions. The method has already been applied in analysing the sinters of thiocyanato-thiocarbamidobismuthates of alkali metals.[14]

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ANALYTICAL REACTIONS OF HYDROXYFLAVONES

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Summary—Newer analytical aspects of the chemistry of hydroxyflavone compounds are reviewed.

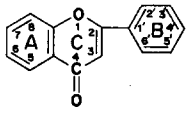
Since the publication of an earlier review[1] on the analytical applications of flavones in 1968, a large number of publications has appeared on the subject, including two more reviews.[2,3] The present article is based on the recent papers and those which were not covered earlier.

A flavone molecule (**I**) can form analytically useful chelates through:

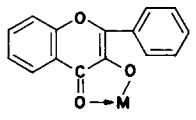
(*i*) the 3-hydroxyl group and the carbonyl (shown in the flavylium structure **II**),

(*ii*) the 5-hydroxy group and carbonyl (shown in **III**),

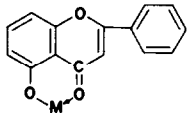
(*iii*) two hydroxy groups present *ortho* to each other in ring B of the flavone molecule as shown in structure **IV**, and



(**I**)



(**II**)



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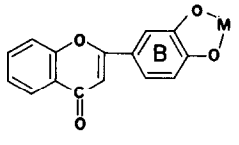
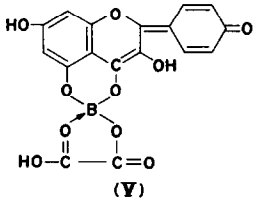


(**IV**)

(*iv*) the formation of multi-ligand complexes incorporating metal, flavone and some other ligands (antipyrine, ClO_4^-, SO_4^{2-}, *etc.*).

These metal chelates are usually coloured and are suitable for the spectrophotometric determination of the metals. Some of them produce characteristic fluorescence and thus the metals can be determined fluorimetrically. Several techniques, chromatography, ring-oven, solvent extraction, *etc.*, have been employed along with photometric and fluorimetric methods to give more selectivity. The compounds have also been used for quantitative precipitation and determination of the metals.

The colour of the metal–flavone chelate or its fluorescence intensity can be quenched with anions. This forms the basis for the indirect determination of the anions. Some anions react directly with flavonoids, giving coloured or fluorescing species suitable for determination. The formation of a boro-oxalate complex with morin (**V**), for instance, has been used in fluorimetric determination of borate.

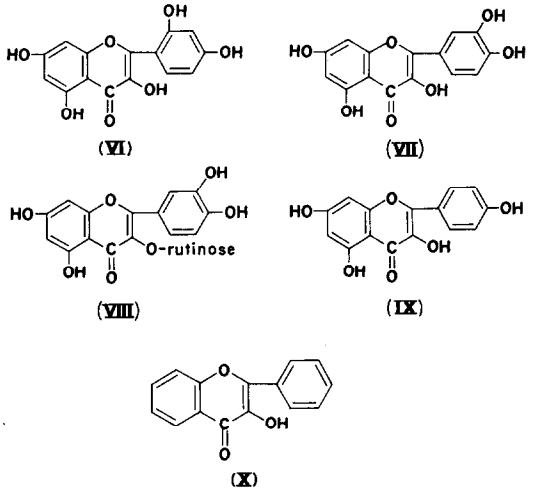


(**V**)

The flavonoids themselves can be identified through the characteristic colour or fluorescence reaction with metals under suitable conditions.[1–4] The spectral bands of flavones show bathochromic shifts on addition of inorganic salt solutions. The shifts are related to the presence of different hydroxyl groups in the molecules. In a similar study, flavonoids have been characterized through these bathochromic shifts and their absorption spectra on paper chromatograms.[5] Flavonols (3-hydroxyflavones) have been distinguished from the other flavones through fluorescence behaviour.[6] In slightly ammoniacal medium, only those flavones fluoresce which have a free or glycosidated hydroxyl group at the C_3 position. In photometric methods for quantitative analysis of flavonoid materials from plant extracts, the accuracy of the result depends on separation of the individual components of the extracts. Paper chromatography,[7–9] microcolumn chromatography on a polyamide sorbent,[10,11] and thin-layer chromatography on polycaprolactam resin powder[12–14] have been found useful for the purpose.

The flavones can be extracted from appropriate plants or synthesized. Most of the analytically important compounds are now commercially available. Amonst them, morin (**VI**) is probably the most extensively studied and used for analytical work. It behaves as a dibasic acid between pH 0.5 and 12.5. Its ioniz-

ation constants (pK_1 and pK_2) have been found[15,16] and the compound has been studied as an extraction reagent.[17] It is quantitatively extracted at pH < 5 while at pH > 11 it is scarcely extracted. Similar compounds frequently employed as analytical reagents are quercetin (**VII**), rutin (**VIII**), kaempferol (**IX**) and flavonol (**X**). In the present survey, the newer analytical applications of these compounds and other flavonoids are outlined.



ANALYTICAL APPLICATIONS

Beryllium and magnesium

In alkaline solution beryllium ions react with morin to give a yellowish-green water-soluble compound which fluoresces in ultraviolet light. The fluorescence emission maximum is at 513 nm and the absorption maximum at 420 nm. The fluorescence reaction is selective (in 0.1–0.5*M* sodium hydroxide) and other ions can be masked. As little as 0.0004 μg of Be/ml can be detected and 0.001 μg determined fluorimetrically. The method is used to determine the metal in the atmosphere, natural water, biological materials and alloys.[1–3] Paper impregnated with morin[18] and a morin-crayon[19] (made by dissolving morin in a mixture of glycerol stearate and paraffin wax) have been used for determining beryllium. Use of the crayon on the ring-oven makes the reaction extremely selective (out of the 62 ions tested, none interferes) and is based on the exceptional instability of the Be–EDTA complex towards ammonia.

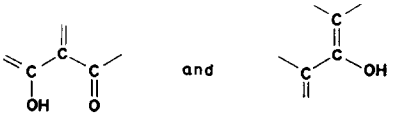
The catalytic oxidation of the Be–morin complex by hydrogen peroxide has been used to determine micro amounts of copper. The beryllium complexes of quercetin and rutin have also been examined.[1–3] The absorption and fluorescence spectra of Be complexes with several 5-hydroxyflavones and 5-hydroxyisoflavones have been studied[20] after their extraction into carbon tetrachloride at pH 8.0–10.0. The beryllium complex with 2-ethyl-5-hydroxy-7-methoxyisoflavone is found to be the most suitable for fluorimetric determination of 0.01–0.30 μg of Be. The fluorescence intensity is measured at 430 nm (excitation at 360 nm).

Magnesium forms a fluorescing complex with morin[21] in phosphate buffer (pH 9.85). The calibration curve is linear in the magnesium range 0.1–0.9 ng/ml. In the determination, the fluorescence is measured at 435.8 nm with excitation by means of a mercury lamp. Heavy metals and large amounts of Ca and Ba interfere.

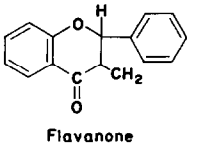
Boron and aluminium

Morin has been extensively used for photometric (sensitivity 0.5 μg/ml) and fluorimetric (sensitivity 0.02 μg/ml) determination of boron in presence of oxalic acid.[1–3,22] The complex shows maximum absorbance at 505 nm and maximum fluorescence at 425 nm. Quercetin and rutin have also been suggested as the photometric reagents. The analytical form of the complex contains B–oxalate–flavone in 1:1:1 ratio. The coloured quercetin complex obeys Beer's law over the range 0–0.5 ppm of B at 445 nm. The method has been applied to determine the element in graphite samples.

A large number of organic reagents are known which form fluorescent compounds with aluminium. Many of these reagents are characterized by the presence of a conjugated system of π-bonds incorporating the enolic hydroxy group and a carbonyl group or a π-bond with a nitrogen atom. Several hydroxyflavones containing the atomic groupings



have been examined[1–3] as fluorimetric reagents for determination of Al, and their sensitivities compared (Table 1). The fluorescence and the colour of the metal complexes formed depend on the number and position of the hydroxy groups in the flavone molecule. The hydroxy groups at 3,5,2′-positions show the greatest effect on the fluorescence. Thus morin (3,5,7,2′,4′-pentahydroxyflavone) and datiscetin (3,5,7,2′-tetrahydroxyflavone) are the most reactive and sensitive reagents amonst the flavones examined. The length of the conjugated π-bond system which includes the reactive groups also has a considerable effect on the sensitivity of the reagents. The presence of a hydrogenated C_2–C_3 bond in flavanones (*e.g.*, hesperitin and hesperidine) leads to a split in the π-bond system and reduces the fluorescence intensity of their aluminium complexes. This explains the low sensitivity of these compounds as reagents for aluminium.

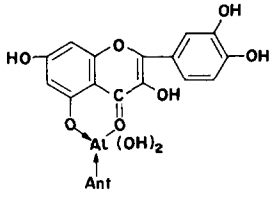


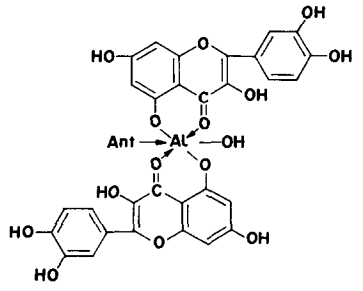
Flavanone

Table 1. Sensitivity and fluorescence detection of Al by flavonoids

Flavonoid	Sensitivity, μg/ml		
	pH 3–4	pH 5–6	pH 10–11
Morin	0.005	0.005	0.05
Datiscetin	0.01–0.02	0.01–0.02	0.10
Datiscin	0.02	0.02	0.10
Quercetin	0.03–0.04	0.03–0.04	—
Rutin	0.05	0.05	—
Quercetrin	0.05	0.05	—
Hesperitin	0.10	0.10	—
Hesperidine	Weak fluorescence		—
Blank solution	No fluorescence	—	—

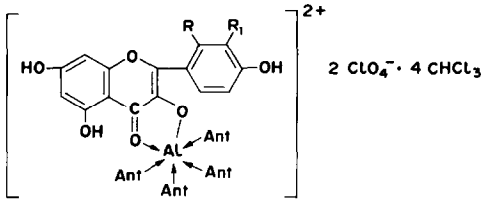
Morin and quercetin have been extensively used as fluorimetric reagents for aluminium.[1–3,23] With the 1:1 Al–morin complex ($K = 2.96 \times 10^6$ at 25°), the sensitivity for the determination is 0.001 μg/ml. The quercetin complex, on the other hand, strongly absorbs the exciting light and gives a much lower quantum yield in spite of its high molar absorptivity. The luminescence reaction between Al and morin also finds application in anion determination.





(In presence of very large excess of quercetin)

To improve the sensitivity and selectivity of Al determination with quercetin, the formation of mixed-ligand complexes was investigated.[24] Aluminium forms two complexes (shown above) on mixing with quercetin and antipyrine. The species can be extracted into dichloroethane and the absorbance of the extract measured at 419 nm. The method has been applied to the determination of Al in standard samples and synthetic rock samples. The detection limit for Al is 0.028 μg/ml. In another study on the formation of mixed complexes, the species containing Al, morin or quercetin, antipyrine and perchlorate ion was extracted into chloroform (structure shown below) and used for the spectrophotometric determination of the metal.[25] The complex obeys Beer's law up to $2 \times 10^{-5}M$ and $3 \times 10^{-5}M$ Al concentration with morin and quercetin respectively.



R = OH, R1 = H (in morin complex);
R = H, R1 = OH (in quercetin complex)

Several other flavonoids,[1–3] *viz.* flavonol, rutin, apigenin and more recently quercemeritrin[26] (3,5,7,3′,4′-pentahydroxyflavone-7-D-glucopyranoside) and kaempferol[27] have been suggested as sensitive reagents for aluminium. The fluorescence of the 1:1 quercimeritrin complex is a linear function of Al concentration in the range 0.002–0.01 μg/ml. The fluorescence is measured at 545–555 nm with excitation at 420–430 nm. The method is used for determining Al in sodium acetate, hydrochloric acid and distilled water—many ions do not interfere.

Gallium, indium and thallium

Several flavone compounds have been examined as photometric, fluorescent and luminescent reagents for gallium, indium and thallium.[1–3] From the physical constants of the complexes (Table 2), it is inferred[28] that all the gallium complexes are more stable than the corresponding indium complexes. Morin has been

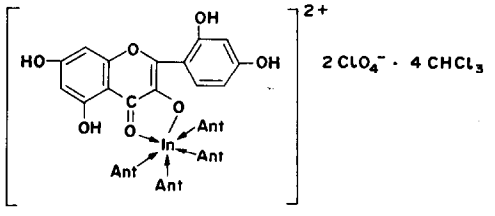
Table 2. Physical constants of Ga and In complexes with morin, quercetin and rutin

Complex	pH	λ_{max}, nm	ϵ, $l.mole^{-1}.cm^{-1}$	K
1:1 Ga–morin	3.6	415–420	4.8×10^4	$2.33–3.23 \times 10^4$
1:3 Ga–quercetin	3.6	450	5.1×10^4	$2.50–4.00 \times 10^{12}$
1:1 Ga–rutin	3.6	405–410	18.4×10^4	$2.33–2.94 \times 10^3$
1:1 In–morin	3.6	410–415	2.9×10^4	$3.85–5.56 \times 10^3$
1:3 In–quercetin	5.0	450	11.0×10^4	$3.03–3.70 \times 10^{11}$

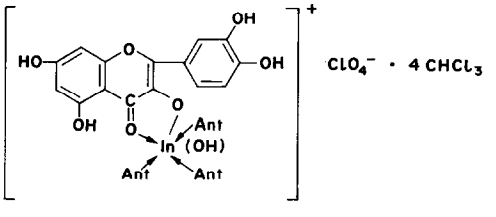
used as a fluorescent metallochromic indicator for titrating 10^{-5}–$10^{-4}M$ Ga and In (and also Sc and Th) within 1% error.[29] The method has been used[30] to determine Ga in semiconducting materials and in arsenide–selenide glasses. The quenching of the luminescence of the Ga–morin complex by oxidizing with Cr(VI) has been made use of in determination of chromium down to 0.01 μg/ml.

Kaempferol acts as a chromogenic reagent[31] in the spectrophotometric determination of 5–10 μg of Ga at pH 5.0 and 6–28 μg of In at pH 4.5 in a 10-ml solution. The extinction is measured at 425 and 430 nm for the Ga and In complexes respectively. The 1:1 Ga–kaempferol complex at pH 3–5 and in 27% ethanol has been used[32] in the determination of the metal in zinc and in hydrochloric acid. Gallium forms a positively charged 1:1 complex with quercetin-3′-glucoside at pH 2.8–3.6. The complex[33] is extracted with butyl acetate and its fluorescence measured at 554 nm. The calibration curve is linear for 0.14–4.2 μg of Ga per 25 ml of solution. Many ions do not interfere in the determination.

The mixed-ligand complex containing Ga with quercetin, antipyrine and perchlorate in 1:1:3:1 ratio has been investigated.[34] The extraction into chloroform is maximal at pH 4.0–5.0. The metal can be determined spectrophotometrically (λ_{max} 445 nm) or fluorimetrically (fluorescence maximum 509 nm) within 3% error. Similarly, mixed-ligand complexes of In with morin (or quercetin) and antipyrine have been extracted into chloroform and correspond to the following structures:[35]



(Mixed-ligand complex with morin)



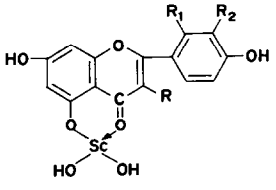
(Mixed-ligand complex with quercetin)

The extracts of the complexes fluoresce in ultraviolet light. The molar absorptivities of the morin and quercetin complexes are 6.0×10^4 and 4.5×10^4 $l.mole^{-1}.cm^{-1}$ respectively. An extraction–photometric method has been developed for determining In in zinc ores.

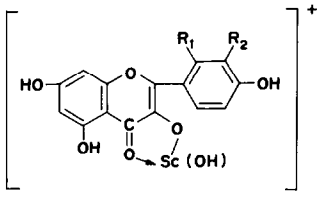
Quercetin has been used in photometric determination of thallium(III)[1-3,36] after extraction of the complex with amyl (butyl or ethyl) acetate (pH 3–5). The absorbance of the raspberry-coloured complex is measured at 510 nm. The method has been applied for the determination of 2–16 μg of Tl/ml in presence of very large amounts of Zn and Cd.

Scandium and the rare earths

The reaction between scandium and polyhydroxyflavones *viz.* morin, quercetin, rutin and kaempferol has been studied and used in spectrophotometric, fluorimetric and complexometric determinations of the metal.[1-3] Two types of complex are formed—fluorescent and non-fluorescent—depending on the pH. Quercetin forms three complexes, two of which are fluorescent; morin gives one fluorescent and one non-fluorescent complex; rutin gives one non-fluorescent compound. All the non-fluorescent and one of the fluorescent quercetin complexes (pH 6.0–6.5) are electrically neutral. The other quercetin complex (pH 5.5–6.0) and the morin complex have a positive charge. The component ratio is 1:1 in all the complexes (structures shown below).

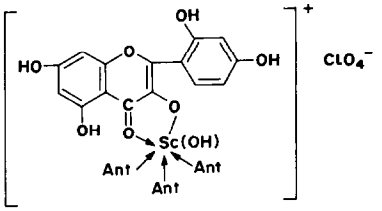


Structure of non-fluorescing Sc complexes
R = R_2 = H; R_1 = OH (morin) R = R_1 = H; R_2 = OH (quercetin)
R = rutinose; R_1 = H; R_2 = OH (rutin)



Positively charged fluorescent Sc complexes
R_1 = OH; R_2 = H (morin) R_1 = H; R_2 = OH (quercetin)

A mixed-ligand complex containing scandium, morin and antipyrine is formed at pH 1.2–4.0 and extracted as an ion-association complex with weakly basic anions (structure given below). The complex can



be used for extractive–photometric (sensitivity 0.1 μg/ml) and extractive–fluorimetric (sensitivity 0.01 μg/ml) determination of the metal. Morin has also been used[29] as a luminescence indicator for the titration of 10^{-5}–$10^{-4}M$ Sc with EDTA at pH 1.78 within

1% error. The determination can be carried out in presence of 500-fold amounts of Ca; 200-fold Y and Mn; 100-fold Mg; 50-fold Zn and Fe(III); 20-fold Be and Cd.

The work on the rare-earth complexes with polyhydroxyflavones was reviewed earlier.[1–3] The optimum pH (2.5) for the formation of the complexes with morin, their absorption and fluorescence emission maxima (410 and 501 nm respectively), molecular extinction coefficients, and the quantum yield have been studied.[3,7] The quantum yield is related to the atomic number of the element. Calibration curves have been constructed for the fluorimetric determination of individual elements. The sensitivity is 0.04 μg/ml.

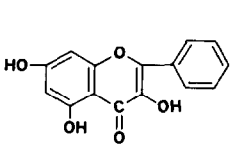
Germanium and tin

The analytical aspects of the reactions of morin, quercetin, quercetin-6′-sulphonic acid, rutin, flavonol and 3-hydroxy-4′-methoxyflavone with Ge have been investigated[1–3,38] in neutral or acidic medium and procedures developed for the photometric determination of the metal. The Ge–rutin complex[38] formed at pH 6.3–7.1 (ϵ 7.1 × 10^3 l.mole^{-1}.cm^{-1} at 400 nm) has a stability constant of 4.95 × 10^5 and the sensitivity is 0.1 μg/ml. Alkali and alkaline earth metals; 500-fold amounts of Mg, Zn, Cd and Mn; 10-fold of Co and Ni; 8-fold amounts of Cu, Al, Se and Te do not interfere, but Ti, Zr, V, Mo and W do.

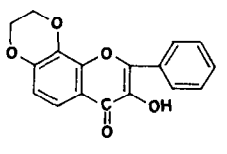
Morin, quercetin, flavonol, kaempferol and 3,4′,7-trihydroxyflavone have been suggested as photometric and fluorimetric reagents for tin(IV).[1–3,39–43] In a fluorimetric procedure, tin is extracted as SnI_4 from sulphuric acid medium into a suitable solvent (to eliminate interference due to other elements), complexed with the flavonol compound and its fluorescence intensity measured. The reactions are highly sensitive. With 3,4′,7-trihydroxyflavone, for example, as little as 0.007 μg of tin can be detected or 0.02 μg determined within 10% error (fluorescence maximum 473 nm, excitation maximum 377 nm). The method has been applied to the analysis of soil and biological tissues.

Titanium, zirconium and hafnium

Morin, quercetin, quercetinsulphonic acid, rutin, kaempferol, galangin and 7,8-ethylenedihydroxyflavonol have been used[1–3] for the spectrophotometric determination of titanium(IV). An extractive–photometric procedure employing quercetin is used to determine Ti in bauxite and in alloys. The extracted species is a 1:1 complex. A 1:2 Ti–quercetinsulphonic acid complex is formed[44] in the pH range 2.2–4.6



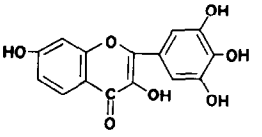
Galangin



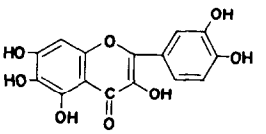
7, 8-Ethylenedihydroxyflavonol

(ϵ 1.6 × 10^4 l.mole^{-1}.cm^{-1}). Beer's law holds over the range 0.05–2.0 μg/ml at 420 nm. In a gravimetric determination of Ti with morin (in sodium hydroxide solution), the complex is precipitated, washed with 0.05*N* sulphuric acid and ignited at 900° before weighing.[45]

Morin, quercetin, quercetinsulphonic acid, rutin, 3,4′,7-trihydroxyflavone, datiscin (the glycoside of 3,5,7,2′-tetrahydroxyflavone), flavonol, flavonol-2′-sulphonic acid, galangin, robinetin, kaempferol and quercetagetin all have been used in photometric or fluorimetric determination of zirconium.[1–3,46–57] The metal can be precipitated from 4*N* sulphuric acid as its complex with morin,[58] ignited at 900° and weighed as ZrO_2.



Robinetin



Quercetagetin

The fluorescence curve of the Zr–datiscin complex is a mirror-image of its absorption curve. The fluorescence intensity is measured at 520 nm. The complex has maximal fluorescence in 6*N* hydrochloric acid, which is the preferred medium for the determination. The procedure has been applied to the determination of Zr in magnesium and zinc alloys. The presence of 100,000 times as much Al and 100 times as much Ag, Cu(II), Cd, Be, Hg(II), Pb, Mn(II), Fe(II), Co(II), Ni(II), In, Ce(III), Y, Cr(III), V(V), Nb(V), Ta(V), W(VI) and U(VI) as zirconium can also be tolerated. Extraction–spectrophotometric procedures have been used to determine Zr in platinum alloys,[47] yttrium and rare-earth compounds[48] and also for group concentration of traces of metals.[49]

The state of quercetin-6′-sulphonic acid in 1–16*N* sulphuric acid has been examined[50] and its protonation constant calculated (p*K* 2.91 ± 0.04). The optimal conditions leading to the formation of its Zr and Hf complexes and their spectrophotometric and fluorescent characteristics (λ^{ab}_{max} 420 nm, λ^{fl}_{max} 501 nm) have been established. The fluorescence of the Hf complex is the more intense. The sensitivities for the fluorimetric determination are 0.04 μg of Zr and 0.02 μg of Hf per ml.

Zr and quercetinsulphonic acid react to form two complexes—1:2 at pH 0.1–0.3 (λ_{max} 420 nm, ϵ 2.25 × 10^4 l.mole^{-1}.cm^{-1}) and 1:1 at pH 1.0–4.0 (λ_{max} 440 nm, ϵ 1.5 × 10^4). The metal in the concentration range 0.04–11.0 μg/ml can be determined at pH 0.1–0.3 without interference from Cu(II), Mg, Ca, Zn, Al, In, Cl^-, NO_3^-, ClO_4^-, SO_4^{2-} and SiO_3^{2-}. The method has been applied to determine Zr in silicates[51] and magnesium alloys.[52]

The fluorescence intensity of the Zr complex with 3,4′,7-trihydroxy-flavone[53] (in 0.6*N* sulphuric acid) has been used (emission at 475 nm, excitation at 417 nm) to detect as little as 0.05 μg of the metal. In

a comparative study[54,55] on the use of flavonol, morin, quercetin and quercetinsulphonic acid as fluorimetric reagents for Zr and Hf, morin was found to be the most sensitive. Increasing acidity increases selectivity but the sensitivity is reduced. Flavonol and morin can be used to detect Zr and Hf in presence of each other.

The formation of the 1:1 yellow zirconium–rutin complex[56,57] (λ_{max} 410 nm, ϵ 1.2×10^4 l.mole^{-1}.cm^{-1}) in 0.3*N* hydrochloric acid and 50% methanol has been used to determine 5.5 ppm of zirconium. The stability constant of the complex is 3.77×10^4.

In a recent study,[59] zirconium(IV) was titrated fluorimetrically with EDTA in the presence of morin. The fluorescence intensity was measured at 518 nm (excitation at 405 nm). The end-point was indicated by the fluorescence intensity falling to zero. Many anions and cations were found not to interfere, but Hg(II) can be tolerated only in amount not exceeding that of Zr, Bi(III) interferes and Hf(IV) is titrated with Zr. The relative standard deviation for titration of 10 ml of a solution containing 1 ppm of Zr does not exceed 1.5%.

Morin and quercetin have been investigated as spectrophotometric and fluorimetric reagents for hafnium.[1–3,60–65] The metal reacts with morin[60,65] (H_5L) in 0.1*N* sulphuric acid, forming a non-fluorescent coloured complex, $[Hf(H_4L)_4]^{2+}$. An uncharged 1:1 complex $[(H_5L)Hf(OH)(SO_4)_2]$, formed in 1*N* sulphuric acid, fluoresces at 510 nm. The fluorescence intensity increases and the absorption decreases with increasing concentration of organic solvent (methanol, ethanol or acetone). In 75% methanol, a hafnium concentration as low as 0.005 μg/ml can be detected. The absorption and luminescence characteristics of the fluorescent complex containing Hf and morin in 1:1 ratio have been studied[65] under optimal conditions (7*N* hydrochloric acid, 30% ethanol). The method permits the determination of 4–24 ng of Hf per ml in presence of an equal concentration of zirconium by passage of the solution through an ion-exchange resin (H^+ form) and measurement of the fluorescence at 501 nm (excitation at 436 nm). The method is ten times more sensitive than that using quercetin.

The spectral and fluorescence spectra of Hf complexes with quercetin have been studied[62] in 5–10*N* hydrochloric acid and 0.2–0.5*N* sulphuric acid. A fluorescent 1:1 compound is formed in hydrochloric acid whereas in sulphuric acid medium a 1:1:1 Hf–quercetin–sulphate complex is formed. Addition of methanol, ethanol or acetone up to a concentration of 38% v/v increases the fluorescence intensity of the complex in hydrochloric acid. The sensitivity of the reaction is 0.04 μg/ml (sulphuric acid) and 0.01 μg/ml (hydrochloric acid) at the fluorescence maximum at 501 nm (excitation at 436 nm). The presence of twice as much Zr does not interfere. With $4.25 \times 10^{-5}M$ quercetin in presence of 8.25*N* perchloric and 9% ethanol, a 200-fold ratio of Zr can be tolerated.[63] Under these conditions, Zr does not fluoresce and the sensitivity for Hf is 0.01 μg/ml. In another procedure, 2% of Hf in zirconium has been determined by measuring the fluorescence (at 498 nm, excitation at 436 nm) of the sample solution in 55% perchloric acid that is 0.015m*M* in quercetin.[61] The distribution of Hf, Zr and Ti on paper in different solvents has been studied.[66] Hf (0.5–8 μg) can be separated from the other two metals by ascending chromatography with a solvent mixture of methyl ethyl ketone and concentrated hydrochloric acid (5:1 v/v). The spots are located by spraying with 0.01% quercetin (in ethanol) and Hf is determined by visual comparison of its fluorescence in ultraviolet radiation with that of a standard.

Thorium and uranium

The complexes of thorium with morin, quercetin, quercetinsulphonic acid, quercetrin (quercetin-3-rutinoside), datiscetin, robinetin, myrecetin, galangin, 3-methygalangin, melanoxetin, chrysin, norwogonin and flavonol-2′-sulphonic acid have been examined.[1–3,46,67,68] The complexes generally contain metal and the ligand in 1:1 or 1:2 ratio. The methods have been employed to determine thorium with these flavonoids. The flavonols are 4–5 times more sensitive than 5-hydroxyflavones. The stability constants range between 10^4 and 10^5.

The optimum conditions to obtain maximum luminescence in the titration of thorium–morin complex with oxalic acid or EDTA have been studied.[67] The amounts of thorium which can be titrated with the two titrants (at pH 1.5–3.0) are up to 20 μg/ml (with oxalic acid) and 50 μg/ml (with EDTA). The presence of sulphate weakens the luminescence of the complex.

Thorium and morin form a 1:3 cationic complex which is extractable into isopentanol as the ion-association complex with perchlorate.[46] The molar absorptivity of the extracted complex (7.3×10^4 l.mole^{-1}.cm^{-1} at 420 nm), its two-phase stability constant and its extraction constant have been determined. A procedure has been developed for extraction and photometric determination of thorium and zirconium in one sample—the method is used to analyse rock salt.

Morin, quercetin, quercetinsulphonic acid, flavonol, galangin and its 3-methyl derivative, 5-hydroxyflavone and its 7-methoxy and 7,8-dimethoxy derivatives, norwogonin, rutin and robinetin have all been examined as spectrophotometric reagents for determination of uranium.[1–3] All the reagents are very sensitive but lack selectivity and a prior separation of uranium from accompanying ions is needed. The complexes contain the metal and ligand in 1:1 or 1:2 ratio except in the case of robinetin, with which a 2: (U:ligand) complex is also formed, involving hydroxyl groups of the B ring of the flavonol molecule.

Arsenic, antimony and bismuth

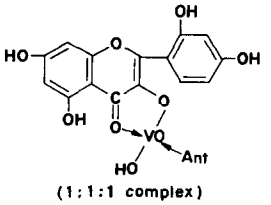
Quercetin has been used[1–3] as a photometric reagent for As(V), Sb(III) and Bi(III). The absorbance in alcoholic medium is measured at 398 nm for the As-complex, 420 nm for Sb and 436 nm for Bi. Flavonol-2′-sulphonic acid and bismuth react to form two complexes. In 0.2–4*N* perchloric acid a 1:1 complex is formed, while a 1:2 (Bi:ligand) complex results over the range from 0.2*N* perchloric acid to pH 5. The higher complex is used for the photometric determination of 0.17–10 μg of Bi per ml at 370 nm.

Antimony (0.5–20 μg) is extracted with benzene from sulphuric acid in presence of potassium iodide (to avoid interference from Au, Be, Al, Sc, Ga, In, Th, Ti, Zr, Hf, V, Cr and Fe). The extract is shaken with 0.2*M* hydrochloric acid and 0.5% morin solution and the fluorescence of the aqueous phase is measured at 420 nm.[39,40]

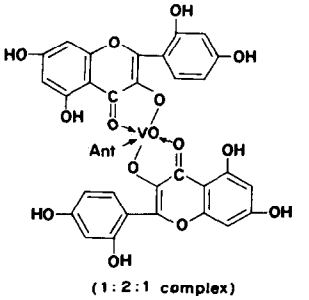
Antimony(III) and kaempferol react in 0.1*M* hydrochloric acid, forming a 1:1 complex (λ_{max} 420 nm). The position and the intensity of the maximum are pH-dependent. The optimum range of determination is 1.9–7.8 ppm of antimony.[69]

Vanadium, niobium and tantalum

The applications of morin, quercetin, rutin and flavonol as spectrophotometric reagents for vanadium have been reviewed.[1–3] Vanadium(IV) or (V) reacts with morin in presence of antipyrine to form yellow complexes which can be extracted with dichloroethane at pH 2–7. The ternary complexes show a characteristic maximum at 420 nm, ϵ 3.75×10^4 l.mole^{-1}.cm^{-1}. They contain vanadium, morin and antipyrine in 1:1:1 and 1:2:1 ratio (structures shown below) irrespective of whether V(IV) or V(V) is used as the starting material. It has been shown by ESR that V(V) is reduced by morin to V(IV), which forms the two complexes—the composition depends on the amount of morin present. In the determination of the metal by use of the dichloroethane extract of the mixed complex at pH 4.5, the presence of alkali and alkaline earth metal ions, Be, Cd, Cr, Mn, Co and Ni can be tolerated.



(1:1:1 complex)



(1:2:1 complex)

Vanadium(IV) and kaempferol react to form a 1:1 complex (λ_{max} 425 nm, ϵ 1.38×10^4 l.mole^{-1}.cm^{-1}) suitable for spectrophotometric determination[70] of ≤2.3 ppm of the metal at pH 4.0, but the method lacks selectivity.

Nb and Ta (in acid solution) have been determined gravimetrically with morin, quercetin and dihydroxyquercetin.[1–3] Quercetinsulphonic acid has been used for photometric determination of Nb, and morin and quercetin are used for Ta.[1–3] Niobium forms with quercetin (H_5A) and hydrogen peroxide a neutral 1:1:1 complex, $NbO(OH)_2H_2O_2(H_4A)$, which fluoresces at 495–500 nm (when excited at 436 nm).[71,72] Methanol, ethanol and acetone increase the fluorescence intensity of the complex. The optimum pH for complexation is 2.1 and a 20-fold ratio of peroxide should be present. The method is suitable for determining 0.09–0.90 μg of Nb per ml in 50% ethanol.

Molybdenum and tungsten

Morin, quercetin, dihydroquercetin, galangin, robinetin and myricetin have been used[1–3] for the spectrophotometric determination of molybdenum. These flavonoids are very sensitive reagents but lack selectivity; a prior separation of molybdenum from other ions is essential. The 1:1 molybdenum–rutin complex (λ_{max} 410 nm, ϵ 8.25×10^3 l.mole^{-1}.cm^{-1}) is formed at pH 3–5.[67] The reaction is used to determine 2.8–5.8 ppm of molybdenum. The fluorescence of the Mo–morin complex[73] at pH 5.0 is greatly enhanced in presence of 20% ethanol or acetone and by cooling to −196°. The fluorescence is linearly related to molybdenum concentration over the range 0.1–1.6 μg/ml. In the presence of ethanol, the fluorescence maximum lies at 480–488 nm (excitation wavelength 436 nm).

Morin has been used for photometric[1–3] and fluorimetric[74] determination of tungsten(VI). The optimal conditions have been established for formation of the 1:1 tungsten–morin complex (pH 5.1–5.4). The complex has maximum absorbance at 410–415 nm and a fluorescence maximum at 500–510 nm. Tungsten concentration in the range 0.003–0.048 μg/ml and fluorescence are linearly related. In the determination, 0.2 μg/ml of Nb(V) and Ta(V) and 0.5 μg/ml of Mo(VI) do not interfere. Flavonol has also been used[1–3] to determine tungsten fluorimetrically at 460 nm (pH 2.5–5.5) in W–Ni steels.

Tungsten forms two complexes with rutin—1:1 at pH 5.0 and 1:3 at pH 7.5. The complexation has been used[57] to determine 3.7–8.9 ppm of the metal. The formation of the 1:2 tungsten–quercetin complex (pH 1.0–1.5, λ_{max} 413 nm, ϵ 1.4×10^4 l.mole^{-1}.cm^{-1}) has been applied for determining W in steel.[75]

Manganese

A kinetic method has been proposed[76] for determining 5–50 ng/ml. It is based on the ability of man-

ganese(II) to accelerate catalytically the oxidation of the beryllium–morin complex by atmospheric oxidation. The fluorescence is measured at 525 nm (excitation at 436 nm). The reaction is strongly dependent on temperature and time.

Iron

Flavonol, morin and quercetin have been used for photometric determination of iron.[1–3] The complexes of iron(III) with hesperitin (1:1 at pH 1.2–2.2, 1:2 at pH 3.5–4.0 and 1:3 at pH 6.5–7.0) and with rutin[57,77] (1:1 at pH < 7 and 1:2 and 1:3 at pH > 7) have also been studied. The use of glycine buffer (pH 3.5) is recommended for determination of the metal with rutin. Beer's law is valid for 0.5–5 μg/ml.[77] Cu(II), Be, Al, UO_2(II), Cr(III), F^-, I^-, CO_3^{2-}, $C_2O_4^{2-}$, $C_4H_4O_6^{2-}$, $B_4O_7^{2-}$, PO_4^{3-} and VO_3^- interfere. Fe(II) also reacts, to form a 1:2 complex at pH > 7.

Anions

Rutin reacts with nitrite in acid medium to produce an orange colour which obeys Beer's law for nitrite from 0.009 to 0.9 mg/ml. The reaction has been used[79] for routine photometric determination of the anion at 425 nm, where the absorbance is maximal.

The quenching of the fluorescence intensity of the Zr–flavonol chelate by fluoride, enables the latter to be determined (up to 10 μg in samples) by measurement of the fluorescence at 460 nm. Al(III), MoO_4^{2-}, $C_2O_4^{2-}$, $C_4H_4O_6^{2-}$ and citrate can be tolerated in at least 10-fold ratio to F^-.

The fluorescence intensity, (F) of the Th–morin complex decreases in the presence of sulphate in accordance with the relationship.[81]

$$F = F_0 \exp[-kc]$$

where F_0 is the intensity in absence of sulphate, c is the molar concentration of sulphate and k is a constant.

Less than 20 μg of sulphate can be determined. The pH of the solution is adjusted to 2.3, Th–morin complex added and the fluorescence is measured at 365 and 500 nm. Iron, fluoride, thiosulphate, phosphate and some organic compounds interfere. Flavonol and quercetin can also be used in place of morin and they afford equal sensitivity. However, with flavonol-2′-sulphonic acid only half the sensitivity is achieved. The method has been applied to the analysis of snow and river waters for their sulphate content.

CONCLUSIONS

It is apparent that hydroxyflavones are very sensitive reagents for several metals and some anions and find wide application in analysis. The selectivity can be improved by making use of extractive techniques and pH variation or through formation of mixed-ligand complexes. Apart from spectrophotometric and fluorimetric methods, the ring-oven and thin-layer chromatography have been used to achieve separation and determination of the elements. Eleven metal ions were separated[82] on filter paper on a ring-oven at 105–110° with 0.05M nitric acid as solvent. After exposure of the paper to ammonia vapour, the ions were located with methanolic morin solution. Quercetin (0.01M) has been used[83] as a spray reagent in thin-layer chromatography and in evaluation of the chromatographed species by ring colorimetry.

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HIGH-PRECISION GRAVIMETRIC COULOMETRY USING THE SILVER–PERCHLORIC ACID COULOMETER: TITRATION OF ARSENIOUS OXIDE WITH ELECTROGENERATED IODINE

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Summary—High-precision gravimetric coulometry with a silver–perchloric acid coulometer is evaluated as an alternative to the conventional titrimetric method. The loss of weight (caused by electrolytic dissolution) of a highly pure silver anode in series with the cathode of a conventional constant-current titration system is measured and related to the number of equivalents of substance titrated. The precision of the method is determined by titrations of the Standard Reference Material 83C arsenious oxide (99.99% pure) with electrogenerated iodine, using biamperometric end-point detection. Depending on the size of the sample, an ultimate precision of 25 ppm is obtained. The assay for 0.5-g samples of the SRM material is $99.993_9 \pm 0.002_5$% purity.

The non-availability of suitably characterized primary-standard reference materials can ultimately limit the accuracy of quantitative determinations. For example, the degree of purity and errors in the atomic weights of the constituents of a reference material cause intrinsic inaccuracies during the characterization of secondary standards or analysis of a sample by comparison with the primary standard.

A primary standard is not needed when constant-current coulometric titration is used to obtain highly accurate analyses, lending support to the proposal to adopt the Faraday as the international standard for titrimetric analysis.[1,2] A number of investigators report precisions for constant-current coulometric titrations well within 100 ppm.[3–10] The current is most often kept constant in these studies by maintaining a constant *IR* drop across a standard resistor. However, monitoring the current in this way becomes inconvenient when the highest precision is desired. Usually it is necessary to analyse large samples, and that requires titration times of several hours.

As an alternative to direct monitoring of current and time, chemical coulometers have been used for current–time integration.[11] Szebelledy and Somogyi,[12] who originated the technique, employed dissolution of a silver anode in silver nitrate solution. In this medium there exists the possibility of formation of silver oxide on the anode surface. VanLente *et al.*[13] used this approach for acidimetric titration with colorimetric end-point detection and obtained a precision of 0.088% for titrations resulting in the dissolution of 0.110 g of silver. In the present paper the precision and accuracy obtainable by gravimetric coulometry have been determined by assay of high-purity arsenious oxide. An assessment of errors is made to evaluate the ultimate limits of the method for determinations of stoichiometry.

THEORY

Arsenic(III) in the form of arsenious acid may be oxidized by electrogenerated iodine according to the equation

$$H_3AsO_3 + I_3^- + H_2O \rightleftharpoons H_3AsO_4 + 2H^+ + 3I^- \quad (1)$$

the I_3^- being formed when I_2 is produced in the presence of I^-:

$$2I^- \rightleftharpoons I_2 + 2e^- \quad (2)$$

$$I_2 + I^- \rightleftharpoons I_3^- \quad (3)$$

The optimum pH-range for a titration based on reaction (1) is 6.5–7.5, which may easily be maintained by use of phosphate buffer. It is stated that iodine may be generated coulometrically under these conditions with a current efficiency of 99.9999% or better at a current density of 1.25–2.50 mA/cm.[6]

A silver anode undergoes electrolytic dissolution in aqueous solutions of 20% w/v perchloric acid initially containing 0.5% w/v silver perchlorate:

$$Ag \xrightarrow{HClO_4,\ AgClO_4} Ag^+ + e^- \quad (4)$$

Metallic silver is insoluble in perchloric acid, whereas silver perchlorate is highly soluble.[14,15] The slow formation of silver oxide according to reaction (5) is not a complicating factor in this medium since it readily reacts with perchloric acid as indicated by reaction (6):

$$2Ag + \tfrac{1}{2}O_2 \rightleftharpoons Ag_2O \quad (5)$$

$$Ag_2O + 2HClO_4 \rightleftharpoons AgClO_4 + H_2O \quad (6)$$

EXPERIMENTAL

Apparatus

A Julie DCS-105 Direct Current Source (Julie Research Laboratories, Inc., New York) was used to provide constant generating current. This instrument is designed to generate precision currents with 1-ppm precision by means of a seven decade Kelvin-Varley voltage divider which provides ultralinear comparison of the built-in precision reference and the output. The reference standard is calibrated periodically with components standardized by the National Bureau of Standards. After calibration, the error for the current employed in this investigation was 0.001%.

Measurements of time were made with a Canberra Industries Model 1491 Nuclear Counter operated with a 1-MHz standard frequency, providing a timing precision of 1 ppm.

A Princeton Applied Research Model 174 Polarographic Analyzer with a Model 174/70 Drop Timer Assembly in the two-electrode mode was used to apply a potential of 150 mV between two 1-cm^2 platinum foil electrodes placed 1 cm apart in the solution, for biamperometric end-point detection. The trace for the end-point was recorded with a Hewlett-Packard Model 680 strip-chart recorder, with the chart-speed adjusted to allow a time resolution of 0.15 sec.

The current-source, timer, and detection-system were grounded through a Wanlass Instruments Model P-1405-Q a.c. power conditioner to eliminate electronic noise from the end-point recording. A diagram of the complete circuit is shown in Fig. 1. A double-pole double-throw switch allowed either flow of current through a suitable dummy resistor, or closing of the circuit including the titration cell, with simultaneous triggering of the timer.

The titration cell was basically the same as that described by Marinenko and Taylor.[6] A 15-cm^2 corrugated platinum sheet served as the generator electrode and a platinum wire spiral was used as the counter-electrode. A second cell, shown in Fig. 2, contained the silver anode and corresponding platinum counter-electrode. A quantity of silver sediment was lost from the electrode in addition to the silver lost through anodic dissolution. During the titration this sediment was collected in the previously weighed quartz crucible shown in the figure. After completion of the titration the crucible was removed from the cell compartment, the silver perchlorate solution drawn off by suction, the sediment rinsed, and the crucible dried and weighed so that the weight of sediment could be determined and included in the calculations. A transfer of silver sediment was thereby avoided, in contrast to the procedure of Craig *et al.*[14] The crucible was constructed from quartz and included a 10-mm diameter fine-porosity quartz frit,

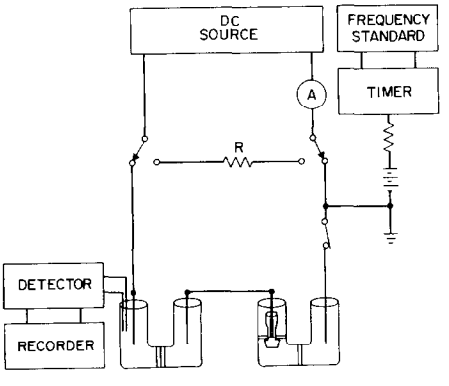

Fig. 1.

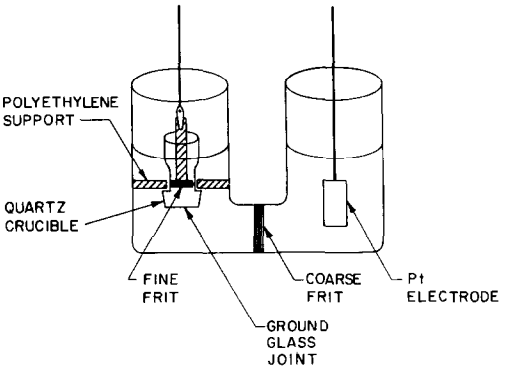

Fig. 2.

since quartz is more stable than other common crucible materials, especially Pyrex, toward atmospheric moisture. The silver anode was situated in the crucible with contact being made to the circuit by an alligator clip with a piece of silver foil acting as a spacer.

All weighings were made with a Mettler semimicro balance (20-g capacity). The sensitivity of the balance was adjusted at regular intervals, with Class M standard weights, which were also used for calibration of the balance weights. All weights were corrected for air buoyancy.

Reagents

Electrolytically pure silver rods (99.9995%) were obtained from Alfa Products. This silver was first purified by electrolysis and then cast in graphite from the melt, to remove any silver oxide present. The purity specification was confirmed by private analysis to ensure that no contamination had occurred before use in this work. Metallic impurities detected by emission spectroscopy were well below 5 ppm.

Silver wire of the same purity was used to suspend the silver anodes from the balance for weighing. The silver foil spacers between the alligator clip and the silver anode were also of this purity.

The concentrated hydrochloric acid and 10% ammonium hydroxide solution used to etch the silver anodes were of J.T. Baker "Ultrex" grade. The silver-anode cell contained a solution of 20% w/v perchloric acid ("Ultrex" grade) and 0.5% w/v silver perchlorate (Alfa Products) in triply distilled demineralized water. To satisfy the current requirements of the platinum cathode in this cell, a small amount of Alfa Products silver oxide (99% pure) was added to the cathode compartment.

Samples consisted of weighed quantities of Standard Reference Material 83c arsenious oxide with an NBS certified assay of 99.99%. These were dissolved in 30% sodium hydroxide solution prepared from Apache Chemicals 99.999% pure sodium hydroxide.

The pH-7 titrant solution, prepared from reagent grade chemicals, was 0.1*M* with respect to potassium iodide, and 0.5*M* with respect to both potassium phosphate and sodium phosphate.

Oxygen was removed throughout the titration with purified nitrogen passed over hot copper and bubbled through a flask containing the titrant solution before entering the cell. The solution in the silver-anode compartment was deoxygenated by passage of prepurified nitrogen.

Procedure

Treatment of silver anodes. The silver anodes were etched in concentrated hydrochloric acid to remove metallic impurities and then, after rinsing, in 10% ammonia solution to remove any surface film. After rinsing, the anodes were dried in a vacuum oven for 1 hr at 100°. Before evacuation, the oven was flushed with a stream of prepurified nitrogen.

The dried silver was cooled under nitrogen in a desiccator.

Plastic gloves were worn and polythene tweezers were used for manipulating the anodes. Sediment collected in the crucible during titration was dried for 1 hr in an oven at a temperature of about 100° under a continuous slow stream of nitrogen.

Arsenious oxide samples. The arsenious oxide was dried at 110° and cooled in a desiccator. The samples were weighed into small Pyrex bottles, which had been cleaned with warm "Ultrex" nitric acid (1 + 1). Samples of 0.05, 0.10, 0.25 and 0.50 g were titrated after being dissolved in 1.0, 1.0, 1.5, and 2.5 ml of sodium hydroxide solution respectively.

Coulometric titration. The potassium iodide solution was pretitrated to react substances capable of reducing the iodine generated. A blank consisting of the same quantity of sodium hydroxide solution as that used to dissolve the sample of arsenious oxide was also titrated. The Pyrex bottle containing the dissolved sample was then added to the titration-cell compartment. Following stirring and bubbling of nitrogen through the solution, a stream of nitrogen was allowed to pass through the cell and the titration of the sample was begun. A generating current of 25 mA was employed. When nearly all the iodine required was generated the current was stopped and the intermediate compartments of the cell were purged (by using nitrogen pressure and vacuum), to ensure titration of all the arsenic present.

Calculation

The appearance of the successive end-points obtained is shown diagrammatically in Fig. 3. The total weight loss of the silver anode less the weight of sediment collected gives the amount of silver lost during the pretitration, blank titration, and sample titration. The total time (t) minus I, II, and IV, the times required for pretitration, blank titration and the post-end-point generation gives the time required for titration of the sample (III). The fraction of total time that is required for the sample-titration is related to the number of equivalents of arsenic by

$$\frac{t - \mathrm{I} - \mathrm{II} - \mathrm{IV}}{t} \times \frac{\text{Ag anode weight loss} - \text{Ag sediment weight}}{107.868\ \mathrm{g}} = \text{equivalents of arsenic titrated} \quad (7)$$

The standard deviation for a given set of results was calculated by the root-mean-square formula and is recorded in Table 1. Confidence limits were deter-

Table 1. Results for titration of As_2O_3 samples

Sample weight, g	Sample	Assay, % As_2O_3	
		Gravimetric integration	Mathematical integration
0.05	1	100.00_6	100.00_4
	2	100.03_1	100.02_5
	3	99.85_8	99.84_2
	4	100.09_3	100.06_6
	5	100.00_3	99.99_9
	6	99.99_3	99.99_7
	7	99.98_0	99.97_6
	Average $99.99_4 \pm 0.07_1$		$99.98_7 \pm 0.07_9$
	$R = 0.23_5$		$R = 0.22_3$
0.10	1	99.992_1	99.996_0
	2	99.986_9	99.983_2
	3	99.990_3	99.987_3
	4	99.972_6	99.971_0
	5	99.993_4	99.989_0
	6	100.063_6	99.998_5
	7	100.009_4	99.996_2
	8	99.934_8	99.988_4
	Average $99.992_9 \pm 0.009_6$		$99.988_7 \pm 0.008_9$
	$R = 0.128_8$		$R = 0.027_5$
0.25	1	99.994_0	99.992_3
	2	99.995_6	99.991_0
	3	99.989_3	99.980_2
	4	99.998_3	99.990_8
	5	99.997_0	99.993_2
	6	99.991_4	99.998_1
	Average $99.994_3 \pm 0.003_4$		$99.989_3 \pm 0.004_7$
	95% Confidence limits $99.994_3 \pm 0.003_6$		$99.989_3 \pm 0.004_9$
	$R = 0.010_0$		$R = 0.013_0$
0.50	1	99.995_8	99.993_3
	2	99.993_0	99.989_5
	3	99.996_3	99.994_2
	4	99.990_2	99.989_1
	5	99.994_3	99.990_3
	Average $99.993_9 \pm 0.002_5$		$99.9913 \pm 0.002_4$
	95% Confidence limits $99.993_9 \pm 0.003_1$		$99.991_3 \pm 0.003_0$
	$R = 0.005_6$		$R = 0.005_1$

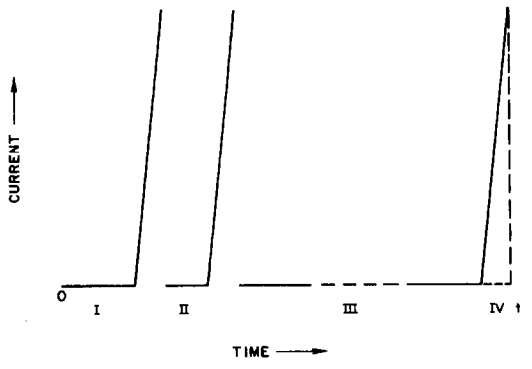

Fig. 3.

mined by the Student t-test. The range R for a set of results is also included in the table. The Q-test was applied to ascertain the validity of any questionable result. As mentioned, the gravimetric results were found to be slightly higher than the mathematical results. The variance ratio or F-test indicates that there is no statistically significant difference between the two sets of results for a given sample size.

RESULTS

Results of titrations of various sample sizes are given in Table 1. A detailed presentation of experimental data is included in Table 2 for the 0.25-g samples.

As indicated in Table 1, an understandable enhancement of precision was obtained by increasing the sample size from 0.05 g to 0.25 g, but this was not as noticeable when the size of sample was increased from 0.25 g to 0.50 g. It is possible that under the conditions of the experiment the limit of precision is being approached. There are several possible limiting factors, including a limitation in the precision of current delivery and a limitation in the precision with which the end-point may be determined. In order to avoid introduction of another variable it was desired to maintain the same generating current throughout rather than to decrease the current in the region of the end-point, as is usually done so that the end-point may be approached more slowly.

At this level of precision inhomogeneity of the arsenious oxide sample could manifest itself. The arsenious oxide generally floats on the surface of sodium hydroxide solution, sometimes being surrounded by an air bubble, revealing the possibility of surface adsorption of gases.

As shown in Table 2, the amount of silver lost as sediment is quite variable. Combined with the possibility of some oxidation of the fine silver particles during drying, this may introduce another non-reproducible variable. Impurities in the silver anodes, weighing errors, manipulation of the cells, losses of arsenic through volatization, and air-oxidation of the iodide solution constitute additional sources of error.

The gravimetric and current-integration results obtained in this work are in good agreement, indicating that the assumption of constant current in equation (7) is reasonable. In general the gravimetric value is larger than the one obtained by integration. This may reflect incomplete recovery of small particles of silver, leading to an error in the measured weight loss. Another factor which may contribute to this apparent error is the dependence of the result on the accuracy of the atomic weight of silver.

The integration value presented here for the assay of NBS 83c arsenious oxide, is in reasonably good agreement with that obtained previously by non-gravimetric high-precision coulometric analyses ($99.986_1 \pm 0.003_2$ for 0.5-g samples).[6]

CONCLUSION

High-precision gravimetric coulometry appears to be a useful alternative to current–time integration for high-precision coulometric titrations. It has the advantage that the experimenter need not continually monitor the generating current, provided a suitably precise current-source is available. Measurements of mass and time are required, both of which may be made with considerable certainty.

The accuracy is ultimately limited by the purity of the silver and the accuracy of its atomic weight, but for the sample sizes used, the accuracy of weighing is at least as important a limiting factor. Weighing errors become less significant and the inaccuracy of the atomic weight of silver becomes more important as the sample size is increased. The error introduced

Table 2. Data for titration of 0.25-g As_2O_3 samples

Sample	As_2O_3, g	Anode weight loss, g	Anode sediment weight, g	Faradaic weight loss due to titration of As(III), g	Assay, %
1	0.252778	0.555955	0.000788	0.555167	99.994_0
2	0.255802	0.560716	0.002951	0.557765	99.995_6
3	0.255273	0.556665	0.001198	0.555467	99.989_3
4	0.252791	0.557970	0.005564	0.552406	99.998_3
5	0.250450	0.555097	0.001671	0.553426	99.997_0
6	0.250876	0.551603	0.000893	0.550710	99.991_4

Average $99.994_3 \pm 0.0034$.

by uncertainty of the atomic weight of silver (which is in a sense a chemical standard) would be eliminated in stoichiometry determinations if all the constituents could be determined by coulometric titration with the silver–perchloric acid coulometer and silver anodes from the same batch.

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PERCHLORIC ACID DISSOLUTION OF GRAPHITE AND PYROLYTIC CARBON

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Summary—Three procedures are described for the wet oxidation, with perchloric acid, of nuclear graphite, pyrocarbon-coated fuel particles, and other carbonaceous materials used in high-temperature gas-cooled nuclear reactors (HTGRs). The first procedure is for dissolution of graphite and pyrolytic carbon, the second for dissolution of milligram quantities of HTGR fuel particles, and the last for dissolution of more easily oxidized carbonaceous materials such as charcoal. These procedures were developed primarily for the dissolution of irradiated materials before fission-product or burn-up analyses, but they are also used for dissolution of unirradiated materials.

Large numbers of samples of irradiated pyrocarbon-coated fuel particles and samples are analysed for fission products and burn-up of heavy metals in support of high-temperature gas-cooled reactor (HTGR) programmes.

Dissolution of these materials is difficult because they are not soluble in the common acids. The graphitic and other carbonaceous material can be burned off in a furnace and the resulting ash dissolved for analysis, but dry-ashing can lead to losses of volatile fission products such as caesium. Other losses arise from the retention of some trace elements on the crucible.

Of the wet-ashing techniques studied at the General Atomic Company, only those procedures employing perchloric acid have been effective. Though mixtures of nitric and sulphuric acids have been used for the dissolution of many organic materials, this combination was found to be ineffective in the dissolution of graphite. The presence of sulphuric acid can also lead to the formation of insoluble precipitates, such as barium and strontium sulphates, which are troublesome in the subsequent analytical procedures.

Gorsuch[1] studied several different wet-oxidation and dry-ashing techniques used in the analysis of organic material for trace elements. He used radioactive tracers to determine the recovery of Pb, Hg, Zn. Se, As, Cu, Co, Ag, Sb, Mo, Cr, Cd, Sr and Fe from cocoa. Several wet oxidation and dry ashing methods were examined for each of the 14 elements listed. Cocoa was used as the organic material because it is available in large quantities, samples are likely to be homogeneous, and it contains several types of organic materials, including fat, which is known to be resistant to oxidation. Gorsuch concluded that the only generalization to be made from his work was that the wet oxidation of organic material with nitric and perchloric acids was the most satisfactory means for the recovery of all the elements studied, except mercury. He used a modified version of the Bethge[2] apparatus for the wet oxidations with perchloric acid.

Smith[3] described wet-oxidation techniques using perchloric acid for a large number of materials, including some organic acids, cellulose, a variety of foodstuffs, ion-exchange resins and motor oil. He alsc discussed the use of catalysts, such as vanadium and chromium, in the oxidation of some materials.

Another paper by Smith[4] dealt with the oxidation of organic matter with perchloric acid at graded oxidation potentials and controlled temperatures. He estimated the oxidation potential of boiling 50% perchloric acid to be 0.8–0.85 V. For boiling 73.6% perchloric acid ($HClO_4 \cdot 2H_2O$), he estimated the potential to be at least 2.0 V. A table relating the boiling point to the perchloric acid concentration was included.

Diehl and Smith[5] reported on the use of mixed perchloric and sulphuric acids for the oxidation of organic matter. They used a modified Bethge apparatus to achieve controlled temperatures and graded oxidation potentials. With the stop-cock open between the flask and the collector, the solution refluxes and the acid concentration remains essentially constant. With the stop-cock closed, the condensed vapours are collected in the reservoir above the stop-cock. This leads to an increase in the acid concentration in the flask and an increase in the boiling point of the solution. The collected condensate can be drained off through the side-arm. By repetition of this operation, the boiling point can be increased stepwise.

SAFETY CONSIDERATIONS

Numerous instances of the detonation of mixtures of hot concentrated perchloric acid and carbonaceous material have been recorded. The purpose of this report is to present stepwise procedures for the dissolution of graphite and certain other carbonaceous materials without danger to individuals in the laboratory.

Chapter 11 of Schumacher's book[6] deals with safety considerations in handling perchloric acid and

perchlorates. A short article on the handling of perchloric acid in analytical work has also been published.[7]

The present paper includes procedures for the following types of samples: macrosamples of graphite and pyrocarbon; carbonaceous material other than graphite; samples in the milligram range, such as individual fuel particles.

It is essential to know the nature of a sample before attempting a wet oxidation with perchloric acid. Applying the procedure for the wet oxidation of graphite to material other than graphite will probably result in an explosion.

Certain materials such as ethyl alcohol form explosive compounds with perchloric acid. Strong dehydrating agents such as sulphuric acid and phosphorus pentoxide can lead to the formation of anhydrous perchloric acid, which reacts explosively with many substances and is itself unstable, exploding spontaneously on standing. Even the use of perchloric acid with metals must be approached with caution: the treatment of bismuth with perchloric acid has been reported to result in explosions.[8]

Wet oxidation techniques for new materials should be tested on milligram samples behind blast shields.

EXPERIMENTAL

The procedures described are specific for the wet oxidation of graphitic samples and non-graphitic types such as charcoal, pitch and organic chemicals. It is imperative to characterize the sample before attempting the most vigorous perchloric acid oxidation. If characterization is uncertain, proceed with the less vigorous oxidation method prescribed for the non-graphitic samples.

Graphite (including pyrolytic carbon) requires very vigorous oxidation conditions for dissolution. The oxidation rate depends on the acid concentration and the temperature of the sample. If the sample is allowed to go to incipient dryness on heating, the sample temperature will rise rapidly, accelerating the reaction rate and frequently leading to an explosion. The oxidation reaction rate can be controlled by keeping an excess of acid in contact with the sample and thus limiting the temperature of the reactants.

The oxidation apparatus consists of an Erlenmeyer flask fitted with a Soxhlet extractor and an air-condenser (Fig. 1). All joints are standard-taper ground glass. The sample and the acid are placed in the flask. The Soxhlet extractor collects the condensed acid and periodically returns it to the flask. This greatly reduces the amount of acid to be added during dissolution and also minimizes the amount of acid passing into the atmosphere. Alternatively a modified reflux collector[2] allows a more convenient removal of the condensate after digestion is complete. The condensate should be removed at reduced heat. The reflux condenser would require an appropriate ground-glass fitting to accommodate the Vigreux air-condenser.

The amount of acid prescribed exceeds the stoichiometric quantity, because of the volume needed to operate the Soxhlet siphon (~25 ml). The minimum volume of perchloric acid to be added should take into account this volume and the sample size. The reaction will consume approximately 4 ml of perchloric acid per gram of graphite. Fuming nitric acid is added initially to destroy any easily oxidizable material (carbon, binder, *etc.*) and to limit the temperature to that of boiling nitric acid.

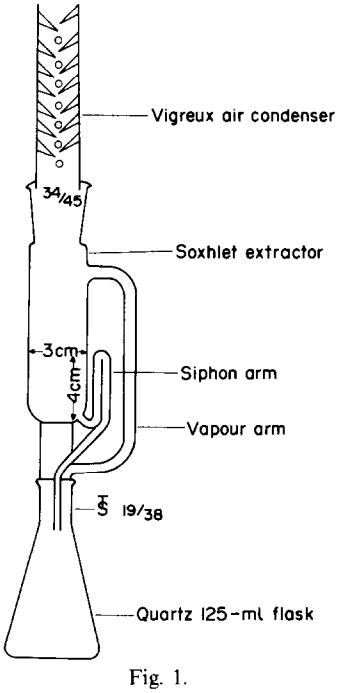

Fig. 1.

Wet oxidation of gram quantities of graphite and pyrocarbon

The method described is for graphite samples of up to about 3 g. Samples substantially larger than this should be dissolved in a 250-ml flask.

Reagents. Perchloric acid, reagent grade, assay 70%; fuming nitric acid, reagent grade, assay 90%.

Apparatus. See Fig. 1 for assembly. The reaction vessel is a quartz Erlenmeyer flask, 125 ml for samples of 1–3 g (19/38 standard taper joint) or 250 ml for samples >5 g (24/40 joint). The Soxhlet extractor has a capacity of about 25–30 ml (50 ml for use with a 250-ml flask). The air-condenser is of Vigreux type with standard taper joint (34/45). A Corning RC 100, 12 × 12 in. hot-plate has been found to be suitable, and will accommodate up to five dissolution assemblies. This unit has a remote Variac control for remote adjustment of temperature.

The fume-cupboard should be made of stainless steel and have a hanging safety glass shield and safety window. There should be no *plastic* or *organic* material in the work area. A piece of transite* on the bottom of the fume-cupboard is satisfactory. The work area should contain only the hot plate(s) and dissolution assemblies (and support stands if necessary). Any chemicals to be added may be brought to the fume-cupboard during the cool phase of the oxidation.

Caution. This procedure is to be used for graphite dissolution *only* and involves a potential hazard. Any manipulations should be performed only when the reaction flask has cooled to about 100°. A thermometer in an Erlenmeyer flask of sulphuric acid placed on the hot-plate along with the samples can be used as temperature-monitor.

Procedure. Pipette into the flask any carriers required for hold-back or subsequent chemistry. Place the sample in the flask and add 5 ml of fuming nitric acid and 50 ml of perchloric acid. Use appropriately more acid for large samples, say 5 ml per g of graphite. Assemble the dissolution apparatus as shown in Fig. 1. Place the assembly on the hot-plate and secure by clamping to a support stand. Set the hot-plate temperature-control to 140–150°. Set the hanging safety shield in place and lower the fume-cupboard safety shield. After the first hour increase the

* Transite is a trademark (John Mansville Corp.) for a compressed asbestos board, and other products.

temperature to 180–190°. Allow the dissolution to proceed until complete. Note the distillation rate of the acid and the volume remaining. Some acid will be consumed for the dissolution, and a small amount may escape. It is imperative to have excess of acid in the flask at all times. When the graphite is entirely oxidized, as indicated by a completely clear solution, collect the excess of acid in the extractor by turning off the hot-plate when the acid level in the extractor is approaching the top of the siphon arm. When the system has cooled to 100° or below, remove the extractor portion of the apparatus and carefully drain the acid into a beaker by means of the siphon. Replace the extractor and turn on the hot-plate to collect more acid if necessary. Turn off the heat; allow to cool. Carefully remove the entire assembly from the hot-plate. The solution in the flask is now ready for further chemistry.

Wet oxidation of milligram samples of fuel particles

Burn-up and fission-product analyses are run on very small samples (1–10 mg) of irradiated fuel particles. These fuel particles are sometimes embedded in a graphite matrix. To effect complete dissolution of the sample, the fuel particles must be pulverized. The following procedure has been developed for the dissolution of this kind of sample.

If the sample contains more than 10 mg of graphite, use the procedure above to dissolve the graphite. Cool, and remove the fuel particles with a disposable transfer pipette. Transfer the particles to a centrifuge tube prepared as described below. If the fission-product content of the matrix graphite is of interest, reserve the perchloric acid solution from the graphite dissolution step.

Apparatus. Plain 40-ml centrifuge tubes (*e.g.*, Corning 8320) are used. Stirring-rods 1/8-in. in diameter are made with rounded ends that fit reasonably well into the conical tip of the centrifuge tube. The tip of the tube is ground and polished with the stirring rod, with the aid of a few mg of 200/400 mesh silicon carbide powder and several drops of alcohol, to produce a good fit of the stirring rod and the conical bottom of the tube. This small grinding surface enables the analyst to grind fuel particles quickly.

The sand-bath used is filled with 100/200 mesh alumina. This provides a white background for viewing the crushed particles. A convenient size of bath is made from a 150-mm diameter Pyrex culture dish filled to a depth of 2 in. with alumina.

The centrifuge tube and stirring rod are cleaned with a dilute detergent solution, then leached with several ml of perchloric acid and a drop of 0.1*N* hydrofluoric acid. The tube is heated in the sand-bath for about 20 min with the stirring rod in place, then removed, cooled and rinsed thoroughly with demineralized water.

Procedure. Transfer the fuel particle sample to a centrifuge tube. Add any carriers needed for subsequent chemistry. Add 3 ml of 70% perchloric acid and 2–5 drops of fuming nitric acid. Place the tube in the sand-bath. Crush the particles by applying pressure on the stirring-rod and rotating it. Lift the rod and allow the debris to settle into the tip of the tube. Continue grinding until all the particles are crushed and pulverized. The fuel will dissolve readily in the acid solution. Dissolution of the graphite is accelerated if it is finely ground. Place the sand-bath on the hot-plate. Lower the fume-cupboard window and turn the hot-plate control to give maximum temperature. Heat until all visible traces of graphite dust are dissolved. Turn off the hot-plate and allow the sample to cool.

Wet oxidation of non-graphitic carbonaceous material

Non-graphitic material such as charcoal, filter paper, pitch, and organic chemicals can be dissolved by wet oxidation or dry-ashing followed by acid dissolution of the ash. The dry-ashing technique is recommended where applicable. The wet oxidation should be reserved for those cases where dry ashing would probably lead to losses of the elements of interest.[1] These materials are more easily oxidized than is graphite and therefore do not require as vigorous a treatment to effect dissolution. Organic solvents can be evaporated to dryness and the residue treated as charcoal or pitch.

The following method can be used for samples weighing several grams.

Procedure. Place the sample in a 250-ml quartz Erlenmeyer flask with a standard taper joint. (Larger or smaller size flasks can be used depending on sample size.) Use an air condenser, Vigreux or straight tube, to serve as a reflux column (an 8–10 in. length of tube is adequate). Add any carriers required for subsequent chemistry, and 20–30 ml of fuming nitric acid in 10-ml portions. Make sure the entire sample is wet and covered with the acid. Swirl the flask gently. Organic matter such as filter paper or cloth will generally disintegrate. Cover the opening of the reflux column with a small "speedy-vap" or watch glass and set the apparatus on the hot-plate. Set the hot-plate control to give a temperature of 100–120°. Allow the dissolution to proceed until complete. It may be necessary to add more acid in the case of charcoal or some organic chemicals. If this is necessary, turn off the hot-plate and allow the vessel to cool for about 10 min. Add more acid as needed.

In the case of charcoal and some other more resistant materials it may be necessary to complete the dissolution by using the perchloric acid procedure. Turn off the heat, allow to cool, remove the condenser, add sufficient perchloric acid to digest the remaining material and to operate the Soxhlet siphon. Assemble the apparatus as in Fig. 1 and proceed with the wet oxidation method for graphite and pyrocarbon.

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DETERMINATION OF HALIDE IONS BY CATHODIC STRIPPING ANALYSIS

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Summary—The determination of halide ions in aqueous solution by cathodic stripping analysis is discussed. It is shown that a linear response is obtained over the concentration range 2×10^{-5}–$10^{-3}M$ for solutions containing only a single halide and that mixtures of halides can usually be analysed. Other interferences are also considered.

While anodic stripping voltammetry has become a familiar technique for the estimation of low levels of metal ions in solution, the equivalent method for the determination of anions, cathodic stripping voltammetry, has received little attention. Indeed there are only a few papers, published several years ago, which describe the determination of trace quantities of a single anion in solution, *e.g.* halides[1–7] and organic sulphur anions;[8] there are also reviews.[9,10] In cathodic stripping analysis the anion to be determined is accumulated at the surface of the electrode, normally silver or mercury, by formation of a layer of the corresponding insoluble metal salt during a pulse towards anodic potentials and the measured parameter is usually the charge needed to strip this layer.

In the period since the publication of the papers mentioned there have been considerable advances in both instrumentation and our understanding of the nucleation and growth processes by which the insoluble layer is formed. It is therefore considered timely to re-examine cathodic stripping voltammetry as a method of analysis for anions. In this paper we report an investigation of the use of a mercury electrode in cathodic stripping analysis for chloride, bromide and iodide, singly or in mixtures. The analyses possible are compared with those claimed for ion-selective electrodes.

EXPERIMENTAL

All solutions were prepared from analytical-grade reagents and triply distilled water. The mercury was also triply distilled. The glassware was cleaned before use by treatment with chromic acid followed by prolonged washing with distilled water.

The experiments were done in a three-electrode, two-compartment cell. The working electrode was a sitting mercury drop formed on a vertical capillary above a syringe operated by a micrometer screw gauge. By means of the micrometer the size of the mercury drop electrode could be made reproducible; the diameter of the drop was measured with a travelling microscope. The auxiliary electrode was a platinum spiral round the working electrode and the reference electrode was a Radiometer type K 401 saturated calomel electrode in a compartment separated from the working electrode by a Luggin capillary. All experiments were carried out in unstirred solution at $19 \pm 2°$. Solutions were deaerated with oxygen-free nitrogen.

Potential pulse and sweep experiments were performed with a Chemical Electronics Valve Potentiostat and Waveform Generator type RB1. To carry out the potential step followed by a sweep, two waveform generators and a purpose-built summing amplifier were employed. Curves of current *vs.* potential and time were recorded on a Hewlett Packard 7035B *x–y* recorder and a Hewlett Packard 1201A memory oscilloscope respectively. Charges associated with the stripping of the mercurous halides were measured with a Hi-Tek Instruments Gated Integrator, triggered by the pulse generator.

RESULTS AND DISCUSSION

Preliminary studies

Figure 1 shows a cyclic voltammogram for $10^{-4}M$ bromide in $1.0M$ sodium perchlorate at a mercury drop electrode; the major features are an oxidation wave, $E_p = +0.17$ V, for the process[11–15]

$$2Hg + 2Br^- \rightarrow Hg_2Br_2 + 2e$$

and a sharp reduction peak, $E_p = +0.06$ V, for the reverse process during the sweep towards negative potentials. In addition to its shape, the reduction peak has all the other characteristics corresponding to a surface process; for example in a series of experiments where the electrode potential was kept for a fixed period at a value at which mercurous bromide is formed and was then swept linearly and rapidly towards negative potentials, the peak current was proportional to scan-rate. Furthermore integration of the anodic and cathodic currents with respect to time on the cyclic voltammogram showed that the charges associated with the formation and removal of the mercurous bromide were equal and hence that all the mercury oxidized remained at the surface as an insoluble mercurous salt.

Similar experiments with chloride and iodide gave the same sort of results except that the potentials for formation and stripping of the mercurous halides were different, see Table 1. These differences immediately suggested the possibility of basing a discriminating analytical method on a double-potential-step technique involving formation of the mercurous halide(s) during a pulse of fixed duration, and strip-

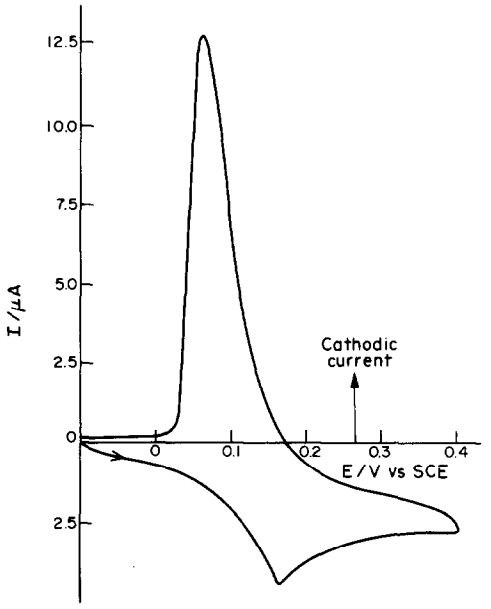

Fig. 1. Cyclic voltammogram of $10^{-4}M$ bromide in $1M$ sodium perchlorate at a mercury electrode. Potential scan-rate 0.03 V/sec.

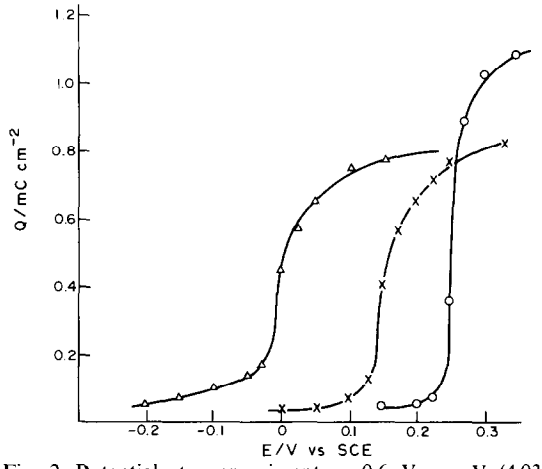

Fig. 2. Potential step experiments -0.6 V$\rightarrow x$ V (4.03 sec)$\rightarrow -0.6$ V. Plots of the charge for stripping mercurous halide, Q, *vs.* potential at which the surface layer of the mercurous halide was formed: $5 \times 10^{-4}M$ halide in $1.0M$ sodium perchlorate. ΔI^-, $\times$ Br^-, $\circ$ Cl^-.

ping during a second pulse; under suitable experimental conditions the charge associated with the reduction process should be proportional to the amount of halide ion reaching the surface of the electrode during the first pulse.

It has already been shown[14] that the formation of mercurous chloride on a mercury anode occurs by successive nucleation and two-dimensional growth of layers of calomel. Potential-step experiments were carried out over a range of potentials, for both iodide and bromide solutions; rising and multipeak transient signals were obtained on the current *vs.* time curves. These were not analysed in detail but it is clear that these mercurous halides are also formed by nucleation and growth mechanisms.

From an analytical viewpoint it may be noted that two important experimental parameters are the potential at which the mercurous halide is formed and the potential at which it is stripped. These were investigated separately, first for solutions containing only a single halide. In the first set of experiments the pulse profile -0.6 V$\rightarrow x$ V (4.03 sec)$\rightarrow -0.6$ V was employed and the charge for the stripping process at -0.6 V was measured and plotted *vs.* the potential (x) at which the mercurous halide was formed. The results of these experiments are shown in Fig. 2. The rising portions of these curves represent the range of potential over which the rate constants for the nucleation and growth processes[16,17] are increasing as the potential is made more positive, whereas in the plateau regions the rate of nucleation and growth is fast compared with mass transport, *i.e.*, the reactions are diffusion-controlled. It may be noted that well-formed plateau regions are observed (in contrast see ref. 5) and that for the same concentration of chloride, bromide and iodide, the charges in the plateau regions are approximately the same. Moreover it is clearly possible, at least for these concentrations, to define potentials where mercurous iodide is formed at a rate determined by the diffusion of iodide ion but the bromide and chloride are not formed, and so on.

Table 1. Cyclic voltammetric data (scan rate 0.03 V/sec) for $10^{-4}M$ solutions of halides in $1.0M$ sodium perchlorate (potentials *vs.* S.C.E.)

	E_p^{OX}, V	E_p^{RED}, V
Cl^-	0.32	0.23
Br^-	0.17	0.07
I^-	-0.05	-0.16

In the second set of experiments the potential profile was -0.6 V$\rightarrow +0.3$ V (4.03 sec)$\rightarrow x$ V and this time the charge for the stripping process was plotted *vs.* the potential at which the stripping took place, see Fig. 3. Again, in the plateau regions, where complete stripping occurs, the charges for all three halides are similar and in each case equal to the charge for the deposition of the halides (Fig. 2).

Both sets of experiments were repeated with solutions containing all three halides and the results are presented in Fig. 4. The comparison of the result with those in Figs. 2 and 3 is of particular importance. It can be seen that (*a*) the potentials at which the precipitation of each halide occurs and (*b*) the charges in the plateau regions are the same for the solutions of a single halide and for the mixture. Hence it may be concluded that there are no primary or secondary (*e.g.* formation of solid solutions) interference effects in the growth or stripping of the mercurous halides. It should also be noted that the stripping waves for chloride and bromide overlap considerably.

The results in Figs. 2–4 would suggest that the following determinations should be possible by use of

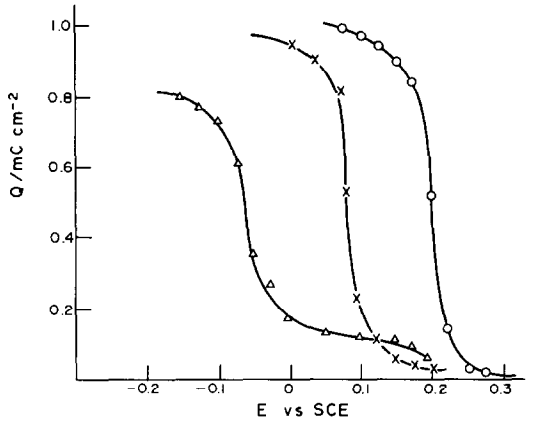

Fig. 3. Potential step experiments -0.6 V $\rightarrow +0.3$ V (4.03 sec) $\rightarrow x$ V. Variation of the charge for the (partial) stripping of the mercurous halide, with potential: $5 \times 10^{-4}M$ halide in $1.0M$ sodium perchlorate. ΔI^-, $\times$ Br^-, O Cl^-.

this cathodic stripping technique:

(*i*) Cl^-, Br^- and I^- in solutions containing only a single halide;

(*ii*) I^- in the presence of excess of Br^- or Cl^-, and Br^- in the presence of excess of Cl^-, by control of the potential in the formation of the mercurous halide;

(*iii*) Br^- in the presence of excess of Cl^- and I^-, and Cl^- in the presence of I^-, by careful control of both the formation and stripping potentials; the tolerance of the chloride determination for bromide will always be low and this determination is probably best carried out by a difference technique using two different deposition potentials such that both halides are deposited at the one, but only one of them at the other.

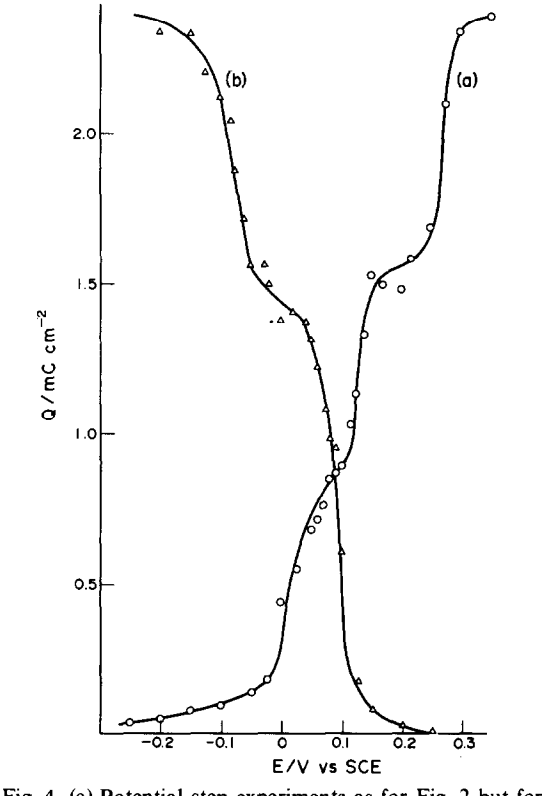

Fig. 4. (a) Potential step experiments as for Fig. 2 but for a solution $5 \times 10^{-4}M$ in each halide (I^-, Br^- and Cl^-), in $0.1M$ sodium perchlorate. (*b*) Potential step experiments as for Fig. 3 but for a solution $5 \times 10^{-4}M$ in each halide in $1.0M$ sodium perchlorate.

Analysis of solutions of a single halide

Suitable potentials for the pulse sequence were chosen from Figs. 2 and 3, and plots of the charge for the stripping reaction *vs.* concentration (over the range 2×10^{-5}–$10^{-3}M$) were constructed for each of the halides. It was found that the relationships between charge Q (C/cm^2) and concentration C (M), were linear and could be represented by the equations

(*i*) iodide: pulse sequence -0.6 V $\rightarrow +0.25$ V (0.4 sec) $\rightarrow -0.6$ V; $10^3Q = 0.46 \times 10^3C + 0.021$; correlation coefficient 0.997

(*ii*) bromide; pulse sequence -0.6 V $\rightarrow +0.4$ V (4.03 sec) $\rightarrow -0.6$ V; $10^3Q = 1.49 = 1.49 \times 10^3C +$ 0.44; correlation coefficient 0.997

(*iii*) chloride; pulse sequence -0.6 V $\rightarrow +0.4$ V (4.03 sec) $\rightarrow -0.6$ V; $10^3Q = 1.30 \times 10^3C + 0.50$; correlation coefficient 0.998.

Changes in the length of the deposition pulse (1 msec–40 sec) and the formation and stripping potentials (provided these were in the plateau regions) had little effect on the linearity of the response. To check the reproducibility, the charge was determined several times at each concentration; typically the measurements were reproducible to within 5% at all concentrations, and much of this variation is probably due to slight irreproducibility in the size of the sitting mercury drop; there is no doubt that the results would be improved by use of a timing circuit and a slowly dropping mercury electrode.

The limits of these plots do not represent the limits of the experimental technique, and by variation of the length of the deposition pulse it is possible to carry out analysis over the range 5×10^{-6}–$10^{-2}M$. Unlike the anodic stripping voltammetric determination of metal ions, however, the lowest detection limit for this analytical procedure cannot necessarily be lowered further by increasing the duration of the deposition pulse or by stirring the solution, because the formation of the mercurous halide layer requires both a nucleation and growth process. There is no certainty that nucleation will occur within the accessible potential range, in very dilute solutions of halide ions.

Analysis of mixtures of halides

The interference of bromide and chloride in the determination of iodide was investigated by determining $5 \times 10^{-4}M$ iodide in the presence of various amounts of the other halides, the optimum pulse profile being chosen on the basis of Fig. 4. The results for bromide ion are shown in Table 2 and it can be seen that the analysis for iodide was only slightly affected by the presence of an equal concentration

Table 2. Determination of $5 \times 10^{-4}M$ iodide in the presence of bromide [potential profile -0.6 V$\rightarrow +0.03$ V (4.03 sec)$\rightarrow -0.60$ V; the experiments were repeated 6 times]

$[Br^-]$,M	Mean charge, mC/cm^2	Std. devn., mC/cm^2
0	0.69	0.012
5×10^{-5}	0.65	0.018
5×10^{-4}	0.67	0.014
5×10^{-3}	0.84	0.048

of bromide but there was considerable error in the presence of tenfold concentration. This is to be expected since the wave for bromide in the charge–potential curve will move to more negative potentials with increasing concentration. The tolerance to chloride ion was substantially better and $10^{-2}M$ chloride ion did not interfere.

The possibilities for the determination of bromide and chloride in the presence of the other halides were investigated only for a solution containing each halide at $5 \times 10^{-4}M$ concentration. The analysis for bromide ion was attempted by choosing a potential profile such that mercurous bromide and iodide were formed during the first pulse and in the second pulse the mercurous bromide was stripped but the mercurous iodide was neither stripped nor further formed; the profile employed was -0.6 V$\rightarrow 0.225$ V (4.03 sec)$\rightarrow -0.025$ V. The charge for $5 \times 10^{-4}M$ bromide in the mixture was 0.603 mC/cm^2, and for the same profile applied to a solution containing only bromide it was 0.599 mC/cm^2.

The chloride analysis was carried out by the difference method since no potential could be found at which chloride was stripped but bromide was not. The profiles employed were -0.6 V$\rightarrow +0.2$ V (4.03 sec)$\rightarrow -0.6$ V and -0.6 V$\rightarrow +0.3$ V (4.03 sec)$\rightarrow -0.6$ V. The differences in the stripping charges should give the quantity of chloride in solution. The charge determined was 0.98 mC/cm^2 compared to 1.04 mC/cm^2 for the profile -0.6 V$\rightarrow 0.3$ V (4.03 sec)$\rightarrow -0.6$ V for a solution containing only chloride.

Hence it would seem that for similar concentrations of halides the cathodic stripping technique can be used to determine all three components provided a suitable set of pulse profiles is employed.

Other interferences

The only species which are likely to interfere seriously are other anions which form insoluble mercurous salts, metal ions which complex the halides, or species which are oxidizable at a mercury anode at the slightly positive potentials used and form a stable soluble product reducible at the potential of the second pulse. This latter category is unlikely to be important and such interferences could in any case be overcome by introduction of a null period between the formation and stripping of the mercurous halide (*i.e.*, a period on open circuit to allow the interfering species to diffuse away from the electrode). Metal ions are unlikely to cause severe interference unless present in high concentration, and any interference could probably be overcome by masking.

The first class of interferents was investigated although it was thought that they could be predicted from a table of solubility products. With $10^{-4}M$ chloride as a model system, it was shown that the addition of perchlorate, nitrate, phosphate and sulphate in $0.1M$ concentration did not interfere in any way. Hydroxide interfered at high concentrations and the technique worked best at pH below 11. Sulphide caused serious interference even when present at $10^{-4}M$.

Comparison of cathodic stripping analysis and ion-selective electrodes

Perusal of the advertising literature supplied by Orion Research Inc.[18] indicates that the lowest detection limits for their halide-selective electrodes are generally similar to those claimed above for cathodic stripping analysis, but the latter technique has the advantage of fewer interferences and greater tolerance for other anions. For example, the liquid-membrane electrode has a wide range of interferences, and equimolar concentrations of bromide or iodide cause difficulties in the determination of chloride with the solid-state membrane. This has been shown above not to be the case with cathodic stripping analysis.

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SHORT COMMUNICATIONS

A HIGHLY SENSITIVE SPECTROPHOTOMETRIC DETERMINATION OF GALLIUM WITH PONTACHROME AZURE BLUE B AND CETYLTRIMETHYLAMMONIUM CHLORIDE

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Summary—A new spectrophotometric method for the determination of gallium with Pontachrome Azure Blue B and cetyltrimethylammonium chloride is described. The sensitivity of the colour reaction between gallium and Pontachrome Azure Blue B is greatly increased in the presence of cetyltrimethylammonium chloride. The gallium complex has maximal absorbance at 680 nm and pH 6.0–6.6. Beer's law is obeyed over the range 0.08–0.6 ppm of gallium; the molar absorptivity is 1.39×10^5 l.mole^{-1}.cm^{-1} and sensitivity 4.9×10^{-4} μg/cm^2. The mole ratio of the complex, the formation constant and effect of interfering ions are described.

The three spectrophotometric methods most widely used for gallium, the Rhodamine B, Malachite Green, and 8-quinolinol procedures, utilize the colour resulting from the formation of complexes.[1,2] Recently, some spectrophotometric methods for metals based on the formation of a ternary complex on a micelle surface formed in the presence of a quaternary ammonium salt have been suggested.[3–6] Pontachrome Azure Blue B (sodium-2″,6″-dichloro-4′-hydroxy-3,3′-dimethylfuchsone-5.5′-dicarboxylate; Colour Index 43830), a triphenylmethane dye, has been used as a spectrophotometric reagent for beryllium and copper,[7] uranium,[8] and scandium.[9]

It has been found that microgram amounts of gallium react very sensitively with Pontachrome Azure Blue B in the presence of a quaternary ammonium salt. This paper describes a highly sensitive method for the determination of gallium based on the formation of such a coloured complex, cetyltrimethylammonium chloride being used. Several conditions under which microgram amounts of gallium can be determined, influence of diverse ions and the composition of the complex are discussed.

EXPERIMENTAL

Reagents

Standard gallium solution. A stock solution of gallium was prepared by dissolving 0.9899 g of gallium metal (99.999% pure) in dilute hydrochloric acid and then diluting it with distilled water to 1 litre ($1.42 \times 10^{-2}M$). The concentration of hydrochloric acid in this solution was 1*M*. The working solutions were made by suitable dilution of this stock solution as required.

Pontachrome Azure Blue B solution. The dyestuff (PAB) was further purified by recrystallization from methanol before use, and an aqueous 0.1% solution ($1.99 \times 10^{-3}M$) was prepared. The solution was stable for at least 3 weeks.

Cetyltrimethylammonium chloride solution ($3.0 \times 10^{-3}M$ (CTMA). Prepared by dissolving 0.960 g in 1 litre of distilled water.

Buffer solution (*pH* 6.5). Made by mixing 0.3*M* nitric acid and 0.3*M* sodium acetate.

All other chemicals used were analytical-reagent grade.

Apparatus

The absorbance measurements were made on a Hitachi automatic recording digital spectrophotometer, 624 type, with matched 1.00-cm quartz cells. The pH measurements were made with a Hitachi-Horiba glass-electrode pH-meter, model M-5.

Standard procedure

Transfer the sample solution containing 2–15 μg of gallium to a 50-ml Erlenmeyer flask. Add 1.0 ml of the CTMA solution, 1.0 ml of the PAB solution, 5 ml of the buffer solution, and a small amount of water to make the volume about 20 ml. Heat the solution in a water-bath at 60–70° for 10 min. After cooling to room temperature, transfer to a 25-ml volumetric flask, dilute to the mark with distilled water, and measure the absorbance of the solution at 680 nm against a reference solution containing the same amounts of reagents.

RESULTS AND DISCUSSION

Absorption spectra

In Fig. 1 curves A and B show the absorption spectra of PAB and its gallium complex at pH 5.0, respectively, while curves C and D show the effect of the addition of CTMA to these solutions at pH 6.5. The formation of the gallium complex is accompanied by a marked increase in the absorbance and a bathochromic shift in the maximal absorption of the complex from 620 to 680 nm.

In order to observe the spectral changes on varying the pH, absorption curves for the gallium complex were prepared at different pH values; the results are shown in Fig. 2. The maximal absorbance of the gallium complex is found at 680 nm above pH 6, and at shorter wavelength at lower pH.

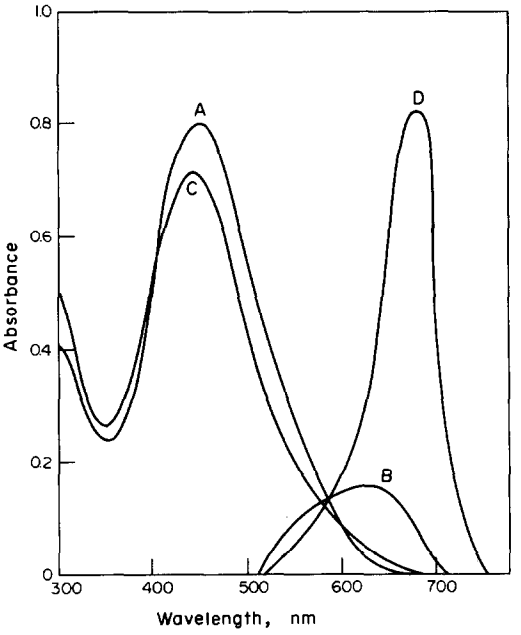

Fig. 1. Absorption spectra of PAB ($8.0 \times 10^{-5}M$) and its gallium complex. (A) Blank for B; $1.16 \times 10^{-5}M$ Ga, pH 5.0, measured *vs.* A; (C) blank for D; (D) $0.58 \times 10^{-5}M$ Ga, $1.2 \times 10^{-4}M$ CTMA, pH 6.5, measured *vs.* C.

Effect of experimental variables

The effect of pH on the absorbance of the gallium complex was examined by measuring the absorbance of the coloured solutions at 680 nm. The results are shown in Fig. 3, from which it can be seen that the maximal absorbance can be obtained in the pH range from 6.0 to 6.6. The reagent blank curve was obtained in the same manner, using the same amounts of reagents. A nitric acid–sodium acetate buffer solution, pH 6.5, was found to be satisfactory for this purpose. The amount of the buffer solution added, over the range from 3 to 15 ml, had no effect on the absorbance measured by the standard procedure.

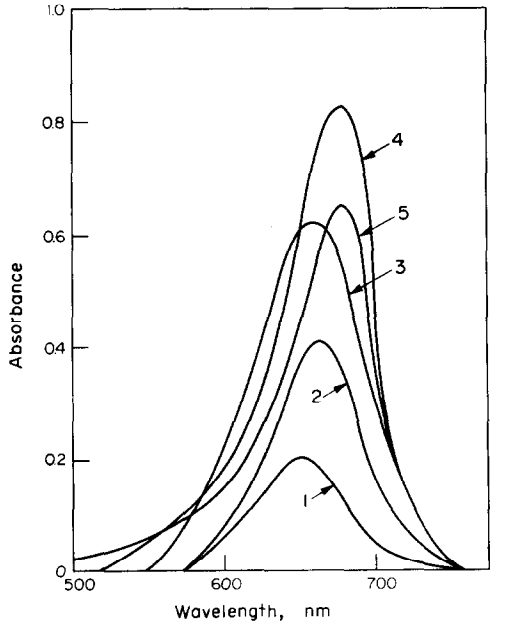

Fig. 2. Absorption spectra of gallium complex at various pH-values. PAB $8.0 \times 10^{-5}M$, Ga $5.8 \times 10^{-6}M$, CTMA $1.2 \times 10^{-4}M$; reference: reagent blank; pH: (1) 3.5, (2) 4.0, (3) 5.2, (4) 6.5, (5) 7.0.

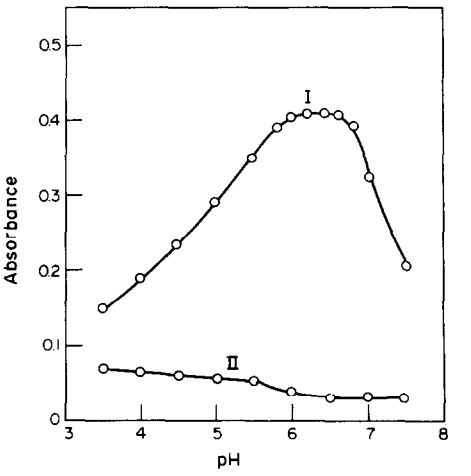

Fig. 3. Effect of pH on colour intensity. I: $8.0 \times 10^{-5}M$ PAB, $1.2 \times 10^{-4}M$ CTMA, $2.9 \times 10^{-6}M$ Ga; reference: reagent blank; II: blank.

The effect of varying the concentration of PAB on the colour development was examined by measuring the absorbance of solutions kept at constant concentration of gallium and CTMA. A 9-fold molar excess of PAB over gallium in a $1.2 \times 10^{-4}M$ CTMA solution was required in order to obtain maximal absorbance. With large excess of PAB, *e.g.* 30-fold molar excess, some precipitate was formed. The optimal amount of PAB was 1.0 ml of a 0.1% solution for less than 0.6 ppm of gallium.

The influence of changes in the concentration of CTMA on the absorbance was determined. The maximal absorbance can be obtained over the range $0.9–1.5 \times 10^{-4}M$ CTMA. The absorbance, however, shows a sharp decrease when the CTMA concentration is $> 2 \times 10^{-4}M$. Hence it is necessary to keep the CTMA concentration constant.

Figure 4 shows the colour-development curves for the heated and the unheated solutions of the gallium complex. At room temperature (20°), 90 min are required for full colour development. When a prepared solution is heated in a water-bath at 60–70°, however, the reaction is greatly accelerated, and the maximum colour development is obtained in 10 min. The absorbance is stable for at least 24 hr.

Calibration curve, sensitivity and reproducibility

A calibration curve for the determination of gallium was prepared by the standard procedure. It obeyed Beer's law

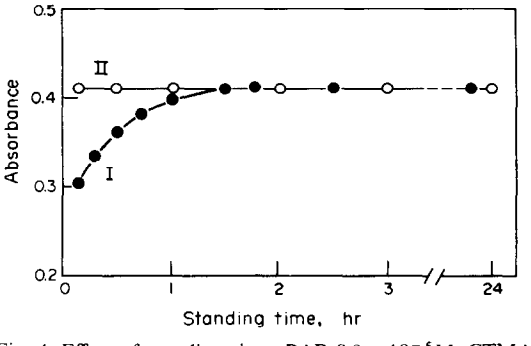

Fig. 4. Effect of standing time. PAB $8.0 \times 10^{-5}M$, CTMA $1.2 \times 10^{-4}M$, Ga $2.9 \times 10^{-6}M$; I: unheated solution. II: heated solution (60–70°).

Table 1. Effect of diverse ions

Ion	Added, μg	Ga found, μg	Ion	Added, μg	Ga found, μg
Ba(II)	250	7.9	Fe(III)	5	14.0
Be(II)	10	16.5	In(III)	100	8.0
Ca(II)	250	8.0	Sc(III)	10	11.2
Cd(II)	250	7.8	Y(III)	100	7.6
Co(II)	250	7.8	La(III)	100	7.8
Cu(II)	50	14.2	Ce(III)	100	7.7
Mn(II)	250	7.6	Nd(III)	100	7.6
Ni(II)	250	8.0	Gd(III)	100	7.9
Pb(II)	250	7.7	Dy(III)	100	7.6
Pd(II)	250	7.9	Er(III)	100	7.8
Zn(II)	250	7.5	Th(IV)	10	14.0
Al(III)	5	15.3	Mo(VI)	100	7.6
Au(III)	100	7.7	U(VI)	10	13.1

Gallium taken: 7.8 μg.

over the range 2–15 μg of gallium in 25 ml of solution. The colour reaction has a molar absorptivity of 1.39×10^5 $l.mole^{-1}.cm^{-1}$ at 680 nm, and the spectrophotometric sensitivity is estimated to be 4.9×10^{-4} μg of gallium per cm^2.

The method is very sensitive. Its sensitivity is much greater than that of the methods using Eriochrome Cyanine R (molar absorptivity, $\epsilon = 2.0 \times 10^4$),[10] Xylenol Orange ($\epsilon = 2.29 \times 10^4$),[11] Catechol Violet and quinine ($\epsilon = 2{,}0 \times 10^4$),[12] 6,7-dihydroxy-2,4-diphenyl-1-benzopyrylium chloride ($\epsilon = 5.6 \times 10^4$),[13] PAR ($\epsilon = 1.02 \times 10^5$),[14] and Chrome Azurol S and CTMA ($\epsilon = 1.15 \times 10^5$).[15]

A standard solution containing 5 μg of gallium was analysed 10 times by the standard procedure. The average absorbance was 0.409 with a standard deviation of 0.002.

Effect of diverse ions

Beryllium, copper(II), uranium(VI), scandium, yttrium and rare-earth elements also form coloured complexes with PAB in weakly acidic solutions.[7–9] These ions were therefore included in a study of possible interference in the determination of gallium. Some common ions, including these ions, were added individually to a solution containing 7.8 μg of gallium, and their effect was examined under the conditions of the standard procedure. The results are summarized in Table 1. It can be seen that some cations, especially aluminium, beryllium, copper(II), iron(III), scandium, thorium and uranium(VI) interfere seriously. Chloride, nitrate, sulphate and acetate are without effect even in large amounts. EDTA and oxalate prevent the formation of the gallium complex.

Small amounts of fluoride ion (less than 50 mg) and phosphate ion (less than 80 mg) have no influence under the conditions of the standard procedure. Sodium fluoride and sodium phosphate can therefore serve as excellent masking agents to prevent the interference of other metals. As shown in Table 2, aluminium, beryllium, scandium and thorium can be effectively masked by fluoride, and scandium, thorium and uranium(VI) by phosphate. However, the influence of copper(II) and iron(III) cannot be eliminated by the addition of these masking agents. Therefore, these ions must be separated by suitable procedures.

Table 2. Effect of fluoride and phosphate as masking agents

Ion	Added, μg	Ga found, μg	
		NaF*	Na_3PO_4†
Be(II)	100	8.2	>15
Cu(II)	50	14.3	>15
Al(III)	100	8.1	>15
Fe(III)	10	12.9	>15
Sc(III)	100	8.2	8.0
Th(IV)	100	8.1	7.9
U(VI)	10	13.0	8.0
	50	15	8.1

Gallium taken: 8.1 μg.
* Addition of 5 ml of 0.1*M* NaF.
† Addition of 3 ml of 0.1*M* Na_3PO_4.

Complex formation

The method of continuous variations was employed to establish the stoichiometry of gallium complex in the presence of CTMA. The constant concentration of CTMA was $1.2 \times 10^{-4}M$, and measurements were made at pH 6.4 and 700 nm. The results indicated that 1:4 complex between gallium and PAB is formed in the presence of CTMA, and a 1:3 complex in the absence of CTMA. These results were confirmed by the mole-ratio method. From the data obtained the formation constant for the complex was estimated to be 7.8×10^{18} for the 1:4 complex.

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SUBSTOICHIOMETRIC DETERMINATION OF ZINC BY THE ISOTOPE-DILUTION METHOD USING A CHELATING AGENT-LOADED RESIN

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Summary—A substoichiometric method for the determination of zinc has been developed. Zinc can be separated from other cations by using an anion-exchanger loaded with a substoichiometric amount of 8-quinolinol-5-sulphonic acid. Interfering metals can be removed beforehand by dithizone extraction. The feasibility of this method for water analysis was also examined.

Recently, the present authors reported a new separation method using ion-exchange based on complexation in the resin matrix.[1] A resin loaded with 8-quinolinol-5-sulphonic acid was also shown to be applicable to the selective preconcentration of chalcophile elements in natural water samples before neutron-activation analysis.[2] An additional advantage of this resin is that the ion-exchange capacity can be varied according to the desired purpose, and therefore substoichiometric separation may be achieved. In the work described below, the possibility of the determination of zinc with substoichiometric amounts of 8-quinolinol-5-sulphonic acid has been investigated.

EXPERIMENTAL

Apparatus

A well-type scintillation counter with an NaI(Tl) crystal was used.

Reagents

Resin loaded with 8-quinolinol-5-sulphonic acid was prepared by adsorption of the reagent on the anion-exchanger, Diaion SA 100 (Cl-form, 100–200 mesh), as described previously.[1] Zinc-65 was obtained from Nippon Isotope Kyokai.

General procedure

To the test solution, add a known amount of zinc (y) containing ^{65}Zn as tracer, and then acetate buffer solution (pH 4.75). Adjust the volume of the test solution to 100 ml. Add 100 mg of the resin (1×10^{-5} mole of 8-quinolinol-5-sulphonic acid/g of dry resin), and stir the mixture for 2 hr with the aid of a magnetic stirrer. Filter the mixture and measure the activity of the resin phase (A_x). Treat a standard solution in exactly the same way and measure the activity of the resin phase (A_y). Calculate the amount of zinc (x) present in the test solution by using the equation

$$x = y(A_x/A_y - 1)$$

Table 1. Substoichiometric separation of zinc(II)

Zinc(II) added, *μg*	Activity of the resin phase, *cpm*
100	1306
200	1684
300	1926
400	2094
500	2168
600	2223
700	2240
800	2236

RESULTS AND DISCUSSION

The influence of pH on the separation of zinc with resin loaded with 8-quinolinol-5-sulphonic acid is shown in Fig. 1, in which the substoichiometric separation is seen to be achieved in the pH range of 4.0–4.8. In this pH-region, the adsorption of zinc(II) on the resin was proportional to the amounts of resin used, indicating that the ion-exchange process based on complexation with 8-quinolinol-5-sulphonic acid in the resin matrix is quantitative. The adsorption is observed to increase at pH > 5.0, probably because of formation of zinc hydroxide.

It was confirmed experimentally that ion-exchange equilibrium was reached within 2 hr. The separation is substoichiometric if the amount of zinc(II) used is > 500 μg (Table 1). Therefore, 600 μg of zinc(II) are added as carrier. A reproducibility test for 100 μg of zinc(II) gave an average value of 109 ± 4 μg (4 determinations).

Since iron(III) and copper(II) interfere with the determination, a preliminary dithizone extraction should be used. When 500 ml of solution containing 100 μg each of zinc(II), copper(II), cadmium(II), mercury(II), cobalt(II) and nickel(II) were taken in a separatory funnel, the pH was adjusted to 7 and 600 μg of zinc and 50 ml of 0.001% dithizone in carbon tetrachloride were added and the solution

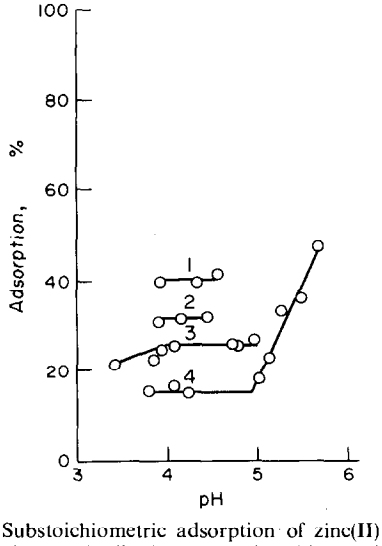

Fig. 1. Substoichiometric adsorption of zinc(II) on resin loaded with 8-quinolinol-5-sulphonic acid. 8-Quinolinol-5-sulphonic acid: 1×10^{-5} mole/gram of dry resin. Resin used (g): 1–0.30, 2–0.20, 3–0.15, 4–0.10.

was shaken, these metals were extracted; shaking the organic phase with 20 ml of 0.1*M* hydrochloric acid stripped the zinc(II), and analysis of the aqueous phase according to the general procedure gave recoveries of 108 ± 4 μg of zinc (5 determinations). The scheme was used for water analysis, and a water sample taken from the Watarase river was found to contain 0.12 ± 0.02 ppm of zinc (5 determinations).

This work was supported in part by a Scientific Research Grant from the Ministry of Education.

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ACETYLACETONE AS CHELATING REAGENT, EXTRACTING SOLVENT, AND ELECTROLYSIS MEDIUM: POLAROGRAPHIC DETERMINATION OF URANIUM(VI) AND IRON(III)

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(*Received* 19 *August* 1976. *Accepted* 9 *December* 1976)

Summary—The chelating reagent acetylacetone has been examined as a polarographic medium; a method for its purification has been developed and it is found that the specific conductance is 4.2×10^{-8} mho/cm, the accessible potential ranges are from −0.16 to −2.26 V *vs.* Ag/0.1*M* $AgClO_4$ for the pure solvent and from −0.35 to −2.20 V in the solvent after extraction. In pure solvent ferric acetylacetonate exhibits one wave and the uranyl complex gives two waves. After extraction from aqueous solution at pH 6.8–7.0, both metal acetylacetonates are reduced more reversibly and at more positive potential than in the pure solvent. Calibration curves are linear in the range 10^{-5}–10^{-3}*M* metal ion in the extract. The direct polarographic determination of uranium and iron in acetylacetone after extraction of the chelate from aqueous solution has been developed.

Acetylacetone (AA) is a polar aprotic solvent slightly miscible with water, and has been used as both an extraction solvent and a chelating reagent in the spectrophotometric determination of many metal ions.[1,2] Because of its tendency to decompose into acetone and acetate and to become discoloured, AA is not suitable for extraction spectrophotometry when the aqueous solution has a pH greater than 7.

Krishen and Freiser reported on the polarographic determination of uranyl ion after its separation from bismuth by extraction with AA; the AA was found not to affect the polarography in aqueous medium.[3] The present communication describes the polarographic determination of uranium(VI) and iron(III) in AA, which acts as the chelating agent for the metal ions, the extracting solvent from aqueous solution, and the medium for the polarographic measurements.

EXPERIMENTAL

Apparatus

A Yanaco Polarograph, Model P8, with three-electrode system was used, at a sweep-rate of 0.2 V/min. The dropping mercury electrode with 60-cm head of mercury had a drop-time of 4.1 sec, and flow-rate of 2.18 mg/sec in open circuit at 25 ± 0.2°. The reference electrode was a silver wire spiral in a 0.1*M* silver perchlorate solution in acetylacetone. A platinum wire spiral was used as the counter-electrode. Deoxygenation was achieved by bubbling oxygen-free nitrogen through the sample for 20 min.

Reagents

A 0.05*M* n-tetrabutylammonium perchlorate (TBAP) solution was used as the supporting electrolyte. Acetylacetonates of uranyl(VI) and iron(III) were prepared by extracting the corresponding chelates into benzene from aqueous solution, and were purified as described by Krishen and Freiser.[3,4] The pH of the aqueous solutions was controlled by the addition of a KH_2PO_4–$Na_2B_4O_7$ buffer solution, and the ionic strength was adjusted to 0.2 with sodium perchlorate.

Purification of solvent

Although many methods have been reported for the purification of acetylacetone for spectrophotometry,[5–7] two procedures were used in this work. The crude solvent was purified by method A below, and after a single use in the experiment was recovered by method B. The drying steps were only necessary for the non-aqueous studies.

Method A. Step 1: reflux over sodium bicarbonate (20 g per litre of analytical grade AA) for half an hour then distil at 48 ± 5° under reduced pressure (20–30 mmHg) through a column packed with helices. Step 2: reflux over phosphorus pentoxide (10 g per litre of AA) and carry out fractional distillation under reduced pressure, using a high reflux-ratio column packed with helices, as before. This method gave about a 60% yield of solvent having a specific conductance of 4.2×10^{-8} mho/cm.

Method B. Step 1: strip the metal ions into an aqueous solution at pH 1 (100 ml of 0.1*M* sulphuric acid per litre of AA for recovery). Step 2: wash with dilute (1:10) ammonia solution (100 ml per litre of AA) and then with

was shaken, these metals were extracted; shaking the organic phase with 20 ml of 0.1*M* hydrochloric acid stripped the zinc(II), and analysis of the aqueous phase according to the general procedure gave recoveries of 108 ± 4 μg of zinc (5 determinations). The scheme was used for water analysis, and a water sample taken from the Watarase river was found to contain 0.12 ± 0.02 ppm of zinc (5 determinations).

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distilled water (100 ml per litre of AA) twice, as described by Meyer and Hopff.[7] Then follow both steps of Method A.

Extraction procedure

Equal volumes (30 ml measured by pipette) of AA and of an aqueous solution containing 10^{-5}–$10^{-3}M$ metal ion were shaken together. The pH was between 6.8 and 7.0. After shaking for about 10 min the two phases were allowed to separate. A 20-ml volumetric flask containing 342 mg of TBAP was then filled to the mark with the organic phase.

RESULTS AND DISCUSSION

Figure 1 shows the polarograms of the acetylacetonates of uranium(VI) (curves *c*, *c'*) and iron(III) (curves *b*, *b'*), and also the residual currents (curves *a*, *a'*) in AA. The accessible potential range in non-aqueous AA was from −0.16 to −2.28 V *vs.* the $Ag/AgClO_4$ electrode, and in the solvent saturated with water, *i.e.*, in the solvent after extraction from aqueous solution, from −0.35 to −2.20 V. These wide potential ranges indicate the utility of AA as an electrochemical medium for non-aqueous polarography.

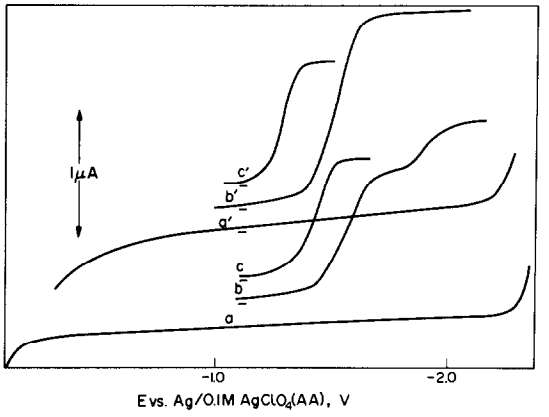

Fig. 1. Polarograms of metal acetylacetonates and residual currents. Supporting electrolyte 0.05*M* TEAP; in non-aqueous solvent acetylacetone, (*a*) residual current, (*b*) $2.0 \times 10^{-4}M$ $UO_2(AA)_2$, (*c*) $2.0 \times 10^{-4}M$ $Fe(AA)_3$. After extraction (*a'*) residual current, (*b'*) $UO_2(AA)_2$ (pH 6.9), (*c'*) $Fe(AA)_3$ (pH 6.8).

In non-aqueous AA ferric acetylacetonate gave a wave with half-wave potential of −1.43 V *vs.* the Ag/Ag^+ electrode. The reciprocal slope of the straight line obtained by plotting E against $\log i/(i_d - i)$ was 85 mV, indicating a rather irreversible one-electron reduction. The diffusion-current constant was 2.06 $\mu A \,.\, l \,.\, mmole^{-1} \,.\, mg^{-2/3} \,.\, sec^{-1/6}$. After equilibration with an aqueous medium buffered at pH 6.8 the ferric acetylacetonate gave a half-wave potential shifted to −1.29 V, and with a slope of 70 mV, indicating greater reversibility in the presence of water.

Uranyl acetylacetonate gave two waves, with half-wave potentials −1.55 and −1.90 V in pure AA. The slope of the log plot for the first wave was 124 mV and the diffusion current constant was 2.00 units. This suggests that in the first wave uranium(VI) is irreversibly reduced to uranium(V). The second wave, for the reduction from uranium(V) to uranium(IV), appears more reversible though the limiting current is smaller than that of the first wave, perhaps because of disproportionation of uranium(V) to uranium(VI) and uranium(IV) at the electrode.

After equilibration with an aqueous medium buffered at pH 6.9 uranyl acetylacetonate exhibits only one wave at a potential close to that of the first wave in the purely non-aqueous medium, at −1.52 V. The slope of the log plot is 99 mV. The wave-height is approximately equal to the sum of the two wave-heights in pure AA, suggesting that reduction is to uranium(IV), and that the disproportionation reaction becomes faster in the presence of water.

The calibration curves for uranium and iron extracted with an equal volume of AA from aqueous solution at pH 6.8–7.0 were linear over the range 10^{-5}–$10^{-3}M$.

It should be possible to determine uranium polarographically directly after extraction from aqueous solution containing any other foreign ion, by adjusting the pH, or adding masking agents. The extraction polarography of other metal cations and inorganic anions in AA will be published in detail elsewhere.

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DALZIN AS AN ANALYTICAL REAGENT FOR ESTIMATION OF TRACE QUANTITIES OF BISMUTH IN LEAD AND NICKEL

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(*Received* 6 *April* 1976. *Revised* 16 *December* 1976. *Accepted* 12 *January* 1977)

Summary—Dalzin forms coloured complexes with many metal ions. The present work deals with its use for determining microgram quantities of bismuth by solvent extraction followed by spectrophotometry. A method for estimation of bismuth in lead and nickel is presented.

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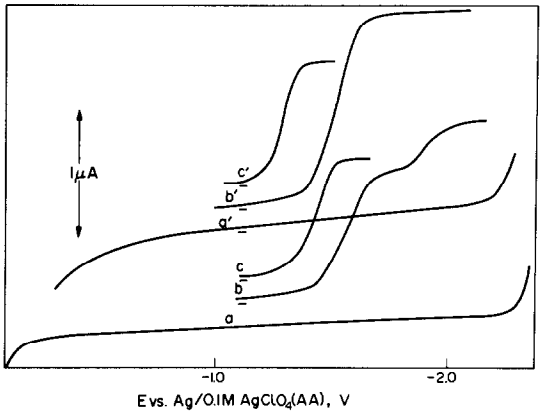

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Summary—Dalzin forms coloured complexes with many metal ions. The present work deals with its use for determining microgram quantities of bismuth by solvent extraction followed by spectrophotometry. A method for estimation of bismuth in lead and nickel is presented.

Dalzin, diallyldithiocarbamidohydrazine, is used for the estimation of bismuth,[1] palladium[2] and cobalt.[3] Conflicting values are reported for the melting point of dalzin prepared by different workers. In the present paper, this problem is resolved and an improved spectrophotometric method for estimating traces of bismuth in lead and nickel is presented. Bismuth is reported to cause increased corrosion of lead and to affect the malleability of nickel.[4, 5]

EXPERIMENTAL

Reagents

Allyl isothiocyanate; hydrazine dihydrochloride; hydrazine sulphate; dioxan, purified by distillation; standard bismuth perchlorate solution (bismuth 10.0 mg/ml) prepared from bismuth nitrate by fuming with perchloric acid, and standardized.[6] All bismuth solutions were kept at pH 1.

Synthesis and properties of dalzin

Method 1.[7] Hydrazine sulphate (0.2 mole) and sodium carbonate (0.2 mole) are dissolved in the minimum quantity of water, then mixed with 0.4 mole of allyl isothiocyanate in 160 ml of alcohol and the mixture is refluxed for 3 hr, then poured into chilled water. Dalzin separates as white shining flakes. It is recrystallized from ethanol and dried under vacuum.

Method 2.[1] Starting from hydrazine dihydrochloride, instead of hydrazine sulphate, dalzin is synthesized and purified as above.

Thin-layer chromatography (TLC). Dalzin is highly soluble in acetone (5% w/v) and sparingly so in chloroform. A 3:1 v/v chloroform–acetone mixture was used for TLC of dalzin on silica gel GF_{254} and silica gel G. The products from the first and second recrystallization were impure, but that from the third showed only a single dark blue spot on GF_{254} and a single white spot on silica gel G (R_f 0.7).

Elemental analysis. The results are given in Table 1.

Potentiometry. One of the enolizable mercapto groups was titrated potentiometrically in 50% aqueous dioxan, and the results indicated a purity of 99.4%.

Melting point. Dalzin decomposes on melting, which may indicate the presence of partially ionic groups.[8] Specimens of dalzin, prepared by both methods, were taken in capillaries which were inserted in the melting point apparatus preheated to 160° (about 20° below the m.p. of dalzin) and heated at 5°/min. Under these conditions a melting point of 186° was found for both specimens.

Determination of bismuth

In lead. A sample of lead (0.5–2 g) containing up to 50 μg of bismuth, is dissolved in 10–20 ml of nitric acid (1 + 1), then heated with 2–3 ml of perchloric acid until most of the acid is fumed off. The fuming is repeated. The cooled salts are dissolved in a few ml of water, 1 ml of 0.02*M* dalzin solution in acetone is added and the solution is diluted to about 50 ml and the pH adjusted to 2.5 with dilute ammonia solution. The solution is transferred to a 100-ml separatory funnel and extracted with 10 ml of chloroform (2 min shaking). The absorbance of the extract is measured at 350 nm against a blank similarly prepared.

In nickel. A sample of nickel (0.3–1 g) containing up to 50 μg of bismuth is decomposed in the same way as lead samples, but with hydrochloric acid instead of nitric acid. The residue from the perchloric acid fuming is cooled, dissolved in a few ml of water, treated with enough 50% w/v sodium citrate solution to give a 10:1 w/w ratio of sodium citrate to nickel; 1 ml of 0.02*M* dalzin in acetone is added, and the solution diluted to ~50 ml with water and adjusted to pH 6.5 with dilute ammonia solution. The determination is completed as for lead samples.

RESULTS AND DISCUSSION

Properties of the complex

The absorption spectra of dalzin and its bismuth complex in chloroform medium are shown in Fig. 1. The

Table 1. Elemental analysis of dalzin

	C, %	H, %	N, %	S, %
First crystallization	42.8	6.3	25.4	26.1
Third crystallization	41.8	6.1	24.3	27.8
Calculated for $C_8H_{14}N_4S_2$	41.45	6.19	24.40	27.50

Table 2. Bismuth in lead and nickel (aqueous phase 50 ml, perchloric acid medium; organic phase 10 ml of chloroform)

No.	Sample	Absorbance at 350 nm	Bismuth found, μg	Error, %
1	Std. Bi 50 μg	0.108	—	—
2	Std. Bi 100 μg	0.210	—	—
3	Pb 0.5 g + Bi 50 μg	0.108	50	nil
4	Pb 1.0 g + Bi 50 μg	0.110	51	+2
5	Pb 2.0 g + Bi 50 μg	0.115	53	+6
6	Ni 10 mg + Bi 100 μg	1.3	very high	—
7	Std. Bi 20 μg	0.045	—	—
8	Std. Bi 50 μg	0.115	—	—
9	Std. Bi 100 μg	0.220	—	—
10	Ni 0.3 g + Bi 100 μg	0.227	104	+4
11	Ni 0.5 g + Bi 50 μg	0.111	50	nil
12	Ni 1.0 g + Bi 50 μg	0.109	49	−2
13	Ni 1.0 g + Bi 20 μg	0.050	22	+10

Nos. 1–6 extractions at pH 2.5, Nos. 7–13 at pH 6.5.

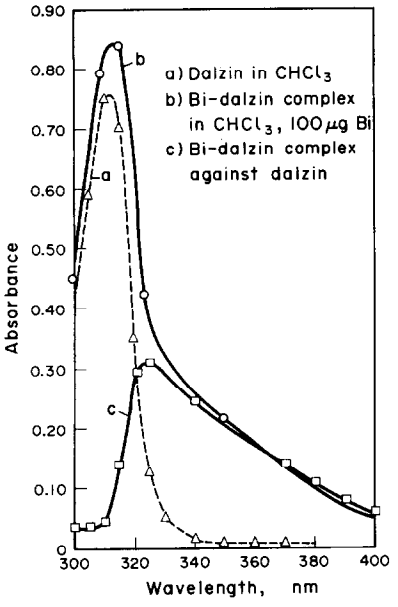

Fig. 1. Absorption spectra of dalzin and its bismuth complex

absorbance of the complex is measured at 350 nm to minimize the effect of surplus reagent. The extraction of the complex starts at pH 1 and increases with pH up to pH 2.5; it is constant at pH >2.5. For extraction of 200 μg of bismuth, 2 ml of $10^{-3}M$ dalzin are sufficient; ten times this amount is used for the determinations. Beer's law is obeyed over the concentration range of 2–25 μg/ml in the extraction. The absorbance remained constant for at least 24 hr.

A pH of 2.5 is suitable for extraction of bismuth in the presence of large amounts of lead, but nickel interferes at this pH. EDTA cannot be used as masking agent for the nickel because its bismuth complex is more stable than the dalzin complex. Citrate masks the nickel but causes incomplete extraction of the bismuth unless the pH is raised to 6.5.

Properties of dalzin

Gupta and Sen Sarma[1] reported a value of 177° and Jacobson and Hanstein[9] reported a value of 186° for the m.p. of dalzin. These discrepancies may be due to the fact that dalzin melts with decomposition and it is difficult to determine the correct m.p. By the modified method described, the m.p. is found to be 186°, for dalzin synthesized by both methods.

Potentiometric titration gave a value of about 9.8 for pK_1. The second dissociation is so weak that the pK-value could not be measured.

Interferences

Palladium and copper interfere. Cobalt is tolerated at the 100 ppm level.

There are many reagents reported for the spectrophotometric estimation of bismuth, *e.g.*, dithizone,[11] thiourea,[10] iodine[11] and diethyldithiocarbamate.[12] In most cases, prior separation of bismuth is necessary, whereas with dalzin direct estimation is possible. The dithizone and diethyldithiocarbamate complexes can be extracted, which leads to increased sensitivity. The sensitivities (Sandell's definition) are given in Table 3. Dalzin is much less sensitive than dithizone. Diethyldithiocarbamate forms strong complexes with elements such as lead and nickel, and either prior separation or the use of cyanide is necessary.

Acknowledgement—The authors wish to express their sincere thanks to Dr. M. Sankar Das, Head, Analytical Chemistry Division, for his constant encouragement and helpful suggestions.

Table 3. Sensitivities of different methods of estimation of bismuth, using solvent extraction

Method	Wavelength, *nm*	Sensitivity, *μg/cm²*
Dithizone	490	0.003
Diethyldithiocarbamate	370	0.020
Dalzin	350	0.040

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TALANTA REVIEW*

APPLICATIONS OF AUGER-ELECTRON SPECTROMETRY

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The radiationless reorganization of atomic electronic shells was first experimentally established by Auger[1–3] in 1923. There was a considerable induction period before the theoretical and experimental research of atomic physicists in the late 1950s and early 1960s led to a greater understanding of the Auger effect. (This work is well documented in references 4 and 5.) The development of electron-stimulated Auger-electron spectrometry (AES) as a powerful tool for the analysis of surfaces began with the work of Harris and of Weber and Peria in 1967. Harris[6] demonstrated the potential of differentiation of the Auger-electron energy-distribution and used the technique in studies of surface segregation[7] and carbon evaporation from a cathode.[8] The important contribution of Weber and Peria[9] was to show that the profusion of low-energy electron diffraction (LEED) instruments available at that time could be modified for use in Auger spectrometry in the differential mode. (The considerable quantity of LEED work carried out in the 1960s is catalogued in the bibliography by Haas *et al.*[10]) Concurrent with these developments increasing efforts were being made to produce electron spectrometers of higher resolution and sensitivity.[11,12] In 1969, Palmberg, Bohn and Tracy[13] demonstrated that the cylindrical-mirror analyser could be used to achieve high sensitivity in AES with resultant increase in the speed of an analysis.

A more recent development has been the use of scanning techniques which make it possible to produce a two-dimensional map or image of the surface distribution of a chosen element. The method can be used in conjunction with "physical" imaging by scanning electron-microscopy. Indeed the AES map can be obtained from Auger electrons produced in the scanning electron-microscope.[14–16] Finally, it is worth pointing out that the advances outlined above have all been carried out during a period of significant improvement in ultrahigh-vacuum technology.

The growth in the number of applications of AES described in the literature has been very marked since approximately 1970. Undoubtedly this has been due to a combination of increasing interest in the surface properties of materials and the unique blend of properties of AES. Not only can an elemental analysis be performed but the technique can also yield information concerning the chemical environment of surface atoms. Furthermore high sensitivity and spatial resolution, and fast responses can be obtained. Recently it has been suggested that because of some of these properties, there is considerable analytical potential for AES in the gas-phase.[17]

This review concentrates on a selection of applications of AES in qualitative surface analysis. Additionally, a discussion of quantification of surface Auger signals and an evaluation of the potential of gas-phase AES are included. A list of some review articles on AES is given at the end of the paper.

SURFACE STUDIES

The great number and variety of published papers on electron-excited AES of surfaces creates difficulties in the task of categorizing material according to the nature of application, material examined or particular Auger technique employed. In the present review, all these topics are discussed with specific examples; however, it should be emphasized that certain studies could clearly be included in more than one area. There is no attempt to encompass the whole field.

Surface chemistry and Auger chemical shift

The adsorption and reactions of gases at a clean metal surface are the main subject of this section. These studies are clearly relevant to problems in corrosion, catalysis, *etc.* (Specific examples of the latter are considered in the next section.) Much of the work in this area has been concerned with the reaction of oxygen with a clean metal surface prepared by thermal treatment and/or argon ion-bombardment.

An early report of an Auger study of metal oxidation was that of Haas and Grant[18] who followed the 164-eV $N_5N_6N_6$ tantalum transition on reaction of a tantalum (110) surface with oxygen. A shift of -6 eV was found when the sample was fully oxidized.

*For reprints of this Review, see Publisher's announcement near the end of this issue, TALR 59.

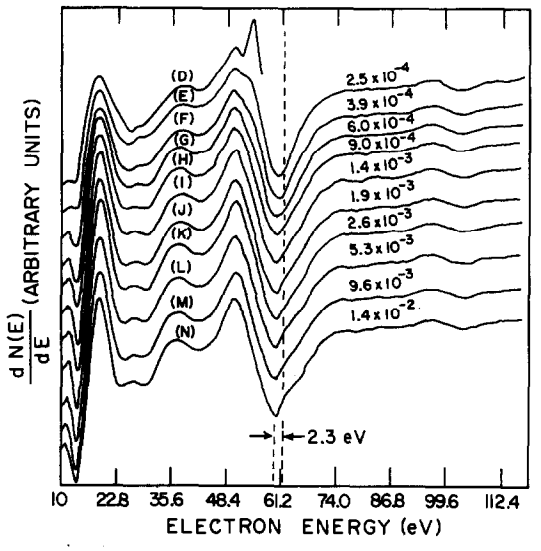

Fig. 1. A. M. Horgan and I. Dalins.[19] Auger-electron spectra showing changes in the $M_{2,3}VV$ peak (61 eV) of nickel on dosing with oxygen. Exposure times are in torr-sec. The dotted line indicates the position of the 61 eV peak of the "clean" Ni(111) surface (by permission of the copyright holders, North-Holland Ltd.).

This type of change of an Auger energy has generally become known as the Auger chemical shift by analogy with the changes in energies of photoemitted electrons in ESCA. The shift is associated with the changes in binding energy of the electrons involved in the Auger transition. An increase in the electropositive character of a metal atom due to oxide formation can be regarded naively as causing a "tightening" of the core levels and hence a shift to higher energies.

Auger transitions can be divided into two categories, (*a*) XYZ and (*b*) XYV or XVV, the members of the latter two often being referred to as valence spectra. Any energy shift in particular XYV or XVV transitions on reaction corresponds to changes in both core level energy and distribution of valence-band electrons. Shifts observed for the type XYZ are considered to be "true" chemical shifts associated only with changes in inner levels caused by valence-band charge-transfer. It should be pointed out that this distinction has not always been made.

In several cases shifts in metal Auger-transition energy (E_{XYZ}) on oxidation have been interpreted by using the empirical equation:

$$E_{XYZ}(z) = E_X(z) - E_Y(z) - E_Z(z + \Delta) \qquad (1)$$

where E_X, E_Y and E_Z are the energies of the levels involved in the Auger transition of the element with the atomic number shown in brackets. The $(z + \Delta)$ term (where Δ is often 1, so the element is the next to z in the Periodic Table) is to allow for the coulombic re-distribution of electrons as a result of ionization. The equation has been quoted in a variety of forms in the literature. Binding energies can be obtained from ESCA for the metal and metal oxide, and approximate Auger energies computed, allowing prediction of Auger chemical shifts.

A good example of the study of a metal–oxygen system is that by Horgan and Dalins[19] who investigated the adsorption of oxygen on the clean (111) surface of a single crystal of nickel. Auger data for a coverage $\theta < 1$ were produced by lightly doping the sample with a molecular beam of oxygen. The results under these conditions were consistent with two chemisorbed states for oxygen adsorbed on the nickel surface. No energy shifts for nickel peaks or the oxygen peak at 516 eV were observed. The coverage condition $\theta > 1$ was produced by maintaining a steady-state gas pressure in the reaction chamber. Studies were confined to the four most intense and easily resolvable nickel peaks at 61 eV ($M_{2,3}VV$), 716 eV ($L_3M_{2,3}M_{2,3}$), 782 eV ($L_3M_{2,3}V$) and 849 eV (L_3VV). Figure 1 shows Auger-electron spectra in the energy range 10–120 eV, which illustrate the changes in the $M_{2,3}VV$ transition on increased doping with oxygen. The 61-eV peak is seen to broaden and undergo a shift to lower energies with increasing oxygen exposure. A final shift of 2.3 eV is reported. Similarly shifts of 1.8 and 2.1 eV are observed for the $L_3M_{2,3}V$ and $L_3M_{2,3}M_{2,3}$ transitions, respectively. The energy changes are rationalized in terms of empirical calculations involving a modified form of equation (1).

Another example of an oxidative study is that of Allen and Wild[20] who examined clean uranium and oxidized uranium surfaces. Figure 2 shows the

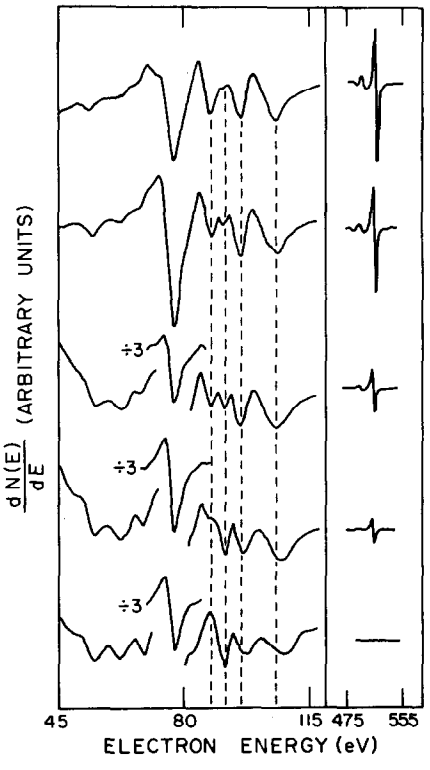

Fig. 2. G. C. Allen and R. K. Wild.[20] Auger spectra from uranium metal foil as a function of oxygen 515-eV peak-height (by permission of the copyright holders, the Chemical Society).

changes occurring in the peaks of the oxide-free surface at 75.5, 53.0, 60.3, 89.9, 95 and 106 eV and the oxygen 515-eV peak, with increased exposure to oxygen. Again several of the peaks change their shape and shift to lower energy. As with the previous study an empirical equation was used to compute Auger energies from ESCA data for the free metal and oxide.

There have been many other studies of metal–oxygen systems of which the following are a few examples—lithium,[21] beryllium,[22–24] sodium,[25] magnesium,[26,27] aluminium,[28] silicon,[29,30] vanadium,[31] chromium,[32] manganese,[28] iron,[26,33–36] yttrium,[37] molybdenum,[38] tungsten,[39,40] platinum,[41,42] samarium, gadolinium and terbium,[43] platinum/tin[44] and silicon/iron alloys.[45]

Experiments have not been confined to the metal–oxygen system, since there have been a number of studies of interactions of other gases, notably CO, with surfaces. The investigation of the adsorption of carbon monoxide and ethylene on a tungsten (100) surface is a typical example.[46] The Auger spectrum in the case of ethylene adsorption at 80 K is attributed to undissociated chemisorbed ethylene. However, the carbon peak shape for adsorption at 300 K is characteristic of surface carbide. The situation with regard to CO may be complicated by the effect of the primary electron beams (in these experiments 2.5 keV) in that the carbide peak shape, indicative of dissociated CO, is observed at both 80 and 300 K. Thus the subjection of the adsorbate to a flux of electrons of 2.5 keV energy *may* cause conversion of virgin CO into another form. The authors of that work quite rightly point out that derivative Auger spectrometry is only useful in indicating the gross changes in the nature of surface-adsorbed species, because of the peak-broadening effects generally observed in "solid-phase" spectra. ESCA spectra have perhaps proved more useful; for example, the dissociation of CO on a molybdenum surface at room temperature has been well characterized.[47]

More recently, high-resolution Auger spectra of surface-adsorbed molecules have been obtained in the non-differentiated mode, in contrast to previous work.[48,49] The spectra of ammonia adsorbed on molybdenum at 450° are indicative of nitride formation whereas at room temperature chemisorption is prominent.[48] The comparison of these spectra with the spectrum of gas-phase NH_3 (obtained in the work of Thompson *et al.*[17]) is interesting (Fig. 3). It is likely that such comparisons will figure more prominently in the literature as the number of available gas-phase spectra increases. Clearly the monitoring of the behaviour of surface-adsorbed species is of considerable importance in catalysis. Similar results to those from the work above have been reported for the interaction of nitrogen with iron and molybdenum.[49]

Other examples of studies of molecules adsorbed on surfaces are silicon/phosphine,[50] aluminium/hydrogen chloride,[51] and silver/sulphur dioxide and carbon dioxide.[52]

Most of the research on gas adsorption has been of this type, where only the interaction of the particular molecule with the surface is considered. However, it is possible to examine a surface reaction between an adsorbed species and molecules in the gas-phase. An example is the work of Bonzel[53] who investigated the kinetics of a surface reaction between adsorbed sulphur and gas-phase oxygen on a copper (110) crystal surface in the temperature range 610–830°. The clean Cu surface was exposed to H_2S and then heated to between 610° and 830° to allow for initial diffusion of some of the adsorbed sulphur into the bulk of the sample. When this process became sufficiently slow the reaction with oxygen was carried out at a constant partial pressure as monitored by a quadrupole mass analyser. The surface sulphur concentration was recorded by AES as a function of time. The only product was SO_2. An analysis of the kinetics of the reaction led to the conclusion that the fast surface reaction between adsorbed sulphur and oxygen probably occurs according to the Langmuir–Hinshelwood mechanism and could be surface-diffusion controlled.

In the last two or three years there has been increased attention paid to the effects of the primary electron beam on gas adsorption. For example, Kirby *et al.*[54,55] have examined electron-beam induced effects on the CO_2 and O_2/silicon systems. It was shown that the impact of the primary beam can create both electronic and thermal effects. Electronically, the

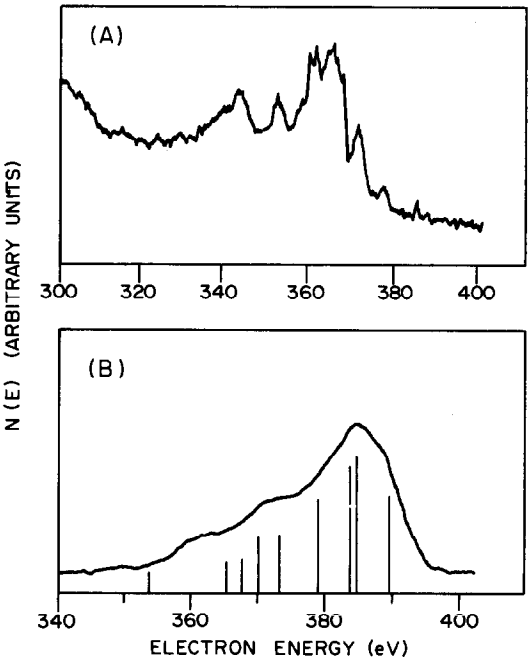

Fig. 3. M. Thompson, P. A. Hewitt and D. S. Woolliscroft.[17] Auger spectrum of NH_3 in the gas-phase (A). (Reprinted with permission: copyright by the American Chemical Society). T. Kawai, K. Kunimori, T. Kondow, T. Onishi and K. Tamaru.[48] Similar spectrum of NH_3 adsorbed on molybdenum at room temperature (B). (By permission of the copyright holders, the American Institute of Physics.)

beam can dissociate surface molecules, desorb molecules and atoms, break bonds in the bulk, and cause surface and bulk excitations. Also, "true secondary" electrons of energy 0–50 eV can reach the surface and cause dissociation of the surface-adsorbed molecules. Local heating by the beam should not be neglected since it may cause, for example, increased diffusion of atomic species such as O into the bulk.

Barrie and Brundle[56] point out that although high beam-currents may be necessary for fast Auger analysis they can have disadvantageous results. These workers compared ESCA and Auger spectrometry of CO adsorbed on polycrystalline molybdenum. Signal intensities in the Auger spectrometry were significantly altered by surface effects induced by the electron beam. Baker and Sexton[57] have shown that electron-beam surface-heating and impact-desorption effects are important in the physisorption of xenon on nickel and platinum. Furthermore, with regard to surface cleaning by inert-gas ion-bombardment before adsorption experiments, the surface structural condition and impurities introduced by ion-implantation have generally not been considered (this topic is discussed in more detail in the section dealing with surface cleaning). Clearly, in the future great care must be taken in the interpretation of Auger data from surface adsorption experiments.

For further detail of electron spectroscopic studies of adsorption of gases and oxidation the reader should consult the review by Brundle.[58]

Catalysis

The potential of AES for the study of heterogeneous catalysis has been cited by several authors, the review by Yates[59] being a good example. In practice many experiments have been concerned with the correlation of the surface elemental composition of a catalyst (obtained by AES) with its performance in chemical processes. For example, Somorjai *et al.*[60] investigated the cleanliness of platinum surfaces with respect to carbon before their use as catalysts for the dehydrocyclization of *n*-heptane to toluene. Takasu and Shimizu[61] used AES to examine the changes in surface composition of copper–nickel plates with pretreatment and related these to catalytic activity. The samples were pretreated by either oxidation and reduction or heat treatment at around 300°. In both cases the surfaces of nickel-rich alloys were enriched with copper, while those of the copper-rich alloys were enriched with nickel. The authors discussed the results in terms of the catalytic activity of copper–nickel alloys for the hydrogenation of ethylene.

Other workers have studied the "working state" of a molybdenum surface on which a reaction occurred between segregated sulphur and ambient oxygen.[62] At temperatures in the range 700–800° it was found that the reaction takes place through direct interaction of oxygen molecules and surface sulphur whereas at higher temperatures of around 1200° it proceeds between sulphur and chemisorbed oxygen. Bhasin[63] examined the AE spectra of two commercial samples of a copper catalyst used for the reaction between methyl chloride and silicon. The surface level of lead in one sample was approximately three times the level in the other catalyst. Apparently such a high level of lead in the "poor" catalyst can be related to the killing of the activity of that particular sample.

It was in 1974 that Yates[59] pointed out that the advance of "clean surface" workers to studies of heterogeneous catalysis was imminent. An examination of the literature today clearly reveals that this progress has taken place, particularly with regard to the techniques that constitute the general area of electron spectroscopy.

Surface cleaning

The advent of studies of surfaces has resulted in the requirement for the rigorous cleaning of the surfaces of single crystals and other materials. The major methods are chemical treatment, sputtering by argon ion-bombardment and cleaving in vacuum. Annealing is frequently used in the first two cases to restore an "ordered" surface. AES is now used routinely to detect surface impurities before and after cleaning. A few examples of AES study of cleaning techniques are considered in this section together with recent work on the structure of ion-bombarded surfaces. Applications of ion-bombardment in repetitive removal of surface layers are discussed at greater length in a later section.

Moon and James[64] examined the effect of HCl vapour-etching (at 800°) of n^+ GaAs (100) substrates doped with silicon, tin or tellurium. Before the etching all Auger spectra were characterized by C, N, O, Ga and As peaks. After treatment the Si and Te-doped samples exhibited unchanged spectra but an accumulation of Sn was observed on the surface of the Sn-doped substrate. The behaviour of the Si and Sn samples, which is contrary to what is expected in terms of the vapour pressure of the elements, was correlated with the equilibrium pressure of Si chlorides being much greater than that of the Sn chlorides (*e.g.*, $P_{SiCL_4}/P_{SnCl_4} \approx 10^7$).

AES data have been recorded for various chemical etchings of n-type germanium wafers.[65] Representative spectra are shown in Fig. 4. The complete list of elements detected was Ge, O, N, C, Ca, F and P although the last three were found only in certain cases. Fluorine contamination was seen only when HF was used. Other workers have examined cleaning by peroxide solutions[66] and abrasion with emery papers.[67,68]

The use of argon ion-bombardment for the cleaning of surfaces before other experiments is widespread. In fact the ion-gun is now a standard fixture on commercial instruments. AES has been used to assess the effectiveness of this technique and also the high-temperature oxygen reaction with reference to nickel (111), nickel (100) and nickel sheet.[69] It was found that heavy carbon deposits on the nickel (100) surface

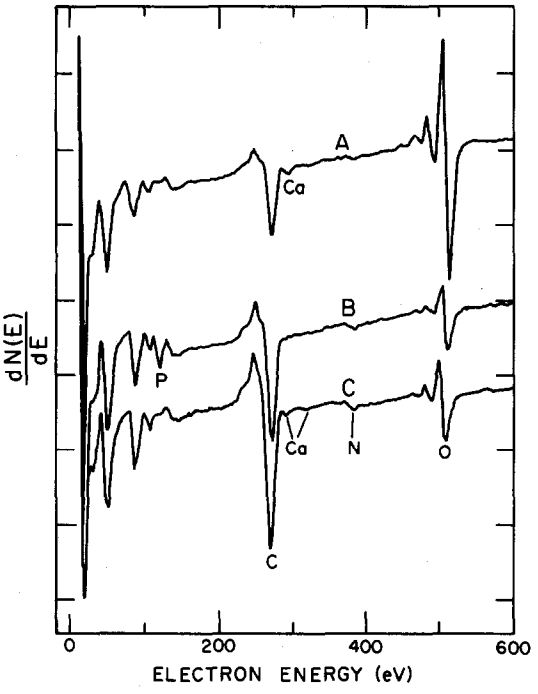

Fig. 4. D. A. Kiewit, I. J. D'Haenens and J. A. Roth.[65] Auger spectra of chemically etched germanium samples. *A*—$HCl:H_2O_2:H_2O$ (1:1:60) + 1%Na_2EDTA, *B*—methanol, acetone, and *C*—$HCl:H_2O_2:H_2O$ (1:1:5). (By permission of the copyright holders, the Electrochemical Society Inc.)

could only be removed after reaction with oxygen at high temperature (~900°) and low pressure (~10^{-6} mmHg). In the case of S on the same surface the contaminant could be removed by argon ion-sputtering at 20° (gun-energy 250 eV and current density 3×10^{-6} A/cm^2) as well as by the oxygen reaction.

Recently Walls, Southworth and Martin[70] carried out a careful study of the effect of ion-bombardment on tungsten surfaces, by AES, LEED and field-ion microscopy (FIM). The last two techniques yield information on the crystalline nature of the surface whereas AES provides an analysis of the inert gas trapped in the surface. FIM images are generally derived from the first atomic layer whereas the AES signal originates (in the case of tungsten electrons) from at least the first six layers, and LEED examines the first two layers. Comparison of FI micrographs of the clean surface with those of the surface after xenon, argon or neon bombardment (800 eV, 1×10^{-6} A/cm^2) showed the surface disorder produced by sputtering. The damage was correlated with the relative sputtering yields of the inert gas ions, *i.e.*, xenon > argon > neon.

Auger analysis of the surface after bombardment with xenon ions (800 eV, 10×10^{-6} A.min.cm^{-2}) revealed that the amount of gas atoms trapped was below the detection limit of the instrument. Furthermore the LEED pattern remained undisturbed. In the case of argon ion-bombardment at 800 eV and 50×10^{-6} A.min.cm^{-2}, argon was detected by means of its peak at 217 eV ($KL_{2,3}L_{2,3}$). With neon, increasing implantation was observed by both Auger and LEED analysis over the bombardment range 10–80 $\times 10^{-6}$ A.min.cm^{-2}. These results are in line with data on trapping probability.

The experiments outlined above emphasise the problems in using ion-bombardment as a cleaning technique before surface studies on, for example, adsorption or catalysis. Subsequently the best species for sputter-cleaning of tungsten surfaces was investigated.[71] From consideration of sputtering yield, trapping probability and surface damage, xenon is the best ion species. However, the authors point out that for cleaning of contaminated rather than pure metal surfaces, other factors may have to be taken into consideration.

Segregation

Perhaps the most important industrial application of AES is in the analysis of segregation of species on a surface or at grain boundaries of metals. Correlation of the results of such studies with the mechanical and chemical properties of materials is now carried out on a routine basis.

Dooley[72] studied surface segregation in zirconium alloys and related the results to previously established properties such as strain-rate sensitivity. Polycrystalline samples were argon ion-sputtered and/or heated to various temperatures before AES analysis. Spectra of a sputtered alloy which contained Sn, Fe, Cr and Ni as minor components are shown in Fig. 5. In the room-temperature spectrum, only zirconium, tin (barely distinguishable), and carbon and oxygen (contaminants) peaks are evident. At 500° the Sn, Fe and C surface-contents increased. Heating to 700° resulted in a decrease of the carbon peak but Fe, Ni and Sn were then present. Between 700 and 900° increasing amounts of sulphur and a general decrease in O and C content were observed. Chromium was only observed at around 900° even though its concentration in the bulk was twice that of nickel. The author related the formation of surface metal carbide to decreased ductility.

The mechanism of the segregation of sulphur from the bulk of a sample of clean polycrystalline molybdenum was examined by the monitoring of sulphur $L_{2,3}M_{2,3}M_{2,3}$ peaks at 152 eV.[73] Dynamic experiments in the temperature range 750–1350° were carried out rapidly over 90 sec and over longer periods of up to 20 min. During the initial stage of segregation the sulphur content at the surface was found to increase linearly with time, implying that there was a constant rate of diffusion of the element from the bulk. The results were said to be consistent with the diffusion of sulphur along grain boundaries. The non-differentiated spectrum (corrected for background) of segregated sulphur measured at high resolution is shown in Fig. 6. The peaks at 152.2 and 155 eV (shoulder) were ascribed to the $L_{2,3}V_2V_2$ and

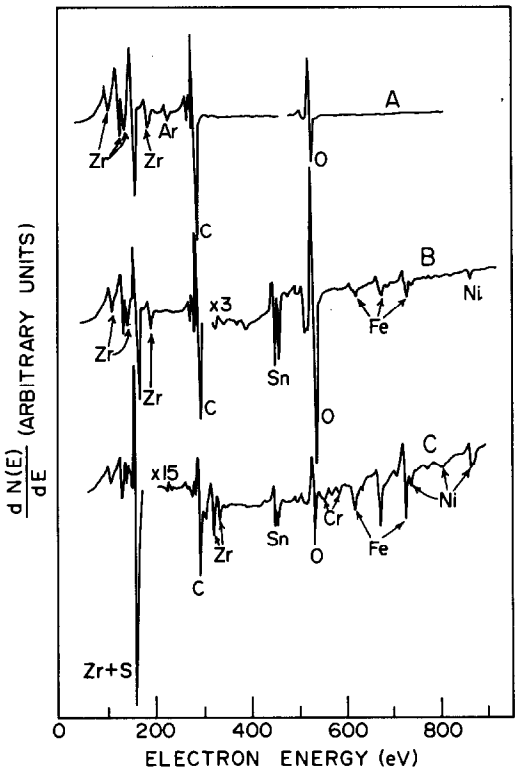

Fig. 5. G. J. Dooley III.[72] Auger spectra of zirconium alloy after argon ion-bombardment. *A*—room temperature, *B*—700°C, *C*—900°C. (By permission of the copyright holders, the American Institute of Physics)

$L_{2,3}V_1V_2$ transitions of molybdenum disulphide, respectively. Hence, the authors were able to glean some information concerning the chemical environment of the segregated element in these experiments.

Further examples of work on segregation are the studies of S, C and P on thorium[74] and S on titanium.[75]

Several workers have attempted to place the surface concentration of segregated species on a quantitative footing. The iron peak at 43 eV and the 119-eV signal of phosphorus were monitored for experiments performed on an Fe–0.063 at% P alloy at various temperatures and times.[76] The equation

$$c_P/c_{Fe} = n_P/n_{Fe} = K(A'_P + b_P)/(A'_{Fe} + b_{Fe}) \quad (2)$$

where c_P and c_{Fe} are surface concentrations, n_P and n_{Fe} are the number of atoms per unit area, A'_P and A'_{Fe} are peak amplitudes, b_P and b_{Fe} are background factors and K is a proportionality constant, was calibrated by measurement of the peak amplitude ratio, A_P/A_{Fe} (in this case corrected for background slope, *i.e.*, (A'_P/A'_{Fe}) and use of the Crank[77] equation for calculation of phosphorus surface concentration under specific conditions. A value of 5.47 was found for the proportionality constant K, which compared favourably with the value of 4.59 computed theoretically on the basis of effective ionization cross-section with inclusion of Coster–Krönig transition contributions.

Another example of empirical quantitative measurement of segregation is the work of Ueda and Shimizu[78] on elements on the surface of an iron–silicon alloy.

In metallurgy, the analysis of segregation at grain boundaries is vital to the understanding of intergranular weakness. This property can result in temper brittleness which is an important problem in the steel industry. AES has proved particularly fruitful in this area. For the study of segregation the specimen is usually fractured under high vacuum to expose a fresh surface for analysis, although this procedure does place obvious constraints on the boundaries to be examined. A good example is the work of Seah and Hondros[79] who examined segregation levels in binary and ternary iron alloys with tin and sulphur over a wide range of temperatures and times. The specimens were heated under vacuum in solid ampoules to develop a similar grain size. After being held at temperatures between 500° and 850° for varying times the samples were water-quenched and then subjected to AES analysis of a cloven area. A comparison of an Auger spectrum typical of a fracture surface with that of pure iron is reproduced in Fig. 7. Tin and sulphur peaks are clearly seen in the spectrum of the alloy.

Depth-concentration profiling

The continuous removal of surface material by inert-gas ion-bombardment (ion-milling) with simultaneous AES monitoring of element concentrations on the "fresh" surface is used to obtain a composition

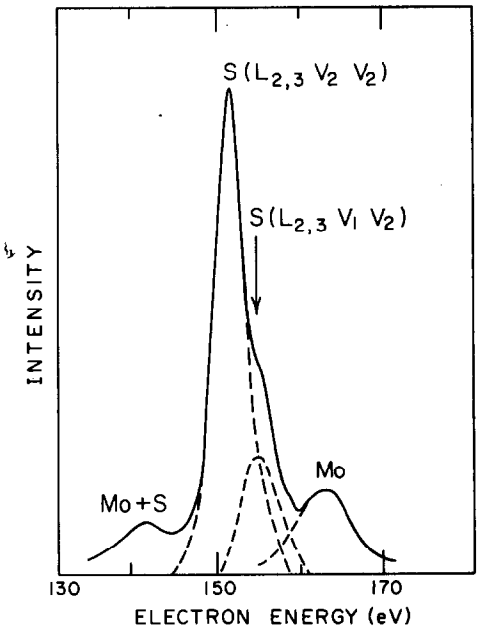

Fig 6. K. Kunimori, T. Kawai, T. Kondow, T. Onishi and K. Tamaru.[73] High-resolution Auger spectrum [$N(E)$ *vs.* E) of sulphur adsorbed on molybdenum. The broken curves are the individual Auger peaks, derived on the assumption of a Gaussian shape. (By permission of the copyright holders, North-Holland Ltd.)

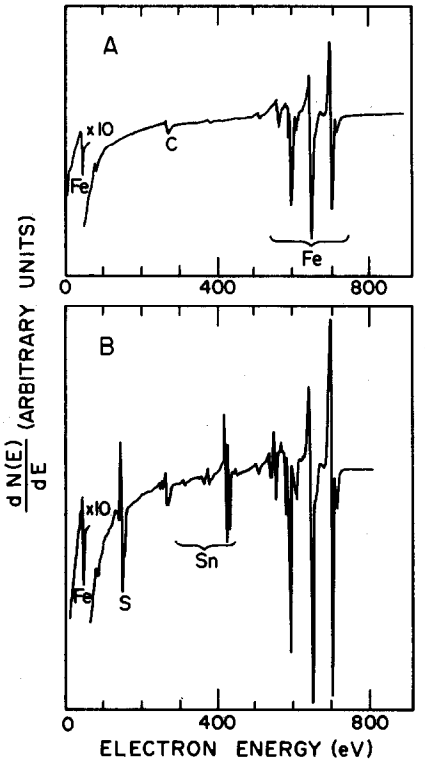

Fig. 7. M. P. Seah and E. D. Hondros.[79] Auger spectra from fracture surfaces. *A*—pure iron and *B*—grain-boundary fracture surface in an iron–1% tin–sulphur ternary alloy quenched from 600°C. (By permission of the copyright holders, the Royal Society.)

profile normal to the solid–vacuum interface. The technique has been applied in several fields, notably to steels, alloys and electrical devices; in this section, some examples of depth-concentration profiling (DCP) are considered together with a brief discussion of the problems associated with interpretation of the profile.

Several of the earlier experiments were performed in a stepwise fashion, often involving transfer of the specimen to the spectrometer, in contrast to the *in situ* method in general use today. For example, Stoddart and Hondros[80] obtained profiles of thin oxide films on stainless steel and an aluminium bronze by a stepwise technique. Samples were ion-etched for various times and then transferred to a spectrometer for Auger analysis. The DCP for the stainless-steel sample is shown in Fig. 8. Enrichment of the oxide layer with Cr, Mn and V is evident whereas with Ni there is depletion. The authors point out that such profiles can be used to analyse protective oxide films that are important in the area of corrosion.

Similar studies by DCP have been carried out on copper/nickel[81,82] and platinum/tin[83] alloys.

Both ramp-etching and *in situ* ion-milling were used by Chang *et al.*[84] in a depth-profiling study of phosphorus-doped SiO_2. The latter is produced by reaction of silane and phosphine with oxygen for electrical application in integrated circuits. The phosphorus and silicon peaks at 120 and 107 eV, respectively, were measured in 12 sec to avoid problems with phosphorus effusion caused by the primary electron beam in the analysis. Figure 9 shows a depth-concentration profile produced by ion-milling of a layer of P-doped SiO_2 (0.5 at% P) on a silicon substrate. The occurrence of a phosphorus-rich layer with an adjacent P-depleted region is evident. From other experiments the authors reached the conclusion that the P-rich layer could not be attributed to phosphorus drift caused by the electron and/or ion beams. Rather, the region could be explained in terms of the rapid reaction of PH_3 at the silicon surface. When the deposition begins the oxide film is thin enough to allow

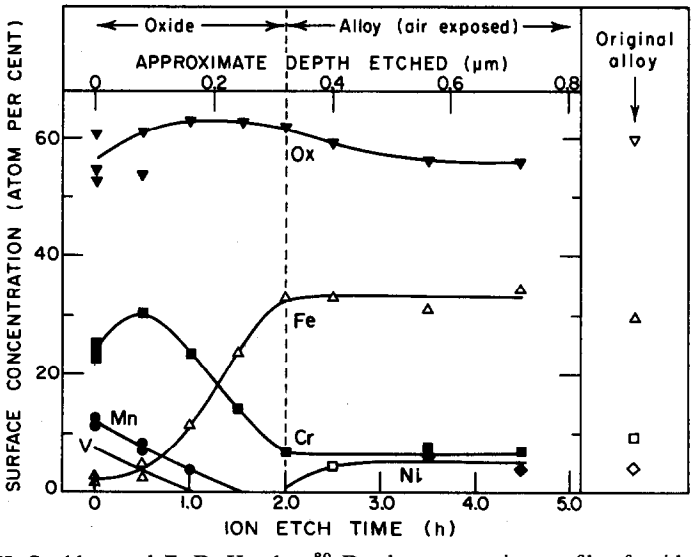

Fig. 8. C. T. H. Stoddart and E. D. Hondros.[80] Depth-concentration profile of oxide layer formed on a stainless-steel sample after 2 hr in air at 900°C. (By permission of the copyright holders, Macmillan Ltd.)

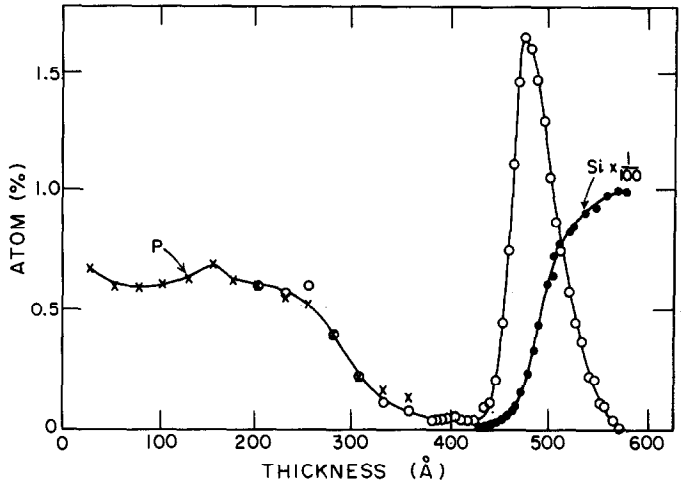

Fig. 9. C. C. Chang, A. C. Adams, G. Quintana and T. T. Sheng.[84] Depth-concentration profile of phosphorus in a P-doped SiO_2 sample (silicon substrate). (By permission of the copyright holders, the American Institute of Physics.)

diffusion of PH_3 to the silicon surface, resulting in a P-rich region. Eventually a steady-state condition is reached, as evidenced by the 0–250-Å region of Fig. 9.

An interesting study was that due to Morabito[85] on the analysis of tantalum films by AES and secondary-ion mass-spectrometry (SIMS). The oxygen, nitrogen and carbon contents of sputtered Ta films have an important bearing on their electrical properties. The homogeneous distribution of these elements in standards prepared by reactive sputtering was established by SIMS and in-depth AES profiling. The results of this investigation demonstrated that, in general, secondary-ion emission is a more sensitive technique than ion-sputtering Auger-spectrometry.

Certain problems associated with ion-sputtering were alluded to in the section dealing with surface cleaning. Because of the nature of the milling technique there are also difficulties in achieving high depth-resolution and an accurate depth-profile. Normally, the depth of sample sputtered is "calibrated" by using the sputtering coefficient of the material under study. However, in a multicomponent system preferential sputtering of one constituent can seriously affect the accuracy of the profile. Other factors to be considered are induced ion-mobility, non-uniform ion-density and destruction of the surface structure (or "roughness"). Recently it was shown that the etching rate can be somewhat higher on that region of the specimen which is exposed to the primary-electron beam than on the area subjected to ion-bombardment only.[86] This effect was attributed to electron-stimulated desorption of surface oxygen with consequent enhanced sputtering in the electron-irradiated area. Thus, the depth-resolution of the DCP technique can be adversely influenced by this artefact.

In earlier applications of DCP many of these factors were largely ignored; however, research activity is currently being devoted to several aspects of the subject. Undoubtedly, the accuracy of the depth profile will increase with information obtained from these experiments.

For further detail on DCP the reader should consult the review by Holloway.[87]

Electrodes and electroplating

Surface composition has an important influence on the nature of electro-deposits. AES has been used with some success in this area; for example, Marcus *et al.*[88] have studied the chemical composition at electro-deposited nickel–nickel interfaces. Nickel laminates were prepared by several cycles of electrodeposition, with intervening polishing and cathodic activation treatment, to give a final thickness of 1 inch. Some samples exhibited minimal resistance to crack formation along a bond. Figure 10*a* shows the AE spectrum from a fracture surface, dominated by characteristic silver peaks. In the spectrum of the surface obtained after argon-ion bombardment (Fig. 10*b*), the peaks due to silver are absent. Thus, the source of the silver deposited at the bond surface was attributed to an activation solution used in a preceding processing step.

A further example of a study of the integrity of electro-deposits is that of Diri and Musket[89] who examined aluminium and uranium samples.

The nature of thin films on the surfaces of platinum anodes in electrolytic cells has been investigated by Johnson and Heldt.[90] Platinum electrodes previously cleaned by inert-gas ion-sputtering were anodized in either sulphuric acid or sodium chloride solution. Only Pt and O peaks were present in the AE spectrum of the surface of Pt anodized in the acid. The results were discussed in terms of the formation of a stable PtO layer. In the case of Pt anodized in sodium chloride solution, Cl was observed as well

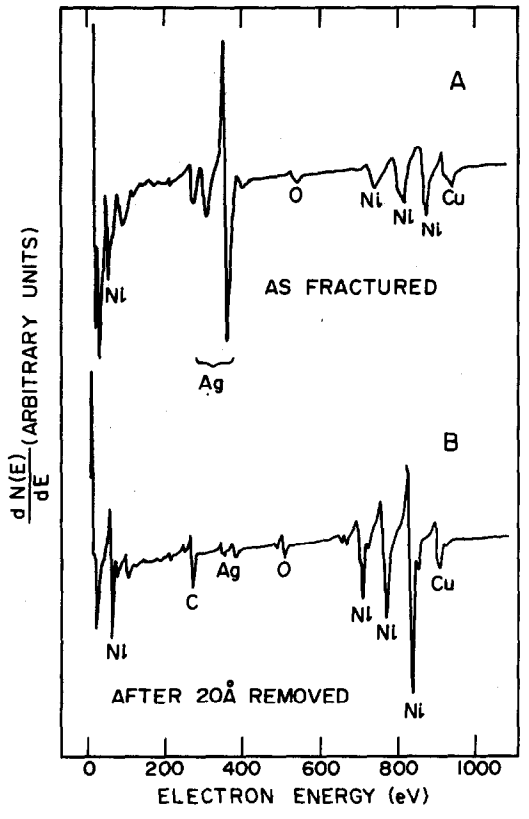

Fig. 10. H. L. Marcus, J. R. Waldrop, F. T. Schuler and E. F. C. Cain.[88] Auger electron spectra of Ni–Ni bond surface. *A*—as fractured and *B*—after 20 Å removed from surface. (By permission of the copyright holders, the Electrochemical Society Inc.)

as Pt and O. These elements were not as strongly bound as the O in the acid-anodized experiment, since they could be partially removed by electron bombardment.

Semiconductors

Several semiconducting materials have been examined by AES for the possibility of surface contamination. For example, Grant and Hass[91] confirmed the work of Taylor[92] regarding the possibility of the Si (111) 7 surface structure being due to an iron impurity. These workers showed that the 45-eV "iron" peak in the Si spectrum is probably due to silicon itself. Further work has shown a similar absence of impurities on Ge (111), GaAs (111), InSb (111)[93] and InAs[94] surfaces.

Alloyed multilayer films have been employed as ohmic contacts to n-GaAs. AES together with DCP was used by Robinson and Jarvis[95] in a study of Ni/Au–Ge contacts on GaAs. Gold and germanium were vacuum-deposited to form a film of eutectic composition on GaAs (100) and GaAs (111) substrates. Nickel was deposited over the Au–Ge and then alloyed at 460° for about 40 sec in a nitrogen atmosphere. Figure 11 shows Auger/depth-composition profiles for the GaAs (111) surface; the curves on the left were obtained before alloying and those on the right after alloying. The results demonstrate that, before alloying, the Ni, Ge and Au covered the substrate in a layered form. After alloying, Ga and As in addition to Ni, Ge and Au are observed near the surface. The authors attribute the relatively high accumulation of Ga near the surface to effusion of the element.

AES and scanning electron microscopy (SEM)

In SEM, changes in collected secondary-electron current with the position of the electron-beam yield information on surface topography. Since the first commercial instrument became available in 1965 the technique has become a powerful research tool. In earlier applications SEM was mainly used to solve problems involving surface topography, but more recently there has been an increasing interest in the correspondence of the surface micrograph with a specific elemental analysis of localized volumes. X-ray spectroscopy combined with SEM is a well-known example of this. In 1970, MacDonald and Waldrop[14,16] demonstrated that the SEM could be interfaced with an Auger spectrometer. Elements in a particular area of a specimen were detected in a point-by-point fashion by high spatial-resolution AES and presented as an Auger-electron image. The image could then be compared with the conventional micrograph. Figure 12 shows the example presented by MacDonald and Waldrop[16] of Auger images (Fe 605 eV and Cu 875 eV) obtained from an iron–copper composite structure. In each image, a point is white if its associated Auger signal-height is at least 25% of the height obtained, just before beginning the image

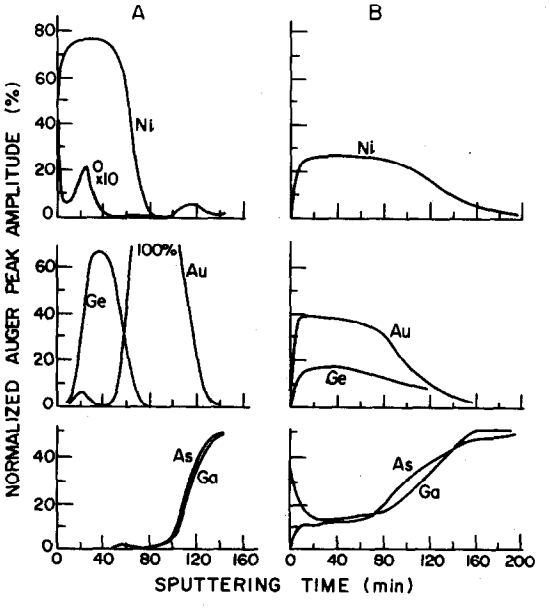

Fig. 11. G. Y. Robinson and N. L. Jarvis.[95] Depth-concentration profile for the ohmic contact structure Ni/Au–Ge on (111) GaAs. *A*—before alloying and *B*—after alloying at 460°C for 40 sec. (By permission of the copyright holders, the American Institute of Physics.)

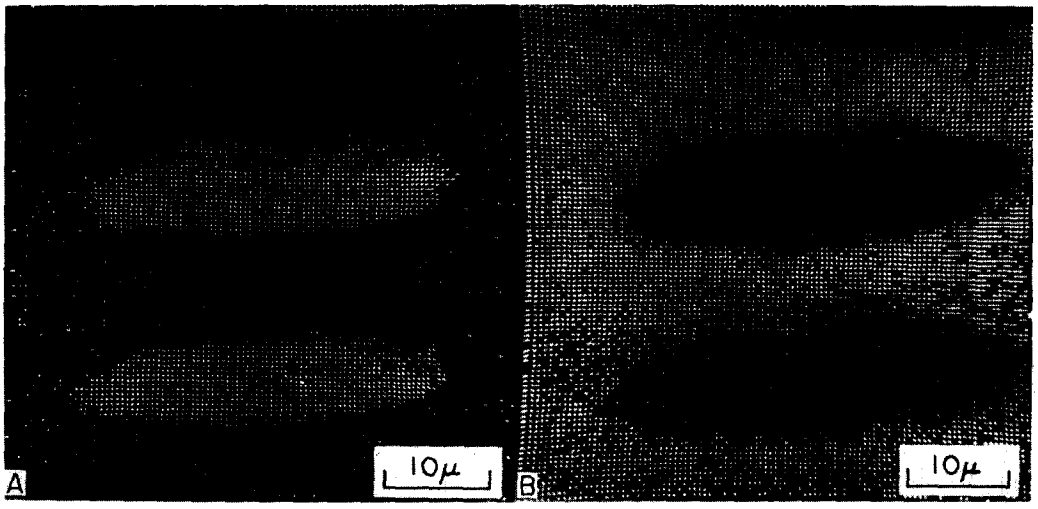

Fig. 12. N. C. MacDonald and J. R. Waldrop.[16] Auger-electron images of an iron–copper composite structure. *A*—iron image and *B*—copper image. (Reprinted by permission of the copyright holders, the American Institute of Physics.)

procedure, from an area known to consist of the corresponding element. The authors pointed out that the spatial resolution is determined by the primary-beam diameter; hence, with the appropriate electron-gun and beam current, submicrometre resolution can be obtained. Furthermore, it shoud be possible to quantify the image by relating the image intensity to Auger peak-height and also to achieve three-dimensional surface analysis by using ion-sputtering.

A number of interesting applications of AES–SEM have been reported in the literature. For example, Marcus *et al.*[88] (see the preceding section) were able to produce an Auger image of the silver present at the surface of the fractured nickel–nickel electrodeposit and compare it with a conventional micrograph (Fig. 13). Another example is the study of Takahashi, Okada and Hotta[96] on the ploughing aspects of frictional force. A sample of MoS_2 was scribed with a diamond tip to determine the relationship between surface damage and change of distribution of elements in the track formed. Auger images of Mo (230 eV) and S (159 eV) showed that the sulphur concentration was higher at the bottom of the track than outside it. This result was associated with the easy cleavage of the crystal because of S–S glide.

The advent of commercial AES–SEM instrumentation should result in the exciting potential for applications in metallurgy, study of electrical devices, for-

Fig. 13. H. L. Marcus, J. R. Waldrop, F. T. Schuler and E. F. C. Cain.[88] Auger-electron image of Ag over bond surface (*A*) and SEM micrograph of same surface (*B*). (Reprinted by permission of the copyright holder, The Electrochemical Society, Inc.)

ensic science and other areas, being fully realized. For an interesting comparison of the possibilities of X-ray, Auger or secondary-ion mass-spectroscopy combined with SEM the reader might consult the paper by Pease.[97] Advantages and disadvantages of the Auger combination as reviewed by this author are reproduced in Table 1.

Table 1. Aspects of AES–SEM[97] (by permission of the copyright holders, Maclean-Hunter Ltd.)

Advantages	Disadvantages
High depth-resolution (5–10 Å)	Spatial resolution 2 μm (?)*
Low detection-limit (10–800 ppm)	High vacuum required
Non-destructive (?)*	Semi-quantitative
Detects elements with $z \geq 3$	Surface-condition dependent
Depth profiling can be used	Difficult to interface AES with SEM
	Slow data acquisition
	Complex instrumentation

* Queries added by the present author.

QUANTIFICATION OF SURFACE AES

The determination of elements present on a surface has been a formidable problem for the Auger spectrometrist for some time. The relationship of the Auger signal to surface concentration is a complex one for several reasons. Inhomogeneity of surface concentration and problems associated with surface morphology are examples. Generally two approaches have been used. The first involves direct or indirect calibration of the surface concentration of a particular element by another technique, and the second is based on experiments concerned with an understanding on a theoretical basis of the factors that contribute to the Auger signal. The latter will be considered first.

Theory

The parameters that contribute to the Auger signal can be written in a simplified expression based on the earlier work of Bishop and Rivière.[98] The Auger current I_A resulting from a transition XYZ in a particular element of concentration N atoms/unit volume is given by

$$I_A = I_P \cdot G \cdot r(E_P) \cdot \tau(E_{XYZ}) \cdot \Phi(E_P, E_X) \cdot \gamma_{XYZ} \cdot N \quad (3)$$

where

I_P = primary current in exciting beam
G = geometrical factor dependent on the instrumental collection efficiency and on the angular distribution of Auger electrons
E_P = energy of exciting beam
$r(E_P)$ = back-scattering factor at E_P
$\tau(E_{XYZ})$ = mean escape depth of electrons with energy E_{XYZ} in the Auger transition XYZ
$\Phi(E_P, E_X)$ = cross-section for ionization of level X of binding energy E_X by an electron of energy E_P
γ_{XYZ} = probability of relaxation by the Auger transition XYZ following ionization of X.

With regard to a particular Auger transition, I_P, E_P and G are generally known; thus the important remaining parameters are r, τ, Φ and γ.

The back-scattering factor r is concerned with the additional contribution to the Auger signal that occurs as a result of ionization by electrons inelastically scattered at the surface. It depends on the energy of the exciting beam E_P and the substrate involved (and therefore E_X). Several workers[98–101] have demonstrated this dependence for a primary beam at normal incidence. Neave, Foxon and Joyce[102] examined Auger yield as a function of primary-beam energy at both normal and glancing incidence, using a silicon (111) surface ($L_{2,3}VV$ Si transition) and a carbon-contaminated silicon surface ($KL_{2,3}L_{2,3}$ C transition). At normal incidence the number of electrons capable of causing ionization, *i.e.*, with energy $> E_X$, reached a maximum at $E_P \sim 6E_X$, whereas at glancing incidence the number continued to increase up to at least $E_P = 22E_X$. Thus, the major determining factor in this case was taken to be the energy distribution of the back-scattered electrons. The contribution of the primary beam was said to be small.

Goto *et al.*[103,104] have used the so-called δ–η method to estimate the contribution of back-scattered electrons to Auger and secondary-electron yields; the system employed was a beryllium deposit on a copper substrate, with normal incidence of the electron beam. The total secondary-electron yield σ and back-scattering coefficient η were obtained experimentally. The true secondary-electron yield δ is found by subtracting η from the total yield. Experiments on Auger electron yield δ_A were carried out at values of E_P from 200 eV to 2.0 keV. Table 2 summarizes the results obtained. In these data, S_A reflects the efficiency of back-scattered electrons in producing Auger electrons and δ_{A_0} the yield due to primary electrons only, both expressed in arbitrary units. Additionally, β_A is the ratio of S_A to δ_{A_0}. The values of r_A are as given by equation (3). The results clearly confirm that back-scattered electrons contribute significantly to the Auger yield, as pointed out by Neave, Foxon and Joyce.

The amount of data available on measurements of electron-scattering lengths or escape-depths τ has

Table 2. Auger-electron characteristics of beryllium[104] (by permission of the copyright holders, North-Holland Ltd.)

E_p *keV*	0.8	1.0	1.5	2.0
S_A	4.0	6.5	6.5	5.5
δ_{A_0}	3.3	2.75	2.15	1.75
β_A	1.2	2.4	3.0	3.1
r_A	1.1	1.2	1.2	1.25

continued to expand over recent years. Values determined by a variety of methods have been assembled by Lindau and Spicer[105] and plotted as a function of the electron energy above the Fermi level for metals and above the valence-band maximum for non-metals (Fig. 14). The logarithmic energy scale ranges from 0 to 3000 eV. The general behaviour is first a sharp decrease with increasing energy followed by a flat minimum in the 50–500 eV range. At higher energies the curve rises again to increased escape-depth. In addition to the large energy-dependence, extremely short τ-values are observed for Cs, Ba, Sr and Yb, and tervalent metals such as Gd and Ce have much greater scattering lengths than bivalent metals such as Ba and Sr. Undoubtedly many more measurements of this parameter will be added in the future. For examples of the techniques involved in escape-depth determination the reader should consult the papers listed in reference 105.

Relatively few measurements of the cross-section Φ (important for AES) have been documented. A significant proportion of those that have been measured have been determined in the gas-phase; for example, Glupe and Melhorn[106] have given K-level cross-sections for the elements in CH_4, N_2, O_2 and Ne. However, a number of semi-empirical expressions have been developed that generally have the form:

$$\Phi(E_p,E_X) = [b/(E_X)^2]f(E_p/E_X) \quad (4)$$

where b is a constant which can take different values, for example, for a K or L level, and f is a function of the ratio of the primary-beam energy to the inner-shell ionization energy. Smith and Gallon used a simple model to estimate Φ by AES for carbon, silicon, selenium, silver, gadolinium and gold. In the equation:

$$I_A = C(I_P\Phi + \alpha\beta) \quad (5)$$

C is a constant and the term $\alpha\beta$ represents the back-scattering contribution. The relative Auger current was measured experimentally for a number of E_p values and the energy-distribution of back-scattered current was also determined. Values of Φ were then computed by an iterative procedure. Generally the cross-sections increase sharply from those for $E_p = E_X$ to a maximum at $E_p \approx 3E_X - 6E_X$, then decrease slowly.

Finally, γ can generally be neglected since it is close to unity, owing to the fact that in conventional AES only shallow inner levels are ionized. Under these conditions the X-ray fluorescence yield is very low compared to Auger-electron production.

Calibration

As with many other analytical techniques, a quantitative analysis can be achieved through calibration procedures, *i.e.*, by correlation of the magnitude of the Auger signal with a measure of surface concentration from another technique. Several independent methods have been used, of which some are direct in that the surface concentration can be obtained from the technique used, whereas others require calibration themselves. Generally, with all these methods, it has been found that there is a linear relationship of surface concentration to Auger-electron count up to monolayer coverage. However, where more layers on a surface are involved the relationship can be somewhat more complex because, for example, of the

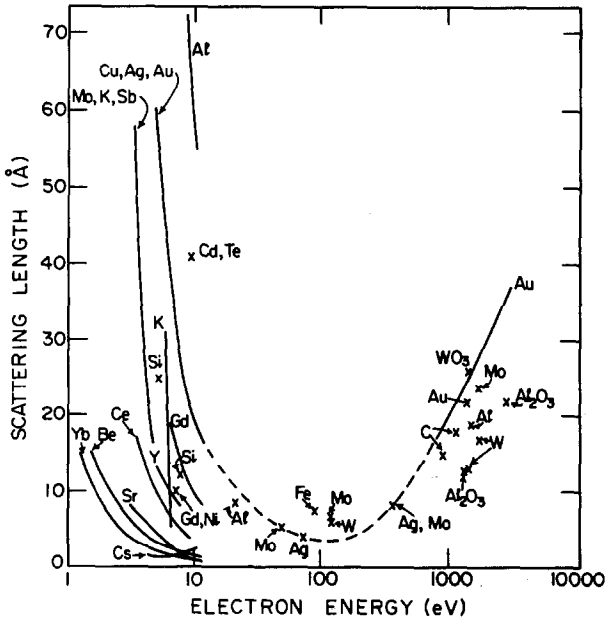

Fig. 14. I. Lindau and W. E. Spicer.[105] Escape depth in Å as a function of the electron energy above the Fermi level for a number of materials. Data sources are listed in reference 105. (By permission of the copyright holders, Elsevier Ltd.)

formation of islands. A few examples of calibration methods are now described.

Perdereau[107] measured the amount of sulphur adsorbed on nickel (111) and (100) surfaces by using hydrogen sulphide labelled with ^{35}S. The amplitudes of the nickel $M_3M_{4,5}M_{4,5}$ peak at 62 eV and sulphur $L_{2,3}MM$ peak at 150 eV were measured as a function of the quantity of sulphur adsorbed on the surface. The radioactivity method for finding the latter was carried out with a precision of $\pm 2 \times 10^{-9}$ g/cm^2. A linear calibration plot was obtained up to saturation of the nickel surface with sulphur. An ion-counting method was used by Thomas and Haas.[108] Sodium, potassium, rubidium and caesium ions from zeolite sources were deposited on a molybdenum (110) surface. The coverage of the surface in each case was calculated from the ion flux to the example. Both alkali-metal ion peaks (Cs 47 eV, Rb 75 eV, K 251 eV) and molybdenum peaks were monitored as a function of coverage. Again linear graphs were obtained under the conditions used.

Several workers[109–111] have employed a quartz crystal oscillator to measure coverage as a function of AE signal. An example of such a quantitative study is that on the adsorption of phosphorus on a silicon (111) surface.[110] In this experiment, a beam of phosphorus particles, largely consisting of P_2 molecules, was impinged at the same rate on both the sample and a quartz crystal oscillator (microbalance) in a series of evaporations. The particles reflected from the silicon and oscillator were monitored by a mass spectrometer to allow determination of the rate of phosphorus adsorption. The ratios of silicon (91 eV) and phosphorus (121 eV) Auger signals were plotted against phosphorus coverage in atoms/cm^2. The main disadvantage with this type of method is that the calibration does not apply to the same surface as that examined by AES. Meyer and Vrakking[99,112] have calibrated Auger peaks by ellipsometry. In ellipsometry the change in the state of polarization of polarized light upon reflection from a surface is measured. The data from the technique can be interpreted quantitatively in terms of surface coverage. The authors have studied the adsorption of O_2 on silicon (111)[99] and PH_3, CH_3SH, CH_3Cl, CH_3OH, NH_2 and other molecules on silicon and germanium surfaces[112] in this manner.

ANALYTICAL POTENTIAL OF GAS-PHASE AES

Despite the growing number of applications of electron-excitation AES in surface studies, relatively little attention has been paid to the analytical potential of the Auger effect in the gas-phase. With the latter it is not necessary to operate the spectrometer in the differential mode as is generally the case with solids. Furthermore, solid-state broadening problems are avoided.[113] Much of the earlier work in the gas-phase was confined to the rare gases.[114–116] In later work, the spectra of several small molecules were recorded, for example N_2, O_2, NO, CO, CO_2 and H_2O,[117] C_3O_2[118] and brominated methanes.[119] Other papers have referred to germanium[120] and organochlorine compounds,[121] and to theoretical analyses of Auger spectra of HF[122] and CH_4.[123]

The possibilities for gas-phase Auger spectrometry in analytical chemistry have recently been discussed by Thompson, Hewitt and Wooliscroft.[17] The factors that contribute to the analytical potential are given below together with one or two comparisons with X-ray excitation.

1. *Qualitative analysis.* The theory of the Auger effect suggests that the technique can provide at least a qualitative elemental analysis for all elements with the exception of hydrogen and helium. Also, in the gas-phase, the valence spectrum observed within the Auger elemental region can yield information about molecular structure. Furthermore, the valence spectrum can be used in a "fingerprint" fashion for the purpose of qualitative identification. With X-ray excitation much of the valence spectrum can be obscured, owing to the energy-width of the exciting source.

2. *Sensitivity and quantitative analysis.* The combination of the availability of electron beams of high flux, and the relatively high inner-shell cross-sections for ionization by electrons leads to the very sensitive nature of the technique. Moreover, the sensitivity is "increased" by multiple excitation from the primary beam, and from back-scattered electrons.

The X-ray flux is considerably smaller and also the cross-sections for ionization of levels of binding energy < 500 eV are lower than with electrons.

3. *Auger theory.* Gas-phase AES offers the opportunity to further understand Auger chemical shifts, ionization cross-sections and Auger quantification.

4. *Surface studies.* Correlation of results for the gas-phase with the spectra of gases adsorbed at surfaces should prove useful in the interpretation of the bonding character of surface-adsorbed species.

Some drawbacks of the technique are as follows.

1. A secondary-electron background is observed, which can be a disadvantage, although this is not as serious as in analysis of solids.

2. Owing to a number of factors such as primary-beam multiple excitation, quantification is difficult.

3. Spectra can be difficult to interpret because of the relatively complex nature of the Auger process and the presence of satellite peaks due to other transitions.

4. The reactivity of the electron must be considered.

5. Instrumentation is both complex and expensive.

Compared to the conventional spectrometer designed for surface work, the gas-phase instrument must include adequate differential pumping for the electron-source, and an electron-energy analysis system capable of greater resolution. A schematic diagram of the spectrometer used by the author is shown in Fig. 15. The electron beam passes through a differential pumping system made between a bridge-piece

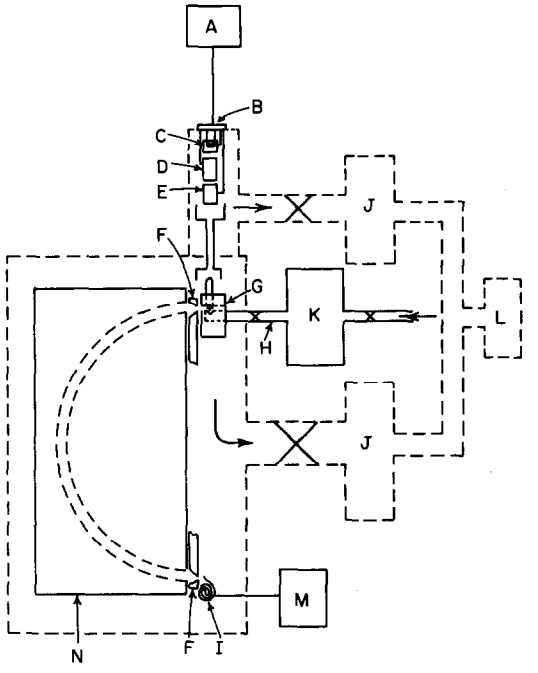

Fig. 15. M. Thompson, P. A. Hewitt and D. S. Woolliscroft.[17] Schematic of gas-phase Auger spectrometer. *A*—electron-gun power-source, *B*—electron-gun base, *C*—gun filament, *D*—focusing anodes, *E*—quadrupoles, *F*—slits, *G*—target chamber, *H*—gas-introduction probe, *I*—electron multiplier, *J*—pumping, *K*—rough pumping, *L*—backing pump, *M*—recorder , *N*—hemispherical analyser. (Reprinted by permission: copyright the American Chemical Society.)

and the electron-gun. The bridge is situated at the entrance side of the analyser and contains a gas-inlet block and vertical inlet tube. Electrons from the tube pass through a variable entrance slit into a 150° hemispherical analyser.

Although this system was used to produce spectra of several molecules, several modifications have been recommended which should increase the sensitivity and ease of application of the instrument.[124]

The sensitivity of the Auger instrument, for a particular transition, can be expressed through the equation

$$I_A = I_p \cdot G \cdot r \cdot \Phi \cdot \gamma \cdot S \cdot P \qquad (6)$$

where P is the gas pressure, S is the probability of Auger-electron escape without prior collision, and the other parameters are as given for equation (3).

As mentioned previously, the potential of AES for sensitive gas analysis lies in the parameter I_p, since high electron fluxes can be obtained with commercial electron-guns. For example, under appropriate conditions, argon present in air is easily detected at 1000 cps. From a quantitative point of view, as with many analytical techniques, it is clearly desirable to calibrate the instrument in terms of Auger count-rate and concentration rather than by use of the several factors in the equation, The importance of one of these parameters, S, is shown in Fig. 16 where the effect of scattering of Auger electrons increases with rising pressure (measured in the differential pumping line).

With respect to the qualitative aspects of the technique, the spectra of molecules in their particular elemental Auger regions are highly characteristic; Fig. 17 shows those obtained from acetylene and ethylene. Interpretation of the spectra can be achieved tentatively through empirical calculations of Auger energies from data from X-ray and ultraviolet photoelectron spectroscopy and equations such as those described previously. For example, the assignment of carbon 1*s*2*m*2*n* transitions of acetylene is given in Table 3.

Where mixtures of gas molecules are involved it is envisaged that prior separation by gas-chromatography will be required. The interfacing of the spectrometer with GLC instruments should present no serious problems in view of the present molecular-separator technology available in analysis by GLC-mass spectrometry.

With regard to the understanding of the Auger chemical shift Siegbahn and co-workers[125] have recently carried out gas-phase AES experiments on several organosulphur and organosilicon compounds. The results were correlated with shifts observed in X-ray photoelectron spectroscopy. It is clear that this area will be a fruitful one for electron spectroscopists in the future.

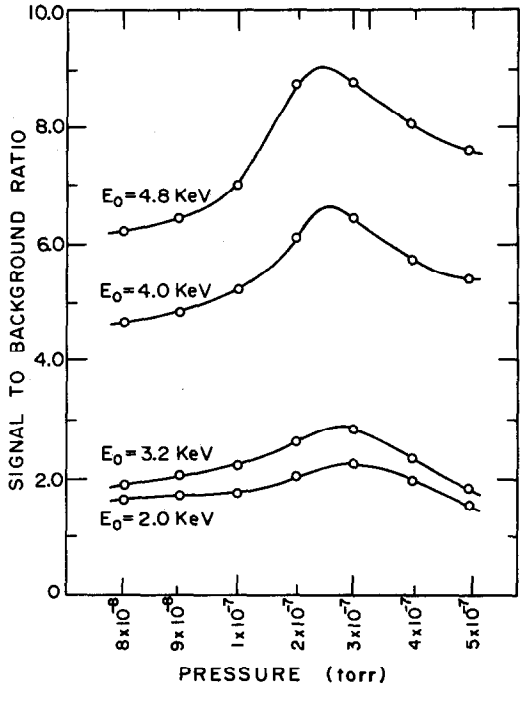

Fig. 16. M. Thompson, P. A. Hewitt and D. S. Woolliscroft.[17] Auger signal-to-background ratio for the argon $2p_{3/2}3p3p$ ($^1D_2$) transition as a function of differential pumping-pressure and incident-beam energy. (Reprinted by permission; copyright by the American Chemical Society.)

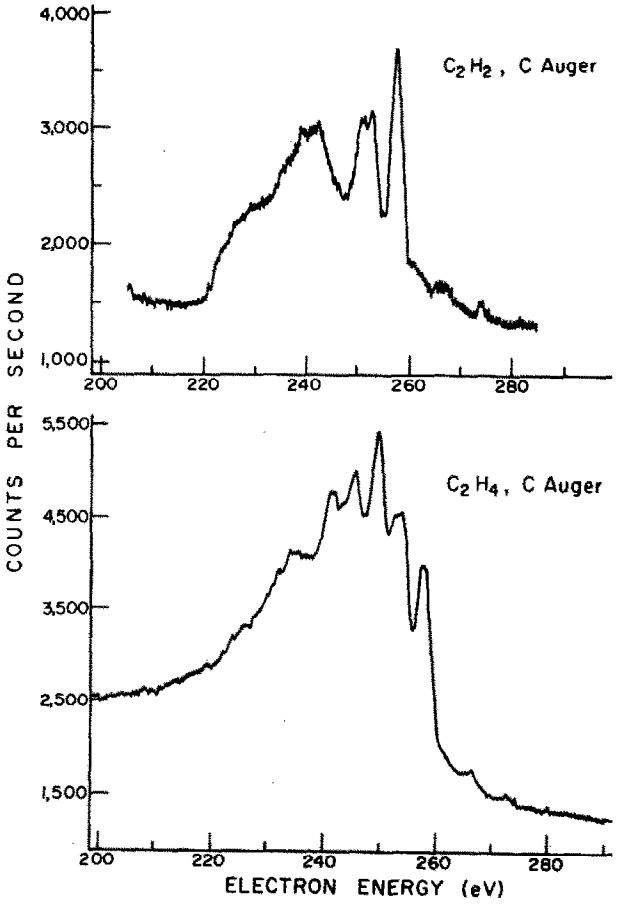

Fig. 17. M. Thompson, P. A. Hewitt and D. S. Wooliscroft.[17] Auger spectra of acetylene and ethylene in carbon 1*s*2*m*2*n* region. (Reprinted by permission; copyright by the American Chemical Society.)

Table 3. Assignment of carbon 1*s*2*m*2*n* Auger transitions of acetylene (adapted from *Anal. Chem.*, 1976, **48**, 1336 by permission. Copyright by the American Chemical Society)

Experimental, *eV*	Empirically calculated, *eV*	Assignment
256.9	256.9	$1s2p\pi^b2p\pi^b$
252.3	252.0	$1s2p\pi^b2p\sigma^b$
250.6	249.9	$1s2p\pi^b2s^*$
247.3	247.1	$1s2p\sigma^b2p\sigma^b$
243.5	242.7	$1s2s\sigma^*2s\sigma^*$
241.9	239.9	$1s2p\sigma^b2s\sigma^*$
238.4	237.8	$1s2s\sigma^b2s\sigma^b$
232.4	232.8	$1s2s\sigma^b2s\sigma^b$

Finally, Vrakking and Meyer[126] have used gas-phase Auger spectrometry with some success to obtain ionization cross-sections for elements in several organic compounds.

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ANALYTICAL APPLICATION OF PORPHYRINS—I

SPECTROPHOTOMETRIC DETERMINATION OF ULTRAMICRO AMOUNTS OF COPPER WITH α,β,γ,δ-TETRA-(3-*N*-METHYLPYRIDYL)PORPHINE

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Summary—A new water-soluble porphyrin, α,β,γ,δ-tetra(3-*N*-methylpyridyl)porphine [T(3-MPy)P], has been synthesized, and its reaction with copper(II) studied spectrophotometrically. Sensitive methods for the determination of copper at ppM level have been established. The spectrophotometric sensitivity and relative standard deviation of the recommended procedure for copper are 0.18 ng/cm^2 (for $A = 0.001$) and 1.0%, respectively. The interference of 19 ions and 20 salts has been examined, and found to be minimal. The methods established could be applied to the determination of copper in water samples with satisfactory results.

Porphyrins and metalloporphyrins have been the subject of many biological and physicochemical studies. Recently, attention has been given to analytical use of porphyrins and their metal complexes, because of their high molar absorptivities and their stability. However, at present, only two porphyrins, α,β,γ,δ-tetraphenylporphine (TPP)[1] and its trisulphonate ($TPPS_3$),[2] have been used as spectrophotometric reagents for traces of zinc and copper respectively.

In this paper, T(3-MPy)P, one of several new water-soluble porphyrins synthesized in our laboratory, is described and moderately selective spectrophotometric methods for the determination of copper at the ppM (parts per milliard) level are reported.

EXPERIMENTAL

Reagents

All reagents used were of analytical-reagent grade unless otherwise described. All solutions were prepared with distilled, demineralized water.

T(3-MPy)P solution. A $6.7 \times 10^{-5} M$ solution was prepared by dissolving 22.8 mg of T(3-MPy)P tetratosylate in 250 ml of water and diluted with water, if necessary. T(3-MPy)P tetratosylate was synthesized by methylation of α,β,γ,δ-tetra(3-pyridyl)porphine [T(3-Py)P] with methyl-*p*-toluenesulphonate.[3] T(3-Py)P was synthesized by refluxing pyrrole and pyridine-3-aldehyde in propionic acid, the method proposed by Adler *et al.*[4] for meso-substituted porphyrins being somewhat modified by the present authors. The results of the elemental analysis of T(3-MPy)P tetratosylate were as follows. Found: C 63.5%; H 4.8%; N 8°.3%; S 9.5%. Calculated for $C_{72}H_{66}N_8O_{12}S_4$: C 63.4%; H 4.9%; N 8.2%; S 9.4%. The details of the method for synthesis will be reported elsewhere, along with the results of spectral studies.

Standard copper(II) solution. A stock aqueous solution containing *ca.* 4 g of $CuSO_4 \cdot 5H_2O$ per litre was prepared, sufficient sulphuric acid to give a pH of *ca.* 1 being added. This stock solution was standardized by titration with EDTA and appropriately diluted to prepare working solutions.

Recommended procedures

Procedure A (Cu less than 13 ppM). Place the sample solution containing less than 0.65 μg of copper(II) in a 50-ml volumetric flask. Add 2 ml of acetate buffer (pH 6) and 2.0 ml of $6.7 \times 10^{-6} M$ T(3-MPy)P solution. Heat for 7 min in a boiling water-bath and allow to cool to room temperature in running water. Add 8 ml of sulphuric acid (1 + 1) and dilute to the mark with water. Measure the absorbance at 434 nm, in 100-mm cells, against water as reference.

Procedure B (Cu 10–130 ppM). Place the sample solution containing less than 3.2 μg of copper(II) in a 25-ml volumetric flask. Add 1 ml of acetate buffer (pH 4) and 1.0 ml of $6.7 \times 10^{-5} M$ T(3-MPy)P solution. Heat for 8 min in a boiling water-bath and allow to cool to room temperature in running water. Add 4 ml of sulphuric acid (1 + 1) and dilute to the mark with water. Measure the absorbance at 434 nm, in 10-mm cells, against water.

Procedure C (Cu 25–250 ppM). Place the sample solution containing less than 6.2 μg of copper(II) in a 25-ml volumetric flask. Add 1 ml of monochloroacetate buffer (pH 3) and 3 ml of $6.7 \times 10^{-5} M$ T(3-MPy)P solution. Heat for 10 min in a boiling water-bath and allow to cool to room temperature in running water. Add 2.5 ml of sulphuric acid (1 + 1) and dilute to the mark with water. Measure the absorbance at 419 nm, in 10-mm cells, against reagent blank.

RESULTS AND DISCUSSION

Absorption spectra

T(3-MPy)P is generally obtained as the tosylate, shown in Fig. 1. Its absorption spectra in aqueous media of different pH are illustrated in Fig. 2. Above about pH 2, the T(3-MPy)P solution is reddish-purple and above pH 2.5, it has absorption maxima at 417 (Soret band, $\epsilon = 2.8 \times 10^5$ l. mole^{-1}. cm^{-1}), 515, 582 and 655 nm and a shoulder at about 550 nm. Below about pH 1, it is green, and in 3*N* sulphuric acid it has absorption maxima at 434 (Soret band, $\epsilon = 3.8 \times 10^5$), 582 and 631 nm. Further, as may be seen from Fig. 2 and Table 1, in moderately or

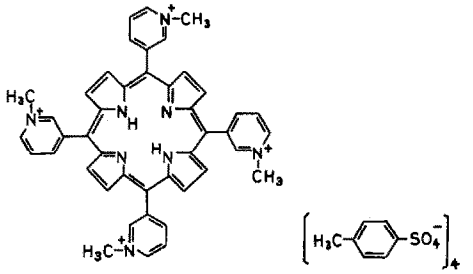

Fig. 1. α,β,γ,δ-Tetra(3-*N*-methylpyridyl)porphine tetratosylate.

strongly acidic media, the Soret band shifts to slightly longer wavelength with increasing acid concentration and its molar absorptivity is dependent upon the nature of the acid. The acid effects are largest in hydrochloric acid solution. The spectra having the Soret band at 417 and 434 nm seem to correspond to the free base form (H_2R) and the diprotonated form (H_4R^{2+}), respectively, and both species are considered to exist as monomers throughout the concentration ranges of proton and T(3-MPy)P, employed, thus behaving similarly to α,β,γ,δ-tetra(4-*N*-methylpyridyl)-porphine [T(4-MPy)P].[3,5]

Figure 3 shows the absorption spectra of the copper(II)–T(3-MPy)P complex under different conditions. Curve **a**, which is measured in the presence of excess of copper(II) against water as reference, has absorption maxima at 420 (Soret band, $\epsilon = 2.7 \times 10^5$), 545 and 630 nm and a shoulder at about 578 nm. On the other hand, the Soret band of curve **b**, obtained in the presence of excess of T(3-MPy)P (against reagent blank as reference), which is of analytical interest, is at 419 nm ($\epsilon = 2.1 \times 10^5$).

As may be seen from the results described above, the molar absorptivities of T(3-MPy)P and its copper(II) complex at each Soret band are extremely large as compared with those of the ligands and complexes commonly used in spectrophotometry—this suggests extremely high sensitivity, and the Soret band of the copper(II) complex is clearly distinguished from that of the H_4R^{2+} form of

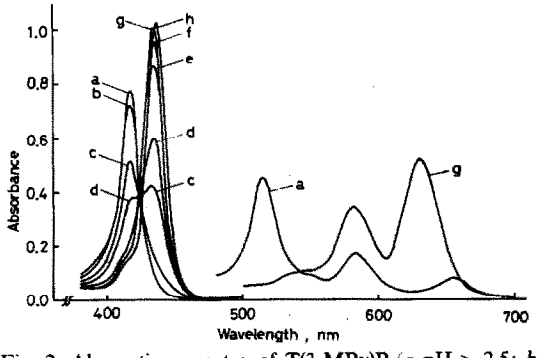

Fig. 2. Absorption spectra of T(3-MPy)P. *a* pH > 2.5; *b*, pH 2.2; *c*, pH 1.8; *d*, pH 1.6; *e*, pH 1.1; *f*, 1*N* H_2SO_4; *g*, 3*N* H_2SO_4; *h*, 18*N* H_2SO_4. The Soret bands are recorded at one-tenth the concentration ($2.7 \times 10^{-6}M$) used for the wavelengths >500 nm.

Table 1. Effect of acids on Soret band of T(3-MPy)P

Medium	Soret band, *nm*	ϵ, $l.mole^{-1}.cm^{-1}$
1*N* HCl	435	3.4×10^5
6*N* HCl	443	3.2×10^5
1*N* H_2SO_4	434	3.6×10^5
3*N* H_2SO_4	434	3.8×10^5
18*N* H_2SO_4	436	3.9×10^5
1*N* HNO_3	432	3.9×10^5
7*N* HNO_3	436	3.8×10^5
1*N* $HClO_4$	432	3.8×10^5
9*N* $HClO_4$	435	3.8×10^5

T(3-MPy)P, although very close to that of the H_2R form. The absorbance measurements for the determination of copper, therefore, should be carried out in acidic media where excess of T(3-MPy)P exists in the H_4R^{2+} form, if the Soret band is used to obtain high sensitivity. However, as the complex formation reaction of T(3-MPy)P with copper(II) is very slow and incomplete in such acidic media, it is preferable to form the complex at somewhat higher pH followed by acidification with acid (*e.g.*, sulphuric acid), and then the absorbance of the excess of reagent is measured at 434 nm against water or that of the complex is measured at 419 nm against a reagent blank.

Reaction rate of complex formation

The rate of formation of T(3-MPy)P complexes with metal ions is generally slow at room temperature. It depends on the kind of metal ion, pH of the solution and the concentrations of T(3-MPy)P and the metal ion, in addition to the reaction temperature. This suggests that selectivity in the determination of metals with T(3-MPy)P can be increased by controling the reaction rate. The complex formation with copper(II) is slow at room temperature, so it is necessary to accelerate the reaction by heating. Figure 4

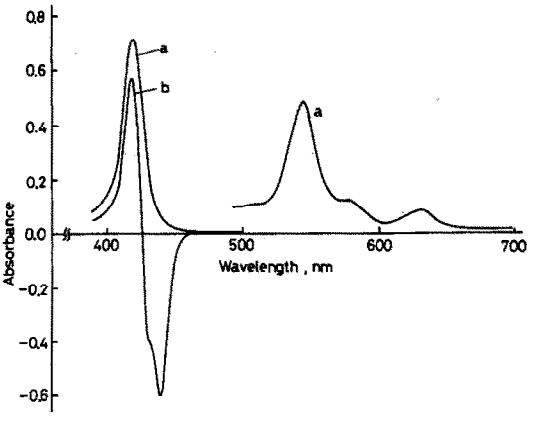

Fig. 3. Absorption spectra of Cu(II)–T(3-MPy)P complex, (*a*) In the presence of excess of copper(II), pH:6. Reference: water. [T(3-MPy)P]: $2.7 \times 10^{-6}M$. (*b*) In the presence of excess of T(3-MPy)P. Reference: reagent blank. [Cu(II)]: 169 ppM, [T(3-MPy)P]: $8.0 \times 10^{-6}M$. Acidified with H_2SO_4 to 2.2*N* after the complex formation is completed at pH 6. The Soret bands are recorded at one-tenth the concentration used for the wavelengths >500 nm.

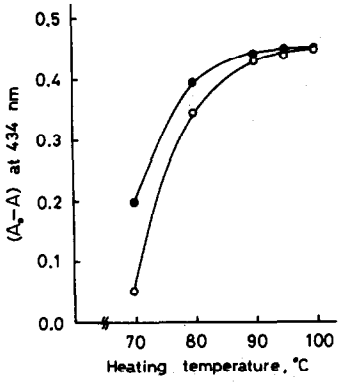

Fig. 4. Effect of heating temperature. [Cu(II)] 81 ppM, [T(3-MPy)P]: $2.7 \times 10^{-6}M$. Heating time: 8 min. Reference: water. —●— pH 4.0, —○— pH 3.5. A_0 and A are the absorbances of reagent blank and sample, respectively.

shows the effect of heating temperature on the degree of complex formation in a fixed heating time (8 min). From Fig. 4, it is seen that the complex formation is accelerated by increasing the temperature or pH, and is complete on heating at 100°.

Effect of heating time

The effect of heating time at 100° was examined with varying pH. The results are shown in Fig. 5, from which it is found that the heating time required for obtaining a constant absorbance can be shortened by raising the pH, and that above pH 3.5, a constant absorbance is obtained within 10 min. On the other hand, other experiments show that the optimum heating time also depends on the copper concentration: the rate of the complex formation decreases with decreasing copper concentration, so it is necessary to heat for a somewhat longer time when the copper concentration is extremely low.

Influence of pH

The influence of pH on the complex formation of T(3-MPy)P with copper(II) at 100° is shown in Fig. 6, from which it is found that (*i*) the lower limit of

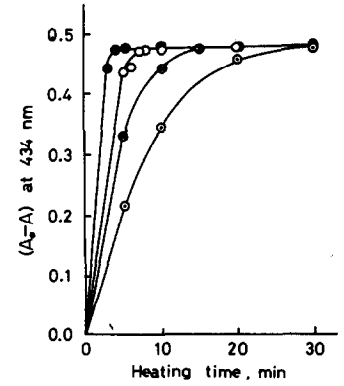

Fig. 5. Effect of heating time at 100°. [Cu(II)]: 85 ppM, [T(3-MPy)P]: $2.7 \times 10^{-6}M$. Reference: water, 10-mm cells. A_0 and A are the absorbances of reagent blank and sample, respectively. —○— pH 2.5, —⊗— pH 3.0, —○— pH 3.5, —●— pH 4.0.

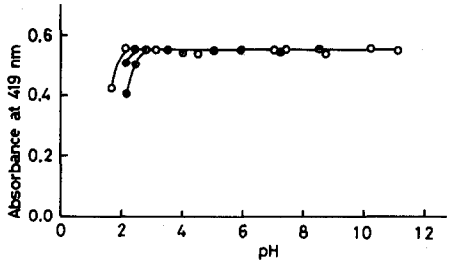

Fig. 6. Influence of pH on the complex formation at 100°. [Cu(II)]: 169 ppM, [T(3-MPy)P]: $8.0 \times 10^{-6}M$. Reference: reagent blank. Heating time: —○— 5 min, —●— 10 min, —○— 30 min.

Table 2. Optimum ranges, sensitivities and molar absorptivities of the recommended procedures

Procedure	Optimum range, *ppM*	Sensitivity for 0.001 absorbance, $\mu g/cm^2$	Molar absorptivity, $l.mole^{-1}.cm^{-1}$
A	1–13	1.8×10^{-4}	3.5×10^5
B	10–130	1.8×10^{-4}	3.5×10^5
C	25–250	3.1×10^{-4}	2.1×10^5

pH, above which a constant absorbance is obtained, is closely related to heating time, (*ii*) a constant absorbance is obtained at pH > 2.2, if the solution is heated for 30 min at 100°, and (*iii*) in order to shorten the heating time, the pH must be raised somewhat.

Amount of sulphuric acid for acidification

As described already, the complex formation reaction is accelerated by increasing pH. On the other hand, at pH > 2, the Soret band of T(3-MPy)P overlaps almost completely with that of the complex. Therefore, it is preferable that the complex formation is taken to completion at a suitable pH above 3, followed by acidification to distinguish the Soret band of T(3-MPy)P from that of the complex. In the recommended procedures, sulphuric acid is used for the aci-

Table 3. Influence of ions and salts

Ions or salts	Tolerance limit
Ca(II), Cd(II), Hg(II), Mg(II), Ni(II), Pb(II)	1000 μg
Ag(I), Al(III), Cr(III), Fe(II), Fe(III),* Ga(III), Mn(II), Zn(II)	100 μg
Co(II), In(III), Pd(II)†, V(IV), V(V)	10 μg
KBr, KI, NaCl, Na_2SO_4, NH_4Cl	0.4*M*
K_2SO_4	0.13*M*
KCl, KNO_3, KSCN, NaBr, $NaNO_3$, $NaClO_4$, NaSCN	0.04*M*
K_3PO_4, KH_2PO_4, Na_2HPO_4.	0.027*M*
Tartrate	0.02*M*
Citrate	0.013*M*
NaI	0.004*M*
$Na_2B_4O_7$	0.002*M*

Cu(II) taken: 2.12 μg.

* One ml of 0.5% hydroxylamine hydrochloride solution was added.

† One ml of 0.01*M* potassium iodide solution was added.

Table 4. Determination of copper in water samples

Sample	Sample taken, *ml*	Cu added, *ng* (*a*)	Cu found, *ng* (*b*)	(*b*)–(*a*) *ng*		Cu content, *ppM*
Tap water	25.0	0	197	197		7.8_6
	25.0	0	201	201		8.0_4
	25.0	0	192	192		7.6_8
					Average	7.8_6
Water of the	25.0	0	192	192		7.6_8
Hirose river	25.0	169	363	194		7.7_6
	25.0	254	450	196		7.8_4
					Average	7.7_6

dification. Fortunately, the complex, once formed, is very stable even in the strongly acidic solution, and constant absorbances are obtained in the sulphuric acid concentration ranges 2.2–3.6*N* in procedures A and B, and 0.4–3.6*N* in procedure C.

Calibration curves

Straight-line calibration curves were obtained for all the procedure recommended. The equations for the curves were

$$\text{Cu (ppM)} = 1.8 \times 10 (A_0 - A) \quad (1)$$

$$\text{Cu (ppM)} = 1.8 \times 10^2 (A_0 - A) \quad (2)$$

$$\text{Cu (ppM)} = 3.1 \times 10^2 A \quad (3)$$

where A_0 and A are the absorbances of the reagent blank and sample respectively, and the equations (1), (2) and (3) correspond to procedures A, B and C respectively. The optimum range for the copper determination, the sensitivity for 0.001 absorbance and the molar absorptivity are summarized for each procedure in Table 2.

Precision test

Twenty-one standard solutions containing 2.12 μg of copper were determined by procedure B. The results gave a relative standard deviation of 1.0%.

Interference studies

Solutions containing 2.12 μg of copper(II) and varying concentrations of each ion or salt to be tested were prepared. The copper was then determined by procedure B. Cations were added in the form of chlorides, nitrates or sulphates; anions were added in the form of the sodium or potassium salts. The limiting value of the concentration of foreign ions or salts was taken as that which caused an error of not more than 3%. The results are summarized in Table 3. Most anions do not interfere with the determination. Interference due to 100 μg of iron(III) or 10 μg of palladium (II) can be removed by the addition of 1 ml of 0.5% hydroxylamine hydrochloride solution and 1 ml of 0.01*M* potassium iodide solution, respectively.

Composition of the complex

Continuous-variation and mole-ratio methods were applied to the copper(II)–T(3-MPy)P system in oorder to determine the stoichiometry of the complex. The results revealed that the ratio is 1:1.

Application of the method

Copper in water samples was determined by procedure A. The results are summarized in Table 4, from which it is seen that copper at the ppM level can be determined with good reproducibility.

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DETERMINATION OF PLATINUM IN ORES BY A COMBINED FIRE-ASSAY AND FLAMELESS ATOMIC-ABSORPTION METHOD

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Summary—A combined fire-assay and flameless atomic-absorption procedure for the determination of platinum in ores is described. Silver beads obtained by cupellation are dissolved in *aqua regia* and made up to standard volume with 6*M* hydrochloric acid, then 50-μl aliquots are injected into a carbon tube. From 0.5 to 5 ppm platinum can be determined with a precision of approximately 5%. The procedure tolerates other platinum metals and gold in the amounts present in the ores analysed.

Much work has been done on the determination of the noble metals by flameless atomic absorption.[1–4] Most of this work however, has been concerned with studies of optimum conditions and interferences from various metals and inorganic acids and very few practical applications have been reported. Janouskova *et al.*[5] determined platinum in reforming catalysts and good agreement with conventional flame atomic-absorption analysis was reported. Bratzel *et al.*[6] determined gold and silver in geological and metallurgical samples in the ng/g range with a carbon-rod atomizer. The results showed good agreement with certified values obtained by a combined fire-assay and flame atomic-absorption procedure.

As part of a comparative study of methods for the determination of platinum in ores conducted in this laboratory, a combined fire-assay and flameless atomic-absorption method was developed and results were compared with previous analyses obtained from independent sources.

EXPERIMENTAL

Apparatus

Lindberg Hevi-duty 20-kW electric furnace. Magnesia cupels produced by Leonard Light Industries (Benoni, South Africa). Crucibles produced by A. P. Green Refractories (Ontario, Canada). Perkin-Elmer 403 Atomic Absorption Spectrophotometer fitted with the HGA-70 flameless atomization device and a deuterium background-corrector. Intensitron platinum hollow-cathode lamp. An Eppendorf 50-μl pipette with disposable tips was used for all injections.

Reagents

Platinum solution (1 mg/ml). Prepared by dissolving 1 g of pure platinum wire (Johnson, Matthey and Mallory) in *aqua regia*. Nitrous oxides were removed by repeated evaporations with concentrated hydrochloric acid. The solution was filtered into a 1-litre flask and made up to the mark with 0.1*M* hydrochloric acid. The solution was standardized with thiophenol,[7] and a second solution was standardized spectrophotometrically[8] against the first, calibrated glassware being used.

Palladium and gold solutions (1 *mg/ml*). Prepared by dissolving the pure metals in *aqua regia*, evaporating to dryness several times with concentrated hydrochloric acid and making up to volume in 0.1 *M* hydrochloric acid.

Rhodium solution (1 *mg/ml*). Prepared by dissolving 0.5838 g of sodium hexachlororhodate (Alfa Inorganics) in 100 ml of 0.1*M* hydrochloric acid.

Iridium solution (1 *mg/ml*). Prepared by dissolving 0.7292 g of sodium chloroiridate (Johnson, Matthey) in 100 ml of 0.1*M* hydrochloric acid.

Silver nitrate solutions (2 *mg/ml and* 20 *mg/ml*). Prepared by dissolving 0.3148 and 3.148 g of silver nitrate (Mallinckrodt, analytical reagent) in 100 ml of doubly distilled, doubly demineralized water.

Lead foil, 0.004-*in. thick.*

Instrumental conditions

Wavelength	265.9 nm
Slit setting	4
Lamp current	28 mA
Drying time	40 sec
Charring time	35 sec
Atomization time	15 sec
Drying temperature	100°
Charring temperature	1100°
Atomization temperature	2600° (10 V)
Water flow	3 l./min
Argon flow	3–5 arbitrary setting
Chart speed	51 mm/min

Several graphite tubes were used in this work. They had all been used to some extent before the platinum injections. Before each analysis the tube was fired to maximum temperature for 2–3 sec. Platinum solutions were then injected. In all cases consistent results were obtained immediately.

Flameless atomic-absorption analysis of platinum standards

Aqueous solutions of platinum were "fired" to determine the optimum concentration range. This was found to be

0.5–5 ppm for 50-μl injections. A slight curvature of the calibration was obtained at higher concentrations.

Platinum standards were prepared by adding μl quantities of stock solutions of silver and platinum to a volumetric flask. A measured volume of nitric acid was added and the solution made up to the mark with hydrochloric acid (1 + 1). Final concentrations of silver and nitric acid were 2 mg and 0.5 ml respectively per 10 ml of solution. Standards were prepared in this manner as it was expected that platinum would be extracted from ores by the classical fire-assay process and concentrated in a 2-mg silver bead. Nitric acid is required to dissolve the silver bead and the hydrochloric acid concentration must be high ($>6M$) to keep silver in solution.

These standards were fired and the calibration curve was found to be linear over the same range as for aqueous solutions. However, the peak-heights had been depressed by approximately 50%. The calibration curves are shown in Fig. 1. The lines for the 6M acid solutions were drawn by the least-squares method. At least 4 injections were made at each concentration. Peak-heights were found to vary considerably from tube to tube, thus it was necessary to draw calibration curves for each analysis.

The results for the 6M acid solutions were compared with those for the same solutions containing 2 mg of silver per 10 ml of solution. Silver depresses the platinum absorbance by 3%. Increasing the silver concentration to 4 mg/10 ml gave no further depression due to silver. Blanks containing only silver in 6M hydrochloric acid were analysed and no signal was obtained at the platinum wavelength.

Acid effects on platinum absorbance

The effects of the addition of sulphuric and phosphoric acids on the determination of platinum in hydrochloric acid were studied. It has been shown in a previous study[9] that the addition of these acids to nitric acid and hydrochloric acid solutions of silver greatly improves the precision for synthetic samples.

The addition of nitric acid to a silver bead containing platinum results in the dissolution of all the silver and some of the platinum. This has been confirmed during this investigation on the fire-assay for platinum and nitric acid alone could not be used as a medium for platinum under these circumstances.

Sulphuric and phosphoric acids (10% v/v) were added to a 4-ppm platinum solution containing silver, nitric acid and hydrochloric acid in the concentrations stated above. These solutions were analysed and the results are shown in Table 1. Each acid reduces both peak-height and precision and this is especially marked in the case of sulphuric acid. Peak-heights were initially consistent at 56 mm, but then became alternately short (~51 mm) and then long (~68 mm), giving the large coefficient of variation. Both acids emitted dense fumes during volatilization and charring time with phosphoric acid present had to be increased to allow argon gas to clear the tube of these fumes. As a consequence of these results neither sulphuric nor phosphoric acids was added to platinum solutions.

Interelement effects

Mutual interferences between noble metals in flameless atomic absorption have been well documented.[3,4] All the interferences listed have been observed when the interfering element is in a large excess, except for one example, that of ruthenium and platinum (1:1 ratio). However, in the platinum ores analysed, ruthenium is either absent or occurs at a much lower level than does platinum. Also there is strong evidence to show that losses of ruthenium are high during the cupellation process[10] and thus the effect of this metal on platinum absorbance was not studied. For similar reasons osmium was also not studied.

Solutions were prepared in a similar manner to that described above, but containing 50 μg of platinum, 25 μg of palladium, 5 μg of gold, 5 μg of rhodium and 2 μg of iridium. These represent the maximum amounts of each metal in the ores to be analysed. The solutions were analysed and the results compared with those for a standard 50-μg platinum solution. The peak-heights were identical, indicating that there is no interference at these levels. Blanks containing the same concentrations of the noble metals with the exception of platinum were also analysed, but no signal was observed at the platinum wavelength.

Base-metal interference was not tested. The only base metal likely to be present in microgram quantities in a silver bead from cupellation is lead. Lead is more volatile than silver and so it is expected that all the lead would be volatilized with silver during the charring cycle.

Flameless atomic-absorption analysis of synthetic samples

The method was tested by synthetic samples prepared by salting lead boats and cupelling to produce a silver bead. Aliquots of standard platinum solutions were added to a boat-shaped container made from a 12.5 × 12.5 cm square of lead foil of 0.010 cm thickness. One ml of 2 mg/ml silver solution was added and the boats were placed in a drying oven for several hr. The boats were then folded into the form of a cube (~25 g), and quickly added to magnesia cupels placed in a furnace at 960°. These cupels had been heated for at least 10 min before use. The furnace door was kept closed for 5 min to allow the lead to melt and then opened by placing a 0.6-cm

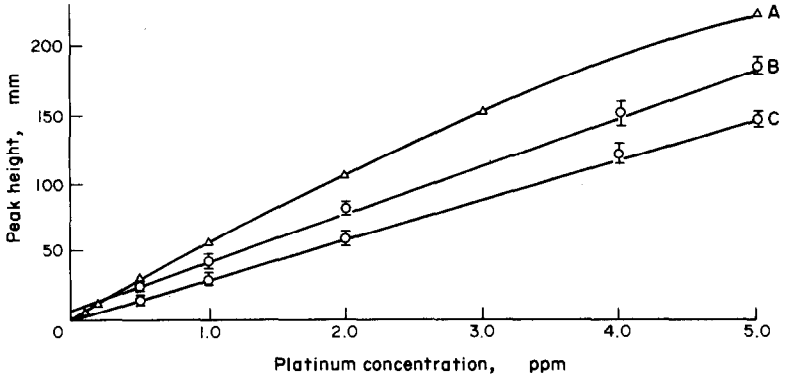

Fig. 1. Flameless atomic-absorption calibration curve for aqueous and hydrochloric acid solutions containing 0.5–5 ppm platinum. A, H_2O: 5-mV scale. B, 50% HCl + 5% HNO_3 + 10 mg Ag/50 ml: 2-mV scale. C, 50% HCl + 5% HNO_3 + 10 mg Ag/50 ml: 5-mV scale. Bars represent standard deviations at the 95% confidence level.

Table 1. Acid effects on platinum absorbance

Acid medium	Peak-height,* *mm*	Coefficient of variation, %
50% HCl + 5% HNO_3	86.4	3.5
50% HCl + 5% HNO_3 + 10% H_3PO_4	81.6	3.6
50% HCl + 5% HNO_3 + 10% H_2SO_4	59.3	12.5

* Average of at least 11 measurements.

thick steel plate under it. Under these conditions the driving of lead occurred at the rate of approximately 1 g/min. When driving was complete the furnace door was closed and the cupellation continued for a further 5 min. Cupels were then slowly withdrawn from the furnace and allowed to cool. When cool the silver beads were transferred to a 10-ml volumetric flask, 0.5 ml of concentrated nitric acid was added and the flask heated by immersion in a beaker of hot water until dissolution of the bead was complete. Then 5 ml of concentrated hydrochloric acid were added and the flask was heated once more to dissolve the silver. The solution was left to cool overnight, and made up to the mark with distilled water. Samples and standards were then analysed, 2 or 3 samples being fired between each standard. A calibration curve was drawn (by the least-squares method) and used to calculate the recoveries of platinum (Table 2). Blanks were run each time but no platinum was detected in them.

Combined fire-assay and flameless atomic-absorption method for ores

Ores for analysis were designated by name or number and originated from the Merensky Reef, South Africa. These ores, which had been crushed fine enough to pass through sieves of 100 and 200 mesh, had previously been analysed for platinum metals and gold.[11,12] The entire ore sample was placed on a large cellophane sheet and rolled or tumbled by lifting alternate corners of the sheet. After 25 min of mixing, the ore was spread out evenly on the cellophane and marked off into 2.5-cm squares. The sample for assay was then obtained by taking small portions from each of the squares. The weights of the ores taken were 1–2 g of float concentrate and 3–7 g for ores S4 and USBM 31. Float concentrate and USBM 31 samples were roasted at 700° for 1 hr before fire-assaying.

Each sample was added to a small-size polyethylene "sandwich" bag containing 85 g of PbO, 21.1 g of Na_2CO_3, 4.5 g of CaO and 2 g of flour. To prevent the flux from becoming too basic, approximately 10 g of silica were added to each ore. Silica (15 g) was used as a blank ore. Silver (2 mg, added as silver nitrate solution) was added to bags containing ores S4 and USBM 31, and 20 mg of silver to the float concentrate samples. Each bag was placed in a crucible pot and the pot in a drying oven at 70° for several hr. After drying, lumps were broken up and the mixture thoroughly shaken for 4–5 min. The crucible pots were placed in the furnace at 950° and heated to 1200° at the maximum rate of the furnace. This normally required 75–90 min. After being held at this temperature for 15 min the crucibles were removed from the furnace and the molten contents poured into conical iron moulds. When cool, slags could be separated from the lead buttons by gentle tapping with a small hammer. Lead buttons were then cupelled to a silver bead as described above.

Table 2. Flameless atomic-absorption of synthetic samples

Platinum added, *μg*	Platinum recovered, *μg**
10.0	10.1 ± 0.5†
20.1	20.5 ± 1.3§
40.2	37.9 ± 1.4†
50.2	46.6 ± 2.0²†

* ± values quoted at the 95% confidence level.
† Average of at least 3 injections for each of 5 samples.
§ Average of at least 3 injections for each of 4 samples.

Table 3. Analysis of ores by combined fire-assay and flameless atomic absorption

	Concentration of platinum, *ppm*§		
	S4[11]	Float concentrate[11]	USBM31[12]
	5.43	77.0	4.56
	4.61*	143.5*	4.25
	5.61	103.7*	5.04
	5.61	76.2	4.25
	5.50	68.2	4.88
	5.58	71.9	4.69
	5.46	78.4	4.28
	4.92	73.2	4.63
Averages	5.44 ± 0.22†	74.2 ± 4.0†	4.57 ± 0.28†
Previous analysis	5.23‡	82.6‡	4.9

* Values rejected at the 95% confidence level.
† ± values quoted at the 95% confidence level.
‡ Analysed by combined fire-assay and flame atomic absorption. NIM Johannesburg, S.A.
§ Average of at least 3 injections.
‖ Average result from 8 laboratories taking part in a "round-robin" analysis included fire-assay/flame atomic absorption, fire-assay/emission spectrography and fire-assay/spectrophotometry. United States Bureau of Mines, Reno, Nevada.

Silver beads from ores S4 and USBM 31 were placed in 10-ml volumetric flasks and the beads from the float concentrate in 100-ml volumetric flasks. The beads were dissolved and the solutions made up to contain 5% nitric acid and 50% hydrochloric acid (v/v). As with synthetic samples, ore samples and standards were analysed so that 2 or 3 samples were fired between each standard. The ore samples were chosen at random for each firing. A calibration curve was again drawn by the least-squares method and the results of these analyses are shown in Table 3.

CONCLUSION

The flameless atomic-absorption method has several advantages. Volatile interferences can be removed by selective volatilization. Palladium, gold, rhodium and iridium (in the amounts found in the ores analysed) do not affect the platinum signal and hence neither prior separation nor the addition of releasing agents is necessary. The method has higher sensitivity and is as fast or faster than most other methods of analysis for platinum in ores. Thus the

flameless atomic-absorption technique offers a feasible alternative to spectrophotometric determinations when highest accuracy and precision are not required or when a very low metal concentration is to be determined.

The combined fire-assay and flameless atomic-absorption method has been shown to be quantitative for platinum in ores and from 0.5–5 ppm of platinum can be determined with a precision of approximately 5%. Results for ores S4 and USBM 31 showed good agreement with independent analyses, while the result for the float concentrate indicated a low, but acceptable, recovery; possibly some platinum was volatilized with silver during the charring stage or was not completely atomized at 2600°. This procedure provides both a concentration and an isolation step (fire-assay), and is combined with a highly selective and sensitive method of analysis. Thus, this method should be applicable to many samples having a variety of matrices and platinum concentrations, but will find particular use for very dilute samples.

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DIE SPEKTROGRAPHISCHE BESTIMMUNG DER VERUNREINIGUNGEN IN PLATIN–RHODIUM-LEGIERUNGEN

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Zusammenfassung—Es waren spektrographische Verfahren zur Bestimmung der Verunreinigungen Ir, Ru, Au, Pd, Ag, Cu, Ni, Fe, Co, Mn, Ti, Pb, Sn, Sb, As, Zn, Al, Si und Mg in Platin–Rhodium-Legierungen zu entwickeln. Dabei galt es, Arbeitsweisen zu finden, die auf eine aufwendige Probenvorbereitung verzichten und für unterschiedliche Materialabmessungen einsetzbar sind. Zur Lösung des Eichproblems wurden für die einzelnen Legierungstypen Standardreihen auf schmelztechnischem Wege und über die Präparation von Metallpulvern hergestellt. Dabei waren für die Begleitelemente Konzentrationsbereiche zwischen $5 \cdot 10^{-4}$% und $1 \cdot 10^{-1}$% zu erfassen. Chemische und spektrographische Prüfungen zeigten, daß die Materialien über eine für Spektralanalyse ausreichende Homogenität verfügen. Im Sinne einer universellen Anwendung wurde als spektrographische Arbeitsweise eine anodische Anregung im Kugelbogen mit einem wassergekühlten Graphitteller als Träger gewählt. Die Methodik gestattet bei Anwendung eines Plangitterspektrographen PGS 2 die Bestimmung der Verunreinigungen in den geforderten Konzentrationsbereichen über weitgehend lineare Eichkurven. Die Variationskoeffizienten liegen für Gehalte um 0,01% zwischen 10% und 30%. Zum Einfluß der Probenform und des Rhodiumgehaltes auf die Meßergebnisse werden vergleichende Untersuchungen angestellt.

Legierungen auf Platin–Rhodium-Basis haben, abgesehen von ihrem herkömmlichen Gebrauch, in den letzten Jahren eine steigende Anwendung besonders als Düsenwannenwerkstoff in der Glasfaserindustrie gefunden. Da solche Materialien extremen thermischen, mechanischen und chemischen Beanspruchungen ausgesetzt sind, hat der Gehalt an speziellen Verunreinigungen einen großen Einfluß auf die Standfestigkeit dieser Werkstoffe. Dieser Umstand führte zu der Aufgabe, Analysenverfahren für die Bestimmung der Begleitelemente in den Legierungstypen PtRh5 (d.h. 5% Rh in Pt), PtRh7, und PtRh10 zu entwickeln. Obwohl chemische Bestimmungsverfahren für die entsprechenden Elemente zur Verfügung stehen,[1] bleibt die Ausarbeitung einer spektrographischen Arbeitsweise unerläßlich. Nur auf diesem Wege sind die geforderte kurzfristige Bereitstellung der Materialkennwerte und damit regulierende und kontrollierende Maßnahmen im Produktionsablauf möglich. Die Forderungen an das Verfahren lassen sich wie folgt zusammenfassen:

Bestimmung der Verunreinigungen Ir, Ru, Au, Pd, Ag, Cu, Pb, Sn, Zn, Sb, As, Fe, Ni, Mn, Co, Ti, Al, Mg und Si in Konzentrationsbereichen $5 \cdot 10^{-4}$–$1 \cdot 10^{-1}$%.

Die Variationskoeffizienten des Bestimmungsverfahrens müssen unter 30% liegen.

Das Verfahren soll für jede anfallende Materialform (Halbzeuge, Pulver) anwendbar und von einer aufwendigen Probenvorbereitung frei sein.

Verfahren zur Spektralanalyse von Platin–Rhodium-Legierungen oder -Pulvergemischen, die die vorangestellten Forderungen voll erfüllen, sind in der Literatur nicht ausgewiesen. Chwastowska, Dybczyński und Kucharzewski[2] beschreiben die Bestimmung von 13 Verunreinigungselementen in Platin–Rhodium-Legierungen. Dieses Verfahren, bei dem die Edelmetalle nachteiligerweise nicht mit erfaßt werden, geht von einer chemischen Vorabtrennung der Matrixelemente aus und ist damit für eine betriebliche Schnellanalyse wenig geeignet. Auch Tosi[3] geht den Weg über die gelöste Probe, arbeitet mit einem Aluminiumoxidüberschuß im Lösungsrückstand und beschränkt sich auf die Bestimmung der Elemente Eisen, Nickel und Chrom. Metallische Proben werden nach der im GOST-Standard 12556-67[4] beschriebenen Arbeitsweise zur Ermittlung höherer Gehalte an Palladium, Iridium und Eisen (0,01–0,20%) eingesetzt. Angaben zur Herstellung einer Eichprobenreihe in metallischer Form fehlen in diesen Arbeiten. Auch die Mitteilung von Kuranov[5] beschränkt sich auf den Hinweis, daß eine Präparation von Platin–Rhodium-Standards über Metallpulver gelingt.

Um eine Arbeitsweise zu finden, die den Forderungen der Aufgabenstellung möglichst nahe kommt, können nur eine Eichprobenpräparation und eine Aufnahmemethodik gewählt werden, wie sie bei uns bereits für die Analyse von Platin[6] und von Palladium[7] zum Erfolg geführt haben. Nach unseren Ergebnissen[8] empfiehlt es sich, die Standards auf schmelztechnischem Wege herzustellen. Dieser Weg bringt den geringsten Arbeitsaufwand und liefert das Probegut in einer Form, die ohne Vorbehandlung für die Analyse einsetzbar ist. Schwierigkeiten bereiten lediglich die Verformbarkeit der Materialien bei Zusätzen >200 ppm sowie die zielgerichtete Dotierung und homogene Verteilung von Elementen wie Silicium, Aluminium und Magnesium in der Matrix.

Der letztgenannte Mangel läßt sich umgehen, wenn die Schmelzeichproben durch über Metallpulver mit Lösungen präparierte Standards ergänzt werden.

Da Platinproben mit unterschiedlichem Rhodiumgehalt für die einzelnen Begleitelemente systematische Abweichungen der Intensitätswerte erwarten lassen, sind für die genannten Legierungstypen getrennte Eichreihen erforderlich. Für die spektrographische Aufnahme muß die Kugelbogentechnik Anwendung finden, da nur auf diese Weise die Eichung eines *direkten* Bestimmungsverfahrens unabhängig von der Probenform zu verwirklichen ist.

EXPERIMENTELLER TEIL

Herstellung der Standards

Für jeden Legierungstyp war auf schmelztechnischem Wege eine Eichreihe, bestehend aus sieben Standards, herzustellen. Als gehaltliche Abstufungen wurden für die meisten Elemente 0,0005; 0,001; 0,002; 0,005; 0,01; 0,02 und 0,05% angestrebt. Lediglich für Iridium, Ruthenium und Eisen war der Konzentrationsbereich 0,002–0,1% gefordert. Als Ausgangsmaterialien dienten Platin (99,999%) und Rhodium (99,99%) in Form von Schmiedestäben bzw. Pulver, deren Reinheit auf chemischem und auf spektrographischem Wege kontrolliert und bestätigt wurde.

Das Schmelzen der Proben wurde in einem Vakuuminduktionsofen bei 1950° und bei 500 mmHg unter Argon vorgenommen. Für Metalle mit hohem Dampfdruck war die Herstellung von binären Vorlegierungen auf Platinbasis erforderlich, die nach den Ergebnissen der chemischen Analyse 2,3% Zn, 2,3% Mg, 3,5% As, 2,8% Sb bsw. 2,4% Pb enthielten. Als Tiegelmaterial wurde Korund verwendet.

Das Schmelzen der Proben mit Sollgehalten von 0,005, 0,01, 0,02 und 0,05% erfolgte bei direktem Zusatz der Elemente bzw. der Vorlegierungen. Eine Verdünnung dieser Legierungen mit Platin und Rhodium im Verhältnis 1:10 führte zu den Standards, deren Dotierungen bei 0,0005, 0,001 bzw. 0,002% lagen. Die in Kupferkokillen abgegossenen Bolzen von 20 mm Durchmesser wurden zu Stäben von 6,5 mm Durchmesser ausgeschmiedet und entsprechend dem Verwendungszweck (chemische Analyse, spektrographische Untersuchungen) zerspant. Standards mit Gehalten > 0,02% erwiesen sich für eine Verformung als zu spröde. In diesen Fällen wurden geeignete Partien des Gußblockes durch Zerspanung in eine für die Spektralanalyse einsetzbare Form gebracht.

Die Herstellung von Standards in Pulverform für die Matrices PtRh5, PtRh7 und PtRh10 gelingt für die den Schmelzproben analogen gehaltlichen Abstufungen der Begleitelemente über eine Präparation von Metallpulvern mit Lösungen.

Ausgangsmaterialien hierzu sind Platin- und Rhodiumpulver entsprechender Reinheit, die durch Aufreiben im Achatmörser und Absieben auf eine Korngröße $\leq 90\,\mu m$ gebracht werden. Den aus diesen Pulvern hergestellten Matrixgemischen mit 5, 7 bzw. 10% Rhodium sind die Beimengungen in Form von Lösungen zuzugeben. Die Menge der Zusätze ist so zu wählen, daß diese Gemische den Forderungen der oberen Bestimmungsgrenze entsprechen. Nach Trocknung der Substanzen werden diese einer Reduktion im Wasserstoffstrom über die Temperaturstufen 100° (1,5 h), 150° (0,5 h), 200° (1,0 h), 300° (1,0 h), 400° (0,5 h), 500° (1,0 h) und 600° (1,0 h) unterzogen und anschließend im Achatmörser 20 Stunden homogenisiert. Eine mechanische Verdünnung dieser Standards über die Verhältnisse 1:2,5; 1:5; 1:10; 1:25; 1:50 mit entsprechenden Mengen Platin- und Rhodiumpulver führt für jeden Gemischtyp zu einer Eichreihe bestehend aus sechs Proben.

Tabelle 1. Gehalte der Schmelzeichproben für die Spektralanalyse von PtRh10-Legierungen (Angaben in ppm)

Element	Probe A 500	A 200	A 100	A 50	A 20	A 10	A 5
Fe	538	1000	494	209	124	71,3	36,5
Mn	491	204	96,5	48,5	21,0	11,5	3,5
Ti	422	189	102	50,5	20,5	10,0	8,0
As	503	226	112	46,0	21,0	13,2	8,6
Pb	508	212	109	58,8	27,6	18,5	11,5
Sb	510	172	93,7	45,8	20,4	9,5	4,6
Sn	489	196	88,5	41,7	19,4	9,6	4,6
Pd	571	219	105	61,1	19,6	10,8	5,8
Au	524	204	100	51,2	21,3	10,1	5,1
Ag	505	226	124	61,6	21,9	11,7	6,1
Zn	619	230	115	65,5	22,6	13,6	8,1
Cu	506	493	207	97,3	49.0	17,4	11,4
Co	497	194	99,9	50,0	19,8	10,1	5,1
Ni	500	206	104	48,3	22,0	10,8	6,2
Ir	480	950	497	146	104	54	27
Ru	530	1030	566	198	113	54	21
Mg	214	35	50	25	7,2	3,8	5,6
Si	293	95	72	32	14,5	11	6,6
Al	2040	411	130	68,8	33,3	19,2	7,1

Prüfung der Standards

Sollen die hergestellten Standards einer spektrographischen Eichung genügen, müssen ihre Begleitelemente eine ausreichend homogene Verteilung in der Matrix aufweisen. Außerdem ist es erforderlich, daß die erhaltenen Konzentrationsstufen weitgehend mit den angestrebten Sollgehalten übereinstimmen.

Für eine verbindliche Festlegung von Eichgehalten müssen für alle interessierenden Begleitelemente chemische Bestimmungsverfahren zur Verfügung stehen, da für keinen Präparationsweg Elementverluste oder das Einschleppen von Verunreinigungen ausgeschlossen werden können. Die Mehrzahl der Elemente ist spektrophotometrisch bestimmbar. Die Magnesiumgehalte sind über Atomabsorptionsspektrometrie zu ermitteln, während Ruthenium und Iridium nur der Aktivierungsanalyse zugänglich sind. Die Variationskoeffizienten der Verfahren liegen normalerweise unter 5%. Lediglich die Aktivierungsanalyse und die Bestimmung von Silicium, Magnesium und Aluminium bei Gehalten unter 0,005% können zu Werten führen, die in der Größenordnung von 20% liegen. Um zu prüfen, ob in den auf schmelztechnischem Wege gewonnenen Eichproben durch die Herstellung bedingte Steigerungen auftreten, wurden die Gehalte der Begleitelemente mit den chemischen Analysenverfahren über die Länge der Schmiedestäbe verfolgt. Da für kein Element eine Konzentrationsänderung über die Stablänge festgestellt werden konnte, war eine Festlegung verbindlicher Eichgehalte über Mittelwertbildung aus den einzelnen Bestimmungen möglich. Die Ergebnisse, wie sie analog auch für die Legierungstypen PtRh5 und PtRh7 erhalten wurden, zeigt Tabelle 1 am Beispiel der Eichreihe für PtRh10.

Die ausgewiesenen Konzentrationen stimmen weitgehend mit den angestrebten Sollgehalten überein. Abweichungen, wie sie bei Eisen, Blei, Iridium und Ruthenium für die niedrigen Gehaltsstufen auftreten, sind auf die Restverunreinigungen der Ausgangsmaterialien, besonders des Rhodiums, zurückzuführen, wirken sich jedoch nicht störend auf die zu erfassenden Konzentrationsbereiche aus. Für Aluminium, Silicium und Magnesium konnten die gewünschten Abstufungen der Gehalte nicht im vollen

Tabelle 2. Magnesium-, Silicium- und Aluminiumgehalte der Pulvereichproben des Typs PtRh10 (Angaben in ppm)

	Probe					
Element	PA 500	PA 200	PA 100	PA 50	PA 20	PA 10
Mg	525	205	104	60	29	22
Si	520	200	120	54	30	17
Al	465	197	93	48,3	17,3	9,3

Umfang erreicht werden. Ihre exakte Dotierung auf schmelztechnischem Wege stößt auf Schwierigkeiten, die nur über eine Präparation von Pulvereichproben zu umgehen sind. Tabelle 2 zeigt dies am Beispiel der Matrix PtRh10. Für die anderen Elemente führt der Weg über die Metallpulver zu gleich guten Ergebnissen wie die Schmelztechnik. Für die Analyse der Pulverstandards sind die gleichen chemischen Bestimmungsverfahren wie für Schmelzproben anwendbar.

SPEKTROGRAPHISCHE VERFAHRENSENTWICKLUNG

Die Aufgabe, Platin–Rhodium-Proben der unterschiedlichsten Form ohne aufwendige Vorbereitung auf ihre Verunreinigungen zu untersuchen, zwingt dazu, für die spektrographische Aufnahme eine Kugelbogentechnik in Verbindung mit einem Plangitterspektrographen PGS 2 einzusetzen. Als Anregungsquelle dient ein stabilisierter Gleichstromdauerbogen, der zwischen einer angespitzten Graphitelektrode (Kathode) und dem anodisch gepolten Probegut brennt. Als Trägerelektrode wird ein Graphitteller mit 12 mm Durchmesser und einer Mulde von 1,5 mm Tiefe angewendet, der auf einem speziellen Kühlsystem[9] sitzt. Diese Anordnung verspricht eine hohe Reproduzierbarkeit der Meßergebnisse und gewährleistet eine ausreichende Nachweisempfindlichkeit für die Bestimmung der geforderten Element-Konzentrationen. Das bei Anwendung der zweiten Spektralordnung gute Auflösungsvermögen der Meßeinrichtung

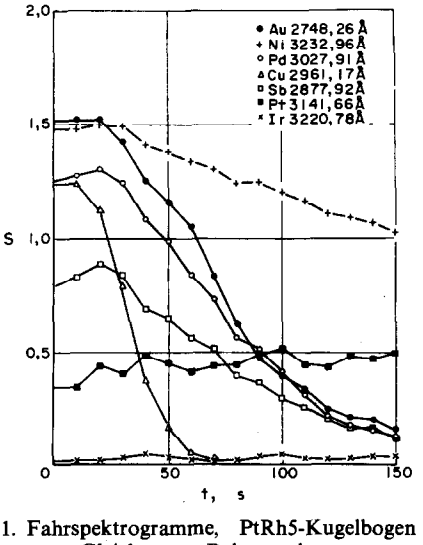

Abb. 1. Fahrspektrogramme, PtRh5-Kugelbogen 12 A Gleichstrom, Pulverproben.

ist notwendig, um bei der linienreichen Platin–Rhodium-Matrix die nachweisgünstigsten Spektrallinien der Begleitelemente einer quantitativen Bestimmung zugänglich zu machen. Eine anodische Anregung von 150 mg-Proben bei 12 A Gleichstrom führt zu den günstigsten Linie-Untergrund-Verhältnissen im Spektrum.

Eine Prüfung des Verdampfungsverhaltens der Matrix und der Begleitelemente ergibt, wie auch die Beispiele in der Abb. 1 zeigen, daß die meisten Elemente (außer Ru und Ir) einer fraktionierten Verdampfung unterliegen und sich somit eine Belichtungszeit von 60 s empfiehlt. Dies gilt im gleichen Maße für Pulverproben wie für die aus den Legierungen gewonnenen Spanproben, unabhängig davon, ob der Rhodiumgehalt 5, 7 oder 10% beträgt, so daß die in Tabelle 3 skizzierte Aufnahmemethodik alle Forderungen der Aufgabenstellung erfüllt. Bei der Analyse von Pulvern sind die 150 mg-Proben vor der spektrographischen Aufnahme zu Tabletten mit 3 mm Durchmesser zu verpressen.

Zur Auswertung der Spektren werden die gemessenen Schwärzungen der Platinvergleichslinien und der Linien der Begleitelemente an einem Rechenbrett in ΔY-Werte überführt. Eine Korrektur des stets unter $S = 0{,}1$ liegenden Spektrenuntergrundes ist dabei nicht erforderlich. Die Aufstellung der Eichkurven erfolgt in den Koordinaten ΔY–log c. Die für die einzelnen Elemente ausgewählten Wellenlängen (Tabelle 4) sind in ihrer Intensität bei der gegebenen Anregung auf die geforderten Konzentrationsbereiche abgestimmt und gelten sowohl für Pulver- als auch für Schmelzproben bei Rhodiumgehalten zwischen 5 und 10%. Unter Verwendung der schmelztechnisch hergestellten Standards und ihrer chemisch ermittelten Begleitelementgehalte wurden Eichkurven für die spektrographische Analyse der Legierungen PtRh5, PtRh7 und PtRh10 aufgestellt. Die damit erfaßbaren Konzentrationsbereiche (Tabelle 4) sind für alle drei Legierungstypen gleich; die angegebenen Grenzgehalte sind als Richtwerte aufzufassen.

Für die meisten Elemente ergeben sich lineare Eichkurven mit Steigungen zwischen 35 und 45°, wie sie für die Edelmetallanalyse nach dem Kugelbogenverfahren üblich sind. Die Abb. 2 und 3 zeigen dies für einige Elemente am Beispiel der Legierung PtRh7.

Abflachungen der Eichkurven, wie sie bei Gehalten > 0,005% Magnesium, > 0,01% Mangan und > 0,01% Gold (Abb. 3) auftreten, sind auf sehr hohe Intensitäten der Analysenlinien zurückzuführen Für Iridium und Ruthenium bleiben die unteren Bestimmungsgrenzen aus Gründen der Nachweisempfindlichkeit auf 0,01% begrenzt (Tab. 4).

Ungünstige Bedingungen liegen, gefördert durch die Verwendung von Korund als Tiegelmaterial, für das Aluminium vor. Eine starke Streuung der Meßergebnisse, hervorgerufen durch mögliche Inhomogenitäten, ließ bei diesem Element keine Zuordnung der chemisch ermittelten Gehalte zu den gemessenen Intensitätswerten zu. Für eine Eichung kommen in

Tabelle 3. Bedingungen der spektrographischen Aufnahme

Trägerelektrode	Graphitteller (T_1–EKL*) mit 12 mm Durchmesser und einer Mulde von 1,5 mm Tiefe, der auf einem Kühlsystem befestigt ist (Wasserdurchfluß 0,5 l./min)
Gegenelektrode	Graphitstab (T_1—EKL*) mit 5 mm Durchmesser und mit einer Kegelspitze (Winkel 25°)
Elektrodenabstand	2 mm
Anregung	Dauerbogen 12 A Gleichstrom, Probe als Anode
Gitter	650 Furchen/mm, Blaze-Wellenlänge in der 1. Spektralordnung bei 5700 Å; Benutzung der 2. Spektralordnung
Einstellung am Spektrographen	Gitterstellung: + 10,51° Spaltschrägstellung: 5,3 Kollimator: 10,0
Spaltbeleuchtung	mit Zwischenabbildung am Kondensor $f = 150$ mm
Zwischenblende	3,2 mm
Filter	Dreistufenfilter
Spaltbreite	0,030 mm
Vorbrennzeit	keine
Belichtungszeit	60 s
Plattenmaterial	ORWO blau extrahart Format 9 × 30 cm
Entwicklung	5 min schaukelnd in Metatyl-Hydrochinon (1 + 5) bei 18°
Fixierung	10 min in saurem Fixierbad nach kurzzeitigem Unterbrecherbad (verd. Essigsäure)
Wässerung	5 min strömend

* VEB Elektrokohle Lichtenberg, DDR.

diesem Fall nur die über Metallpulver und Lösungen präparierten Standards in Betracht.

Die über die präparierten Pulverstandards aufgestellten Eichkurven (Abb. 4 und 5) führen hinsichtlich Kurvenverlauf und erfaßbarem Konzentrationsbereich zu den gleichen Ergebnissen, wie sie bereits für Schmelzproben erhalten wurden.

Sehr vorteilhaft ist, daß die gelungenen Dotierungen der Pulverproben (Tab. 2) gestatten, auch für die Elemente Magnesium, Silicium und Aluminium den geforderten Gehaltsbereich (0,001 bis 0,05%) über sinnvolle gehaltliche Abstufungen zu erfassen.

SPEKTROGRAPHISCHE HOMOGENITÄTSPRÜFUNG, REPRODUZIERBARKEITEN

Das entscheidende Maß für eine ausreichend homogene Verteilung der Verunreinigungen in der Matrix und damit für die Eignung der hergestellten Standards zu Eichzwecken sind die erreichbaren Variationskoeffizienten für die einzelnen Elemente. Diese Werte wurden für jeden Legierungs- und Gemischtyp an $N = 20$ spektrographischen Aufnahmen von Proben mit Gehalten bei 0,01% ermittelt. Die Ergebnisse zeigt Tabelle 5.

Für die Mehrzahl der Elemente ergeben sich Werte,

Tabelle 4. Wellenlängen, Filterstufen und Konzentrationsbereiche für die Analyse von Platin–Rhodium-Legierungen

Analysenlinie, Å	Filterstufe, % D	Vergleichslinie Å	Filterstufe, % D	Konzentrationsbereich, %
Au 2748,26	100	Pt 2744,83	100	0,0005–0,05
Pb 2802,00	100	Pt 2744,83	100	0,001–0,05
Sb 2877,92	100	Pt 2744,83	100	0,0005–0,05
Mn 2933,06	100	Pt 2744,83	100	0,0005–0,05
Sn 3009,15	100	Pt 3041,22	100	0,0005–0,05
Si 2516,12	100	Pt 2541,35	100	0,001–0,03
As 2349,84	100	Pt 2541,35	100	0,0007–0,05
Co 3044,01	100	Pt 3041,22	100	0,0005–0,05
Ni 3232,96	100	Pt 3041,22	100	0,0006–0,05
Pd 3027,91	100	Pt 3041,22	100	0,0005–0,06
Cu 2961,17	100	Pt 2744,83	100	0,001–0,05
Ir 3220,78	100	Pt 3041,22	100	0,01–0,1
Fe 3021,07	100	Pt 3041,22	100	0,003–0,1
Zn 3282,33	100	Pt 3041,22	100	0,001–0,03
Ti 3234,52	100	Pt 3041,22	100	0,0007–0,05
Ag 3382,89	10	Pt 3041,22	100	0,0005–0,02
Mg 2802,70	10	Pt 2744,83	100	0,0005–0,01
Ru 2678,76	100	Pt 2541,35	100	0,01–0,1
Al 3082,16	100	Pt 3041,22	100	

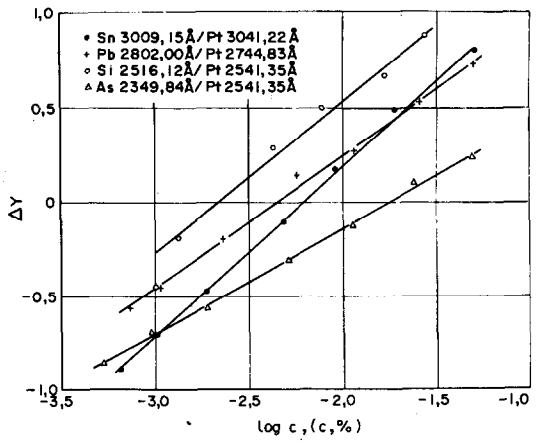

Abb. 2. Eichkurven für die Bestimmung von Sn, Pb, Si und As in PtRh7-Legierungen.

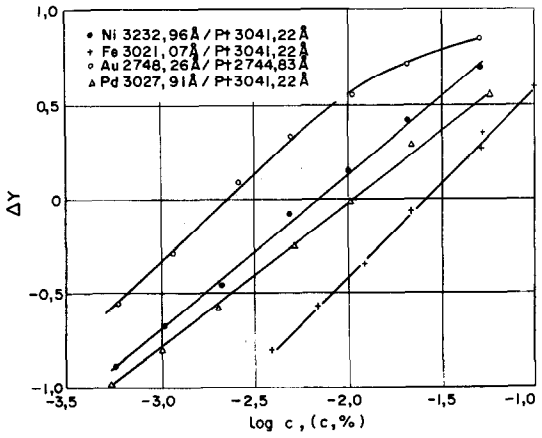

Abb. 3. Eichkurven für die Bestimmung von Ni, Fe, Au und Pd in PtRh7-Legierungen.

die die Forderung $\leq 30\%$ weit unterbieten und damit bestätigen, daß die Standards über eine für die geforderte Spektralanalyse ausreichende Homogenität verfügen. Eindeutige Unterschiede zwischen den einzelnen Legierungs- und Gemischtypen sind nicht festzustellen.

Variationskoeffizienten $\geq 25\%$ sind auf eine zu geringe Steigung der Eichkurven (Silber, Magnesium, Aluminium, Silicium) oder auf Unregelmäßigkeiten im Verdampfungsvorgang (Titan, Magnesium, Silicium, Aluminium) zurückzuführen.

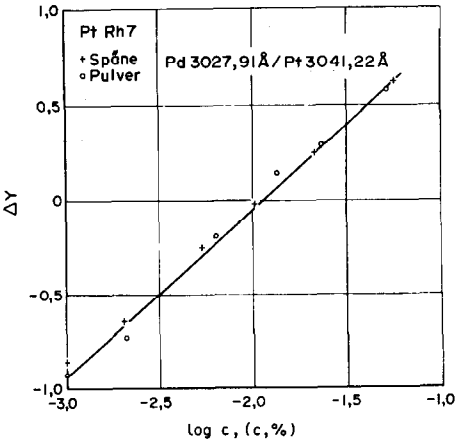

Abb. 4. Gemeinsame Eichkurve für die Bestimmung von Pd in Schmelz-und Pulverproben des Typs PtRh7.

EINFLÜSSE DER PROBENFORM UND DES RHODIUMGEHALTES AUF DIE MESSERGEBNISSE

Für die Anwendung der entwickelten Bestimmungsverfahren war es notwendig zu prüfen, ob massive Proben (Halbzeuge, Späne) und Pulverproben spektrographisch miteinander vergleichbar sind. Da für beide Probeformen Eichreihen zur Verfügung stehen, sind derartige Untersuchungen möglich.

Führen sie bei Anwendung der gleichen Arbeitsweise zu identischen Eichkurven, so wären Pulverproben über schmelztechnisch hergestellte Standards und Legierungsproben über Pulverstandards analysierbar. Derartige Bedingungen würden die Durchführung von Routineanalysen entscheidend vereinfachen.

Die Ergebnisse der Messungen, durchgeführt für die Matrixzusammensetzungen PtRh5, PtRh7 und PtRh10 über die geforderten Konzentrationsbereiche, zeigen die Abb. 4 und 5 am Beispiel der Bestimmung von Palladium und Silicium in PtRh7.

Es ergibt sich, daß Pulver- und Spanproben bei Rhodiumgehalten von 5, 7 und 10% für die meisten

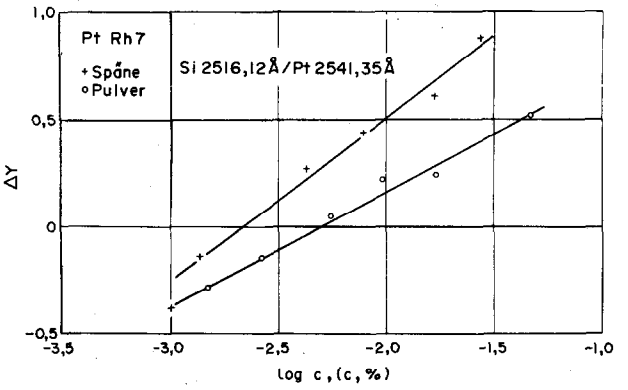

Abb. 5. Eichkurven für die Bestimmung von Si in Schmelz- und Pulverproben des Typs PtRh7.

Tabelle 5. Variationskoeffizienten (%) für die Bestimmung der Begleitelemente (je zu 0,01%) in PtRh-Legierungen und-Pulvergemischen ($N = 20$)

	Schmelzproben			Pulverproben		
Element	PtRh5	PtRh7	PtRh10	PtRh5	PtRh7	PtRh10
Zn	18	13	16	19	14	19
Pd	14	13	14	13	9	14
Ti	31	34	33	22	24	27
Ni	11	10	14	9	9	11
Ir	13	10	12	16	14	12
Co	9	16	14	9	8	16
Sn	11	10	13	14	11	14
Fe	7	7	9	10	7	12
Cu	19	14	18	12	11	9
Sb	17	12	18	9	11	14
Pb	14	14	14	23	25	25
Au	18	14	19	13	15	18
Ru	11	10	15	8	9	13
Si	17	19	26	21	27	29
As	21	16	23	18	14	23
Mn	19	22	24	12	17	21
Ag	29	31	30	27	29	23
Mg	24	39	28	41	45	48
Al				49	38	48

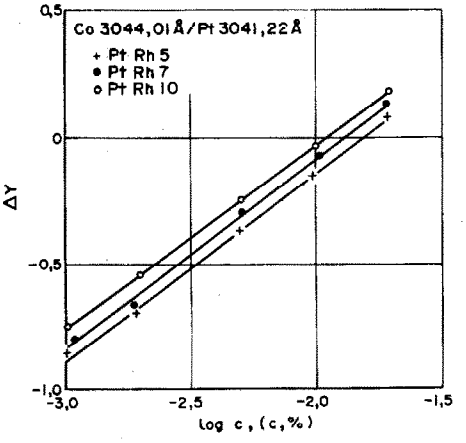

Abb. 6. Eichkurven für die Bestimmung von Co in PtRh5-, PtRh7- und PtRh10-Legierungen.

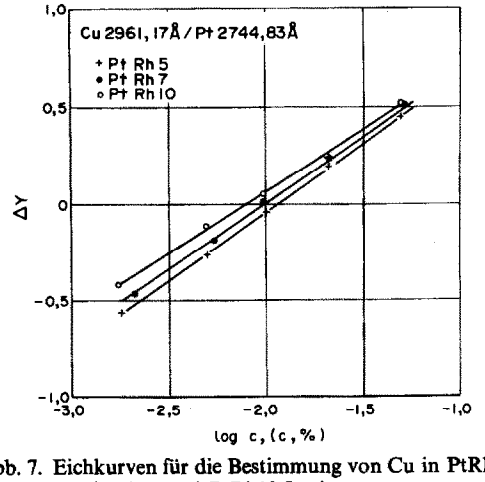

Abb. 7. Eichkurven für die Bestimmung von Cu in PtRh5-, PtRh7- und PtRh10-Legierungen.

Elemente eindeutig zu gemeinsamen Eichkurven führen. Die Abweichungen einiger Meßpunkte vom gezeichneten Kurvenverlauf sind völlig regellos und liegen im Streubereich der chemischen und spektrographischen Bestimmungsverfahren. Lediglich für die Bestimmung des Siliciums (Abb. 5) ergeben sich eindeutig voneinander abweichende Eichkurven. Die Ursache für diese Erscheinung ist offensichtlich darin zu suchen, daß sich legiertes Silicium (Schmelzproben) und Siliciumdioxid (Pulverproben) hinsichtlich Verdampfung und Anregung bei Anwendung einer Kugelbogentechnik unterschiedlich verhalten.

Ergebnisse von Vergleichsuntersuchungen an den drei Eichreihen (Schmelzproben) zum Einfluß des Rhodiumgehaltes auf die Bestimmung der Verunreinigungen zeigen die Abb. 6 und 7 am Beispiel der Elemente Kobalt und Kupfer.

Die durch Unterschiede in der Matrixzusammensetzung hervorgerufenen Abweichungen der Eichfunktionen äußern sich in Parallelverschiebungen und teilweise in einer geringen Änderung der Steigung der Kurven. Diese Erscheinungen treten für alle Begleitelemente auf, wenn auch nicht immer so ausgeprägt wie in den gezeigten Beispielen. Eine quantitative Abschätzung dieser Effekte[8] ergibt, daß sich zumindest die zwischen den Legierungstypen PtRh5 und PtRh10 auftretenden Abweichungen der Eichkurven eindeutig aus dem Streubereich der Bestimmungsverfahren hervorheben.

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Summary—A spectrographic method was required for the determination of traces of Ir, Ru, Au, Pd, Ag, Cu, Ni, Fe, Co, Mn, Ti, Pb, Sn, Sb, As, Zn, Al, Si and Mg in platinum–rhodium alloys without the need for a lengthy sample-preparation step. For calibration purposes, samples similar in composition to the alloys were prepared both by melting samples of the pure metals to which traces had been added, and by thorough mixing of metals in powder form, covering the concentration range 5×10^{-4} to 10^{-1}%. Chemical and spectrographic tests showed that the homogeneity of the samples was more than adequate for the purpose. The spectrographic procedure used anodic excitation in a globule arc and a water-cooled graphite plate as sample-carrier, together with a plane-grating spectrograph PGS 2. Calibration curves were linear over wide sections of the concentration ranges of interest. For levels around 0.01% the coefficients of variation lay between 10 and 30%. Results were compared for differently prepared samples and for alloys with varying rhodium contents.

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DETERMINATION OF 30 ELEMENTS IN COAL AND FLY ASH BY THERMAL AND EPITHERMAL NEUTRON-ACTIVATION ANALYSIS

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Summary—Thirty elements are determined in coal and fly ash by instrumental neutron-activation analysis using both thermal and epithermal irradiation. Gamma-ray spectra were recorded 7 and 20 days after the irradiations. The procedure is applicable to the routine analysis of coals and fly ash. Epithermal irradiation was found preferable for the determination of Ni, Zn, As, Se, Br, Rb, Sr, Mo, Sb, Cs, Ba, Sm, Tb, Hf, Ta, W, Th and U, whereas thermal irradiation was best for Sc, Cr, Fe, Co, La, Ce, Nd, Eu, Yb and Lu. Results for SRM 1632 (coal) and SRM 1633 (fly ash) agree with those of other investigators.

Instrumental activation-analysis with thermal neutrons (INAA) is a versatile technique for the determination of many elements in a variety of geological materials. Even though many earth science laboratories currently employing this technique are situated at some distance from a nuclear reactor, which means that the analysis is restricted to long-lived nuclides ($t_{1/2} > 1$ day), the number of elements that can be determined is still considerable.

Recently the determination of trace elements in coal and its combustion products has become an important issue in several countries because of greater appreciation of the environmental effects of the burning of coal. Block and Dams,[1] in a feasibility study of INAA applied to coal analysis, listed about 25 elements which may be determined in coals by use of the long-lived nuclides. From the information given in their paper on the normal concentration ranges found in coals and the detection limits attainable by INAA, it can be concluded that about 15 elements in this group can be determined satisfactorily in most coal samples. A more recent study[2] on trace elements in the National Bureau of Standards coal (SRM 1632) and fly ash (SRM 1633) reference materials indicates that the number may be extended to about 20, if SRM 1632 can be considered as representative of coals in general.

Instrumental activation-analysis with epithermal neutrons (ENAA) is advantageous for the determination of a number of minor and trace elements in silicate rocks.[3,4] Many of these elements have isotopes with high I/σ_0 ratios (resonance activation integral/thermal neutron-activation cross-section) leading to long-lived γ-emitting nuclides on epithermal activation. On the other hand, most nuclides (of elements present in rocks) that yield major activities on thermal-neutron activation (^{23}Na, ^{41}K, ^{45}Sc, ^{59}Co, ^{139}La, ^{151}Eu) show correspondingly low I/σ_0 ratios. Since the gamma-ray spectra of long-lived nuclides in coals and fly ash that have been irradiated with thermal neutrons are somewhat similar to those of similarly treated rock samples, there was reason to believe that ENAA might be advantageous in the case of coals and their combustion products. In a recent study,[5] concerned with short-lived radionuclides, ENAA was shown to be advantageous for several elements. In the present investigation, the application of ENAA to elements yielding long-lived nuclides by (n, γ) reactions is reported. For each of the 30 elements studied, a comparison of results obtained by the thermal and epithermal irradiation technique is presented. The nuclear data of interest in connection with ENAA of coals are shown in Table 1. As in the study of short-lived nuclides,[5] the standard reference materials SRM 1632 and SRM 1633 were used as test materials.

EXPERIMENTAL

Epithermal-neutron activation

Samples of about 0.1 g were wrapped in 30 × 30 mm sheets of aluminium foil and packed into a 1-mm thick cadmium box (20 mm inner diameter, 12 mm inner depth) which allows about 20 samples or standards to be irradiated together. A multielement standard, made by grinding an obsidian sample from Horse Mountain, Oregon to < 200 mesh and spiking with appropriate concentrations of Ba, Co, Cr, Cs, Rb, Sb, Ta, Zr, Sc, La, Eu and Tb, was used as a monitor for most of the elements studied. The multielement standard was calibrated against pure solutions and the U.S.G.S. standard rocks. For Ni, As, Se, Br, Sr, Mo, Sb, W and U, standards were made by evaporating aliquots of dilute solutions onto 30 × 30 mm sheets of aluminium foil. Irradiations were carried out in the JEEP-II reactor (Kjeller, Norway) in a position where the thermal neutron flux was about 1.5×10^{13} n.cm^{-2}.sec^{-1} and the cadmium ratio of ^{197}Au was about 3.0. The irradiation time was 2 days for coals and 1 day for ash samples.

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Table 1. Nuclear data of interest in the epithermal activation analysis of coals based on long-lived nuclides ($t_{1/2} > 1$ day)

Element	Radionuclide	Half-life	σ_0[6]	I[7]	I/σ_0
Sc	^{46}Sc	84 d	25	11	0.44
Cr	^{51}Cr	27.8 d	16.0	8.5	0.53
Fe	^{59}Fe	45.1 d	1.14	1.2	1.1
Co	^{60}Co	5.3 y	37.5	75.0	2.0
Ni	^{58}Co*	71 d	—	—	—
Zn	^{65}Zn	245 d	0.82	1.6	2.0
As	^{76}As	26.4 h	4.4	63	14
Se	^{75}Se	120 d	55	500	9.1
Br	^{82}Br	35.4 h	3.0	50	17
Rb	^{86}Rb	18.7 d	0.45	7	16
Sr	^{85}Sr	65 d	0.57	7.5	13
Zr	^{95}Zr	65 d	0.075	0.38	5.1
Mo	^{99}Mo	66.7 h	0.14	7.5	54
Sb	^{122}Sb	2.7 d	6.2	180	29
	^{124}Sb	60.3 d	4.0	120	30
Cs	^{134}Cs	2.05 y	30.0	465	16
Ba	^{131}Ba	12.0 d	11	270	15
La	^{140}La	40.2 h	9.0	11	1.2
Ce	^{141}Ce	32.5 d	0.58	0.49	0.84
Nd	^{147}Nd	11.1 d	1.4	2.8	2.0
Sm	^{153}Sm	46.8 h	210	2900	14
Eu	^{152}Eu	12.4 y	5300	7000	1.3
Tb	^{160}Tb	72.1 d	25	400	16
Tm	^{170}Tm	130 d	106	1700	16
Yb	^{169}Yb	32 d	3200	25000	7.8
Lu	^{177}Lu	6.7 d	2050	600	0.29
Hf	^{181}Hf	42.5 d	12.6	28	2.2
Ta	^{182}Ta	115 d	22	700	32
W	^{187}W	24 h	37	420	11
Th	^{233}Pa	27.4 d	7.4	82	11
U	^{239}Np	2.35 d	2.72	280	103

* Formed by the ^{58}Ni(n,p)^{58}Co reaction.

Thermal-neutron activation

Samples of about 0.1 g and standards as described above were weighed into polyethylene mini-vials (5 mm internal diameter, 1.0 cm depth) which were heat-sealed. Irradiations were carried out for 1 hr in the RT-3 tube of the National Bureau of Standards Reactor (Gaithersburg, Maryland) at a thermal-neutron flux of about 5×10^{13} n.cm^{-2}.sec^{-1}.

Activity measurements and data reduction

The samples from both irradiation modes were subjected to gamma-ray spectrometry, 7 days after the irradiation. The detector used had a resolution of 1.7 keV for the 1332-keV peak of ^{60}Co, and a relative efficiency of 11%. Gamma-ray analysis was performed again after about 20 days, with a detector having a resolution of 2.0 keV for the 1332-keV peak and a relative efficiency of 12%. By use of a 4096-channel pulse-height analyser and automatic sample-changers, the samples were counted for 1 hr each, and the data recorded on magnetic tape. In no case did the dead-time for any sample exceed 10%.

The spectra were processed on an IBM 370 computer, using the program SPECTRA.[8] The program employs a sensitive and specific search algorithm which examines both the first and second derivatives of the spectrum. The peak areas were determined by the "Wasson method",[9] using five channels. Multiplets were analysed by a non-iterative fit of symmetrical gaussian peaks to the spectral features. The precision and accuracy of this procedure have been found to be comparable to those obtainable with more complex and time-consuming procedures.[10]

RESULTS AND DISCUSSION

Comparisons of the two methods with respect to precision and accuracy were made by analysing five replicates of the National Bureau of Standards coal (SRM 1632) and fly ash (SRM 1633) standard reference materials. The results are given in Tables 2 and 3 for the epithermal and thermal irradiations, respectively. In Tables 4 and 5, the assumed "best" values from this work are compared with literature values. In most cases, agreement with the literature data is satisfactory. The aim of the present work was not only to determine for which elements ENAA would be the preferred technique, but also to see how ENAA compared for those elements expected to be determined more favourably by INAA. This information would be useful in judging in which cases ENAA, thermal INAA, or a combination of the two, would be the preferred method for the determination of a specified number of elements.

Sc, Fe, Co. These elements are determined with a high precision in INAA. The ENAA results show a precision of 3% or better for these elements. For Sc and Fe, the INAA results are more precise. In the case of Co, the I/σ_0 ratio is in the intermediate region (2.0), and there is no appreciable difference between ENAA and INAA. When Sc is determined by ENAA, it becomes necessary to consider the interference from the fast-neutron induced reaction ^{46}Ti(n,p)^{46}Sc, which is usually negligible in thermal-neutron studies. In the present case, where the fast-neutron flux in the irradiation position was about 5% of the thermal-neutron flux, the correction amounts to about 2%.

Cr. For chromium, the precision by INAA was about 2% and 4% for the fly ash and the coal respectively. As expected from the low I/σ_0 ratio of ^{50}Cr (0.53), the conditions are significantly worse in the case of ENAA, where the precision is only about 10%. Furthermore a correction of the order of 10% for the contribution from the ^{54}Fe(n,α)^{51}Cr reaction has to be introduced in this case.

Ni. In the thermal-neutron irradiated samples, no peak was observed for ^{58}Co produced from Ni by fast neutrons. By ENAA, nickel could be determined at the 10% precision level. The results compare favourably with the literature values shown in Tables 4 and 5.

Zn. The conditions for the determination of zinc seem to be similar for both techniques. In ENAA the ratio of ^{65}Zn to the major interfering nuclide ^{46}Sc is increased by a factor of about 4. On the other hand, the interference from the 1115.3-keV γ-ray of ^{160}Tb to the 1115.5-keV peak of ^{65}Zn becomes about 8 times more important in the case of ENAA.

As. From the high I/σ_0 ratio of ^{76}As, one would expect ENAA to yield superior results. The fact that ^{82}Br, which is a major activity in irradiated coals, shows even greater enhancement by ENAA than does ^{76}As, probably explains why the results by the two techniques show similar precision.

Table 2. Elemental concentrations in NBS coal (SRM 1632) and NBS fly ash (SRM 1633) by instrumental activation-analysis using epithermal neutrons, *ppm*

Element	Nuclide measured	γ-Energy, *keV*	Decay time, days	NBS 1632 Mean	NBS 1632 Relative s.d., %	NBS 1633 Mean	NBS 1633 Relative s.d. %
Sc	^{46}Sc	1120	20	3.95 ± 0.06	1.5	25.6 ± 0.5	1.8
Cr	^{51}Cr	320	20	20.6 ± 2.3	11.1	135 ± 14	10.4
Fe, %	^{59}Fe	1099	20	0.841 ± 0.025	3.0	5.91 ± 0.16	2.8
Co	^{60}Co	1174	20	5.70 ± 0.12	2.1	41.0 ± 0.6	1.5
Ni	^{58}Co	811	20	16.4	—	98.5 ± 9.5	10.1
Zn	^{65}Zn	1115	20	37 ± 6	15.9	200 ± 8	4.2
As	^{76}As	559	7	6.3 ± 0.2	3.2	59.1 ± 4.8	8.1
Se	^{75}Se	264	20	3.0 ± 0.3	8.8	10.8 ± 0.8	7.3
Br	^{82}Br	618	7	19.6 ± 0.4	2.1	9.2 ± 0.8	8.9
Rb	^{86}Rb	1076	20	18.3 ± 1.1	6.0	108.4 ± 3.7	3.4
Sr	^{85}Sr	514	7	159 ± 14	8.9	1520 ± 35	2.3
Zr	^{95}Zr	757	7	<100	—	310 ± 70	23
Mo	^{99m}Tc	140	7	3.08 ± 0.12	3.8	25.3 ± 1.6	6.2
Sb	^{122}Sb	564	7	3.2	—	5.9 ± 0.5	7.9
	^{124}Sb	1691	20	2.8	—	6.03 ± 0.23	3.8
Cs	^{134}Cs	795	20	1.52 ± 0.11	7.5	8.42 ± 0.22	2.6
Ba	^{131}Ba	496	20	306 ± 20	6.5	2510 ± 50	2.1
La	^{140}La	1596	7	10.8 ± 0.8	7.3	84.0 ± 3.6	4.3
Ce	^{141}Ce	145	20	22.6 ± 2.2	9.6	150.6 ± 3.3	2.2
Sm	^{153}Sm	69	7	1.41 ± 0.06	4.3	10.4 ± 0.9	8.3
Tb	^{160}Tb	879	20	0.274 ± 0.012	4.4	2.01 ± 0.06	3.0
Yb	^{169}Yb	177	20	0.95 ± 0.05	4.9	5.9 ± 0.3	4.9
Hf	^{181}Hf	482	20	0.83 ± 0.06	7.4	6.7 ± 0.3	4.0
Ta	^{182}Ta	1221	20	0.273 ± 0.009	3.4	2.00 ± 0.06	3.1
W	^{187}W	685	7	0.71 ± 0.07	10.3	3.9 ± 0.4	10.5
Th	^{233}Pa	311	20	3.12 ± 0.10	3.2	24.0 ± 0.5	2.1
U	^{239}Np	277	7	1.45 ± 0.04	3.1	12.2 ± 0.6	4.8

Table 3. Elemental concentrations in NBS coal (SRM 1632) and NBS fly ash (SRM 1633) by instrumental activation analysis using thermal neutrons, *ppm*

Element	Nuclide measured	γ-Energy, *keV*	Decay, time, *days*	NBS 1632 Mean	NBS 1632 Relative s.d. %	NBS 1633 Mean	NBS 1633 Relative s.d. %
Sc	^{46}Sc	1120	20	3.80 ± 0.05	1.2	26.7 ± 0.2	0.8
Cr	^{51}Cr	320	20	20.8 ± 0.8	3.9	129.2 ± 2.7	2.1
Fe, %	^{59}Fe	1099	20	0.901 ± 0.019	2.1	6.20 ± 0.05	0.8
Co	^{60}Co	1174	20	6.01 ± 0.16	2.6	40.3 ± 0.4	1.0
Zn	^{65}Zn	1115	20	39 ± 6	14.5	201 ± 6	2.9
As	^{76}As	559	7	6.1 ± 0.4	6.6	61.5 ± 2.4	3.9
Se	^{75}Se	264	20	3.7 ± 0.7	19.0	10.6 ± 1.3	12.4
Br	^{82}Br	618	7	19.2 ± 0.6	3.2	9.2 ± 0.6	6.9
Rb	^{86}Rb	1076	20	19.4 ± 2.3	11.9	110 ± 9	8.3
Sr	^{85}Sr	514	20	190	—	1480 ± 60	4.4
Zr	^{95}Zr	757	20	<250		410	—
Sb	^{122}Sb	564	7	3.0	—	6.1 ± 0.4	6.5
	^{124}Sb	1691	20	2.7	—	5.9 ± 0.5	9.2
Cs	^{134}Cs	795	20	1.49 ± 0.22	14.7	8.4 ± 0.5	5.5
Ba	^{131}Ba	496	20	309 ± 24	7.6	2550 ± 30	1.3
La	^{140}La	1596	7	10.3 ± 0.5	4.9	85.3 ± 3.8	4.4
Ce	^{141}Ce	145	20	19.5 ± 0.7	3.4	149.6 ± 2.0	1.3
Nd	^{147}Nd	91	20	8.7 ± 1.0	11.8	57.8 ± 1.6	2.8
Sm	^{153}Sm	69	7	1.38 ± 0.09	6.6	12.1 ± 1.4	11.5
Eu	^{152}Eu	1408	20	0.38 ± 0.04	10.7	2.69 ± 0.09	3.2
Tb	^{160}Tb	879	20	<0.5	—	1.99 ± 0.16	8.0
Yb	^{169}Yb	177	20	0.88 ± 0.09	10.4	6.2 ± 0.2	2.9
	^{175}Yb	396	7	0.84 ± 0.07	8.8	6.6 ± 0.4	5.3
Lu	^{177}Lu	208	7	0.109 ± 0.11	10.1	0.94 ± 0.09	9.5
Hf	^{181}Hf	482	20	0.91 ± 0.11	12.4	7.0 ± 0.4	5.6
Ta	^{182}Ta	1221	20	0.30	—	2.01 ± 0.14	7.0
Th	^{233}Pa	311	20	2.87 ± 0.09	3.2	23.8 ± 0.4	1.8

Table 4. Elemental concentrations in NBS coal (SRM 1632); comparison of present data with literature values, *ppm*

Element	Present work preferred values†	Ondov *et al.*[2]	Nadkarni[11]	Ruch *et al.*[12]	Klein *et al.*[13]	Chattopadhyay and Jervis[14]	Millard and Swanson[15]	Steinnes and Rowe[5]	NBS* Certified value
Sc	3.80 ± 0.05 T	3.7 ± 0.3	3.50 ± 0.08	3.81 ± 0.47	4.5	3.58 ± 0.35	4.1		
Cr	20.8 ± 0.8 T	19.7 ± 0.9	18.9 ± 2.2	20.3 ± 2.9	21 ± 2	21.6 ± 2.1	20.6		20.2 ± 0.5
Fe (%)	0.901 ± 0.015 T	0.84 ± 0.04	0.85 ± 0.06	0.93 ± 0.08	0.84	0.869 ± 0.041	0.903		0.87 ± 0.03
Co	5.70 ± 0.12 E	5.7 ± 0.4	5.13 ± 0.57	5.58 ± 0.21	5.9	5.50 ± 0.40	6.2		(6)
Ni	16.4 E	18 ± 4	12.1 ± 0.7	18.4 ± 2.1	14.5	13.5 ± 1.2			15 ± 1
Zn	37 ± 6	30 ± 10	32 ± 3	37.2 ± 17.4	34	37.5 ± 2.8			37 ± 4
As	6.3 ± 0.2 E	6.5 ± 1.4	4.61 ± 0.32	5.7 ± 0.13	5.5	5.75 ± 0.37		6.5 ± 1.2	5.9 ± 0.6
Se	3.0 ± 0.3 E	3.4 ± 0.2	2.44 ± 0.08	2.8 ± 0.11	3.05	3.03 ± 0.28			2.9 ± 0.3
Br	19.6 ± 0.4 E	19.3 ± 1.9	15.2 ± 1.4	18.2 ± 2.3	14.2			19.5 ± 0.3	
Rb	18.3 ± 1.6 E	21 ± 2	16.3 ± 3.7	22.5 ± 3.7	19.5		24		
Sr	159 ± 14 E	161 ± 16	1.02 ± 0.05	145 ± 9	144	1.33 ± 0.1	129	161 ± 9	
Mo	3.08 ± 0.12 E			3.2 ± 0.4	3.4	0.20 ± 0.02			
Sb	3.0 ET	3.9 ± 1.3	3.06 ± 1.4	3.4 ± 0.8	4.45	3.09 ± 0.26			
Cs	1.52 ± 0.11 E	1.4 ± 0.1	1.32 ± 0.11	1.8 ± 0.3	1.4	0.35 ± 0.04	2.6	1.36 ± 0.10	
Ba	306 ± 20 E	352 ± 30	311 ± 25	366 ± 34	405	314 ± 20	280	338 ± 14	
La	10.3 ± 0.5 T	10.7 ± 1.2	7.89 ± 0.15	11.3 ± 0.4	10.5		11.3	11.4 ± 0.5	
Ce	19.5 ± 0.7 T	19.5 ± 1	19.7 ± 0.56	23.3 ± 2.7	18.5		20		
Nd	8.7 ± 1.0 T						10.7		
Sm	1.41 ± 0.06 E	1.7 ± 0.2	1.66 ± 0.16	1.8 ± 0.1			1.6	1.38 ± 0.10	
Eu	0.38 ± 0.04 T	0.33 ± 0.04	0.37 ± 0.02	0.41 ± 0.03	0.21		0.4	0.299 ± 0.022	
Tb	0.274 ± 0.012 E	0.23 ± 0.05	0.40 ± 0.02				0.5		
Yb	0.84 ± 0.09 T	0.7 ± 0.1	0.69 ± 0.04	0.78 ± 0.07			0.8		
Lu	0.109 ± 0.011 T	0.14 ± 0.01	0.12 ± 0.005	0.15 ± 0.01			0.1		
Hf	0.83 ± 0.06 E	0.96 ± 0.05	0.89 ± 0.02	1.10 ± 0.15	0.95		1.1		
Ta	0.273 ± 0.006 E	0.24 ± 0.04	0.24 ± 0.01	0.21 ± 0.02	0.17		0.3		
W	0.71 ± 0.07 E	0.75 ± 0.17		0.74 ± 0.3				0.75 ± 0.17	
Th	3.12 ± 0.10 E	3.2 ± 0.2	1.28 ± 0.06	3.65 ± 0.49	3.0		3.2		(3.0)
U	1.45 ± 0.04 E	1.41 ± 0.07	1.2 ± 0.1	1.46 ± 0.35	1.26		1.43	1.46 ± 0.02	1.4 ± 0.1

* Numbers in parentheses are information values.
† T = Thermal; E = Epithermal.

Table 5. Elemental concentrations in NBS fly ash (SRM 1633); comparison of present data with lieteature values, ppm

Element	Present work† preferred values	Ondov *et al.*[2]	Nadkarni[11]	Klein *et al.*[13]	Chattopadhyay and Jervis[14]	Millard and Swanson[15]	Steinnes and Rowe[5]	NBS* Certified value
Sc	26.7 ± 0.2 T	27 ± 1	25.1 ± 0.5	32	20.7 ± 2.1	29.1		
Cr	129.2 ± 2.7 T	127 ± 6	113 ± 1.5	138	131 ± 6.1	180		131 ± 2
Fe (%)	6.20 ± 0.05 T	6.2 ± 0.3	6.17 ± 0.41	6.37	6.08 ± 0.52	6.69		
Co	40.3 ± 0.4 T	41.5 ± 1.2	36.7 ± 3.9	46	35.4 ± 2.8	42		38
Ni	98.5 ± 9.5 E	98 ± 9	100 ± 5	109	96.8 ± 3.2			98 ± 3
Zn	201 ± 6 T	216 ± 25	212 ± 14	208	214 ± 16			210 ± 20
As	61.5 ± 2.4 T	58 ± 4	67.6 ± 0.9	54	60.7 ± 2.6		58.0 ± 2.0	61 ± 6
Se	10.8 ± 0.8 E	10.2 ± 1.4	9.1 ± 0.2	9.35 ± 0.03	9.48 ± 0.8			9.4 ± 0.5
Br	9.2 ± 0.6 T	12 ± 4	7.52 ± 0.46	6.0			7.7 ± 1.5	
Rb	108.4 ± 3.7 E	125 ± 10	111 ± 13.5	120				112
Sr	1520 ± 35 E	1700 ± 300	1406 ± 80	1301	1373 ± 95	1390	1430 ± 60	1380
Zr	310 ± 70 E	301 ± 20			301 ± 22	500		
Mo	25.3 ± 1.6 E				1.52 ± 0.15			
Sb	6.0 ± 0.2 E	6.9 ± 0.6	6.72 ± 0.35	7.8	7.14 ± 0.56			
Cs	8.42 ± 0.22 E	8.6 ± 1.1	5.81 ± 1.4		0.63 ± 0.06	9.4	8.2 ± 0.9	
Ba	2550 ± 30 T	2700 ± 200	2700 ± 200	2780	2610 ± 210	2490	2540 ± 50	
La	84.0 ± 3.6 T	82 ± 2	64.1 ± 1.6	82		80	81.2 ± 3.3	
Ce	149.6 ± 2.0 T	146 ± 15	161 ± 35			169		
Nd	57.8 ± 1.6 T		60.5 ± 1.5			81		
Sm	12.1 ± 1.4 T	12.4 ± 0.9	13.6 ± 0.88	15			11.4 ± 1.6	
Eu	2.69 ± 0.09 T	2.5 ± 0.4	2.62 ± 0.05	2.86		3.1	2.44 ± 0.19	
Tb	2.01 ± 0.06 T	1.9 ± 0.3	3.12 ± 0.02			1.8		
Yb	6.6 ± 0.4 T	7 ± 3	5.53 ± 0.14			6.8		
Lu	0.94 ± 0.09 T	1.0 ± 0.1	1.01 ± 0.02			1.2		
Hf	6.7 ± 0.3 E	7.9 ± 0.4	7.52 ± 0.02	10.8		8.2		
Ta	2.00 ± 0.06 E	1.8 ± 0.3	2.04 ± 0.03	1.6		2.2		
W	3.9 ± 0.4 E	4.6 ± 1.6					4.2 ± 0.4	
Th	24.0 ± 0.5 E	24.8 ± 2.2	32.2 ± 0.2	26		26		(24)
U	12.2 ± 0.6 E	12.0 ± 0.5	11.3 ± 0.3	11.8		11.7	12.7 ± 0.5	11.6 ± 0.2

* Numbers in parentheses are information values.
† T = Thermal; E = Epithermal.

Se. The results from ENAA show the higher precision, especially for SRM 1633. A correction for the contribution of the 264.1-keV γ-ray of ^{182}Ta is necessary in both cases.

Br. Bromine is determined with similar precision in both materials. In cases of ash samples with substantially lower bromine content than SRM 1633, the epithermal technique would appear to be advantageous.

Rb. Investigations on silicate rocks have shown that ENAA is superior to thermal INAA for this element,[4,16] and this is also true for coal and fly ash. The precision is improved by a factor of about 2 in both cases.

Sr. Strontium is difficult to determine in the coals by thermal INAA, but ENAA yields satisfactory results. At the higher concentration level present in the fly ash, the results from both techniques are similar.

Zr. The I/σ_0 ratio of 5.0 for ^{94}Zr indicates that ENAA should be slightly more advantageous for this element and this appears to be the case. Zirconium is not a good element for instrumental activation analysis, however; the only nearly satisfactory result obtained was for SRM 1633 by ENAA.

Mo. This element can hardly be detected by thermal INAA and is subject to a large interference from ^{235}U fission. ENAA appears to give precise results for fly ash and coal. The ^{235}U(n,f) reaction has an I/σ_0 ratio of only 0.47 and the reduced fission interference requires only a small correction. Results for NBS 1632 agree with those of Ruch[12] and Klein[13] but disagree with those of Chattopadhyay.[14]

Sb. As in earlier studies,[2,5] it was confirmed that antimony is inhomogeneously distributed in SRM 1632. For SRM 1633, the results based on ^{122}Sb show similar precision for both techniques, which may be explained by the similar I/σ_0 ratios associated with the formation of ^{82}Br and ^{122}Sb. ENAA seems to be the more precise technique when ^{124}Sb is used.

Cs. For caesium, ENAA shows the higher precision, as expected from the high I/σ_0 ratio of ^{133}Cs.

Ba. Considering the high I/σ_0 ratio of 15 for ^{130}Ba, it appears surprising that both techniques show similar precision. At lower barium levels in coals, however, ENAA has been shown to be preferable.[17] The 28.4-hr ^{135m}Ba isotope, which is associated with an even higher I/σ_0 ratio, was observed in most of the spectra, but with peak intensities substantially lower than those of the 496-keV peak of ^{131}Ba when recorded 7 days after the irradiation.

La. The results for La are similar by both techniques.

Ce. Cerium is determined with high precision by thermal INAA. Even though the I/σ_0 ratio of ^{140}Ce is as low as 0.84, the results obtained by ENAA are also of fairly good quality. The interference from ^{235}U fission is somewhat less in the case of ENAA and only a small correction is needed. On the other hand, the interference from the 145.4-keV γ-ray of ^{233}Pa, which is in most cases negligible in thermal INAA, becomes significant in ENAA.

Nd. Results of good precision were obtained by thermal INAA after correction for the contribution from ^{235}U fission. In the case of ENAA, the determination proved to be difficult, especially in the case of the fly ash. This may be due to higher relative interference from the 86.8-keV peak of ^{160}Tb in the case of ENAA.

Sm. There is no significant difference between the results obtained by the two techniques for samarium. As in the study based on a short irradiation[5] our results for Sm in SRM 1632 are slightly lower than most of the published data.

Eu. This is a case where thermal INAA is the superior technique. The ^{152}Eu peaks obtained after ENAA were rather poor, and therefore no results are reported here.

Tb. For this element, ENAA is clearly the technique of choice, showing a precision of about 5% for the coal and 3% for the fly ash. The 879-keV peak of ^{160}Tb was not detected in SRM 1632 after thermal neutron activation and 20 days' delay.

Tm. Considering the I/σ_0 ratio associated with the formation of ^{170}Tm, ENAA would seem to be the more advantageous alternative for the determination of thulium. Calculations based on the 84.3-keV peak after ENAA, however, yielded results that were about three times higher than would be expected for samples with a normal rare-earth distribution. Probably the peak was not resolved from the 84.7-keV peak of ^{182}Ta. Even the peaks of ^{233}Pa and ^{160}Tb at 86.6 and 86.8 keV respectively may have interfered with the thulium determination.

Yb. Ytterbium can be determined by means of both ^{169}Yb (177.0 keV) and ^{175}Yb (396.1 keV). In ENAA ^{169}Yb is the only real possibility because of the low I/σ_0 ratio of ^{174}Yb. The results obtained by thermal INAA are similar in precision and accuracy for both nuclides. The data based on ^{169}Yb are similar for both irradiation techniques.

Lu. Lutetium is determined with a precision of about 10% in both materials by INAA. The epithermal activation technique is not applicable because of the low I/σ_0 ratio of ^{176}Lu (0.29).

Hf. The precision for hafnium is about 10% for the coal and 5% for the fly ash by both techniques. The precision seems to be slightly better with ENAA.

Ta. For this element, use of ENAA gives a very significant improvement, which is to be expected from the high I/σ_0 ratio (32) of ^{181}Ta.

W. The determination of tungsten after decay for 1 week is difficult at this concentration level, both for the coal and fly ash. ENAA brings about a significant improvement, yielding results with a precision of about 10%.

Th. Thorium is one of the elements for which ENAA has been shown to give a significant advantage for analysis of silicate rocks.[4,16] In SRM 1632 and SRM 1633, the concentrations are sufficiently high

for a very satisfactory precision to be obtainable also by INAA. At lower concentration levels, ENAA would be the technique of choice for thorium ($I/\sigma_0 = 11$).

U. The I/σ_0 ratio of 103 makes ENAA very good for uranium. While it is difficult to determine U in coal and fly ash by thermal INAA, this element is determined with a precision of about 3–4% by ENAA. Results compare favourably with those obtained by γ-ray counting of natural radioactivity[2] and isotope-dilution mass-spectrometry.[13]

On the basis of this study, the elements may be classified as follows.

1. Elements where ENAA is of definite advantage in comparison with thermal INAA: Ni, Mo, Rb, Sr, Cs, Tb, Ta, W, U.

2. Elements where the results from this work show no appreciable difference, but ENAA would be preferable at lower concentration levels: As, Se, Br, Zr, Sb, Ba, Hf, Th.

3. Elements where the results from this work show no appreciable difference, but thermal INAA would be preferable at lower concentration levels: Sc, Fe, Co, Zn, La, Sm, Yb.

4. Elements where thermal INAA is of definite advantage: Cr, Ce, Nd, Eu, Lu.

For a number of these elements, determined by means of radionuclides with half-lives exceeding 50 days, significantly better results might have been obtained with both ENAA and INAA by carrying out another later counting, for example, after 6 weeks, with longer counting times. However, for the purpose of this study, which had the objective of analysing a reasonably large number of samples in a relatively short period of time, only the two measurements were made.

Some specific sources of error and practical limitations of ENAA as applied to geological materials have been discussed in detail elsewhere.[3] Since the samples concerned in this work are similar to silicate rocks in most significant respects, the discussion need not be repeated here. The high carbon content of the coals might bring about different activation ratios in samples and standards in ENAA because ^{12}C is a very good neutron moderator.[5] In the present work, however, appreciable differences between the results obtained by the two irradiation techniques were not observed for SRM 1632, either for high (Cs, Ta) or low (Sc, Cr) I/σ_0, which indicates that possible moderation of neutrons within the coal sample did not affect the accuracy of the results. The significance of interfering nuclear reactions in thermal INAA and in ENAA have been discussed above each element wherever appropriate.

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SPECTROPHOTOMETRIC DETERMINATION OF SELENIUM IN CONCENTRATES AND HIGH-PURITY COPPER METAL WITH 3,3′-DIAMINOBENZIDINE AFTER SEPARATION BY XANTHATE EXTRACTION*

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Summary—A method for determining 0.0001–0.10% of selenium in copper, nickel, molybdenum, lead and zinc sulphide concentrates is described. After sample decomposition, selenium is reduced to the quadrivalent state by heating in a 4*M* hydrochloric acid–5*M* sulphuric acid medium, then extracted into chloroform as the xanthate, and ultimately determined spectrophotometrically with 3,3′-diaminobenzidine. Small amounts of iron, lead and copper, and an appreciable amount of molybdenum are co-extracted as xanthates but do not interfere. More than 5 mg of antimony will cause low results. The proposed method was developed primarily for concentrates, but it is also applicable to high-purity copper.

The development of methods for the determination of elements at the 1-ppm level in diverse sulphide concentrates is an important aspect of the Canadian Certified Reference Materials Project at CANMET. Because selenium is a common trace constituent in sulphide ores,[1] a method was needed for its determination.

The distillation of selenium(IV) bromide or the reduction of selenium to the elemental state in acid solution is usually employed for its separation.[2] However, recent work by the author on the chloroform extraction of metal ethyl xanthate complexes from hydrochloric acid media[3] suggested the possibility of a new separation procedure for selenium based on its solvent extraction as the xanthate. In subsequent work, chloroform extraction of arsenic[4] and tellurium[5] ethyl xanthates from $\geq 11M$ hydrochloric acid media was utilized in the determination of these elements in sulphide concentrates, after their preliminary separation from most of the matrix elements by co-precipitation with hydrous ferric oxide from an ammoniacal medium. Because it has been reported that selenium can also be separated by the same co-precipitation procedure,[2] it was considered that a similar method might be developed for selenium. Consequently, the possible application of these combined separation procedures was investigated in the present work, but this approach was later dropped.

This paper describes the successful determination of selenium in copper, nickel, molybdenum, lead and zinc sulphide concentrates, and in high-purity copper metal, after its separation from the matrix elements —without prior separation by co-precipitation with iron(III)—by chloroform extraction as the xanthate from a 4*M* hydrochloric acid–5*M* sulphuric acid medium. Selenium is ultimately determined spectrophotometrically by a modification of a method reported by Cheng,[6] which involves the measurement of the toluene extract of the selenium(IV)–3,3′-diaminobenzidine complex. Although the author[3,7] and several previous investigators[8] have found that selenium forms an extractable xanthate complex, the application of this system as a separation step before the determination of selenium has not, to the author's knowledge, been reported previously.[9] Some advantages of the proposed method over those involving distillation, precipitation of elemental selenium, neutron-activation, and hydride reduction in conjunction with atomic-absorption spectroscopy are its simplicity, sensitivity and relative specificity. It also requires no special apparatus.

The determination of selenium by flameless (carbon rod) atomic-absorption spectroscopy was also investigated but was abandoned because of the poor reproducibility.

EXPERIMENTAL

Reagents

Standard selenium solution, 10 μg/ml. Dissolve 0.1000 g of pure selenium metal by heating gently with 25 ml of concentrated nitric acid, cool, and dilute to 1 litre with water. Dilute 10 ml of this stock solution to 100 ml with water. Prepare fresh as required. (The purity of the selenium metal was confirmed by the potassium permanganate oxidation–iron(II) back-titration method.)[10]

3,3′-Diaminobenzidine tetrahydrochloride, 0.2% w/v solution. Prepare just before use.

4M Hydrochloric acid–5M sulphuric acid solution. Slowly add 280 ml of concentrated sulphuric acid, with stirring, to ~350 ml of water. Allow the solution to cool to room temperature, then add sufficient 0.5% w/v potassium permanganate solution to oxidize any reducing impurities

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present. Add 340 ml of concentrated hydrochloric acid and dilute to 1 litre with water.

Tartaric acid, 20% w/v solution.

EDTA, disodium salt, 4% w/v solution.

Formic acid, 10% v/v.

Potassium ethyl xanthate, 20% w/v solution. Prepare fresh as required.

Ammonia, 50% v/v.

Nitric acid, 50% v/v.

Sulphuric acid, 50% v/v.

Perchloric acid, 5% v/v.

Toluene, analytical-reagent grade.

Chloroform, analytical-reagent grade.

Procedures

Calibration curves. Add 2 ml of concentrated perchloric acid to each of seven 100-ml beakers; then, by burette, add to the last six beakers, 0.5, 1, 2.5, 5, 7.5 and 10 ml, respectively, of standard 10 μg/ml selenium solution. The first beaker contains the blank. With the exception of the blank, evaporate each solution until fumes of perchloric acid appear (Note 1), then wash down the sides of the beaker with water and evaporate the solution just to fumes of perchloric acid again to ensure the complete removal of nitric acid. Cool to room temperature, then add to each beaker 1 ml of 20% tartaric acid solution, 5 ml of 4% EDTA solution and 2 ml of 10% v/v formic acid and dilute each solution to ~25 ml with water. Adjust the pH of each of the resulting solutions to 1.25 ± 0.05 with 50% v/v ammonia solution, add 5 ml of freshly prepared 0.2% 3,3′-diaminobenzidine solution, mix thoroughly, and allow to stand for 45 min to complete the complex formation. Adjust the pH to 6.75 ± 0.15 with 50% v/v ammonia solution and 5% v/v perchloric acid, if required (Note 2), then transfer each solution to a 125-ml separatory funnel, marked at 50 ml, and dilute to the mark with water. By pipette, add 20 ml of toluene, stopper, and shake for 2 min. Allow several min for the layers to separate, then drain off and discard the lower aqueous layer. Drain the toluene layers into dry 40-ml centrifuge tubes and centrifuge for 1 min. Determine the absorbance of the blank and each of the four extracts of lowest selenium content, at 420 nm, against toluene as the reference solution, using 40-mm cells. Determine the absorbance of the blank and each of the five extracts of highest selenium content in a similar manner, using 20-mm cells. Correct the absorbance value obtained for each selenium–3,3′-diaminobenzidine extract by subtracting that obtained for the blank. Plot μg of selenium *vs.* absorbance for each series of measurements.

Concentrates. Depending on the expected selenium content, transfer 0.2–0.5 g of powdered sample (Note 3) to a 250-ml beaker. Add ~2 g of potassium chlorate, moisten with a few ml of water, cover and carefully add 20 ml of concentrated nitric acid in small portions. Heat gently until the sample is decomposed (Note 4), then add 30 ml of 50% v/v sulphuric acid and heat until the evolution of brown oxides of nitrogen ceases. Remove the cover, wash down the sides of the beaker with water, and carefully evaporate the solution until fumes of sulphur trioxide just appear (Note 5). Cool, wash down the sides of the beaker with 10 ml of concentrated nitric acid (Note 6). Cover, and heat the solution until the evolution of brown oxides of nitrogen ceases, then remove the cover and evaporate the solution until fumes of sulphur trioxide just appear. Cool, wash down the sides of the beaker with water, and again evaporate the solution just to fumes to ensure the complete removal of nitric acid. Cool to room temperature, add 20 ml of water, mix and add 17 ml of concentrated hydrochloric acid. Heat the solution to the boiling point and boil gently for 10 min to reduce selenium to the quadrivalent state. Cool the solution to room temperature, then filter it through glass-fibre filter paper (Note 7) into a 125-ml separatory funnel. Wash the beaker three times with 4*M* hydrochloric acid–5*M* sulphuric acid contained in a plastic wash-bottle. Wash the paper and residue four times with the mixed acid solution, then discard the paper and residue. Carry a blank through the whole procedure.

Add 10 ml of chloroform to the blank and sample solutions, followed by 1 ml of freshly prepared 20% potassium ethyl xanthate solution, stopper, and shake for 1 min. Allow at least 5 min for the layers to separate, then drain the chloroform phase into a 125-ml separatory funnel. Extract the aqueous phase twice more, in a similar manner, with 10-ml portions of chloroform and 1 and 0.5 ml of xanthate solution, respectively. Wash the aqueous phase by shaking it for ~30 sec with 5 ml of chloroform. Add 30 ml of water to the combined extracts, stopper, and shake for 1 min. Allow several min for the layers to separate, then drain the chloroform phase into a 150-ml beaker. Add 5 ml of chloroform and 0.5 ml of xanthate solution to the aqueous phase, stopper, and shake for 1 min. After the layers have separated, drain the chloroform phase into the beaker containing the initial extract. Wash the aqueous phase twice, by shaking for ~30 sec each time, with ~3 ml of chloroform and add the washings to the beaker containing the extract. Add 10 ml of 50% nitric acid and 2 ml of concentrated perchloric acid to the combined extracts and heat in a hot water-bath to remove the chloroform. Cover the beaker, heat until the evolution of brown oxides of nitrogen ceases, then remove the cover, wash down the sides of the beaker with water, and evaporate the solution just to fumes of perchloric acid (Note 1). Cool, wash down the sides of the beaker with water, evaporate to fumes of perchloric acid again to completely remove nitric acid, then cool to room temperature (Note 8).

If the sample contains 100 μg or less of selenium, proceed with the additions of tartaric acid, EDTA and formic acid solutions to both the sample and blank solutions. Adjust the pH to 1.25 ± 0.05 and determine selenium as described above.

If the sample contains more than 100 μg of selenium, add 3 ml of concentrated perchloric acid and 2.5 ml of 20% tartaric acid solution to both the sample and blank solutions. Transfer the solutions to volumetric flasks of appropriate size (50 or 100 ml) and dilute to volume with water. Transfer suitable aliquots (up to 20 ml) of both solutions to 100-ml beakers and, if necessary, add sufficient concentrated perchloric acid and 20% tartaric acid solution so that 2 ml and 1 ml, respectively, are present (Note 9), then proceed with the additions of EDTA and formic acid solutions, the pH adjustment and the subsequent determination of selenium as described above.

Copper metal. Transfer 0.5 g of sample to a 250-ml beaker, cover and add ~5 ml of water and 10 ml of concentrated nitric acid. When the dissolution of the sample is complete, add 30 ml of 50% v/v sulphuric acid and heat until the evolution of brown oxides of nitrogen ceases. Remove the cover, wash down the sides of the beaker with water, and carefully evaporate the solution until fumes of sulphur trioxide just appear (Note 5). Cool, wash down the sides of the beaker with water, and again evaporate the solution until fumes of sulphur trioxide just appear, to ensure the complete removal of nitric acid. Cool and add 20 ml of water and 17 ml of concentrated hydrochloric acid and boil the solution gently for ~5 min. Cool to room temperature, transfer the solution to a 125-ml separatory funnel, using 4*M* hydrochloric acid–5*M* sulphuric acid to wash the beaker, and proceed with the extraction of selenium xanthate and the subsequent determination of selenium as described above.

Notes

1. Prolonged fuming or evaporation of the solution to dryness will cause low results for selenium.[11,12]

2. If EDTA precipitates during complex formation, difficulty will be experienced in adjusting the pH of the solution to 6.75 ± 0.15 until the precipitate has dissolved. If this occcurs, adjust the pH to 7–7.5, swirl the beaker until the precipitate dissolves, then adjust the pH to the recommended value with 5% v/v perchloric acid.

3. The use of larger samples is not recommended because of the high metal ion content of the resultant solution. This may result in the formation of sulphate salts that are not completely soluble in the strongly acidic medium used for the extraction of selenium xanthate.

4. If some elemental sulphur is still present, add 1 or 2 ml of 20% v/v bromine in carbon tetrachloride and heat gently until the bromine and carbon tetrachloride have been removed.

5. Prolonged fuming results in an appreciable loss of selenium by volatilization. At this, and subsequent stages, the evaporation of the solution should be discontinued as soon as fumes of sulphur trioxide appear.

6. Nitric acid is added to dissolve any elemental selenium that may have been formed by reduction with sulphur dioxide or hydrogen sulphide in preceding stages.

7. Filtration of the solution through ordinary filter paper is not recommended. Enough carbonaceous material is dissolved by the strongly acidic solution to cause partial reduction of selenium to the elemental state, particularly if the solution is allowed to stand for some time before the extraction of selenium xanthate. Some lead chloride may pass through the filter paper but this does not interfere in the extraction of selenium.

8. If the sample contains an appreciable amount of molybdenum, an insoluble white molybdenum compound may form when the solution is evaporated to fumes of perchloric acid. If this occurs, add ~5 ml of water, then add dropwise sufficient 25% w/v sodium hydroxide solution to dissolve the precipitate. Depending on the expected selenium content of the sample, either add the recommended volumes of tartaric acid, EDTA and formic acid solutions, adjust the pH of the resulting solution to 1.25 ± 0.05 with concentrated perchloric acid and proceed as described, or add the recommended volumes of concentrated perchloric acid and tartaric acid solution, then transfer the solution to a volumetric flask of appropriate size and proceed as described.

9. The selenium(IV)–diaminobenzidine complex is not completely extracted into toluene under the proposed conditions.[6] Consequently, to avoid error resulting from variation in the final salt content of the aqueous phase during extraction (and subsequently in the degree of extraction), the general composition of the sample solution should be approximately the same as that of the solutions employed for calibration purposes.

RESULTS

Spectrophotometric determination of selenium by the 3,3′-diaminobenzidine method

Low and erratic results were obtained for selenium in initial tests in which Cheng's method[6] was applied to pure selenium solutions. This was found to be caused by the high initial pH (2–3) recommended by Cheng before the addition of 3,3′-diaminobenzidine and the subsequent formation and extraction of the selenium(IV) complex into toluene. Tests showed that consistent and reproducible results are obtained when the pH of the solution is in the range 1.0–1.5 before the addition of the reagent. An intermediate pH of 1.25 ± 0.05 was chosen for subsequent work. In subsequent work tartaric acid was also employed during complex formation to prevent possible hydrolysis of other metal ions.

Separation of selenium by extraction of its ethyl xanthate complex

Previous work[3] showed that selenium(IV) [or probably selenium(II) after reduction by xanthate] can be quantitatively extracted into chloroform from 0.1–10*M* hydrochloric acid. It was also found in that and subsequent work, in which methods involving xanthate extraction from ≥11*M* hydrochloric acid were developed for arsenic[4] and tellurium[5] in ore concentrates, after their preliminary separation by co-precipitation with iron(III), that the extraction of iron(III), copper(II), molybdenum(VI) and certain other species [antimony(III) and (V), bismuth, tin(IV) and nickel] is minimal from ≥10*M* hydrochloric acid media. Initially, it was considered that a similar method, involving both separation procedures, might be developed for selenium. However, this approach was ultimately abandoned because it was found that the iron collection method does not yield complete recovery of selenium(IV) from a strongly ammoniacal medium, and that small amounts are lost by volatilization at room temperature from strongly acidic hydrochloric acid media, particularly on standing. Similar losses of selenium have been reported by previous investigators.[13–15]

It is known that a strongly oxidizing sample-decomposition step, in which selenium is oxidized to selenium(VI), is necessary for the decomposition of sulphide ores.[16] It is also known that selenium(VI) can be quantitatively reduced to the quadrivalent state, without loss by volatilization, by boiling in a 4*M* hydrochloric acid medium.[14,15] Because the reduction of selenium to the quadrivalent state is required for its extraction as the xanthate, and because it was found that it can also be quantitatively extracted into chloroform from fairly concentrated sulphuric acid media, the extraction of selenium(IV) from a 4*M* hydrochloric acid–5*M* sulphuric acid medium was investigated as a possible means of separating it directly from large amounts of the matrix elements under consideration; if higher concentrations of sulphuric acid are used, the density of the resultant solution precludes the use of chloroform in the extraction.

Preliminary experiments with 4*M* hydrochloric acid–5*M* sulphuric acid solutions of selenium(IV) yielded low results which were found to be caused by the co-extraction of a small amount of hydrochloric acid into the chloroform phase. This resulted in a partial loss of selenium, due to volatilization as the chloride, when the xanthate extract was treated with nitric and perchloric acids and the resultant solution was ultimately evaporated to fumes of perchloric acid. Further work showed that μg-amounts of selenium are also potentially lost to the aqueous phase when the chloroform extract is washed with water to remove co-extracted hydrochloric acid.

However, this can be recovered readily by adding xanthate solution to the wash solution and re-extracting the selenium. Experiments showed that up to at least 500 μg of selenium(VI) will be quantitatively reduced to selenium(IV) by boiling for ~10 min in a 4*M* hydrochloric acid–5*M* sulphuric acid medium, and can be quantitatively extracted into chloroform as the xanthate in three successive extractions and separated from the co-extracted hydrochloric acid as described above. Complete recovery of selenium (500 μg) was obtained when the procedural steps described above were applied to synthetic (0.5-g samples) copper, nickel, zinc, lead and molybdenum concentrates after sample decomposition by the proposed procedure.

Effect of diverse ions

Cheng[6] found that in the absence of elements that oxidize the reagent [*e.g.*, vanadium(V)], and in the presence of EDTA as a complexing agent for iron(III), copper(II) and other elements, 3,3′-diaminobenzidine is a relatively specific reagent for selenium, and that interference from coloured ions [chromium(III), nickel, copper(II) and cobalt] can be eliminated by extracting the selenium(IV) complex into toluene. From previous work,[3] the author expected that tellurium(IV), gold(III), platinum(IV) and palladium(II) would be co-extracted, to a certain extent, as xanthates from a 4*M* hydrochloric acid–5*M* sulphuric acid medium. Because gold, platinum and palladium occur in sulphide concentrates, and the effect of these elements had not been studied previously by Cheng,[6] tests were conducted which ultimately showed that 500-μg quantities of gold(III) and platinum(IV) interfere by oxidizing diaminobenzidine, yielding low results for selenium. Palladium(II) (500 μg) also causes low results for selenium because of the formation of a white precipitate which results in emulsification in the toluene phase. However, subsequent tests showed that up to at least 100 μg each of gold and platinum and 50 μg of palladium will not interfere. Moderate amounts (500 μg) of tellurium(IV) also do not interfere.

Table 1. Recovery of selenium from synthetic concentrate samples

Matrix and nominal composition, %	Total Se present, %	Se found, %
Cu concentrate (33.52 Cu, 30.01 Fe, 34.16 S)	0.0051_4	0.0052_2
	0.0056_4	0.0056_4
	0.0096_4	0.0094_0
	0.0146	0.013_7
	0.0546	0.052_1
	0.1046	0.100_3
Mo concentrate (12.7 Mo, 1.1 Fe, 56.6 insoluble material*)	0.0046_1	0.0044_8
	0.0051_1	0.0051_4
	0.0091_1	0.0086_5
	0.0141	0.013_2
	0.0541	0.052_6
	0.1041	0.100_5
Pb concentrate (65.5 Pb, 18.8 S, 4.5 Zn, 1.2 SiO_2, 10.3 Fe, 0.07 Ag)	0.0037_3	0.0037_6
	0.0042_3	0.0042_2
	0.0082_3	0.0080_0
	0.0132	0.013_2
	0.0532	0.051_8
	0.1032	0.100_3
Zn concentrate (44.7 Zn, 31.6 S, 7.4 Pb, 0.8 SiO_2, 11.0 Fe, 0.01 Ag)	0.0009_9	0.0009_4
	0.0014_9	0.0015_2
	0.0054_9	0.0050_4
	0.0105	0.010_2
	0.0505	0.049_4
	0.1005	0.097_5
Ni-Cu concentrate (11.89 Ni, 10.83 Cu, 32.04 Fe)	0.0079_1	0.0081_5
	0.0084_1	0.0084_5
	0.0124_1	0.012_0
	0.0174	0.013_8
	0.0574	0.057_6
	0.1074	0.106_5

Duplicate determinations of selenium in the Cu, Mo, Pb and Zn concentrates by the proposed method gave 0.0046_8 and 0.0046_0, 0.0041_2 and 0.0041_0, 0.0032_2 and 0.0032_4, and 0.0005_0 and 0.0004_8%, respectively. Four determinations of selenium in the Ni-Cu concentrate gave 0.0077_4, 0.0069_0, 0.0076_5 and 0.0073_5%.

* Predominantly talc.

Analysis of the solutions remaining after the extraction and subsequent determination of selenium in the synthetic concentrates described previously (compositions given in Table 1) showed that only small amounts of iron (20–30 μg), nickel (10–20 μg), zinc (3–8 μg) and lead (35–190 μg) are co-extracted with selenium xanthate. Copper is co-extracted to a greater extent, *viz.* 0.6–0.7 mg at the 170-mg level. Copper xanthate is not appreciably soluble in chloroform and some of the insoluble yellow compound may be retained in the chloroform phase during extraction, but this does not interfere in the extraction of selenium. Neither copper nor any of the above co-extracted elements interferes in the subsequent determination of selenium. Although molybdenum is appreciably co-extracted as the xanthate from a 4*M* hydrochloric acid–5*M* sulphuric acid medium, ~300 mg of molybdenum (which is the approximate molybdenum content of a 0.5-g sample of a pure molybdenum sulphide concentrate), do not interfere in the xanthate extraction, and the co-extracted molybdenum (up to ~30 mg) does not interfere in the subsequent determination of selenium. Similar tests showed that 500 mg each of nickel, zinc and copper also do not interfere in the proposed method. Moderate amounts of chromium (50 mg), bismuth (50 mg), manganese (50 mg), vanadium (25 mg), tin (20 mg) and arsenic (20 mg) can be present in the sample without causing error in the selenium result. Antimony (more than 5 mg) causes low results for selenium because it is appreciably co-extracted as the antimony(V) chloro-complex from a 4*M* hydrochloric acid medium.[3] This results in the formation of an insoluble compound when the extract is treated with nitric and perchloric acids and ultimately evaporated to fumes of perchloric acid.

Table 2. Determination of selenium in commercial-purity copper rods

Sample[17]	Recommended value, *ppm*	Se found, *ppm*
SSC–1	7.3	8.8, 9.0
SSC–2	2.6	2.8, 3.4
SSC–3	3.9	4.8, 5.0
SSC–4	2.9	3.4, 3.6

Applications

The proposed method was applied to the analysis of a series of five synthetic concentrates (200-mesh commercial-grade sulphide concentrates), in which selenium, added to the powdered samples in the form of a standard solution, was varied from 0.0005 to 0.10%. It was also applied to samples of four certified reference, commercial-purity copper rods. The results of these analyses are given in Tables 1 and 2.

DISCUSSION

Table 1 shows that the results obtained for the synthetic copper, molybdenum, lead and zinc concentrate samples agree favourably with the calculated amount of selenium present. Those obtained for the synthetic nickel–copper concentrate samples are also in good agreement with the calculated amount present, although it was found that the concentrate employed was not homogeneous with respect to its selenium content; the mean value of the four results obtained for the concentrate (reported in the footnote to Table 1) was used to calculate the total amount present. Unfortunately, nickel and molybdenum concentrates of low selenium content and of higher nickel and molybdenum contents than those shown in Table 1 could not be obtained. However, the method is applicable to these concentrates because, as stated previously, large amounts of nickel (500 mg) and molybdenum (300 mg) do not interfere in the determination of selenium by the proposed method.

The results obtained for the copper rods are slightly higher than the recommended values, but in general agreement with them.

It is to be emphasized that the predominant source of operator error is that resulting from prolonged fuming of the sample solution to fumes of sulphur trioxide to remove nitric acid. An appreciable amount of selenium is lost by volatilization under these conditions. The evaporation of the solution should be discontinued as soon as fumes of sulphur trioxide appear. Undoubtedly, this accounts for the slightly low results obtained for some of the synthetic concentrate samples (Table 1), particularly at the higher levels of selenium.

The proposed method is suitable for samples containing 0.0001% or more of selenium. Probably samples containing approximately 0.02% or more can be analysed by flame atomic-absorption spectroscopy after the separation of selenium by the proposed method.

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TRACE DETERMINATION OF CARBON AND OXYGEN IN TUNGSTEN BY SPARK-SOURCE MASS-SPECTROGRAPHY

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Summary—A high pumping-speed vacuum system, incorporating a mechanical cryo-pump, was designed and built to attach to the source of a spark-source mass-spectrometer to reduce the partial pressure of carbon- and oxygen-containing gases. Pressures in the 10^{-10} mmHg range were obtained, which provide a suitable environment for the determination of carbon and oxygen in tungsten. The effect of the partial pressure of CO on carbon and oxygen determination has been studied and characterized. A determination limit of 1 ppm has been achieved for these elements in tungsten.

The determination of carbon and oxygen by a spark-source mass-spectrograph (SSMS), unlike the determination of metallic species, requires special attention and care. Background gases in the mass-spectrometer ion-source, notably CO, CO_2, C_xH_y, and H_2O, are usually high and set the lower limit for the detection of carbon and oxygen. In addition, the effect of background gases on the determination of carbon and oxygen by SSMS is dependent on the nature of the material being analysed. Background gases are an important limitation in the analysis of an active metal such as tungsten, but not in the analysis of semiconductors, noble metals, or non-reactive metals, exemplified by germanium, gold, or copper respectively. Special techniques are needed to reduce the amount of residual gases and maintain low background-gas pressure, especially during sparking.

Cryogenic methods to lower the amount of background gases in the mass-spectrometer ion-source have been studied and shown to be useful for certain analyses. One of the first applications of cryogenics to mass spectrometry was reported by Hickam and Sweeney.[1] They attached a Dewar flask of liquid helium to the ion-source of the mass spectrometer. Because of mechanical limitations, pumping speeds were improved only slightly, to 25 l./sec. Harrington *et al.*[2] incorporated a charcoal-covered copper surface directly into the ion-source of a Nuclide Graf 2 mass spectrograph. Liquid nitrogen was used to cool the charcoal surface before sparking. The ion-source was "rough-pumped" with an untrapped mechanical pump and the ion-source chamber was not baked out before the analysis. The technique, however, was shown to be effective in reducing the interferences on the photoplate that were due to hydrocarbon lines and the water background. This experimental arrangement[3] was useful for measuring carbon, oxygen and nitrogen in iron and zinc at the 10–30 and 1–2 ppm levels, respectively. In addition, favourable analytical results were reported for carbon and oxygen in zone-refined tungsten rod at the 4 and 2 ppm levels, respectively.

Other workers in the field have previously reported the need for reduced ion-source pressures to determine carbon and oxygen at the 1 ppm level in various materials. For example, Socha and Willardson[4] took another approach which involved replacing the diffusion pump with a high-speed ion-pump to minimize the contribution of organic species emanating from the diffusion pump, and measured the gas content of GaAs as a function of source-pressure and pumping speed. Konishi *et al.*[5] recognized that materials such as GaAs dissociate during sparking, leaving metallic deposits over the inside walls of the ion-source. The evaporated material then acts like a getter for the background gases as well as overcoating those regions which are sources of desorbed gas. GaAs "free" from carbon and oxygen was used as a counter-electrode to spark against Fe, Ni, and Cu samples, with modest success in the 50-ppm range for carbon and oxygen.

More recently, Clegg *et al.*[7] incorporated a liquid helium–liquid nitrogen system into their ion-source and showed extremely good results for oxygen and carbon in semiconductors. Beske *et al.*[8] incorporated a surface cooled with liquid helium into the mass-spectrometer ion-source in a study of oxygen in copper and silicon, and concluded that it was possible to detect oxygen in metals down to 1 ppm.

The best technique for determination of low concentrations of carbon and oxygen in reactive materials is the combination liquid helium–liquid nitrogen cryo-pumping system, but there are still several disadvantages. First, the use of the two liquefied gases is expensive and tedious. Secondly, at the end of an experiment, it is troublesome to bring the cryo-panel up to room temperature. There are also problems associated with the construction of the apparatus,

namely in the use of vacuum feed-throughs and concentric coils and shields which, in addition, require more space in the source-chamber.

In previous work at this laboratory, the use of a copper "doughnut" filled with liquid nitrogen and with and without adsorbent material, was found unsatisfactory for the determination of carbon and oxygen in tungsten. This paper describes the resultant further work, involving a combination of a mechanical cryo-pump and a high-speed diffusion-pumping system, adapted to a modified ion-source chamber of an AEI MS702 mass spectrometer. The combination of the two incorporates all of the advantages of the previously described systems. In addition, the rate of analysis is improved because the pump-down takes 30 min and warm-up less than 15 min, and the limiting factor is the length of time needed for the analysis itself.

This work will show that it was not possible to measure carbon and oxygen concentrations at the ppm level in tungsten with an AEI MS702 mass spectrograph when base-pressures in the ion-source were in the 10^{-7} mmHg range used by Harrington *et al.*,[3] base-pressures of 10^{-10} mmHg being found necessary.

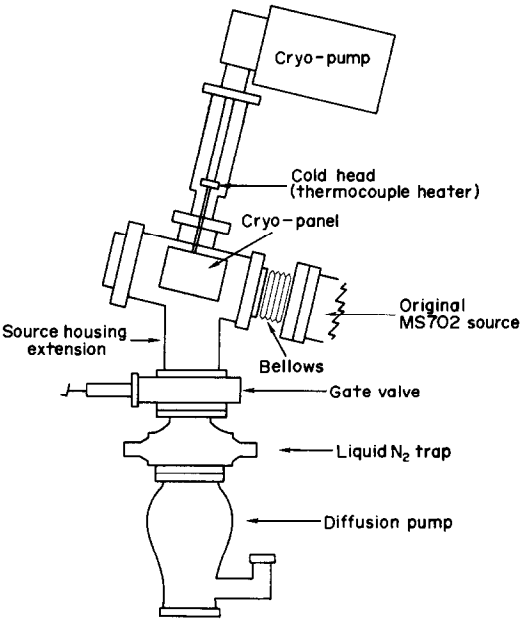

Fig. 1. Schematic representation of the auxiliary pumping system attached to the ion-source of the AEI MS702 mass spectrometer.

EXPERIMENTAL

Apparatus

The ion-source chamber of a conventional AEI MS702 SSMS has been redesigned and extended to include a commercial mechanical cryogenic assembly (Cryogenic Technology, Inc., Waltham, MA) with an ultimate temperature of 9 K and a power-capacity of 1 kW at the operating temperature. In addition, this unit has a built-in heater for heating the copper panel to 350 K. A high-speed diffusion pump with polyphenyl ether and a large liquid-nitrogen trap are included, primarily for pumping hydrogen. The ion-source is evacuated, from atmospheric pressure, by a zeolite trap cooled in liquid nitrogen, the use of which eliminates the very undesirable problem of oil-contamination due to mechanical rough-pumping.

An EAI Quadrupole 250 mass spectrometer and a nude ionization gauge for monitoring the gas-background and source pressures, respectively, are mounted on the source-chamber. An ultrahigh-vacuum variable-leak valve for introduction of gas is also included on the source chamber.

Figure 1 is a schematic drawing of the apparatus and shows the modifications and additions which were designed and built to adapt these new units to the SSMS. They include a stainless-steel bellows transition piece between the original source and the source-housing extension and a movable carriage (not shown) which supports the housing extension, stainless-steel gate-valve, liquid-nitrogen trap and diffusion-pump assembly. This entire new assembly must be separable from the original ion-source to expedite sample-changing and source-cleaning. This is accomplished by means of the carriage and use of flexible water- and fore-pump hoses.

Operating characteristics

The pumping speed of the new liquid-nitrogen trap–diffusion pump combination is estimated to be 1000 l./sec, and the pumping speed of the cryo-panel is dependent upon its temperature and the area of the copper surface. The surface area of the cryo-panel can be large, but is limited in this application by the space available in the source and by mechanical problems with the mounting. A cryo-surface 150 cm^2 in area was fabricated from 10-mil copper sheet and the estimated pumping speed for all species except hydrogen, helium and neon is 1500 l./sec, whereas the original pumping conditions gave a pumping speed in the ion-source of about 4 l./sec.

It is important to note the performance of the instrument before the modifications. The ion-source pressures were originally measured at the liquid-nitrogen trap above the original source-diffusion pump, a significant distance from the ion-source chamber where the sample-sparking occurs. Table 1 shows a comparison of source-pressures under various operating conditions, measured with the nude ionization gauge in the ion-source chamber. The ion-source pressures are actually two orders of magnitude higher than those recorded by the original source ion-gauge (IG1); the nude ion-gauge (IG2) located in the ion-source measures the true source-pressure.

Typical quadrupole mass-spectra of the background gases in the ion-source before sparking and during sparking are shown in Fig. 2. For comparison purposes, it should be noted that the spectrum in 2a was recorded at 3 times the amplifier sensitivity used for that in 2b. It can be seen that the two dominant species which increase during sparking are H_2 and CO. This large increase in CO is very significant in the determination of low levels of carbon and oxygen in tungsten. Other species, CH_4,

Table 1. Comparison of ion-source pressures

Apparatus	IG2*, *mmHg*	
	Without cryo-pump	With cryo-pump
Standard MS702†	1×10^{-6}	5×10^{-9}
Large diffusion pump and liquid-nitrogen trap	1×10^{-8}	3.5×10^{-10}

* Nude ionization gauge in source
† IG1 6×10^{-8} mmHg.

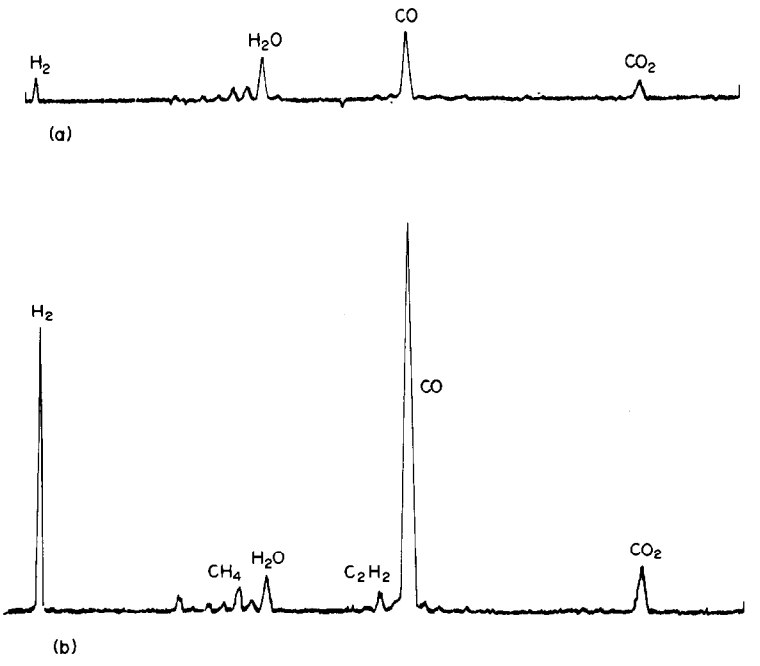

Fig. 2. Quadrupole mass spectra of silicon sample recorded (*a*) before sparking, 5×10^{-10} mmHg, amplifier sensitivity 1×10^{-7} A; (*b*) during sparking, 2×10^{-8} mmHg, amplifier sensitivity 3×10^{-7} A.

C_2H_2, and CO_2, also increase but to a lesser degree and therefore are less important in carbon and oxygen determinations.

Sample preparation

Two commercially available tungsten wires designated A and B were analysed along with a sample used as a standard. This standard was a high-purity ingot of electron-beam zone-refined (EBZR) tungsten obtained from Materials Research Corporation, Orangeburg, NY. All samples were etched before analysis, with a 1:1 mixture of concentrated hydrofluoric and nitric acids and then rinsed several times in distilled water and finally in methanol. They were air-dried briefly before being mounted in tantalum sample-holders with nylon tweezers.

Experimental conditions

All samples were sparked under the conditions shown in Table 2. The etched samples were loaded into the ion-source and positioned so that the two pieces could be sparked end-to-end. After an overnight bake at approximately 150°C and with the cryo-pump on, the pressure in the source was typically 5×10^{-10} mmHg. After presparking, four consecutive independent analyses were recorded for each sample, two per photoplate.

Typically, 30-nC exposures were recorded on Ilford Q-2 photoplates. The photoplates were developed for 5 min in diluted (1:1) Kodak D-19 solution, fixed for 2.5 min, then rinsed for approximately 20 min. The air-dried plate was read on a microdensitometer where the background and line intensities were recorded. These data and other necessary input information were typed on computer cards and analysed by an IBM 370/158 system. Two independent calculations were used, one based on the Siedel function and the other on the Hull equation, in a program written by Bey and Allard.[9] The data were corrected for photoplate mass-sensitivity and sensitivity factors.[10] The values presented in the tables are an average of those obtained in the two calculations and have been converted into ppm (w/w).

Table 2. Operating parameters for the AEI MS702

rf-Voltage, %	50
Repeat rate	300/sec
Pulse width	200 μsec
Source pressure	
Before spark	$\sim 5 \times 10^{-10}$ mmHg
During spark	$\sim 1 \times 10^{-8}$ mmHg
Ion-beam chopper	
Repetition rate	2×10^3–2×10^6/sec
Pulse width	10 μsec
Amplitude	7 V, negative
Left-hand electrode	Vibrated during sparking
Accelerating voltage	18 kV
Magnet current	240 mA
Prespark	Usually 5–10 nC before each analysis

RESULTS

Effect of CO on carbon and oxygen determinations

The importance of the residual gases in the determination of carbon and oxygen in tungsten by SSMS can be shown by measuring the concentrations of these elements under differing ambient conditions. Results taken with and without use of the cryo-panel are shown in Table 3. With the cryo-panel at 273 K, the apparent concentrations of carbon and oxygen are quite high. Significant improvement is noted when the temperature is lowered to 77 K. This would correspond to the conditions reported in the literature, for use of a liquid-nitrogen cryo-panel without an absorbent. This may be sufficient when analysing non-active materials but it is evident from this work that these are not the "true" concentrations for carbon and oxygen in an active material such as tungsten.

Table 3. Analysis of W wire as a function of cryo-temperature

Temperature, *K*	C, *ppm*	O, *ppm*
273	2200	840
77	75	20
14	13	2.2

The improvement in going from 77 K to 14 K is that the background carbon and oxygen species CO, CH_4 and CO_2 are now being pumped by the cryo-panel. This results in a further reduction in the apparent carbon and oxygen concentration measured.

As a further demonstration of the effect of the background gas on the measurement of carbon and oxygen, a series of experiments was performed by back-filling the chamber with CO or Ar at various pressures while sparking. Tungsten and gold electrodes were analysed separately in this manner and the results are shown in Fig. 3. It can be seen that at a given partial pressure of CO, different materials yield significantly different apparent concentrations for carbon. This result arises from the differences in the reactivity of the materials. Tungsten, being very reactive with respect to CO, yields results 1000 times those for gold. On the other hand, at an argon partial pressure of 10^{-6} mmHg, tungsten and gold both give an apparent argon value of 1 ppm.

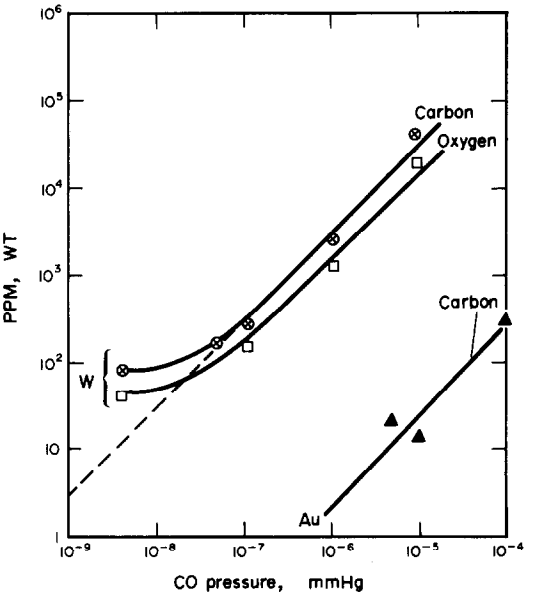

Fig. 3. Carbon and oxygen concentrations *vs.* the partial pressure of CO for tungsten, and carbon concentration *vs.* the partial pressure of CO for gold.

Analytical data

The average analytical results for carbon and oxygen in the tungsten samples A and B are shown in Table 4. Also shown, where possible, is a comparison with results obtained by other analytical methods.

Precision and accuracy

In a typical analysis by SSMS, no standards are used for calibration; instead, the matrix isotopes are used as an internal standard. When this method is used with a photoplate as detector, the precision is said to be 20–30%, while the error may be as large as a factor of 3–5.

The precision of this work was established by using the "best" sample available, Sample A tungsten wire. Table 5 gives the values obtained by using several photoplates, several different sample loadings and analysis on different days with somewhat varying conditions, such as initial starting pressures and the source baked or unbaked.

The carbon and oxygen concentrations were calculated to be 13 and 2.2 ppm respectively, the standard deviations being 3 and 0.7 ppm, corresponding to a precision of 25–30%. The carbon results for both sample A and the EBZR material are in good agree-

Table 5. Precision figures for sample A—tungsten wire, *ppm* (w/w)

C	O
17	2.5
17	2.7
11	1.3
12	1.7
8	1.3
14	2.1
13	2.5
16	3.4
12	1.9
15	2.7
7	
12	
Mean 13	2.2
Std. devn. 3	0.7

Table 4. Comparison of results for carbon and oxygen, *ppm* (w/w)

	Sample A		Sample B		EBZR W	
	C	O	C	O	C	O
SSMS (corrected values)	13	2.2	14	1.7	3	2.0
Combustion/GC*	16	—	—	—	—	—
Vacuum fusion†	—	—	—	—	—	<10
Combustion-conductometric†	—	—	—	—	<3	—

* GTE Labs
† Manufacturer's result

ment with those obtained by other techniques. Less reliable data by alternative techniques are available for the oxygen, but the value of 2.2 ppm is certainly not in disagreement with the manufacturer's figure of < 10 ppm.

DISCUSSION

It cannot be stressed too strongly that the capability of the SSMS for the determination of interstitial species at the 1-ppm level and lower, notwithstanding the importance of the background gases in the ion-source, is directly dependent on the material being analysed. Tungsten, a very reactive material, is particularly sensitive to the residual gases and consequently is difficult to analyse for carbon and oxygen. Inert elements such as gold and germanium are affected only slightly by the background gases, so the detection limits for the interstitial species will be lower than for tungsten.

The contribution of the background gases to the determination of carbon and oxygen is twofold, a gas-phase effect and a surface effect. The gas-phase contribution, present under all circumstances of sparking, is small and not as significant as the surface effect. The lower limit of determination of carbon and oxygen in non-reactive materials will be 1 ppm for a partial pressure of 10^{-6} mmHg of CO, which is essentially the magnitude of the gas-phase effect. The surface contribution is dependent on the sample material, and proportional to the accommodation coefficient of the residual gas with the sample and the spark duty cycle.[13] For tungsten, this is particularly critical and results in a detection limit of about 1 ppm for 10^{-9} mmHg of CO.

CONCLUSIONS

It has been demonstrated that a mechanical cryopanel at 14 K in conjunction with a high-speed diffusion pump is an effective and trouble-free addition to a modified ion-source of a conventional SSMS. It provides enhanced pumping for carbon- and oxygen-containing gases, particularly during sample-sparking. The reduced partial pressures permit measurement of carbon and oxygen at the 1 ppm level in reactive materials such as tungsten and the 1 ppM (part per milliard) level for materials such as Ge or Au, provided the partial pressures of these species do not rise above about 10^{-9} mmHg during sparking.

The system asssembled for this work, in addition to the advantages already discussed in conjunction with the measurement of carbon and oxygen, provides an advantage in the measurement of impurities in materials which readily form hydrides. This is true, for example, for the rare earths, where the intense line of a matrix hydride may appear to be an impurity which is not in fact present. The pumping system described here will maintain the hydrogen partial pressures at low levels, thereby minimizing the formation of these molecular ions and simplifying photoplate interpretation.

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INVESTIGATION BY AUTOMATED DIFFERENTIAL PULSE ANODIC-STRIPPING VOLTAMMETRY OF THE PROBLEM OF STORAGE OF DILUTE SOLUTIONS

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Summary—The storage of dilute solutions of metal ions before their laboratory analysis presents a difficult problem in the examination of many environmental samples. By utilizing the solution container as an electrochemical cell and employing the method of differential pulse anodic-stripping voltammetry at a hanging mercury drop electrode, it is shown that an automated read-out system in an enclosed environment can be developed for monitoring the solution–container interactions that occur over short or extended periods of time. In the present work, interactions of dilute solutions (1–10 μg/l.) of cadmium(II), lead(II), copper(II), zinc(II), and thallium(I) in glass, polyethylene and Teflon containers have been investigated at various pH values and in different ionic environments. The results demonstrate the importance of factors other than pH.

The increasing interest in the environment has created a challenge to analytical chemistry. However, the ever-increasing need for trace determinations of species at the parts per milliard (ppM) level has presented many problems to the analytical chemist. Though on-site monitoring of samples is an ideal often striven for, most trace determinations are still performed in the laboratory, and careful sample collection and storage followed by laboratory analysis is the usual procedure for trace determinations.[1]

Even if extreme care is taken in collection of a liquid sample, to assume that the sample remains unchanged between collection and analysis is rather naive.[2] Very dilute solutions such as those usually examined in environmental work have been shown to interact considerably with the containers in which they are stored,[2–11] so the environmental systems cannot be assumed to be stable when their surroundings are altered. Such interactions between dilute solutions and containers[12–17] have been manifested in the case of trace metal determinations at the 1–100 ppM level (10^{-8}–$10^{-6}M$).

Losses of trace metals to containers are well documented and have been attributed to adsorption onto the walls of the containers. In effect, the walls of a container can act as an ion-exchanger, so adsorption of metal ions from solution should be expected.[18] Conversely, of course, ions already adhering to the sides of the containers can be desorbed, resulting in contamination of the sample.

The optimum conditions for storage of dilute solutions are by no means clear, despite the considerable literature on the subject. Acidification with nitric acid in general inhibits, and in some cases prevents, the loss of metal ions by adsorption,[2,12,15] and severe losses have been incurred when solutions were stored at pH 6.[7,12,19] Bubić *et al.*[7] claim that for zinc, copper, lead and cadmium, polyethylene is a better container than borosilicate glass (Pyrex), but Eicholz *et al.*[8] maintain that Pyrex is better for zinc and several other ions. Other workers[12,14] show no preference for either polyethylene or glass containers. Struempler reported that in polyethylene containers appreciable losses of lead can occur even at pH 2. In contrast to Struempler's findings, Florence[20] reported only slow uptake of lead by polyethylene at pH 6 and no appreciable uptake at pH 2. On the other hand, Petrie and Baier,[21] using liquid-scintillation spectrometry of ^{210}Pb to study the principal lead(II) transport processes occurring in anodic-stripping voltammetric analysis of sea-water, reported that the concentration of lead after 95 min was reduced by 84% at pH 8.2, 78% at pH 4.6 and 39% at pH 3.0. Evaluation of the storage of dilute solutions therefore needs to occupy a considerable portion of the environmental analyst's time, as each system may need to be examined individually.

With improvements in polarographic instrumentation and electrodes[22,23] anodic-stripping voltammetry is now being widely used in the trace determination of metals in environmental samples. However, despite the fact that ppM levels can be monitored directly, this technique has not been widely employed to investigate the problem of storage of dilute solutions. Such studies have usually been undertaken by atomic-absorption spectrometry or radioactive tracer methods.

In the present communication we wish to demonstrate how the technique of differential pulse voltammetry at a hanging drop mercury electrode can be

very conveniently employed to monitor automatically the concentration of species in a sealed system (the container) over a lengthy period of time. Conventionally, voltammetric determinations involve transfer of sample from the storage container to a glass electrochemical cell. However, it is easy to construct an electrochemical cell from any desired material, so the container and cell can be one and the same vessel. Since anodic-stripping voltammetry is essentially non-destructive, *in situ* monitoring of concentration as a function of time is easily achieved, and apart from the contact of the solution with the electrodes, the solution–container interactions can thus be directly monitored in an enclosed system. In this work, data on Pyrex, polyethylene and Teflon containers were obtained to determine the most favourable conditions for storage of dilute solutions of cadmium, lead, copper, zinc and thallium at the ppM level in several different media.

EXPERIMENTAL

Instrumentation

All anodic-stripping voltammetry with differential pulse read-out was performed with a Princeton Applied Research (PAR) Analyzer Model 174A coupled to an Automated Electroanalysis Controller Model 315. In initial experiments, a Model 9323 PAR Hanging Mercury Drop Electrode requiring manual setting of the electrode area was used as the working electrode. Subsequently, the Automated Hanging Mercury Drop Electrode System Model 314 was employed to provide a fully automated system. An $Hg/HgSO_4$ [saturated K_2SO_4 or $(NH_4)_2SO_4$] electrode was used as the reference electrode and platinum wire as the auxiliary electrode. The usual calomel or Ag/AgCl reference electrodes were not used, because of the potentially deleterious effect of chloride contamination on the determination of copper. Argon was used to remove oxygen from the solution before each electrochemical measurement. To prevent evaporation of the solvent, the argon was presaturated before entering the cell, by passing it through a bubbler containing the supporting electrolyte being used. All measurements were performed at room temperature (21–23°). A Radiometer pHM 62 pH meter was used for pH-measurements.

Chemicals

All standard solutions were prepared from analytical-reagent grade chemicals. The supporting electrolytes, nitric acid, potassium nitrate and tetraethylammonium perchlorate were also made from analytical reagent grade chemicals, with doubly distilled water.

Procedure

To keep possible sources of contamination to a minimum, the polarographic cells were used as the container under investigation. Pyrex cells were constructed in the university's glass workshop; polyethylene and Teflon cells were cut from conventional storage bottles to fit the cell top.

The polarographic cells were cylindrical with a diameter of 6.0 cm and a volume of 200 ml. The solution volumes used in each experiment were 100.0 ml.

Pretreatment of the cells was found to be of prime importance for their performance. Washing the cells with chromic acid was not considered, as chromium has been shown to adhere to the container walls despite numerous washings with water.[24] Concentrated nitric acid was preferred for washing purposes, as it had been shown to be a good cleansing agent.[25] The Pyrex and Teflon cells were boiled three times for 3 hr in concentrated nitric acid before their first use and then for a minimum of 3 hr between all subsequent uses. Electrodes were also cleaned in this manner. The polyethylene cells were soaked rather than boiled in nitric acid, as boiling deforms these containers. This initial process with nitric acid was intended to "age" the cells by reacting active surface sites with the strongly adsorbing hydrogen ion, and these containers were therefore expected to show less adsorption than a new untreated cell. Reproducible results were obtained with this pretreatment. Unless in use or being cleaned, containers were filled with the supporting electrolyte to be used in the anodic-stripping experiments. All rinsing of cells was also done with supporting electrolyte.

In all investigations two or more species were determined simultaneously to provide a means of discerning instrumental effects as opposed to container effects. It is unlikely that the metal ions examined show identical adsorption characteristics, in view of their separation by means of ion-exchange resins.[26] Thus any uniform change of all of the differential pulse peak-heights in any given determination was attributed to an instrumental effect such as incorrect area of the hanging drop mercury electrode, while any relative changes in a peak or peaks were taken to indicate a change in concentration of the corresponding species, caused by interaction with the container.

Reagent purity is usually an important consideration in studies at the ppM level, and acids and supporting electrolytes frequently have to be carefully purified before use. In the present work, however, such a step could be eliminated by adopting the following procedure. The electrolyte to be examined (100.0 ml) was added to the cell and a differential pulse anodic-stripping polarogram was recorded. Known concentrations of the species to be monitored were then added by addition of 1.0 ml of a standard solution. Since peak-heights were found to be a linear function of concentration for all species examined, the initial concentration of species in the background electrolyte could be determined. This concentration plus the added concentration could therefore be used to represent the initial concentration to be examined as a function of time. Impurity levels were conveniently incorporated into the experiment in this way. At frequent intervals during the course of the experiment, the peak-heights of the anodic stripping curves were measured. The first data point was obtained 5 min after addition of the species being monitored. During the first 30 min of the experiment data points were obtained every 5 min. For the next 16–24 hr data points were collected at approximately 30-min intervals and then at about 2-hr intervals until the termination of the experiment. At the conclusion of the experiment another standard addition experiment was performed to verify that the final concentration was the same as that estimated by direct monitoring of peak-heights.

This standard addition determination was performed by addition of 1, 2, 3 and 4 times the volume of standard solution added at the start of the experiment.

The metal ion solutions used in standard addition experiments were prepared by successive dilution from $10^{-2}M$ standard solutions.

The differential pulse anodic-stripping experiments were performed with a pulse amplitude of 50 mV and a duration of 0.5 sec between pulses. A 3-min period with stirring (Teflon-coated stirring bar and magnet) and a 30-sec equilibration period without stirring were employed for the controlled-potential electrolysis. The potentials for conditioning of the electrode and for the electrolysis were those appropriate for the system being investigated.

RESULTS AND DISCUSSION

Environmental samples are generally extremely complex, and in sea-water for example, organically and colloidally bound metals may need to be considered. In the present investigation, it was believed simplest to use labile metal ions as model systems. Consequently, in initial studies the solutions contained metal ions dissolved in 1% nitric acid or 0.1*M* potassium nitrate at pH 6. The acidic medium was used to simulate the common procedure of acidifying samples immediately after collection, and the other medium was at a pH at which several investigations have previously suggested that substantial loss to containers can occur. In the media chosen, all the metal ions examined were assumed to be aquated cations of the type $[M(H_2O)_x]^{y+}$.

In perfecting the procedure, a series of short-term (1 day) experiments was undertaken on Cd, Cu and Pb in 1% nitric acid and 0.1*M* potassium nitrate, in Pyrex, polyethylene and Teflon containers. Frequent monitoring of the peak-current as a function of time revealed that provided the containers had undergone extensive aging and pretreatment no change in peak-height (concentration) occurred (within the limit of experimental error, *i.e.*, results consistent to ±3% over a 24-hr period). Table 1 shows a typical set of data for the initial and final concentration determined by the method of standard additions, confirming the validity of the data obtained by monitoring of peak-heights rather than concentrations during the 24-hr period. Thus, the somewhat surprising result was obtained that in glass, polyethylene or Teflon containers, no apparently rapid interaction of the solution with the containers occurs for the three metals examined, in a closed measurement system and at two different pH-values.

Table 1. Short-term monitoring of cadmium, lead and copper concentrations in Pyrex, polyethylene and Teflon (24 hr)

		Concentration of trace metal, *ppM*		
		Cadmium	Lead	Copper
Pyrex				
1% HNO_3	Initial	1.2	2.2	1.0
	Final	1.1	2.4	1.0
0.1*M* KNO_3	Initial	3.3	4.8	1.5
	Final	3.9	5.0	1.7
Polyethylene				
1% HNO_3	Initial	7.3	8.8	5.7
	Final	6.0	8.5	5.9
0.1*M* KNO_3	Initial	2.6	3.4	3.0
	Final	2.8	3.0	4.0
Teflon				
1% HNO_3	Initial	1.8	3.5	1.4
	Final	2.5	4.1	1.4
0.1*M* KNO_3	Initial	1.5	2.8	2.5
	Final	1.8	3.3	3.3

Results obtained by method of standard additions.
Peak-heights measured at 48 time-intervals during the course of the experiment were essentially constant (average deviation ±3%).

Monitoring of zinc, cadmium, copper, lead and thallium in 1% nitric acid or 0.1*M* potassium nitrate (pH 6) medium over a two-week period revealed that except for copper no interaction with the containers occurred. In 1% nitric acid, copper appears to be slowly leached from each of the containers, although to differing degrees. Initial and final concentrations

Table 2. Long-term determination of zinc, cadmium, lead, thallium and copper in Pyrex, polyethylene and Teflon (2 weeks)

		Concentration of trace metal, *ppM*				
		Cadmium	Lead	Copper	Zinc	Thallium
Pyrex						
1% HNO_3	Initial	1.2	2.5	1.5	1.7	4.9
	Final	1.7	1.6	9.7	2.1	5.6
0.1*M* KNO_3	Initial	1.4	9.0	3.3	2.0	6.3
	Final	1.2	9.2	2.6	2.1	5.5
Polyethylene						
1% HNO_3	Initial	1.5	9.0	4.5	1.7	11.2
	Final	1.6	9.1	7.9	2.7	12.2
0.1*M* KNO_3	Initial	1.3	2.3	1.6	3.0	2.0
	Final	1.1	3.2	2.7	3.0	1.7
Teflon						
1% HNO_3	Initial	1.2	2.6	1.4	6.7	3.6
	Final	2.2	3.2	15.3	8.3	3.8
0.1*M* KNO_3	Initial	1.9	3.8	2.6	2.0	2.3
	Final	3.0	3.3	2.9	2.2	3.2

Results obtained by the method of standard additions.
Except for copper in 1% HNO_3, peak-heights measured at 186 time-intervals during the course of the experiment were essentially constant (average deviation ±3%). For copper in 1% HNO_3 the peak-height increased as a function of time to give a final value consistent with results obtained by the method of standard additions.

of each element are presented in Table 2 and it can be seen that Teflon introduced the greatest increase in copper concentration. It is interesting to note that when analysed, a sample of Teflon contained more copper than did one of polyethylene.[27] At pH 6 the copper concentration remains unchanged, indicating that the source of contamination is the displacement of copper impurities from the container by the strongly adsorbed hydrogen ion.[28] Zinc can be determined directly in nitric acid media by differential pulse anodic-stripping voltammetry,[29] although this is not often reported as possible.

Preferential adsorption may also explain the observations made for the samples at pH 6. The literature contains many reports that severe losses of metal ion occur at this pH. The striking difference between the solutions employed in this study and many of those used in earlier work is the high concentration of potassium (and nitrate) present and that the metal species are cationic in the media chosen rather than neutral or anionic as may be the case in other media. Thus, it may be the presence of the univalent cation which swamps out possible adsorption sites by virtue of its relatively very high concentration. If the metal ion exists as an anionic species, then of course it would be the anion that would be important. Two cases of little or no loss at pH 6 have been reported; the first was storage of silver ions in sodium thiosulphate/sodium chloride media,[13] and the second was that of mercury in potassium iodide solution.[30] Adsorption of silver onto the container was found to increase when the sodium chloride concentration decreased from 0.1 to 0.001 *M*. It was also found that 0.001 *M* potassium iodide inhibited mercury adsorption onto polyethylene. In both cases the metal was probably present as an anionic complex, and the possibility that anions such as chloride or iodide, in relatively large excess, may inhibit losses of anionic metal complexes from dilute solutions needs to be considered. In the examples studied in the present work, it is the cation of the supporting electrolyte which is likely to be important and 0.1 *M* tetraethylammonium perchlorate was used as the medium for investigating the problem of storing dilute solutions (pH 6). The tetraethylammonium cation is considerably more bulky than the potassium cation and was believed to be less likely to inhibit metal-ion adsorption.

Table 3 shows quite clearly that even in 16 hr substantial losses of lead and copper to the container occurred for glass and polyethylene in particular, while the cadmium concentration remained unaltered in all containers. The data in Table 3 are qualitatively in agreement with those in the literature. That is, cadmium ions do not strongly interact with the container even at pH 6,[15] whereas lead does, even when polyethylene replaces glass as the container. The substantially superior performance of Teflon as a container when 0.1*M* Et_4NClO_4 is used as a supporting electrolyte was confirmed by studies of extended duration. The cadmium, lead and copper concentrations did not decrease significantly over a whole week, whereas, as Table 3 shows, in glass or polyethylene significant losses of lead and copper occurred within 16 hr.

Table 3. The determination of cadmium, lead and copper in 0.1*M* Et_4NClO_4 when stored in Pyrex, polyethylene and Teflon (16 hr)

		Concentration of trace metal, *ppM*		
		Cadmium	Lead	Copper
Pyrex				
	Initial	1.2	6.2	4.1
	Final	1.3	3.0	2.0
Polyethylene				
	Initial	1.2	8.9	3.1
	Final	1.0	4.0	1.4
Teflon				
	Initial	1.2	6.0	3.3
	Final	1.3	5.0	3.2

In view of the several results pertaining to electrodes and their interaction with solutions,[21,31,32] it seems appropriate to comment on some of the experimental aspects of the electrode arrangement used in the present investigation. As described in the experimental section, all electrodes underwent the same chemical treatment as the containers. Furthermore, an $Hg/HgSO_4$ reference electrode was used in preference to the more usual chloride-containing calomel or Ag/AgCl reference electrodes. Any leakage of chloride which could occur over the long duration of these experiments was believed to be a more potentially serious problem than leakage of sulphate, since the latter is not electroactive at mercury electrodes and does not tend to form complexes with the cations examined. Finally, the reference electrode and auxiliary electrode were separated from the solution under investigation by a salt bridge containing the solution to be examined. With these precautions no evidence could be obtained that the presence of the electrodes modified the behavior of the system being examined.

The possible influence of the mercury necessarily introduced into the solution during the progress of the experiment is less certain, although deliberate variation in the quantity of elemental mercury present as a pool in the bottom of the container was shown to have no effect on the results.

These results demonstrate that the technique of differential pulse anodic-stripping voltammetry provides a useful and simple method for studying the problem of storage of dilute solutions. Data obtained suggest that although loss of metal species at pH 6 has been extensively investigated and compared with storage at pH < 2 a significant variable sometimes seems to have been overlooked. At low pH (*e.g.*, in 1% nitric acid) samples are stored at relatively high ionic strength where the adsorption characteristics of the cation (hydrogen ion) and anion determine the extent

of interaction of the container and solution. At higher pH, the matrix of the sample is at least as important as the pH. In the environmental samples the matrix can be exceedingly complex, but is often of high ionic strength. Furthermore, the metal species present can exist as inorganic cations, or anions, or as organically bound species, depending on the matrix. It is therefore not necessarily the case that adsorption onto the container will occur because a solution has a pH $\gg$ 2 and that solutions must be acidified to prevent this occurring. However, if the metal ion of interest can be determined by anodic-stripping voltammetry, then by utilizing the container as the electrochemical cell, it is possible to evaluate, easily and reliably, the container and conditions for suitability for storing the species to be determined.

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SHORT COMMUNICATIONS

HYDROUS ZIRCONIUM OXIDE AS AN ANION-EXCHANGER

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Summary—Samples of hydrous zirconium oxide have been prepared under varying conditions of precipitation, and their anion-exchange properties are reported. The effect of electrolyte concentration, time of equilibration and drying temperature on anion-exchange capacity has been studied. Stoichiometry of exchange, chemical stability and regeneration power of the exchanger have also been investigated. Distribution coefficients of various anions are reported, and some pairs of anions have been separated on the basis of the sorption data.

Hydrous oxides form an important class of synthetic inorganic ion-exchangers and show anion- and cation-exchange properties at pH-values below and above their isoelectric points. With the revival of interest in synthetic inorganic ion-exchangers, a sufficient amount of work has been done on the cation-exchange[1,2] behaviour of hydrous zirconium oxide (HZO). Much less information exists on its anion-exchange properties.[3–5] The present work has been undertaken to investigate its anion-exchange properties systematically and explore the utility of the material for the separation of various anions.

Samples of HZO have been prepared under varying conditions of precipitation and examined for their chloride uptake. The effect of electrolyte concentration, time of equilibration and drying temperature on exchange-capacity has been studied. The stoichiometry of Cl^-–NO_3^- exchange has been examined. The chemical stability and regeneration power of the exchanger have also been investigated. Distribution coefficients (K_d values) for various anions have been determined, and on the basis of the sorption data some representative separations of analytical interest have been achieved.

EXPERIMENTAL

Reagents

All chemicals used were of analytical purity. The isotope ^{36}Cl, procured from BARC, Bombay, was used for checking the stoichiometry of uptake.

Instrumentation

The pH-measurement were carried out with a Cambridge Bench pH-meter. A Bausch and Lomb Spectronic 20 spectrophotometer and Radelkis Oscillotitrator Model 302 were used. Beta-counting of ^{36}Cl was done with a Geiger-Müller counter.

Preparation of the exchanger

HZO samples were prepared by mixing 0.1*M* zirconium oxychloride and ammonia or sodium hydroxide solutions in different [Zr]/[OH] ratios (Table 1). The alkali was added to the zirconium solution except for samples ZA3 and ZS3, where the order was reversed. The precipitate was kept overnight with the mother liquor at room temperature (32 ± 3°), filtered off, washed with demineralized water and dried at 70 ± 2°. The dried exchanger was then broken down to the required particle size by immersion in demineralized water and/or by grinding. It was then converted into the NO_3^--form by washing it in a column with a mixture of sodium nitrate and nitric acid at 0.1*M* total ionic strength and acidity 0.01*M*. The sample was air-dried and then equilibrated over a saturated solution of ammonium chloride (79% relative humidity) to constant weight.

Ion-exchange capacity

The time required for attainment of maximum chloride uptake capacity was determined by equilibrating the NO_3^--form of the exchanger (100–200 mesh) with a solution of 0.09*M* sodium chloride in 0.01*M* hydrochloric acid for different intervals of time and found to be about 5 min. The effect of chloride ion concentration on capacity was studied by varying the sodium chloride concentration at a constant acidity of 0.01*M* hydrochloric acid. Reproducible results were obtained for chloride uptake capacity, the standard deviation being 0.04 meq/g. The uptake became maximal at a chloride concentration of 0.1*M* or more. However, reproducible results could not be obtained for the chloride release capacity of these samples. When HZO is converted into the chloride form and washed with demineralized water to remove the extraneous chloride ions, some of the adsorbed chloride ions are also lost to the washings. Hence only the chloride uptake capacity is reported here.

Table 1. Preparation and properties of HZO ion-exchanger

Sample	[Zr]/[OH]	Chloride uptake, *meq/g*
ZA1	1:1	colloidal
ZA2	1:2	1.09
ZA3	1:2	1.03
ZA4	1:3	1.05
ZA5	1:4	1.01
ZA6	1:5	0.98
ZS1	1:1	colloidal
ZS2	1:2	1.05
ZS3	1:2	1.03
ZS4	1:3	1.01
ZS5	1:4	0.96
ZS6	1:5	0.95

ZA—precipitated with ammonia.
ZS—precipitated with sodium hydroxide.

Table 2. Effect of drying temperature on capacity (ZA2)

Drying temperature, °C	Capacity, *meq/g*
32 ± 3*	1.09
50	0.91
110	0.75
160	0.74
220	0.74
300	0.72
340	0.44
600	0.28

* Equilibrated over saturated solution of NH_4Cl.

The stoichiometry of uptake for chloride ions was examined by equilibrating almost carrier-free chloride tracer at different concentrations of nitrate ion, and log K_d was found to be a linear function of log $[NO_3^-]$, with a slope of -1.

Chemical stability

This was examined by keeping about 200 mg of the exchanger in contact with 50 ml of the solution for 24 hr with intermittent shaking, and then determining the zirconium content spectrophotometrically[6] in the supernatant liquid. Treatment with 1*M* hydrochloric acid produced a zirconium concentration of 64 mg/l., and 0.10*N* and 1.0*N* sulphuric acid gave values of 12 and 60 mg/l. respectively. Lower concentrations of these acids, nitric acid up to 1.0*M*, 1*M* sodium chloride or potassium nitrate, demineralized water, alcohol, acetone and benzene were without effect.

Effect of drying temperature

The samples were heated at different temperatures and then cooled over silica gel. The capacity fell with increase in drying temperatures (Table 2).

Regeneration power

The chloride uptake capacity was found to change in the course of six regeneration cycles with 0.09*M* sodium nitrate–0.01*M* nitric acid as regenerant, from 1.09 to 0.94 meq/g.

Distribution studies and separations

Distribution coefficients (K_d) for different anions were determined by batch operation. About 200 mg of the exchanger in nitrate form was loaded with 10 ml of $2 \times 10^{-3}M$ aqueous solution of the anion (Table 3).

Separations on a 100–200 mesh HZO column (5 × 0.58 cm) were carried out by loading with less than 20% of the breakthrough capacity for each anion. Elution was started after 5 min, at a flow-rate of 10–15 ml/hr.

Table 3. Distribution coefficients of some anions on HZO in NO_3^--form (ZA2)

Anion	Taken as	K_d*
Cl^-	KCl	278
Br^-	KBr	201
I^-	KI	130
SCN^-	KSCN	322
MoO_4^{2-}	Na_2MoO_4	50
$S_2O_3^{2-}$	$Na_2S_2O_3$	205
SO_4^{2-}	K_2SO_4	1566
CrO_4^{2-}	K_2CrO_4	$>10^4$
$Fe(CN)_6^{4-}$	$K_4Fe(CN)_6$	127
PO_4^{3-}	Na_2HPO_4	$>10^4$

* K_d = meq per g of exchanger/meq per ml of solution.

RESULTS AND DISCUSSION

It is apparent from Table 1 that the variation in [Zr]/[OH] ratio, order of mixing of reagents and the type of alkali used in the preparation of the samples do not appreciably affect the chloride uptake capacity of the exchanger. However, sample ZA2 had the highest ion-exchange capacity and therefore all other studies were carried out with that sample only. A constant value for the chloride uptake was obtained after 10 min of equilibration with a 0.1*M* chloride medium. The exchanger is stable in alkalis, different electrolyte solutions, alcohol, benzene, acetone and 0.1*N* mineral acids. It is fairly resistant to heat treatment and retains about 70% of its anion-exchange capacity even after heating to 300°.

The distribution studies reveal that for halide ions the distribution coefficients decrease with the increasing ionic radius, Cl^- (1.81 Å)> Br^- (1.95 Å)> I^- (2.16 Å). A similar sequence was observed on hydrated tin(IV) oxide.[7] Further, it is observed that HZO has a high affinity for SO_4^{2-}, CrO_4^{2-}, and PO_4^{3-}. Therefore, it can be used for separations involving these anions. Details of the separations carried out are presented in Table 4. The elution curves are sharp and above 90% recovery is obtained for each anion.

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Table 4. Separation of anions on nitrate form of HZO

Ions separated	Elution system
Cl^-, CrO_4^{2-}	Cl^- with 8 ml of 1*M* $NaNO_3$, 2-ml H_2O wash, CrO_4^{2-} with 8 ml of 3*M* NH_3
Br^-, CrO_4^{2-}	Br^- with 8 ml of 1*M* $NaNO_3$, 3-ml H_2O wash, CrO_4^{2-} with 8 ml of 3*M* NH_3
I^-, CrO_4^{2-}	I^- with 9 ml of 1*M* $NaNO_3$, 3-ml H_2O wash, CrO_4^{2-} with 8 ml of 3*M* NH_3
$S_2O_3^{2-}$, SO_4^{2-}	$S_2O_3^{2-}$ with 14 ml of H_2O, SO_4^{2-} with 12 ml of 3*M* NH_3
$S_2O_3^{2-}$, CrO_4^{2-}	$S_2O_3^{2-}$ with 16 ml of H_2O, CrO_4^{2-} with 14 ml of 3*M* NH_3
MoO_4^{2-}, CrO_4^{2-}	MoO_4^{2-} with 10 ml of 0.09*M* NaCl/0.01*M* HCl, 2-ml H_2O wash, CrO_4^{2-} with 8 ml of 3*M* NH_3
MoO_4^{2-}, PO_4^{3-}	MoO_4^{2-} with 9 ml of 0.09*M* NaCl/0.01*M*, HCl 3-ml H_2O wash, PO_4^{3-} with 8 ml of 3*M* NH_3
SCN^-, $Fe(CN)_6^{3-}$	SCN^- with 8 ml of 0.5*M* NaCl/0.1*M* HCl, 2-ml H_2O wash, $Fe(CN)_6^{4-}$ with 8 ml of 1*M* NH_3/2*M* NH_4Cl

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CONSTRUCTION OF A NEW Hg^{2+}-SELECTIVE LIQUID-STATE ELECTRODE

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Summary—The construction and basic characteristics of a new liquid-state Hg^{2+}-selective membrane electrode are discussed. The membrane consists of the PAN chelate of Hg(II), dissolved in $CHCl_3$. The linear response range of the electrode is 10^{-1}–$10^{-5}M$ Hg^{2+} with a slope of 28.5 mV/decade of concentration. The response time of the electrode in dilute solutions is less than 3 min, and in concentrated solutions it is only a few sec. The electrode has been used in precipitation or complexation titrations in which Hg^{2+} is involved (*e.g.*, in the determination of some organic compounds in drug synthesis).

The development of ion-selective membrane electrodes has seen spectacular achievements in the last few years. Theoretically, it should be feasible to construct such electrodes for any ionic species. However, in practice there are a number of difficulties, depending on the nature of the ion towards which the electrode should be selective.

The construction of some solid-state Hg^{2+}-selective membrane electrodes has been proposed in the literature, with electroactive substances such as HgS precipitated on the surface of a graphite rod,[1] HgS or HgSe cemented with epoxy resin,[2] HgS deposited on Ag_2S/Ag,[3] Ag_2HgI_4 with epoxy resins,[4] AgI and Ag_2S mixture pressed into pellets[5] and Ag_2HgI_4, $CuHgI_4$ or Tl_2HgI_4 (as pressed powders).[6]

Recently, the construction of ion-selective liquid-membrane electrodes sensitive to Hg^{2+}, consisting of mercury(II) chelates dissolved in suitable organic solvents, has been described.[7–9] In the present paper we describe the construction and use of a new electrode of this type, based on the Hg(II)–PAN chelate dissolved in chloroform.

EXPERIMENTAL

Apparatus and reagents

The e.m.f. measurements were performed at room temperature in stirred solutions, with an electronic potentiometer (Servogor, Goerz Electro, Vienna). The potentiometric titration curves were recorded with a TTT 2 pH/mV-meter and an ABU 12 Autoburette and Titrigraph SBR 2c recorder (Radiometer). A saturated calomel electrode (K 401, Radiometer) was used as reference electrode, and this was connected to the sample solution by a saturated potassium nitrate bridge. All reagents used were of analytical grade.

Preparation of the liquid membrane

To obtain the liquid membrane 20 ml of $10^{-2}M$ mercuric nitrate at pH 6.2 (adjusted with hexamine) were shaken in a separating funnel for 3 min with 20 ml of chloroform containing 0.0249 g of PAN, the phases were separated and the organic layer was dried by passage through anhydrous sodium sulphate, transferred to a 100-ml flask and diluted to volume with chloroform. The concentration of the chelate in this solution was $5 \times 10^{-4}M$.

Construction of the electrode

The construction of the electrode has been described previously[10,11] and consists of impregnating the support material (a graphite rod 15 mm long, 6.5 mm diameter, made water-repellent) with the Hg^{2+}–PAN solution in chloroform. The internal reference electrode is eliminated by using a stainless-steel wire introduced into the graphite rod. The electrode is stored in the Hg^{2+}–PAN solution and is washed with distilled water between measurements.

RESULTS AND DISCUSSION

The electrode function, E–pHg

The e.m.f. measurements were made with the electrochemical cell

$$\text{Hg}^{2+}\text{-selective membrane electrode} \;\Big|\; \text{Hg}^{2+}\ (C_{\text{Hg}^{2+}}),\ \mu = 0.5\,(\text{KNO}_3) \;\Big|\; \begin{matrix}\text{satd.}\\ \text{KNO}_3\end{matrix} \;\Big|\; \text{SCE} \quad \text{(I)}$$

where $C_{Hg^{2+}}$ is the Hg^{2+} concentration, ranging from 0.1 to $10^{-6}M$. The e.m.f. is given by

$$E_1 = E'_0 + 0.0285 \log[\text{Hg}^{2+}] \qquad (1)$$

where E'_0 is the conditional standard potential of the electrode under the conditions of use of cell (I). The measurements were carried out at constant ionic strength ($\mu = 0.5$, KNO_3), and the junction potential was kept constant.

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The electrode function, E–pHg

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$$\text{Hg}^{2+}\text{-selective membrane electrode} \;\Big|\; \text{Hg}^{2+}\ (C_{\text{Hg}^{2+}}),\ \mu = 0.5\,(\text{KNO}_3) \;\Big|\; \begin{matrix}\text{satd.}\\ \text{KNO}_3\end{matrix} \;\Big|\; \text{SCE} \quad \text{(I)}$$

where $C_{Hg^{2+}}$ is the Hg^{2+} concentration, ranging from 0.1 to $10^{-6}M$. The e.m.f. is given by

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Table 1. Selectivity coefficients, $K_{Hg^{2+},M^{z+}}$ [the nitrates of the respective metals at a concentration of 0.1*M*, pH 1 and $\mu = 0.5$ (KNO_3)]

M^{z+}	$K_{Hg^{2+},M^{z+}}$
Cd^{2+}	8.81×10^{-5}
Cu^{2+}	1.38×10^{-4}
Ni^{2+}	7.94×10^{-5}
Co^{2+}	4.47×10^{-5}
Zn^{2+}	2.76×10^{-5}
Mn^{2+}	1.58×10^{-5}
Pb^{2+}	3.55×10^{-5}
Bi^{3+}	1.05×10^{-5}
Al^{3+}	4.17×10^{-4}
Mg^{2+}	1.70×10^{-4}
Ag^{+}	7.25
Fe^{3+}	2.40×10^{5}

The electrode response was linear over the range 10^{-1}–$10^{-5}M$ $Hg(NO_3)_2$, with a slope of 28.5 mV/pHg. Extrapolation to pHg = 0 gives 523 mV for E_0' *vs.* SCE, a value approaching that of the Hg^{2+}-selective membrane electrodes constructed previously.[8,9] The inability to obtain better sensitivity for this electrode is probably due to the adsorption of Hg^{2+} ions at the end of the electrolyte bridge and on the surface of the glass vessel.

Influence of pH

The pH range over which the potential remains constant for a given pHg is relatively narrow because of the hydrolysis of Hg^{2+}, and is 0–2 for pHg = 1, 0–2.5 for pHg = 2 and 0–3.5 for pHg = 3. The direct potential measurements for calibration of the electrode were done at pH 1 (adjusted with nitric acid).

Table 2. Reproducibility of potential measurements (averages of 12 measurements during 5 weeks)

Hg^{2+},*M*	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}
E, *mV*	379 ± 5	406 ± 4	434 ± 3	466 ± 3	495 ± 3

Response time of the electrode

The characteristic dynamic response is a most important factor in use of the electrode for direct potentiometric determinations or in potentiometric titrations. The response characteristics of the electrode were evaluated by introducing the electrode into mercuric nitrate solutions of different concentrations but identical acidity (pH 1) and noting the e.m.f. values as a function of time. The response time of the electrode in dilute solutions (pHg < 4) is less than 3 minutes, and in concentrated solutions is only a few seconds.

Selectivity of the electrode

Selectivity coefficients, $K_{Hg^{2+},M^{z+}}$, were calculated by the method of Srinivasan and Rechnitz,[12] from the relation

$$\log K_{Hg^{2+},M^{z+}} = \frac{E_{II} - E_I}{28.5} + \log[Hg^{2+}] - \log[M^{z+}]^{2/z} \quad (2)$$

where E_I is the e.m.f. of cell (I) for $C_{Hg^{2+}} = 0.1M$, and E_{II} is the e.m.f. of an electrochemical cell of the type

$$\begin{array}{c}Hg^{2+}\text{-selective}\\ \text{membrane}\\ \text{electrode}\end{array} \left| \begin{array}{c} M^{z+}\ (C_{M^{z+}} = 0.1M),\\ \mu = 0.5\,(KNO_3)\end{array} \right| \begin{array}{c}\text{satd.}\\ KNO_3\end{array} \left| \text{SCE} \right. \quad \text{(II)}$$

where M^{z+} represents any of the main metallic cations that form more or less stable chelates with PAN. In all

Table 3. Potentiometric determination of some halogenated organic compounds with the Hg^{2+}-selective membrane electrode

No.	Organic compound	Taken, *mg*	Found *mg*	% X
1.	Ethanolamine hydrochloride	3.452	3.48	36.7
	$Cl_{theor.}$ = 36.37%	6.904	6.94	36.5
		10.356	10.32	36.2
2.	Chloroethylamine hydrochloride	12.634	12.58	60.9
		25.268	25.2	61.0
	$Cl_{theor.}$ = 61.17%	37.902	38.4	61.9
3.	*p*-Acetylaminobenzenesulphochloride	10.532	10.64	15.3
		21.064	20.8	15.0
	$Cl_{theor.}$ = 15.18%	31.596	30.4	14.6
4.	*p*-Toluenesulphochloride	9.845	9.94	18.8
		19.690	19.5	18.5
	$Cl_{theor.}$ = 18.61%	29.535	29.4	18.5
5.	2,3,5,6-Tetrahydro-6-phenyl-imidazo(2,1-b)thiazole hydrochloride	7.255	7.18	14.6
		14.510	14.37	14.6
		21.765	21.8	14.8
	$Cl_{theor.}$ = 14.74%			
6.	4′-(β-Piperidinoethoxy)-2-carbomethoxybenzophenone hydrochloride	18.324	18.4	8.83
		36.648	36.4	8.72
		54.972	54.7	8.73
	$Cl_{theor.}$ = 8.78%			
7.	2,2′-Diphenyl-4-piperidino-butyramide methyl bromide	13.527	13.41	19.0
		27.054	27.2	19.3
	$Br_{theor.}$ = 19.18%	40.581	40.8	19.3
8.	Novocaine hydrochloride	10.750	10.76	13.0
		21.500	21.6	13.1
	$Cl_{theor.}$ = 13.00%	32.250	32.0	12.9

cases the nitrates were used at pH 1. The values of the selectivity coefficients may be seen in Table 1.

The interference of Fe^{3+} is overcome by addition of fluoride.

Reproducibility of potential measurements

The reproducibility was tested for the range 10^{-1}–$10^{-5}M$ mercuric nitrate; the values in Table 2 are the average of 12 measurements during a five-week period, and prove the excellent stability of the electrode.

ANALYTICAL APPLICATIONS

The electrode was used with good results as an indicator electrode for complexation and precipitation potentiometric titrations including mercuric ions.

The potentiometric titration of mercuric nitrate with EDTA at pH 6 (hexamine buffer) gave a large potential jump at the equivalence point, and a maximum error of 0.5% for titration of 18–46 mg of Hg(II) with 0.1*M* EDTA. Cations forming EDTA-complexes with stability constants comparable to or higher than that of the Hg(II) complex will interfere, and so will silver. The interference of Fe(III) can be overcome by adding fluoride.

The electrode was equally satisfactory as indicator electrode for the potentiometric titration of I^-, Br^-, SCN^- and Cl^-, and was therefore used for the determination of some halogenated organic compounds used in the drug industry. Some of the results obtained are presented in Table 3. In the case of compounds 2, 3 and 4 the halide was obtained in ionic form by refluxing the sample for 30 min with 20% sodium hydroxide solution. The first four compounds in the table are important intermediates in organic synthesis, and the others are pharmacologically active.

This electrode has also been used for the determination of sodium benzyldithiocarbamate (an important intermediate in the synthesis of the fungicide 3-benzyl-5-carboxymethyltetrahydro-1,3,5-thiadiazin-2-thione, sodium salt) and can be used for the determination of other dithiocarbamates used on a large scale as fungicides in agriculture or as accelerators in the rubber industry.

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OXYGEN DETERMINATION IN ORGANIC FLUORINE COMPOUNDS BY MEANS OF A GLASSY-CARBON PYROLYSIS TUBE

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Summary—A conventional apparatus for determination of oxygen in organic compounds has been improved for application to organic fluorine compounds. A feature of the apparatus is the use of a pyrolysis tube made of glassy carbon instead of quartz, which eliminates effects due to hydrogen fluoride produced in pyrolysis of the sample. Ten analyses of dexamethasone with the apparatus gave a mean value of 20.44% for oxygen (theory, 20.38%), with a standard deviation of 0.16%. Oxygen in 9 organic fluorine compounds was accurately determined by using the apparatus, with an average error of +0.1%. One analysis by a gravimetric or a coulometric method took about 40 or 25 min, respectively.

Determination of oxygen in organic fluorine compounds is of importance, as shown by the great demand for it, and various methods and apparatus for the determination have been reported. The pyrolysis tube used for determining oxygen in organic compounds is usually made of quartz, but this gives erroneously high results for fluorine compounds because the hydrogen fluoride produced in the pyrolysis reacts with silicon dioxide to produce water.

Three methods are available for elimination of this source of error. First, the hydrogen fluoride is made to react with an absorbent previously packed in the pyrolysis tube, and produce a stable fluoride. The second method is to coat the inner wall of the pyrolysis tube with a substance stable to hydrogen fluoride. The third is to employ a pyrolysis tube made of a material that does not react with hydrogen fluoride.

cases the nitrates were used at pH 1. The values of the selectivity coefficients may be seen in Table 1.

The interference of Fe^{3+} is overcome by addition of fluoride.

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Table 1. Analytical results for oxygen in organic fluorine compounds

Sample	Sample taken, *mg*	CO_2, *mg*	O found, %	O calcd., %	Difference, %
2-Fluoroacetamide	3.255	1.877	20.9_7		+0.2
C_2H_4FNO	4.465	2.585	21.0_5	20.76	+0.3
	3.644	2.095	20.9_0		+0.1
o-Fluorobenzoic acid	3.499	2.191	22.7_7		−0.1
$C_7H_5FO_2$	4.092	2.566	22.8_0	22.84	−0.0
	3.927	2.482	22.9_8		+0.1
p-Fluorobenzoic acid	3.840	2.395	22.6_8		−0.2
$C_7H_5FO_2$	4.223	2.650	22.8_2	22.84	−0.0
	3.825	2.415	22.9_6		+0.1
9-Fluoro-11β,21-dihydroxy-16α-	4.316	2.051	17.2_8		+0.3
methylpregna-1,4-diene-3,20-dione	4.475	2.112	17.1_6	17.00	+0.2
$C_{22}H_{29}FO_4$	4.026	1.888	17.0_5		+0.1
9-Fluoro-11β,16α,17,21-tetra-	4.021	2.437	22.0_4		−0.1
hydroxypregna-1,4-diene-3,20-	3.741	2.284	22.2_0	22.09	+0.1
dione 16,17-*O*-acetonide	4.189	2.550	22.1_3		+0.0
$C_{24}H_{31}FO_6$					
9-Fluoro-11β,17,21-trihydroxy-	4.206	2.376	20.5_4		+0.2
16α-methylpregna-1,4-diene-3,20-dione	4.156	2.342	20.4_9	20.38	+0.1
$C_{22}H_{29}FO_5$	3.795	2.110	20.2_2		−0.2
4,4,4-Trifluoro-1-phenyl-	3.420	1.385	14.7_2		−0.1
1-3-butanedione	3.806	1.553	14.8_4	14.80	+0.0
$C_{10}H_7F_3O_2$	3.934	1.624	15.0_1		+0.2
$C_{21}H_{25}FO_3$	4.035	1.580	14.2_4		+0.3
	4.127	1.615	14.2_3	13.94	+0.3
	3.978	1.540	14.0_8		+0.1
$C_{24}H_{31}FO_5$	3.207	1.705	19.3_3		+0.2
	4.436	2.330	19.1_0	19.12	−0.0
	3.658	1.950	19.3_8		+0.3

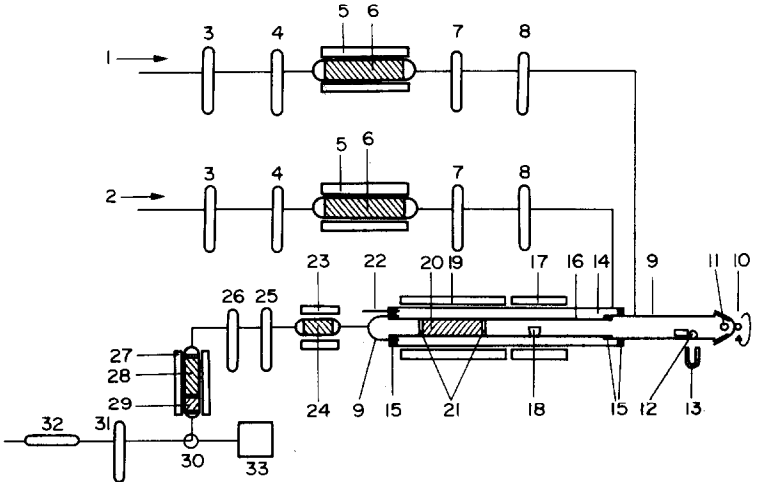

Fig. 1. Diagram of oxygen determination apparatus. 1: carrier gas inlet (nitrogen or argon), 2: inlet for protection gas (nitrogen or argon), 3: silica-gel drying tube, 4: flowmeter, 5: heating furnace (550°), 6: porous copper, 7: purifying tube (sodium hydroxide), 8: purifying tube (magnesium perchlorate), 9: glass tube attached to glassy-carbon tube, 10: sample inlet, 11: flushing hole, 12: iron ball, 13: magnet, 14: quartz tube for protection, 15: adhesive, 16: glassy-carbon tube, 17: sample heater, 18: sample boat, 19: combustion furnace, 20: platinized carbon, 21: glassy-carbon wool, 22: outlet for protection gas, 23: heating furnace (100°), 24: quartz wool, 25: purifying tube (silica gel), 26: purifying tube (sodium hydroxide), 27: heating furnace (150°), 28: iodine pentoxide, 29: porous copper, 30: three-way stop-cock, 31: purifying tube, 32: absorption tube, 33: coulometric apparatus.

Mázor[1] reported the use of magnesium nitride in the section of tube immediately after the one where the sample is heated. The hydrogen fluoride reacts with it to form magnesium fluoride and ammonia. As reported by Monar[2] and Volodina *et al.*,[3] barium chloride is similarly useful for the removal of hydrogen fluoride.

Meade *et al.*[4] considered that preconditioning of quartz pyrolysis tubes was required in the determination of total oxygen in fluorine-containing organometallic compounds and used several injections of a hydrocarbon such as iso-octane for the purpose. We have succeeded in determining oxygen in thallium compounds by coating the inner wall of pyrolysis tube with carbon, produced by the pyrolysis of naphthalene in a stream of an inert gas,[5] but have not yet applied the coating method to the determination of oxygen in organic fluorine compounds.

A platinum pyrolysis tube has been recommended.[6] We have determined oxygen and fluorine simultaneously in organic fluorine compounds by using a platinum pyrolysis tube,[7] but in the section of tube that was packed with carbon and heated at 1100–1120° fine crystals of platinum carbide formed in the tube within 10 days, causing cracking all over the surface of this section. Ehrenberger *et al.*[8] and Schwarzkopf and Schwarzkopf[9] used a nickel pyrolysis tube successfully.

In this paper we report the results of an attempt to use a glassy-carbon pyrolysis-tube. Glassy carbon is the general term for carbon produced through solid-phase carbonization. The product is hardly graphitized, showing no or few well-formed crystals of graphite, is isotrophic, shows a glassy appearance and lustre when cut or broken, and permits little gas to penetrate it. These properties are similar to those of glass, hence the name of glassy carbon. Among glassy carbons now commercially available are Cellulose Carbon® by GFC (England), Vitreous Carbon® by The Plessy Co. (England), Carbone Vitreux® by Le Carbone Lorraine (France), Glassy Carbon® by Tokai Carbon Co., Ltd. (Japan). The last-named was chosen for our work.

The carbon dioxide produced in blank determinations with a glassy-carbon pyrolysis tube was approximately 50 μg in 25 min, a value nearly the same as that obtained by using a quartz pyrolysis tube. Oxygen was determined as easily with a glassy carbon tube as with a quartz tube.

EXPERIMENTAL

Samples

The samples used were compounds of which the carbon, hydrogen and fluorine contents had been confirmed analytically.

Reagents

The reagents used were the same as those in our previous paper.[10]

Apparatus

A glassy-carbon tube (Glassy Carbon GC-20, Tokai Carbon Co., Ltd.) with an inside diameter of 10 mm, outside diameter of 13 mm and length of 500 mm was employed. It has the following physico-chemical properties:[11] heat-resistance (heat-treatment temperature), 2000°; apparent specific gravity, 1.47–1.50; porosity, 1–3%; gas permeability, 10^{-10}–10^{-12} cm^2/sec.

The apparatus shown in Fig. 1 was used. To eliminate the effect of any hydrogen fluoride resulting from the pyrolysis, a tube packed with quartz wool (and heated at 100°) was connected to the glassy-carbon pyrolysis tube and a purifying tube of silica gel followed it. The other apparatus components and their layout were the same as those previously reported.[10,12]

Procedure

This was the same as that for oxygen determination in organic compounds, described in our previous paper.[10]

RESULTS AND DISCUSSION

Blank determinations conducted immediately after assembly of the apparatus showed that 150 μg of carbon dioxide were produced in 25 min, whereas the blank value for carbon dioxide obtained after the apparatus had been heated for 10 hr was 50–60 μg/25 min. The blank value for a quartz tube has been found by us to be usually 50–60 μg/25 min.

Analyses of standard sucrose (51.41% O) and benzoic acid (26.20% O) for oxygen gave mean values of 51.44 and 26.28%, respectively. Ammonium fluoride was then analysed by the same method with the same apparatus, in order to remove small amounts of impurities in the inner wall and platinized carbon of the glassy-carbon tube before the determination of oxygen in organic fluorine compounds. When five 5-mg samples of ammonium fluride were analysed in succession, the value for oxygen obtained was about 50 μg/25 min.

Dexamethasone was then analysed for oxygen 10 times successively. The average oxygen content was 20.44% with standard deviation 0.16%; the theoretical value is 20.38%.

Table 1 gives the results for 9 organic fluorine compounds; the average error is +0.1%.

One analysis took about 40 min by a gravimetric method and about 25 min by a coulometric method.

This method seems to be applicable not only to fluorine compounds but also to compounds containing alkali metals, which cannot be analysed by use of a quartz tube.

Acknowledgements—The authors are indebted to Dr. Nobuo Suzuki, Development Laboratories, Hoechst Japan Limited, for his encouragement and to Dr. Shigehiko Yamada, Tokai Carbon Co., Ltd., for the generous supply of glassy-carbon tubes. Thanks are also due to Mr. Eichi Nakamura for his assistance in the early stages of the work.

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A NEW BORON-SELECTIVE RESIN DERIVED FROM GUAR GUM

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Summary—A boron-selective resin has been prepared by cross-linking of a natural plant hydrocolloid (the polysaccharide guaran from guar seeds). Concentration and separation of boron can be achieved on this resin through complexing of boron with the *cis*-hydroxyl groups in the polymer. The method has been applied to the determination of boron.

The endosperm of guar seed (*Cyanaposis tetragonolobus*) consists of a polysaccharide gum (guaran, a galactomannan) which has been extensively used as a hydrocolloid in the food, paper and certain other industries.[1] Since galactose and mannose units in this polysaccharide both contain a pair of *cis*-hydroxyl groups, it undergoes reversible, pH-dependent gelling with boron.[1]

Cross-linking of guar-gum with cyanuric chloride or epichlorhydrin gives an insoluble, water-swellable polymer, which retains its ability to complex boron. Preparation of a boron-binding resin by amination of chloromethylated polystyrene with *N*-methylglucamine has been reported by Rosset and co-workers,[2,3] but such polymers with a hydrophobic styrene backbone are less compatible with aqueous solutions.

In this communication we report the use of a guar-based resin for separation and concentration of boron, as an alternative to the popular method based on volatilization of methyl borate.[4]

EXPERIMENTAL

The insoluble guaran resin was prepared from guar gum purified by ethanol precipitation. Guar gum (100 g) was soaked in an aqueous acetone solution (1:1, 200 ml). Cyanuric chloride (10 g) dissolved in acetone (100 ml) and sodium hydroxide solution (6.5 g in 20 ml of water) were added. The temperature of the reaction mixture rose to 45–50°. After aging for 24 hr, the pale yellow mass was poured into water, acidified with acetic acid, filtered off, extensively washed with water and acetone, and air-dried, to give a resin with a moisture content of 8–10% and 80% having a particle size of 30–50 mesh. The pH of an aqueous suspension of the resin was 6.8–7.2. The resin swelled in water to nearly three times its volume, and had a cation-exchange capacity of 2–3 meq/g for Na^+. The boron-exchange capacity was determined by adding 1 g of the air-dried resin to 100 ml of 0.05*M* sodium tetraborate containing 1.0 ml of 0.1*M* sodium hydroxide. After equilibration for 2 hr, the resin was filtered off and washed with 0.01*M* sodium hydroxide. Boron in the combined washings and filtrate was determined by titration with 0.01*M* hydrochloric acid to a pH of about 7, measured accurately with a pH-meter, followed by addition of 5 g of mannitol and titration of the liberated acid to the same pH with 0.01*M* sodium hydroxide (1 ml of 0.01*M* NaOH corresponds to 0.108 mg or 0.01 meq of boron).

From the difference between the amount of boron originally present in the solution and that remaining after complexation with the resin, the exchange capacity of the resin was found to be 4.2 meq/g. Separation and concentration of boron was investigated by using a resin column (25 × 0.9 cm) prepared from 10 g of resin slurried in 150 ml of 0.01*M* sodium hydroxide. A flow-rate of 2.5 ml/min was obtained with a hydrostatic pressure of 20 cm.

A boron solution containing 1–5 meq of boron and 1.0 ml of 0.1*M* sodium hydroxide was slowly passed through the column. No boron could be detected in the effluent. After all the solution has been passed through the column, the complexed boron was eluted with 0.05*M* hydrochloric acid, followed by water as a wash. Boron in the eluate was determined as above. A concentration of 20–40 fold was readily achieved (see Table 1).

Determinations of boron in some naturally occurring compounds are given in Table 2. The boron in water samples was directly concentrated by passage of the sample through the resin column, and other samples were ashed according to standard procedures.[5] The residue from the ashing was leached with water and boron separated on the resin column. Boron in these samples was also determined by direct titration by standard methods.[5]

Table 2 shows that the results obtained by the proposed method are comparable to those obtained by the direct method.

Preliminary investigations have shown that resins of this type also act as molecular sieves, and work is in progress to separate macromolecules by using these resins as gel-filtration media, similarly to Sephadex gels.[6]

Acknowledgement—One of us (R.B.) is thankful to Shri S. K. Das, Director (Survey and Research), Ground Water Department, Government of Rajasthan, Jodhpur, India, for his encouragement and interest in this work.

Table 1. Concentration and recovery of boron from resin column

Volume of original solution, *ml* (*a*)	Volume of eluate with 0.01*M* HCl/H_2O, *ml* (*b*)	Boron added, *meq*	Boron found in eluate, *meq*	Concn. achieved, (*a*/*b*)
250	25	1.50	1.48	10
500	25	1.50	1.46	20
1000	40	2.50	2.46	25
2000	50	4.50	4.44	40

Table 2. Determination of boron in some naturally occurring substances

Sample	Boron found, *ppm*	
	Present method	Alternative method[5]
Water	2.32	2.31
Plant material	4.10	3.98
Milk	3.52	3.48
Butter	4.65	4.78

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TENSAMMETRIC DETERMINATION OF MICROGRAM AMOUNTS OF VANADIUM BY CATALYTIC OXIDATION OF *o*-AMINOPHENOL

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(*Received* 28 *August* 1976. *Accepted* 10 *December* 1976)

Summary—A tensammetric method is proposed for the determination of microgram amounts of vanadium, based on catalysis of the oxidation of *o*-aminophenol with sodium chlorate in acidic solution (pH 2.0). The oxidation product gives a very sensitive tensammetric wave; under optimum conditions, the wave-height is proportional to the concentration of vanadium. From 0.2 to 3.0 μg of vanadium can be determined in a final volume of 50 ml. Mo(VI), W(VI), Mn(VII), Ce(IV) and large amounts of Al(III) and Fe(III) cause positive errors, and Hg(II) and thiosulphate negative errors. Interference from Fe(III), Al(III) and Cu(II) can be eliminated by solvent extraction with oxine at about pH 8.0.

The most widely adopted catalytic methods for the determination of various ions have been based on spectrophotometry. Procedures for the determination of trace amounts of vanadium by catalytic oxidation of gallic acid, α-naphthylamine and *p*-phenetidine have been reported by Fishman and Skougstad,[1] Tanaka and Awata,[2] and Bontschev and Jeliazkowa.[3]

We have already used catalytic oxidation of *o*-aminophenol by dissolved oxygen for the determination of copper.[4] This paper describes the determination of small amounts of vanadium by catalysis of the chlorate oxidation of *o*-aminophenol.

EXPERIMENTAL

Reagents

o-Aminophenol. Purified as reported previously,[4] and a $5 \times 10^{-3}M$ solution prepared with deoxygenated redistilled water.

Vanadium(V) stock solution, $10^{-3}M$. Prepared by dissolving 0.194 g of sodium vanadate ($NaVO_3 \cdot 4H_2O$) in 1 litre of freshly redistilled water, and further diluted as required.

Standard silicate samples. JG-1 (Granodiorite) and JB-1 (Basalt) were obtained from the Geological Survey of Japan.

All other reagents employed were of analytical-reagent grade.

Apparatus

All the polarograms were recorded with a Yanagimoto PA-101 polarograph. The flow-rate of the dropping mercury electrode was 1.46_8 mg/sec and the drop-time was 4.25 sec in air-free redistilled water (30°) in open circuit and with a mercury height of 68 cm. For a.c. polarographic measurements, a small a.c. voltage (15 mV, 60 Hz) was superimposed on the applied d.c. potential.[5]

Recommended procedure

Take 0–7 ml of $10^{-5}M$ vanadium(V) standard solution in 50-ml standard flasks, add to each 5 ml of 0.2*M* sodium chlorate and 10 ml of 2.5*M* sodium perchlorate–perchloric acid mixture, and warm to 50°. Add 5 ml of $5 \times 10^{-3}M$ *o*-aminophenol as quickly as possible, shake, and dilute to 50 ml with warm (50°) redistilled water. Place the flasks in a water-bath kept at 50 ± 0.1°, and allow to stand for 2 hr. Cool to 30° to quench the reaction. Transfer a portion of the solution into a polarographic cell and record the a.c. polarogram between +0.3 and −0.2 V *vs.* S.C.E.

RESULTS AND DISCUSSION

Polarography of o-aminophenol and its oxidation product

o-Aminophenol is known to be oxidized slowly by dissolved oxygen in neutral or alkaline solution, to 2-amino-3-phenoxazone,[6,7] which gives a very sensitive a.c. polarographic wave at about −0.4 V *vs.* S.C.E. (at pH 8.0). Figure 1 shows the polarographic waves of *o*-aminophenol and its oxidation product (at pH 2.0).

Oxidation of *o*-aminophenol with sodium chlorate is very slow at pH below 3, and no a.c. wave is observed. However, very small amounts of vanadium(V) accelerate the oxidation and a very high a.c. wave is observed.

Table 2. Determination of boron in some naturally occurring substances

Sample	Boron found, *ppm*	
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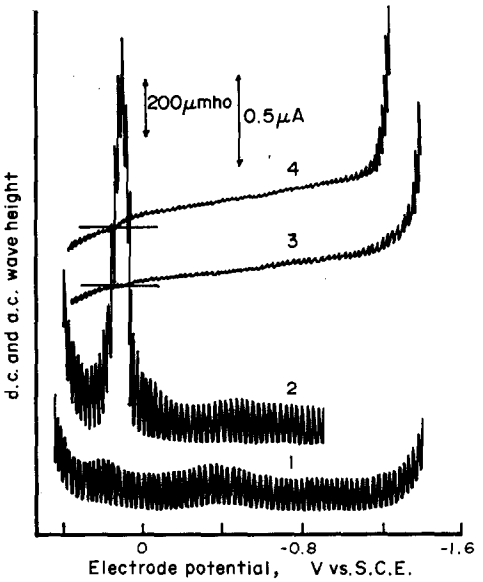

Fig. 1. Polarograms (d.c. and a.c.) of *o*-aminophenol and its oxidation products 0.5*M* $NaClO_4$–$HClO_4$ (pH 2.0), 0.02*M* $NaClO_3$, $5 \times 10^{-4}M$ *o*-aminophenol, after standing for 2 hr. 1: a.c. polarogram, 2: same as (1) except solution $10^{-6}M$ in vanadium (V), 3: d.c. polarogram, 4: same as (3) except solution $10^{-6}M$ in vanadium (V).

From study of the electrocapillary curves, temperature coefficients of the a.c. wave-height, and relation between the a.c. wave-height and concentration of the oxidation product,[8] it is concluded that the a.c. wave is a tensammetric one.

The infrared spectrum of the oxidation product shows the absorption of the 1,2,4,5-substituted aromatic radical δ_{CH} band at 850 cm^{-1} and of the quinone radical $\nu_{C=O}$ in the 1660-cm^{-1} region.[9]

From these results, it is suggested that the oxidation product is the corresponding 2-amino-3-phenoxazone, and the mechanism of the catalytic oxidation in this case may be the same as in the case of the oxidation with dissolved oxygen.[4] Vanadium(V) oxidizes *o*-aminophenol, then the vanadium(IV) produced is reoxidized to vanadium(V) by the sodium chlorate. Further oxidation of *o*-aminophenol proceeds by repetition of these reactions.

Choice of conditions

Effect of temperature and reaction time. The rate of the catalytic oxidation in acidic solution is markedly affected by changes in temperature. It was found that the reaction at 50 ± 0.1° was suitable for the accurate determination of 0.2–3.0 μg of vanadium(V) in a final volume of 50 ml.

The effect of reaction time on the wave-height was examined for a solution that was $5 \times 10^{-4}M$ in *o*-aminophenol, 0.02*M* in sodium chlorate, $4 \times 10^{-7}M$ in vanadium(V) and 0.5*M* in sodium perchlorate–perchloric acid. The results are shown in Table 1.

Because vanadium(V) is regenerated by oxidation with sodium chlorate, a longer reaction time results in a greater

Table 1. Effect of reaction time on the a.c. wave-height

Time, *min*	Wave-height, *μmho*	Time, *min*	Wave-height, *μmho*
30	82.3	150	445.5
60	193.2	180	503.6
90	268.6	210	542.2
120	384.0	240	570.4

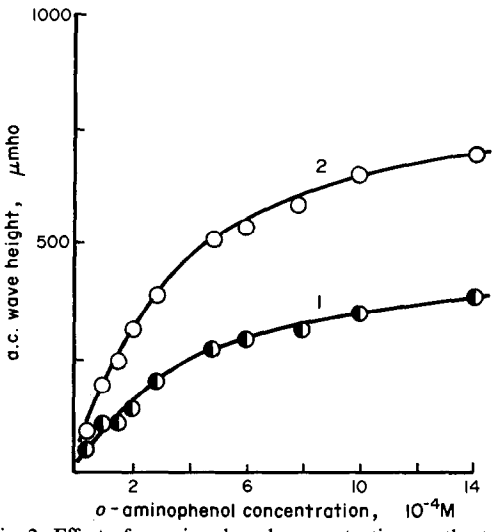

Fig. 2. Effect of *o*-aminophenol concentration on the tensammetric wave-height: 0.5*M* $NaClO_4$–$HClO_4$ (pH 2.0), 0.02*M* $NaClO_3$, $5 \times 10^{-7}M$ vanadium(V). Reaction time, 1, 1 hr; 2, 2 hr.

a.c. wave-height. However, from a practical point of view a reaction time of 120 min is suitable for the determination of 0.2–3.0 μg of vanadium in 50 ml. If the reaction time is increased, the method may be extended down to 0.05 μg of vanadium.

Effect of pH. When vanadium(V) is absent, no wave is observed after reaction times of up to 6 hr at pH < 4. However, at pH > 4 an a.c. wave due to oxidation of *o*-aminophenol by dissolved oxygen appears. Therefore, the determination should be carried out at pH 2–3.

Table 2. Interference by various ions

Element added	Concn. of interferent, *mg/50 ml*	V(V) found, *μg*	Recovery, %
Ag(I)	2.2	1.02_5	101.5
Co(II)	1.2	1.04_5	103.5
Mn(II)	5.5	1.03_4	102.4
Cu(II)	0.7	1.06_2	105.2
Hg(II)	0.2	1.03_4	102.4
Zn(II)	2.7	1.02_3	101.3
Se(IV)	0.8	1.02_5	101.5
Te(II)	1.3	0.99_7	98.7
Fe(III)	1.2	1.03_4	102.4
Al(III)	2.7	1.00_4	99.4
Bi(III)	4.2	1.03_8	102.8
As(III)	1.5	1.02_5	101.5
Ce(IV)	0.15	1.07_9	106.8
Zr(IV)	0.06	0.99_8	98.8
Cr(VI)	0.12	1.04_8	103.8
Mo(VI)	0.06	1.05_2	104.2
W(VI)	0.12	0.99_0	98.0
Mn(VII)	0.03	1.06_4	105.3
NO_2^-	4.0	1.01_7	100.7
NO_3^-	60	1.03_4	102.4
Cl^-	1.5	0.99_8	98.8
SCN^-	0.3	0.99_9	98.9
acetate	60	1.04_2	103.2
SO_3^{2-}	16	1.03_8	102.8
SO_4^{2-}	20	0.99_9	98.9
$S_2O_3^{2-}$	0.23	0.82_4	81.6
PO_4^{3-}	1.0	1.02_8	101.8
tartrate	0.3	0.98_8	97.8

Table 3. Determination of vanadium in standard silicate samples by the recommended procedure

Sample	Weight taken, *mg*	Vanadium found, *ppm*	Content certificate, *ppm*	Standard deviation, *ppm*
JG-1	50	22.8	24	0.8
		23.0		
		23.8		
		23.6		
JB-1	10	195	200	7.9
		190		
		188		
		198		

Effect of sodium chlorate concentration. The rate of oxidation increases with chlorate concentration up to 0.02*M*, and then becomes constant. Thus, the solution should be 0.02*M* in sodium chlorate.

Effect of o-aminophenol concentration. Varying amounts of the reagent were added to a series of standard solutions [(0.02*M* sodium chlorate, $5 \times 10^{-7}M$ vanadium(V) and 0.5*M* sodium perchlorate–perchloric acid solution (pH 2.0)]. The effect on the wave-height is shown in Fig. 2.

In each case, the wave-height increases with increasing concentration of *o*-aminophenol, but as the oxidation of *o*-aminophenol by dissolved oxygen can no longer be disregarded at concentrations above $10^{-3}M$, the working concentration of *o*-aminophenol was fixed at $5 \times 10^{-4}M$.

A linear calibration curve with zero intercept was obtained for 0.2–3.0 μg of vanadium(V) in a final volume of 50 ml.

The detection limit is one order of magnitude lower than that of the catalytic determinations using spectrophotometric procedures.[2,3]

Interferences

Since all tensammetric waves are very sensitive to surfactants, the effect of other surfactants on this tensammetric wave was studied: 0.01% gelatin, which is weakly adsorbed in the whole potential range, and 0.05*M* pyridine, which gives a negative tensammetric wave, depressed the tensammetric wave-height of the oxidation product by about 20%, whereas 0.05% methyl cellosolve and 0.005% alkyl phenol and ABS detergent, which is commonly used in laboratories, showed no effect.

The effects of diverse ions on the determination of 1.01 μg of vanadium are summarized in Table 2.

Of the cations examined, zirconium(IV), chromium(VI), molybdenum(VI) tungsten(VI) and manganese(VII) cause serious interferences if present in 30–120-fold w/w ratio to V(V). Thiosulphate ion (in 230-fold w/w ratio) is the only interfering anion.

Interference from manganese, cerium(IV), iron(III), copper(II) and aluminium can easily be eliminated by extraction with oxine at about pH 8.0. As proposed by Talvitie,[10] molybdenum and tungsten can be separated from vanadium by oxine extraction at pH 4.0 and subsequent stripping of vanadium with sodium borate buffer.

Determination of vanadium in a standard silicate rock

Vanadium was determined in the standard silicate samples JG-1 (Granodiorite) and JB-1 (Basalt) by the following procedure. The sample (50 mg for JG-1, 10 mg for JB-1) is decomposed with perchloric acid–hydrofluoric acid mixture and the solution slowly evaporated to dryness. The residue is dissolved in 3 ml of hot 6*M* nitric acid, then 5 ml of 1% oxine solution in acetic acid are added and the pH is adjusted to 8.0–10.0 with concentrated ammonia solution. The oxinates of copper, ferric iron and aluminium are extracted with two 10-ml portions of alcohol-free chloroform, and the aqueous phase is boiled to remove dissolved chloroform. The pH is adjusted to 2.0 with 1*M* perchloric acid and the vanadium determined by the procedure described. The results, shown in Table 3, are in good agreement with the certificate values.[11] Four samples can be analysed in three hours.

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ESTIMATION OF METHIONINE AND ITS METAL COMPLEXES BY OXIDATION WITH CHLORAMINE-T AND DICHLORAMINE-T

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Summary—A simple method for the estimation of methionine (HMt) in aqueous solution has been developed, based on its oxidation with chloramine-T and dichloramine-T at room temperature. The direct titration, with visual or potentiometric end-point, involves a two-electron change, corresponding to the formation of methionine sulphoxide. Most amino-acids do not interfere, but cysteine, glutathione and thiourea are oxidized under these conditions. A back-titration procedure in which methionine is oxidized in 0.1*M* sodium hydroxide by excess of chloramine-T with a four-electron change corresponding to the formation of methionine sulphone has also been developed. Methionine is oxidized to the respective nitrile, however, with excess of dichloramine-T. The methods have also been employed in estimating methionine in two of its soluble complexes, $[NiMt]ClO_4$ and $Na[AgMt_2]$.

During our investigations on the behaviour of some thiols and amino-acids with organic haloamines,[1–3] it was noticed that methionine (HMt) undergoes stoichiometric oxidation with chloramine-T (CAT) and dichloramine-T (DCT) under specified conditions and that the methods could be employed for a volumetric estimation of the compound in solution. Methionine is an essential amino-acid, an intermediary in dietary metabolism, and the only amino-acid which is excreted in urine in normal quantities. Being an important plant protein it is also a constituent of algae. Methionine has been oxidized to the sulphoxide with iodine,[4] bromine in acetic acid,[5] potassium bromate,[6] and iodine monochloride,[6] whereas oxidants such as $NaClO_2$,[7] H_2O_2[8] and bromide–bromate mixture[5] are found to convert it into the corresponding sulphone. During the present investigations, it was found that methionine can be estimated with CAT and DCT by a direct titration, with a visual end-point (indigo carmine as internal indicator) or a potentiometric end-point, or by a back-titration method.

The methods were found to yield accurate and reproducible results with methionine and were also useful for estimating methionine in its complexes.[9]

EXPERIMENTAL

Reagents

DL-Methionine was purified by recrystallization from aqueous solution. The purity of the sample was checked by titration with perchloric acid[10] and by paper chromatography. Aqueous solution of methionine (~ 2 mg/ml) were prepared in triply distilled water or in buffer solutions of pH 1–8.

Solutions of CAT and DCT were prepared as before.[1–3] A 0.1% aqueous solution of indigo carmine was used as indicator. Analytical-grade reagents were used for other solutions.

Direct titration

Visual end-point. To the methionine (4–50 mg in aqueous solution) add ~ 1 ml of glacial acetic acid, 1 ml of 10% potassium bromide solution, 0.1–0.2 ml of indicator and 10–20 ml of water and titrate with 0.01 or 0.02*N* CAT to the appearance of a pale yellow colour. The indicator correction is 0.1 ml with 0.01*N* CAT and 0.05 ml with 0.02*N* CAT.

Table 1. Extent of oxidation of methionine in different solvent and buffer media with excess of chloramine-T

Medium	mmole CAT used / mmole HMt taken	Medium	mmole CAT used / mmole HMt taken
0.10*N* H_2SO_4	3.31	pH 1	3.46
0.25*N* H_2SO_4	3.27	pH 2	3.94
0.50*N* H_2SO_4	3.13	pH 3	4.11
0.10*M* HCl	3.52	pH 4	3.99
0.25*M* HCl	3.46	pH 5	3.62
0.50*M* HCl	3.36	pH 6	3.35
0.10*M* $HClO_4$	3.24	pH 7	3.22
0.25*M* $HClO_4$	3.08	pH 8	2.90
0.50*M* $HClO_4$	3.00	0.075*M* NaOH	2.00
0.5*M* HOAC	4.14	0.100*M* NaOH	2.00
1.0*M* HOAC	3.96	0.125*M* NaOH	2.00
		0.25*M* NaOH	1.47

HMt taken = 0.066 mmole; CAT = 1.0 mmole; time = 60 min. HCl–KCl buffer (pH 1,2). Potassium biphthalate–HCl buffer (pH 3). Sodium acetate–acetic acid buffer (pH 4–6). Borax–boric acid buffer (pH 7, 8).

Oxidations with DCT are done in the same way but the glacial acetic acid is unnecessary and the methionine solution is diluted to about 50 ml before titration. Indicator corrections are the same as with CAT.

Potentiometric end-point. Use a platinum indicator electrode and calomel reference electrode. The end-point is clearly defined only if 1 ml of 10% potassium bromide solution and 1–5 ml of glacial acetic acid are added.

Back-titration

Add the sample containing 3–15 mg of methionine to 50 ml of 0.1*N* CAT in an iodine-flask containing enough sodium hydroxide to give an overall alkalinity of 0.1*N*. Shake the reaction mixture and after 60 min, add 20 ml of 2*N* sulphuric acid and 20 ml of 20% potassium iodide solution and titrate the liberated iodine with standard thiosulphate solution. Run a blank with CAT solution alone.

Alternatively add the aqueous sample solution containing 2–25 mg of methionine to 25 ml of 0.1*N* DCT in an iodine-flask and dilute to about 250 ml to give a water content of 85–92% in the reaction mixture. After 60 min, titrate the excess of DCT as above. Run a blank with DCT alone.

RESULTS AND DISCUSSION

Some typical results of direct titration of methionine with CAT and DCT with visual and potentiometric end-points are shown in Table 2. The two-electron change observed can be represented as follows:

$$CH_3SRH + R'NClNa\ (\text{or } {}^1/_2R'NCl_2)$$
$$+ H_2O \rightarrow CH_3\overset{\overset{O}{\|}}{S}SRH + R'NH_2 (\text{or } {}^1/_2R'NH_2)$$
$$+ NaCl\ (\text{or } HCl)$$

$R' = p\text{–}CH_3C_6H_4SO_2$ and

$R = -CH_2CH_2CH(NH_2)COO^-$

Paper chromatography with benzyl alcohol saturated with water was used to identify the products—the sulphonamide ($R_F = 0.91$; 0.5% vanillin in 1% hydrochloric acid in ethanol as spray reagent)[2,3] and methionine sulphoxide ($R_F = 0.67$; spray reagents for methionine).

Cysteine, glutathione and thiourea interfere, but cystine, glycine, serine, threonine, leucine, proline, histidine, glutamic acid and urea (~ 0.05 mmole each) do not.

The four-electron change observed with CAT in the back-titration method can be explained as follows:

$$CH_3SRH + 2R'NClNa$$
$$+ 2H_2O \rightarrow CH_3\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}RH + 2R'NH_2 + 2NaCl.$$

The sulphonamide and methionine sulphone ($R_F = 0.56$) were detected by paper chromatography as described above.

Oxidations with DCT can be represented as

$$CH_3SRCHNH_2COOH + 2R'RNCl_2$$
$$+ 2H_2O \rightarrow CH_3\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}RCN$$
$$+ 2R'RNH_2 + 4HCl + CO_2$$

$(R = -CH_2CH_2-)$

$(R' = p\text{–}CH_3C_6H_4SO_2)$

The presence of the nitrile in the reaction products was detected by its colour reaction with hydroxylamine and iron (III).[11]

Cysteine, cystine, glutathione, serine and threonine (~ 0.05 mmole) interfered in the back-titration procedure. Typical results were correct within 0.5%.

A further application of the proposed techniques is in the estimation of methionine in its soluble metal complexes. Two complexes [NiMt] ClO_4 and $Na[AgMt_2]$ where

Table 2. Estimation of methionine and its metal complexes with chloramine-T and dichloramine-T (direct titration, amounts in *mg*)

Visual end-point						Potentiometric end-point					
Methionine		$[NiMt]ClO_4$		$Na[AgMt_2]$		Methionine		$[NiMt]ClO_4$		$Na[AgMt_2]$	
Taken	Found	Taken	Found	Taken	Found	Taken	Found	Taken	Found	Taken	Found
Oxidation with CAT											
4.09	4.11	3.10	3.10	3.20	3.21	4.92	4.93	3.30	3.31	7.79	7.81
10.22	10.23	4.97	4.98	8.01	8.02	9.84	9.86	6.61	6.63	15.58	15.59
16.35	16.28	6.21	6.21	16.02	16.04	14.75	14.85	9.91	9.94	23.37	23.4
20.44	20.5	7.45	7.44	19.22	19.3	19.67	19.8	13.22	13.25	31.16	31.2
24.53	24.6	9.31	9.31	24.02	24.0	24.59	24.6	16.52	16.57	38.95	39.1
30.66	30.7	12.42	12.48	28.83	28.8	29.51	29.6	19.82	19.9	46.74	47.0
40.88	40.9	18.62	18.7	32.03	32.1	—	—	—	—	—	—
51.10	51.2	24.83	24.9	40.04	40.2	—	—	—	—	—	—
Oxidation with DCT											
4.24	4.26	3.16	3.15	3.31	3.30	5.49	5.49	3.09	3.09	8.11	8.10
10.60	10.57	6.32	6.31	8.28	8.27	10.98	10.97	6.18	6.19	16.21	16.20
16.96	17.03	9.48	9.46	13.25	13.30	16.47	16.46	9.27	9.28	24.32	24.4
21.20	21.2	11.38	11.43	16.56	16.59	21.96	21.9	12.36	12.38	32.42	32.5
25.44	25.6	12.64	12.68	19.87	19.8	27.45	27.6	15.45	15.47	40.53	40.6
31.80	31.9	15.80	15.83	24.84	24.9	32.94	33.1	18.54	18.6	48.63	48.8
42.40	42.5	18.96	19.0	33.12	33.1	—	—	—	—	—	—
53.00	53.1	25.28	25.3	41.40	41.4	—	—	—	—	—	—

Mt = $CH_3SCH_2CH_2CH(NH_2)COO^-$, were prepared[9] and their composition was checked. Aqueous solutions of the complexes (0.6 mg/ml for the nickel complex and 1.5 mg/ml for the silver complex) were employed and direct titrations with visual and potentiometric end-points were carried out with 0.01*N* CAT or DCT, as indicated for methionine, and 0.1*N* solutions for the back-titration method. Some typical results are shown in Table 2.

The dependence of the stoichiometry and the potential break on the presence of KBr during the direct titration of methionine with CAT and DCT indicates that elemental bromine is probably responsible for oxidation of the amino-acid to the corresponding sulphoxide:

$$RNCl^- + 2Br^- + 2H^+ \rightarrow Br_2 + R'RNH_2 + Cl^-$$

$$CH_2SRH + Br_2 + H_2O \rightarrow CH_3{-}\overset{\overset{O}{\|}}{S}{-}RH + 2HBr.$$

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THE ANALYSIS OF HUMAN BREATH AND URINE FOR ORGANIC COMPONENTS WITH CHROMATOGRAPHIC AND MASS SPECTROMETRIC TECHNIQUES: A REVIEW*

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Since the conception of gas chromatography by Martin and Synge,[1] the technique has been rapidly developed, and it is at present the most widely used analytical tool in the physical sciences. The advent of open tubular columns[2] was a breakthrough for analysis of complex mixtures. Chromatographic analysis of complex mixtures with many different classes of trace components is being applied to present-day analytical problems in fields such as air and water pollution, petroleum and coal research, flavour studies, food products, cigarette smoke and medicine.

Characteristic chromatograms or "fingerprints" associated with trace components in body liquids and effluents are termed metabolic profiles. Much could be learned about human metabolism if these metabolic profiles could be correlated, by pattern-recognition analysis, with nutrition, physical exercise, seasonal and diurnal variations, genetic make-up, and physiologic and pathologic state,[3] *etc.*

Urine and breath are two obvious choices from the body fluids and effluents for analysis; their collection does not require the disruption of any bodily processes and avoids the possibility that the trauma associated with collection (*e.g.*, of blood or similar samples) may influence the substituents present. Breath offers certain advantages over urine in that it is already in a convenient physical form for analysis by gas chromatography and it gives information about those bloodstream components that readily pass the alveolar-pulmonary membrane, in contrast to those filtered by the kidneys.

HISTORY

The use of urine examination (mainly of physical properties) in the diagnosis of disease has been known from the first recorded medical practices. Uroscopy became so popular among the physicians of the middle ages that the practice and the practitioners were depicted in art and literature. The eighteenth century marked the beginning of scientific methods in urine analysis.[4] Since that time urine analysis has advanced along with chemical analysis.

In the late eighteen-hundreds it was recognized that the physiologic state of man and his environmental conditions were reflected in his expired air.[5] Few advances were made until the advent of gas chromatography because of the lack of analytical technique. Even then analyses were somewhat limited owing to the lack of suitable concentration methods.[6–9] In the present decade analytical techniques have progressed far enough for correlation of breath analysis with disease to become a real possibility. Dubowski[10] has recently published a review on the present state of breath analysis.

METHODS FOR PROFILE ANALYSIS

Liquid chromatography (LC) and gas chromatography (GC) both have their place in the establishment of metabolic profiles. GC offers high resolution and rapid analysis, but not all substances are volatile or convertible into volatile form. It has been estimated that approximately 25% of the several thousand known biologically occurring compounds can be determined by GC. For substances such as proteins, peptides, nucleic acids, nucleotides, nucleosides, most co-enzymes and co-factors, cytochromes, porphyrins and bile pigments, GC cannot be used.[11] LC is more suitable for these components.

Liquid chromatographic techniques

A research group at Oak Ridge National Laboratory published a number of articles on use of LC for the separation of complex biological mixtures. Members of the group also published two reviews dealing primarily with their work in this area.[12,13] They developed an automatic analyser for the separation and determination of ultraviolet-adsorbing components.[14] Their system was composed of a heated high-pressure anion-exchange column, an acetate-buffer elution system, and a recording photometer. A typical urine sample took 40 hr for analysis

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and produced more than 100 chromatographic peaks. More than 180 different components were separated from urine that had been concentrated by sorption processes.[15] Minimum detectable quantities (MDQs) of less than a microgram were observed for many components. Fifty of the ultraviolet-absorbing compounds were identified by spectral maxima, GC methylene-unit retention values, and mass spectral peaks.[16]

More recently the Oak Ridge group coupled anion- and cation-exchange columns and achieved higher resolution, with detection of up to 17% more ultraviolet-absorbing compounds, and a reduction of analysis time to 14 hr.[17] They later developed a multicolumn, high-resolution chromatograph[18] and a multicolumn, high-pressure injection valve for the simultaneous injection into parallel columns.

They also developed a carbohydrate analyser composed of a temperature-controlled, high-pressure anion-exchange separation system.[14] The eluate was mixed with phenol and sulphuric acid and monitored by a recording continuous-flow colorimeter. The eluent was a borate buffer, giving anionic sugar borate complexes. A typical urine sample required a 24-hr analysis time and gave about 40 peaks. The sample preparation for both analysers consisted of filtration to remove particulate matter and ultrafiltration for samples such as blood serum which have a high concentration of proteins.

Katz, Pitt and Jones[19] of the Oak Ridge Research Center also described a detection system for the sensing of oxidizable compounds after anion-exchange chromatography. Detection relied on the fluorescence of the cerium(III) produced by the reaction of the eluted compounds with cerium(IV). This cerate-monitor was used in series with a UV-monitor because the latter was relatively insensitive to aromatic acids. For a sample of urine the cerate-monitor detected approximately 25 more peaks than the UV-monitor. MDQs were in the microgram range. This system was improved by extending the column elution range and shortening the time required from 2 days to 1 day.[20] The improved system was used for examining serum as well as urine.

Systems for organic acids and amino-acids have not been as well developed as the carbohydrate and UV-analysers, but they do show promise. A system for the analysis of organic acids was designed by Rosevear, Pfaff and Moffitt.[21] The separation medium was activated silicic acid and the eluent was a chloroform, t.-amyl alcohol and water mixture. The eluent was monitored colorimetrically after the addition of an ethanol solution of Neutral Red. The time required for elution was approximately 6 hr, with the separation of more than 40 constituents from urine. MDQs were less than a microgram for some components.

The determination of amino-acids has been attempted with many different methods. The method of Moore and Stein[22] is currently in use in most laboratories dealing with protein and peptide analysis. About 30 urinary substances (including amino-acids) can be detected with this low-resolution ion-exchange separation. Much effort has been expended in automating and refining the technique.[23]

Hamilton[24] presented a high-resolution method of analysis for amino-acids and related compounds. He was able to separate 175 compounds in human urine with a high-pressure temperature-controlled cation-exchange column. Ninhydrin was used for the detection, with monitoring at two wavelengths. A single analysis took as much as 65 hr. Submicrogram MDQs were demonstrated.

Brown[25] wrote a book on the use of LC in biomedical applications, covering instrumentation, experimental methods and data treatment. Several references to profiles and other analyses of biomedical interest were given, including nucleotides, steroids, vitamins, amino-acids, lipids, carbohydrates, drugs and their metabolites, *etc.*

Young, Epley and Goldman[26] studied the influence of diet on the composition of serum and urine. For their analyses they used the Oak Ridge UV- and carbohydrate analysers and an amino-acid analyser. In general, water excretion tended to increase and quantities of most urinary components tended to decrease while the subjects were on a chemically defined low-bulk diet of "Vivonex". Further studies need to be done to establish which compounds arose from endogenous metabolism and which were dietary in origin.

Gas-chromatographic techniques for non-volatiles

Jellum, Stokke and Eldjarn[11,27–29] did research with a large number of patients, using a GC–mass spectrometry (MS)–computer (COM) system for the establishment of metabolic profiles. Their work was primarily with urine samples but some serum and biopsy samples were also analysed. The system consisted of five GCs equipped with flame-ionization detectors (FIDs). One of the GCs was interfaced to a single-focusing MS through a molecular separator of the glass-frit type. An on-line computer was used for the MS data-acquisition and an off-line computer was used for the MS library-search. Following is a brief summary of the types of compounds separated by their procedures: (1) ether-soluble substances that are volatile (lower hydrocarbons, alcohols, aldehydes, ketones, short-chain free fatty acids, *etc.*); (2) substances volatile at higher temperatures (higher alcohols, aldehydes, ketones, aliphatic and aromatic hydrocarbons, phenols, barbiturates, and other heterocyclics); (3) acidic metabolites in the form of methyl esters; (4) derivatives of amines, amino-acids, and simple dipeptides; (5) derivatives of carbohydrates and certain amino-sugars; (6) derivatives of acidic compounds (*e.g.*, drug metabolites released on acid hydrolysis); (7) total amino-acid and amine content, including those liberated by acid hydrolysis. Samples from several patients could be run in one day with the system, and 500–1000 total peaks were obtained.

They made several observations about such work: (1) the intake of drugs, even seemingly innocuous ointments, complicates the pattern; (2) urine varies considerably from person to person (the difficulty is considerably decreased by using fresh morning urine, which is relatively characteristic of endogenous metabolism); (3) large amounts of benzoic acid are regularly encountered and may indicate the presence of bacteria in urine. There are several micro-organisms that contain a hippuricase which hydrolyses hippuric acid to glycine and benzoic acid.

Horning and co-workers did considerable work on the use of GC–MS or GC–MS–COM for obtaining metabolic profiles.[30,31] They published methods for the isolation, derivative formation and analysis of human adult and infant urinary steroids, serum (or plasma) and urinary sugars and sugar alcohols, serum and urinary acids, serum acids of the Krebs cycle and related compounds, and many acidic and neutral drugs and drug metabolites. Methods for amines were under study. The isolation was done by solvent extraction, ion-exchange, column or thin-layer chromatography, or enzymic or chemical hydrolysis. This step can be considered as a low-resolution high-capacity method for the separation of classes of compounds. Horning's group discussed several derivative-formation procedures for the different classes. Their GCs were equipped with packed glass columns and an FID, MS, or electron-capture detector (ECD). The ECD was used for analysis of steroids which had been converted into halogenated derivatives.

Horning and his associates developed a system which utilized glass open tubular columns for the same type of analyses as those above.[32–34] They used a glass injection system which consisted of a packed precolumn and a gas-phase splitter. The precolumn provided complete sample evaporation before the splitter zone, trapped contaminating non-volatiles, and prevented decomposition or adsorption of components. They used a coating technique in which the liquid phase contained very fine particles of silaned silica powder.

Rutten and Luyten[35] worked with steroid analysis, using glass open tubular columns. They compared three types of pretreatment for the glass: etching, silaning, and surface-active agents. They found the use of a surface-active agent, with a static coating-procedure, to be the best method. The pretreatment of urine consisted of enzymatic hydrolysis and isolation and purification of the steroids by either a classical extraction technique or with Amberlite XAD-2 and Amberlyst A-26, and finally formation of methoxime trimethylsilyl derivatives. Approximately 35 peaks were detected with an FID in about 1 hr for the urine of a normal male.

Hutterer *et al.*[3] used a GC–MS–COM system to separate and identify metabolic products of low molecular weight in microlitre quantities of physiological fluids. Their samples were first deproteinated and silylated, a process which produced derivatives of amino-acids, sugars, organic acids, drugs, *etc.* The products were extracted and then separated on a packed glass column, the effluent being split between an FID and an MS. In one example of a blood-serum sample 46 chromatographic peaks were obtained in about 75 min. The number of peaks was increased by sorbing the non-polar components with Amberlite XAD-2 and eluting them with an organic solvent.

Amino-acid analysis can be done with GC as well as LC techniques. Tucker and Molinary[36] did this by using a modified method of Gehrke *et al.*[37] The sample (urine, plasma, or cerebrospinal fluid) was first passed through a cation-exchange column and then the amino-acids were converted into *N*-trifluoroacetyl n-butyl esters. The GC was equipped with two packed glass columns and dual FIDs. The instrumental time needed was about 1 hr.

Chalmers and Watts[38–40] developed methods for the quantitative extraction and GC analysis of urinary organic acidic metabolites. The acids were extracted by anion-exchange chromatography with subsequent freeze-drying of the extracted acids, conversion of the dry acids into volatile trimethylsilyl derivatives, and then GC analysis. Loss of some low molecular-weight acids was minimized by forming less volatile derivatives of these compounds before the freeze-drying. In a later article, Chalmers, Bickle and Watts[41] point out that the previous methods were unsatisfactory for short-chain aliphatic acids with between one and five carbon atoms. These acids were either lost by volatilization on freeze-drying or had trimethylsilyl esters that were eluted with the solvent and reagents used. These authors suggested an alternative method for these acids, using a cation-exchange column to remove metal ions and other cations and to release the free acid from its salt. GC analysis was then performed directly on the liquid. They claimed this method was better than solvent extraction[42,43] or steam distillation[44] because these methods were not quantitative for acids. The acids have an unfavourable partition coefficient between water and organic solvent. Steam distillation resulted in dilution of the acids by a factor of 4–5. This can be avoided, but the acid conditions necessary could cause artifact formation.

Gas chromatographic techniques for volatile compounds

Volatile compounds are convenient to determine because they require no pretreatment. However, standard analysis techniques for effluents have not so far been concerned with the volatile substances present. As a result, much useful information from this source has been ignored though more attention has been paid to it recently, especially to breath samples.

Zlatkis and co-workers published several articles along these lines. Zlatkis and Liebich[43] used liquid–liquid extraction for preparation of concentrates and GC–MS for the analysis of urine samples. The urine was extracted with ethyl ether, distilled at low temperature under reduced pressure, and concentrated

to a few microlitres. The GC column was a 150 m × 0.5 mm inner diameter stainless-steel capillary coated with Dowfax 9N15. A longer column was used in connection with the MS. The GC–MS interface was a two-stage jet molecular separator of the Becker–Ryhage type. Approximately 300 compounds were separated, 40 of which were identified by MS. The extraction method was compared with high-vacuum distillation of urine; very little difference was observed. Characteristic components included dimethylsulphone, pyrrole, 4-heptanone, allyl isothiocyanate, several alkyl furans, ketones, and lactones. Semiquantitative data were obtained by measuring the peak areas in the chromatograms and by adding known amounts of identified components to samples before isolation. The concentration of the components ranged from 10 to 100 μg in a 24-hr urine sample. Differences between the chromatograms of the various samples were primarily quantitative in nature. Some components were invariably found in high concentrations while others were much more variable. However, chromatograms from an individual remained fairly constant over a three-month period. This indicated that perhaps these variations are characteristic of the individual rather than a result of diet. Zlatkis and Liebich reported that preliminary results from subjects on a chemically defined low-bulk diet (Vivonex) showed that the chromatograms from an individual do remain relatively unchanged.

Later Zlatkis and co-workers began using an isolation technique from flavour research, viz, headspace analysis, and adsorption on the porous polymer "Tenax".[45–47] The headspace above a urine sample at 100° was swept with helium and the gases passed through a water condenser and trapped on the Tenax column. In some cases ammonium sulphate was added to increase volatilization. The Tenax was then transferred to a modified injection port and the components were thermally desorbed onto a cooled pre-column. The analytical column was a 100 m × 0.5 mm inner diameter nickel capillary coated with either "Emulphor ON 870" or "Emulphor-O"; both are polar liquid phases. Detectors used were an FID, a flame-photometric detector (FPD), and/or an MS. The analysis time was about 2.5 hr and total time required was less than 4 hr. Multiple sampling and evaluations of storage conditions and container size all showed similar profiles. Fifty-one components of urine were identified by MS, including ketones, alcohols, aldehydes, pyrroles and pyrazines. Twenty-five of these compounds were also found when extraction with diethyl ether was used. Many deviations were probably due to increase in the sample concentration caused by the adsorption technique. Dimethylsulphone, a major component found by the extraction method, was not detected by the headspace method, whereas a number of isomeric hydrocarbons were.

The system was also used for breath profiles.[46] Samples taken on two different days and consisting of 50 exhalations from a subject breathing ultrapure air were analysed. Profile differences could easily result from substances taken into the mouth as well as from decay products caused by oral bacteria. No attempt was made to identify the components.

Zlatkis *et al.*[48] also used the system for the analysis of volatiles from serum and plasma. Chromatograms were obtained in approximately 1 hr and were not as complex as those for urine. Characteristic components in serum were ethanol, 4-methyl-2-pentanone, hexanal, 1-butanol, 2-hexanol, 2-heptanone, and benzaldehyde.

Liebich and Al-Babbili[49] studied some of the parameters involved in a system such as the one described above. They studied the effects of the temperature of the cooling water, the desorption temperature, and the sampling temperatures and time. They recommended the following: cooling water temperature 12°, desorption temperature 300°, and sampling at a temperature of 90° for 1 hr.

Recently Zlatkis and Andrawes[50] used diethyl ether extraction and concentration on glass wool for analysis of volatiles in serum. The chromatograms obtained by this method were as complex as those obtained by other concentration methods.

Pauling and co-workers analysed volatiles from urine and breath by high-resolution techniques.[51–53] The urine sample was kept at pH 7 with a phosphate buffer. Samples were concentrated by headspace collection and a cold-trap. The column was a 1000 ft × 0.03 in. inner diameter stainless-steel capillary coated with SF 96 silicone oil. The detector was a modified FID. The major change in the detector was use of a platinum cylinder topped by a platinum-rhodium mesh cone as an ion-collector. This system permitted the quantitative determination of approximately 280 substances from urine vapour in 6 hr and 250 from breath in 2.5 hr. Integration, peak-matching, and various statistical pattern-recognition procedures were performed by computer. These investigators fed their subjects on Vivonex for several days before analysis. A relative standard deviation of about 10% was found for measurements of individual peaks repeated on successive days, whereas for a regular diet the fluctuations were several times larger. Pauling *et al.* described an automatic system controlled by computer.[52] They claimed that this apparatus was suitable for the routine analysis of about 200 volatile components of human urine. Up to 350 compounds could actually be counted on a chromatogram but many of them were (1) not present in most urine samples or (2) inadequately resolved, or (3) lost to a variable extent in the urine vapour procedure so that large errors occurred in their measurement.

Hartigan *et al.*[54] designed and used a nitrogen-sensitive thermionic detector as well as an FID for the analysis of urine volatiles. Headspace collection and 2 mg of Tenax GC adsorbent were used for isolation of the volatile components. The column was a 55 m × 0.22 mm inner diameter glass capillary coated with SF 96 silicone oil. Analysis time was about 2

hr. Novotny *et al.*[55] later extended the range of samples to include urine, serum and cerebrospinal fluid. They also analysed urine samples after treatment with β-glucuronidase and sulphatase which cleave glucuronides and sulphates. Two liquid phases of differing polarities, Emulphor ON-870 and SF 96, were used. McConnell and Novotny[56] described the automation of their system and discussed the reporting of retention data. They recommended selecting one peak out of a profile as a reference and reporting the retention times relative to it.

Conkle[5] wrote his dissertation on the GC–MS analysis of breath samples for organic and inorganic compounds. In one series of experiments a rebreathing system was employed which accomplished a twofold increase in concentration. The GC columns were packed 1/8-in. stainless-steel tubes and the detectors used were FID, ECD, thermal conductivity, and MS. Seventy-two compounds were separated and 69 were identified by MS. Their production rates were also determined. Four compounds, freon, methylchloroform, 1-butene and ethanol, were found in all of the samples and 14 compounds were found in 80% of the samples. A significant number of compounds were contaminants from the collection system.

Stoner, Cowburn and Craig[57] examined the volatile metabolites in plasma. Solvent extraction was used for concentration. A GC equipped with packed glass columns and an FID was used for separation and detection. In an hour, 21 peaks were eluted, four of which were incompletely resolved from the solvent peak. Recovery of ^{14}C-napthalene, the internal standard, was found to be 95% by scintillation counter.

Concentration techniques

In the methods for volatiles reviewed above, several concentration methods were used. Many researchers have evaluated these and other techniques; some of their conclusions are given here.

Novotny *et al.*[55] compared cryogenic trapping, freezing of the sample in an empty tube, direct injection into a capillary column, and adsorption on a polymer. The first two methods have problems associated with water interference, solvent impurities, and formation of artifacts. On-column cryogenic concentration is technically difficult because of the large volumes of gas used and is limited to stationary phases which stay liquid at low temperature. Bellar and Lichtenberg[58] commented that liquid/liquid extractions with organic solvents provide erratic or low extraction efficiencies. Large detector-responses to solvents and solvent impurities could cause serious interferences.

Of the adsorbents available, most of the common ones, silica gel, alumina, charcoal, *etc.*, have excessive surface activity toward many organic compounds and have high affinity for water. Novotny *et al.*[55] examined Tenax (or Tenax GC), poly(2,6-diphenyl-*p*-phenylene oxide), for its usefulness as a GC adsorbent. They examined the effect of water, losses due to irreversible adsorption, and explained qualitative and quantitative changes in chromatograms when different sampling techniques were used, on the basis of frontal and displacement chromatography and selective properties of the adsorbent. They concluded that Tenax was a suitable adsorbent for a wide range of both polar and non-polar organic compounds. However, there was considerable dependence on sampling technique, so quantitative and sometimes even qualitative data must be treated with caution.

Zlatkis *et al.*[45] examined three different adsorbents: "Porapak" P, "Carbon Molecular Sieve", and Tenax. They found Tenax to be the best because of its high temperature stability (upper limit 375°).

Bellar and Lichtenberg[58] used a dynamic system in which a purge gas was bubbled through the sample, rather than collection of headspace gases for the analysis of volatiles in water. This should quantitatively remove the water-insoluble volatiles from the sample and thus provide a direct measure of their original concentration in the aqueous phase. Water-soluble compounds were only qualitatively transferred. They found the method applicable to organic compounds with a solubility of less than 2% in water and with boiling points less than 150°. They tried several adsorbents: silica gel, Porapak Q, "Chromosorb" 103, and Tenax. Chromosorb 103 and Tenax were found to be most satisfactory but they used Tenax because of its higher temperature stability.

Versino, de Groot and Geiss[59] cited the following advantages for the dynamic enrichment on adsorption columns: (1) the adsorbed compounds can be thermally desorbed; (2) the adsorption and desorption procedures can be easily automated; (3) the dynamic enrichment allows the complete adsorption of substances having a retention volume lower than the sample volume passing through the adsorption column, and for more volatile compounds an equilibrium concentration is established that is proportional to the concentration in the original sample; (4) the sampling can be performed *in situ*. They found that for Tenax the adsorption and desorption efficiencies were better than 90% for different classes of compounds, both hydrophobic and hydrophilic. Columns conditioned at elevated temperatures under a continuous flow of gas had a tendency to produce peaks belonging to the biphenyl, n-terphenyl and triphenylene class. This was alleviated by filling the column with nitrogen, then stopping the gas-flow, at elevated temperatures. This allowed the polymer to form cross-links.

Butler and Burke[60] studied Tenax, Chromosorb 101 and 102, and Porapak P, Q, R and T. Their conclusions were that Porapak Q and R had the best overall sampling capacities as measured with acetonitrile. t.-butanol, methyl-ethyl ketone and benzene as molecular probes. They recommended Tenax for high-boiling components because of its high temperature stability and low retention volumes. They said

that work was under way on the use of pellicular beads as adsorbents.

Mass spectrometry

As seen above, the components in a profile are identified almost exclusively by MS. The small sample size required with open tubular columns makes other techniques impractical. One of the basic problems with GC–MS systems is interfacing the GC column effluent, which contains primarily carrier gas, with the reduced pressures of the MS. Several methods have been used for this.[61,62] For open tubular columns direct coupling is possible.[63–65]

Fales *et al.*[66] compared various ionization techniques available for use with biologically important compounds. Electron impact is normally used, but chemical ionization, field ionization, and field desorption also have their applications. Gordon and Frigerio[67] discussed the use, in biological research, of mass fragmentography, *i.e.*, the simultaneous monitoring of one or more fragment ions, rather than the conventional scanning of the total ion spectrum.

Waller[68] edited a book on biochemical applications of MS. Topics discussed were MS in instrumentation, including coupling of GC with MS, computerization of MS data, and various applications. Henneberg *et al.*[69] and Novotny *et al.*[62] also reviewed the use of computers in GC–MS work.

Open tubular columns

Open tubular columns have separation efficiencies per unit of length similar to those of packed columns but their relatively low pressure drops allow the use of much longer lengths. The longer columns result in greatly enhanced resolution. There are two types of open tubular columns, wall-coated (WCOT) and support-coated (SCOT) columns. The WCOT columns have a liquid phase coated on the inside of the column whereas the SCOT columns have the walls of the tubing coated with a support material which is then itself coated with a liquid phase. In practice the SCOT columns give better separation of compounds with low boiling points whereas WCOT columns are better for compounds with high boiling points. Ettre[70] predicted this behaviour from theoretical considerations.

Inner tubing diameters ranging from 0.01 to 0.03 in. have been used. The larger diameter columns can accommodate larger sample sizes and they reduce the danger of plugging during the coating procedure, but they do so at the sacrifice of efficiency. Longer columns must be used to obtain comparable resolution.

Glass may eventually become the tubing material of choice for biological samples; however, it does have drawbacks, including fragility, difficulty in the adhesion of a liquid phase, and short usable life of the liquid phase. Several authors have discussed the use and preparation of glass open tubular columns.[71,72]

METABOLIC PROFILES

An increasing number of diseases are being recognized as products of a metabolic disorder that is the result of some defect in biochemical processes. Some 150–200 of the known genetic disorders are single-gene diseases and are inborn errors of metabolism in the strict sense. About 0.3% of live births show these single-gene diseases. Since a few thousand enzymes and structural proteins are known, it is likely that the 150–200 known inborn errors are only part of the total number. Inborn errors affecting enzyme activity will usually result in an accumulation of substrate or substrate derivatives and a decreased amount of product or substances derived from the product. If the accumulated compounds are small molecules and are water-soluble, they will probably show high concentrations in the blood, urine or breath. Accumulation of high molecular-weight compounds that are sparingly soluble in water will usually give rise to storage diseases.[73] With the high-resolution analyses now available these inborn errors of metabolism can be detected with greater efficiency.

Jellum *et al.*[28] used their GC–MS system for (1) the finding of normal metabolites of unknown metabolic origin, (2) the discovery of new, unknown metabolic disorders, and (3) the diagnosis of known metabolic disorders. They could detect 70 of the known metabolic disorders and they discovered five new disorders.[73] Many different researchers have studied specific metabolic disorders.[3,36,42]

Other disease states can also be determined with these high-resolution systems. These cases may not be easily diagnosed because relatively small changes in profiles occur. Jellum *et al.*[27–29] did work on various types of cancer, hepatic disorders, ketosis (*e.g.*, patients in a diabetic coma), metabolic acidosis and alkalosis, and toxic products produced on sterilization of intravenous nutrition. Horning *et al.*[34] characterized normal and pathological states of steroids and studied the developmental changes of steroids in the newborn. Zlatkis *et al.*[45] studied patients with diabetes mellitus. Subjects being treated with insulin had high concentrations of pyrazines, cyclohexanone, lower aliphatic alcohols and octanols. Liebich and Al-Babbili[49] and Liebich[74] also studied patients with diabetes mellitus and undergoing different treatments and found abnormal concentrations of fiver lower aliphatic alcohols and two ketones. There was, however, considerable variation between different stages and forms of the disease.

These analytical systems could also be used for the determination of toxic or noxious compounds,[75] including drugs[30,31,34,76] and alcohol[77,78] and in the analysis of compounds occurring in minute quantities.[27]

Orthomolecular medicine is defined as the preservation of health and treatment of disease by maintaining the optimum concentration of essential substances. In the past the practice of orthomolecular

medicine has been a trial-and-error procedure. High-resolution systems could make quantitative the determination of many components that are necessary for this kind of treatment.[51]

CONCLUSIONS

The use of high-resolution gas and liquid chromatographic and associated ancillary techniques has rapidly developed highly sensitive and selective tests for a seemingly endless array of physiological disorders. Many of these, *e.g.*, inborn enzyme errors, have until recently been totally unknown in origin. However, such analyses are often only qualitative, or pseudo-quantitative for relatively few components. The tremendously large number of compounds which can be simultaneously determined in a given body-effluent sample, especially urine, makes GC metabolic profiles uniquely suitable for population-screening tests, as demonstrated by Pauling[79] in his work with quantitative chromatographic analysis in orthomolecular medicine. Important future application of

Table 1. Methods for metabolic profile determination

Subject	Technique	Topic	References
Profile analysis	Reviews		10, 12, 13
	Liquid chromatography	amino-acids	22–24
		automated analysis	14, 17, 18
		book	25
		carbohydrate determination	14
		dietary influences	26
		organic acids	21
		serum analysis	14, 20
		urine analysis	14–16, 19–22, 24
	Gas chromatography for non-volatiles	amino-acids	30–34, 36, 37
		biopsy samples	11, 27–29
		glass open tube columns	32–35
		organic acids	38–41
		plasma	36, 37
		serum	3, 11, 27–34
		steroids	30–34
		sugar alcohols	30–34
		sugars	30–34
		urine	3, 11, 27–34, 36, 41
	Gas chromatography for volatiles	breath	5, 45–48, 53, 97, 98
		cerebrospinal fluid	54, 55
		cold traps	51–53
		extraction	43, 45, 47
		mass spectrometry	43, 61, 62
		plasma	57
		porous polymer	45–48
		serum	50, 54, 55
		urine	43, 45–48, 54, 55
	Concentration	cryogenic trap	55
		extraction	43, 45, 58
		porous polymers	45–48, 55, 58–60
		solid adsorbents	45, 55, 58–60
	Mass spectrometry	biochemistry	68
		fragment identification	67
		gas chromatography	43, 61, 62
		high capacity pumps	82, 83
		molecular separators	80, 81
		open tubular columns	63–65
		reviews	62, 69
	Open tubular columns	glass columns	71, 72
		mass spectrometry	65
		SCOT and WCOT columns	70
Metabolic profiles and disorders		acidosis	27–29
		alkalosis	27–29
		alcohol	77, 78
		cancer	27–29
		diabetes	45, 49, 74
		drugs	30, 31, 34, 76
		hepatic disorders	27–29
		ketosis	27–29
		noxious compounds	75
		"orthomolecular" medicine	51, 79
		pattern recognition	90–93
		urine profiles	3, 28, 36, 42, 73

organic-component analysis of body effluents will undoubtedly be made in adapting these techniques to routine health-screening tests, but at present formidable problems exist. Regardless of whether low dead-volume[80,81] molecular separators or high-capacity pumps[82,83] are used in mass spectrometers, the extremely small sample required, widely varied component concentrations (often ranging over several order of magnitude) and ultrahigh time-resolution capabilities of modern capillary gas chromatographs necessarily result in loss of reliability in mass spectrometric data for component identification. For efficient process-control, data-accumulation, work-up, storage, and screening-correlations, highly complex integral computer systems become an essential requirement.[65] Manual data-evaluation of component retention-times and response-values is necessarily precluded for screening populations, because of the sheer bulk of data to be handled. Commercial software is available for computer-aided data-evaluation. Statistical computations[84–89] and pattern-recognition techniques offer [90–93] promise in streamlining classification of metabolic profiles or "fingerprints" as indicators of various physiological disorders. The necessity for preadministration of synthetic standard (*e.g.*, Vivonex) diets[51–53] over a period of several days makes it rather cumbersome to use metabolic profiles in screening, but may prove to be well worth the extra effort (compared to that needed for present automated multichannel chemical tests) when the utility of simultaneous, multicomponent body-fluid analyses is more widely realized.

The most advanced as well as the most common form of breath analysis to date is probably the test for ethyl alcohol.[94–96] However, a wide array of clinically significant components has been determined in breath, including volatile metabolic products, common drugs, anaesthetics, respiratory gases, and environmental air pollutants. The physiological aspects of breath-sampling have been outlined very well in a review by Dubowski,[10] but the most serious limitation, namely environmental contamination, to applications of breath profiles in health-related problems, was omitted. Breath analysis will be more adequately developed in future work, because it offers unique advantages as a biological sample. Among these are that it is simple to collect, it may be repeatedly sampled over a short period, it does not require elaborate preseparation steps, and its collection is not traumatic, even for children.[97] The promise of breath analysis is that it can provide information not available from urine analysis. Differences and difficulties in analysis may arise for several reasons: (1) daily variations in individuals' metabolism may be significant and may affect breath and urine differently; (2) the urine components are present in much larger quantities; (3) the lungs are more liable to be affected by atmospheric contamination; (4) the breath components are present in such small quantities that contamination from the sampling system itself is likely; (5) bacteria in the oral cavity may produce volatile organics which are not necessarily present in urine but may be in breath; (6) variations between individuals are unresolved; (7) diet effects on breath and urine are unresolved; (8) breath analysis reflects those components which readily pass the alveolar-pulmonary membrane in contrast to those filtered by the kidneys; (9) digestive processes may affect breath relatively more than urine, as has been observed for hydrogen[97] and other gases.[98]

Breath and urine remain exciting areas for research in clinical chemistry since their full potential has yet to be tapped.

The information in Table 1 summarizes the major references.

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MANIPULATIONS, pM′–pH DIAGRAMS AND ACCURACY IN DETERMINATION OF METALS*

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Summary—Manipulations done with metal ion solutions can influence the accuracy of a determination. During a manipulation, when a non-homogeneous solution in a non-equilibrium state is dealt with, polynuclear hydroxide compounds and/or a hydroxide precipitate may be formed, which generally do not immediately disappear after homogenization of the solution. Deviations from the equilibrium state that is expected after homogenization, may not be negligible during the subsequent analysis. A part of the metal content escapes determination and systematic errors arise. The magnitude of the error depends upon the nature of the particular metal to be determined and the manipulations performed. The influence of the manipulations can be understood and foreseen by studying the behaviour of the metal ions in solution by means of a pM′–pH diagram. In this diagram regions can be indicated where the experimental conditions correspond to the formation of a hydroxide precipitate and polynuclear hydroxide complexes. The momentary state of the solution during a manipulation can be represented by a point. This point changes its position as the manipulation proceeds, describing a locus through the diagram. The locus depends upon the initial conditions and the particular manipulation performed. If the locus penetrates one of the "error" regions, the corresponding compounds will be formed and the error of the determination will increase. Conversely, if the locus is adapted so as to avoid penetration of the regions for polycomplexation and precipitation, the error is found to decrease remarkably.

Traditionally, chemical research is largely empirical, with an initial guess investigated experimentally, and the process improved by consideration of the results, *i.e.* optimization by feed-back. This approach is not in itself wrong, but it can be considerably shortened by proper use of chemical knowledge.

Consider complexometry for example. Procedures for moderately concentrated metal solutions ($10^{-2}M$) are easily found simply by trial and error because the experimental conditions can be varied between wide limits without affecting the results. When dilute solutions are dealt with, however, the choice of factors such as pH, buffer concentration and indicator is much more restricted, making the chances of finding the optimum conditions solely by trial and error rather small. In general a systematic theoretical approach is necessary, followed by an experimental check of the validity of its predictions. However, this experimental check is itself often invalidated by manipulative errors, as the experimentalist is insufficiently aware of the correlation between the accuracy of an analysis and the manipulation history of the solution tested. This holds for all techniques in which metal ion solutions are used, and in general a strict scheme of manipulation has to be followed when such a solution is prepared for a particular analysis.

The origin of the errors is the formation of polynuclear hydroxide complexes and/or a hydroxide precipitate during and just after certain manipulations performed on an initially homogeneous solution at equilibrium. If a reagent solution is added, a non-equilibrium situation will be created because of the concentration gradients between the reagent and the solution it is entering, no matter how efficient the stirring. If localized conditions correspond to those necessary for formation of polynuclear hydroxide complex or a precipitate, these compounds will be formed at least partly, and may persist in the system even after the solution has been mixed thoroughly enough to be thought homogeneous, even though the final conditions do *not* correspond to the formation of the complex or precipitate. In such a case, which occurs much more often than we are aware of (especially when the compounds concerned have low reactivity or exhibit inert behaviour), a fraction of the metal content will escape determination in the subsequent analysis.

The proof of this is that the accuracy increases when the manipulations are conducted in such a manner that such conditions do not arise in the solution.

This phenomenon was first encountered with the complexometric titration of aluminium[1] and tin.[2] Later, remarkable improvements were made in the determination of bismuth, thorium, zirconium and the rare-earth elements by applying the same ideas. It was found that even in the standardization of dilute EDTA solutions with copper the error can be decreased from above 1% to less than 0.3% by taking

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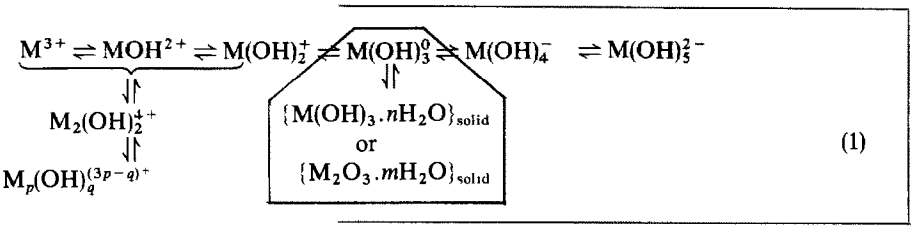
into account the precipitation phenomena. This paper describes the necessary theory.

An exact description of what happens as a consequence of a particular manipulation is neither possible nor necessary. It is sufficient to study the metal hydroxide equilibrium system, which is best done by use of logarithmic diagrams, in which the influence of side-reactions between the metal ion and other ions present in the reaction medium can also be incorporated. Side-reactions of this kind that lead to precipitate formation will not be considered here, however.

pM–pH DIAGRAMS

Consider a medium in which hydroxide formation is the only reaction in which the metal ion is involved, and for argument's sake suppose the ion to be tervalent, M^{3+}. The reaction scheme for hydroxide formation can be set out as below.



(1)

The system has two independent variables; the concentrations of the various species depend on both the total concentration of M and the pH. If an additional demand is set, only one degree of freedom remains, a relationship exists between the metal-ion concentration and pH, and a curve can be drawn on the logarithmic diagram, reflecting the particular demand. In what follows we shall be concerned with the borderline for maximum solubility, and the conditions under which not more than 1% of the metal ion is present as a polynuclear hydroxide complex.

According to Ringbom,[3] a system of co-existing equilibria can be divided into a main reaction [in our case the enclosed part of scheme (1)] and the competitive side-reactions, covering all other reactions. The total concentration [M′] of the metal ion that is not involved in the main reaction is a much more suitable working parameter than the concentration $[M^{3+}]$ of free metal ion and is related to it[3] by Ringbom's side-reaction coefficient: $\alpha_{M(X)} = [M']/[M^{3+}]$. If OH^- is the only side-reaction component we have

$$\alpha_{M(OH)} = ([M] + [MOH] + [M(OH)_2] + \cdots + 2[M_2(OH)_2] + \cdots)/[M] \quad (2)$$

(charges will be omitted for convenience and greater generality).

For convenience, we will restrict ourselves for the moment to the case where polycomplexation does not occur to a measurable extent, which always happens when [M′] is small enough.

For the reaction

$$M + iH_2O \rightleftharpoons M(OH)_i + iH \quad (3)$$

the overall stability constant $*\beta_i$ is introduced in accordance with the IUPAC notation:[4]

$$*\beta_i = \frac{[M(OH)_i][H]^i}{[M]} \quad (4)$$

Substitution of this equation in equation (2) and omission of the polycomplex terms gives:

$$\alpha_{M(OH)} = 1 + 10^{(pH + \log *\beta_1)} + 10^{(2pH + \log *\beta_2)} + \cdots 10^{(mpH + \log *\beta_m)} \quad (5)$$

We can call this α_{mono}. Generally, because of the form of equation (5), the pH-range can be divided into distinct regions in each of which one of the hydroxide complexes predominates, and for which $\alpha_{M(OH)}$ can be approximated by the corresponding term in equation (5):

$$\log \alpha_{M(OH)} \simeq (ipH + \log *\beta_i) \quad (6)$$

$$(i = 0,1,2,\cdots m; \log *\beta_0 = 0)$$

giving a series of straight lines on a graphical representation of log α *vs.* pH (see Fig. 1), the curve for $\log \alpha_{M(OH)}$ *vs.* pH being the rounded-off line connecting the line-segments corresponding to the highest values of log α. Note that the difference between the curve and the straight lines is generally smaller than log 2, and cannot be larger than log m; in practice it is thus negligible in comparison with the usual uncertainties in $\log *\beta_i$. The straight lines can be regarded as acceptable approximations.

When polynuclear complexes with the general formula $M_p(OH)_q$ are formed in solution the system of straight lines outlined above can be supplemented with lines corresponding to these polycomplexes. The stability constant of the complex can be defined as

$$*\beta_{q,p} = \frac{[M_p(OH)_q][H]^q}{[M]^p} \quad (7)$$

(note the reversal of p and q in accordance with IUPAC notation). Introduction of (7) into the general formula (2) for the side-reaction coefficient leads to the addition of the term

$$\Sigma \frac{p[M_p(OH)_q]}{[M]} = \Sigma p \frac{*\beta_{qp}[M]^{(p-1)}}{[H]^q} = \alpha_{poly} \quad (8a)$$

to the total side-reaction coefficient:

$$\alpha_{M(OH)} = \alpha_{mono} + \alpha_{poly} \quad (8b)$$

There are two possibilities. The first is that the mononuclear complexes predominate, in which case α_{poly} can be neglected and equation (6) can be used for α_{mono} as before. The second is that α_{mono} can be neglected, and then replacement of [M] in equation (8a) by $[M']/\alpha_{M(OH)}$ gives:

$$\alpha_{poly} = \Sigma p {}^*\beta_{qp}[M']^{(p-1)}/[H]^q \alpha_{M(OH)}^{(p-1)} \qquad (9a)$$

If only one complex is formed, then

$$\log \alpha_{poly} = \log \alpha_{M(OH)} = \left(\frac{q}{p}\right)\mathrm{pH} + \left\{\frac{\log {}^*\beta_{qp} + \log p}{p}\right\} + \left(\frac{p-1}{p}\right)\log [M'] \qquad (9b)$$

This equation leads to a set of parallel straight lines in the $\log \alpha$ *vs.* pH diagram, dependent on the total concentration of metal M involved in the side-reactions. When more than one polynuclear complex is formed, every such complex gives rise to a set of straight lines corresponding to equation (9b). It should be noted that equation (9b) also holds for the mononuclear complexes ($p = 1$) and thus can be regarded as the general formula for the straight lines in the $\log \alpha_{M(OH)}$ *vs.* pH diagram. In Fig. 1 $\log \alpha_{poly}$ is drawn for different scandium concentrations. The binuclear hydroxide $Sc_2(OH)_2^{4+}$ is predominantly formed only at scandium concentrations above $10^{-3}M$.

Equations (9a) and (9b) can be used to derive the borderlines for precipitation and 1% polycomplexation, as follows.

Precipitate formation

For a metal ion M^{n+} a precipitate of the general composition $M(OH)_n$ is formed when the limiting concentration of this compound is exceeded. This concentration may be expressed as

$$[M(OH)_n]_{max} = {}^*K_{sn} \qquad (10)$$

which can be combined with equation (4) to give the well-known formula for the solubility product:

$$\frac{[M^{n+}]_{max}}{[H]^n} = {}^*K_{sn}/{}^*\beta_n = {}^*K_{s0} \qquad (11)$$

From this equation $[M^{n+}]$ can be removed by substituting $[M']/\alpha_{M(X)}$ for it. This leads to the general formula for the borderline of the precipitation region, holding also in the presence of a ligand X

$$p[M']_{max} = -\log {}^*K_{s0} + n\,\mathrm{pH} - \log \alpha_{M(X)} \qquad (12)$$

Assuming that hydroxide formation is the only side-reaction taking place in solution, we can substitute equation (5) in (12). However, knowing that $\alpha_{M(OH)}$ can be split into separate terms for distinct pH-regions, we can do the same here and substitute equation (9b) in equation (12), obtaining

$$p[M']_{max} = (np - q)\mathrm{pH} - (p\log {}^*K_{s0} + \log {}^*\beta_{qp} + \log p). \qquad (13)$$

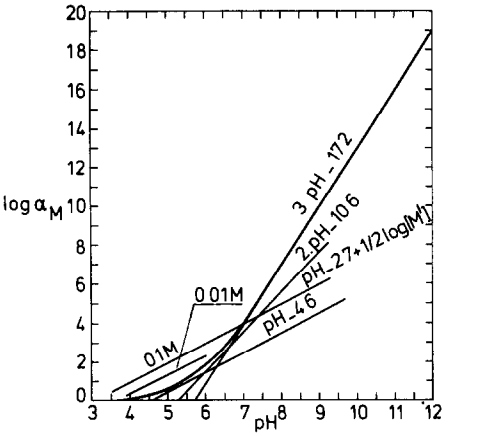


Fig. 1. $\log \alpha_{M(OH)}$ *vs.* pH for scandium, calculated with $\log {}^*\beta_1 = -4.6$, $\log {}^*\beta_2 = -10.6$, $\log {}^*\beta_3 = -17.2$, $\log {}^*\beta_{22} = -5.8$, $\log {}^*\beta_{43} = -14.0$ and $\log {}^*\beta_{53} = -17.5$. The exact curve (without polycomplexation) and the straight-line approximations are drawn, as well as the straight lines for the polycomplex $Sc_2(OH)_2$ at total scandium concentrations of 0.01 and 0.1*M*.

Equation (13) represents a linear relation between pM′ and pH, so in the pM′–pH diagram we get a number of straight lines. The curve for log pM′ is the rounded-off line connecting the line-segments corresponding to the *lowest* pM′-values [note the negative sign of log α in (12)]. The curve can be calculated more exactly by using the logarithm of equation (9a). In Fig. 2 the exact precipitation borderline is drawn for Sc, together with the straight lines from (13). If we take into account the uncertainty in the data used for the calculations, it is obvious that approximation by rounding-off the straight lines is adequate for most purposes.

Polynuclear complex formation

The concentration borderline for precipitation differs in principle from that for polycomplexation. The first is theoretically a sharp boundary, the second is not, so we have to stipulate a concentration restric-

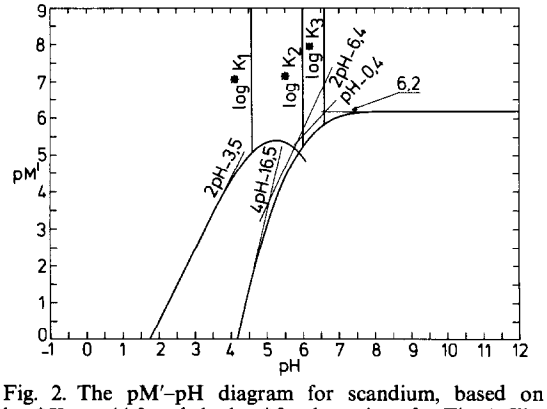


Fig. 2. The pM′–pH diagram for scandium, based on $\log {}^*K_{s0} = 11.0$ and the $\log {}^*\beta$ values given for Fig. 1. The precipitation borderline and 1% borderline for the polycomplex $Sc_2(OH)_2$ are given together with the straight-line approximations. The $\log {}^*K_i$ lines are also drawn, indicating the predominance regions for monocomplexes $Sc(OH)_i$ ($i = 0,1,2,3$).

tion for inert polycomplexes which may be formed. We may assume that polycomplexes will not interfere when less than 1% of [M'] is in the form of a polycomplex; at the most 1% of M then escapes from the quantitative analysis. Further restriction to a 0.1% limit shifts the line only a few tenths of a log unit. This restriction can be expressed mathematically as

$$\frac{p[M_p(OH)_q]}{[M]} < \frac{10^{-2}[M']}{[M]} = 10^{-2}\alpha_{mono} \quad (14)$$

By appropriate substitutions the general formula for the "1%-borderline" is found to be

$$p[M']_{1\%} = \left\{\frac{q\text{pH} - p\log\alpha_{mono}}{(p-1)}\right\} + \left\{\frac{\log {}^*\beta_{qp} + 2 + \log p}{(p-1)}\right\} \quad (15)$$

which gives a series of straight lines for various pH-regions as before. In Fig. 2 the borderline is given for the $Sc_2(OH)_2^{4+}$ complex. The line is mainly composed of two straight parts, pM' = 2pH − 3.5 and pM' = −2pH + 17.7. In the pSc'–pH diagram vertical lines are also drawn at $pH = p^*K_i = p^*\beta_i - p^*\beta_{i-1}$. These lines form the boundaries of the predominance regions of the $M(OH)_i$ species.

If other complexing species are present besides OH^-, the calculations become more complicated because $\alpha_{M(total)}$ will then depend on the concentration of these species as well as on [M'] and pH. This situation will be dealt with later.

MANIPULATION OF SOLUTIONS

The pM'–pH diagram is said to give information about equilibrium situations. But what does equilibrium mean when different data are found in the literature for "aged" and for "fresh" precipitates? The analytical chemist doing gravimetric analysis will be interested in a diagram with a line for the aged precipitate, but the analyst doing volumetric analysis will eschew even the faintest precipitate and so be interested in the line corresponding to the fresh precipitate only. Because of our interest in the behaviour of metals in solution, the pM'–pH diagrams in this paper have been constructed from data corresponding to media at 20° and an ionic strength of 0.05, and for fresh precipitates.

The importance of the diagrams is that a particular set of experimental conditions can be represented by a point P and that a locus is described by P as the conditions change during a manipulation. In the following, some common manipulations will be considered. The constants used were selected from the literature and corrected for the ionic strength and other parameters of the system. They were generally in good agreement with the critical values listed by Baes and Mesmer.[5]

Dilution

Suppose for example that 100 mg of scandium are dissolved in 1.5 ml of perchloric acid (1 + 1) which afterwards acts as an indifferent medium. The solution will be about 1 ml in volume and contain 2 mmole of Sc and 2 mmole of surplus perchloric acid. Thus to a first approximation p[Sc'] = −0.3 and pH = −0.3 (point P_0 in Fig. 3 corresponds to these values). When the solution is diluted homogeneously with water, [Sc'] and [H] change by the same factor; the same value has to be added to both p[Sc'] and pH. Point P shifts along a 45° line; a tenfold dilution shifts the experimental conditions to agree with point P_1 (Fig. 3). If the dissociation of water is taken into account, the dilution line will finally approach pH 7 asymptotically. The production of H^+-ions because of the hydrolysis of scandium is neglected; it causes only a slight shift of the line.

In practice, dilution will not occur homogeneously. Considering the solution in this non-homogeneous state it follows that the dilution factors will range from zero to infinity. If we divide the solution into a large number of small parts, each of which is different but itself approximately homogeneous, the points P_i corresponding to these parts will lie on or near the dilution line and be spread over the whole line. In the case of Sc the region of polycomplexation is penetrated (Fig. 3); in the case of Bi the precipitation region is also entered (Fig. 4).

Generally, polycomplexes and precipitates form rapidly, which means that these compounds are formed even during a short penetration of the regions.

After homogenization of the solution the points P_i will telescope to one final point which theoretically may lie outside the polycomplex and precipitation regions. However, the compounds have a low reaction velocity and the restoration of equilibrium does not take place completely within a reasonably short time. This is the reason for less accurate results being obtained. Its importance depends upon the accuracy desired, the reaction velocities and the particular technique used for the analysis. For instance, in atomic-absorption spectrometry polynuclear complex formation will seldom decrease the absorption signal. In complexometry both phenomena usually interfere.

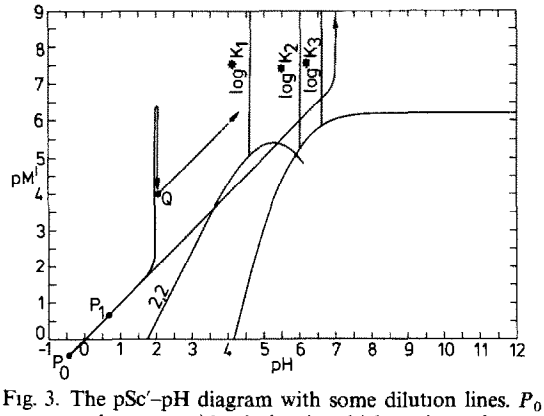


Fig. 3. The pSc'–pH diagram with some dilution lines. P_0 corresponds to an acid solution in which a piece of scandium has been dissolved, and P_1 to a 10-fold dilution of this solution.

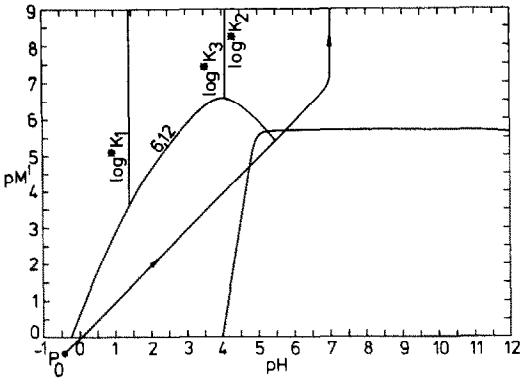


Fig. 4. The pBi'–pH diagram calculated with $\log {}^*\beta_1 = -1.40$, $\log {}^*\beta_2 = -5.45$, $\log {}^*\beta_3 = -9.50$ and $\log {}^*\beta_4 = -22.30$, $\log {}^*\beta_{12,6} = 0.33$ and $\log {}^*K_{s0} = 3.80$. The polycomplex region and precipitation region are penetrated by the line for dilution with water, starting from P_0 which corresponds to a solution obtained by dissolving a piece of Bi in a concentrated acid.

The question is in which way dilution interference can be prevented. If dilutions are made with 0.01*M* perchloric acid, the dilution line will asymptotically approach pH 2. If the dilution factor for Sc is 10^4, point *Q* in Fig. 3 is reached after homogenization. This medium can be diluted further with water without problems; the 45° line does not penetrate the polycomplex of precipitation region. From the diagram for tin(IV) (Fig. 5) it follows that when a strongly alkaline solution is diluted, precipitation will also occur. *P*, lying near the horizontal axis at pH 14, shifts along a 135° line towards lower pH and will penetrate the precipitation region at about pH 11. Aluminium in alkaline solution is present as $Al(OH)_4^-$, so the slope of the tangent of the precipitation borderline (which is always equal to the electric charge of the predominantly occurring ion) is equal to −1. In this case dilution will not cause precipitation: the dilution locus of *P* has the same slope (Fig. 6).

In Fig. 4, P_0 lies nearly at the 1% polycomplex borderline. If such a Bi solution is diluted with an acid solution of pH 1, the (6,12)-polycomplex region is penetrated and about 10% of the bismuth will be converted into $Bi_6(OH)_{12}$. It turns out practically that the $Bi_6(OH)_{12}$ complex completely dissociates on further dilution at the pH 1 level. Whether this is a matter of kinetics or inaccuracy in the polycomplex equilibrium constant and so in the line position, is not known at the moment, but a deeper penetration of the region to values above pH 3 always leads to inaccurate titration results with drifting end-points. The atomic-absorption results are also then less accurate.

In the case of tin(IV) the point P_0 near the origin lies behind the precipitation line, which agrees with the fact that when tin is dissolved in concentrated nitric acid precipitation occurs.

Dilution is one of the most common operations and will lead to specific problems for every metal. It also forms an integral part of many other manipulations but this is not always recognized. For instance when a tin(IV) solution is poured into a beaker that has just been rinsed and is still wet, some SnO_2 precipitates and an error of a few per cent will occur. Rinsing of a glass electrode after pH-adjustment, and adding a reagent solution which is not sufficiently acidic are other errors which can easily be committed unwittingly. When EDTA is added to a cold aluminium solution we deal almost solely with dilution during this manipulation, as EDTA hardly reacts with Al^{3+} at room temperature. This implies that the polynuclear hydroxide is formed, which—even on heating—reacts only slowly with EDTA, and a few per cent error can be expected. The remedy is acidification of the EDTA to pH 2.5 and homogeneous neutralization with hexamine by boiling.[1]

In many cases it is possible to find a suitable pathway to avoid error, but as the different manipulations are closely related, let us first discuss some of them individually.

Neutralization

Suppose that a strongly acidic concentrated metal solution at pH_{P_0} is neutralized homogeneously with a dilute solution of a strong base of $pOH = pC_{base}$. The first additions act like a dilution, so approximately a 45° line is followed near P_0. When the solution has been diluted by the factor $10^{(pC_b - pH_{P_0})}$ its pH approaches pC_b and the pH will change with a jump to a pH-value near $(14 - pC_{base})$, just as in an acid–base titration. Further additions act only as a dilution; the pH will asymptotically approach the value $(14 - pC_{base})$. Summarizing, we can say that the neutralization line consists of three parts: a 45° line through the starting point P_0, a horizontal part at the level $pM' = pM'_{P_0} + (pC_{base} - pH_{P_0})$ and a verti-

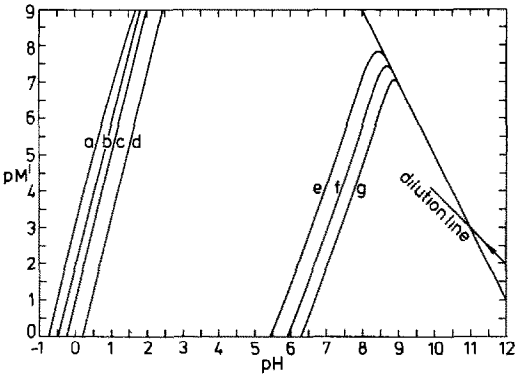


Fig. 5. The pSn(IV)'–pH diagram. The precipitation borderline *a* has been calculated with $\log {}^*\beta_1 = -1.0$, $\log {}^*\beta_6 = -22.0$ and $\log {}^*K_{s0} = -3.0$. Tin(IV) forms no polycomplexes as far as is known. The lines b, c and d correspond to chloride concentrations of 0.7, 1 and 2*M* respectively and have been calculated with $\log \beta_{SnCl_6} = 2.0$. The lines e, f and g correspond to EDTA concentrations of 10^{-4}, 10^{-3}, 10^{-2} and $10^{-1}M$ respectively, and have been calculated with $\log K_{SnY} = 34.50$. The dissociation constants of EDTA were taken as 10.34, 6.24, 2.75 and 2.07 for pK_4, pK_3, pK_2 and pK_1 respectively.

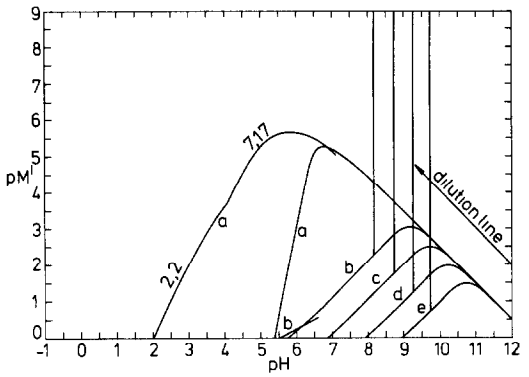


Fig. 6. The pAl′–pH diagram. The following hydrolysis constants have been used for the calculation of the precipitation and polycomplex borderline a: $\log {}^*\beta_1 = -4.3$, $\log {}^*\beta_2 = -9.3$, $\log {}^*\beta_3 = -15$, $\log {}^*\beta_4 = -22$, $\log {}^*\beta_{22} = -6.3$, $\log {}^*\beta_{15,6} = -47$, $\log {}^*\beta_{32,13} = -104.5$, $\log {}^*\beta_{34,13} = -97.6$, $\log {}^*\beta_{17,7} = -48.8$ and $\log {}^*K_{s0} = 9.50$. Three complexes were found to contribute to the 1% polycomplex borderline, namely the complexes (2,2), (7,17) and (13,34) of which the last only contributes just before the precipitation borderline. In view of the uncertainties in these constants only the first two complexes will be considered. The lines b, c, d and e correspond to EDTA concentrations of 10^{-4}, 10^{-3}, 10^{-2} and $10^{-1}M$ respectively and have been calculated with the stability constants $\log K_{\mathrm{AlY}} = 16.70$, $\log K^{\mathrm{H}}_{\mathrm{AlHY}} = 2.5$, $\log K^{\mathrm{OH}}_{\mathrm{AlYOH}} = 8.1$ and $\log K^{2\mathrm{OH}}_{\mathrm{AlY(OH)_2}} = 11.80$. The dissociation data for EDTA were those given for Fig. 5. The vertical lines indicate the pH limit above which the Al–EDTA complex is transformed into $Al(OH)_4^-$ to the extent of >1% in dilute solutions.

cal part at $pH = pH_{base} = (14 - pC_{base})$. (See *e.g.*, Fig. 7, branch II).

When the basic solution has a concentration higher than that of the acid solution at pH_{P_0}, the 45° line will not occur and the horizontal line starts immediately at P_0. So far we have considered homogeneous equilibrium situations, and should now consider what happens in practice between addition and homogenization, when we deal with non-homogeneous situations. The neutralization reaction can be regarded as proceeding instantaneously, and because diffusion takes place very slowly, it can be assumed that the neutralization and dilution phenomena are always close to equilibrium in individual sections of the solution. So just as for dilution we can assume here that the corresponding points P for small parts of the solution are statistically spread along the dilution line. Deviations from the line may be regarded as small. This means that the addition of a solution of sodium hydroxide will lead to a deep penetration of the precipitation region and that precipitate formation can be expected in most cases. Just as in dilution, the production of H^+-ions during the formation of soluble mono- or polynuclear hydroxides can be neglected in consideration of the position of the neutralization line; it will shift the line only a few tenths of a logarithmic unit.

The presence of anions of weak acids and bases has a large influence on the shape of the neutralization line, however. When, for instance, ammonia at a concentration C_{am} is added to a metal ion solution (pM'_{P_0}, pH_{P_0}) containing acetic acid at a concentration of C_{ac} and with P_0 near the origin, the following neutralization line will be approximately followed. When $pC_{am} > pH_{P_0}$, a 45° (dilution) line through P_0 will first be followed. At $pM' = pM'_{P_0} + (pC_{am} - pH_{P_0})$ a horizontal part starts. Near $pH = pK_{ac}$ (4.7) a vertical jump occurs as a consequence of the buffer action as the acetic acid is neutralized. The height of the jump depends on C_{ac} and C_{am} and can be approximated by $(pC_{am} - pC_{ac})$, *i.e.* the logarithm of the dilution factor and hence the amount by which pM′ increases. A further small addition of ammonia causes a horizontal jump through the "equivalence" point at pH = 7.1 until $pH \sim p^*K_{am}$ (9.4), the ammonia "half-titration" value. A further addition of ammonia largely dilutes the solution; the pH will slowly approach the value $pH = \frac{1}{2}(14 + p^*K_{am} - pC_{am})$ for a pure ammonia solution. (The second part of this path coincides with branch III in Fig. 7).

This example demonstrates how a pathway can be constructed in the pM′–pH diagram. It also shows how pM′-jumps can be generated by the addition of weak acids and bases, jumps that can be used to create alternative pathways in order to prevent unwanted hydroxide reaction. An overshoot of pH during the neutralization of acids can be prevented by using buffer solutions with a pH 1 unit higher than that of the equimolar buffer; 80% of the buffer capacity then remains available for neutralization. When even this procedure leads to too-high pH-values, use can be made of an acidified hexamethylenetetramine (hexamine) solution which releases ammonia on heating, thus neutralizing the solution homogeneously and controllably. The addition of solids should be avoided. In the vicinity of solids high local concentrations will occur, and with salts of weak acids extreme pH-values may arise.

SIDE-REACTIONS WITH OTHER IONS

In the theoretical section the side-reaction coefficient was taken as $\alpha_{M(OH)}$ for the construction of the pM′–pH diagram. When other ions are added to the solution, because of neutralization for instance, a contribution to $\alpha_{M(total)}$ can be expected. Considering all possible side-reactions is something of a labour of Sisyphus. We shall restrict ourselves to some examples of complexometric titrations.

When other ions X form predominating complexes with M, $\alpha_{M(X)}$ will be larger than $\alpha_{M(OH)}$, which implies that $p[M']_{max}$ will decrease and new lower-lying lines appear in the pM′–pH diagrams as the borderlines for precipitation and polycomplexation. In Fig. 5 the chloride and EDTA lines are drawn. It follows that tin metal can be dissolved in concentrated hydrochloric acid without the precipitation of SnO_2; point P_0 near the origin stays outside the SnO_2 region if the chloride concentration is $>2M$. If a solution with

[Cl] ~ 2*M* is diluted tenfold with 1*M* perchloric or nitric acid, the pH remains about 0, pM′ becomes 1 and [Cl] will be about 0.2 *M*. The result is that *P* now lies in the precipitation region as the borderline has shifted faster than *P*. If the solution is diluted with 1*M* hydrochloric acid, [Cl] gradually changes from 2*M* asymptotically towards 1*M*. Under these circumstances point *P* remains outside the precipitation region and no SnO_2 precipitate is formed. Tin(IV) can be determined complexometrically by a back-titration procedure, but the EDTA solution which is added should be acidified to pH = 0 and have [Cl] = 1*M*. (The concentration of EDTA has to be $< 7 \times 10^{-3} M$ because of precipitation of H_4Y.)[2] After addition of the EDTA, which quickly reacts with Sn(IV) at room temperature, we have to consider the EDTA lines in the pM′–pH diagram. It is known[2] that Sn(IV)–EDTA dissociates near pH 7, forming a precipitate. From this phenomenon we can calculate the lines in Fig. 5. The implication is that the strongly acidic Sn(IV)–EDTA solution should not be neutralized with a sodium hydroxide or ammonia solution. The best method is to add a solution of hexamine acidified to pH 5–6 (to prevent crossing the borderline during the addition) and then to heat the solution to raise the pH by hydrolysis of the hexamine. In this way very accurate tin determinations are possible.[2]

From the pM′–pH diagram for Cu it is obvious that neither a precipitate nor a polycomplex will be formed when a piece of copper is dissolved in nitric acid and the solution is diluted with water up to point (4,4) (Fig. 7, branch I). When sodium hydroxide is added to adjust the pH to 5.5 for the complexometric titration with TAR as indicator, a 4–5% error is found (branch II).

Addition of a dilute ammonia solution ($10^{-2} M$) also gives a penetration of the precipitation region under curve b (branch III). In practice an error of about 1% is found. The addition of enough concentrated ammonia gives an error of only 0.3% because the neutralization line passes over the lines e,f,g corresponding to ammine-formation. However, it is found experimentally that a few slips can still occur. Very accurate results are obtained when the solution is neutralized with a solution of acetate or hexamine of pH 6 (branch IV). It may also be mentioned that when an ammoniacal solution of copper ($10^{-2} M$) is titrated at pH 9.5 with trien (triethylenetetramine) with an ion-selective electrode used for the end-point determination, the trien should also be made ammoniacal. If not, then if the Cu–NH_3 solution is diluted locally with titrant by a factor of 10 the borderline shifts 4 log units upwards while point *P* at (2,9.5) shifts only 1 unit, and *P* is passed by the borderline (see Fig. 7). This explains the poor response of the electrode after a few determinations, because of the nearly irreversible hydroxide precipitation at the electrode surface.

The addition of EDTA to an aluminium solution has already been discussed. The pH can be slowly increased on heating if hexamine is added. When the Al–EDTA complex is completely formed and a final pH-adjustment is needed, it follows from Fig. 6 that in nearly all cases of practical interest ($C_{Al} < 10^{-2} M$) the neutralization line lies above the precipitation line, so no precipitate will be formed. However, the Al–EDTA still dissociates at high pH-values, forming $Al(OH)_4^-$ which only slowly reforms Al–EDTA on lowering of the pH. The formation of the soluble tetrahydroxo-complex leads to irregular results in this case.

In general it can be postulated that systematic errors may be expected when more than 1% of the metal–EDTA complex has been hydrolysed. This 1%-limit can mathematically be expressed as

$$\Sigma[M(OH)_n] = [MY]/100 \qquad (16)$$

whence, with

$$\alpha_{M(Y)} = 1 + [Y']K'_{MY} \sim [Y']K'_{MY} \qquad (17)$$

we can derive the equation

$$\log \alpha_{M(Y)} - \log \alpha_{M(OH)} = 2 \qquad (18)$$

For a given excess of EDTA present in the solution [Y′] is fixed and equation (18) can be satisfied at a definite value of the pH. In Table 1 a survey is given for some metal–EDTA combinations. Its importance is to make it obvious that the addition of complexing agents such as EDTA or DCTA does not always guarantee freedom from the errors that can arise during manipulations. Even when the precipitation region is not penetrated, systematic errors may be

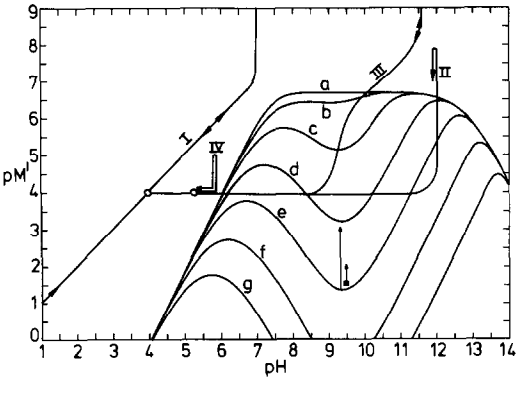


Fig. 7. The pCu′–pH diagram. Although some polycomplex data have been reported, no polycomplex line was found in calculations with these data. The precipitation borderline a is based on $\log {}^*\beta_1 = -8.0$, $\log {}^*\beta_2 = -14.8$, $\log {}^*\beta_3 = -27.3$, $\log {}^*\beta_4 = -40.4$ and $\log {}^*K_{s0} = 8.1$. The lines b–g correspond to ammonia concentrations of 0.01, 0.03, 0.1, 0.3, 1 and 3*M* respectively and have been calculated with $\log \beta^H_{NH_4} = 9.4$ and $\log \beta_{Cu(NH_3)_i} = 4.13$, 7.61, 10.54 and 12.60 for i = 1,2,3 and 4 respectively. Line I corresponds to dilution with water, and lines II–IV correspond to dilution with water to point (4,4) followed by neutralization with 0.01*M* NaOH, concentrated NH_3 solution, and acidified hexamine, respectively. The square dot illustrates precipitate formation in an ammoniacal solution of copper at pH 9.5 by a tenfold dilution with a medium not containing ammonia.

Table 1. The pH-limits for dissociation of metal–EDTA complexes (the concentrations of EDTA given are those of the excess present)

Species	Dissociation into a precipitate, 100% EDTA	Dissociation into soluble hydroxide complexes		
		$10^{-4}M$ EDTA	$10^{-3}M$ EDTA	$10^{-2}M$ EDTA
Ag(I)	13.7	12.4	13.0	13.5
Al(III)	10.0	8.2	8.7	9.2
Ce(III)	11.0	10.7	11.1	11.4
Cu(II)	>14	13.8	>14	>14
Fe(III)	12.2	12.1	12.6	13.1
Ga(III)	8.1	7.9	8.4	8.9
Hg(II)	no ppte.	12.7	13.7	>14
In(III)	12.5	11.7	12.2	12.6
Pb(II)	no ppte.	13.4	13.7	>14
Sc(III)	11.7	11.7	12.2	12.7
Sn(II)	no ppte.	8.9	9.2	9.6
Sn(IV)	7.0	—	—	—
Th(IV)	8.6	8.7	9.2	9.7
Y(III)	12.3	>14	>14	>14
Zn(II)	no ppte.	12.2	12.5	12.8
Zr(IV)	4.4	3.5	4.1	4.6

The limiting pH-values for the bivalent Ba, Ca, Cd, Co, Fe, Mn, Ni and Sr, are all above 14.

introduced by the addition of a neutralizing agent with a pH exceeding the values given in Table 1.

When EDTA is present in solution, in a back-titration procedure for instance, the amount of EDTA is mostly related to the amount of M present. This has a mathematical consequence if the metal–EDTA complex can hydrolyse to form a precipitate. Suppose that EDTA is added in 100% excess. This means that the concentration of free EDTA (Y) equals the total concentration of M, now present as MY. If we consider the formation of MY as a side-reaction and the precipitation as the main reaction, it will be obvious that MY predominates, so $\alpha_{M(total)}$ can be approximated by $\alpha_{M(Y)}$. Substituting equation (17) into equation (12) for the precipitation borderline and taking into account that $pM' = pY'$ we get

$$\log {}^{*}K_{s0} + \log K'_{MY} - n\text{pH} = 0 \qquad (19)$$

This equation gives a definite value for the pH at which precipitation starts. This precipitation limit is surprisingly low for some metals (see Table 1).

CONCLUSIONS

It has been shown that specific pitfalls may exist in the common operations of analytical chemistry, and examples have been used to give some insight into manipulation errors and to show that a number of small sins can easily be committed and are mostly overlooked as an origin of errors. Some of the most important consequent improvements possible are as follows. When acidic solutions of multivalent metal ions, especially Bi(III), Ga(III), Al(III), Fe(III), Zr(IV), and the lanthanide ions, have to be diluted, sufficiently acidified water should always be used. Buffer substances such as sodium acetate and hexamine should never be added in the solid state. In general all additions should be of liquids at the right pH. Thus acidified water should be used for rinsing glass-electrodes, making up to the desired volume in volumetric flasks, making reagent solutions, *etc.* Even EDTA, used as a titrant, must sometimes be acidified; examples are titrations of tin(IV), bismuth, zirconium and gallium. These small changes in routine procedures may improve the results remarkably. In general a critical inspection should be made of every manipulation. This can be done with the aid of the pM′–pH diagram, which nowadays can easily be constructed by means of a computer. The purpose of this paper was to reconsider old matters in a special way, to give the reader what is hoped to be a useful tool for solving problems.

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APPLICATIONS DE LA COLORIMETRIE DE PRECISION A LA MICROANALYSE ELEMENTAIRE

DOSAGES DE L'ALUMINIUM, DU COBALT, DE L'ÉTAIN ET DU FER: QUELQUES REMARQUES RELATIVES AU DOSAGE DU TITANE, DU PLATINE, DU PALLADIUM, DU MOLYBDÈNE ET DU PHOSPHORE

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Résumé—Le prélèvement analytique de masse inférieure à 5 mg est attaqué par voie humide dans un micromatras du type Kjeldahl. L'aluminium, le cobalt, l'étain, le fer sont dosés par colorimétrie spectrophotométrique en mettant en oeuvre les réactions suivantes: formation d'un complexe aluminium–alizarine S–calcium, cobalt(II)–tiron, étain(IV)–phénylfluorone, fer(III)–tiron.

La colorimétrie de précision, déjà mise en oeuvre dans notre Service pour de nombreux microdosages,[1–4] a été appliquée au microdosage de l'aluminium, du cobalt, de l'étain et du fer dans les substances organiques après attaque par voie humide.

Les complexes ou ions colorés auquels il est fait appel pour les dosages colorimétriques sont indiqués, ci-après, et les références bibliographiques sont citées dans le tableau 2.

Aluminium. Le réactif alizarine S–calcium forme un complexe orange rouge avec l'aluminium(III) à pH 4,4–4,7.

Cobalt. Le tiron forme un complexe jaune vert avec le cobalt(II) à pH 9,6.

Etain. La phénylfluorone forme un complexe orangé avec l'étain(IV) en milieu acide. Cette colorimétrie s'est avérée délicate et les résultats mal reproductibles tant qu'une quantité minimale d'ions SO_4^{2-} n'a pas été introduite.[5] La gélatine a été adoptée pour stabiliser la solution colloïdale du complexe.[6]

Fer. Le tiron forme un complexe rouge avec le fer (III) à pH 9,5–9,8 et un complexe bleu à pH 3,5–4,5. La colorimétrie à pH 9,5–9,8 a été adoptée dans notre Service du fait de sa meilleure sensibilité, mais la colorimétrie à pH 3,5–4,5 est à envisager lors de la présence de certains éléments qui gênent à pH 9,8 et ne gênent pas à pH 3,5–4,5.[7] Le tiron a semblé à priori intéressant puisqu'il se complexe avec le fer(III), forme obtenue après attaque par voie humide de la substance à analyser alors que la majeure partie des réactifs employés se complexent avec le fer(II).

PARTIE EXPERIMENTALE

L'attaque du type micro-Lorenz modifié, qui fournit la "solution d'attaque" après dilution du contenu du matras, les prélèvements, la préparation de "blancs de solution d'attaque" (même mode opératoire que pour une attaque proprement dite, mais sans introduction de substance à analyser) de "solutions d'essais à blanc de réactifs", les prélèvements d'aliquotes, la préparation de solutions étalons (introduction dans les fioles de colorimétrie de p mg d'élément sous forme de solution titrée au lieu de solution d'attaque) ont été antérieurement décrits dans la publication de Debal *et al.*[4]

La colorimétrie est effectuée sans recours à une courbe d'étalonnage. La quantité inconnue d'élément P mg contenue dans la fiole de colorimétrie est calculée à partir de p par une simple règle de proportionnalité:

$$P = \frac{pD}{d}$$

où D est l'absorbance de la solution inconnue et d la moyenne des absorbances de solutions étalons contenant p mg d'élément. Toutes les absorbances sont mesurées par rapport à des "solutions d'essais à blanc de réactifs".

Réactifs

Les réactifs sans mention spéciale sont des réactifs Prolabo "pour analyses". Les réactifs employés tant pour l'attaque par voie humide que pour la colorimétrie sont uniquement cités sous la rubrique attaque. L'eau utilisée est distillée au laboratoire dans un appareil en acier inoxydable.

Aluminium

Attaque. Acide sulfurique (p.s. = 1,83); acide nitrique (p.s. = 1,38); acide chlorhydrique (p.s. = 1,19).

Colorimétrie. Chlorure de calcium: dissoudre 14 g de carbonate de calcium ($CaCO_3$) dans 50 ml d'acide chlorhydrique 6*M*. Porter à ébullition pendant 2 mn. Ajuster à 1 litre avec de l'eau après refroidissement.

Alizarine sulfonate de sodium: solution aqueuse à 0,14%. La solution est stable plusieurs semaines.

Solution tampon à pH 4,4–4,7: solution contenant 140 g d'acétate de sodium $NaCH_3COO, 3H_2O$ et 60 ml d'acide acétique (p.s. = 1,05), par litre de solution aqueuse.

Solution titrée d'aluminium à 0,500 mg/ml: dissoudre 0,500 g d'aluminium en copeaux à 99,99% (Fluka) dans

40 ml d'acide chlorhydrique 6*M* en présence d'un peu de platine (petite plaque par exemple); chauffer doucement pour faciliter la réaction, laisser dissoudre le temps nécessaire (pouvant dépasser la journée) à température ambiante; ajuster ensuite à 1 litre avec de l'eau.

Solution titrée d'aluminium à 0,010 mg/ml: diluer avec de l'eau une partie de la solution précédente.

Cobalt

Attaque. Acide sulfurique (p.s. = 1,83); acide nitrique (p.s. = 1,38); eau oxygénée (110 vol.).

Colorimétrie. Tiron: solution aqueuse à 0,2% à préparer au moins 3 à 4 heures avant emploi. La solution doit être incolore et ne se conserve que quelques jours à l'abri de la lumière.

Ammoniaque (p.s. = 0,90).

Papier pH permettant de mesurer le pH à 0,5 unité près.

Solution tampon à pH 9,6: solution aqueuse contenant 53,5 g de chlorure d'ammonium et 115 ml d'ammoniaque (p.s. = 0,90) par litre de solution.

Solution titrée de cobalt à 1 mg/ml: dissoudre 4,94 g de nitrate de cobalt $Co(NO_3)_2\ 6H_2O$ dans le l'eau, ajouter 10 gouttes d'acide nitrique (p.s. = 1,38) et ajuster à 1 litre avec de l'eau. La solution est stable plusieurs mois.

Solution titrée de cobalt à 0,050 mg/ml: diluer avec de l'eau 50 ml de la solution précédente, ajouter 10 ml d'acide chlorhydrique (p.s. = 1,19) et ajuster à 1 litre avec de l'eau.

Etain

Attaque. Mêmes réactifs que ceux utilisés pour le cobalt.

Colorimétrie. Acide chlorhydrique (p.s. = 1,19).

Gélatine en poudre: solution aqueuse à 0,4% à préparer chaque jour. Dissoudre la gélatine dans l'eau bouillante en agitant.

Méthanol à 99,8% redistillé.

Phénylfluorone: dissoudre 0,050 g de phénylfluorone dans 50 ml de méthanol et 1 ml d'acide chlorhydrique (p.s. = 1,19); compléter à 500 ml avec du méthanol; la solution est stable plusieurs jours, et doit être renouvelée dès qu'elle cesse d'être limpide.

Solution titrée d'étain à 0,500 mg/ml: dissoudre 1 g d'étain en grenailles dans 100 ml d'acide chlorhydrique (p.s. = 1,19); la dissolution est complète à température ambiante au bout de quelques jours; ajuster ensuite à 2 litres avec de l'eau distillée; Charlot[8] accélère la dissolution en chauffant doucement mais il faut se méfier de la volatilité du chlorure d'étain; Leblond[5] signale que la présence d'acide sulfurique évite la perte par volatilisation du chlorure d'étain. Nous avons constaté que les solutions préparées avec l'acide chlorhydrique seul étaient plus stables que celles qui contiennent de l'acide sulfurique.

Solution titrée d'étain à 0,010 mg/ml: diluer la solution précédente avec de l'acide chlorhydrique 0,5*M*.

Glycocolle: solution aqueuse à 10%: dissoudre dans l'eau presque bouillante en agitant (le glycocolle—glycine *p.a.* Merck—a toujours donné satisfaction). La solution est utilisable plusieurs semaines sous réserves de la filtrer si elle perd, tant soit peu, sa limpidité. La concentration finale en glycocolle est la même que celle indiquée par Dymov *et al.*[6] puisqu"on utilise 10 ml de glycocolle à 10% au lieu de 5 ml de glycocolle à 20% lequel a tendance à recristalliser lors du refroidissement de la solution.

Fer

Attaque. Mêmes réactifs que ceux utilisés pour le cobalt.

Colorimétrie. Tiron: solution aqueuse à 0,5%. La solution doit être incolore et ne se conserve que quelques jours à l'abri de la lumière.

Ammoniaque (p.s. = 0,90).

Solution tampon à pH 9,8: solution aqueuse contenant 10 g d'hydrogénocarbonate de sodium ($NaHCO_3$) et 5 g de carbonate de sodium (Na_2CO_3) par litre de solution.

Solution titrée de fer à 0,500 mg/ml: dissoudre 4,317 g d'alum de fer et d'ammonium $Fe_2(SO_4)_3(NH_4)_2SO_4$, $24H_2O$ dans un peu d'eau et 5 ml d'acide sulfurique (p.s. = 1,83). Ajuster à 1 litre avec de l'eau. La solution est stable plusieurs mois.

Solution titrée de fer à 0,020 mg/ml: ajouter 5 ml d'acide sulfurique (p.s. = 1,83) à 40 ml de la solution précédente et ajuster à 1 litre avec de l'eau.

Attaques par voie humide

Diverses méthodes sont mises en oeuvre selon l'élément à doser, elles sont reportées dans le tableau 1.

Colorimétrie

Les conditions de la colorimétrie sont indiquées dans le tableau 2. Les réactifs sont introduits dans la fiole jaugée "de colorimétrie" de capacité *f* dans l'ordre indiqué dans la colonne *R* de ce tableau. Trois sortes de solutions sont

Tableau 1. Attaques par voie humide

*E**	*m**	Operations successives effectuées en micromatras
Al	1 à 5	0,8 ml H_2SO_4 + 3 à 4 gouttes HNO_3; Eb* = 15 2 fois 2 à 3 gouttes HNO_3; Eb = 15 + 15 3 fois 0,5 ml HCl; Eb = 10 + 10 + 10
Co	1 à 5	0,8 ml H_2SO_4 + 3 à 4 gouttes HNO_3; Eb = 15 2 fois 2 à 3 gouttes HNO_3; Eb = 15 + 15 3 fois 3 à 4 gouttes H_2O_2; Eb = 15 + 15 + 15
Sn[9,10]	2 à 5	0,8 ml H_2SO_4 + 3 à 4 gouttes HNO_3; Eb = 15 2 fois 2 à 3 gouttes HNO_3; Eb = 15 + 15 3 fois 4 à 5 gouttes H_2O_2; Eb = 15 + 15 + 15 1 ml H_2O bouillante; Eb = 0
Fe	1 à 5	0,8 ml H_2SO_4 + 9 à 10 gouttes HNO_3; Eb = 15 2 fois 7 à 8 gouttes HNO_3; Eb = 15 + 15 3 fois 5 à 6 gouttes H_2O_2; Eb = 15 + 15 + 15

* Signification des symboles:

E: Elément dosé dans des substances organiques.

m: Masse du prélèvement analytique en mg. Si les teneurs en éléments sont faibles, il est possible d'élever *m* au dela des valeurs indiquées. De même, il est possible d'abaisser *m* si l'on dispose de très peu d'échantillon.

Eb: Durées d'ébullition exprimées en minutes; ces valeurs sont donnés à titre indicatif; les vapeurs nitreuses doivent être totalement chassées lors de la dernière addition d'acide chlorhydrique ou d'eau oxygénée. Eviter toute évaporation à sec.

Tableau 2. Colorimétrie

E	*F*, ml	*f*, ml	*P*, mg	*DO**	*e**, cm	*λ**, nm	*t**	*R*
Al[11,12]	50 ou 100	100	0,01 à 0,05 0,05 à 0,07	0,13 à 0,6 0,3 à 0,4	2 1	490	1 à 3 h	*w* ml *A* ml chlorure de calcium: 2 ml *V** = 50 ml tampon: 25 ml alizarine: 5 ml H_2O
Co[13]	50 ou 100	50	0,01 à 0,1 0,1 à 0,2	0,06 à 0,6 0,3 à 0,6	2 1	340	45 mn à 3 h	*w* ml *A* ml tiron: 5 ml ajuster à pH 9 environ (ammoniaque 5*M*) *V* = 35 ml tampon 10 ml H_2O
Sn[5,6]	100 Introduire d'abord 3 ml HCl 6*M* dans chaque fiole	50	0,01 à 0,03 0,03 à 0,05	0,2 à 0,6 0,3 à 0,5	2 1	520	35 à 45 mn	*w* ml *A* ml H_2SO_4 0,5*M*: 10 ml† HCl 1*M*: 2 ml† gélatine: 1 ml phénylfluorone: 5 ml glycocolle: 10 ml H_2O
Fe[7,14]	50 ou 100	50	0,01 à 0,2 0,2 à 0,4	0,04 à 0,8 0,4 à 0,8	2 1	480	1 à 4 h	*w* ml *A* ml tiron: 2 ml ajuster à pH 7–8 coloration rouge carmin (ammoniaque 5 ou 10*M*) tampon 15 ml H_2O

* Signification des symboles.
F: Capacité de la fiole dans laquelle est dilué le contenu du matras dans le cas de prélèvements aliquotes;
DO: Absorbance;
e: Epaisseur de la cuve de colorimétrie;
λ: Longueur d'onde à laquelle est effectuée la mesure;
t: Temps d'attente avant la lecture de l'absorbance sur le spectrophotomètre;
V: Volume approximatif de solution après addition d'eau;
† Pour les solutions étalons voir la section *Resultats et Discussion.*
F, *f*, *P*, *e*, *λ* peuvent éventuellement être modifiés pour des cas particuliers.

ainsi préparées de façon similaire:[4] solutions inconnues, solutions étalons, solutions d'essais à blanc de réactif. Toutefois introduire dans la fiole de colorimétrie

—dans les cas des solutions inconnues

(1) soit le volume total $A = s$ ml de la solution d'attaque, soit lors de prélèvements de parties aliquotes des volumes $A = a_1 \ldots A = a_i \ldots A = a_n$ avec $a_1 > \ldots a_i \ldots > a_n$,

(2) un volume w de "blanc" de solution d'attaque avec $w = s - s = 0$, $w = a_1 - a_1 = 0 \ldots, w = a_1 - a_i \ldots, w = a_1 - a_n$ selon que $A = s$, $A = a_1 \ldots, A = a_i \ldots, A = a_n$;

—dans les solutions étalons

$A = v$ ml de solution titrée

$w = a_1$ ou s ml de "blanc de solution d'attaque" selon que l'on procède ou non au prélèvement de parties aliquotes;

—dans les solutions d'essais à blanc

$w = a_1$ ou s ml de "blanc de solution d'attaque".

Calculs

Teneur centésimale en élément *E*:

$$x = \frac{100\,PF}{ma_i}\,\%$$

RESULTATS ET DISCUSSION

Quelques résultats représentatifs sont indiqués dans le tableau 3.

Dans le cas du cobalt les résultats semblent plus précis lorsqu'on a chassé les vapeurs nitreuses par l'eau oxygénée au lieu de l'acide chlorhydrique (qui présente pourtant l'avantage de chasser plus rapidement ces vapeurs).

Au début de l'étude du microdosage de l'étain les contenus des matras étaient systématiquement portés à l'ébullition pendant 20 mn après l'addition d'eau bouillante. Cette ébullition s'est avérée inutile; il en est de même pour le dosage du titane des substances inorganiques.

En utilisant, pour l'attaque des substances organiques contenant du fer, le même mode opératoire que pour celles contenant du cobalt, un précipité blanchâtre apparait souvent dans les solutions obtenues après attaque; il peut en général être remis en solu-

Tableau 3. Exemples de résultats

E	Composé	Teneur en élément, %*			
		m, *mg*	$\bar{x}_i$	$\bar{x}$	*T*
Al	Ethyl-2 hexanoate d'aluminium	4,582	8,2	8,2	8,17
		5,520	8,1		
		5,528	8,5		
		3,618	8,2		
		4,302	8,0		
	Acétylacétonate d'aluminium	4,624	8,2	8,3	8,32
		4,730	8,5		
		5,750	8,4		
		2,245	8,3		
		4,056	8,3		
Co	Cyclohexylbutyrate de cobalt	3,273	14,6	14,7	14,83
		3,469	14,5		
		2,946	14,7		
		2,760	15,1		
		4,244	14,4		
Sn	Bis (éthyl-2 hexanoate) de dibutylétain	2,399	22,9	22,8	22,86
		4,325	22,5		
		3,698	22,6		
		3,245	23,1		
		2,292	23,1		
	Tétraphenylétain	3,300	27,4	27,8	27,78
		2,164	27,5		
		2,499	28,1		
		2,930	28,1		
		2,444	27,7		
Fe	Ferrocene	1,417	29,8	29,9	30,02
		3,101	30,2		
		0,868	29,9		
		2,506	29,6		
		4,370	30,0		
	Trisbenzoylacétonate de fer(III)	3,252	10,4	10,3	10,36
		5,182	10,2		
		3,454	10,4		
		3,847	10,4		
		5,130	10,3		

* x_i: résultats trouvés
$\bar{x}$: moyenne des résultats trouvés
T: teneur calculée

tion par addition de 1 ml d'eau puis en portant 15 mn à l'ébullition. Les ébullitions en présence d'eau provoquent souvent des soubresauts avec projections et sont, de ce fait, à éviter, si possible. Avec les quantités de réactifs indiquées pour le fer dans le tableau 1, un précipité blanc est rarement observé jusqu'ici, celui-ci semble lié à un chauffage trop intensif des matras. Il est, en outre, recommandé d'ajouter avec précautions (risques de projections) l'eau oxygénée dans la solution encore chaude alors qu'on laisse habituellement refroidir les solutions avant d'y ajouter des réactifs.

En ce qui concerne la colorimétrie de l'aluminium, l'introduction d'une trop grande fraction de solution d'attaque perturbe les résultats (affaiblissement de la coloration). L'aliquote prélevée doit donc être comprise entre le dixième et le quart du volume total de la "solution d'attaque". Cette dernière attaque n'est pas neutralisée avant l'addition du tampon.

L'absorbance de la solution d'éssais à blanc de réactifs est élevée (*DO* de l'ordre de grandeur de 0,18 en cuve de 1 cm), elle décroit légèrement quand la quantité de blanc de solution d'attaque introduit croit. Avec certains modèles de spectrophotomètres, il est préférable d'effectuer toutes les mesures d'absorbance par rapport à l'eau et de soustraire des *DO* celle de la solution d'essais à blanc de réactifs.

Pour la colorimétrie du cobalt la précision des résultats est meilleure si l'aliquote prélevée ne représente pas plus de la moitié de la "solution d'attaque".

La colorimétrie de l'étain s'est avérée délicate: il importe d'introduire des ions SO_4^{2-} et il faut que l'acidité finale (chlorhydrique + sulfurique) soit sensiblement constante. A cette fin, les volumes des aliquotes doivent rester compris entre 10 et 15 ml et dans ce cas, il convient d'introduire dans toutes les fioles de colorimétrie 10 ml d'acide sulfurique 0,5*M* et 2 ml d'acide chlorhydrique 1*M*, sauf pour la préparation des solutions étalons. Il faut, pour ces dernières, tenir compte de l'acidité de la solution titrée qui n'est pas négligeable (milieu 0,5*M*). Par exemple, pour une solution étalon contenant 0,020 mg d'étain soit 2 ml de solution titrée renfermant 1 ml d'acide chlorydrique 1*M*, il faut introduire 10 ml d'acide sulfurique 0,5*M* et 2 − 1 = 1 ml d'acide chlorhydrique 1*M*.

Pour une solution étalon contenant 0,050 mg

d'étain, soit 2,5 ml d'acide chlorhydrique 1 *M*, il faut introduire seulement 10 − (2,5 − 2) = 9,5 ml d'acide sulfurique 0,5*M*, les 2 ml d'acide chlorhydrique ayant déjà été introduits par la solution étalon.

Dans ces conditions, toutes les solutions sont limpides et l'absorbance de la solution d'essai à blanc est de l'ordre de grandeur de 0,02, en cuve de 1 cm.

Pour la colorimétrie du fer, moins sensible que les précédentes, il est possible de ne pas prélever d'aliquote et d'utiliser la totalité de la solution d'attaque lorsque les teneurs en fer sont faibles. La présence de cette solution d'attaque diminue un peu la stabilité du complexe fer–tiron, c'est pourquoi il est recommandé (*cf* tableau 2) de ne pas attendre plus de 4 h pour effectuer les mesures spectrophotométriques.

Le tiron sert aussi d'indicateur de pH; il permet de suivre la neutralisation avant l'addition de tampon.

Eléments gênants

L'influence de la présence simultanée d'éléments (quelques dixièmes de mg pour 1 ou 2 mg de prélèvement analytique) a été étudiée.

Dosage de l'aluminium. As, B, Be, Br, Ca, Ce (légère coloration orangée au moment de l'attaque), Cd, Cl, Co, Cr, F, Hg, K, I, Li, Mg, Mn, N, Na, Ni, P, Pd, Pt, Se, V ne gênent pas. Ba ne gêne plus après filtration préalable de la solution d'attaque.

Sb conduit à l'obtention de résultats légèrement erronés par excès.

Bi, Cu, Fe, Mo, Pb, Sn, Te, Ti, Zn gênent.

Dosage du cobalt. As, Br, Cl, F, Ge, Hg, I, K, Li, Mg, N, Na, P, Pd, Sb, Se ne gênent pas.

En présence de platine, les solutions d'attaque sont jaunes et les résultats obtenus sont erronés par excès (correction à étudier).

Cd, Cr, Zn, conduisent à des résultats très légèrement erronés par excès.

Al, B, Ba, Be, Bi, Ca, Cu, Ce, Fe, Mo, Mn, Pb, Nb, Ni, Sn, V, Zr gênent.

Dosage de l'étain. Br, Cl*, Co, Cu, F, K, N, Ni, P, Pb†, Pd (coloration orangée au moment de l'attaque), Pt, S ne gênent pas.

Ce, Nb et Bi conduisent à l'obtention de résultats légèrement erronés par excès.

Fe, Mo, Ti, V, Zr gênent.

Dosage du fer. As, B, Ba, Be, Bi, Br, Cd, Cl, F, I, K, Mg, Mo, N, Na, Ni, P, Pd, Pt, Sb, Se, Sn, Te, V, Zn, Zr ne gênent pas.

Ag, Co ont tendance à conduire à l'obtention de résultats erronés par excès lorsque les quantités dépassent 0,1–0,2 mg dans le prélèvement analytique.

Mn, Ti gênent.

Remarques complémentaires relatives aux éléments, objets d'une publication antérieure[4]

Dosage du titane. Be, Bi, Ca, Cd, Ge, La, Mn, Re, Te, Th, Zr ne gênent pas. V gêne.

Pour le microdosage de titane[4] utiliser de l'acide oxalique à 2,5% et non à 25%.

Dosage du platine. Bi, Ca, Co, Cu, F, La, Mn, Sn ne gênent pas.

Hg gêne.

Dosage du palladium. Al, Ca, Co, Cu, Hg, Mg, Mn, Ni, Th, Zr ne gênent pas.

Dosage du molybdène. Bi, Ca, Cd, Fe, Mg, Ni, Ru, Zn ne gênent pas.

Dosage du phosphore. Be, Bi, Ce, Cs, Er, Eu, Gd, In, Mn, Ta, Tl, Zr ne gênent pas.

CONCLUSION

Les méthodes spectrophotométriques, associées à une attaque par voie humide, ont été appliquées au dosage de plusieurs éléments en fonction de problèmes effectivement posés. Le microdosage du phosphore est le plus universel, celui du cobalt l'est beaucoup moins et une étude complémentaire serait nécessaire s'il apparaissait que les hétéroéléments gênants se rencontraient souvent simultanément dans les molécules organiques, ce qui n'est pas, actuellement, le cas. L'étude du dosage de plusieurs autres éléments, par ces méthodes, est encore en cours.

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* Le chlorure d'étain est volatil mais d'après Leblond[5] la présence d'acide sulfurique empêche les pertes par distillation.

† Le précipité qui apparait au moment de la reprise par l'eau du contenu du matras disparait pendant la dilution en fiole.

Summary—The sample (up to 5 mg) is destroyed by using a wet process in a glass flask of the Kjeldahl type. Aluminium, cobalt, tin and iron are determined spectrophotometrically. The following reactions are used: complexation of aluminium by Alizarin Red S and calcium, cobalt(II) by tiron, tin(IV) by phenylfluorone, iron(III) by tiron.

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EXTRACTIVE SEPARATION AND SPECTROPHOTOMETRIC DETERMINATION OF TUNGSTEN AS PHOSPHOTUNGSTEN BLUE

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Summary—Phosphotungsten blue is produced by tin(II) reduction of tungstate solution complexed with phosphate at a w/w ratio of W/P = 5, in 4*M* hydrochloric acid medium, and extracted with isoamyl alcohol; thus tungsten is separated from Fe(III), Ni, Co, Cr(III), V(V), As(V), Sb(III), Bi, Si, U(VI), Ca and Cu(II). In presence of bismuth (0.5 mg/ml), ⩾99.7% W is separated in a single extraction. After alkaline back-extraction, tungsten is determined spectrophotometrically as phosphotungsten blue; it is measured at 930 nm in aqueous solution or at 900–960 nm after isoamyl alcohol extraction, the Beer's law ranges being 0.08–0.6 and 0.16–0.72 mg/ml respectively. The methods are shown to give satisfactory results in the analysis of practical samples containing some milligrams of tungsten.

Few methods exist for extractive separation and determination of milligram amounts of tungsten. Only the inorganic complexes with thiocyanate,[1] peroxide,[2] chloride,[3] fluoride[4] and phosphate[5] have been proposed for such a separation and thiocyanato tungstate(V) complex has hitherto been the only coloured inorganic complex available for determination of tungsten. Apart from the recent titrimetric[6] and spectrophotometric[7] methods based on the thiocyanato complex, there are few satisfactory methods for the rapid determination of macro amounts of tungsten in industrial and natural samples.

It has long been known that reduction of phosphotungstate produces an extractable blue colour. Although (extracted) phosphomolybdenum blue has been used extensively for determination of phosphorus[8] and for separation[9] and determination[10] of molybdenum, the corresponding phosphotungsten blue has not been utilized analytically. As relatively few elements form heteropoly-blue species, the extraction of phosphotungsten blue should be useful for separation of tungsten from many elements and for its determination.

EXPERIMENTAL

Reagents and solutions

Tungsten solution. Sodium tungstate was dissolved to give a solution containing W at the mg/ml level: this was standardized[6] by titration with iron(III).

Phosphate solution. Trisodium orthophosphate was dissolved to give a 10-mg/ml solution of P and further dilutions were made as required.

Tin(II) chloride solution. A 40% w/v solution in concentrated hydrochloric acid.

Bismuth solution. Sodium bismuthate was dissolved in 1*M* hydrochloric acid to give a bismuth concentration of 10 mg/ml.

Isoamyl alcohol. Fractionally distilled with a Vigreux column and the 128–130° fraction used.

Samples

Synthetic samples. These were prepared by mixing solutions of the ions in the proportions shown in Table 3.

Ferrotungsten. The sample (0.3 g) was carefully fused with sodium peroxide (3 + 1 g) in a nickel crucible.[11a] The melt was dissolved in 30 ml of concentrated hydrochloric acid in a beaker. The nickel crucible was rinsed with 10 ml of hydrochloric acid (1 + 1), and then with hot water. A sufficient amount of phosphate (about 30 mg of P) and then the rinsings were added to the beaker, then the solution was boiled for 5 min. Any tungstic acid precipitated, because insufficient phosphate had been added, was filtered off and redissolved in alkali. After addition of more phosphate this solution was mixed with the rest of the tungsten solution, which was then diluted accurately to 250 ml. Portions (10 or 20 ml) were taken for analysis, allowance being made, when adjusting the conditions, for the acid and phosphorus present in the solution.

High-speed steel. The sample (0.5 g) was dissolved in 20 ml of phosphoric/sulphuric acid,[11b] the solution was heated and 3 ml of phosphoric acid were added. Concentrated nitric acid was added dropwise to dissolve carbides, then the solution was evaporated to fumes. Water containing 5 ml of concentrated hydrochloric acid was added and the solution was again heated until its volume was reduced to 2–3 ml. Water, and 10 ml of concentrated hydrochloric acid were added and the solution was heated until it just boiled. After cooling, the solution was diluted to exactly 100 ml. Any tungstic acid precipitated was redissolved as above. Aliquots (10 or 20 ml) were taken for analysis, their phosphorus content and acidity being allowed for in adjusting the conditions.

Separation of tungsten as phosphotungsten blue

A slightly alkaline sample of tungstate solution containing 4–100 mg of W was placed in a separating funnel, then sufficient phosphate solution was added to adjust the w/w ratio of W/P to 5. One ml of bismuth solution and 2 ml of tin(II) chloride solution, then sufficient 12*M* hydrochloric acid to adjust the total acidity to 4*M* in a final volume of 20 ml, were added. After a wait of 2 min the mixture was shaken for 20 sec with 15 ml of isoamyl alcohol. On settling, the layers were separated. For >20 mg of W, the aqueous phase was shaken again with a further 5 ml of solvent.

The solvent phase was shaken (for 1 min each time) with 15 ml of distilled water, then dilute alkali (containing ten or more drops of saturated sodium hydroxide solution to give rapid separation of layers), and finally very dilute alkali (containing 2 drops of saturated sodium hydroxide solution). Saturated sodium hydroxide solution was added to the combined aqueous extracts until any precipitated tin hydroxide redissolved. Any remaining hydroxide precipitate was filtered off, then the solution was diluted to 50 ml. Tungsten was determined by either of the procedures described below.

When iron was present, 2–4 times its weight of ascorbic acid was dissolved in the solution before addition of the phosphate.

Spectrophotometric determination

After extraction with isoamyl alcohol. An aliquot of the strongly alkaline solution from the separation procedure, containing up to 18 mg of tungsten, was placed in a separating funnel. Sufficient phosphate solution to make the w/w ratio of W/P equal to 0.5–0.9 was added, followed by 3 or 4 drops of thioglycollic acid, 5 ml of tin(II) chloride solution and, without delay, enough hydrochloric acid to adjust the total acidity to 5*M* in a final volume of 25 ml. After 5 min, the solution was shaken with 20 ml of isoamyl alcohol for 20 sec. After separation, the organic phase was filtered into a 25-ml standard flask through a dry filter paper (Whatman No. 41) and diluted to the mark. The absorbance of the solution was measured against isoamyl alcohol at 900 nm in a 1-cm cell.

Without solvent extraction. A suitable aliquot of the alkaline solution from the separation, containing not more than 15 mg of tungsten, was diluted with distilled water to 25 ml in a standard flask after addition of the reagents used in the procedure above. The absorbance was measured after 20 min at 930 nm against distilled water.

RESULTS AND DISCUSSION

The use of the reduced ternary P–Mo–W complex has been proposed[12–14] for the spectrophotometric determination of tungsten. This complex takes 1 hr to reach maximum absorbance, and the absorbance then decreases at a constant rate, Beer's law is not obeyed and many important elements interfere.[13] The binary heteropoly tungsten blues have not previously been proposed for the determination of tungsten or the heteroatom.

Extractive separation of tungsten as phosphotungsten blue

Of the various possible reducing agents for making phosphotungsten blue, only mercury and tin(II) chloride seemed promising. Tin(II) chloride is preferable to mercury because it permits more efficient extraction at lower concentrations of tungsten. Phosphotungsten blue is only slightly extracted by amines (<5%), and amyl acetate and methyl isobutyl ketone extract it partially (~50%). Isoamyl alcohol and tributyl phosphate extract it almost quantitatively but the former is more selective. The degree of extraction of phosphotungsten blue with isoamyl alcohol depends on the acid concentration, showing an increase up to 4*M* acidity and then remaining almost constant up to 7*M* (Fig. 1, curve A). The amount extracted is maximum at a w/w ratio of W/P = 5, (Fig. 1, curve B), and is ⩾98% for W/P ratios in the range 1–8. The concentration of tin(II) and the reaction time also affect the efficiency of extraction, which reaches a maximum with 4% w/v $SnCl_2$ and a reaction time of 2 min but with only slight decreases at higher values (Fig. 1, curves D and C). Shaking for 20 sec is sufficient for quantitative extraction. The degree of extraction also depends on the tungsten concentration; it increases as the tungsten concentration increases up to 1 mg/ml, and then decreases slightly as the tungsten concentration increases to 5 mg/ml, when only a single extraction is done (Fig. 1, curve E). The fraction extracted continues to increase with tungsten concentration up to 5 mg/ml when a second extraction with 5 ml of solvent is carried out (Fig. 1, curve E'). If the optimum conditions are used, 99.0% of the tungsten can be extracted. Repeated extractions of the raffinate give very little

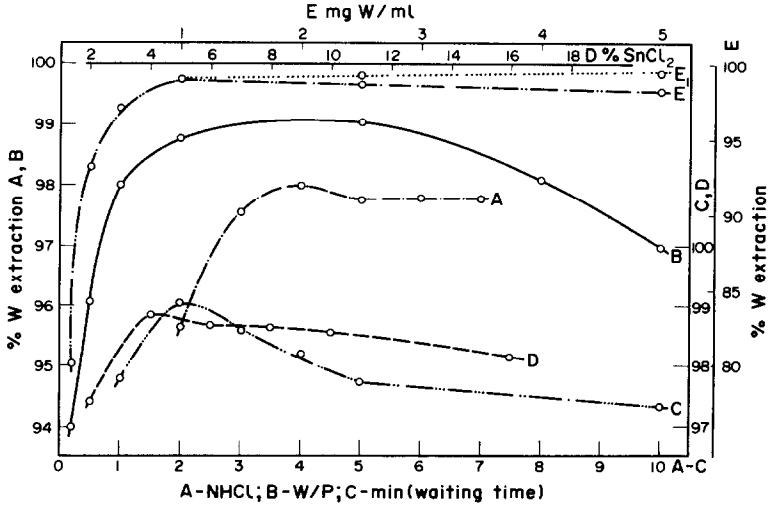

Fig. 1. Dependence of amount of phosphotungsten blue extracted on various parameters (a curve and the corresponding scale are labelled with the same letter). Tungsten concentrations: A–D 1 mg/ml.

Table 1. Effect of anions on the amount of phosphotungsten blue extracted†

Salt added	Amount g	Tungsten extracted§ %
—	—	99.0
Sodium sulphate*	1.0	98.6
Sodium chloride*	1.0	97.4
Potassium chloride*	1.27	95.0
Potassium acetate	1.0	97.5
Potassium citrate	1.0	95.0
Oxalic acid	0.54	97.4
Sodium oxalate	0.81	95.4
Potassium oxalate	1.0	93.6
Potassium hydrogen fluoride	1.0	76.3
Potassium nitrate*	1.0‡	95.2

† W = 1 mg/ml.
* Added before reduction.
§ By difference; W in aqueous phase determined by Hg–SCN^- method.[7]
‡ Some fading of blue colour.

Table 2. Coextraction of diverse elements and their effect on the extraction of phosphotungsten blue*

Other element	Amount (mg)	Extraction of: Other‖ element (%)	Tungsten† (%)	Tungsten‡ (%)
—	—	—	99.0	99.7
Fe(III)§	200	0.02	97.5	99.7
Ni(II)	120	0	97.4	99.7
Co(II)	120	0	98.1	99.78
Cr(III)	100	0.03	85.2	99.79
V(V)	10	4–5	94.5	98.88
Mn(II)	10	0	98.7	99.75
As(V)	10	~0.1–0.2	99.3	—
Sb(III)	10	3.5	99.5	—
Bi(V)	10	0.7	99.7	—
U(VI)	20	0.7	94.7	98.54
Ca(II)	20	—	99.0	99.68
Cu(II)	20	0.3	99.45	—
Si(IV)	50	~0.4	99.0	99.65

* W = 1 mg/ml.
† By difference; W in aq. phase detd. by Hg-SCN method.[7]
‡ After addition of 10 mg Bi to aq. phase.
§ Added ascorbic acid before stannous chloride reduction.
‖ Detd. by conventional colorimetric methods[16,17] in the filtrate from alkaline back extract.

improvement when the tungsten concentration drops to μg/ml levels.

Chloride, sulphate and acetate do not affect the extraction to any extent; citrate, nitrate and oxalate decrease the amount extracted by about 2–4% while fluoride decreases it by about 20% (Table 1). Sodium and potassium decrease the amount extracted by about 2 and 4% respectively. The blue colour does not form in the presence of tartaric acid; the slight blue turbidity which appears slowly is not extractable.

At the concentrations usually present in real samples, calcium, manganese, iron, cobalt and nickel either do not affect the amount of tungsten extracted or decrease it only slightly; uranium, vanadium and chromium decrease it by 5–14%, while arsenic, copper, antimony and bismuth increase it by 0.3–0.7% (Table 2). These elements themselves are only slightly extracted. Complete or almost complete (>99.3%) removal of the elements may be effected by filtration of the alkaline back-extract: only antimony and vanadium remain (about 3–5%). Tungsten is not lost by adsorption onto the small amount of hydroxide precipitate filtered off from the alkaline back-extract. Molybdenum is extracted along with tungsten and has to be removed first by other methods. About 70% of the tin from the stannous chloride reductant is

Table 3. Analysis of samples by the proposed methods of separation and determination

Sample composition*, *mg*		
Matrix	W added	W found, *mg*
Co(60), Cr(20)	20.0	20.0, 20.1
Fe(272.4), Cr(80), Ni(28) Mn(2)	16.0	16.0, 16.0§
Fe(47.2), Co(40), Cr(3)	9.0	8.98
Co(45), Cr(15)	40.0	40.0, 40.1
Ni(50)	50.0	50.0
Fe(6.6), Mn(5), Sn(0.6), Bi(0.12), Ca(0.05)	29.9	30.0, 29.9
Ferrotungsten A	75.2%†	75.0% 75.3%‡ 75.0%‖
High speed steel super rapid extra 500	18.0%†	17.8%

* The first six samples are analogous to Stellite, Midvale HR, K.S. magnet steel, Haynes metal, nickel–tungsten and Spanish wolframite respectively.
† Reported value confirmed by thiocyanate methods.[6,7]
§ Tungsten determined by the thiocyanate method.[7]
‡ Tungsten separated by the thiocyanate method.[1]
‖ Tungsten separated by the phosphotungstate method.[5]

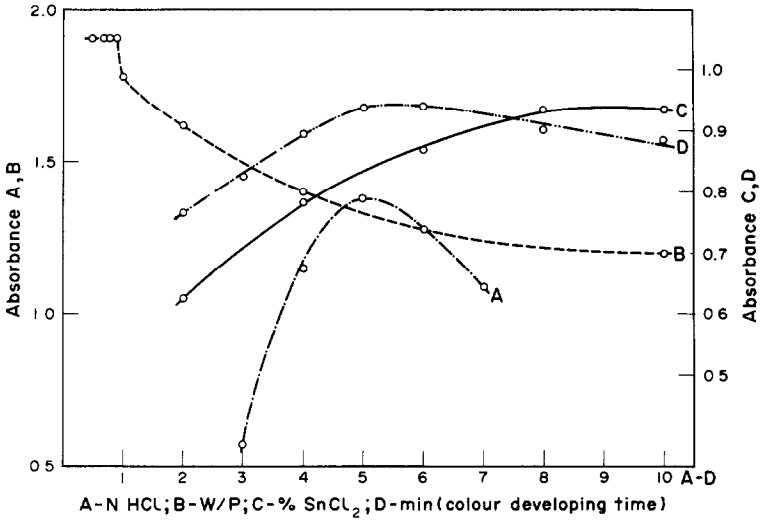

Fig. 2. The effect of various parameters on the absorptivity of phosphotungsten blue after extraction with isoamyl alcohol (a curve and the corresponding scale are labelled with the same letter). Tungsten concentrations: A and B—1 mg/ml. C and D—0.5 mg/ml.

extracted, but it need not be removed if tungsten is determined by the thiocyanate method or by the proposed phosphotungsten blue method. The uranium and vanadium which remain after the separation procedure applied to samples containing normal levels of these elements do not interfere. The xanthate[15] method can be used for removal of molybdenum, in which case most of the tin would also be removed, but tungsten then has to be determined by the thiocyanate method.

Because of the ineffectiveness of further isoamyl extractions of the raffinate, and because of the deleterious effects of other elements on the amount of tungsten extracted, the system would have had little analytical utility but for the peculiar behaviour of bismuth in increasing the amount of tungsten extracted to 99.7% (Table 2) even in the presence of other elements which normally suppress extraction. If 10 mg of Bi are added before the reduction, at least 99.7% of the tungsten is removed in a single extraction for tungsten up to 1 mg/ml, and after two extractions for solutions containing up to 5 mg/ml. When vanadium (0.5 mg/ml) and uranium (1 mg/ml) are present, 98.9 and 98.5% of the tungsten are extracted, respectively. As a second extraction is not so effective, lower amounts of these elements should be present for a more complete extraction.

Determination of tungsten as phosphotungsten blue

The colour of phosphotungsten blue can be utilized for determination of tungsten. However, the conditions for optimum absorptivity of phosphotungsten blue are different from the optimum conditions for its extraction by isoamyl alcohol.

The absorptivity also depends on the acid concentration, and has a maximum value at 5*M* (Fig. 2, curve A), but it increases with increasing phosphorus concentration between w/w ratios of W/P of 20 and 0.9 then remains constant at lower ratios down to 0.5 (Fig. 2, curve B). The absorptivity increases as the tin(II) chloride concentration is increased to 8% then remains nearly constant with further increase to 10% (Fig. 2, curve C). For measurements in aqueous solution, full colour development takes 20 min, but if the coloured species is to be extracted, the maximum absorptivity is obtained if the extraction is made between 5 and 6 min after the solutions are mixed (Fig. 2, curve D). Extraction for 10–20 sec gives the optimum results, because the absorptivity decreases on longer shaking with the solvent.

If mercury is used for the reduction, the blue complex extracted is unstable. There is a rapid fall in the absorbance, probably because of absence of reductant in the solution.

The spectrum of phosphotungsten blue in the visible region is shown in Fig. 3, curves A and B.

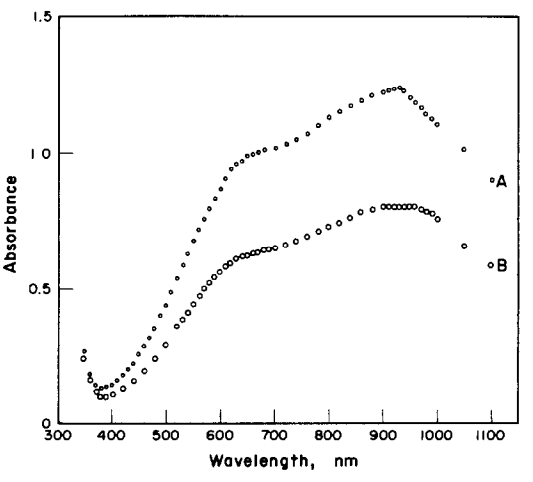

Fig. 3. Absorption spectra of phosphotungsten blue. A—in aqueous solution; B—in isoamyl alcohol.

Beer's law is obeyed for 4–18 mg of W in 25 ml of isoamyl alcohol at λ_{max} 900–960 nm and for 2–15 mg of W in 25 ml of aqueous solution at λ_{max} 930 nm. The absorbance decreases in isoamyl alcohol and increases in aqueous solution at a constant rate of 0.001/min for up to 1 hr, and any delay in measurement can be allowed for accordingly.

If the determination is to be done after the proposed extractive separation of tungsten, the calibration graph should be prepared by applying the same procedure to standard tungstate solutions; with any other separation method, the calibration graph may be prepared by using sodium tungstate solutions directly.

Nickel and cobalt interfere in the tungsten determination by causing a considerable decrease in the absorbance, and iron and vanadium suppress it almost completely. In the presence of molybdenum, a purple complex with λ_{max} at 560–570 nm is extracted. Therefore, tungsten can be determined as phosphotungsten blue only after separation, by means of the proposed procedure or by any other suitable method, from these seriously interfering elements, which are very commonly present in industrial and natural samples.

A disadvantage of using the back-extract from the proposed separation procedure is that development of the blue colour is slow and the aqueous solution becomes turbid because of hydrolysis of tin. Addition of 3 or 4 drops of thioglycollic acid before acidification prevents this hydrolysis and speeds development of the blue colour. Larger amounts of thioglycollic acid cause turbidity, however.

Applications

A single extraction of phosphotungsten blue with isoamyl alcohol separates 4–100 mg of tungsten from most elements except molybdenum and tin, and silica need not be removed by dehydration. The mg amounts of tungsten can then be determined spectrophotometrically as phosphotungsten blue. The methods are simple, rapid and applicable to all natural and industrial tungsten-containing materials. The proposed methods for separation and determination together take ~40 min for a single sample and give reproducible and satisfactory results with an overall maximum error of 0.2% for 5–60 mg of tungsten (Table 3) after correction by calculation, or by using a suitable calibration graph to allow for the extraction being only 99.7% efficient. Determination of tungsten by the proposed method after other separation procedures, [1,5] and determination of tungsten by the thiocyanate[7] method after the proposed separation method give similar results (Table 3).

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ATOMIC-ABSORPTION SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF MANGANESE WITH THENOYLTRIFLUOROACETONE

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Summary—An atomic-absorption spectrophotometric method for the determination of traces of manganese in solution with thenoyltrifluoroacetone (TTA) is described. Manganese(II) is extracted with 0.01*M* TTA in methyl isobutyl ketone (MIBK) at pH 9.5. The atomic-absorption of the organic phase at 279.5 nm is measured. Except for chromium, iron, hafnium, niobium, nickel, rhodium, tin, titanium and zirconium, microquantities of many other cations and anions do not interfere. Iron can be removed by MIBK extraction before the TTA extraction. The sensitivity of the method was 1.6 ng/ml for 1% absorption in aqueous solution. The method was successfully applied to the analysis of environmental waters. Manganese in the filtered fractions of water samples was reliably determined with relative standard deviations of 7% at the 5 μg/l. level and 1% at 50 μg/l.

Traces of manganese in aqueous solution have been determined by spectrophotometry or atomic-absorption spectrophotometry (AAS) after separation and/or concentration by means of evaporation, precipitation, co-precipitation, solvent extraction, ion-exchange, extraction and ion-exchange, and chelating resins. In water analysis by AAS, it is usual to use solvent extraction to increase the sensitivity and avoid interference by other elements. Many studies on determination of traces of manganese in natural, drinking, tap, tank and waste waters *etc.* by AAS with chelate-complex extraction have been reported. Ammonium pyrrolidinedithiocarbamate (APDC) and sodium or ammonium diethyldithiocarbamate (DDTC) are frequently used as the chelating agents.[1–11] Although methyl isobutyl ketone (MIBK) is often the preferred solvent,[4] the manganese complexes of APDC and DDTC are rather unstable in MIBK.[2,3,6,7,9,11]

Thenoyltrifluoroacetone (TTA), another familiar chelating agent for separation or concentration of metals by solvent extraction, has been used for determination of manganese spectrophotometrically[12–14] or by flame photometry.[15,16] The present paper describes a sensitive method for determination of traces of manganese by AAS with manganese(II)–TTA/MIBK as extraction system. The TTA complex is stable in MIBK medium. The established method has successfully been applied to the analysis of environmental waters.

EXPERIMENTAL

Apparatus

A Perkin-Elmer 403 Atomic Absorption Spectrophotometer equipped with a standard air–acetylene burner head and Intensitron manganese hollow-cathode lamp was used. The instrumental settings used are summarized in Table 1. An automatic shaker and 100-ml separatory funnels with Teflon stop-cocks were used for the extractions. The pH-measurements were done with a pH-meter or pH test-papers.

Reagents

Standard manganese solutions. A 1.00-mg/ml stock solution was prepared by dissolving 0.100 g of pure manganese metal in 10 ml of 7*M* nitric acid and diluting to exactly 100 ml with water. Solutions of lower concentration were prepared by appropriate dilution.

Hydroxylamine hydrochloride solution, 2.5% w/v.

TTA solution, 0.01*M*. TTA (0.88 g) dissolved in 400 ml of MIBK.

Buffer solution (pH 9.5). Ammonia solution (1*M*) was added to 1*M* ammonium chloride to adjust the pH to 9.5 (pH-meter).

All other solutions were prepared from analytical reagent-grade chemicals without further purification.

Procedures

TTA extraction. Take not more than 40 ml of the sample solution, containing 0.08–200 μg of manganese, in a separatory funnel. Add 1 ml of hydroxylamine hydrochloride solution and mix well. Add 5 ml of buffer solution

Table 1. Atomic-absorption conditions for manganese determination

Wavelength	279.5 nm
Lamp current	20 mA
Slit-width	1 mm (0.7 nm spectral band-width)
Burner-height	at position 14
Burner-slot	0.5 × 104 mm
Air:	
pressure	30 psig
flow-rate	24.0 l./min
Acetylene:	
pressure	8 psig
flow-rate	6.2 l./min
Sample feed-rate	3.0 ml/min
Read-out time	11 sec

and dilute to 50 ml with water and mix well. Then, using a Thymol Blue pH test-paper, adjust the pH to 9.5 with dilute ammonia solution if necessary. Add 5.0 ml of TTA solution and shake vigorously for 1 min. Let the solution stand for 20 min, then drain off and discard the aqueous phase (containing a small amount of white bubbles). Aspirate the organic phase into an oxidizing air–acetylene flame and measure the atomic-absorption (described below as absorbance, for convenience) at 279.5 nm.

Construct a calibration curve by taking 0 (corresponding to a reagent blank), 0.10, 0.25, 0.50, 1.25 and 2.50 μg of manganese, then proceeding as described above for the TTA extraction. Run a reagent blank through the entire procedure.

Removal of iron by MIBK extraction. Before the TTA extraction, adjust the sample volume to 40 ml and add 40 ml of concentrated hydrochloric acid. Mix well, and then add 10 ml of MIBK and shake vigorously for 1 min.

Drain off and transfer the aqueous phase to a 200-ml quartz dish. To decompose residual organic matter, add 2 ml of concentrated nitric acid and heat gently for a while. Add 1 ml of 60–70% perchloric acid and evaporate the solution until white fumes appear (*i.e.*, nearly to dryness). Dilute the residue to *ca.* 40 ml with water, then carry out the TTA extraction.

RESULTS AND DISCUSSION

TTA extraction of manganese

The absorbances of the manganese complex and reagent blank solutions remained constant for at least a week at room temperature.

Effect of pH. Manganese was quantitatively extracted in the pH range 8.5–9.5 as seen in Fig. 1.

Effect of hydroxylamine hydrochloride concentration. Hydroxylamine hydrochloride was necessary to keep the manganese in oxidation state II. A concentration of 0.05% hydroxylamine hydrochloride in the resulting solution is sufficient.

Effect of TTA concentration. Any TTA concentration oetween 0.001*M* and 0.2*M* is suitable for the manganese levels used, and 0.01*M* was chosen as being convenient (see below, *Separation of the phases*).

Shaking time. Although a shaking-time of 1 min has been adopted, the extraction is complete after 10 sec of shaking.

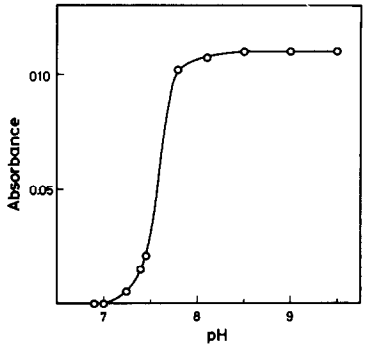

Fig. 1. Effect of pH on TTA extraction of 2.50 μg of manganese in 50 ml of aqueous phase containing 1 ml of hydroxylamine hydrochloride solution. Dilute ammonia solution was used in pH adjustment before addition of 5.0 ml of TTA solution.

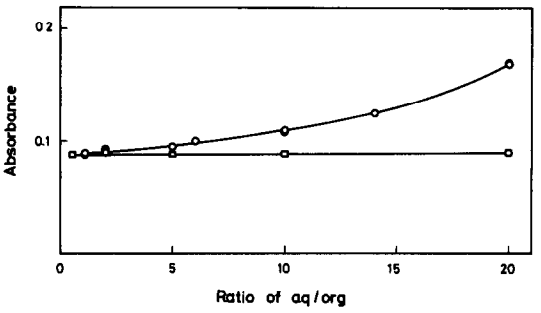

Fig. 2. Effect of ratio of aqueous to organic phase on TTA extraction of 2.50 μg of manganese. ○, 5.0 ml of 0.01*M* TTA solution; ●, 5.0 ml of 0.15*M* TTA solution; □, after correction for volume of organic phase after shaking.

Separation of the phases. After the shaking, an emulsion is formed. With increasing concentration of TTA, the separation of the phases becomes more difficult. After 15–20 min standing, white bubbles which do not contain manganese remain in the aqueous phase.

Calibration curve. Linear calibration curves are obtained for the manganese concentration ranges 0–0.9 μg/ml of organic phase when the burner slot is parallel to the optical path (normal position) and 0–50 μg/ml when the slot is at 90° to the optical path.

The sensitivity is about 7 times as great for MIBK extracts as for aqueous solutions (0.02 μg/ml for 1% absorption for organic solutions and 0.13 μg/ml for aqueous solution).

Effect of phase-volume ratio. The volume of aqueous phase was varied in the range 2.5–100 ml and the volume of organic phase (0.01 and 0.15*M* TTA) was kept constant at 5.0 ml, giving a phase-volume ratio ranging from 0.5 to 20. As indicated in Fig. 2, the absorbance increases exponentially with increasing phase ratio (or volume of aqueous phase). For example, the absorbances were 0.110 and 0.169 at aq/org = 10 and 20, respectively However, it was also found that the 5.0 ml of MIBK had decreased to 4.0 and 2.6 ml after shaking with 50 and 100 ml of aqueous phase respectively. Therefore, the increase in absorbance is merely due to the dissolution of MIBK. So, in this extraction system, it is important to keep the volume ratio of aqueous and organic phases constant. If the extraction is carried out from 100 ml of aqueous solution with 5.0 ml of TTA–MIBK solution, the absorbance must be corrected from the decrease in the volume of organic phase.

Interferences. The possible interference of a large number of cations and anions in the TTA extraction of 2.50 μg of manganese was examined. Most of the metals were used as sulphate, nitrate or chloride. For an error of 0.1 μg of manganese the tolerance limits for interfering cations and anions are summarized in Table 2. The oxidation states of the metals are those before addition of hydroxylamine hydrochloride.

Chromium, iron, hafnium, niobium, nickel, rhodium, tin, titanium and zirconium interfere strongly even at low concentrations, and most other metals

Table 2. Effect of diverse ions on determination of manganese

Addition		Mn found, μg	Addition		Mn found, μg
Al(III)	0.50 mg	2.5	Ni(II)	50 μg	2.5
	1.0 mg	2.3		0.10 mg	2.3
Bi(III)	5.0 mg*	2.5		1.0 mg	1.7
	10 mg*	2.2		10 mg	0.1
Ca(II)	5.0 mg	2.5	Os(IV)	0.10 mg	2.5
	10 mg	2.2		1.0 mg	2.4
Ce(IV)	1.0 mg	2.5		5.0 mg	2.0
	5.0 mg*	0.3		10 mg	1.8
	10 mg*	0.2	Pr(III)	5.0 mg*	2.5
Co(II)	0.10 mg	2.5		10 mg*	1.8
	1.0 mg	1.8	Re(VII)	0.10 mg	2.5
	5.0 mg	0.2		1.0 mg	2.4
	10 mg	0.1		10 mg	0.6
Cr(III)	10 μg	2.5	Rh(III)	10 μg	2.5
	25 μg	2.4		25 μg	1.2
	50 μg	1.8		0.10 mg	0.7
	0.10 mg*	1.3		10 mg*	0.1
	1.0 mg*	0.5	Sb(III)	0.10 mg	2.5
	10 mg*	0.3		1.0 mg	2.3
Cu(II)	1.0 mg	2.5		5.0 mg	1.7
	5.0 mg	1.9		10 mg	1.1
	10 mg	0.4	Si(IV)	1.0 mg	2.5
Dy(III)	1.0 mg	2.5		5.0 mg	1.3
	5.0 mg*	1.8		10 mg	0.6
	10 mg*	1.5	Sm(III)	1.0 mg	2.5
Er(III)	1.0 mg	2.5		5.0 mg*	2.1
	5.0 mg*	1.9		10 mg*	2.0
	10 mg*	1.6	Sn(II)	25 μg	2.5
Eu(III)	1.0 mg*	2.5		50 μg	2.2
	5.0 mg*	1.9		0.10 mg	1.8
	10 mg*	1.8		1.0 mg	0.2
Fe(III)	10 μg	2.5	Sr(II)	1.0 mg	2.5
	25 μg	2.4		10 mg	2.6
	50 μg	2.2		100 mg	3.1
	0.10 mg	2.0	Tb(III)	1.0 mg	2.5
	1.0 mg*	1.1		5.0 mg*	2.2
	10 mg*	0.9		10 mg*	0.2
Ga(III)	1.0 mg	2.5	Ti(IV)	10 μg	2.5
	5.0 mg	2.2		25 μg	2.1
	10 mg	1.7		0.10 mg	1.5
Gd(III)	1.0 mg	2.5		10 mg*	0.2
	5.0 mg*	2.3	Tm(III)	1.0 mg	2.5
	10 mg*	2.2		5.0 mg*	2.0
Hf(IV)	10 μg	2.5		10 mg*	0.4
	25 μg	2.4	W(VI)	5.0 mg	2.5
	0.10 mg	2.2		10 mg	2.4
	10 mg*	0.5	Y(III)	1.0 mg*	2.5
Ho(III)	1.0 mg*	2.5		5.0 mg*	1.3
	5.0 mg*	1.8		10 mg*	0.2
	10 mg*	1.4	Zn(II)	1.0 mg	2.5
In(III)	0.10 mg	2.5		5.0 mg*	2.4
	1.0 mg	2.3		10 mg*	1.3
	5.0 mg*	2.0	Zr(IV)	25 μg	2.5
	10 mg*	1.5		50 μg	2.3
Li(I)	5.0 mg	2.5		0.10 mg	2.1
	10 mg	2.4		1.0 mg	1.7
Mg(II)	1.0 mg	2.5		5.0 mg*	0.9
	5.0 mg	1.9		10 mg*	0.6
	10 mg	1.5	CN^- (as KCN)	5.0 mg	2.5
Nb(V)	50 μg	2.5		10 mg	2.3
	0.10 mg	2.2	F^- (as NaF)	5.0 mg	2.5
	1.0 mg*	1.5		10 mg	2.3
	10 mg*	1.5	SCN^- (as KSCN)	5.0 mg	2.5
				10 mg	2.4

* Precipitate arises in the aqueous phase.

Table 3. Results of manganese determinations in environmental water samples

Type of water	Location	Manganese, *ppM* With MIBK extn.*	RSD, %	Without MIBK extn.†
Drinking	Water supplies in JAERI	4.6 ± 0.3	6.5	4.6, 5.0
Waste (1)-A	Waste stream of No. 1 in JAERI	14.7 ± 0.3	2.0	14.5, 14.5
Waste (2)-A	Waste stream of No. 2 in JAERI	23.8 ± 0.3	1.3	23.7, 23.7
Lake	L. Akogi, Ibaraki	50.8 ± 0.5	1.0	50.9, 51.5
River (1)	R. Kuji, 0.8 km from the estuary, Ibaraki	19.7 ± 0.4	2.0	20.2, 19.7
River (2)	R. Kuji, 10 km from the estuary, Ibaraki	32.5 ± 0.4	1.2	32.4, 32.4

Before the determination, all the samples were treated with hydrochloric acid at the sampling site and passed through a 0.45-μm Millipore filter; 40.0 ml of each sample were used for the determination.

* Av. ± $\sigma(n = 5)$.

† Determined without MIBK extraction for removal of iron.

(except strontium) give low results when present at high concentration, but 10 mg each of silver, arsenic(V), barium, beryllium, cadmium, caesium, germanium, mercury(II), iridium, lanthanum, molybdenum(VI), lead, palladium(IV), rubidium, selenium-(IV), tellurium(VI), thallium(I) and vanadium(V), and 20 mg each of potassium and sodium did not interfere. Anionic interferences were restricted to cyanide, fluoride and thiocyanate; 10 mg each of bromide, carbonate, perchlorate, iodide, nitrate, sulphate and thiosulphate did not interfere, nor did borate (54 mg), chloride (20 mg), citrate (950 mg), phosphate (30 mg) and tartrate (730 mg). However, addition of tartrate to the aqueous phase before the extraction did not prevent the interferences.

Removal of iron by MIBK extraction

The interference of iron is sometimes a serious problem in water analysis, so iron was removed by MIBK extraction[16] before the TTA extraction, ~94% of the manganese remaining in the aqueous phase after a single MIBK extraction. Although *ca.* 6% of the manganese is lost in the extraction, 10 mg of iron can be separated satisfactorily from 0.1–5.0 μg of manganese.

Application to environmental waters

The method was applied to the analysis of environmental waters such as drinking, waste, lake and river waters. Immediately after the water samples were taken, 10 ml of concentrated hydrochloric acid were added per litre of sample. The solution was then passed through a 0.45-μm Millipore filter previously washed with 500 ml of 0.01*M* hydrochloric acid. Table 3 shows the analytical results obtained by applying the established method to six water samples. As indicated in the table, 5–50 ppM (parts per milliard) of manganese in the filtered fractions of environmental water samples can be determined with relative standard deviations of 7–1%. It is also seen that removal of iron by MIBK extraction is not necessary for the water samples tested.

The volume of sample used for the extraction was varied from 10 to 40 ml and the amount of manganese found was plotted against sample volume, a linear relation being found. Tests with known amounts of manganese added to each sample solution and determined with and without MIBK extraction for removal of iron gave 96–104% manganese recovery, showing that the extraction was quantitative.

A method involving evaporation and AAS was used to check the reliability of the method (Table 4). The results obtained by both methods were in good agreement for all the samples. The proposed method, however, needs much smaller volumes of sample and shorter analysis time than the evaporation method.

CONCLUSIONS

Manganese at concentrations of a few ppM in aqueous solutions can be determined by AAS with a single-step extraction of manganese(II) with TTA/MIBK. It is important to keep the volume ratio of aqueous and organic phases constant, because of the dissolution of MIBK in the aqueous phase. As it is easy to concentrate the manganese by a factor of up to 20 by the TTA extraction, the sensitivity is increased. The method is simple and rapid, with high sensitivity, satisfying precision and reliability, in addition to a broad determination range.

Table 4. Comparison of results of manganese determinations by two methods

Sample	Manganese, *ppM* Proposed method		Evaporation-AAS method*	
Waste (1)-B	15.6	16.0	15.1	16.0
Waste (2)-B	17.9	17.3	17.0	18.0

* One litre of each sample was reduced to 20 ml by evaporation. Values were obtained by use of a calibration curve.

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SHORT COMMUNICATIONS

COMPARISON OF METHODS FOR THE DETERMINATION OF VANADIUM IN SEA-WATER

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Summary—Procedures for the determination of vanadium in sea-water have been independently developed at two laboratories. The separation and concentration steps were distinctly different and quantification was by neutron activation or atomic absorption. Both methods provide a reliable measurement of vanadium concentration at natural levels in sea-water.

Analytical procedures for the determination of vanadium in sea-water have been developed independently at two laboratories. Each of the methods incorporated a separation and concentration step to eliminate interference by the sample matrix. In the first case vanadium and a vanadium tracer were co-precipitated from solution with ferric hydroxide;[1] in the second, a vanadium thiocyanate complex was formed and separated by sorption on an anion-exchange resin. The co-precipitated vanadium was determined by neutron-activation analysis (NAA); in the ion-exchange procedure the vanadium was determined by atomic-absorption spectrometry (AAS) on the eluate. This report compares the results obtained when samples of water collected from the Adriatic Sea and the Pacific Ocean were analysed by both methods.

EXPERIMENTAL

Samples

The sea-water was collected at a depth of 20 ft off the end of the pier at the Scripps Institution of Oceanography, La Jolla, California, and at two locations (Lignano and Ancona) in the Adriatic Sea. The waters were acidified with concentrated hydrochloric acid (10 ml/l.) at the time of collection, then filtered through a 0.45 μm membrane and stored in acid-leached polyethylene containers.

Neutron-activation analysis procedure

Chemicals and tracer. Iron carrier solution was prepared by dissolving 99.999% pure iron powder in *aqua regia* and diluting with distilled water to a final concentration of 10 mg/ml. Vanadium-48 solution in the carrier-free form was prepared as vanadium(IV) in 0.1*M* hydrochloric acid. Vanadium standard (2 μg/ml) was made from a commercial 1000-ppm standard prepared from ammonium metavanadate. Other reagents used were of analytical reagent grade.

Instruments. The ^{48}V tracer was gamma-counted with an NaI(Tl) well-type detector coupled to a scaler. The neutron-induced ^{52}V was measured with a 38-cm^3 Ge(Li) detector associated with a 4096-channel pulse-height analyser. The pulse-height data were transferred onto magnetic tape and thence into a computer, which provided the net counting rate for the 1434-keV photopeak of neutron-activated vanadium.

Isolation of vanadium from sea-water. Iron carrier (1 mg/100 g of sample) was added to a weighed amount ($\leq$ 100 g) of acidified sea-water. A known ^{48}V activity, usually about 10^4 cpm, was also added. Some samples were also treated with 0.1 ml of the vanadium standard at this stage. The solution was kept at 70–80° for 1 hr to facilitate exchange between the various oxidation states of vanadium in solution. After cooling, the pH was adjusted to about 7 with 8*M* ammonia and the precipitate was coagulated by warming and collected on a sintered-glass disc of medium porosity, washed with water to remove residual salts and dissolved in a small volume of 8*M* nitric acid. The solution was transferred to a 7-ml polyethylene irradiation vial and brought to a final weight of 5.00 $\pm$ 0.05 g with 8*M* nitric acid (4.13 ml). The recovery of ^{48}V in this solution was determined by comparison of its gamma-ray activity with that of a tracer standard (to provide information on the amount of sample solution transferred to the vial).

Blanks and standards. Three blanks were prepared, namely 100 μl of the iron carrier solution in 8*M* nitric acid, 8*M* nitric acid, and 8*M* ammonia. The standards were also made up in 8*M* nitric acid and contained 0.2 μg of vanadium. Blanks, standards and samples all had the same volume, obtained by weighing the solutions, the specific gravity of which was known.

Irradiation and measurement. Samples, blanks and standards were irradiated sequentially, each for 180 sec, in the pneumatic tube assembly of the TRIGA nuclear reactor at the University of California, Irvine, California. The thermal-neutron flux at the terminal end of this assembly is 3×10^{12} n.cm^{-2}.sec^{-1}. After irradiation the sample was transferred to a 14-ml polyethylene vial, and the original vial was rinsed once with 1.5 ml of distilled water, the rinse being added to the irradiated solution. The sample

Table 1. Effect of various eluents on the recovery of vanadium sorbed as the thiocyanate complex on Dowex 1

Eluent		V added to 1 litre of artificial sea-water, μg	V found in eluate, μg
Volume, *ml*	Composition		
150*	Methanol–6*M* HCl (9:1 v/v)	5.0	4.95*
150	1*M* $HClO_4$–1*M* HCl	5.0	2.4
150	2*M* $HClO_4$–1*M*HCl	5.0	1.2
50	6*M* HCl	5.0	0.0

* If a much smaller volume is used (100 ml or less) the elution of vanadium is not quantitative.

was positioned in the centre of the Ge(Li) detector and separated from it by a plastic beta-particle absorber, 2 cm thick. The gamma-ray pulses were accumulated for 180 sec, commencing 90 sec after the end of the irradiation. The instrumental dead-time at the beginning and end of the counting interval was recorded. The 1434-keV photopeak of ^{52}V was corrected for the mean dead-time value and the isotopic yield in the initial isolation step. The corresponding quantity of vanadium was calculated by simple proportion from standards corrected for dead-time.

Atomic-absorption procedure

All reagents were of analytical-reagent grade unless otherwise stated. The preparation of vanadium standard and aluminium chloride solutions was described earlier.[2] The ion-exchanger was Dowex 1, X8 (100–200 mesh; chloride form); 4 g of it were soaked in a few ml of the pretreatment solution and the slurry transferred to form the ion-exchange column,[3] the same solution being used as a rinse. The pretreatment solution consisted of 100 ml of distilled water, 1 ml of concentrated hydrochloric acid, 1 g of potassium thiocyanate and 0.5 g of ascorbic acid and was prepared fresh daily. The eluent solution was a 9:1 v/v mixture of methanol and 6*M* hydrochloric acid. To avoid the formation of air-bubbles in the resin-bed this solution should not be prepared immediately before use, but preferably one day in advance; the mixture is stable for at least one month.

Artifical sea-water was made by dissolving the following chemicals in 1 litre of distilled water: NaCl (28.0 g), KCl (0.8 g), $MgSO_4 \cdot 7H_2O$ (5.33 g), $CaCl_2 \cdot H_2O$ (1.33 g).

Preliminary experiments. The effect of the following eluents on the recovery of vanadium (from synthetic sea-water) sorbed as the thiocyanate complex on Dowex 1 was examined: 150 ml of methanol–6*M* hydrochloric acid (9:1 v/v); 150 ml of 1*M* perchloric acid–1*M* hydrochloric acid: 150 ml of 2*M* perchloric acid–1*M* hydrochloric acid: 50 ml of 6*M* hydrochloric acid.

The recovery of up to 200 μg of vanadium in 1 litre and of 12 μg of vanadium in 5 litres of synthetic sea-water was also studied.

Procedure. In each litre of acidified sea-water used, 10 g of potassium thiocyanate and 5 g of ascorbic acid were dissolved and the solutions were let stand for 2–3 hr. Artificial sea-water was treated in the same way, except that known amounts of vanadium were added. These samples (1–3 litres) were passed through the ion-exchange column at a flow rate of 1.7 ml/min. The resin was then washed with 20 ml of distilled water and vanadium eluted with 150 ml of eluent solution.

The vanadium eluate was slowly evaporated under an infrared lamp, the residue dissolved in 10 ml of 6*M* hydrochloric acid containing 1 ml of the aluminium chloride solution, and vanadium determined by atomic-absorption spectrophotometry.[2] For calibration, suitable standard solutions were aspirated before and after each batch of samples.

RESULTS

No measurable amounts of vanadium were detected in the blank materials examined by NAA. Only the methanolic hydrochloric acid eluent removed vanadium quantitatively from the resin column (Table 1). The results summarized in Table 2 show that vanadium up to 200 μg is quantitatively sorbed on the resin from up to 5 litres of sample and recovered by elution.

The analysis of the sea-water samples is shown in Table 3. The average concentration and standard deviation of the Pacific Ocean waters (μg/l.) were 2.00 ± 0.09 by NAA and 1.86 ± 0.12 by AAS. For the Adriatic water the corresponding values were 1.69 and 1.71 at the Lignano location and 1.64 and 1.73 in the vicinity of Ancona. The difference between the values for the same sea-water is within the range to be expected from the standard deviations observed.

DISCUSSION

In the NAA procedure the irradiation assembly is such that a sample size of up to 5 ml may be accommodated. It was inconvenient to transfer the dissolved iron carrier quantitatively to the irradiation vial and still keep within the volume limitation. Accordingly, less than the entire sample was irradiated. Knowledge of the fraction of the sample undergoing analysis was provided by the ^{48}V measurement. For the 14 samples analysed, the fraction transferred ranged from 88.8 to 94.8%.

In the pulse-height analysis of the samples, the dead-time (which represents the percentage of time that gamma-ray pulses were not accepted by the spectrometer) ranged from 9 to 30% at the start of counting. The decrease in dead-time over the counting interval was usually about 5% and occurred linearly as estimated for several samples by recording dead-time meter readings at about 15-sec intervals during the course of measurement. With the irradiation schedule used, about 15000 counts per μg of vanadium are acquired in the photopeak area. Fractions of a microgram may be determined even with the modest neutron flux used.

Table 2. Effect of vanadium concentration and sample volume on recovery

Volume, *l.*	V added, μg	V found in eluate, μg
1.0	40	42.0
1.0	200	194
2.0	12	12.0
3.0	12	11.9
4.0	12	12.2
5.0	12	12.3

Table 3. Results of vanadium determinations in sea-water samples

Sample	Volume, *l.*	Vanadium concentration, *μg/l.* NAA	AAS
Pacific Ocean			
(Scripps Pier)	1		1.80
	1		2.00* (2.0)
	2		1.90*
	3		1.73
	0.098	1.99†	
	0.098	2.00§ (0.20)	
Adriatic Sea			
(Shore near Lignano	3		1.71
Sabbiadoro, Italy)	0.041	1.69	
(Shore near Ancona,	3		1.73
Italy)	0.043	1.64	

* Results after subtraction of the quantity of vanadium added to the sample before the ion-exchange or co-precipitation step. The amount added (in μg) is shown in parentheses.

† Average of 12 determinations, standard deviation 0.10 μg/l.

§ Average of two samples, average deviation 0.01 μg/l.

In the AAS method, ascorbic acid is added to the acidified water sample to reduce vanadium to the quadrivalent state. This reacts with thiocyanate to form an anionic complex which is strongly retained on the Dowex 1 (thiocyanate form). Co-adsorbed with the vanadium are the thiocyanate complexes of uranium,[4,5] molybdenum,[6] cobalt,[7,8] cadmium,[8] zinc,[9] copper,[10] mercury[10,11] and iron(III).[4] Only part of the molybdenum is co-eluted with the vanadium by the methanol–hydrochloric acid. All other elements are strongly retained because they form stable anionic chloride complexes. The methanolic hydrochloric acid must be used as eluent because the vanadium thiocyanate complex is very strongly sorbed ($K_d > 10^4$) and cannot be destroyed by application of aqueous acid. Similar observations apply to uranium.[4]

The thiocyanate passing into the eluate during elution does not interfere during the subsequent evaporation to dryness. The washing step preceding the elution of vanadium removes residual potassium thiocyanate and ascorbic acid from the ion-exchange column.

Though the NAA method is inherently more sensitive than the AAS method, both procedures give a reliable measurement of vanadium in sea-water at the natural levels of concentration.

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DETERMINATION OF ALUMINIUM IN AEROSOLS BY FLAMELESS ATOMIC-ABSORPTION SPECTROMETRY

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Summary—A method is reported for the determination of aluminium in aerosols collected on Whatman 41 cellulose filters. In the destruction procedure, provision was made to eliminate silica by hydrofluoric acid treatment. Analysis of the solutions was performed by the flameless atomic-absorption technique. The accuracy was checked by using data from instrumental neutron-activation analysis (INAA) and standard reference materials. An analogue integrator gave a better linearity and detection limit than conventional peak-reading.

Aluminium is one of the few elements that are present at parts per hundred levels in particulate matter in air. Other elements present in high concentration are Na, K, Mg, Ca, Zn, Si, Pb and Fe.[1] One important feature of aluminium is its potential use as a monitor in air-pollution measurements, as this element mainly originates from natural sources. If the concentrations of pollutants are expressed by reference to that of aluminium, the influence of the natural background variations can be taken into account.

The determination of aluminium by flame atomic-absorption techniques is quite difficult, unless the nitrous oxide–acetylene flame is adopted. Flameless atomic-absorption avoids many interference problems while permitting the use of very small samples. Although some interferences have been studied previously,[2] both anionic and cationic interferences of potential importance when aerosols are dealt with were investigated in this work. Extensive use was made of an analogue integrator which is a simplified version of that described by Cox.[3]

EXPERIMENTAL

Instrumentation

Use was made of a Perkin-Elmer 503 spectrometer in conjunction with an HGA 74 furnace and its programmable power supply. Auxiliary equipment was a Perkin-Elmer deuterium correction-unit (No. 3030875) and a type-56 recorder. The light-source was an aluminium hollow-cathode lamp (Activion Glass Ltd.). The working current for this lamp is 20 mA, but later tests showed that running it at 10–15 mA kept the background noise level to a minimum. A 20-μl Eppendorf pipette was used for the injection of solutions into the furnace. For some experiments an energy-dispersive X-ray fluorescence analysis system (Kevex 0810) connected to a Northern Econ II multichannel analyser was used.

The integrator used in this work is shown in Fig. 1. This unit automatically corrects for base-line drift. To minimize drift, it is important to use the high signal output from the spectrometer (1 V for an absorbance of 1), resulting in negligible electronic drift.

Reagents and standard solutions

All reagents used in this work were of the "Pro Analysis" grade. Water was distilled in a quartz apparatus. The primary aluminium standard was prepared by dissolving exactly 1 g of aluminium in 10 ml of 12*M* hydrochloric acid. Dilution gave a 1000-ppm stock solution which was used for all further work. A constant hydrochloric acid concentration was maintained when preparing dilute solutions. This gave a shelf-life of more than 6 months for concentrations as low as 0.2 ppm. All solutions were stored in polyethylene flasks.

Instrumental parameters

The optimum ashing and atomization conditions were determined by introducing into the furnace 4-ng amounts of aluminium in 20 μl of 0.1 *N* acid. Measurements were made at 309 nm with a 0.7-nm spectral band-width. Signals were recorded for ashing times of 15 and 30 sec. Figure 2 shows signal–temperature curves obtained with use of hydrochloric, nitric and sulphuric acids. Similar results were obtained with phosphoric acid, but when this acid is heated at below 1000°, smoke formation occurs during atomization. It is apparent from Fig. 3 that the presence of perchloric acid leads to irreproducible results.

The following programme was selected.
Drying 100°, 30 sec (20 ml)
Ashing 1500°, 15 sec
Atomization 2700°, 10 sec
Burn-out 2700°, 10 sec

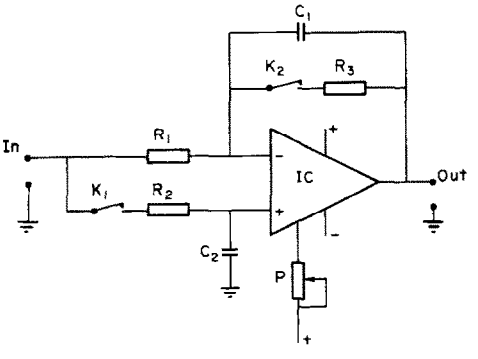

Fig. 1. Schematic diagram of analogue integrator. $R_1 = R_2 = 1\,M\Omega$; $R_3 = 1\,k\Omega$; $P = 10\,k\Omega$; $C_1 = 1\,\mu F$; $C_2 = 5\,\mu F$; $IC = 40\,J$ analog devices.

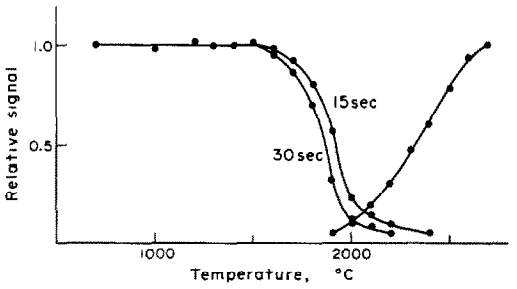

Fig. 2. Ashing and atomization curves for HCl, H_2SO_4, HNO_3 and H_3PO_4.

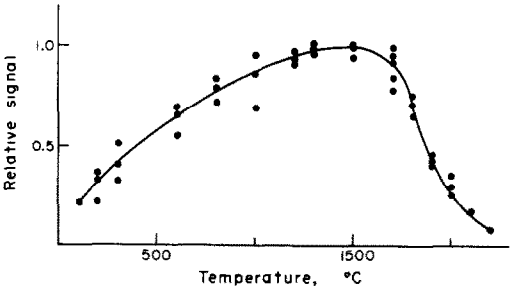

Fig. 3. Ashing curve for $HClO_4$.

Except when indicated, use was made of the gas-stop mode.

Spectral characteristics

The four most important spectral lines of aluminium, at 308, 309, 394 and 396 nm, were investigated. Other lines were not detected because of their lower relative intensities.

Experiments were made with 4 ng of aluminium in 0.1*M* hydrochloric acid and the results are shown in Table 1. The spectral band-width was 0.7 nm (according to the Perkin-Elmer instructions).[4]

The upper limit for linearity is defined as the amount of aluminium at which the absorption deviates by 10% from the straight line relationship. The relative sensitivity of 1.00 for the 309-nm gas-stop conditions corresponds to an absolute sensitivity of 4.5 ± 10^{-11} g of aluminium for 1% absorption. As the 309 and 396 nm spectral lines are the most sensitive and the most intense, they are suitable for a low detection limit. At 396 nm it was preferable to reduce the band-width to 0.2 nm as saturation of the detector could occur, presumably because of radiation from the oven in the near-visible region of the spectrum.

The detection limits given in Table 2 were calculated for the 3σ criterion. It is apparent from Tables 1 and 2 that both the linearity and the detection limits are improved when the integrator is used.

Interferences

Anions. The interference of several anions was studied with 4 ng of aluminium and measurement at 309 nm. Results for the five most common acids (HCl, H_2SO_4, HNO_3, H_3PO_4, and $HClO_4$) are shown in Fig. 4. This representation is equally valid for peak-height and peak-area measurements as no significant difference between the values obtained was noted. All curves were normalized at 0.0001*M* hydrochloric acid. Clearly no serious interference is observed except when perchloric acid is present. This has some drawbacks as far as the destruction of the sample is concerned, because standard destruction methods often include the use of perchloric acid

Cations. Again 4-ng amounts of aluminium in 0.1*M* hydrochloric acid were introduced and the absorbance was measured at 309 nm. An interference study was made for Na, K, Mg, Ca, Zn, Si, Pb and Fe. Although it is expected that in most aerosols the w/w ratio of any element to aluminium will not exceed 10, the interference was investigated up to a ratio of 500. Departure from the expected signal was always smaller than 3 and 25% for ratios of 10 and 500 respectively. Deuterium correction and peak-integration gave similar results. It can be concluded that cationic interference is negligible when dealing with most aerosols.

Destruction procedure

A simple and rapid preliminary destruction of the organic material has been used. It consists of a 30-min heating cycle in a muffle furnace at 600°. A prolonged heating cycle of up to 8 hr gave no evidence of aluminium losses. The procedure was compared with a wet nitric acid destruction but no significant difference in results was noted.

After this treatment, 10 ml of nitric acid are added to the ash and the material is quantitatively transferred into a Teflon beaker. Approximately 0.5 ml of hydrofluoric acid (48%) is added and the solution heated in an oil-bath to dryness. The quantities given are suitable for 10-cm^2 pieces of filter paper. This step is necessary because otherwise a considerable fraction of the sample remains undissolved. A comparison was made of the remaining solid phase, after a classical wet digestion with nitric and perchloric acids with that obtained when the step using hydrofluoric acid was included in the procedure. The results listed in Table

Table 1. Linearity and relative sensitivity

Wavelength *nm*	Gas-flow mode	Upper linearity limit, *ng*		Relative sensitivity
		Peak-height measured	Peak-area measured	
308		280	420	25
308	mini-flow	22	26	1.8
308	gas-stop	16	20	1.5
309		60	60	9.1
309	mini-flow	8	10	1.2
309	gas-stop	7	9	1.0
394		200	340	25
394	mini-flow	50	60	2.7
394	gas-stop	36	50	2.2
396		120	160	9.1
396	mini-flow	26	34	1.2
396	gas-stop	24	32	1.1

Table 2. Detection limits

Wavelength, *nm*	Band-width *nm*	Detection limit, *ng* Peak-height measured	Peak-area measured
309	0.7	0.12	0.07
396	0.2	0.32	0.08

Table 3. Composition of solid-phase residue after destruction

Element	Remaining solid phase after destruction, % Without HF	With HF
Mg	2.6	0
Al	14	1.7
Si	72	0
K	13	0
Ca	10	0.3
Ti	65	16
Fe	2.5	0.3
Mn	2.9	0.1
Ni	0.5	0
Cu	0	0
Zn	0.4	0
Pb	0.1	0

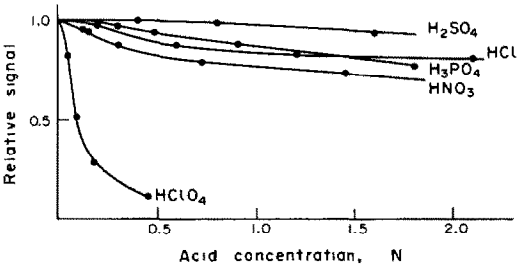

Fig. 4. Anionic interferences.

3 were obtained by filtering the solutions obtained by both procedures (0.4-μm Nucleopore filter) and performing a multielement analysis of the filter by energy-dispersive X-ray fluorescence. The most important element not completely brought into solution is titanium, probably because it is present as TiO_2. The residual 1.7% of aluminium affects the accuracy of the analysis to a negligible extent.

Accuracy

To investigate the accuracy, four different types of samples with known aluminium content were selected: seven WH 41-filters, a standard gelatin sample, and coal and fly-ash standard reference materials. Peak area was used for all measurements.

Table 4. Analysis of gelatin, coal and fly ash

Sample	Aluminium concentration Literature	This work
Gelatin	55 ± 2 ppm	60 ± 2 ppm
Coal	1.85 ± 0.13%	1.65 ± 0.12%
Fly ash	12.7 ± 0.05%	13.8 ± 0.2%

The WH-41 filters. Seven filters loaded with urban aerosol were analysed by INAA at the Institute of Nuclear Sciences in Ghent, Belgium. The aluminium concentration is reported with 5% precision. Two separate analyses following the procedure described were made for each filter. The mean deviation with respect to INAA is about 12% but filter inhomogeneities are to some degree responsible for the observed deviations.

Gelatin, coal and fly ash. The method was also tested on samples other than aerosols. A gelatin reference material available from Kodak Industrial Laboratories (TEG-50-A), containing 25 elements in concentrations of about 50 ppm,[5] was analysed.

The accuracy was also checked by using coal and fly-ash standard reference materials from NBS (SRM 1632 and SRM 1633). None of these materials has been officially certified for the aluminium concentration, but literature data are available.[6] These results and the mean of four individual runs for each sample are listed in Table 4.

CONCLUSION

Instrumental parameters and spectral characteristics were investigated and optimized. With the exception of ClO_4^-, no serious interference from other ions should occur when dealing with aerosols.

Analogue integration yielded better results than peak-height measurement as far as linearity and detection limit are concerned.

Accuracy tests showed good agreement with literature data on widely different matrices.

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DETERMINATION OF THIOUREA AND ITS ORGANIC DERIVATIVES WITH IODINE TRICHLORIDE

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Summary—Thiourea and its organic derivatives and thiosemicarbazide are determined in water, methanol or glacial acetic acid medium by reaction with an excess of iodine trichloride in the presence of mercuric chloride. The reaction is complete in 15 min. The excess of iodine trichloride is evaluated by adding potassium iodide and titrating the liberated iodine with thiosulphate. A variety of organic thioureas can be determined with an average accuracy and precision of 0.2%.

A number of oxidimetric methods have been published for the determination of thiourea and its organic derivatives. The most widely used procedure for thiourea involves oxidation with hypoiodite.[1] The reaction is essentially complete in about 4 min and a longer reaction time of up to 30 min has no effect. Bromine in acid medium can also be used for thiourea.[2] Gupta[3] determined *N*-phenyl-, *N*,*N*'-methylphenyl-, *N*,*N*-ethylphenyl- and *N*,*N*'-diphenylthiourea with bromate–bromide mixture in acid medium, and the first three of these with iodine in presence of sodium bicarbonate. In both cases the main reaction involves removal of sulphur from the thiourea to give the corresponding urea and sulphate. The iodimetric determination is limited to water-soluble thioureas. In bromimetric determination, the aryl group undergoes nuclear bromination and thus the total consumption of bromine varies with the sample. Unfortunately, even under the optimum conditions, the consumption of bromine differs from the theoretical and, therefore, an empirical correction has to be made.

Tiwari and Pande[4] titrated thiourea and its allyl and phenyl derivatives with *N*-bromosuccinimide, the reaction products being thought to be the corresponding urea and elemental sulphur.

Organic derivatives of thiourea are not particularly soluble in water, and this imposes a limit on the concentration range that can be analysed in aqueous medium. Verma and Bose[5] titrated *N*-phenylthioureas in glacial acetic acid with lead tetra-acetate. This procedure is not applicable to diphenyl and alkyl thioureas. A cerimetric titration in acetonitrile proposed by Verma and Kumar[6] is applicable only to thiourea and its *N*-substituted alkyl derivatives. Phenyl iodosoacetate has also been applied in 40–80% acetic acid to determine *N*-aryl and alkyl thioureas.[7]

Hydrochloric acid solutions of iodine monochloride and iodine trichloride have been used extensively as analytical

Table 1. Determination of thioureas with iodine trichloride

	Purity, %		Deviation, %	
	Present method*	Comparison method	Av.	Max
Thiourea	98.2	98.0	0.1	0.1
Thiosemicarbazide	99.5	99.3	0.1	0.1
N-Allylthiourea	97.6	97.4	0.1	0.2
N-Methylthiourea	99.1	99.2	0.1	0.1
N-Butylthiourea	96.4	96.1	0.1	0.1
N-Phenylthiourea	98.9	99.3	0.2	0.3
N-*o*-Tolylthiourea	98.6	98.2	0.2	0.3
N-*p*-Anisylthiourea	97.8	97.6	0.2	0.4
N-*m*-Chlorophenylthiourea	99.6	99.4	0.2	0.3
N-Phenyl-*N*'-methylthiourea	96.8	97.2	0.3	0.4
N,*N*'-Diphenylthiourea	99.8	99.5	0.1	0.3
sym-bis(*o*-Tolyl)thiourea	99.3	99.0	0.2	0.5
sym-bis(*p*-Tolyl)thiourea	98.4	98.1	0.3	0.4
2-Methylthiouracil	99.0	98.7	0.4	0.6

* Average of 8 determinations

reagents. Kagan and co-workers[8–11] worked out volumetric determinations for many organic substances with these reagents, based on substitution, addition or oxidation reactions. In oxidations, they noted that both reagents react similarly. Thiourea is oxidized to its disulphide on titrating with iodine monochloride.[12] A similar method is described for alkyl and aryl derivatives of thiourea.[13] These reagents have also been used for titrating mercaptans in presence of starch and iodide.[14]

A rapid and precise procedure is described in the present communication for determination of thiourea and its alkyl and aryl derivatives with iodine trichloride. The samples are dissolved in water, methanol or glacial acetic acid and treated with an excess of iodine trichloride in the presence of a sufficient amount of mercuric ions. After completion of the reaction the excess of oxidant is evaluated iodimetrically.

EXPERIMENTAL

Reagents

Iodine trichloride solution, 0.1*N*. A simple method of preparation was used,[8] based on the reaction $KI + 2KIO_3 + 12HCl \rightarrow 3ICl_3 + 6H_2O$. For 1 litre of 0.1*N* iodine trichloride, dissolve 3.57 g of potassium iodate in 100 ml of hot water. After cooling add 1.38 g of potassium iodide, 41.7 ml of concentrated hydrochloric acid and dilute to 1 litre. Standardize iodimetrically.

Thioureas. As a check independent methods were used to determine the purity of samples. Thiourea[1] and thiosemicarbazide[15] were determined by hypoiodite oxidation, alkylthioureas by non-aqueous cerimetric titration,[6] phenylthioureas by bromine oxidation[3] and Pb(IV) titration.[5] Diphenylthiourea was determined by non-aqueous alkalimetric titration[16] and other diarylthioureas and 2-methylthiouracil by total sulphur analysis by the volumetric Carius method.[17]

The methanol and glacial acetic acid were reagent grade solvents.

Procedure

Take a sample solution in water, methanol or glacial acetic acid, containing 0.02–0.1 meq of –NHCSNH– group, in a 200-ml flask with a ground-glass stopper. Add 10 ml of a saturated aqueous solution of mercuric chloride followed by about 100% excess of iodine trichloride solution, with swirling. Allow the flask to stand for 15 min. When 2-methylthiouracil is being determined, immerse the flask for 5 min in a water-bath heated to 60° and then cool. Add 20% aqueous solution of potassium iodide until the first formed brick-red precipitate of mercuric iodide dissolves, then 5 ml more. Titrate the liberated iodine with 0.04*M* thiosulphate delivered from a 10-ml burette, with starch as indicator. Run a blank determination.

RESULTS AND DISCUSSION

The method yielded results accurate and precise to about 0.2% for a variety of thioureas. It is found that the amount of excess of oxidant has a marked effect on the reaction velocity. With 200% excess of the reagent the reaction is complete in about 5 min. Mercuric chloride is added to the reaction mixture, ostensibly to complex the iodide ions formed by reduction of iodine trichloride, but no mercuric iodide is apparently precipitated, presumably because the reduction product from the titrant is iodine monochloride and not iodide. This view is supported by the observation that on addition of excess of iodine trichloride to a suspension of mercuric iodide in water a clear solution results. In view of all this, the reaction of iodine trichloride with thioureas in presence of mercury(II) can be written as follows:

$$RNH \cdot CS \cdot NHR' + 4ICl_3 + 5H_2O \rightarrow RNH \cdot CO \cdot NHR' + H_2SO_4 + 4ICl + 8HCl$$

The reaction of thiosemicarbazide is

$$2NH_2 \cdot CS \cdot NHNH_2 + 10ICl_3 + 8H_2O \rightarrow 2HCN + 2N_2 + 2H_2SO_4 + 10ICl + 20HCl$$

Similar products were proposed by Suchomelová and Zýka[18] for the reaction of thiosemicarbazide with lead tetra-acetate. Semicarbazide reacts with iodine trichloride in the presence of mercury(II) according to the equation

$$NH_2 \cdot CO \cdot NHNH_2 + ICl_3 \rightarrow HCN + N_2 + ICl + 2HCl$$

The reaction is quantitative and complete in 5 min with about 50% excess of oxidant added.

In the absence of mercury(II), molecular iodine is liberated and if this is to be titrated extra care is needed to prevent the escape of iodine. Furthermore, the reaction becomes slow and a period of about 40 min is required for complete oxidation in the presence of about 200% excess of oxidant. The consumption of iodine trichloride is, however, the same as that in the presence of mercury(II).

Iodine trichloride is a powerful oxidant and reacts with several compounds. Hydrazine, ascorbic acid, thiophene, hydrogen sulphide and mercaptans interfere seriously. Compounds that can be tolerated even when present in large amounts include glucose, alanine, formic acid, urea, glutaric acid, butylamine, diethylamine and carbon disulphide.

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DETERMINATION OF THIOL GROUPS WITH *o*-DIACETOXY-IODOBENZOATE

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Summary—*o*-Diacetoxyiodobenzoate is used for determining thiol groups by two procedures. In the first, thiols are titrated directly with the reagent at pH 6–8, with leuco-2,6-dichlorophenolindophenol and potassium iodide as indicator. In the second, thiols are treated at pH 7 with an excess of the reagent, the surplus being determined by reaction with excess of mercaptoacetic acid followed by back-titration of the latter with iodine. Both procedures yield results within 0.2% of the theoretical.

Cysteine and glutatione have been determined with *o*-iodosobenzoate[1,2] according to the reaction

$$2RSH + OI\text{–}C_6H_4\text{–}COOK \rightarrow RSSR + I\text{–}C_6H_4\text{–}COOK + H_2O$$

An excess of the reagent is added to the sample solution and the residual amount is evaluated iodimetrically. However, this procedure needs some preliminary tests to ascertain the excess of reagent to be used if high results are to be avoided. Moreover, the excess of reagent should be titrated immediately after its addition. In the present work two simple methods are proposed which do not suffer from these shortcomings. In the first method a solution of the sample is titrated directly with a standard solution of potassium *o*-diacetoxyiodobenzoate [$(AcO)_2I\text{–}C_6H_4\text{–}CO_2K$] within the pH range 6–8, with leuco-2,6-dichlorophenolindophenol and potassium iodide as indicator; at the end-point a blue colour is formed. The end-point is sharp, stable and reproducible. Starch and potassium iodide can also be used as indicator, but the blue colour then has a tendency to fade and slightly high results are observed. This procedure is recommended for individual thiol groups even in the presence of several possible interferents. In the second method the thiol solution is treated with an excess of *o*-diacetoxyiodobenzoate and the surplus is evaluated by adding a measured excessive amount of mercaptoacetic acid solution and back-titrating the surplus of the latter with iodine. The results remain unaffected even by using 200% excess of the oxidant and titrating after 10 min. This procedure does not require any orienting tests and is expected to be useful for the determination of both free and sluggishly reacting thiol groups in natural products.

EXPERIMENTAL

Reagents

o-Diacetoxyiodobenzoate solution, 0.05*N*. Prepared by adding to the acid reagent a slight excess of 1*M* potassium hydroxide and diluting to standard volume. It is standardized iodimetrically and diluted as required.

Mercaptoacetic acid, 0.05*M*. Standardized iodimetrically.[5]

Phosphate buffer (pH 7). Prepared by dissolving 117.7 g of K_2HPO_4 and 44.1 g of KH_2PO_4 in 1 litre of water.

Leuco-2,6-dichlorophenolindophenol. Prepared by adding 0.5 g of potassium acetate to 25 ml of 0.05% solution of the sodium salt of the indicator and bleaching the blue colour by dropwise addition of 0.05% ascorbic acid solution. The reduced indicator is oxidized on exposure to air and hence decolorization before use is necessary.

Procedure 1

Dissolve an accurately weighed amount of sample, containing 0.05–1.0 meq of thiol group, in 10 ml of water and add 5 ml of phosphate buffer and 5 ml of water. Add 1 ml of leuco-2,6-dichlorophenolindophenol indicator together with about 50 mg of potassium iodide. Titrate slowly (5 ml of titrant per min) with 0.01*N* *o*-diacetoxyiodobenzoate reagent for up to 0.25 meq of thiol group and 0.05*N* titrant for larger amounts. Near the end swirl the solution for 10 sec between adding drops of titrant; the end-point is the appearance of the vivid blue colour of the oxidized form of indicator.

Procedure 2

Weigh a sample containing 0.1–1.0 meq of thiol group and dissolve it in 10 ml of water. Add 5 ml of phosphate buffer and 10 ml of suitably diluted *o*-diacetoxyiodobenzoate solution so that there is about 50–100% excess. Swirl the contents of the flask for about 30 sec and add a measured excess of 0.05*M* mercaptoacetic acid and 3 ml of 1*M* sulphuric acid. After 30 sec titrate the residual mercaptoacetic acid with 0.04*N* iodine, to a starch indicator end-point. Run a blank determination.

RESULTS

In Table 1, results are given for the determination of some water-soluble thiols by the proposed methods. The first procedure was also applied to ascorbic acid and sodium thiosulphate and their determination provides a useful means for standardizing the *o*-diacetoxyiodobenzoate solution (Table 2).

3-Mercaptopropionic and mercaptosuccinic acid, having the thiol group attached to the carbon atom β to the carboxyl group, give erroneous results in procedure 1; glutathione gives incorrect results in procedure 2.

Interferences

Thiourea and thiosemicarbazide cause +4% and +2% error respectively when present in amounts 5–6 times that of the thiol. Hydroquinone, thiosulphate, ascorbic acid and sulphide react quantitatively. Species that react with thiol groups must be absent (*e.g.*, silver, mercury and copper

Table 1. Determination of thiol groups with *o*-diacetoxyiodobenzoate

Sample	Purity, %		
	Procedure 1*	Procedure 2*	Comparison method
Cysteine	98.5	98.2	98.3 Hydroxymercuribenzoate[3]
Glutathione	97.6	—	97.8 Iodimetry[4]
2-Mercaptoethylammonium chloride	97.9	97.8	98.0 Iodimetry[5]
Mercaptoacetic acid	80.2	80.6	80.4 Chloramine-T titration[6]
2-Mercaptoethanol	98.7	99.0	98.8 ICl titration[7]
2-Diethylaminoethanethiol hydrochloride	98.1	98.0	98.3 Pb^{4+} titration[8]
Ethanethiol	95.6	95.2	95.4 Iodimetry[5]
2-Mercaptopropionic acid	97.4	97.5	97.3 Br^{+} titration[9]
Glycerol-1-thiol	79.2	79.2	79.0 Iodimetry[5]

* Mean of 10 determinations; relative standard deviations are 0.1–0.2% for procedure 1, 0.1–0.3% for procedure 2.

Table 2. Determination of ascorbic acid and sodium thiosulphate

Sample	Amount, *mg*	
	Procedure 1	Iodimetric determination
Ascorbic acid	0.56	0.62
	2.51	2.48
	5.63	5.70
	10.14	10.08
	25.52	25.65
Sodium thiosulphate	0.41	0.38
	1.10	1.18
	5.67	5.72
	9.26	9.32
	19.43	19.38

form insoluble mercaptides; unsaturated compounds such as acrylonitrile and methyl methacrylate form addition compounds; acetone forms mercaptals; oxidizing agents produce various compounds).

Alanine, cystine, 4-aminobenzoic acid, glycine, urea, formaldehyde, carbohydrates, cyanide, chloroacetic acid, thiocyanate and formate (which may interfere in one or another of the other methods for thiols) were tested and found not to interfere.

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ANALYTICAL APPLICATION OF ORGANIC REAGENTS IN HYDROPHOBIC GEL MEDIA—IV

SELECTIVE PRECONCENTRATION OF COBALT(II) WITH 1-NITROSO-2-NAPHTHOL GEL*

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Summary—Cobalt is selectively extracted from solution onto gel beads impregnated with 1-nitroso-2-naphthol. A concentration factor of 67 has been achieved by passing 2 litres of sea water containing 0.05 ppm of cobalt over the beads at a flow-rate of 40 ml/hr. The cobalt is eluted from the beads with methyl isobutyl ketone.

We have already reported the use of gel beads treated with dithizone and thiothenoyltrifluoroacetone for the selective trapping of mercury(II) in aqueous samples.[1] As a continuation of that study we now report the selective trapping of cobalt(II) at the ppm level from aqueous samples.

The gel beads used were of cross-linked polystyrene, and were swollen with chlorobenzene containing 1-nitroso-2-naphthol. During the complex-formation reaction, cobalt(II) was oxidized in the beads to cobalt(III) with the formation of the tris-chelate. Cobalt(III) could not be back-extracted even with concentrated mineral acids, but the chelate was easily eluted from the gel-beads by a small amount of methyl isobutyl ketone (MIBK) and the cobalt subsequently determined.

A similar investigation using polyurethane sponge support has been reported recently, but nothing was mentioned about the recovery of cobalt from the reagent matrix.[2]

EXPERIMENTAL

Reagents

1-Nitroso-2-naphthol (analytical grade) was recrystallized twice from ligroin, and had m.p. 110.4–110.8°. All other reagents were of analytical grade.

Procedures

Preparation of the gel beads and the column. Two g of dry polymer beads (60–80 mesh) were soaked with 15 ml of 0.01*M* solution of 1-nitroso-2-naphthol in chlorobenzene for 24 hr at room temperature. The gel beads, after centrifugation, were packed into a glass tube in a manner similar to that described previously,[1] to give a column of 1.0 cm^2 × 10 cm. The interstitial volume in the column was about 5 ml. The reagent concentration, as calculated from the solvent taken up by dry polymer beads, was 5×10^{-6} mole per ml of the gel bed.

Gel column operations. All aqueous solutions to be subjected to the column operation were presaturated with chlorobenzene.

The pH of the sample solution containing a known amount of metal ions was adjusted to the appropriate value with a sodium acetate–perchloric acid buffer solution. The solution was charged into the column top by gravity flow at a flow-rate of 1.7 ml/min, and the eluate was collected in 10-ml fractions, which were analysed for metal ions by atomic-absorption spectrophotometry.

The cobalt(III) chelate from the gel bed column was recovered by eluting with MIBK at a flow rate of 0.4 ml/min. As the elution proceeds, the gel column shrinks to one third of its original volume because of loss of the solvent responsible for swelling. Forty ml of eluent were sufficient to recover the chelate from the gel bed of the dimensions given.

Partition coefficient of the reagent. The partition coefficient of 1-nitroso-2-naphthol in chlorobenzene was determined by shaking 10 ml of the organic phase with a mixture of 9 ml of 0.1*M* sodium perchlorate and 1 ml of 1*M* sodium acetate–perchlorate buffer. The concentration of the reagent in the aqueous phase was determined spectrophotometrically. Measurements were made on solutions ranging in concentration from 0.01 to 0.2*M* and in pH from 4.5 to 6.6.

RESULTS AND DISCUSSIONS

1-Nitroso-2-naphthol forms a 1:2 chelate (metal to ligand ratio) with cobalt(II), which oxidizes spontaneously to give the 1:3 chelate of cobalt(III).[3–7] This chelate is so inert that it does not dissociate even in strong acid or alkali, hence 1-nitroso-2-naphthol has been widely used as a selective reagent for the separation and photometric determination of cobalt.

Thus, it seemed reasonable to attempt the selective trapping of trace cobalt in aqueous samples by use of a column of polystyrene gel beads impregnated with a chlorobenzene solution of 1-nitroso-2-naphthol.

The distribution coefficient of the reagent between chlorobenzene and water was found to be 540 ± 35, slightly higher than the value of 350 in an MIBK–water system,[8] and almost independent of the reagent concentration and pH. Thus the reagent is retained in the gel

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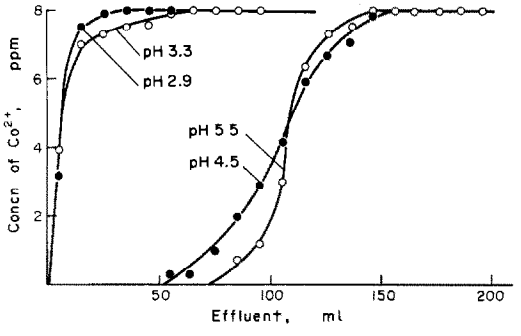

Fig. 1. Effect of pH on the break-through curve of 1-nitroso-2-naphthol gel column. 1-Nitroso-2-naphthol: 5.84×10^{-5} mole.

beads and hardly distributed into the aqueous phase, which is useful for continuous column extraction.

The oxidation of cobalt(II) is brought about mainly by the reagent itself; the overall reaction being:

$$4HL + Co^{2+} = CoL_3 + H_2L^{\cdot} + 2H^+ \qquad (1)$$

where $H_2L^{\cdot}$ represents a semiquinone-type radical species resulting from one-electron reduction of the reagent molecule.[3] Although no definite products from the radical species have been characterized so far, the stoichiometry of reaction (1) is considered to be 1:4.[3-7]

However, in the proposed process, where a large volume of water which has been exposed to air is passed through the column, it is possible that the reagent may be regenerated in part or in whole by aerial oxidation or by disproportionation of the reduced intermediates. Therefore, the stoichiometry in the column process may be between 1:4 and 1:3.

As illustrated in Fig. 1, the extraction behaviour in the column process is entirely dependent upon the pH of the aqueous phase, in agreement with that in the batch process. If the extraction capacity is estimated on the assumption of 1:3 stoichiometry (metal to reagent ratio), the extraction at pH 5.5 is 74% of capacity, and the original yellow colour of the reagent gel turns to red-violet over the entire length of the column. With decrease in the pH of the aqueous phase, the extent of extraction decreases remarkably; 70, 5 and 3% of the extraction capacity at pH 4.5, 3.3 and 2.9 respectively.

The flow-rate also affects the extraction behaviour in the column process. Increased flow-rate causes earlier breakthrough of cobalt, but the elution curve becomes less steep (Fig. 2). However, the total amount of cobalt trapped on the column does not seem to be affected so much by the flow-rate within this range.

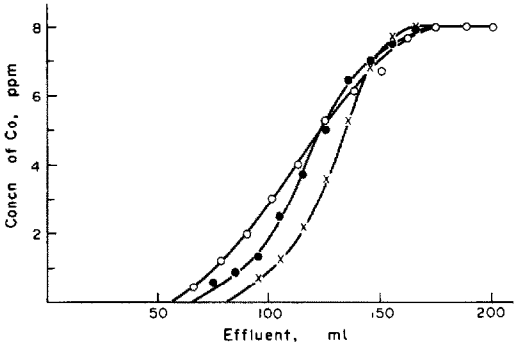

Fig. 2. Effect of the flow-rate on the break-through curve of the gel column. 1-Nitroso-2-naphthol: 5.8×10^{-5} mole. Flow-rate (ml/min): —○— 18.2, —●— 7.5, —×— 4.4

Table 1. Extraction of cobalt at pH 5.5 and back-extraction of cobalt chelate with MIBK

Concn. of Co in the sample, *ppm*	5	1	0.5	0.1	0.1*	0.05*
Amount of sample passed, *ml*	50	250	500	1000	1000	2000
Flow-rate, *ml/hr*	27.3	55.6	50.0	62.5	76.9	40.0
Total amount of Co retained by the column, *mg*	0.25	0.25	0.25	0.10	0.10	0.10
Volume of MIBK, *ml*	38.0	36.2	30.0	28.6	34.0	30.0
Co recovered, *mg*	0.23	0.22	0.24	0.096	0.093	0.095
Recovery, %	92	88	96	96	93	95
Concentration factor	1.5	6.9	16.7	35.0	29.4	66.7

* Sea-water spiked with cobalt.

Table 2. Effect of diverse ions on the extraction and back-extraction of cobalt (1-nitroso-2-naphthol 5.84×10^{-5} mole)

	Copper			Nickel		
Concn. of Co, *ppm*	5	1	0.5	5	1	0.5
Concn. of Cu or Ni, *ppm*	5	1	20	5	1	20
Amount of sample passed, *ml*	300*	200	200*	300*	200	200*
Total amount of Co retained by the column, *mg*	—	0.2	0.1	—	0.2	0.1
Co extracted onto gel†, *mg*	0.625	—	—	0.604	—	—
Cu or Ni extracted onto gel†, *mg*	0.600	—	—	0.312	—	—
Co recovered, *mg*	0.654	0.185	0.067	0.624	0.217	0.100
Recovery %	104	92.5	66.8	103	109	100
Cu or Ni recovered, *mg*	0.495	0.201	1.00	0.282	0.162	0.832
Recovery %	82.4	100.5	—	90.4	81	—

* Exceeding the capacity of the gel column.
† Estimated from breakthrough curve.

The resulting cobalt(III) chelate can be easily recovered by simply eluting the gel beads column with MIBK for the final cobalt determination. Table 1 summarizes the results of the preconcentration of cobalt at ppm or sub-ppm level in water, and the back-extraction of cobalt chelate with MIBK. The sample solution, adjusted to pH 5.5, was passed through the gel-bead column. The amount of cobalt recovered in the MIBK-extract agreed fairly well with that in the initial sample and the concentration factor attained was as high as 67. Diverse ions at the concentrations found in sea-water do not interfere with the selective extraction of cobalt.

Metal ions such as copper(II), nickel(II) and iron(III), if present in higher concentrations, may also be extracted onto the column under these conditions, but, in contrast to cobalt, these metal ions can be easily back-extracted with 2*M* hydrochloric acid, just as in the solvent extraction process.[9]

The extraction behaviour of copper is similar to that of cobalt. At pH 5.5, the extraction is almost quantitative (based on 1:2 chelate formation) and is 17% at pH 3.5. Accordingly, the extraction of copper competes with that of cobalt, and cobalt cannot replace copper from the corresponding chelate in the gel matrix. This is to be expected since the log β_2 values for the Co(II) and Cu(II) chelates are 22.81 and 23.37 respectively. Thus, in the presence of a large excess of copper, the extraction capacity may not be reached by cobalt. On the other hand, if the sample contains comparable amounts of copper and cobalt, both ions are equally extracted onto the gel column, from which copper can be back-extracted with 2*M* hydrochloric acid, while cobalt is not. Some typical examples are shown in Table 2.

The extraction of nickel is less effective than that of cobalt, as expected from the formation constant (log $\beta_2 = 21.6$), 73% being extracted at pH 5.5 and 83% at pH 6.5. Thus, when a sample solution containing a large excess of nickel is treated with the gel column, cobalt is extracted preferentially, so that a red-violet zone of cobalt(II) chelate appears gradually from the top of the column. Some examples are also shown in Table 2.

Iron(III) is known to be extracted with this reagent as the tris-chelate from a fairly acid solution. However, the extraction of iron onto the gel column at pH 5.5 is not complete, owing to partial hydrolysis of iron(III). At the same time, cobalt is likely to be co-precipitated with iron(III) hydroxide at this pH. Therefore, iron, if present in a moderate excess, has to be masked with citric acid, which is a common buffering agent in the nitrosonaphthol extraction of cobalt(II).[11]

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DETERMINATION OF THALLIUM IN ROCK AND SOIL SAMPLES

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Summary—The fluorescence of the chloro-complexes of thallium(I) is made the basis of a method for determination of traces of thallium. The procedure is applied to the determination of thallium in rocks or soils.

Because of the low abundance of thallium and the relatively high detection limits for this element by flame photometric procedures, wet-chemical techniques must be applied when analysing for thallium. Although the detection limit for atomic fluorescence is given as 0.008 $\mu g/cm^3$, this technique is not suited for routine analysis due to fluctuations arising from source instabilities when electrodeless discharge lamps are used. The fluorimetric procedures by which sufficiently low detection limits can be realized are those which utilize the quenching of the fluorescence of Cochineal Red and uranyl sulphate[2] or the fluorescence of thallium(I) chloro-complexes[3,4] or the complex with Rhodamine B.[5,6] These determinations are usually preceded by concentration steps achieved by ion-exchange,[7] solvent extraction[8] or co-precipitation.[9]

Since the blank values obtained by the Rhodamine B fluorimetric method[6] are appreciably higher than those reported for the chloro-complex method,[3,4] the latter seems to have added advantages due to the improved signal-to-noise ratio.

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The resulting cobalt(III) chelate can be easily recovered by simply eluting the gel beads column with MIBK for the final cobalt determination. Table 1 summarizes the results of the preconcentration of cobalt at ppm or sub-ppm level in water, and the back-extraction of cobalt chelate with MIBK. The sample solution, adjusted to pH 5.5, was passed through the gel-bead column. The amount of cobalt recovered in the MIBK-extract agreed fairly well with that in the initial sample and the concentration factor attained was as high as 67. Diverse ions at the concentrations found in sea-water do not interfere with the selective extraction of cobalt.

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EXPERIMENTAL

Reagents

All reagents used were *pro analysi* grade. The exchange resin was Bio-Rad AG 50W-X8,200-400 mesh.

Apparatus

Ion-exchange column, 65 mm long, in a borosilicate glass tube 10 mm in diameter. Teflon bombs and beakers. Farrand spectrofluorimeter; for analysis the excitation and analysing monochromators were fitted with 20-μm slits. The instrument was fitted with a 150-W xenon d.c. arc-lamp and an R213 (Hamamatsu) photomultiplier tube. The setting of the microammeter was 0.1 or 0.3 so that the voltage on the photomultiplier could be kept as low as possible. "Agla" micrometer syringe.

Procedure

To a 1-g sample in a Teflon bomb add 1 ml of concentrated perchloric acid and 10 ml of concentrated hydrofluoric acid, heat to 180° and allow to digest for approximately 1 hr; if no Teflon bomb is available, place the sample and acids in a covered Teflon beaker and heat in an air-bath at 180° for 4 hr. Remove the sample from the bomb and place it in a Teflon beaker. Evaporate the silicon tetrafluoride and excess of hydrofluoric acid. To the salts add 2 ml of perchloric acid and evaporate nearly to dryness; again add 1 ml of perchloric acid and 5 ml of saturated boric acid solution and evaporate to dryness, taking care not to decompose the perchlorates.

Dissolve the salts in water, then add a little chlorine water to oxidize all thallium to Tl(III). Add enough hydrobromic acid to bring its concentration to 1*M* and extract with 10 ml of methyl isobutyl ketone (MIBK), shaking for 10 min. Extract with an additional 3-ml portion of MIBK. Evaporate the MIBK at 30–35° in a scrubbed air-stream. Dissolve the residue in acid and dilute so as to obtain 25 ml of solution that is 0.1*M* in hydrochloric acid. Add a little chlorine water to ensure complete oxidation to Tl(III), since Tl(I) is strongly sorbed on the ion-exchanger. Pass the sample through the ion-exchange column and collect the first 40 ml of eluate and wash-water, add one drop of perchloric acid and evaporate this solution to destroy any organic matter and dissolved ion-exchange resin. Dissolve the residue in *ca.* 5 ml of $10^{-4}M$ perchloric acid, and add some saturated SO_2-water. Expel SO_2 by gentle heating. To this solution add 2.338 g of sodium chloride, dissolve it and dilute to 10 ml. Measure the luminescence at 430 nm, with excitation at 245 nm. Prepare a calibration curve by using appropriate quantities of TlCl solution, drying them at 100°, adding 2.338 g of sodium chloride and diluting to 10 ml.

RESULTS AND DISCUSSION

The precision of the method was rigorously tested by analysis of a granitic rock sample; the estimated relative standard deviation was 9.2% (8 samples). Duplicate analyses were made of the six new series US Geological Survey Standard Rocks, with the results shown in Table 1. Other analyses for thallium in these samples are included for comparison.

Dissolution of the sample

Tracer experiments with ^{204}Tl have shown that no significant loss occurs when a typical silicate sample is dissolved in hydrofluoric acid containing hydrochloric, nitric or perchloric acid. According to Matthews and Riley,[6] up to 40% of the thallium may be lost on prolonged heating with these acids, however.

A silicate sample, spiked with 1 μg of Tl and ^{204}Tl, was heated under an infrared lamp with a perchloric–hydrochloric acid mixture; after evaporation, the residue was dissolved and transferred to a counting dish, evaporated again and counted. An apparent loss of 6–30% of the ^{204}Tl was obtained (in comparison with the same amount of ^{204}Tl placed directly in a counting dish). To determine whether this loss was due to the evaporation, an aliquot (equivalent to 0.05 g of sample) of a solution made from a granite was evaporated directly in a 5-ml Teflon counting dish, and spiked just before reaching dryness at 180°. The count-rate did not alter appreciably after additional evaporation of five 4-ml portions of nitric, hydrochloric or perchloric acids or combinations of these acids with hydrofluoric acid. The apparent minor gains or losses found in the counting after each portion had been evaporated to dryness, were never more than 6% and can be ascribed to a change in the geometry of the sample in the counting dish and not to losses by evaporation.

Separation

Although the separation of Tl(III) from the matrix on a strong acid cation-exchange resin is feasible, the time taken makes the extraction of $HTlBr_4$ into MIBK more attractive. The extraction was monitored by flame emission at 377.6 nm and found to be quantitative if the concentration of the hydrobromic acid is higher than 0.2*M*. Iron(III), however, begins to be extracted from a hydrobromic acid concentration of 0.8*M*, and dichromate [formed from chromium(III) by fuming perchloric acid] is also extracted appreciably. To eliminate these fluorescence quenchers, they are reduced by SO_2, the excess of which is easily removed by heating; after oxidation of Tl(I) with chlorine water, all traces of other metals are removed by passing the solution through a small cation-exchange column.

Table 1. Determination of thallium ($\mu g/g$) in US Geological Survey Standard Rocks

Rock	Present work	Matthews[6]	Wahler[10]	Champ[11]
AGV-1 Andesite	0.43	0.39	0.27	1.6
BCR-1 Basalt	0.48	0.59	0.36	—
DTS-1 Dunite	0.74	0.13	<0.05	—
G-2 Granite	0.96	1.02	0.84	1.3
GSP-1 Grandiorite	1.78	1.87	0.7	1.6
PCC-1 Peridotite	0.28	0.35	<0.05	—
W-1	0.35	—	<0.05	—

Table 2. Fluorescence signal (arbitrary scale) for 2 ppm Tl(I) in 4*M* chloride solutions ("Specpure" reagents were used)

Type of chloride	NH_4^+	H^+	Li^+	Na^+	K^+	Rb^+	Cs^+
Fluorescence intensity	69	55	60	78	77	81	83

Fluorescence intensity

The excitation wavelength, 230 nm for maximum intensity, showed a slight dependence on chloride concentration; the emitted wavelength showed a broad peak, with maximum intensity at 430 nm. These results are in accordance with those of Curtice and Scott.[12] A small peak at 460–490 nm is also observed; this is a second-order reflection of the excitation peak. The fluorescence intensity is a function not only of chloride concentration but also of the cation associated with the chloride, as shown in Table 2.

It is apparent that caesium chloride, which gives the highest fluorescent emission, would be the most suitable, and high chloride concentrations can be obtained with it (9.6*M*), which give an intensity twice that with the 4*M* medium. Because of the high cost of this reagent, sodium chloride was used in all subsequent analyses. Lithium chloride is also capable of yielding high chloride concentrations (10.7*M* saturated solution), but the products available other than high-purity or ultrapurity grade quenched the fluorescence. It had been noticed that the highest fluorescence intensity with the commercially available lithium chloride was with a 3*M* solution, and that it decreased at higher LiCl concentrations. A similar result was observed with reagent-grade hydrochloric acid, the peak fluorescence being obtained with 4*M* acid.

Reduction

Since the thallium is in the tervalent state when eluted from the column, it has to be reduced to the univalent state to give the fluorescing species. Tin(II) and hydroxylammonium chloride are suitable for the reduction but quench the fluorescence considerably. Sulphur dioxide was found to be suitable. Although it absorbed and/or quenched the signal, the excess could be removed by gently boiling, and this minimized the quenching.

Table 3. Quenching of fluorescence of 1 ppm thallium

Element	Quenching, % *A**	*B**	*C**
Pb(II)	76	20	3
Cu(II)	98	55	13
Fe(III)	100	81	19
Mn(II)	55	15	4
Cr(III)	60	15	5
Ag(I)	60	10	2
NO_3^-	75	25	5

* Concentration of quenching agent: *A* 100 ppm, *B* 10 ppm, *C* 1 ppm. Sulphate, perchlorate, boric acid, calcium, magnesium and aluminium at the 100-ppm level did not quench the fluorescence.

Interferences

A number of cations and anions were investigated to ascertain their degree of quenching. The results are shown in Table 3.

Conclusion

The toxic nature of thallium makes its determination in the body and the environment important. The determination of thallium by measuring the fluorescence offers a method with a low detection limit and excellent sensitivity. The proposed method can be applied to various matrices, as the major components are separated by extraction and ion-exchange; all the ions that quench the fluorescence are also removed.

The advantage of this method is that no calibration standards are needed; thallium chloride is used as the standard. If need be, any sample can be analysed for thallium by this method and then used as a calibration standard in other faster, but less precise, instrumental methods.

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USE OF A DESK PROGRAMMABLE COMPUTER FOR CALCULATING THE CALIBRATION CURVE OF A PHOTOGRAPHIC EMULSION FOR SPECTROGRAPHIC ANALYSIS

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Summary—A computer method for calculating the calibration curve for emulsion-covered glass plates used to interpret densities of lines for quantitative spectrographic work is reported. It follows a slightly modified ASTM graphical method, which is also described, to establish preliminary and emulsion calibration curves. Once the curves are established, the relative intensities are obtained from transmission data pairs for concentration lines and an internal standard line. The program is written in BASIC.

In the past 10 years many reports have been published on the application of computer programming for the calibration of photographic emulsions. Calculating boards[1] and rules[2] have essentially been replaced by read-outs from large and small computers. The authors have generally chosen programs that follow graphical methods of calibration,[3–8] though some, *e.g.*, Margoshes and Rasberry,[9] have taken a different approach by assuming a linear relation between functions of the relative exposure and of the microphotometer readings. Most of the graphical methods appear to be unduly complex; for example, data are generally converted into Seidel or "modified" Seidel transformations, the principles involved in Kaiser transformations are employed, or dedicated computers are used.

Our laboratory wanted a program that would follow our present slightly modified ASTM method of calibration,[10] which is simple in principle. We sought a computer method that would print out preliminary and emulsion calibration curves so that a convenient check could be made on the original data when desired, and more points added to the preliminary curves if necessary, because the accuracy of the read-out is limited by the original microphotometer data.

With our program, the emulsion calibration equation is obtained and stored in the memory of the calculator. To find a relative intensity, two transmission readings (one from the element in question and the other from an internal standard) are entered into the computer. Checking the emulsion calibration is simplified by printing out the preliminary curve with the original data superimposed on it. A program originated to follow our existing "hand emulsion-calibration" method, uses a Hewlett-Packard 9830-A calculator with an 8K memory storage. An X–Y plotter is attached to plot curves originated by the data from the computer.

PROCEDURE FOR EMULSION PLATE CALIBRATION

Cassette, rotation and position settings on the spectrograph are adjusted so that the wavelength region 2750–3450 Å can be photographed. A 50-mg/ml solution of iron is sparked for a 20-sec and a 40-sec exposure. Details of the excitation conditions used with our spectrograph are given in Appendix A. A 7-step filter, with segments in ratios of powers of 2 is placed between the spark and the entrance slit of the spectrograph to attenuate the exposure.

Lines in the wavelength region 3,000–3,200 Å are measured by densitometer. Transmittances (between 1.5 and 92%) are listed as DARK $\%T$ if they refer to the portion of the line corresponding to the second step of the filter and LIGHT $\%T$ for the portion corresponding to the third step. The preliminary curve (P.C.) is plotted on linear graph paper, 15 × 10 in, from about 50 such lines-pairs (Fig. 1). This is the first stage in the ASTM method.

The second stage is the construction of the emulsion calibration or H & D (Hurter and Driffield) curve and it is this curve that is ultimately used in relating transmission to relative intensity. To construct this curve a DARK $\%T$ point is chosen on the preliminary curve as low in value as possible but above the intercept of the curve with the ordinate. The corresponding LIGHT $\%T$ is obtained and is called the % transmission ($\%T$) and assigned the number 7. The next LIGHT $\%T$ point to be obtained is

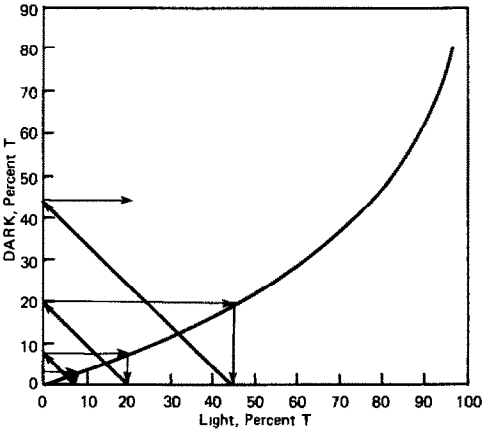

Fig. 1. Preliminary curve, exemplifying method of successive determination of DARK % T and LIGHT % T values.

assigned the number 6 and is the LIGHT $\%T$ value corresponding to the DARK $\%T$ point numerically equal to the $\%T$ value number 7 and read from the P.C. This method is continued until $\%T$ values have been obtained for numbers 5, 4, 3, and 2.

These $\%T$ values are then plotted as ordinates (log scale) against their numbers on 8.5 × 11 in. 2-cycle semi-log paper, the abscissa being marked off from 1 to 8 with ten divisions between each number (Fig. 2). A straight line is drawn connecting points "six" and "seven" and extended to the abscissa. Intermediate points are then taken so that the calibration curves can be drawn more accurately. A number between 7 and 8, *e.g.*, 7.5, is chosen and the corresponding $\%T$ value is read from the straight line on the emulsion calibration curve. The DARK $\%T$ point that is numerically equal to this $\%T$ value is located on the P.C. and called $\%T_i$ and a corresponding LIGHT $\%T$ value on the P.C. is read off and assigned the number 6.5. The process is then continued until the $\%T$ values for numbers 5.5, 4.5, 3.5, and 2.5 have been obtained. Additional starting points such as 7.8, 7.6, *etc.*, are chosen and used to obtain enough data points for the emulsion calibration curve to be drawn precisely. Tables 1 and 2, in conjunction with Figs. 1 and 2, illustrate the method. This emulsion calibration curve is then expanded on 15 × 10 in. 2-cycle semi-log paper. The scale of the ordinate remains the same, but the abscissa is expanded and two curves are plotted, one above the other, the upper for 2–5 and the lower for 5–8, each major division corresponding to 0.1 and each minor division to 0.02.

The last stage involves construction of a rule. On a piece of cardboard approximately 28 × 1.5 in., the longitudinal mid-line is drawn. The underside of the line is marked off to correspond exactly in position to the numbers on the expanded calibration curve, so that 8 is the last point at the right-hand end of the rule. The $\%T$ values corresponding to the numbers are then laid off on the upper side of the line, by aligning the rule and calibration graph and using a set-square and ruler for marking off. The result is shown diagrammatically in Fig. 3.

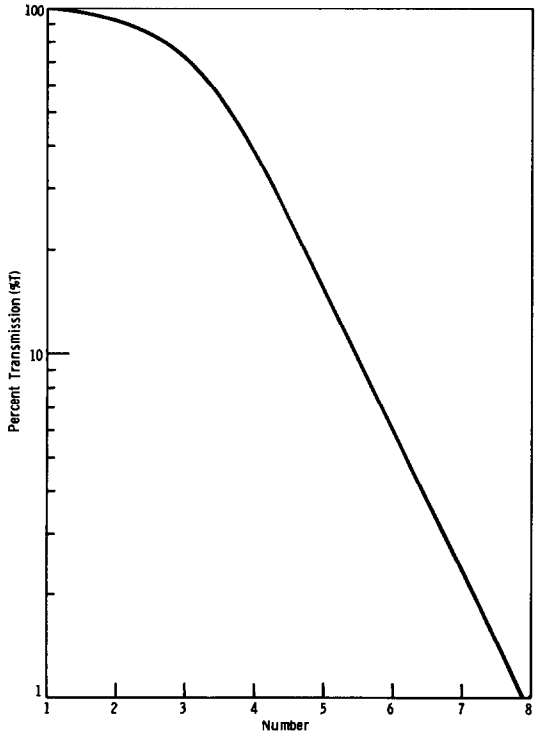

Fig. 2. Emulsion calibration curve.

Table 1. Typical raw "DARK" and "LIGHT" data points used to establish the preliminary curve equation

DARK $\%T$	LIGHT $\%T$
8.7	24.5
5.1	14.7
42.1	77.1
65.1	91.9
11.1	29.1
59.5	85.8
49.7	81.1
30.5	58.1
38.1	73.3
2.9	6.2

Table 2. Typical values for establishing the emulsion calibration equation

NUMBER	LOG $\%T$	LIGHT $\%T$
7	0.4047	2.54
6.6	0.5671	3.69
6.2	0.7295	5.36
5.8	0.8917	7.79
5.4	1.0528	11.29
5.2	1.1328	13.58
4.8	1.2907	19.53
4.3	1.4806	30.24
3.7	1.6859	48.52
3.3	1.7974	62.72
2.5	1.9318	85.47

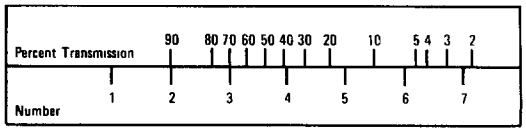

Fig. 3. Condensed calibration rule.

The rule has the approximate range 92.0–2.0% transmission. Densitometer readings of lines in the calibrated wavelength region on photographic plates can then be interpreted for the elements under study. The $\%T$ values for the known and for the internal standard are read from the glass emulsion. An ordinary ruler graduated in the same fractions as the abscissa on the semi-logarithmic paper used is laid with its zero on the higher $\%T$. The number of subdivisions on the ruler from the zero to the point which corresponds to the lower $\%T$ is the relative intensity for that pair of $\%T$ values. By continuation of this process for pairs of known and internal standards lines, an analytical curve can be established on semi-log paper, with the log axis labelled concentration and the linear axis relative intensity.

HEWLETT-PACKARD CALCULATOR METHOD

The equation of the preliminary curve can be determined and the curve generated by a plotter by means of the polynomial regression procedure outlined in the MATH PAC book supplied with the H.P. computer.[11] In this method, a set of data points is fed into the calculator and the coefficients of a polynomial of up to the 20th degree are produced by use of a least-squares fit. The DARK $\%T$ and LIGHT $\%T$ data used for the preliminary curve are entered

into the H.P. program. From the operations chart in Appendix B, it is seen that the calculator asks for the maximum degree of the polynomial. The higher this degree, the longer the time intervals required between inputs of the data pairs because the calculator must solve the required equation for each data pair. As the data are loaded, they can be stored and corrected if necessary. Various degrees of polynomial were examined and it was found that a 6th degree equation gave a sufficiently high correlation coefficient for practical use. The equation used is:

$$T_l = A_0 + A_1(T_d) + \ldots\ldots A_6(T_d)^6 \quad (1)$$

where T_l = LIGHT % transmission, T_d = DARK % transmission, A_0, A_1 *etc.* = coefficients of the polynomial equation.

The upper f6 block in the operations chart shows that a plot of the preliminary curve and a lower degree polynomial equation can now be obtained.

A table of T_d and T_l data pairs is now required. The output data are the DARK $\%T$ values from 1 to 80% at 1% intervals and the corresponding calculated LIGHT $\%T$ values. A plot of the data is a smooth curve essentially identical with a curve drawn from the original data.

The coefficients of the 6th degree polynomial are now used to generate the tables of LIGHT $\%T$ and NUMBER, used to formulate the emulsion calibration curve. T_d is set equal to unity in the polynomial, which is then solved for T_l, the value of which is stored in the table along with the NUMBER 7. The computer then sets $T_d = T_l$ and solves the new equation. In this manner, values of T_l are established for NUMBERS 7, 6, 5, 4, 3, and 2. A linear relation is assumed to hold from NUMBER 7 to NUMBER 6 and, by extension, to the NUMBER corresponding to $1\%T$.

From the equation of this straight line, the computer calculates NUMBER values and corresponding T_l values. For example, the T_l value corresponding to NUMBER 7.5 is obtained, set equal to T_d and placed in polynomial (1) which is then solved to yield the new T_l values corresponding to NUMBER 6.5. In similar fashion, NUMBER values from 6.9 to 2.1 at 0.1 intervals are obtained, and are stored in a table. The data from this table are then used to generate the coefficients for the equation:

$$\text{NUMBER} = B_0 + B_1(\log T_l) + \ldots\ldots B_6(\log T_l)^6 \quad (2)$$

The operations chart (Appendix B) indicates the flexibility of use of equation (2). As shown in the lower f6 block, it is possible to print a table of Log T_l values *vs.* NUMBER, plot the curve, or print out relative intensity for each pair of transmission points entered. The last is done by using equation (2) and substituting the $\%T$ for a known element (obtained from the line density) for T_l and solving for NUMBER. The procedure is repeated for $\%T$ for an internal standard and another NUMBER is obtained. The computer subtracts these two NUMBERS and the difference is called the RELATIVE INTENSITY. This process is continued (as outlined for the method done by hand) for pairs of known and internal standard lines. An analytical curve is printed out on semi-log paper. Once the coefficients of the emulsion calibration curve equation have been determined, this equation can be used with a desk-top calculator with lower memory capacity. The program is given in Appendix C and is written in BASIC.

Acknowledgements—The author is indebted to Dr. Gary L. Hagnauer and Mrs. Anna Hansen for their assistance with the H.P. computer program and to Mr. Frederick Valente who suggested this time-saving approach.

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APPENDIX A

Equipment
- Baird 3-m spectrograph, 2.75 Å/mm reciprocal linear dispersion
- Jarrell-Ash Varisource
- Jarrell-Ash Microphotometer

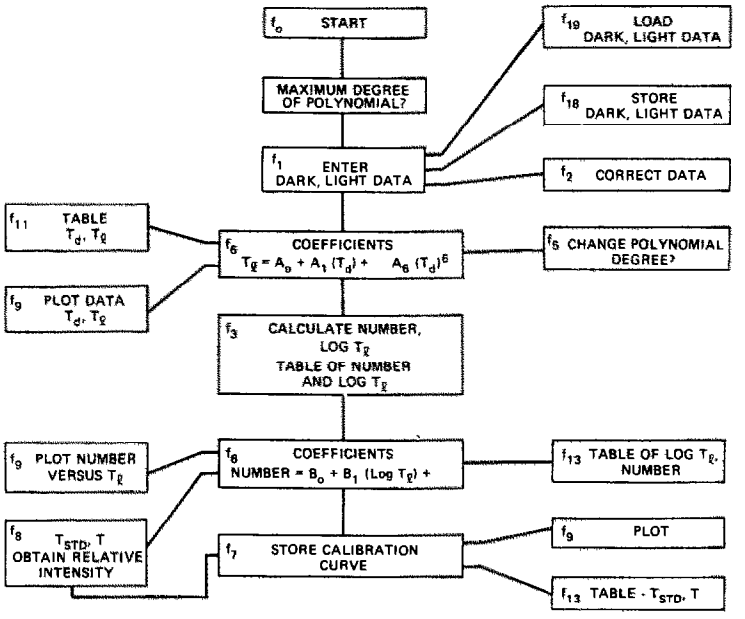
Instrumental parameters
- Spark–18,000 V (a.c.), 3 breaks per half-cycle, 6–6.5 A
- Analytical gap 3 mm
- Auxiliary gap 6 mm
- Sample-electrode Ultra Carbon 106
- Counter-electrode Ultra Carbon 105 U
- Prespark duration 20 sec

Photographic parameters
- Plates Eastman Kodak SA 1
- Developer Eastman Kodak D19
- Development time 3.5 min
- Development temperature 20°C

Spectral range of calibration 2750–3450 Å
Spectral lines read in range 3000–3200 Å

APPENDIX B

H. P. CALCULATOR OPERATIONS CHART



T_g = Percent transmission of light line
T_d = Percent transmission of dark line

APPENDIX C

HEWLETT-PACKARD CALCULATOR

PROGRAM FOR GLASS PLATE EMULSION CALIBRATION

f_0

```
10  For I=1 to 22
20  C[I] = B[I] = 0
30  Next I
40  For I = 23 to 253
50  C[I] = 0
60  Next I
70  B[I] = 1
80  W = N = S1 = S2 = S3 = S4 = S5 = I1 = 0
90  Disp "Max Degree Polynomial";
100 Input D2
110 Print "Max Degree Polynomial = "D2
120 D1 = D2
130 Print
140 End
```

f_1

```
10  Format F 4.0, 2F 12.4
20  Print "Enter Prelim Calibrn Data"
30  If N ≠ 0 then 70
40  Print "No." Tab 10 "DARK" Tab 22 "LIGHT"
50  I1 = 0
60  I1 = I1 + 1
70  Disp "Dark, Light = ";
80  Input G[I1], H[I1]
90  Y = H[I1]
100 B [2] = G [I1]
110 Write (15, 10) N+1, G[I1], H[I1]
120 Y = FN X 1
130 Go to 60
140 End
```

f_2

```
10  If W = 0 then 40
20  Disp "Not allowed"
30  End
40  Disp "Wrong No., Dark, Light = ";
50  Input I, Y, B[2]
60  G[I] = Y
70  H[I] = B[2]
80  Print "Delete: Dark = "G[I]" Light = " H[I]
90  Y = FNX (-1)
100 Disp
110 End
```

f_3

```
10  I1 = 0
20  Print "Polynomial Degree = " D1
30  Print "Relative I Log T Light"
40  X2 = 1
50  X = 1
60  X1 = 8
70  If X1 < = 2 then 210
80  Y = B[D1 + 1]
90  For J = D1 to 1  Step -1
100 Y = Y * X + B[J]
110 Next J
120 X = Y
130 If X > 100 then 210
140 X1 = X1-1
150 If X1 < = 2 then 210
160 I1 = I1 + 1
170 H[I1] = X1
180 G[I1] = L G T X
190 Print X1, G[I1], X
200 Go to 70
210 X2 = X2 - 0.1
220 If X2 = 0 then 290
230 I1 = I1 + 1
240 G[I1] = (G[2] - G[3]) * X2 + G[2]
250 X1 = 6 + X2
260 X = 10 ↑ G [I1]
270 H[I1] = X1
280 Go to 190
290 Y = FN Y1
300 End
```

f_4

```
10  Def FNX (Z)
20  For I = 2 to D2
30  B[I+1] = B[I] * B[2]
40  Next I
50  B[D2 +2] = Y
60  R = 0
70  For I = 1 to D2 + 2
80  For J = I to D2 + 2
90  R = R + 1
100 C[R] = C[R] + B[I] * B[J] * Z
110 Next J
120 Next I
```

```
130  S1 = S1 + B[2] * Z
140  S2 = S2 + B[2]↑2 * Z
150  S3 = S3 + Y * Z
160  S4 = S4 + Y *Y * Z
170  S5 = S5 + B[2] * Y * Z
180  N = N + Z
190  Return 0
```

f_5

```
10  Disp "New Polynomial Degree = ";
20  Input D1
30  Print "Degree of Polynomial = " D1
40  End
```

f_6

```
10  If N < = D2 - W then 340
20  If D1 < = D2 - W then 50
30  Disp "Max Deg = "; D2 - W
40  End
50  If W = 0 then 330
60  T = 0
70  For I = 1 to D1 + 1
80  B[I] = 0
90  For J = 1 to D1 - I + 2
100 R = (I + J - 1) * (D2 + 2 -0.5 * (I + J))
110 B[I] = B[I] + C[T + J] * C[R]
120 Next J
130 T = I * (D2 + (3-I)/2)
140 Next I
150 R1 = 0
160 For I = 2 to D1 + 1
170 R1 = R1 + C [I*(D2 + (3-I)/2)]↑2
180 Next I
190 T0 = C[(D2 + 1) * (D2 + 2)/2]
200 T0 = T0 - C[D2 + 1]↑2
210 Print
220 Print "Coefficients"
230 Print
240 Format F3.0, E12.4
250 For I = 1 to D1 + 1
260 Write (15, 240) "B("I-1") = "B[I]
270 Next I
280 Print
290 Print
300 Print "R Square = " R1/T0
310 Print
320 End
330 If N > D2 then 360
340 Disp "Not Enough Points"
350 End
360 P = W = 1
370 D2 = D2 + 1
380 For J = 1 to D2
390 Print C[P]
400 C[P] = SQR C[P]
410 For I = 1 to D2 - J + 1
420 C[P + I] = C[P + I]/C[P]
430 Next I
440 R = P + I
450 S = R
460 For L = 1 TO D2 - J
470 P = P + 1
480 For M = 1 to D2 + 2 - J - L
490 C[R + M - 1] = C[R + M - 1] - C[P] * C[P + M -1]
500 Next M
510 R = R + M - 1
520 Next L
530 P = S
540 Next J
550 T = (D2 + 1) * (D2 + 2)/2
560 For I = 1 to D2 - 1
570 T = T - 1 - I
580 C[T] = 1/C [T]
590 For J = 1 to D2 -I
600 P = D2 + 1 - I - J
610 P = P * (D2 + 1 - (P-1)/2) - I
620 R = P - J
630 S = 0
640 U = I + J + 1
650 Y = P
660 For K = 1 to J
670 Y = Y + U - K
680 S = S - C[R + K] * C[Y]
690 Next K
700 C[P] = S/C[R]
710 Next J
720 Next I
730 C[1] = 1/C[1]
740 Go to 60
```

f_7

```
10  B[22] = D1
20  Print "Store X = F (Log T) Calibration"
30  Disp "Store File # = ";
40  Input I
50  Print "Store File #" I
60  Store Data I, B
70  End
```

f_8

```
10  Print "Diff X Evaluation"
20  Disp "T(STD), T = ;
30  Input T1, T2
40  Print "T (STD) = " T1
50  Print "T = " T2
60  T1 = LGTT1
70  T2 = LGTT2
80  X1 = X2 = B[D1 + 1]
90  For J = D1 to 1 Step -1
100 X1 = X1 * T1 + B[J]
110 X2 = X2 * T2 + B[J]
120 Next J
130 Print "X(STD) = " X1
140 Print "X = " X2
150 Print "X(STD) - X = "X1 - X2
160 Go to 20
170 End
```

f_9

```
10  Disp "Re-plot Axis";
20  Input Z9
30  If Z9 = 0 then 390
40  Disp "X(Max) = ";
50  Input B2
60  Disp "X(Min) = ";
70  Input A2
80  Disp "Y(Max) = ";
90  Input B1
100 Disp "Y(Min) = ";
110 Input A1
120 C2 = (D2 - A2)/10
130 C1 = (B1 - A1)/10
140 Scale A2, B2 + 2*C2, A1, B1, +2*C1
150 Plot A2 + (B2 - A2)/2.2, A1 + C1/4
160 Label (*, 3,2,0, 2/3)
170 Letter
180 Plot A2 + C2/4, A1 + (B1 - A1)/2.2
190 Label (*, 3, 2, PI/2, 2/3
200 Letter
220 Offset C2, C1
230 XAXIX A1, C2, A2, B2
240 YAXIS B2, C1, A1, B1
250 YAXIX A2, C1, A1, B1
260 XAXIX B1, C2, A2, B2
270 Label (*, 2, 1.7, 0, 2/3)
280 For Y = A1 to B1 Step 2*C1
290 Plot A2, Y, 1
300 CPLOT -5.4, -0.34
310 Label (380, 2, 1.7, 0, 2/3) Y
320 Next Y
330 For X = A2 to B2 Step 2*C2
340 Plot X, A1, 1
350 CPLOT - 3.8, -1
360 Label (380, 2, 1.7, 0, 2/3) X
370 Next X
380 Format F 5.1
390 For X = A2 to B2 Step C2/10
400 Y = B[D1 + 1]
410 For J = D1 to 1 Step -1
420 Y = Y * X + B[J]
430 Next J
440 Plot X, Y
450 Next X
460 Disp "Plot Data Points";
470 Input Z9
480 If Z9 = 0 then 550
490 PEN
500 For K = 1 toI11
510 Plot G[K], H[K]
520 CPLOT -0.3, -0.3
530 Label (*) "O"
540 Next K
550 PEN
560 Plot -1.2 * C2, -C1
570 PEN
580 Go to 10
```

f_{11}

```
10  Format 2F 12.4
20  Print Tab 9 "X Dark" Tab 21 "Y Light"
30  For I = 1 to 79 Step 2
40  Y = B[D1 + 1]
50  For J = D1 to 1 Step -1
60  Y = Y* I + B[J]
70  Next J
80  Write (15, 10) I, Y
90  Next I
100 For I = 80 to 100 Step 1
110 Y = B[D1 + 1]
120 For J = D1 to 1 Step -1
130 Y = Y * I + B[J]
140 Next J
150 Write (15, 10) I, Y
160 Next I
170 End
```

```
f13
  10  Format 2 F 12.4
  20  Print Tab 9 "X" Tab 21 "T"
  30  For I = 0.3 to 2 Step 0.05
  40  Y = B[D1 +1]
  50  For J = D1 to 1 Step -1
  60  Y = Y * I + B[J]
  70  Next J
  80  Write (15, 10) Y, 10↑I
  90  Next I
 100  End

f14
  10  Def FNY(Z)
  20  Disp "Max Degree Polynomial";
  30  Input D2
  40  Print "Degree Polynomial = " D2
  50  D1 = D2
  60  Print I1
  70  For I = 1 to 22
  80  C[I] = B[I] = 0
  90  Next I
 100  For I = 23 to 253
 110  C[I] = 0
 120  Next I
 130  I3 = 0
 140  B[1] = 1
 150  W = N = S1 = S2 = S3 = S4 = S5 = 0
 160  I3 = I3 + 1
 170  B[2] = G[I3]
 180  Y= H[I3]
 190  Y = FN X1
 200  Print I3, G[I3], H[I3]
 210  IF I3 = I1 - 1 then 230
 220  Go to 160
 230  End

f17
  10  Print "Load X = F ( Log T) Calibration"
  20  Disp "Load File # = " ;
  30  Input I
  40  Print "Load File # " I
  50  Load Data I, B
  60  D1 = D2 B[22]
  70  Print "Degree Polynomial = " D1
  80  End

f18
  10  Disp "Store Date, File # = ";
  20  Input I
  30  Store Data I
  40  End

f19
  10 Disp "Load Data, File # = ";
  20  Input I
  30  Load Data I
  40  Format F 4.0, 2 F 12.4
  50  Print "No." Tab 10 "Dark" Tab 22 "Light"
  60  I1 = 0
  70  I1 = I1 + 1
  80  Y = H[I1]
  90  B[2] = G[I1]
 100  Write (15, 40) N + 1, G[I1], H[I1]
 110  Y = FNX1
 120  Go to 70
 130  End
```

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A NEW ION-EXCHANGE TEST FOR DETECTION OF KETONES ON THE MICROGRAM SCALE

SAIDUL ZAFAR QURESHI and IZZATULLAH
Department of Chemistry, Aligarh Muslim University, Aligarh, India

(*Received* 11 *January* 1977. *Revised* 11 *February* 1977. *Accepted* 26 *February* 1977)

Summary—A test for the detection of certain ketones is based on the reaction with 1-chloro-2,4-dinitrobenzene in the presence of an anion-exchange resin in the OH^- form, to give a violet colour on the resin bead surface.

A number of tests for the detection of the carbonyl group have been described by Feigl.[1] A new spot-test for aliphatic aldehydes and ketones is based on their interaction with 2,3-dimethyl-2,3-bis(hydroxyamino)butane[2] to form an anhydro product which is converted into an intensely coloured stable nitronyl nitroxide free radical on addition of sodium periodate. However, benzaldehyde interferes with the test. Another test for aldehydes and ketones is described by Bajaj[3] and covers a number of reducing sugars, aliphatic aldehydes, heterocyclic aldehydes, aromatic aldehydes and ketones. Sawicki[4] has described a test for acetonyl compounds, based on the thermochromic reaction with 2-hydroxyl-1-naphthaldehyde to produce a brilliant green colour. Acetophenone, heptanone and pentanone gave negative results. A general spot-test for ketones is based on its interaction with pentacyanoaquoferrate to produce a red colour.[5] Another spot-test for aliphatic ketones, described by Anger,[6] uses alkaline *m*-dinitrobenzene as the condensation reagent. Ion-exchange resin beads have been successfully used as the detection medium for a number of organic functional groups.[7–12] The present communication for the detection of ketones is based on such a technique.

EXPERIMENTAL

Reagents

A 1% solution of 1-chloro-2,4-dinitrobenzene in distilled ethanol, and solutions of ketones in distilled ethanol.

Dowex 1 × 10 (50–100 mesh) in the OH^--form.

Procedure

Place about 4–6 ion-exchange beads (in the OH^--form) on a white spot-plate and blot them dry with a filter paper. Add one drop of the test solution, followed by a drop of reagent solution. A violet-pink colour is developed on the bead surface if the test solution contains a ketone. The sensitivity of the test may be improved if freshly regenerated resin is used while still moist.

RESULTS

The following ketones gave a positive result: acetone, acetophenone, ethyl methyl ketone, cyclohexanone, cyclopentanone, methyl n-amyl ketone and benzyl methyl ketone. A negative test was obtained with benzophenone, methyl n-propyl ketone, methyl isobutyl ketone and ethyl

```
f13
  10  Format 2 F 12.4
  20  Print Tab 9 "X" Tab 21 "T"
  30  For I = 0.3 to 2 Step 0.05
  40  Y = B[D1 +1]
  50  For J = D1 to 1 Step -1
  60  Y = Y * I + B[J]
  70  Next J
  80  Write (15, 10) Y, 10↑I
  90  Next I
 100  End

f14
  10  Def FNY(Z)
  20  Disp "Max Degree Polynomial";
  30  Input D2
  40  Print "Degree Polynomial = " D2
  50  D1 = D2
  60  Print I1
  70  For I = 1 to 22
  80  C[I] = B[I] = 0
  90  Next I
 100  For I = 23 to 253
 110  C[I] = 0
 120  Next I
 130  I3 = 0
 140  B[1] = 1
 150  W = N = S1 = S2 = S3 = S4 = S5 = 0
 160  I3 = I3 + 1
 170  B[2] = G[I3]
 180  Y= H[I3]
 190  Y = FN X1
 200  Print I3, G[I3], H[I3]
 210  IF I3 = I1 - 1 then 230
 220  Go to 160
 230  End

f17
  10  Print "Load X = F ( Log T) Calibration"
  20  Disp "Load File # = " ;
  30  Input I
  40  Print "Load File # " I
  50  Load Data I, B
  60  D1 = D2 B[22]
  70  Print "Degree Polynomial = " D1
  80  End

f18
  10  Disp "Store Date, File # = ";
  20  Input I
  30  Store Data I
  40  End

f19
  10 Disp "Load Data, File # = ";
  20  Input I
  30  Load Data I
  40  Format F 4.0, 2 F 12.4
  50  Print "No." Tab 10 "Dark" Tab 22 "Light"
  60  I1 = 0
  70  I1 = I1 + 1
  80  Y = H[I1]
  90  B[2] = G[I1]
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```

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Table 1. Limit of detection of ketones

Ketone	Concentration, *M*	Volume, *ml*	Amount detected, *μg*
Cyclopentanone	0.001	0.005	0.4
Cyclohexanone	0.010	0.002	1
Acetophenone	0.010	0.005	6
Benzyl methyl ketone	0.010	0.002	3
Acetone	0.100	0.005	30
Ethyl methyl ketone	0.100	0.005	35
Methyl n-amyl ketone	0.100	0.005	60
Mesityl oxide	0.050	0.006	30

isopropyl ketone. A number of other organic compounds were found not to interfere with the test. They include *hydrocarbons and their derivatives* (benzene, toluene, xylene, carbon tetrachloride, nitrobenzene, bromobenzene, *o*-dichlorobenzene); *carbohydrates* (lactose, rhamnose, fructose, glucose, starch, sucrose, agar-agar); *acids* (formic, acetic, propionic, tartaric, oxalic, benzoic, citric); *aldehydes* (formaldehyde, acetaldehyde, crotonaldehyde, cinnamaldehyde, isovaleraldehyde, salicylaldehyde, anisaldehyde, *p*-dimethylaminobenzaldehyde); *nitriles* (acetonitrile, benzonitrile, propionitrile, mandelonitrile and butyronitrile); *amides* (acetamide, benzamide, phthalimide, oxamide, salicylamide, acetanilide, succinimide); *amino-acids* (glutamic acid, aspartic acid, methionine, cysteine, creatine, L-proline, glycine, α-alanine); *phenols* (pyrogallol, resorcinol, 1-naphthol, 2-naphthol, *m*-cresol, phenol); *ethers* (dioxan, anisol, diethyl ether); *alcohols* (methyl, ethyl, isopropyl, n-butyl, isoamyl, glycerol); *heterocyclic bases* (pyridine, piperidine); *amines* (ethylamine, triethanolamine, dicyclohexylamine, aniline, ethanolamine and *N*-phenyl-1-naphthylamine).

The following compounds gave characteristic colours (shown in brackets): methylamine (yellow), dimethylamine (yellow), indole (brown) and pyrrole (brown).

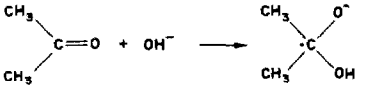
The limit of detection for a number of ketones was determined and the results are summarized in Table 1.

About 1 μg of cyclopentanone could be detected in the presence of aniline (0.37 mg), acetamide (3.5 mg), *o*-anisidine (1 mg), benzaldehyde (1.3 mg), benzene (0.6 mg), dioxan (0.2 mg), fructose (11 mg), ethyl acetate (7 mg), phenol (0.1 mg), pyridine (3.2 mg), methylamine (24 mg) and methanol (45 mg).

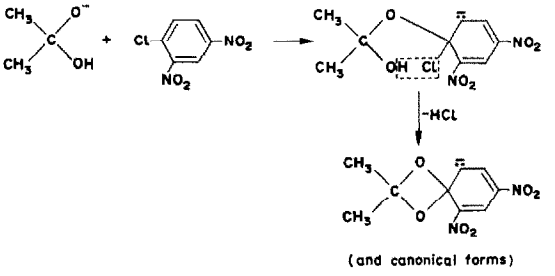
DISCUSSION

The ion-exchange test was positive with a number of ketones but in a few cases, *e.g.*, methyl n-propyl, methyl isobutyl and ethyl isopropyl ketones negative results were obtained. The reactivity of the carbonyl group is affected by steric hindrance, that is, it decreases with the size of the substituents.[13] This explains the negative results obtained with methyl isobutyl and ethyl isopropyl ketones. Similarly acetophenone gives a positive test while benzophenone does not. In benzophenone the carbonyl group is sandwiched between two phenyl groups which inhibit the addition of the OH^- group. The sensitivity for benzyl methyl ketone is greater than that for acetophenone. This is because in acetophenone the phenyl group is directly linked to the >C=O group and has an effect on the addition of the OH^- group.[14] In benzyl methyl ketone, the phenyl group is not directly linked to the >C=O group, and this effect is reduced.

The reaction between ketones and 1-chloro-2,4-dinitrobenzene in a basic medium can be regarded as proceeding as follows. In a basic medium there is a reversible addition of OH^- to the carbonyl group:[13]



The anion produced acts as a nucleophile and adds at the reagent carbon-atom bearing the chlorine atom, the reaction being promoted by the presence of the nitro groups:[13]



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ANALYTICAL DATA

ACID DISSOCIATION OF 2-MERCAPTOHISTAMINE AND ITS RELATED COMPOUNDS

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Summary—The acid dissociation constants of 2-mercaptohistamine hydrochloride (2-MH) and its related compounds ergothioneine (Erg), 2-mercaptoimidazole (MI), *N*-methyl-2-mercaptoimidazole (MMI) and histamine dihydrochloride were determined by potentiometry at 15°, 25° and 35° and $\mu = 0.1$ ($NaClO_4$). The values of ΔH and ΔS for the ionization equilibria were calculated. The magnitude of ΔH (9.5 kcal/mole) for pk_{a_1} of 2-MH is similar to the value ΔH = 9–10 kcal/mole found for the ionization of a number of amino groups. The value ΔH = 7.4 kcal/mole for pk_{a_2} of 2-MH is similar to the values for the ionization of a variety of thiols (ΔH = 5–7 kcal/mole). Such values were not obtained for Erg, MI and MMI, which suggests that 2-MH exists mainly in the thiol form, whereas Erg, MI and MMI are in the thione form.

2-Mercaptohistamine (2-MH), which contains both mercaptoimidazole and amino groups, is an analogue of ergothioneine (2-mercaptohistidine trimethyl betaine, Erg), and is estimated as a biologically active substance.[1] The thiol (C—SH) or thione (C=S) forms of Erg are presumed to be related to its biological activity.[2] The physicochemical properties of Erg[3–6] and such related compounds as 2-mercaptoimidazole,[3–7] *N*-methyl-2-mercaptoimidazole[7] and 2-thiolhistidine[8] in aqueous solution have been investigated by potentiometry and spectrometry. 2-MH, which is the most important analogue of Erg, was synthesized in 1932,[9] but its physicochemical properties have not previously been determined.

This paper reports the acid dissociation constants and thermodynamic parameters for 2-MH, determined by potentiometry. The involvement of the thiol rather than the thione form in the dissociation of 2-MH is strongly indicated.

EXPERIMENTAL

Materials

2-Mercaptohistamine hydrochloride was prepared according to the method of Fraser and Raphael,[10] and recrystallized from 80% acetic acid, mp. 241–2° (uncorrected; Fraser and Raphael give 244–5°). This compound gave only one spot on thin-layer chromatography (silica gel; solvent, ethanol–28% ammonia solution 3:1; $R_f = 0.64$), and the structure was identified by both infrared and nuclear magnetic resonance spectroscopy. 2-Mercaptoimidazole (MI), recrystallized from water, m.p. 221–2°, *N*-methyl-2-mercaptoimidazole (MMI), recrystallized from alcohol, m.p. 243–4°, ergothioneine and histamine dihydrochloride were obtained commercially. Carbonate-free potassium hydroxide solution was prepared by the method of Armstrong.[11] Other reagents used were guaranteed grade.

Potentiometric titration

The potentiometric titrations were done with a Hiranuma Titrator TB-101 and Titrigraph Rat 101 equipped with a Denkikagaku-keiki MC-30 combination electrode adjusted with standard solutions. A solution containing 2 mmole of the compound in 10 ml was titrated with carbonate-free 0.1*M* potassium hydroxide, under nitrogen and with magnetic stirring. The ionic strength was adjusted to 0.1 with sodium perchlorate. The potentiometric measurements were made at 15 ± 0.1°, 25 ± 0.1° and 35 ± 0.1°.

Calculation

Ionization constants were calculated according to the method of Schwarzenbach.[12] When ΔH was constant over the temperature range used, ΔH was calculated from

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

and ΔS from

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

where K_1 and K_2 are the equilibrium constants at absolute temperatures T_1 and T_2 respectively. Otherwise ΔH and ΔS were calculated by the method of Fujishiro *et al.*[13]

RESULTS AND DISCUSSION

The ionization constants and thermodynamic parameters are summarized in Table 1. The ionization constants were not influenced by the speed of titration within the range used. The ionization constants of Erg, MI and MMI agreed well with the values previously reported.[3–7] The dissociation constants of thiolhistidine were determined as $pk_{a_1} = 1.84$, $pk_{a_2} = 8.47$ and $pk_{a_3} = 11.4$,[8] pk_{a_2} and pk_{a_3} being assigned to the deprotonation of the amino and thiol groups, respectively, by analogy with the constants for cysteine and histidine. As shown in Table 1, the pk_a values of Erg, MI and MMI are similar to those for the thiol groups of various types of thiol compound, but the thermodynamic parameters, especially the entropy change, are different from those for thiol groups. Therefore, a simple comparison of the dissociation constants alone may lead to an erroneous assignment of the pk_a values. A plot of $T\Delta S$ against ΔH is linear for Erg, MI and MMI, but the point for 2-MH is well away from the line. This result shows that for 2-MH there is an additional factor besides

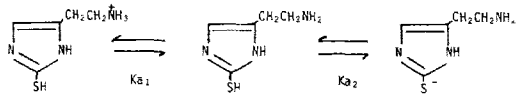

Chart 1. Probable ionization equilibrium of 2-mercaptohistamine.

the simple solute–solvent interaction[14] which is presumed to exist in the other three compounds.

The magnitude of $\Delta H_1 = 9.5$ kcal/mole for pk_{a_1} of 2-MH compares favourably with values of $\Delta H = 9$–12 kcal/mole for the ionization of a number of α-amino-acid esters,[15] ethylamine,[16] glycine[17] and histamine.*[18] Also, the values of $\Delta H_2 = 7.4$ kcal/mole and $\Delta S_2 = -28$ cal.mole^{-1}.deg^{-1} for pk_{a_2} are similar to the values $\Delta H = 5$–7 kcal/mole and $\Delta S = 20$–30 cal.mole^{-1}.deg^{-1} for the ionization of a variety of thiols.†[19–21] On the basis of the thermodynamic data, the predominant ionization processes appear to be those given in Chart 1. Therefore, it would be concluded that the first and second deprotonation steps of 2-MH are those of the amino and thiol groups, respectively. On the other hand, with such compounds as Erg, MI and MMI, the thermodynamic data imply that the thiol forms are not involved in the deprotonation process, but that the thione forms are, as described previously.[3–7]

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*For histamine, pk_{a_1} was related to the deprotonation of imidazole from the results in Table 1 and reference 18.

† On the basis of thermodynamic data, pk_{a_2} for cysteine esters and cysteamine was related to the deprotonation of the thiol group.[20,21]

Table 1. Acid dissociation constants and thermodynamic parameters of 2-mercaptohistamine and related compounds ($\mu = 0.1$ $NaClO_4$)

Compound	Temp. °C	pk_{a_1}	pk_{a_2}	ΔG_1 kcal/mole	ΔG_2 kcal/mole	ΔH_1 kcal/mole	ΔH_2 kcal/mole	ΔS_1 cal.mole^{-1}.deg^{-1}	ΔS_2 cal.mole^{-1}.deg^{-1}
2-Mercaptohistamine·HCl	15	9.36 ± 0.01	11.74 ± 0.05	12.3	15.5			−9.7	−28.6
	25	9.12 ± 0.02	11.62 ± 0.03	12.4	15.8	9.5	7.4	−9.7	−28.2
	35	8.86 ± 0.04	11.37 ± 0.06	12.5	16.0			−9.6	−27.9
Ergothioneine	15	10.72 ± 0.04		14.1				−9.0	
	25	10.44 ± 0.04		14.2		11.6		−8.7	
	35	10.11 ± 0.02		14.3				−8.5	
2-Mercaptoimidazole	15	11.47 ± 0.03		15.1				−0.7	
	25	11.21 ± 0.03		15.3		14.9		−1.0	
	35	10.74 ± 0.03		15.1				−1.5	
N-Methyl-2-mercapto-imidazole	15	12.15 ± 0.06		16.0				+2.8	
	25	11.64 ± 0.04		15.9		16.8		+2.8	
	35	11.31 ± 0.03		15.9				+2.8	
Histamine·2HCl	15	6.40 ± 0.01	10.10 ± 0.02	8.3	13.3			−4.8	−11.0
	25	6.13 ± 0.01	9.82 ± 0.01	8.4	13.4	7.0	9.5	−4.9	−13.0
	35	6.05 ± 0.01	9.62 ± 0.01	8.5	13.6			−4.8	−15.0
Imidazole[18]	15	7.31							
	25	7.12				7.5		−6.7	
	35	6.93							
Ethylamine[16]	0	11.4							
	25	10.8	9.10			9		−19	
Glycinate[17]	0.4	10.25							
	30	9.44				10.2		−9.5	
	48.8	9.00							
Cysteine methyl ester[20]	25	6.59	9.10			9.15	5.28	0.8	−24
Cysteine ethyl ester[21]	25	6.56	8.98			8.0	4.9	−2.4	−24.7
Ethylmercaptan[19]	25	10.61				6.42		−27	
Mercaptoethanol[19]	25	9.72				6.21		−23.7	
β-Mercaptopropionate[19]	25	10.84				6.10		−29.2	
Mercaptoacetic acid[19]	25	10.68				6.28		−27.8	

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ANNOTATION

AMPLIFICATION REACTIONS

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Although amplification reactions were known in the last century and were studied extensively by Hungarian workers at the beginning of the present century,[1–3] it was not until Leipert[4] described his method for the determination of iodine in organic compounds on the micro scale, that wide interest was aroused. Until that time it had been necessary to complete the microdetermination of iodine in organic compounds gravimetrically, because titrimetric methods were unreliable owing to the unfavourable equivalent of iodine. It was probably around this time that the term "amplification" was first used. Shortly afterwards, Vieböck and his co-workers[5] used a similar method to determine alkoxyl indirectly by oxidation of the iodide liberated from the distilled alkyl iodide.

Mohr[6] had first used the reaction in 1853, but with chlorine water as the oxidant. Winkler (1900) also used chlorine water,[7] and Hunter (1909)[8] later used sodium hypochlorite. Bromine water, which is a much more convenient oxidant, appears to have been used for the first time by Bugarszky and Horvath[9] (1909). Despite the earlier origins of this reaction it became referred to widely (albeit incorrectly) as the Leipert procedure.

The term "amplification" has been used in a variety of cases where the conventional reaction for a particular determination is replaced by another reaction by which a more favourable measurement can be made. It is doubtful whether the term "amplification" should be used when this is so. Unfortunately, no serious attempt has yet been made to define these reactions. I once stated "there are two kinds of amplification reaction; direct and indirect. In direct amplification reactions, the quantity of the constituent sought is amplified directly and is measured as such (*e.g.*, iodine in the Leipert reaction), whereas in indirect amplification, species associated with the desired constituent (*e.g.*, iodine in the Vieböck method) is amplified in quantity and measured",[1] but this is a different kind of classification and does not specify which reactions can legitimately be classed as true amplification reactions.

As our own studies in this field have extended,[10,11] it has become apparent that there are more types of amplification reactions than previously considered. This has also been stressed by Fritsche and Weisz.[12] Undoubtedly, the various types need to be more clearly defined. When we speak of amplification (or "multiplication" which is often used synonymously), we should mean that the species to be determined is multiplied as in the Leipert reaction or that an associated species is multiplied as in the Vieböck–Brecher reaction. In such examples the amplification and the more favourable analytical factor are obvious. However, in several types of reaction which have been referred to as "amplification reactions" there is no multiplication either of the desired species or of an associated one. We have been guilty ourselves of using this loose terminology. In some cases the term is used even when the normal equivalence has not been enhanced. For example, the indirect determination of arsenic(III) by oxidation with cerium(IV), followed by fluorometric determination of the excess of cerium(IV),[13] is called an amplification because the ratio of cerium to arsenic is 2:1, but incorrectly so because this is the normal equivalence in this reaction and therefore there is no amplification. In a more recent paper,[14] hydrazine is oxidized with periodate and the iodate formed is determined iodimetrically. This is termed amplification because thrice the amount of titrant is consumed as that in the normal direct iodimetric determination of hydrazine. Again, this can hardly be called amplification, because it is not iodine that is being used as the reagent, but periodate.

Although it is a straightforward matter to see that such a reaction does not involve amplification, other examples present greater problems.

1. "Amplification" through an organic molecule

When metals are determined, for example by precipitation with oxine, followed by treatment of the precipitate with bromine or another oxidant, the improved equivalence is obtained because of the favourable consumption of bromine by oxine, or by the complete destruction of oxine by an oxidant [cerium(IV) or permanganate]. There is no multiplication of any constituent.

2. "Amplification" through heteropoly acid formation

A similar situation exists in this example. The desired constituent attaches to itself large amounts of another radical. The favourable measurement is obtained by then measuring these large amounts (*e.g.*, molybdenum in $H_3PO_4 \cdot 12MoO_3$) in order to determine phosphorus. Again there is no actual multiplication. Although the system is different from type *1* in the type of chemical bonding, both systems provide the same type of enhancement of the equivalence.

3. Extension of a reaction beyond its "normal" stage

Nitrate can be reduced by iron(II), but the equivalence depends on the conditions.[15]

Acid conditions

$$NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow 3Fe^{3+} + NO + 2H_2O \quad (A)$$

Alkaline conditions

$$NO_3^- + 2Fe(OH)_2 + H_2O \rightarrow NO_2^- + 2Fe(OH)_3 \quad (B)$$

With a catalyst and under alkaline condition, however, nitrite is reduced further, to ammonia.

$$NO_2^- + 6Fe(OH)_2 + 5H_2O \rightarrow NH_3 + 6Fe(OH)_3 + OH^- \quad (C)$$

Thus we get a much more advantageous reduction of nitrate.

$$NO_3^- + 8Fe(OH)_2 + 6H_2O \rightarrow NH_3 + 8Fe(OH)_3 + OH^- \quad (D)$$

This is not a multiplication, yet a more favourable measurement has been achieved. This same reaction has been used to determine cobalt by means of formation of cobaltinitrite, and a 37-fold enhancement obtained.[16]

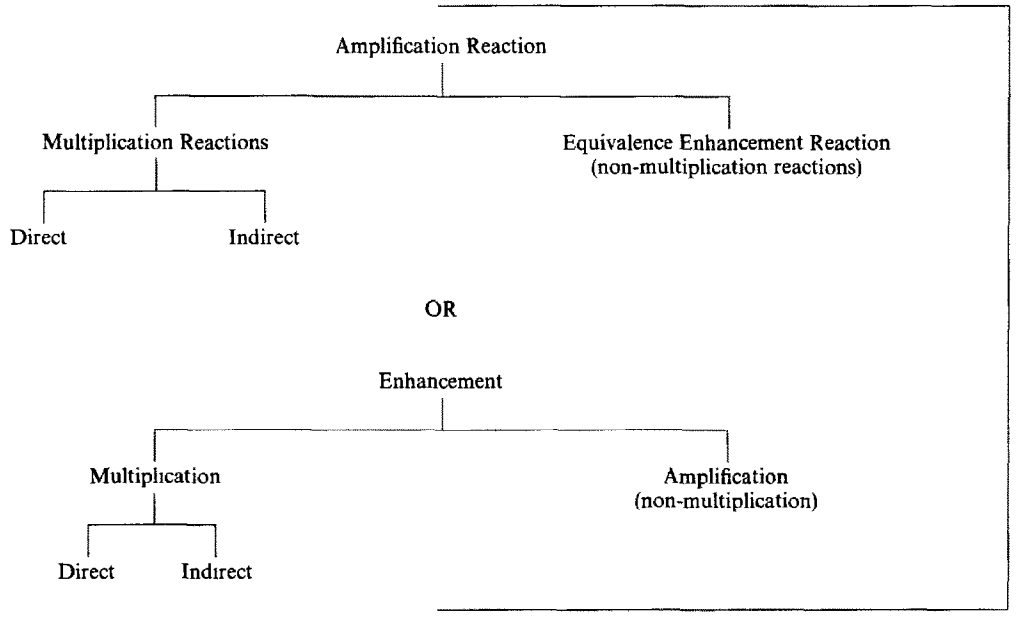
4. The direct titration of iodide with hypochlorite

$$I^- + 3ClO^- \rightarrow IO_3^- + 3Cl^-$$

If we titrate with standard hypochlorite to the exact equivalence point and then add an excess of iodide and titrate the liberated iodine with thiosulphate, the system is similar to the Leipert reaction and so is true multiplication. But if we do nothing further after reaching the endpoint except measure the amount of hypochlorite consumed, the same 6-fold consumption of titrant (in terms of stoichiometry) will have been obtained, but there has not been any multiplication.

Although it is not completely clear, the Oxford Dictionary implies that "amplification" means "enlargement" or "enhancement"; and "multiplication" means "breeding" or "reproduction". If this difference is accepted (it will be recalled that "multiplication" and "amplification" are used synonymously) we could use "multiplication" to describe Winkler–Leipert and Vieböck type reactions and "amplification" for the overall effect of enhancing the equivalence ratio. There is no real need in the definition to classify reactions such as *1–4*, different from each other though they may be: this would complicate the definition and would be carrying classification too far.

Thus we could have:



The first classification has the advantage that it retains the most-widely used and long-established term to describe the overall effect. The second classification has the advantage that "enhancement" is probably a better word to describe the overall effect, but with the disadvantages that "amplification" would have a much more restricted meaning.

There are still some difficulties. Some may argue that Reaction *D* is not an enhancement of the equivalence ratio; it is simply the equivalence for that particular reaction. This criticism could only be overcome by comparing the reaction with that used in the conventional method. But if the newer enhanced reaction replaced the conventional method at all levels, the difficulty would reappear, for one could then ask what has been enhanced.

Unless these difficulties can be overcome it is may be best to exclude non-multiplication reactions of this type from the definition.

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AMPEROMETRIC COMPLEX-FORMATION TITRATIONS WITH A DROPPING BISMUTH AMALGAM ELECTRODE IN HALIDE MEDIUM

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Summary—The use of the dropping bismuth amalgam electrode has been investigated for the selective determination of metal ions in the presence of large concentrations of halides by means of amperometric complex-formation titrations, using normal pulse polarography. Concentrations of metal ions down to $3 \times 10^{-7} M$ have been determined with adequate accuracy in the presence of about $0.1 M$ chloride or $0.01 M$ bromide. Calculated and experimental current–voltage curves have been compared and found to be in reasonable agreement.

Since the introduction by Michel[1] of anodic amperometry at mercury electrodes as a method of end-point detection for complex-formation titrations several applications of this method have been described in the literature.[2–4] Although the dropping mercury electrode is more reproducible and easier to prepare, the rotating mercury electrode has been recommended because of its higher sensitivity.

At present a similar or even better sensitivity can be obtained with dropping electrodes provided that polarographic pulse techniques are used.[5] Of these pulse techniques normal pulse polarography with increasing pulse amplitude has the additional advantage that during most of the time a potential can be applied at which no interfering reaction occurs. Recently attention has been paid to the unfavourable influence of halides, caused by the formation of insoluble mercury(I) halides or of mercury(II) halide complexes.[6] The influence of halides is very marked at lower pH values. In order to avoid these limitations, an attempt has been made in this work to investigate the possibility of using metal amalgam indicator electrodes for amperometric titrations. The choice of the metal was based on the criteria that its cation should form strong complexes with the ligand to be used as the titrant but should have a lower tendency than mercury to form complexes or insoluble products with halides. Bismuth fulfils both requirements and its amalgam, which can be prepared easily, is liquid, is stable in the presence of water and can be used as a dropping electrode. With such an electrode the influence of halides is much less marked than it is with mercury alone. No information on the use of a dropping amalgam electrode as indicator electrode in amperometry has been found in the literature.

THEORETICAL

Theoretical current–voltage relationships will be derived for the anodic dissolution of bismuth from a dropping bismuth amalgam electrode (DAE) in the presence of chloride and EDTA in order to test the possibility of using this electrode in complexometric titrations. The treatment will be given according to den Boef and Freese.[6] A comparison will be made with the experimental data.

Four different cases have been considered: (*i*) the formation of the insoluble bismuth hydroxychloride, $Bi(OH)_2Cl$; (*ii*) the formation of bismuth hydroxide; (*iii*) the formation of a mixture of bismuth–chloride complexes; (*iv*) the formation of bismuth–EDTA complexes in a medium containing EDTA. The derivation of the current–voltage relationships is based in all cases on the assumptions that all equilibria are established rapidly and that the Nernst equation is obeyed:

$$E = E^0_{(Bi^{3+},Bi^0)} + \frac{RT}{3F} \ln \frac{a_{Bi^{3+}}}{a_{Bi^0}} . \qquad (1)$$

As no information is available[7] on the formation of intermetallic compounds of bismuth and mercury, this effect is not taken into consideration.

According to Galus[7] we can assume that $a_{Bi^0} = [Bi^0]$ as long as the mercury is not saturated with bismuth, so that at the surface $(a_{Bi^0})_s = [Bi^0]_s$. As a first approximation the activities in the solution are considered to be equal to concentrations and we can write

$$E = E^0_{(Bi^{3+},Bi^0)} + \frac{0.059}{3} \log \frac{[Bi^{3+}]_s}{[Bi^0]_s} . \qquad (2)$$

Several alternatives will be considered:

(*i*) the formation of the insoluble bismuth hydroxychloride at the electrode surface according to the reaction:

$$Bi^{3+} + 2OH^- + Cl^- \rightleftharpoons Bi(OH)_2Cl \ (\rightleftharpoons BiOCl).$$

This reaction may be described in terms of surface concentrations by

$$K_{so}^{Bi(OH)_2Cl} = [Bi^{3+}]_s[OH^-]_s^2[Cl^-]_s.$$

The current–voltage relationship for this case is given by:

$$E = E^0_{(Bi^{3+},Bi^0)} + \frac{0.059}{3}\log K_{so}^{Bi(OH)_2Cl} - \frac{0.118}{3}\log[OH^-]_s - \frac{0.059}{3}\log[Cl^-]_s - \frac{0.059}{3}\log[Bi^0]_s. \quad (3)$$

Assuming that steady-state conditions are established, we can substitute for the surface concentrations

$$[Cl^-]_s = \frac{i_d^{Cl^-} - i}{k_{Cl^-}} \quad (4)$$

and

$$[Bi^0]_s = \frac{i_d^{Bi^0} - i}{k_{Bi^0}}. \quad (5)$$

With $[OH^-]_s = [OH^-]_{bulk}$ this leads to:

$$E = E^0_{(Bi^{3+},Bi^0)} + \frac{0.059}{3}\log K_{so}^{Bi(OH)_2Cl} - \frac{0.118}{3}\log[OH^-] - \frac{0.059}{3}\log\frac{i_d^{Cl^-} - i}{k_{Cl^-}} - \frac{0.059}{3}\log\frac{i_d^{Bi^0} - i}{k_{Bi^0}}. \quad (6)$$

(*ii*) In the case of formation of bismuth hydroxide, the reaction at the electrode surface is:

$$Bi^{3+} + 3OH^- \rightleftharpoons Bi(OH)_3\ (\rightleftharpoons Bi_2O_3)$$
$$K_{so}^{Bi(OH)_3} = [Bi^{3+}]_s[OH^-]_s^3.$$

The current–voltage relationship is given by:

$$E = E^0_{(Bi^{3+},Bi^0)} + \frac{0.059}{3}\log K_{so}^{Bi(OH)_3} - \frac{0.177}{3}\log[OH^-] - \frac{0.059}{3}\log\frac{i_d^{Bi^0} - i}{k_{Bi^0}}. \quad (7)$$

(*iii*) In the case of the bismuth–chloride complexes, the reaction at the electrode surface is:

$$Bi^{3+} + nCl^- \rightleftharpoons BiCl_n^{3-n}.$$

As we are mainly interested in the influence of halide concentrations that are large relative to the concentration of bismuth, $[Cl^-]_s$ may be taken as being equal to $[Cl^-]_{bulk}$. The current–voltage relationship can then be given by:[6]

$$E = E^0_{(Bi^{3+},Bi^0)} - \frac{0.059}{3}\log\alpha_{Bi(Cl)_{bulk}} + \frac{0.059}{3}\log\frac{i}{k_{Bi^{3+}}} - \frac{0.059}{3}\log\frac{i_d^{Bi^0} - i}{k_{Bi^0}} \quad (8)$$

(*iv*) The equation for the potential of the electrode in the case of bismuth–EDTA complex formation is given by:

$$E = E^0_{(Bi^{3+},Bi^0)} - \frac{0.059}{3}\log K'_{BiEDTA} + \frac{0.059}{3}\log\frac{i}{i_d^{EDTA} - i} - \frac{0.059}{3}\log\frac{i_d^{Bi^0} - i}{k_{Bi^0}} \quad (9)$$

where $K' = [BiEDTA]/[Bi'][EDTA']$; the charges of the ions have been omitted. The presence of chloride and hydroxide ions may lead to a decrease in the value of K'_{BiEDTA}. For the evaluation of these relationships the following constants were taken from the literature: log $K_{so}^{Bi(OH)_2Cl} = -30.8$;[8] log $K_{BiEDTA} = 26.7$;[8] $E^0_{(BiO^+,Bi^0)} = 0.32$ V ($BiO^+ + 2H^+ + 3e \rightleftharpoons H_2O + Bi^0$);[9] $\log{}^*\beta_{1,2} = -4{\cdot}7$ ($Bi^{3+} + 2H_2O \rightleftharpoons Bi(OH)_2^+ + 2H^+$);[10] log $\beta_1 = 2.4$; log $\beta_2 = 3.5$; log $\beta_3 = 5.4$; log $\beta_4 = 6.1$; log $\beta_5 = 6.7$ and log $\beta_6 = 6.6$ ($Bi^{3+} + nCl^- \rightleftharpoons BiCl_n^{3-n}$);[11] log $\alpha_{EDTA(H)} = 13.7$ (pH 2) and log $\alpha_{EDTA(H)} = 6.6$ (pH 5).[11]

The value $E^0_{(Bi_3{}^+,Bi^0)} = -0.015$ V *vs.* SCE is calculated from $E^0_{(BiO^+,Bi^0}$ and $^*\beta_{1,2}$. The remaining values, *viz.* $i_d^{Bi^0}$, i_d^{EDTA} and the concentration of bismuth in the amalgam were determined experimentally. For $[Bi^0] = 1.2 \times 10^{-3}M$ (see experimental) the value $i_d^{Bi^0} = 8.0\,\mu A$ gives $k_{Bi^0} = 7 \times 10^3\,\mu A.mole^{-1}$ and for $[EDTA]_{bulk} = 10^{-4}M$, $i_d^{EDTA} = 0.65\,\mu A$ results

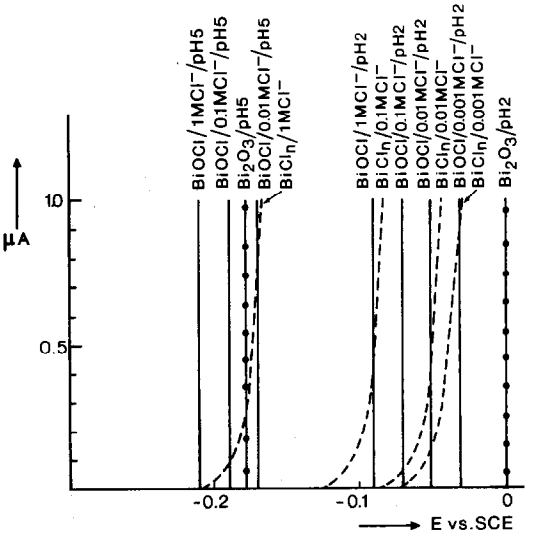

Fig. 1. Current–voltage curves, calculated according to equations (6), (7) and (8) at both pH 2 and 5 and at different concentrations of chloride. Solid lines: equation (6); marked solid lines: equation (7); dotted lines: equation (8).

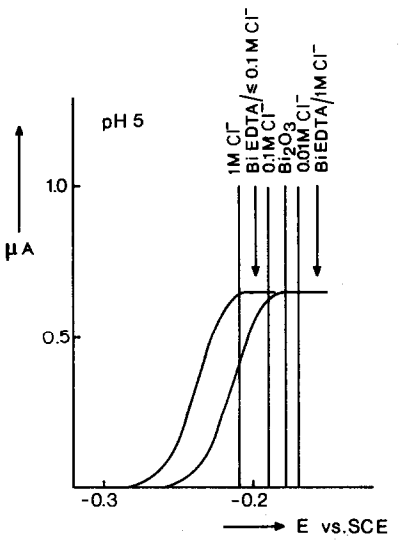

Fig. 2. Current–voltage curves, calculated according to equations (9) and (6) at pH 5 for different concentrations of chloride.

in $k_{EDTA} = 6.5 \times 10^3\ \mu A.1.mole^{-1}$. It seems possible to assume that the values K_{Cl^-} and $k_{Bi^{3+}}$ are about equal to k_{EDTA}.

Figure 1 shows some current–voltage curves calculated on the basis of equations (6), (7) and (8) for both pH 2 and 5 and for different chloride concentrations.

Figures 2 and 3 give some current–voltage curves calculated by means of equation (9) and the curves obtained for chloride solutions in the absence of EDTA, under the same conditions assumed for Fig. 1.

A similar theoretical treatment can be applied to solutions containing bromide or iodide. However, iodide will interfere because mercury–iodide complex formation predominates over the reaction between bismuth and EDTA.

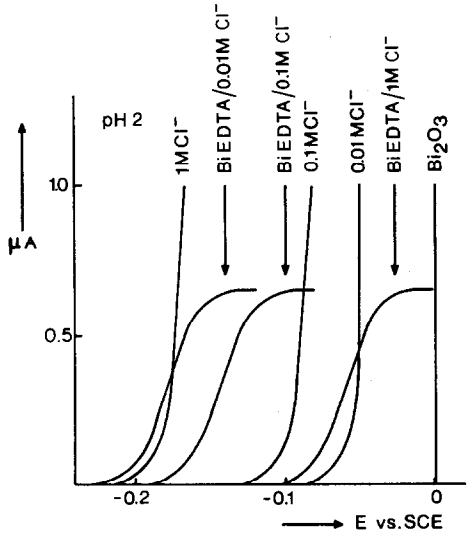

Fig. 3. Current–voltage curves, calculated according to equations (9), (6) and (8) at pH 2 for different concentrations of chloride.

EXPERIMENTAL

Apparatus

The amalgam for the DAE (Fig. 4) is prepared by electrolytic reduction of bismuth oxynitrate solution A ($10^{-2}M$ $BiONO_3$ in $1M$ nitric acid) at a mercury pool B in a glass cell C. In the bismuth solution A is immersed the second working electrode D, consisting of a platinum wire in a glass tube E and separated from solution A by a sintered glass disc F. A coulometer (Metrohm E 211-A) is used to generate and control the amount of the bismuth in the amalgam. During the electrolysis with constant current the solution and the amalgam are stirred simultaneously by bubbling nitrogen through them both. Oxidation of the amalgam is avoided by preparing and storing it under an atmosphere of nitrogen and maintaining it at −0.3 V *vs.* SCE, when not in use. A $1.2 \times 10^{-3}M$ concentration of bismuth in the amalgam was used throughout the experiments. This concentration was determined by linear-sweep voltammetry (5 mV/sec) on a hanging drop of the amalgam. The total quantity of charge consumed by oxidation of the bismuth was measured by integration of the well developed anodic peak. From this and the volume of the amalgam drop, the concentration of the bismuth in the amalgam was calculated.

All experiments were performed with a PAR model 174 polarographic analyser in the normal pulse mode. All potential values were referred to SCE.

A 10-ml titration cell (Fig. 5) was constructed with a narrow outlet at the bottom in order to minimize the contact between the amalgam and the test solution. The mercury level was kept constant by connection to a reservoir with a large cross-sectional area. In this way the introduction of bismuth ions into the test solution by chemical oxidation of the amalgam was minimized.

The cell was siliconed with dimethyldichlorosilane and subsequently heated at 200° for 2 hr, in order to reduce

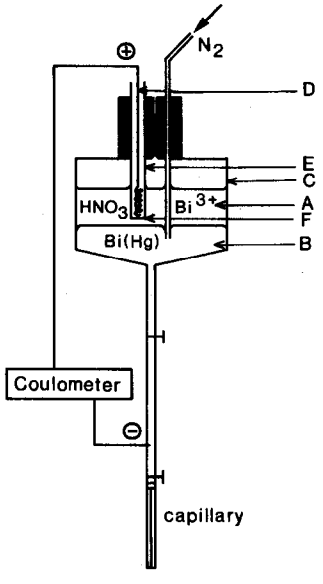

Fig. 4. Apparatus for the preparation of the bismuth amalgam and its use as a dropping electrode. A: solution of $0.01M$ $BiONO_3$ in $1M$ HNO_3; B: mercury pool; C: glass cell; D: platinum wire as second working electrode; E: glass tube; F: fritted glass disc.

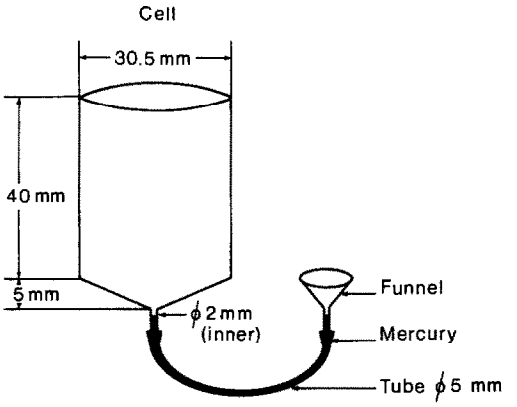

Fig. 5. Titration cell (10-ml).

adsorption of metal ions from the solution onto the walls of the cell. The vessel was covered with a Teflon lid provided with holes for the salt bridge, the platinum auxiliary electrode, the DAE, a gas inlet tube and the tip of the burette. Traces of oxygen were removed from the nitrogen by passage over a column containing an activated copper oxide catalyst (B.T.S. catalyst, BASF, Ludwigshafen). Before entering the cell the nitrogen passed through a wash-bottle filled with the supporting electrolyte. The titrant was added by means of a microburette (Metrohm E 457).

Reagents

Quartz-distilled water was used in all experiments. Stock solutions ($10^{-3}M$) of metal ions and EDTA were prepared from analytical grade chemicals, but the potassium chloride and potassium bromide were of Suprapure quality (Merck). Samples for analysis were prepared just before use.

Procedure

The sample was placed in the titration cell and deaerated for 15 min. The nitrogen flow was then redirected over the solution and an anodic polarogram was recorded. The applied e.m.f. selected was at the foot of the anodic wave in the case of a direct titration and at the diffusion plateau in the case of a back-titration.[5] The rest potential was set at a value about 200 mV more negative than the $E_{\frac{1}{2}}$-value of the anodic wave. The potential was scanned until the proper working potential was reached and then kept at this value. The current was recorded after about 7 drops in order to ensure that the memory circuits had become fully charged. After each addition of titrant solution, nitrogen was bubbled through the solution for about 1 min for deaeration and mixing. The titration was continued until 100% excess of titrant had been added. The end-point was at the intersection of the two straight lines on the graph.

RESULTS AND DISCUSSION

A comparison of the experimental current–voltage curves with the theoretical curves calculated for pH 2 from equations (6) and (8) (Fig. 6) shows that the experimental curves occur at more positive potentials than were predicted. This difference might be attributed to several factors.

No values of $E^{0}_{(Bi_3^+, Bi^0)}$ are to be found in the literature; its value has to be calculated from other standard potentials and equilibrium constants, some of which are possibly unreliable.

The literature values of the stability constants of the bismuth chloride complexes corresponded to an ionic strength of 2, which is higher than in our experiments. A lower ionic strength will lead to lower values of the concentration constants, causing a shift of the calculated curves to more positive potentials.

In the case of the more concentrated chloride solutions ($1M$) in our experiments, a correction is needed for the diffusion potential across the diaphragm of the reference electrode;[12] a correction of 14 mV as mentioned by Bates[13] seems appropriate.

From equations (7) and (9) it can be calculated that bismuth–hydroxide complex formation will predominate over the formation of BiEDTA above pH 9. Therefore, determinations were restricted to acidic solutions (pH ≤ 5).

The shift towards negative potentials of the anodic dissolution wave for bismuth amalgam in the presence of EDTA, which depends on the pH (Figs. 7 and 8), makes it possible to measure the EDTA concentration and thus to detect the end-point in a complexometric titration in halide medium.

A series of d.c. polarograms for different concentrations of EDTA at pH 3 in solutions of perchloric acid showed that there is a linear relationship between the height of the anodic ligand wave and the concentration of the ligand (Fig. 9). This holds as long as the ratio of the concentration of the free ligand to the concentration of bismuth in the amalgam does not exceed a value of about 0.7.

The anodic dissolution wave of bismuth amalgam in the presence of EDTA and chloride is somewhat more pronounced than would be expected on the basis of available equilibrium data. The formation of a ternary complex between bismuth, EDTA and chloride could explain this fact, which results in a lower limit of determination for the titrations in the

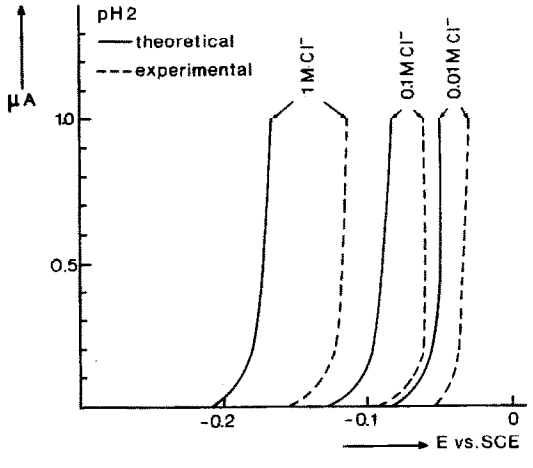

Fig. 6. Current–voltage curves, calculated according to equations (6) and (8) at pH 2 for different concentrations of chloride (dotted lines). Corresponding experimental current–voltage curves (solid lines).

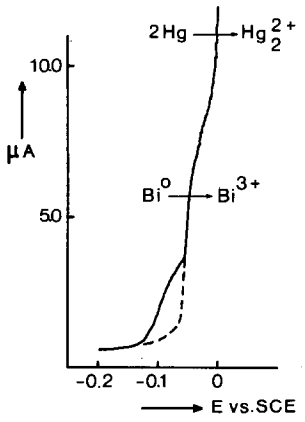

Fig. 7. Current-sampled d.c. polarograms of 0.1*M* KCl at pH 2·4 ($HClO_4$) in presence (——) and absence (-----) of $3 \times 10^{-4}M$ EDTA.

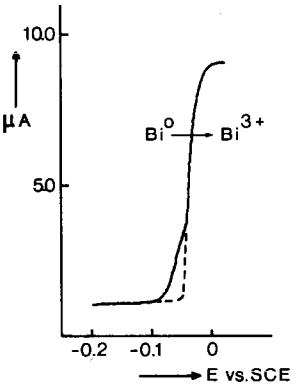

Fig. 8. Current-sampled d.c. polarograms of 0.1*M* KBr at pH 3 ($HClO_4$) in presence (——) and absence (-----) of $3 \times 10^{-4}M$ EDTA.

presence of chloride. Potentiometric curves for the titration of bismuth with EDTA (bismuth amalgam electrode), as well as photometric titration curves for the same reaction, indicate that the conditional stability constant is approximately ten times greater in chloride than in perchlorate medium. No difference was observed in the absorption spectra of BiEDTA in the presence and absence of chloride.

Meyers and Osteryoung[14] have compared normal and differential pulse polarographic detection for the titration of copper(II) with EDTA, using the cathodic wave of free copper(II) ions. Both methods give signals of about the same magnitude at a given potential, but the differential pulse technique has a larger signal-to-noise ratio and hence a better sensitivity. A similar behaviour was observed in the present investigation for complexometric titrations using the anodic wave of the ligand. However, normal pulse polarography was preferred as the indication method for other reasons, the main one being that the anodic dissolution of bismuth as bismuth–EDTA—the indicating reaction—always introduces a systematic error. Since in the case of normal pulse polarography the indicating reaction only occurs during a fraction of the total time needed for the titration, this systematic error will be negligible in all cases. In the case of differential pulse polarography systematic errors caused by anodic dissolution of bismuth as bismuth–EDTA might occur under certain conditions.

Titration errors may arise from:

oxidation of amalgam, which can occur at the narrow outlet at the bottom of the cell;

adsorption of metal ions on the walls of the cell;

contamination of the reagents by trace amounts of metal ions which also react with EDTA under the experimental conditions.

This last effect was thought to arise in the titration of $2 \times 10^{-6}M$ EDTA with Pb(II) (Table 1) in the presence of 0.1*M* analytical grade potassium chloride. Although a tenfold decrease in this chloride concentration did not produce a tenfold decrease in the systematic error, the use of Suprapure quality potassium chloride or bromide did improve the results significantly.

In order to illustrate the applicability of the method several direct titrations have been carried out as well as some back-titrations. Table 2 shows some results obtained in the presence of large amounts of halides and some other metal ions. Titrations of Hg(II) are impossible because the conditional constant is too low owing to the strong complexation with chloride; this effect might be used for masking. Determinations of Fe(III) with EDTA as titrant were not successful

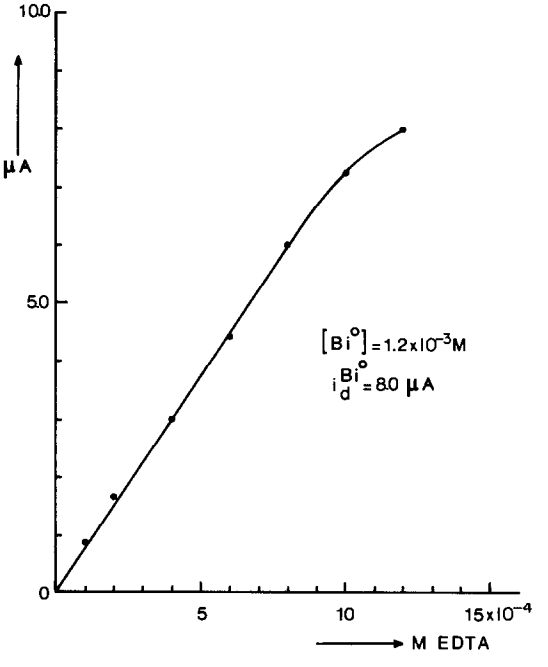

Fig. 9. Plot of the height of the anodic wave of EDTA *vs.* the concentration of the EDTA at a $1.2 \times 10^{-3}M$ bismuth concentration in the amalgam.

Table 1. Determination of EDTA with Pb(II) at pH 4.8 (acetate buffer) at an indication potential of −0.14 V *vs.* SCE

Amount of EDTA, *μg/10 ml* taken	found	Error, %	Std. devn., % (no. of detns.)	[KCl], *M*
5.58	4.83	−13.4	2.0(3)	0.1
5.58	5.13	−8.0	5.6(5)	0.01
5.58	5.60	+0.3	4.8(5)	0.1 "Suprapure"

Table 2. Determination of metal ions and EDTA in the presence of halide ions

Titrant	D/B*	pH	Medium	Indication potential, *V vs.* SCE	Concentration of other ions, *M*	Species titrated, *μg/10 ml* taken	found	Error %	Std. devn. % (no. of detns.)
Pb(II)	B	4.8	acetate buffer	−0.14	0.05 Cl^-	0.983 Zn(II)	0.966	−2.7	2.0(4)
Pb(II)	B	4.8	acetate buffer	−0.14	0.05 Cl^-	0.327 Zn(II)	0.304	−7.0	2.0(4)
Pb(II)	B	4.8	acetate buffer	−0.14	0.01 Br^-	0.983 Zn(II)	0.973	−1.0	2.5(3)
EDTA	D	2	$HClO_4$	−0.07	0.05 Cl^-	3.48 Th(IV)	3.42	−1.7	3.0(3)
EDTA	D	2	$HClO_4$	−0.07	0.01 Br^-	3.48 Th(IV)	3.48	—	3.0(3)
EDTA	D	2	$HClO_4$	−0·07	0.05 Cl^-	1.16 Th(IV)	1.09	−6.0	5.0(3)
Pb(II)	D	4.8	acetate buffer	−0.14	0.1 Cl^-	5.58 EDTA	5.60	+0.3	4.8(5)
Th(IV)	D	2	$HClO_4$	−0.07	0.05 Cl^- 1.5×10^{-6} Fe(III)	11.17 EDTA	10.42	−6.7	3.0(3)
Pb(II)	D	4.8	acetate buffer	−0.14	0.05 Cl^- 10^{-6} Hg(II)	7.44 EDTA	6.88	−7.5	3.2(3)
Th(IV)	B	4.8	acetate buffer	−0.04	0.05 Cl^-	0.89 Ga(III)	0.88	−1.1	2.3(3)
Th(IV)	B	4.8	acetate buffer	−0.04	0.01 Br^-	0.89 Ga(III)	0.88	−1.1	3.7(4)

* D = direct titration. B = back-titration.

because of incomplete formation of the Fe(III)–EDTA complex, even after 30 min of heating at pH 2 or 4.8. A successful back-titration of $5 \times 10^{-6} M$ Fe(III) appeared to be possible with DTPA (diethylenetriaminepenta-acetic acid) and Th(IV) at pH 4.8. At lower concentrations of Fe(III) this reaction remains incomplete, even after heating. This may explain the fact that roughly equimolar amounts Fe(III) do not interfere in the determination of other metal ions.

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APPLICATION OF POLYETHYLENE GLYCOL FOR "ELECTROCHEMICAL MASKING" IN DIRECT-CURRENT POLAROGRAPHY

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Summary—The use of polyethylene glycols (PEG) of molecular weight from 200 to 15,000 for electrochemical masking has been investigated. A pH-4.4 tartrate buffer was found to be the most suitable supporting electrolyte, and 0.1% the optimum PEG concentration. PEGs of m.w. below 600 had little effect on the waves examined, and are useless for electrochemical masking. Under the conditions chosen, the waves of Bi(III), Sb(III) and In(III) are completely suppressed; the Cd(II) and Pb(II) waves are shifted to more negative potentials, and the Tl(I) wave is scarcely affected by PEGs. The Cu(II) wave behaves differently from the others. A method is proposed for the determination of lead and/or thallium in the presence of up to 5000-fold w/w ratios of bismuth, antimony or indium. The determination of both lead and thallium is only possible when the amounts are not too different, as the waves are quite close. Copper(II) interferes.

Electrochemical masking, which is based on the electrochemical effect of adsorption of an electrochemically inactive organic substance onto the electrode surface, is insufficiently utilized in polarographic analysis. Examples include the determination of thallium in the presence of a 1000-fold quantity of copper,[1] thallium with a 500-fold quantity of cadmium,[2] iron(III) or lead with a 2000-fold amount of copper,[3] and copper with a 1000-fold amount of bismuth.[4] Interesting results have been reported in some other papers.[5–8] It is worth noting the successful investigations in a.c. polarography, where specifically adsorbed electrochemically inactive organic substances have been used.[3,9–12] The non-ionic surface-active substance Triton X-100 has most often been used,[1,3,4,6,7] also camphor,[1,3,4] propan-2-ol,[3] cation-active *N*-tetrabutylammonium sulphate,[2] decylamine,[10] dodecylamine,[11] and anion-active Benex.[9] Most of the supporting electrolytes used have contained strong complexing agents such as EDTA,[1,3,4] diethylenetriaminepenta-acetic acid,[7] 1,2-diaminocyclohexanetetra-acetic acid,[12] tartrates,[3] citrates[9,11] and oxalates.[10]

The polyethylene glycols (PEGs) would seem to be worth investigating as electrochemical masking reagents. They are known to be adsorbed on the dropping mercury electrode,[13–17] and to suppress some polarographic waves.[8,18–21] The various oligomers are readily soluble in water and are available with a wide range of molecular weights. Investigations on the effect of the molecular weight of the PEGs on their ability to suppress polarographic waves must be preceded by a suitable choice of the supporting electrolyte composition and by an evaluation of the effect of PEG concentration.

EXPERIMENTAL

Equipment and reagents

Investigations were performed with a Radelkis polarograph type OH-102 and two dropping electrodes with characteristics $m = 2.95$ mg/sec and $t_0 = 2.88$ sec, for selecting the supporting electrolyte, and $m = 1.11$ mg/sec and adjustable drop-life time $t_r = 3.0$ sec, for the remaining investigations. The mercury pool counter-electrode served also as reference electrode, and its potential was regularly checked against a saturated calomel electrode by means of a high-resistance millivoltmeter. Measurements were made in a vessel kept at 20°. Solutions were deaerated with purified nitrogen.

Polyethylene glycols were obtained from Carl Roth (molecular weights 200–6000) and Fluka A.G. (the others), and were used without additional purification.

Investigations

The effect of adding PEGs, of various molecular weights and at several different concentrations, was studied by recording polarographic waves of a number of ions in solutions of different pH. Investigations covered the following species: iron(III), copper(II), bismuth(III), antimony(III), lead(II), thallium(I), tin(II), indium(III), cadmium(II), zinc(II), nickel(II), cobalt(II), chromium(III), gallium(II) and oxygen. The media used were 1*M* hydrochloric acid, 0.5*M* sodium sulphate, 1*M* acetate buffer (pH 4.7), 1*M* sodium hydroxide, ammonia buffer (1*M* ammonium chloride + 1*M* ammonium hydroxide), and tartrate buffer (pH 4.4: 0.4*M* disodium tartrate + 0.1*M* sodium hydrogen tartrate). The concentration of each metal ion was $5 \times 10^{-4}M$ and the oxygen level in each electrolyte was that of a saturated solution. To the solutions were added 0.005% or 0.1% of PEGs with molecular weight 300, 1500 or 4000, and the results were compared with those obtained from solutions which contained 0.01% of gelatin.

RESULTS

The half-wave potentials for the metal ions in the presence of 0.1% of PEG (m.w. 4000) are shown in

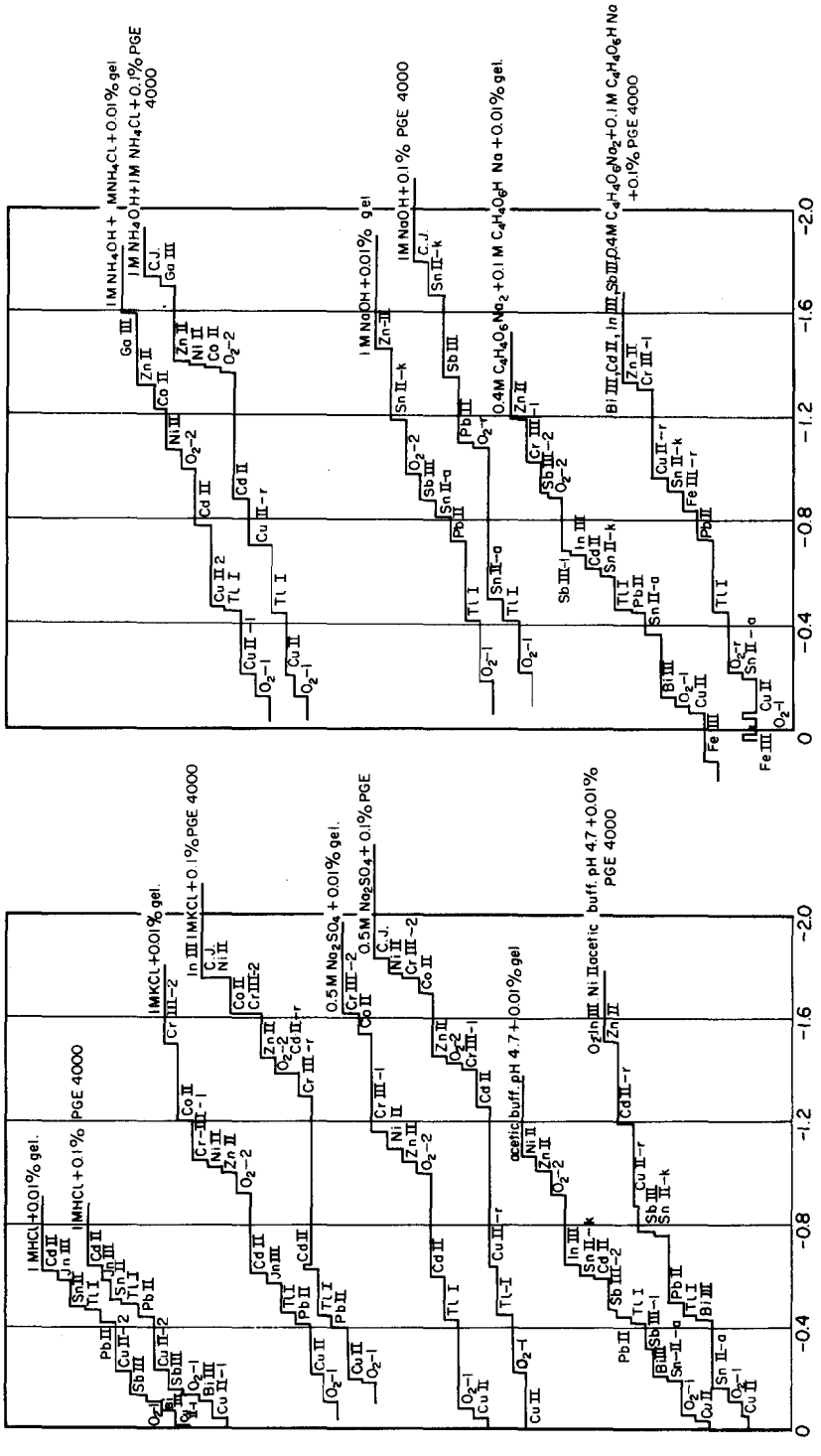

Fig. 1. Polarographic "spectra" in various supporting electrolytes with and without addition of 0.1% of PEG with molecular weight of 4000.

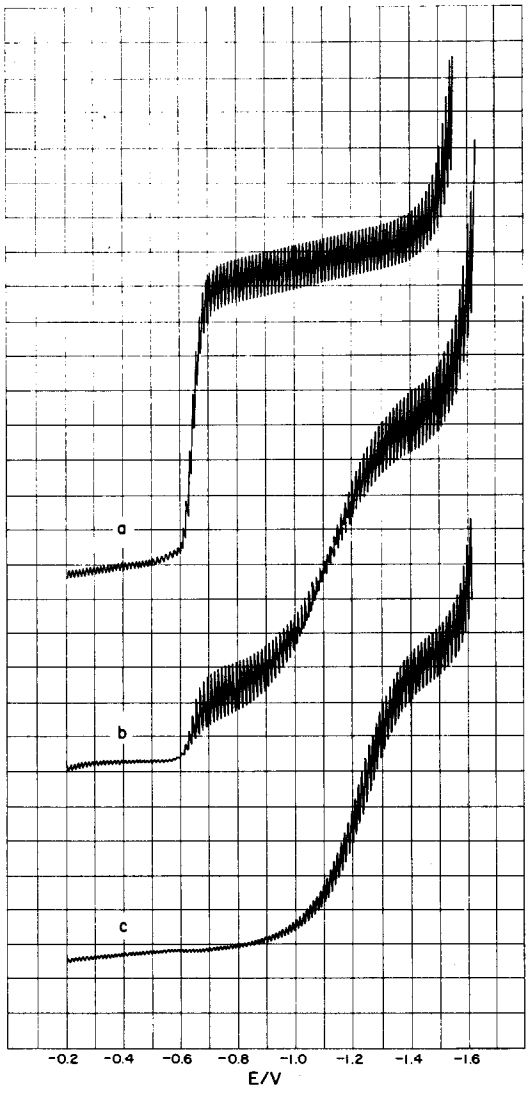

Fig. 2. Example of wave suppression by PEG: cadmium wave in the tartrate buffer, pH 4.4. (*a*) without PEG, but with 0.01% gelatin. (*b*) 0.004% PEG, m.w. = 600. (*c*) 0.05% PEG, m.w. = 600.

Fig. 1. When a wave was split to such an extent that the half-wave potentials of both parts could be determined, this is indicated in the figure as a step of half the usual height, as for example, for antimony(III) in tartrate solutions without PEG. When two clearly formed waves were observed they are marked as if they were waves obtained with two different depolarizers, and are identified by numbering in the order in which they occurred. When addition of PEG suppressed the wave and gave rise to a new one at a more negative potential the step in the figure is identified with an "r", *e.g.*, in tartrate solution Fe(III)–r. We shall call these waves "induced" waves (see Fig. 2 for the cadmium waves). If the PEG caused a peak to form, this is marked symbolically on the diagram by a rectangular peak with leading-edge height equal to the polarographic wave height and trailing edge height equal to that after the polarographic wave was passed. The small waves associated with a sudden change in the double-layer capacity, which were observed between −1.6 and −2.0 V, are marked C.J.

In tartrate solution, which proved to be the best supporting electrolyte of those considered, the effect of changing the molecular weight of the PEG was examined for the cadmium wave. The results obtained are shown in Fig. 3. For further investigations a PEG concentration of 0.1% was selected, as it ensured the maximum influence on the waves examined.

A wider range of PEG molecular weights was covered in investigations on the waves of thallium(I), copper(II), lead(II), cadmium(II), bismuth(III), antimony(III) and indium(III) in tartrate solution at pH 4.4. The PEG concentration was kept at 0.1% and the molecular weight was varied from 200 to 15,000. The results obtained are displayed in Figs. 4 and 5. Figure 4 illustrates changes in the height of the primary waves (solid line) and of the new waves at more negative potentials for copper and lead (dotted line) as a function of the molecular weight of the PEG. In addition, for copper and bismuth, the current at the minimum (see Fig. 6) is also plotted as a function of the PEG molecular weight (shown as a dashed line). Currents are relative, being normalized to that recorded in the absence of PEG. In the case of lead the dotted line depicts the combined height of the primary and the new waves. The height of the new cadmium wave could not be determined, because of interference from the background current.

Figure 5 shows the width of the "induced" waves of cadmium, lead, thallium and copper, as a function of the PEG molecular weight. These are taken from

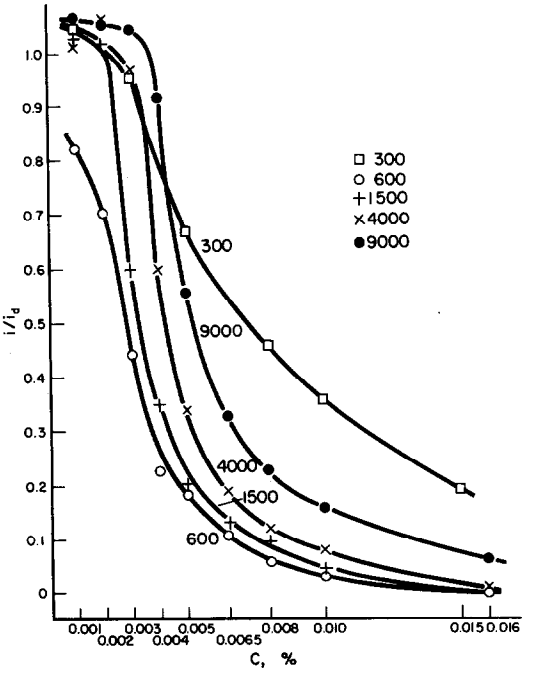

Fig. 3. The effect of the PEG concentration and molecular weight on the suppression of the cadmium wave in tartrate buffer at pH 4.4.

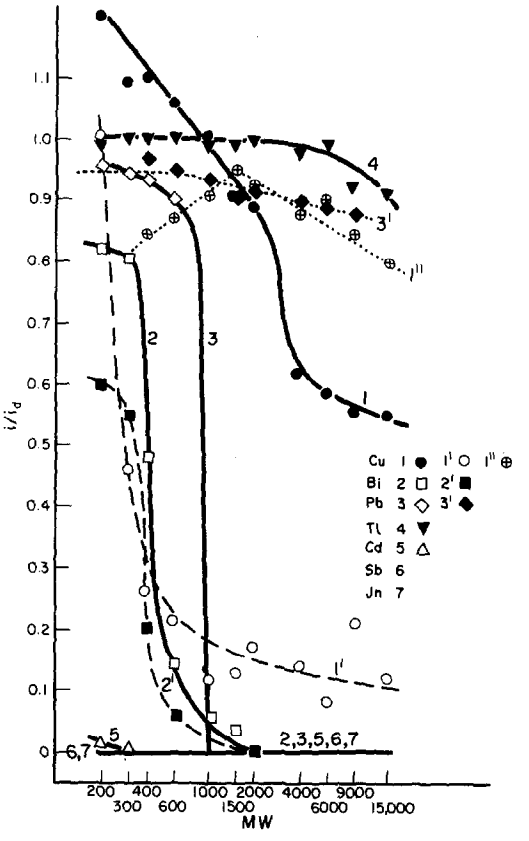

Fig. 4. Relative heights of primary wave (solid line), induced wave (dotted line) and minimum (dashed line) of ions examined in the presence of 0.1% of PEG, of various molecular weights, in tartrate supporting electrolyte (pH 4.4), 1–Cu(II); 2–Bi(III); 3–Pb(II); 4–Tl(I); 5–Cd(II); 6–Sb(III); 7–In(III).

the polarograms, and cannot be calculated, as the shapes of the "induced" waves do not fit that predicted by the normal equation for a polarographic wave. For the sake of clarity the results for copper are displayed separately (Fig. 5): they are dealt with in the discussion section.

As the surface-active PEGs used had a marked effect on the life-time of the mercury drop, the variation of wave-height with drop-life was investigated for copper and lead. The results are summarized in Table 1.

The possibility was then considered of determining lead and thallium in the presence of large amounts of bismuth, antimony and indium, working under what seemed to be the optimum conditions of 0.1% of PEG, m.w. 4000, in a tartrate buffer at pH 4.4.

Of these combinations, that of lead in the presence of a large excess of bismuth offers the greatest difficulty under normal conditions, as the bismuth wave occurs at a far lower potential than that of the lead wave. Results for the determination of lead and thallium in the presence of a 500-fold amount of bismuth are shown in Table 2. As the lead and thallium waves are not widely separated (by only about 0.25 V), it is not possible to determine a small amount of one in the presence of a large amount of the other.

DISCUSSION

Choice of electrolyte

The preliminary investigations, aimed at enabling the most suitable supporting electrolyte to be chosen, revealed that analytically useful results were only to be obtained by using the tartrate buffer. In this buffer,

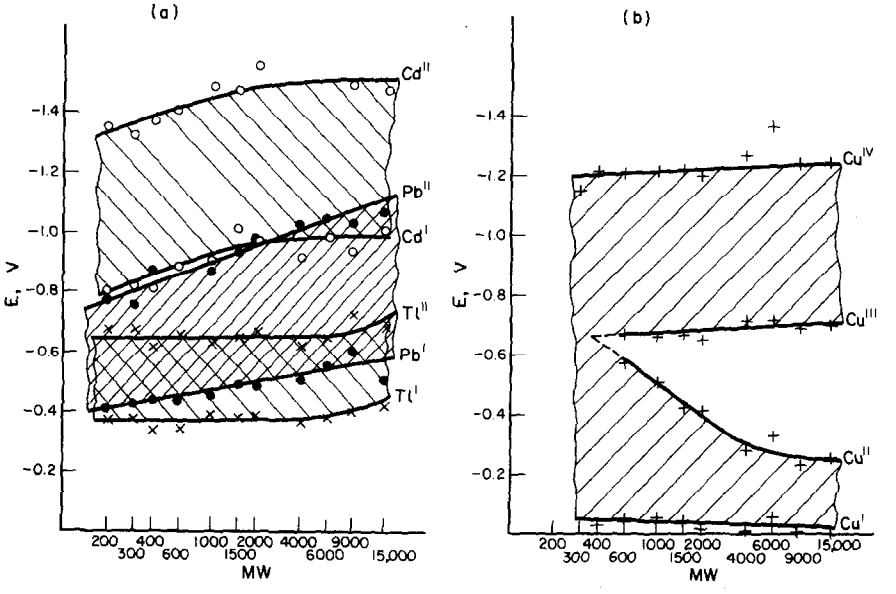

Fig. 5. Width of the waves of thallium, lead and cadmium (*a*) and copper (*b*) in tartrate supporting electrolyte (pH 4.4) with 0.1% of PEG of various molecular weights.

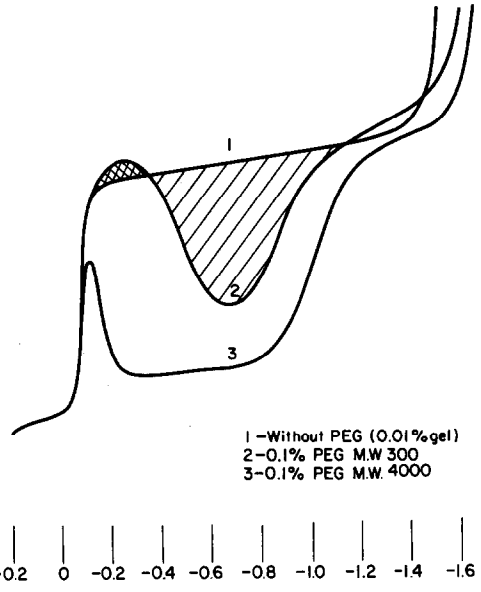

Fig. 6. The copper wave obtained in the absence, (1) and in the presence of 0.1% PEG with molecular weight of 300 (2) and 4000 (3) in tartrate supporting electrolyte (pH 4.4).

and in the presence of 0.1% of PEG (m.w. 4000), the waves of bismuth, antimony and indium are completely suppressed while the waves of lead and thallium(I), which coincide in the absence of PEG, become separated by about 0.25 V. The other supporting electrolytes did not offer any advantages for analytical purposes. In 1*M* hydrochloric acid the addition of PEG makes little or no difference. In 1*M* potassium chloride or 0.5*M* sodium sulphate in the presence of 0.1% PEG (m.w. 4000) the waves are shifted towards more negative potentials, so no waves are observed between −0.7 and −1.2 V (*vs.* SCE). The new waves are not advantageous, however. A similar situation arises with an ammoniacal supporting electrolyte. The wave-shifts caused by adding PEG to the 1*M* sodium hydroxide electrolyte are also not applicable but analytical use might be made of the damping of the indium(III) and nickel(II) waves in acetate buffer.

Concentration of PEG

A thorough study of the importance of the molecular weight and concentration of the PEG was confined to the cadmium wave as it seemed to be typical of the group considered. It can be seen that increasing the PEG concentration from 0.001% to 0.01% results in a very substantial change in the diffusion current (Fig. 3) and that further increasing the concentration causes the current to approach zero asymptotically. It was therefore assumed that a concentration of 0.1% would be sufficient to cause the maximum possible effect. As this concentration does not markedly affect the viscosity of the solutions and therefore also not the wave-heights, it can be used for practical purposes.

Table 1. Effect of drop life-time on the induced waves of copper and lead in tartrate solution (pH 4.4) containing 0.1% PEG with molecular weight of 4000

Depolarizer	Drop life-time, *sec*	Height of induced wave, *μA*	Peak-height,* *μA*
Cu(II)	1.5	1.00	0.81
	3.0	1.08	1.00
	5.0	1.24	1.13
Pb(II)	1.5	1.12	
	3.0	1.33	
	5.0	1.50	

* Applies only to Cu(II).

Table 2. Precision and accuracy of the determination of lead and thallium in the presence of a large amount of bismuth which is masked "electrochemically" by addition of 0.1% of PEG (m.w. 4000)

		Added				Found			
Series	No. of tests	Bi mM	Pb *μM*	Tl *μM*	Ratio Bi:Pb:Tl	Pb *μM*	Tl *μM*	*S** *μM*	S_r†,%
I	10	50	100	—	500:1:0	96	—	2.5	2.6
II	9	50	200	—	500:2:0	202	—	3.9	1.9
III	8	50	—	100	500:0:1	—	97	1.5	1.6
IV	10	50	—	200	500:0:2	—	198	3.4	1.7
V	9	50	100	100	500:1:1	103	99	Pb 6.5	6.0
								Tl 2.6	2.5
VI	9	50	200	200	500:2:2	200	199	Pb 7.5	3.8
								Tl 6.4	3.2

* Standard deviation.
† Relative standard deviation.

Molecular weight of PEG

The effect of the molecular weight of the PEG on the heights of the waves studied is shown in Fig. 4. In general, low molecular-weight samples (200–400) had comparatively little effect, while a sample of molecular weight 2000 in many cases completely suppressed the waves, except for lead, thallium, and to some extent copper.

However, the change in the height of the primary wave should be considered not on its own, but in relation to the height of the wave, and to the apparent width of the "induced" wave, as indicated in Fig. 5. The small reduction in the thallium wave (line 4, Fig. 4) is caused by the shift in the wave illustrated in Fig. 5. With lead the effect is much more marked—the primary wave is completely suppressed by PEGs with molecular weights over 1000, but if the height of the "induced" wave, which is very close to the primary wave, is measured, the wave-height is hardly affected by high molecular-weight PEGs. On the other hand, the potential range occupied by the waves increases with increasing PEG molecular weight, and also shifts to more negative potentials. This results in a limited separation of the lead wave from the thallium wave, which occurs at the same potential in the tartrate buffer in the absence of PEG and does not shift to more negative potentials as the lead wave does.

The primary cadmium wave is almost completely suppressed by PEGs of all molecular weights while the "induced" wave appears at more negative potentials and tends to merge with the electrolyte breakdown current at high molecular weights. For a PEG of molecular weight 4000 the cadmium wave coincides with the lead wave.

Even low molecular-weight PEGs depress the copper wave, but do not suppress the polarographic maximum—this is only done by higher molecular weight samples. The result is the rather odd shape of the curve for copper in Fig. 4, where the solid line represents the height of the wave plus the maximum, the dashed line the substantially depressed wave, and the dotted line the "induced" wave. Figure 6 shows the polarograms obtained with PEGs of molecular weights 300 and 4000.

The bismuth wave is completely suppressed by PEGs of molecular weight above 2000, and the waves of antimony and of indium by all the samples of PEGs. Of the various combinations which could be analysed by making use of the masking by PEGs, that of lead in the presence of a large amount of bismuth was selected as being typical and of most interest, and also as being quite impossible by polarography without the addition of PEG. The results shown in Table 2 are satisfactory, and show further that both lead and thallium can be determined together, though with poorer precision. The 500-fold amount of bismuth does not represent the limiting case: if $10^{-5}M$ is taken as the lower limit of determination of lead by d.c. polarography and $5 \times 10^{-2}M$ as the solubility of bismuth in the tartrate electrolyte, it would seem that a 5000-fold Bi:Pb ratio could just be tolerated. It should be mentioned that the solubility of bismuth in this electrolyte is higher than in most others.

Drop life-time

Measurements made on solutions of lead and copper (Table 1) show that the wave-heights do depend on the drop life-time, and the heights of the "induced" waves more so than those of the primary waves. To minimize errors from this source the drop life-time must be kept constant, and in addition, the solutions must be kept at constant temperature, because the adsorption of the PEG varies as the temperature changes.

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USE OF DIETHAZINE HYDROCHLORIDE FOR THE EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF URANIUM AND AS A REDOX INDICATOR

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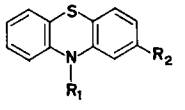
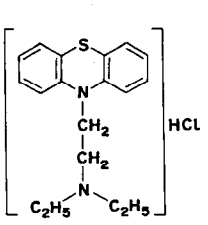
Summary—Optimum conditions have been established for the formation and extraction of the complex formed from diethazine, thiocyanate and uranium(VI). An extractive spectrophotometric method for the determination of uranium(VI) is described. Experimental conditions have been also established for the direct titrimetric determination of uranium(IV) with potassium dichromate, using diethazine hydrochloride as redox indicator. Interferences have been considered.

As pointed out in our earlier work,[1–3] phenothiazine derivatives exhibit a number of interesting analytical properties due to their characteristic structure (the presence of chemically active sulphur and nitrogen atoms and of substituents in positions 2 and 10).

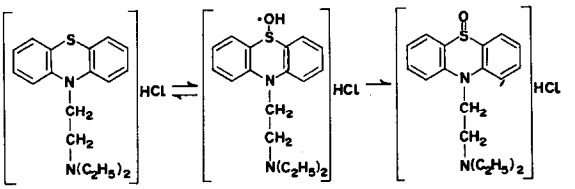


Of these properties the most important are the liability to oxidation by means of many oxidizing agents [for example $K_2Cr_2O_7$, NH_4VO_3, $Ce(SO_4)_2$, $KBrO_3$, KIO_3, KIO_4, $NaNO_2$, H_2O_2], with the formation of coloured compounds, and the ability to form easily extractable ion-association complexes with anionic complexes of a number of metals. The properties mentioned are the basis of the application of phenothiazine derivatives as reagents for spectrophotometric and gravimetric determination of some metals[4–8] and as redox indicators.[9–13]

In the present work, the use of diethazine hydrochloride for the extractive spectrophotometric and dichromate-titration determination of uranium has been examined. We have found that diethazine hydrochloride [10-(3-diethylaminopropyl)phenothiazine hydrochloride] reacts in acid medium with uranium(VI) thiocyanate complexes, forming a yellow compound $(DT \cdot H)_2[UO_2(SCN)_4]$, where DT denotes diethazine. This compound is fairly soluble in chloroform but sparingly soluble in water. This property has been exploited for the development of an extractive spectrophotometric method for the determination of uranium(VI).



We have also found that diethazine hydrochloride forms a coloured oxidation product with $K_2Cr_2O_7$ and a number of oxidants[14] in acid medium. The oxidation proceeds in two stages. First a stable coloured radical form is formed reversibly, then the free radical is irreversibly oxidized by strong oxidants to the colourless sulphoxide.[12] The mechanism can be represented as follows:



This property enables diethazine hydrochloride to be used as indicator in various redox titrations,[9] its transition potential being 0.76 V in 0.5*M* sulphuric acid at 20°.[15,16]

EXPERIMENTAL

Reagents

Uranium(VI) solution, 0.01*M*. Prepared from uranyl acetate. Standardized gravimetrically with 8-hydroxyquinoline.[17]

Uranium(IV), 0.05*M solution in* 0.5*M sulphuric acid*. Prepared from pure uranyl acetate solution in 1.0*M* sulphuric acid, reduced in a Jones reductor then aerated for about 10 min to oxidize any uranium(III) to uranium(IV). Standardized with ceric sulphate.[18]

Potassium dichromate solution, 0.01*N*.

Diethazine hydrochloride (DT.HCl), 0.05*M and* 1% *solutions in* 0.5*M hydrochloric acid*. Standardized gravimetrically with silicotungstic acid.[19]

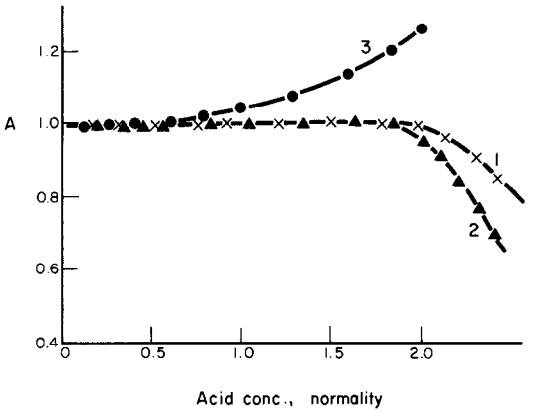


Fig. 1. The dependence of absorbance on the acid concentrations. $CUO_2^{2+} = 3.2 \times 10^{-4}M$; $C_{DT} = 0.01M$; $C_{NH_4SCN} = 0.1M$; $\lambda = 400$ nm. *1*—HCl; *2*—H_2SO_4; *3*—HNO_3.

Ammonium thiocyanate, 5M and 1M solutions.
Hydrochloric, sulphuric and nitric acids, 5N.
Analytical-grade reagents and doubly distilled water were used throughout.

Extraction of uranium

Procedure of investigation. The course of the formation and extraction of the yellow thiocyanate–uranyl–DT compound depends on the acidity of the solution, the thiocyanate and DT.HCl concentrations and on the nature of the solvent used. These factors were investigated as follows. Suitable amounts of uranyl acetate solution, 1*N* hydrochloric or sulphuric acid, 1*M* ammonium thiocyanate and diethazine hydrochloride solution were mixed (in that order) in a 50-ml separating funnel, and diluted to 10 ml. The mixture was shaken vigorously until a distinct precipitate appeared. Then 10 ml of organic solvent (chloroform, ethyl acetate, isoamyl alcohol, diethyl ether, carbon tetrachloride or benzene) were added in portions. The extracts were combined in a 10-ml volumetric flask. The absorbance was measured at 400 nm in 10-mm cells, against the organic solvent as reference. Chloroform was found to be the most suitable extractant, giving quantitative extraction without extracting the uranium thiocyanate complex.

Optimum extraction conditions. The absorbance of the chloroform extract is constant when the aqueous phase acidity is varied from 0.05 to 1.8*N* hydrochloric or sulphuric acid (Fig. 1). Nitric acid cannot be used because at concentrations above 0.5*M* it oxidizes diethazine hydrochloride to a red product. The absorbance is maximal and constant when the thiocyanate concentration is above 0.15*M* and there is at least a 12-fold excess of DT with respect to UO_2^{2+}. The extraction coefficient of uranium is 99.9 from a medium 0.3*M* in hydrochloric acid, 0.3*M* in thiocyanate and 0.01*M* in diethazine hydrochloride.

The volume ratio of aqueous to organic phase does not affect the extraction within the range from 1:1 to 1:8.

The absorption spectrum has a maximum at 315 nm (Fig. 2), with molar absorptivity 2.3×10^4 l. mole^{-1}.cm^{-1}. Because the reagents absorbance at 315 nm, analytical measurements were made at 400 nm (molar absorptivity 6.6×10^3 l. mole^{-1}.cm^{-1}).

Composition of the complex. The method of continuous variations showed the mole ratio UO_2^{2+}:DT·H to be 1:2. To establish the ratio UO_2^{2+}:SCN^- the method of equilibrium shift was used, and log $A_x/(A_o - A_x)$ was found to be a linear function of log [SCN^-] with a slope of 4, indicating UO_2^{2+}:SCN^- = 1:4. Thus the compound extracted is $(DT \cdot H)_2[UO_2(SCN)_4]$ where DT·H represents protonated diethazine. This formula was confirmed by chemical analysis of the precipitate, dried at room temperature to constant weight. The diethazine was determined spectrophotometrically,[20] uranium titrimetrically with ceric sulphate, and thiocyanate argentometrically. Found: DT·H 54.0%; U 21.4%, SCN^- 20.9%; calculated for $(DT \cdot H)_2([UO_2(SCN)_4]$: DT·H 54.2%; U 21.6%, SCN^- 21.1%.

Solubility in water and organic solvents. The solubility of the complex in water was determined spectrophotometrically,[20] and found to be $1.4 \times 10^{-7}M$. The solubility in organic solvents, determined as described earlier,[5] is relatively high, *e.g.*, acetone, 0.98*M*; chloroform, 0.12*M*; ethanol, 0.038*M*; benzene, 0.0076*M*; diethyl ether, $1.3 \times 10^{-4}M$; carbon tetrachloride, $1.1 \times 10^{-4}M$.

Extractive determination of uranium

The extraction of the compound into chloroform can be used for the spectrophotometric determination of uranium(VI).

Procedure. In a 50-ml separating funnel place up to 5 ml of $10^{-3}M$ uranium solution, 1 ml of 3*M* hydrochloric acid, 2 ml of 1*M* ammonium thiocyanate, 2 ml of 0.05*M* diethazine hydrochloride and dilute to 10 ml with water, shake the funnel vigorously until a compact precipitate forms, then extract with chloroform. Transfer the extracts to a 10-ml standard flask, and dilute to the mark with chloroform. Measure the absorbance at 400 nm against chloroform as reference.

Beer's law is obeyed over the uranium concentration range 10–100 μg/ml in the chloroform extract. The error does not exceed ±2.0%. The time needed for a determination is about 20 min.

Na^+, K^+, Ca^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+}, Mn^{2+}, Mg^{2+}, Ni^{2+}, Al^{3+}, Cl^-, CH_3COO^-, SO_4^{2-}, tartrate and citrate do not interfere with the determination. Oxalate, tartrate and cations which form coloured thiocyanates (Co^{2+}, Cu^{2+}, Fe^{3+}, Bi^{3+}, Ti^{4+}, Mo^{5+}, W^{5+}) interfere.

Diethazine hydrochloride as redox indicator in titration of uranium(IV) with dichromate

We have found that diethazine hydrochloride is easily oxidized in acid medium by potassium dichromate with the formation of a pink-red oxidation product. The optimal conditions for formation of this product have been established.

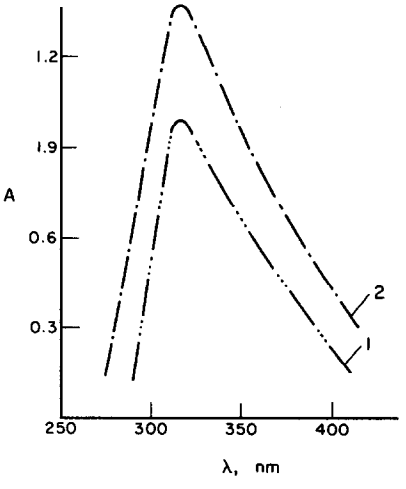


Fig. 2. Absorption spectra of chloroform solutions of thiocyanate–uranyl–DT complex. *1*—$C_{UO_2^{2+}} = 1.5 \times 10^{-4}M$; *2*—$C_{UO_2^{2+}} = 2.2 \times 10^{-4}M$; UO_2^{2+}:DT = 1:2; $C_{NH_4SCN} = 0.3M$; $C_{HCl} = 0.3M$.

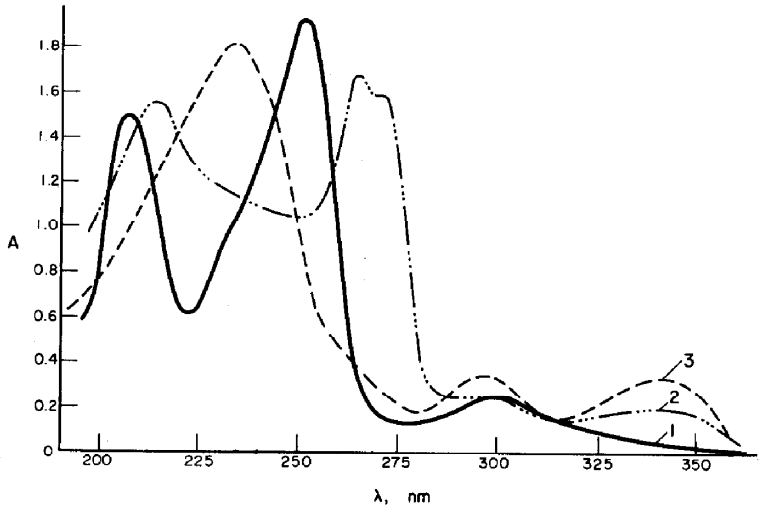


Fig. 3. Ultraviolet-region absorption spectra of aqueous solutions of diethiazine hydrochloride: *1*—reduced form; *2*—free radical; *3*—sulphoxide. $C_{DT} = 6 \times 10^{-5}M$; $C_{HCl} = 0.5M$; $K_2Cr_2O_7$:DT = 1:6 (curve 2), 2:3 (curve 3).

The absorption spectra of the oxidation product obtained in various concentrations of sulphuric, hydrochloric and phosphoric acid were recorded and show that the absorbance is maximal for 1.0–2.2*N* hydrochloric or phosphoric acid medium, and for the same range of sulphuric acid concentration but only after 10–15 min. Nitric acid cannot be used because at concentrations above 0.5*M* it also oxidizes diethazine hydrochloride.

The absorbance in 1.5*M* hydrochloric acid medium is maximal when the molar ratio $K_2Cr_2O_7$:DT·H is 1:6.

Absorption spectra of the reduced and oxidized forms. As already mentioned, diethazine hydrochloride is oxidized reversibly by dichromate to a pink-red free radical, which is further oxidized irreversibly to a colourless sulphoxide. In Fig. 3 the spectra (in the ultraviolet range) of the reduced and oxidized forms are shown. The spectrum of the free radical shows a bathochromic shift and the sulphoxide a hyperchromic shift with respect to the reduced form in the range 225–285 nm. Figure 4 gives the spectrum of the oxidized form in the visible range. Table 1 summarizes the results.

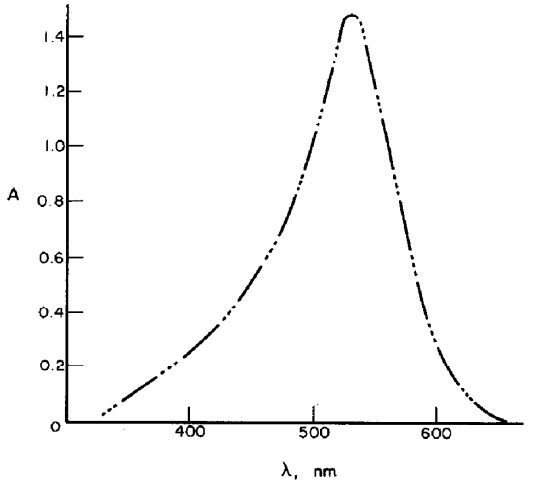


Fig. 4. Visible-region absorption spectrum of aqueous solution of free radical of diethazine hydrochloride. $C_{DH} = 2.5 \times 10^{-4}M$; $K_2Cr_2O_7$:DT = 1:3; $C_{HCl} = 2M$.

Titration of uranium(IV). Diphenylamine, diphenylaminesulphonic acid,[21] 5,6-dimethylphenanthroline,[22] β-colubrine, brucine,[23] *N*-phenylanthranilic acid, diphenylbenzidine[24] and triphenylmethane dyes[25] have been used in the titration of uranium(IV) with potassium dichromate. We find that diethazine hydrochloride can be employed satisfactorily as a reversible indicator in uranium(IV)–dichromate titrations at room temperature in hydrochloric or sulphuric acid medium, and that it is superior to diphenylamine and *N*-phenylanthranilic acid. Table 2 shows some results. Oxidants such as Ce(IV), V(V), HNO_3, and reductants such as Fe(II), Sn(II), Mo(V), will interfere.

Table 1. Values of λ_{max} and ϵ of non-oxidized forms of DT and the DT oxidation product

Form of DT	λ_{max}, *nm*	ϵ, *l. mole.*$^{-1}$ *cm*$^{-1}$
non-oxidized	207	2.5×10^4
	252	3.2×10^4
	301	4.1×10^3
free radical	209	2.5×10^4
	265	2.8×10^4
	272	2.6×10^4
	513	5.9×10^3
sulphoxide	235	3.0×10^4
	295	5.2×10^3
	342	5.0×10^3

Table 2. Titration of uranium(IV) with 0.01*N* $K_2Cr_2O_7$ (diethazine hydrochloride as indicator)

Uranium(IV) *mg*	$K_2Cr_2O_7$ consumed, *ml* Theoretical	Experimental ($\bar{X} \pm S$)
4.34	3.65	3.66 ± 0.01
7.06	5.93	5.95 ± 0.02
8.83	7.42	7.41 ± 0.01
11.95	10.04	10.00 ± 0.02
16.37	13.76	13.83 ± 0.04
20.23	17.00	16.95 ± 0.02
24.25	20.38	20.44 ± 0.02

S = Standard deviation

Procedure. Adjust the acidity to 1.0–3.0*N* in hydrochloric or sulphuric acid and add a small amount of syrupy phosphoric acid (2–4 ml) to catalyse the reduction of the oxidized form of diethazine by uranium(IV). Add 1 ml of 0.1% DT·HCl solution for a titration volume of 60–100 ml and titrate. The colour changes from green to dark red at the end-point. Apply a correction for the indicator blank (<0.05 ml of 0.01*N* potassium dichromate).

In the titration of uranium(IV) with potassium dichromate Fe^{2+}, Sn^{2+}, Mo^{5+}, Ce^{4+}, VO_3^- and HNO_3 interfere.

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THE SPECIFICITY CHARACTERISTIC OF ANALYTICAL METHODS—I

NON-SPECIFICITY COEFFICIENTS

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Summary—Two types of non-specificity coefficients are defined. These coefficients quantitatively characterize the change caused in an analytical result by the presence of interferents. The first of these coefficients describes a parallel shift of a calibration curve and the second a shift in the slope. The properties of these coefficients and of their practical application as characteristics of a method are discussed. The approach described may be used to characterize the specificity of an analytical method when the calibration curve is linear and the presence of an interferent causes a parallel shift of the curve or changes its slope but not its shape.

NOTATION USED

B_{rel} —relative error of an analytical method
c_d —concentration of the component to be determined (analyte)
c_b —concentration of the interferent
k_d —slope of calibration curve
k_p —proportionality constant relating an interferent concentration to the component R'_b of the interfering signal
k_a —proportionality constant relating an interferent concentration to the component R''_b of the interfering signal
K_P —non-specificity coefficient that characterizes the influence of an interferent on the parallel shift of the calibration curve
K_A —non-specificity coefficient that characterizes the influence of an interferent on the slope of the calibration curve
m —number of components to be determined (analytes)
n —number of interfering components
R —total analytical signal emitted by a sample
R_d —analytical signal emitted by the analyte
R_b —total interfering signal
R'_b —component of an interfering signal responsible for parallel shift of the calibration curve
R''_b —component of an analytical signal responsible for a change of the slope of the calibration curve
S_P —specificity of an analytical method
S_L —selectivity of an analytical method

INTRODUCTION

A great many new or modified analytical methods are published, but when an analyst wants to choose the optimal method for a particular problem, he runs into difficulties because the characteristics of these methods given by the authors are very often not comparable. Hence in the last few years attempts have been made to systematize and make quantitative the description of the characteristics of analytical methods. The most important of these characteristics are: accuracy, precision, sensitivity, upper and lower limits of detection, specificity and selectivity. They have all been discussed critically by Wilson.[1–4] Such concepts as accuracy, precision, sensitivity and limit of detection are already defined more or less precisely and in common use, but the terms specificity and selectivity are ambiguous and very often used interchangeably.

Belcher[5] and Betteridge[6] have suggested characterizing the selectivity qualitatively by means of the "selectivity index". The advantages and disadvantages of this proposition were discussed in later papers,[7,8] but only in connection with analytical reagents and reactions. More recently Anastassiadis and Common,[9] Świętosławska[10] and Kaiser[11] have discussed the concepts of selectivity and specificity as characteristics of analytical methods and proposed mathematically-formulated definitions permitting quantitative description of these characteristics by means of numerical values. Unfortunately these authors have suggested three different definitions of specificity. The Anastassiadis and Common definition characterizes the specificity of a single-component method with respect to a single interfering substance. Świętosławska defines the specificity as the reciprocal of the error caused by the bias of all interferents that are present in the sample. The most general is Kaiser's approach. He defines the selectivity and specificity for any multicomponent analytical procedure and the "partial specificity" for characterizing single-component determinations.

The numerical values of the Świętosławska and Kaiser characteristics are valid only for fixed concentrations of all components of a sample. For practical purposes they can only be used if the method fulfils some simplifying assumptions. Moreover, they describe only the combined effect of all the interferents, whereas for the practising analyst the information of primary interest is a numerical description of the

effect of individual interferents. The last problem was discussed in detail by Wilson.[4]

The present paper does not give yet another definition of specificity. Instead it suggests the use of two coefficients that describe quantitatively the specificity of an analytical procedure in relation to the individual interferents. These coefficients can characterize both the specificity and selectivity of a method (if these terms are distinguished) without finally defining these concepts, just as the standard deviation characterizes precision without defining the concept of precision.

The terms "analytical method", "characteristic of an analytical method" and "interferent" are still ambiguous and it is necessary to state precisely their meaning to avoid misunderstandings. In this paper all these terms are used in the same sense as they are defined by Wilson.[1,4] They can be formulated shortly as follows:

Analytical method—a complete analytical procedure.
Characteristic of an analytical method—an experimentally-determined value for a parameter of fundamental importance in assessing the suitability of the method for any given purpose.
Interferent—a substance that causes systematic error in the analytical results.

DEFINITION OF NON-SPECIFICITY COEFFICIENTS

All analytical methods are based on the relation between an analytical signal and the concentration of the component to be determined (analyte). The concept of the analytical signal is universal. It may be the intensity of a radiation, absorbance, values of various electrochemical or electrical parameters, as well as the volume of a titrant or weight of a precipitate. If a method is not totally specific, then the measured signal R is a function of the concentration not only of the analyte c_d but also of other components of the sample c_{b_i} that interfere in the determination. This function:

$$R = F(c_d, c_{b_1}, \ldots, c_{b_n}) \tag{1}$$

is the calibration function of the method. Usually the value of this function is unknown and the participation of an individual component in the emission of the measured signal cannot be calculated simply on the basis of its concentration. After the transformation of this function into a Taylor's series it may be approximated locally (over a small range of concentrations) as a surface of the first order in an n-dimensional space. For a larger concentration range, comparable with that found in real analytical samples, approximation as a surface of the second order gives better results. The function then has the form:

$$R = k_0 + k_d c_d + k_{p_1} c_{b_1} + \ldots + k_{p_n} c_{b_n} + k_{a_d} c_d^2 + k_{a_1} c_d c_{b_1} + \ldots + k_{a_n} c_d c_{b_n} + \ldots + k_{a_{nn}} c_{b_n}^2 \tag{2}$$

where k_0 *etc.* are the proportionality coefficients and there are $(\frac{1}{2}n^2 + \frac{5}{2}n + 3)$ of them. The form of this equation is too complicated for use in analytical practice but it can be simplified if the following assumptions are made.

1. The analytical signal is equal to zero when the concentration of analyte and the concentrations of all interferents are equal to zero. Then $k_0 = 0$.
2. The analytical signal is a linear function of the concentration of analyte and of every individual interferent.
3. The effects of individual interferents are independent of the ratios of their concentrations.

The first assumption is fulfilled by all analytical methods, because the signal emitted when all the components of the sample are at zero concentration may easily be eliminated by means of a blank. The second assumption is also fulfilled by most methods, but not by others, *e.g.*, atomic spectroscopy methods. The third assumption is the most dubious, but experimental examination indicates that it may be accepted for various types of methods,[12] but must be verified in every case, and again atomic spectroscopy methods do not satisfy it.

With these assumptions taken into account, equation (2) may be transformed into

$$R = k_d c_d + \sum_{i=1}^{n} k_{p_i} c_{b_i} + \sum_{i=1}^{n} k_{a_i} c_d c_{b_i} \tag{3}$$

or for one interferent:

$$R = k_d c_d + k_p c_b + k_a c_d c_b \tag{4}$$

The analytical sense of equation (4) is presented graphically in Fig. 1. The total analytical signal R consists of the signal R_d emitted by the analyte, and the interfering signal R_b. The analyte signal is a linear function of the analyte concentration

$$R_d = k_d c_d \tag{5}$$

The interfering signal R_b consists of two components R_b' and R_b''. The component R_b' is responsible for the parallel shift of the calibration curve and depends on

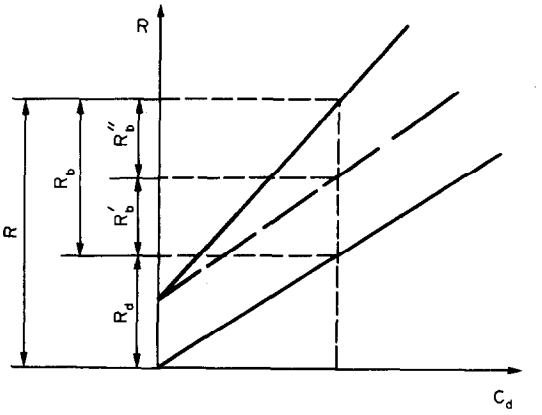

Fig. 1. Graphical representation of the characteristics of the interfering signal components.

the interferent concentration only:

$$R'_b = k_p c_b \quad (6)$$

The component R''_b is responsible for the change in slope of the calibration curve and depends on the concentration of both analyte and interferent:

$$R''_b = k_a c_d c_b \quad (7)$$

It is necessary to note that the term "interfering signal" means the difference between the value of the total signal emitted by the sample and the value of the signal emitted by the analyte. Defined in this way, the interfering signal contains not only the real signal R'_b emitted by the interferent (or interferents), but also the influence (R''_b) of the interferent on the analyte signal. The value of the second component is equal to zero when the concentration of the analyte is equal to zero. It is evident that the interfering signal can be either positive or negative.

The relative error of the analytical result when an interferent is present is given by

$$B_{rel} = \frac{R - R_d}{R_d} = \frac{R'_b + R''_b}{R_d}. \quad (8)$$

Taking into account (5), (6) and (7) we get

$$B_{rel} = \frac{k_p c_b + k_a c_d c_b}{k_d c_d} \quad (9)$$

This equation contains three constants: k_p, k_a and k_d. Putting

$$\frac{k_p}{k_d} = K_P \quad (10)$$

and

$$\frac{k_a}{k_d} = K_A \quad (11)$$

gives

$$B_{rel} = K_P \frac{c_b}{c_d} + K_A c_b \quad (12)$$

When n interferents are present in the sample and all fulfil the simplifying assumption that their effect is independent of the ratios of their concentrations, then

$$B_{rel} = \frac{1}{c_d} \sum_{i=1}^{n} K_{P_i} c_{b_i} + \sum_{i=1}^{n} K_{A_i} c_{b_i} \quad (13)$$

The constants K_P and K_A are the "non-specificity coefficients". They are coupled in pairs and every pair characterizes the influence of one interferent on the analytical results obtained by means of a particular analytical method. The analytical significance of these coefficients may be described as follows.

K_P is the relation of the "parallel shift" component of the interfering signal emitted by unit concentration of interferent, to the signal emitted by unit concentration of analyte. It is dimensionless.

K_A is the relation of the "slope-changing" component of the interfering signal, emitted at unit concentration ratio of interferent to analyte, to the signal emitted by unit concentration of analyte. The dimension of this coefficient is concentration^{-1}.

The reciprocals of these coefficients may be called "specificity coefficients", but the non-specificity coefficients are more convenient from the practical point of view.

PROPERTIES OF NON-SPECIFICITY COEFFICIENTS

The numerical values of the non-specificity coefficients must be found experimentally for every interferent and they are valid only for the analytical method used and the range of concentration for which they were found.

For a completely specific method the measured signal is dependent on only the concentration of analyte and completely independent of the type and concentrations of other components of the sample. All non-specificity components are then equal to zero. If the method is not totally specific, as is usual in analytical practice, at least one of the non-specificity coefficients for at least one interferent is different from zero, with an absolute value which is the higher, the less specific the method.

The practical values of the coefficient K_P are between 0 and 1. On the basis of equations (5), (6) and (10) we can write

$$R'_b = K_P \frac{c_b}{c_d} R_d \quad (14)$$

and if $K_P = 1$ and $c_b = c_d$, then $R'_b = R_d$. The interfering component R'_b is equal to the signal emitted by the analyte at equal concentrations of analyte and interferent, when the coefficient K_P is equal to unity. That means the method is totally non-specific with respect to this interferent.

The determination of a reasonable upper limit for the value of K_A is much more complicated. Because of the dimension of this coefficient its numerical value depends on the concentration units used. Moreover, the absolute value of R''_b depends not only on K_A and on the relation of c_b to c_d but also on the absolute concentration of analyte. On the basis of (5), (7) and (11) we can write:

$$R''_b = K_A c_d \frac{c_b}{c_d} R_d \quad (15)$$

and assuming $c_b = c_d$,

$$\frac{R''_b}{R_d} = K_A c_d \quad (16)$$

The interfering component R''_b is equal to the signal emitted by the analyte at equal concentrations of analyte and interferent and the method must be regarded as totally non-specific with respect to this interferent when $K_A = 1/c_d$. Usually in analytical practice the value of K_A is about 10^{-3} (concentration unit)$^{-1}$ or less.

APPLICATION OF NON-SPECIFICITY COEFFICIENTS

In all thorough descriptions of analytical methods the authors give the list of elements or compounds that may be present in the sample and can interfere. Sometimes they also give the concentrations at which a significant interfering effect was found. In general the conclusions concerning the amount of foreign species which can be tolerated without causing interference are based on subjective criteria. In the last few years, however, some ideas have been proposed for objective interpretation of the existence of an interference effect. Maurice and Buijs[13] have proposed a general test for estimation of total interferences in an analytical procedure and Wilson[4] has given a design for estimation of the interference effect of individual species. Both methods warn only against the interferences tested and give only qualitative information. In contrast, presentation of a list of interferents together with their non-specificity coefficients could allow quantitative prediction of the interferent effect as a function of the concentrations of the analyte and interferents.

When using the non-specificity coefficients as a characteristic of an analytical method it is necessary to remember that this method must fulfil some assumptions. In general, these coefficients may be used when a shift (parallel or angular) of the calibration curve is caused, but not a change in shape. The magnitude of this shift must be proportional to the interferent concentration, otherwise the coefficients K_P and K_A are not constant over the whole concentration range. In that case they can be replaced by the simple function $K_{(P,A)} = f(c_b)$, which usually allows the exact characteristic to be obtained. If the dependence of the interferent effect on the interferent concentration is considerably non-linear, the non-specificity coefficients cannot be used. This is often the case with atomic spectroscopy methods.

The proposed non-specificity coefficients describe the relations between the signals emitted by the analyte and interferents, and thus characterize the effect of interfering species and thereby the specificity or selectivity of the analytical method, whatever the final definitions of these concepts. Therefore the coefficients K_P and K_A not only directly characterize the specificity but may also be used for expressing the specificity or selectivity according to the definitions proposed by various authors. All the definitions proposed to date are based on more far-reaching simplifying assumptions than those used for the non-specificity coefficients, and only the coefficient K_P is needed to describe them. These definitions[9–11] and their transformation by means of the non-specificity coefficients are presented below. For simplification the original definitions are given in the notation used in this work.

Specificity according to Anastassiadis

$$S_P = \frac{\frac{R_d}{c_d}}{\frac{R_d}{c_d} + \frac{R_b}{c_b}} = \frac{1}{1 + K_P} \tag{17}$$

Specificity according to Świętosławska:[10]

$$S_P = \frac{k_d c_d}{\sum_{i=1}^{n} |k_{b_i} c_{b_i}|} = \frac{c_d}{\sum_{i=1}^{n} |K_{P_i}| c_{b_i}} \tag{18}$$

Partial specificity according to Kaiser:[11]

$$S_p = \frac{k_d}{\sum_{i=1}^{n} |k_{b_i}|} - 1 = \frac{1}{\sum_{i=1}^{n} |K_{P_i}|} - 1 \tag{19}$$

Selectivity according to Kaiser:[11]

$$S_L = \operatorname*{Min}_{j=1\ldots m} \frac{k_d}{\sum_{i=1}^{n} |k_{b_i}|} - 1 = \operatorname*{Min}_{j=1\ldots m} \frac{1}{\sum_{i=1}^{n} |K_{P_i}|} - 1 \tag{20}$$

Equation (19) describing what Kaiser calls "partial specificity" is comparable with the specificities defined by the other authors [equations (17) and (18)]. Kaiser's "total specificity" is omitted here, because it is not comparable with the other equations. However, this total specificity may also be expressed by means of the coefficient K_P.

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THE SPECIFICITY CHARACTERISTIC OF ANALYTICAL METHODS—II

ESTIMATION AND EXPERIMENTAL VERIFICATION OF THE NON-SPECIFICITY COEFFICIENTS

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Summary—A procedure for estimation of non-specificity coefficients by use of small amounts of standard samples is described. This procedure enables also the simultaneous verification if the specificity of a method with respect to the investigated interferent may be characterized by means of these coefficients. Four various analytical methods were tested and a good agreement of experimentally found values of interferent effects with the values calculated by means of non-specificity coefficients have been stated.

NOTATION USED

a —intercept of a straight line graph on the ordinate
b —slope of the straight line
c_b —concentration of interferent
c_d —concentration of analyte
c_r —relative concentration of interferent, relation of c_b to c_d
K_P and K_A —non-specificity coefficients
R —total analytical signal
R_d —analytical signal of analyte
R'_b —"parallel shift" component of interfering signal
s_x —standard deviation for results indicated by subscript
S_L mean "lack of fit" square
S_W mean "within group" square
q —number of standards in series
t —number of parallel determinations of a standard sample

INTRODUCTION

In Part I,[1] two kinds of non-specificity coefficient were defined and the possibility of their application to the characterization of analytical methods was discussed. Here we present a procedure for estimation of these coefficients and its experimental verification for such methods as spectrophotometry, polarography and coulometry.

All the interferents investigated affect the analytical results very strongly and would usually be separated from the analyte before measurement of the analytical signal; they were specially chosen because such large effects are particularly difficult to characterize quantitatively, and thus provide a good test of the proposed ideas. In addition, the results obtained are easily presented graphically.

ESTIMATION OF NON-SPECIFICITY COEFFICIENTS

The non-specificity coefficients must be calculated from the experimental data obtained by analysis of standard samples. The standards must be prepared separately for every interferent tested. The most precise way to estimate the coefficients is to prepare a set of calibration curves with varied interferent concentration, followed by calculation of the coefficient values for every curve, which shows whether the values are constant over the concentration range of interest. However, such a method is uneconomic, because if every curve is based on q standards and the method is tested against q concentrations of interferent, it is necessary to prepare q^2 standard samples plus the standards used for preparation of the normal calibration curve in absence of interferent. Because the value of q cannot be lower than 3, testing of the method for even one interferent requires at least 9 standards, and to improve the confidence limits of the results it is recommended to make $q = 5$ or 6. Such a procedure is very time-consuming even with solution samples, for which the preparation of standards is relatively simple, and it may not be used in analytical practice.

Appropriate choice of the interferent concentrations in the standard samples allows simplification of the testing procedure, however. According to the equations (4) and (5) Part I,[1] the analytical signal of the analyte is

$$R_d = k_d c_d \tag{1}$$

and the total analytical signal in the presence of one interferent is

$$R = k_d c_d + k_p c_b + k_a c_d c_b. \tag{2}$$

The ratio of R to R_d is

$$R_r = 1 + \frac{k_p}{k_d} c_r + \frac{k_a}{k_d} c_b \quad (3)$$

where c_r is the relative concentration of interferent ($c_r = c_b/c_d$).

Taking into account the definitions of K_P and K_A we obtain

$$R_r = 1 + K_P c_r + K_A c_b. \quad (4)$$

When a series of standards is prepared so that c_r is constant, then R_r is a function of c_b only. This function $R_r(c_b)$, described by equation (4), enables us to calculate the K-values and to test their constancy by means of q standards. When $R_r(c_b)$ is linear, then K_P and K_A are constant and they are described by the parameters of its regression line:

$$K_P = \frac{a - 1}{c_r} \quad (5)$$

$$K_A = b \quad (6)$$

The standard deviations and confidence limits of the K-coefficients may be calculated from the standard deviations of a and b:

$$s_{K_P} = s_a/c_r \quad \text{and} \quad s_{K_A} = s_b. \quad (7)$$

In the calculation of the regression parameters and verification of the linearity it is important that the variances of all measurements should be homogeneous. In chemical analysis the variance of the measurements usually increases with increasing concentration and this requirement is not fulfilled. It is therefore necessary to use weighting factors in all the statistical calculations and hence the dispersion of the measurements at various concentrations ought to be estimated. The variances of the R_r-values can be calculated from the variances of corresponding values of R_d and R, taking into account the law of propagation of errors. The variations in parallel determinations of R_d and R are not correlated, so the following simplified formula may be used:

$$s^2_{R_r} = \frac{s^2_R}{R_d^2} + \frac{R^2}{R_d^4} s^2_{R_d} \quad (8)$$

The general schedule of measurements shown in Table 1 is sufficient for complete calibration of an analytical method. The variances of R_d and R as well as of R'_b must be estimated experimentally on the basis of t parallel determinations on standard samples. The minimum value of t may be taken as 3, but if it does not lead to too much extra work this number ought to be higher, *e.g.*, 5 or 6. In practice, an interferent rarely affects the dispersion of results significantly and the magnitude of the variance is dependent only on the magnitude of the analytical signal. Because small errors in estimation of s^2_R or $s^2_{R'_b}$ values do not have a significant influence on the values of the calculated coefficients the variances of R and R'_b may be taken as equal to the variance of R_d obtained for a standard that emits a corresponding magnitude of signal. The variance of R need be determined experimentally only for the range of concentration where R significantly exceeds R_d, but such cases happen rather rarely in practical analysis.

When t parallel determinations are done, then the values given in Table 1 represent the mean values and their variances. When the variances for R or R'_b are taken as the same as for R_d, then the values of R and R'_b can be based on single determinations and the variances of single determinations must also then be used.

For all interferents for which $R_r(c_b)$ is linear, the values of the measurements tabulated in columns 6 and 7, 11 and 12 *etc.* are redundant and can be omitted. The calculations are carried out according to the following scheme.

Calculation scheme 1

1. Calculate the values of $R_{r_1} \ldots . R_{r_q}$ as the ratios of values of R (Table 1, column 8) to corresponding values of R_d (column 3).

2. Calculate the variances $s^2_{R_r}$ from the corresponding variances s^2_R and $s^2_{R_d}$.

3. Calculate the parameters a and b of regression line $R_r(c_b)$ by the least-squares method, using the weighting factors, and then calculate the variances s^2_a and s^2_b.

Table 1. Schematic table of measurements

	Analyte			Interferent A					Interferent B					
					$c_{r_A} =$						$c_{r_B} =$			
Standard No.	c_d	R_d ($c_b = 0$)	$s^2_{R_d}$	c_b ($c_b = c_{r_A} \cdot c_d$)	R'_b ($c_d = 0$)	$s^2_{R'_b}$	R (c_r = const.)	s^2_R	c_b	R'_b	$s^2_{R'_b}$	R	s^2_R	etc.
1	2	3	4	5	6	7	8	9	10	11	12	13	14	
1	c_{d_1}			$c_{r_A} \cdot c_{d_1}$					$c_{r_B} \cdot c_{d_1}$					
2	c_{d_2}			$c_{r_A} \cdot c_{d_2}$					$c_{r_B} \cdot c_{d_2}$					
.	.			.					.					
.	.			.					.					
.	.			.					.					
.	.			.					.					
q	c_{d_q}			$c_{r_A} \cdot c_{d_q}$					$c_{r_B} \cdot c_{d_q}$					

Note. The values of c_{d_1}, c_{d_2} ..... c_{d_q} and c_r are dependent only on the concentration ranges of interest. The data given in columns 6 and 7, 11 and 12 *etc.* are necessary only when $R_r = R_r(c_b)$ is not linear.

4. Using the weighting factors, calculate the "within-group" sum of squares of results [*i.e.*, $\Sigma(\bar{y}_i - y_i)^2$] and the "lack-of-fit" sum of squares, which is the difference between the residual sum of squares about the regression and the "within-group" sum of squares.

5. Calculate the mean "lack-of-fit" square (S_L) and mean "within-group" square (S_w) and apply the F-test to verify the hypothesis of linearity of $R_r(c_b)$:[2]

$$F = S_L/S_w.$$

6. If $F > F_{tab}$ the function $R_r(c_b)$ is linear. Calculate the values of the K_p and K_A coefficients and their standard deviations.

An example of calculation according to scheme 1 of K-values for spectrophotometric determination of uranium with respect to thorium as interferent is given in Appendix I.

When an analytical method does not fulfil all the simplifying assumptions made in deducing the K-coefficients, then the function $R_r(c_b)$ is not linear and at least one of the K-coefficients is not constant. If the interferent signal R_b is responsible for the deviation from the linearity and this effect is not large, the specificity of the method may be characterized by means of K-coefficients expressed as linear functions of c_b. In such a case the K_P-value must be calculated from the functions $R_d(c_d)$ and $R'_b(c_b)$, the second of which describes the component of the interfering signal that is responsible for the parallel shift of the calibration curve and is independent of the concentration of analyte (see Part I).[1] For this purpose it is necessary to prepare an additional series of standards (see columns 6, 11 *etc.* in Table 1) that contain the corresponding concentrations of interferent ($c_b = c_r c_d$) but no analyte. The total number of standards necessary for testing the method with respect to such an interferent is $2q$. The K-coefficients must then be calculated according to scheme 2.

Calculation scheme 2

Steps 1–5 are in scheme 1.

6. When $F < F_{tab}$ calculate the parameters of the regression lines for $R_d(c_d)$ and $R'_b(c_b)$, using the weighting factors, verify the linearity by means of the F-test and check whether $R_d(0) = 0$ and $R'_b(0) = 0$ by means of the t-test. $R_d(0)$ and $R'_b(0)$ may be accepted as equal to zero when the corresponding values of $|a|/s_a$ are less than t_{tab}.

Note. When $R_d(c_d)$ or $R'_b(c_b)$ is linear and does not pass through the origin then the analytical procedure is incorrect, *e.g.*, it is necessary to use a blank correction.

7*a*. When $R_d(c_d)$ and $R'_b(c_b)$ are linear and pass through the origin K_P must be constant. Calculate its value as the relation of the slope of $R'_b(c_b)$ to that of $R_d(c_d)$.

7*b*. When $R'_b(c_b)$ is not linear, calculate the local values of k_p and then the local values of K_P as the ratio of k_p to k_d, find the parameters of the regression line of $K_P(c_b)$ and verify its linearity. If it is linear then $K_P = a + bc_b$. Its confidence limit may be estimated only locally for individual c_b-values: $K_P \pm s^2_{a+bc_b} \cdot t_{0.95(q-2)}$.

Note. If $R_d(c_d)$ is not linear or $K_P(c_b)$ is not linear and not constant, the specificity of the method relative to the interferent tested cannot be characterized by means of the K-coefficients.

8. Using the constant value of K_P or local values of K_P, calculate the local values of K_A and their variances.

9. When $K_P \neq$ const., test whether $K_A =$ const. by means of the t-test.

Note. K_a may be constant despite $R_r(c_b)$ not being linear, when only the R'_b-signal is responsible for this deviation from linearity.

10. If $K_A \neq$ const. calculate the parameters of the regression line $K_A(c_b)$ and verify its linearity. When it is linear K_A may be expressed as $K_A = a + bc_b$ and its confidence limit may be estimated only locally (see 7*b*).

Note. If $K_A \neq$ const. and $K_A(c_b)$ is not linear, the specificity of the method relative to the interferent tested cannot be characterized by means of the K-coefficients.

An example of calculation (according to scheme 2) of the K-coefficients for coulometric determination of uranium with molybdenum as interferent is given in Appendix II.

Sometimes the coefficient K_A ought to be expressed as a linear function of the analyte concentration; then all the operations given in step 10 must be carried out for $K_A(c_d)$. The expression of the K-coefficients as linear functions is necessary when the influence of the interferent on the analytical signal is approximated better by a second-order function than a linear function and it usually concerns the coefficient K_A that describes the inter-effect between the analyte and the interferent. The application of this procedure widens the possibilities of the approach. It is particularly useful when the K-coefficients are used for mathematical correction of the analytical results obtained in the presence of certain interferents, some of which do not fulfil the simplifying assumptions well. The K-coefficients can also be expressed by means of functions other than linear, but this complicates the problem and finds application only for special cases.

The procedure described allows the complete testing of an analytical method for all interferents of interest by use of relatively few standards, and also whether the simplifying assumptions are satisfied. However, it does not permit verification of the assumption that the activity of individual interferents is independent of their mutual proportions in the sample. One way of verifying this is to compare the result for a standard mixture containing known concentrations of the analyte and all interferents of interest with the result (corrected by means of the K-coefficients) for a sample containing the same concentration of pure analyte.

The complete statistical evaluation of the data used

for calibration of an analytical method according to schemes 1 and 2 is rather arduous and requires the use of a computer. However, particularly when the results are read from a graphical calibration curve, a much simpler procedure can often be used, that gives sufficiently correct results. The estimation of the parameters of all the test-functions as well as the verification of their linearity may be done graphically and the K-coefficients calculated. simply on the basis of these parameters.

EXPERIMENTAL

Apparatus

Unicam SP 500 spectrophotometer. Radelkis OH-102 polarograph with dropping mercury and calomel electrodes. Equipment for controlled-potential coulometry based on the Tacussel PRT-500 Lc potentiostat with IG-38 integrator. Minicomputer.

Methods used

1. Spectrophotometric uranium(VI) determination with Arsenazo-III according to Savvin (without extraction).[3]
2. Spectrophotometric manganese determination with formaldoxime according to Marczenko.[4]
3. Polarographic determination of uranium(VI) in 2N sulphuric acid medium according to Kolthoff and Harris.[5]
4. Controlled-potential coulometric determination of uranium(VI) in 5N sulphuric acid medium according to Farrar *et al.*[6]

Standard samples

The standard samples used for testing the methods above were prepared according to Table 1.

Table 2. K_P and K_A values for spectrophotometric determination of uranium(IV) with Arsenazo III (uranium concentration range 0–20 μg/10 ml)

Interferent	Interf. concn. range, μg/10 ml	K_P	K_A (μg/10 ml)$^{-1}$
Th	0–20	0.95	-1.16×10^{-2}
Ce	0–20	1.62	-7.30×10^{-3}
Gd	0–15	1.64	-7.75×10^{-3}

Table 3. K_P and K_A values for spectrophotometric determination of manganese with formaldoxime (manganese concentration range 0–25 μg/10 ml)

Interferent	Interf. concn. range μg/10 ml	K_P	K_A (μg/10 ml)$^{-1}$
Ni	0–20	1.30	0
Fe	0–40	0.43	0
Co	0–300	0.053	-3.00×10^{-4}
Mo	0–1000	0	3.70×10^{-5}

Table 4. K_P and K_A values for polarographic determination of uranium(VI) (uranium concentration range 0–1000 μg/10 ml)

Interferent	Interf. concn. range μg/10 ml	K_P	K_A (μg/10 ml)$^{-1}$
V	0–400	0.357	5.58×10^{-4}
Cu	0–200	0	-5.02×10^{-4}
Mo	0–250	2.336	8.01×10^{-5}

Table 5. K_P and K_A values for coulometric determination of uranium(VI) (uranium concentration range 0–4 mg/sample)

Interferent	Interf. concn. range mg/sample	K_P	K_A (mg/sample)$^{-1}$
V	0–0.5	2.242	0.506
Mo	0–0.5	5.366	3.069–5.433 c_b
Fe	0–1.25	2.010	0
Cu	0–2.0	3.607	0
Ce	0–0.6	0.669	0

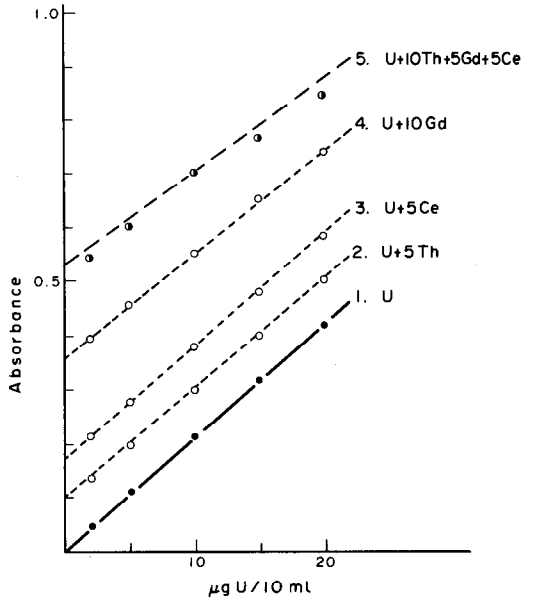

Fig. 1. Comparison of experimentally determined (points) and calculated (dashed lines) interference effects in the spectrophotometric determination or uranium. 1—Uranium; 2–4—individual interferents; 5—mixture of interferents. The numbers by the symbols of interferents indicate the concentrations in μg/10 ml.

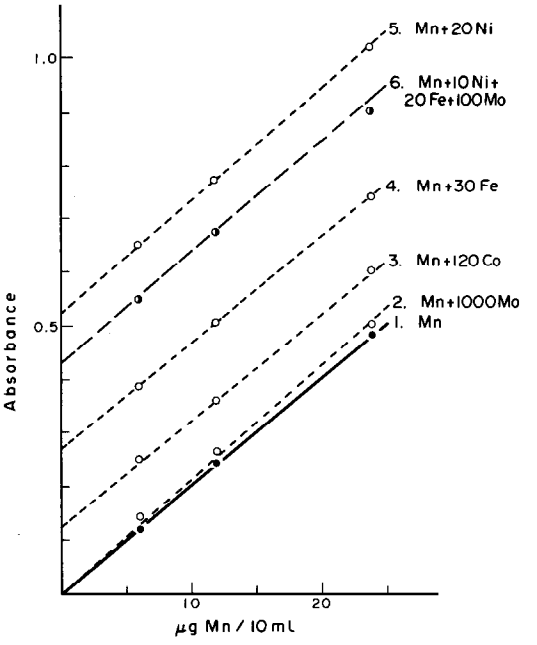

Fig. 2. Comparison of experimentally determined (points) and calculated (dashed line) interference effects in spectrophotometric determination of manganese. 1—Manganese; 2–5—individual interferents; 6—mixture of interferents. The numbers by the symbols of interferents indicate the concentrations in μg/10 ml.

RESULTS AND DISCUSSION

The possibility of applying the non-specificity coefficients for determining the practical specificity characteristics of the four methods mentioned above was investigated. Each method was tested with respect to the strongest interferents. The K_P and K_A values obtained experimentally are shown in Tables 2–5. The full data and calculations for an example of each computation scheme are given in Appendices I and II.

The comparison of the experimental results with the results corrected by means of the K-coefficients is presented in Figs. 1–4. The points plotted represent the experimental values of the analytical signal for the analyte in presence of one interferent or a mixture of some interferents. The continuous line represents the normal calibration curve in the absence of interferents and the dashed lines represent the theoretically calculated values, *i.e.*, the calibration curve values corrected by means of the K-coefficients for a defined concentration of one interferent or a mixture of interferents.

It is seen from Tables 2–5 that for 15 interferents tested in the four methods the K-coefficients are constant and that only in one case, molybdenum in the coulometric determination of uranium, the coefficient K_A must be described by a linear function. The agreement of the calculated and experimental values is excellent for the determinations in presence of single interferents in all the methods investigated. This fact confirms that the K-coefficients may be used successfully as a characteristic of analytical methods and that the proposed calibration procedure based on a small number of standards gives sufficiently precise results. The worst situation is for the multi-interferent mix-

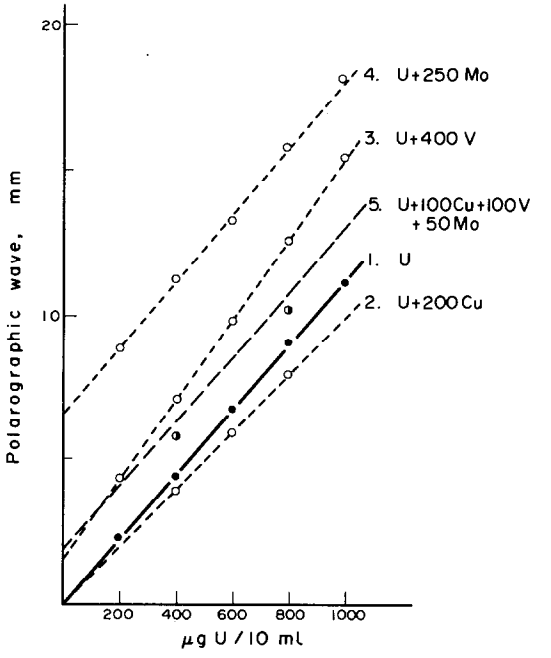

Fig. 3. Comparison of experimentally determined (points) and calculated (dashed lines) interference effects in polarographic determination of uranium. 1—Uranium; 2–4—individual interferents; 5—mixture of interferents. Numbers by the symbols of interferents indicate the concentrations in μg/10 ml.

ture. In this case the deviations of the calculated results from the experimental are significantly larger than the reproducibility of the methods. However, taking into consideration the very strong interfering signals and the possibility of accumulation of errors made in the estimation of K-values for single interferents, the additivity of interfering signals can be accepted as established.

On the basis of these experiments we conclude that the non-specificity coefficients characterize quantitatively the specificity of the analytical procedures investigated.

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APPENDIX I

Calculation of K_P and K_A values for spectrophotometric determination of uranium(VI) in presence of thorium.

Note. All statistical calculations presented in Appendices I and II were carried out according to the formulae given by Brandt[7] and Bevington.[8]

Number of standards in series; $q = 5$.

Number of parallel determinations of each standard: $t = 5$.

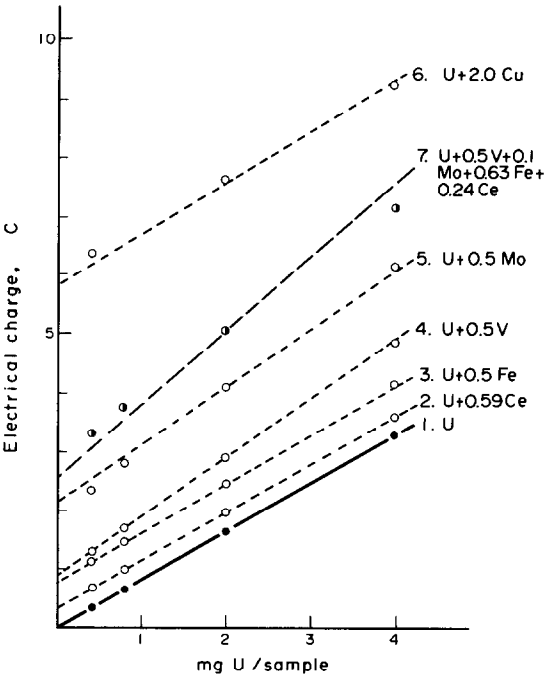

Fig. 4. Comparison of experimentally determined (points) and calculated (dashed lines) interference effects in coulometric determination of uranium. 1—Uranium; 2–6—individual interferents; 7—mixture of interferents. Numbers by the symbols of interferents indicate the concentrations in mg per sample.

Relative concentration of interferent: $c_r = 1$.

c_d and c_b in μg/10 ml.

R_d and R in absorbance units.

All R_d and R values are the mean values of five measurements and the variances are the variances of these means.

Experimental data

Standard No.	c_d	R_d	$s^2_{R_d} \times 10^6$	c_b	R	$s^2_R \times 10^6$
1	2	0.043	0.2	2	0.085	0.8
2	5	0.107	0.8	5	0.198	0.8
3	10	0.214	1.8	10	0.388	3.2
4	15	0.319	5.0	15	0.568	12.8
5	20	0.428	5.0	20	0.742	28.8

Calculated values of the total relative signal R_r

Standard No.	c_b	R_r	$s^2_{R_r} \times 10^4$
1	2	1.977	8.6
2	5	1.850	3.2
3	10	1.813	2.0
4	15	1.781	2.8
5	20	1.734	2.4

Regression parameters of $R_r(c_b)$:

$a = 1.92$; $b = -9.68 \times 10^{-3}$; $S_L = 1.621 \times 10^{-2}$; $S_W = 8.951 \times 10^{-4}$; $F = 18.10 > F_{0.95(1,3)} = 10.13$; R_r (c_b) is linear.

$s_{K_P} = 0.03$; $s_{K_A} = 2.3 \times 10^{-3}$; $t_{0.95(3)} = 3.18$; $K_P = 0.92 \pm 0.09$ and $K_A = -0.01 \pm 0.007$ $(\mu g/10\ ml)^{-1}$.

APPENDIX II

Calculation of K_P and K_A values for coulometric determination of uranium(VI) in presence of molybdenum

Number of standards in series: $q = 5$.

Number of parallel determinations of each standard: $t = 5$.

Relative concentration of interferent: $c_r = 0.1$.

c_d and c_b in mg/sample.

R_d, R'_b and R in coulombs.

All R_d, R'_b and R values are the mean values of five measurements and the variances are the variances of these means.

Experimental data

Standard No.	c_d	R_d	$s^2_{R_d} \times 10^6$	c_b	R'_b	$s^2_{R'_b} \times 10^6$	R	$s^2_R \times 10^5$
1	0.2	0.162	1.8	0.02	0.086	1.8	0.275	0.32
2	0.5	0.409	1.8	0.05	0.216	1.8	0.685	0.98
3	1.0	0.812	5.0	0.10	0.435	7.2	1.455	2.0
4	2.0	1.621	7.2	0.20	0.868	9.8	3.133	4.6
5	4.0	3.254	20.0	0.40	1.742	12.8	6.157	18.0

Calculated values of total relative signal R_r

Standard No.	c_b	R_r	$s^2_{R_r} \times 10^5$
1	0.02	1.586	29.5
2	0.05	1.675	8.9
3	0.10	1.792	5.5
4	0.20	1.933	2.8
5	0.40	1.892	2.4

Function $R_r(c_b)$:

$a = 1.75$; $b = 0.445$; $S_L = 1.84 \times 10^{-2}$; $S_W = 8.51 \times 10^{-3}$; $F = 2.16 < F_{0.95(1,3)} = 10.13$; $R_r(c_b)$ is not linear.

Function $R_d(c_d)$:

$a = 1.41 \times 10^{-3}$; $b = 0.811$; $s_a = 0.005$; $t = 0.28 < t_{0.95(3)} = 3.18$; $S_L = 2.10$; $S_W = 1.4 \times 10^{-4}$; $F = 1500 \gg F_{0.95(1,3)} = 10.13$.

$R_d(c_d)$ is linear and passes through the origin.

Function $R'_b(c_b)$:

$a = -9.90 \times 10^{-4}$; $b = 4.36$; $s_a = 6.9 \times 10^{-4}$; $t = 1.44 < t_{0.95(3)} = 3.18$; $S_L = 0.793$; $S_W = 1.46 \times 10^{-6}$; $F = 5.4 \times 10^5 \gg F_{0.95(1,3)} = 10.13$; $R'_b(c)_b$ is linear and passes through the origin; $s_{K_P} = 0.047$; $K_P = 5.37 \pm 0.15$.

Local values of K_A

Standard No.	c_b	K_A	$s^2_{K_A}$
1	0.02	2.45	6.4×10^{-3}
2	0.05	2.76	3.2×10^{-4}
3	0.10	2.55	5.2×10^{-5}
4	0.20	1.98	7.2×10^{-6}
5	0.40	0.89	1.6×10^{-6}

Function $K_A(c_b)$:

$a = 3.07$; $b = 5.46$; $S_L = 1.17$; $S_W = 1.19 \times 10^{-4}$; $F = 9800 \gg F_{0.95(1,3)} = 10.13$; $K_A(c_b)$ is linear.

$K_A = 3.07 - 5.46\ c_b$ (mg/sample)$^{-1}$.

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MASS-SPECTROMETRIC MULTIELEMENT ANALYSIS OF COPPER AND COPPER-BASE ALLOYS, WITH ELECTRICAL DETECTION

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Summary—Relative sensitivity coefficients have been determined for 21 elements in copper and its alloys, with iron as an internal standard, by spark-source mass-spectrometry with electrical detection and magnetic peak-switching. Twenty calibration standards ranging from pure copper to 60%-copper alloys were used. The sensitivity coefficients measured appear to be independent of the elemental concentration and are obtained with a mean precision of 15%.

Accurate quantitative analysis by spark-source mass-spectrometry requires determination of relative sensitivity coefficients by analysis of calibration standards. In this work the relative sensitivity coefficients of a number of elements in copper and copper alloys are determined by spark-source mass-spectrometry with electrical detection. The sensitivity coefficient S_R, for an element x in a given matrix is defined as

$$S_R\left(\frac{x}{y}\right) = \left(\frac{C_x}{C_y}\right)_{\text{determined}} \Big/ \left(\frac{C_x}{C_y}\right)_{\text{true}}$$

where y is the reference element. Iron was preferred to copper as the reference element. The matrix element is more homogeneous and is more accurately certified but it has no low-abundance isotope; the large matrix ion-currents may cause instability of the electron multiplier[1] and saturation of the output signal. Moreover, with iron as a reference, the results can be compared directly with those obtained in a previous study of the steel matrix.[2]

Several authors have published experimentally determined sensitivity coefficients for the analysis of copper with photoplate detection.[3] The coefficients reported in this paper were determined by using electrical detection and magnetic peak-switching. The previous study[2] for steel samples showed that this mode of operation is more precise than the photographic method of analysis. Although the mass resolution with electrical detection is considerably lower than with photoplate detection it is adequate because the copper spectra are not too complicated. Nevertheless, in order to detect possible spectral interferences, the complete mass spectra were first recorded with photoplate detection.

EXPERIMENTAL

The mass spectrometer was a radio-frequency spark-source double-focusing instrument with Mattauch–Herzog geometry (JMS-01 BM-2, JEOL, Tokyo) equipped with an electrical detection system (MS-ED-01).

Samples

Spark-source mass-spectrometry requires very homogeneous samples because very small amounts of material are consumed. Copper reference materials especially prepared for spark-source mass-spectrometry are not available. The samples used here were selected from standard reference materials intended primarily for optical emission and X-ray spectrometry and were tested for homogeneity.

The samples cover a wide range of composition from very pure copper to 60%-copper alloy (brass). They were chosen in such a way that the S_R values of as many elements as possible could be determined in several samples.

Five copper-base alloys, available from the National Bureau of Standards, Washington, D.C. were chosen as reference materials: SRM 1101 and 1102 (Cartridge Brass B and C), SRM 1106 and 1108 (Naval Brass A and C) and SRM 1121 (Beryllium Copper). They are wrought materials in the form of discs, 32 mm in diameter and 19 mm thick. Table 1 lists the certified concentrations. According to the certificates, these values are not expected to deviate from the "true" concentration by more than ± 1 in the last significant figure reported; for a subscript figure, the deviation is not expected to be more than ± 5. The values in brackets are not certified, but are given for information. The standard deviation of the certified values was assumed to be half the specified uncertainty of ± 1 or ± 5 in the last significant figure.

From the three series of graded dilute copper alloys prepared by Johnson Matthey Ltd., London, for use in spectrochemical analysis, eight reference materials were analysed. These standards contain the impurity element listed in Table 2. These samples are available in the form of rods 3 mm in diameter and 90 mm long, except for sample CA 4 (1.6 × 100 mm). The analysis reports do not give information on the precision of the results listed, but the same assumptions were made as for the NBS data.

From the Canada Centre for Mineral and Energy Technology, Ottawa, four commercial-purity copper rods (SSC 1–4) were used. They are intended as reference materials for spectrographic purposes and are in the form of hot-rolled rods, 8 × 300 mm. Table 3 gives the recommended values and the corresponding standard deviations.

In addition, copper samples containing standardized platinum contents of 100, 12 and 1.2 ppm w/w from the BCR (Community Bureau of Reference, Commission of the European Communities, Brussels) were analysed. They were prepared by successive dilutions of platinum in copper by means of high-frequency levitation melting.[4] The

Table 1. Composition of the NBS copper-base alloy standard reference materials, %w/w

Element	NBS-SRM 1101 Cartridge Brass B	NBS-SRM 1102 Cartridge Brass C	NBS-SRM 1106 Naval Brass A	NBS-SRM 1108 Naval Brass C	NBS-SRM 1121 Beryllium Copper CA-172
Be	0.0005_5	0.0000_3			1.89
Al	0.0006	0.0007			0.07
Si	(0.005)	(0.002)			0.11
P	0.002_0	0.004_8			(0.005)
Cr					(0.002)
Mn	0.005_5	0.004_5	0.005	0.025	(0.00_4)
Fe	0.037	0.011	0.004	0.050	0.08_5
Co					0.29_5
Ni	0.013	0.005	0.025	0.033	0.012
Cu	69.6_0	72.8_5	59.0_8	64.9_5	97.4_9
Zn	30.2_6	27.1_0	40.0_8	34.4_2	(0.01)
As	0.009	0.004			
Ag	0.003	0.0010			(0.005)
Cd	0.005_5	0.004_5			
Sn	0.016	0.006	0.74	0.39	0.01
Sb	0.012	0.005			
Te	0.001_5	0.000_3			
Pb	0.05	0.020	0.032	0.063	(0.002)
Bi	0.000_4	0.000_5			

Table 2. Composition of the Johnson Matthey dilute copper alloy standards, %w/w

Series CA				Series CB			Series CC			
Element	CA 3	CA 4	CA 6	Element	CB 0	CB 1	Element	CC 1	CC 3	CC 5
Cr	0.003	0.0018	0.0003	Si	0.049	0.02	Be	0.0300	0.0065	0.0012
Ga	0.004	0.0021	0.0005	Mn	0.046	0.018	P	0.0230	0.0050	0.0008
Ag	0.006	0.0020	0.0006	Fe	0.023	0.011	Zn	0.0230	0.0060	0.0015
Sn	0.005	0.0015	0.0006	Co	0.052	0.02	As	0.015	0.004	0.001
Sb	0.0043	0.0010	0.0005	Ni	0.033	0.015	Se	0.016*	0.0040*	0.0008*
Pb	0.005	0.0024	0.0007				Te	0.0150	0.0055	0.0015
Bi	0.008	0.0023	0.0009							

* Calculated from the dilution of the master alloy.

samples are discs with a diameter of 10 mm and a thickness of 1.5 mm. They have been investigated by several techniques such as neutron, photon and charged-particle activation analysis, atomic-absorption spectrometry, emission spectrography, X-ray fluorescence analysis, isotope dilution methods and spark-source and low-voltage discharge mass-spectrometry. The weighted mean of all analyses is specified as 98.5 ± 0.1, 11.75 ± 0.03 and 1.18 ± 0.01 ppm, respectively.

The sample used for testing the dynamic range of the electron multiplier was Johnson Matthey high-purity platinum wire (diameter 0.5 mm) with a total metallic impurity content lower than 10 ppm.

Sample preparation. Two cylindrical rods (2 mm diameter) were machined from the samples; the ends were flattened to a thickness of 1 mm as proposed by Franzen and Schuy.[5] The sparking surfaces were ground flat and the electrodes etched in dilute nitric acid (*p.a.*), washed with distilled water and rinsed in acetone (*p.a.*). They were sparked off at least 10 min before starting the measurements.

Table 3. Composition of the certified commercial purity copper rods from the Canada Centre for Mineral and Energy Technology

	Recommended value and standard deviation, *ppm*			
Element	SSC-1	SSC-2	SSC-3	SSC-4
Fe	39 ± 7	32 ± 7	40 ± 9	50 ± 9
Ni	18 ± 3	3 ± 1	48 ± 8	25 ± 4
Zn	33 ± 8	16 ± 5	15 ± 4	30 ± 7
As	1.2 ± 0.5	1.2 ± 0.6	5 ± 2	2.8 ± 0.5
Se	7 ± 2	2.6 ± 0.8	3.9 ± 0.7	2.9 ± 0.8
Ag	19 ± 6	14 ± 3	16 ± 4	21 ± 5
Cd		10 ± 1		19 ± 3
Sn	55 ± 7	10 ± 2	12 ± 2	21 ± 3
Sb	2.6 ± 0.5	5.8 ± 0.7	2 ± 1	11 ± 1
Te	4.6 ± 0.8	1.2 ± 0.5	2.5 ± 0.6	1.4 ± 0.4
Pb	65 ± 7	6 ± 1	5 ± 2	16 ± 1
Bi	1.2 ± 0.3	0.10 ± 0.04	0.59 ± 0.01	0.23 ± 0.05

Mass-spectrometric procedure

The instrumental parameters selected were identical to those used for the analysis of iron and steel samples,[2] except for the following. The width of the collector slit was adjusted to 350 μm instead of 250 μm in order to reduce the effect of instability of the magnetic field. No extra interferences were caused by the resulting mass-resolution degradation, as the spectra were rather simple. With the sparking conditions as for steel samples, it was impossible to obtain stable sparking for a sufficient length of time as the copper and brass electrodes soon made contact and fused together. Therefore the "Variac" setting which controls the input to the radiofrequency oscillator was lowered to 2.5 kV, which corresponds to a spark-source voltage of about 40 kV. Nevertheless, for the brass samples, stable sparking remained difficult.

RESULTS AND DISCUSSION

Linearity of the electron-multiplier response

Unlike iron, the matrix element in this study has no low-abundance isotope and therefore the matrix ion-current up to which the electron multiplier response remained proportional to the input current was first established. For all the isotopes of a well-chosen matrix element, the collector current was integrated until a 1-nC charge had been collected at the total ion-beam monitor. Each individual current integration took about 15 sec. Platinum was selected since it has 6 stable isotopes with abundances ranging

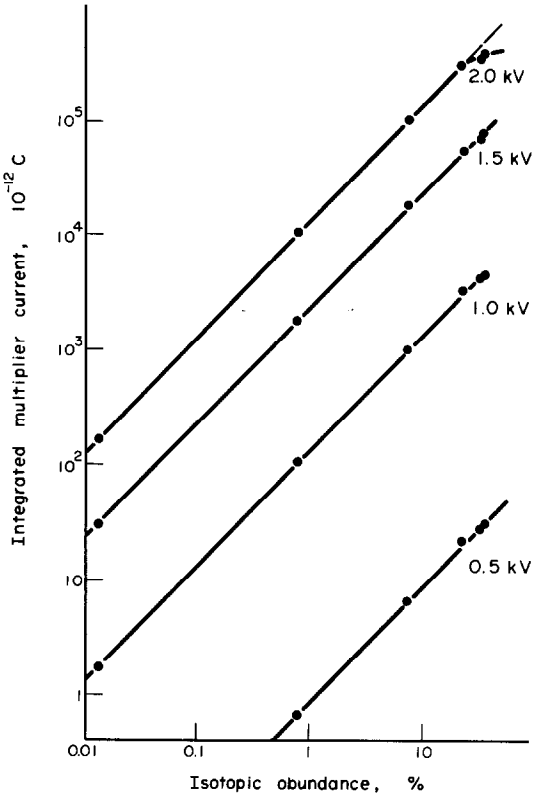

Fig. 1. Electron-multiplier response at different multiplier voltages.

from 0.013 to 33.8%. It was shown that none of these isotopes suffered interference from impurities. It was possible to measure integrated multiplier currents between 3×10^{-13} and 10^{-6} C. To cover this range, the measurements had to be carried out at several electron-multiplier voltages. Figure 1 shows that saturation occurs at an integrated current of 3×10^{-7} C. This corresponds to a multiplier current of about 2×10^{-8} A and a dynamic range of 10^6.

Consequently, it is difficult to use copper as an internal standard because it cannot be measured with the same multiplier voltage as impurities at the ppm-level. Iron was therefore used as the reference element. As the iron concentration is above 30 ppm in every sample, it is possible to measure copper *vs.* iron.

Qualitative analysis

The interferences detected in the spectra are listed in Table 4. The trailing superscript refers to the positive charge of the ion; the plus signs of the charge superscripts are omitted since all ions are of positive charge. The charge superscript is omitted entirely for species having a single positive charge. Interferences below 15% were corrected for by using interference-free isotopes of the interfering element.

Nearly all elements had one or more isotopes that were free from interference. Only beryllium in the samples NBS-SRM 1101, 1102 and JM CC5, aluminium in NBS 1101, silicon in NBS-SRM 1101 and

Table 4. Interferences in copper and copper alloy spectra

Element	Isotope	Interference	Interfered in sample	Interfered in sample but corrected by use of the species in brackets
Be	9	$^{63}Cu^{7}$	NBS 1101, 1102; JM CC 5	JM CC 1, 3 ($^{65}Cu^{7}$)
Al	27	$^{54}Fe^{2}$	NBS 1101	NBS 1102 ($^{57}Fe^{2}$)
Si	28	$^{56}Fe^{2}$	NBS 1101, 11102	NBS 1121, JM CB 0.1 ($^{57}Fe^{2}$)
	29	$^{58}Ni^{2}$	NBS 1101, 1102; JM CB-O, 1	NBS 1121 ($^{61}Ni^{2}$)
	30	$^{60}Ni^{2}$	NBS 1101, 1102; JM CB-O, 1	NBS 1121 ($^{61}Ni^{2}$)
Cr	54	^{54}Fe	NBS 1121	
Fe	54	^{54}Cr, $^{108}Cd^{2}$		SSC-1,3(^{52}Cr), SSC-2,4 (^{52}Cr, $^{111}Cd^{2}$)
	56	$^{112}Cd^{2}$,$^{112}Sn^{2}$	NBS 1106	SSC-2,4($^{111}Cd^{2}$)
	57	$^{114}Cd^{2}$,$^{114}Sn^{2}$	NBS 1101, 1102, 1106, 1108; SSC-2,4	SSC-1,3($^{119}Sn^{2}$)
	58	^{58}Ni	all samples	
Ni	58	^{58}Fe,$^{116}Cd^{2}$, $^{116}Sn^{2}$	NBS 1106, 1108	NBS 1101, 1102 ($^{119}Sn^{2}$); NBS 1121, SSC-1,3($^{54,56,57}Fe$, $^{119}Sn^{2}$); SSC-2,4($^{54,56,57}Fe$, $^{111}Cd^{2}$, $^{119}Sn^{2}$)
	60	$^{120}Sn^{2}$	NBS 1106, 1108; SSC 1,2	NBS 1101, 1102, 1121; SSC-3,4($^{119}Sn^{2}$)
	61	$^{122}Sn^{2}$	NBS 1101, 1102, 1106, 1108, 1121; SSC-1,4	
	62	$^{124}Sn^{2}$	NBS 1101, 1102, 1106, 1108, 1121; SSC 1,2,4	SSC-3($^{119}Sn^{2}$)
	64	^{64}Zn	all samples except JM CBO, 1	
Zn	64, 66	background Cu, CuH^{+},	NBS 1121; JM CC 3,5; SSC-1,4	
Se	77	^{65}Cu C, ^{63}Cu N	JM CC 3,5; SSC 1-4	
	80, 82	CuOH	all samples	
Cd	112, 114, 116	Sn	all samples	
Sn	112, 114, 116	Cd	NBS 1101, 1102; SSC-2,4	
	122, 124	Te	NBS 1101, 1102; SSC-1,4	
Te	120, 122, 124	Sn	NBS 1101, 1102; SSC-1,4	
	123	^{123}Sb	NBS 1101, 1102; SSC-1,4	
	125	*	NBS 1101; SSC-2,4	
	126, 128, 130	Cu_2^{+}	all samples	

* Charge transfer in electric field

1102, nickel in NBS-SRM 1106 and 1108, selenium in the BCR-samples and tellurium in NBS-SRM 1102 and SSC-2, 3 and 4 could not be determined by using magnetic peak-switching under the conditions used in this work. The sensitivity coefficients of these elements were determined in several of the other samples.

Brass and beryllium copper standards

The relative sensitivity coefficients of the elements certified by the National Bureau of Standards in brass and beryllium-copper samples were determined. Six channels were available on the instrument used; one was used for the internal standard, the others for isotopes of the elements to be measured. For each isotope, 8 successive integrations were carried out before switching to the next isotope. The integrated monitor charge was about 1 nC. The entire sequence was repeated at least 10 times and the experiments were carried out in 2 or more groups over a one-month period. The results were averaged and the corresponding relative standard deviation was calculated from

$$s = \frac{100}{\bar{C}} \sqrt{\frac{(C_i - \bar{C})^2}{n-1}}\,\%$$

where C_i is an individual concentration, $\bar{C}$ the mean concentration and n the number of analyses.

All interference-free isotopes were used. Whenever more than one isotope was available, the weighted average concentration and the corresponding standard deviation was calculated from

$$\bar{C} = \frac{\Sigma(C_i/s_i^2)}{\Sigma(1/s_i^2)}$$

and

$$s = \frac{100}{\bar{C}} \frac{\sqrt{N}}{\sqrt{\Sigma(1/s_i^2)}}\,\%$$

where N is the number of reference materials used. The S_R values were calculated by using the data in Table 1.

The results are summarized in Table 5. The standard deviations listed take into account only the precision of the measurements and not the uncertainties in the certified concentrations. The average relative standard deviation for all elements is 13% compared with 10% found previously for iron and steel samples. This might be attributed to the less homogeneous distribution of some elements and to the fact that with the brass samples it was difficult to obtain stable sparking conditions.

Dilute copper alloy standards

The same experiments were performed on 8 dilute copper alloys from Johnson Matthey. As iron was not certified in series CA and CC, copper was used as the internal standard and the S_R-values were recalculated by using the S_R value of copper *vs.* iron, as determined in the samples from series CB. The results are listed in Table 6 and the average relative standard deviation for all elements is 10%.

Certified commercial-purity copper rods

To extend the composition range of the copper samples studied to lower concentrations, four reference materials from the Canada Centre for Mineral and Energy Technology were analysed. They consist of high-purity copper doped with some impurities. The results are listed in Table 7. The average relative standard deviation for all elements is 13%, suggesting that these materials are less homogeneous than the Johnson Matthey samples. Radermacher and Beske[6] also found indications of poor homogeneity, even with a low-voltage discharge ion-source mass-spectrometer.

Table 5. Experimentally determined S_R values for brass and beryllium copper for the NBS standards*

Element	SRM 1101		SRM 1102		SRM 1106		SRM 1108		SRM 1121	
	S_R	s, %	S_R	s, %	S_R	s, %	S_R	s, %	S_R	s, %
Be									0.68	6
Al			1.2	25					1.31	6
Si									0.92	6
P	1.6	21	1.6	15					(1.6)	7
Cr									(1.25)	6
Mn	1.6	10	1.32	6	1.4	8	1.29	7	(2.0)	10
Fe	1	—	1	—	1	—	1	—	1	—
Co									0.81	6
Ni	0.65	8	0.75	10					0.70	6
Cu	0.55	5	0.60	6	0.53	6	0.61	5	0.65	5
Zn	1.0	10	0.95	7	0.75	6	0.87	10	(1.7)	10
As	2.2	20	2.3	17						
Ag	2.8	15	1.5	12					(2.5)	10
Cd	2.4	25	2.5	15						
Sn	2.9	16	2.0	21	2.8	15	2.7	17	3.2	13
Sb	2.6	21	2.7	20						
Te	3.1	25								
Pb	3.7	17	4.3	25	3.4	20	3.2	20	(4.5)	20
Bi	2.2	17	1.8	21						

* Where no value is indicated, either a certified concentration is unavailable or an interference occurs.

Table 6. Experimentally determined S_R values for the Johnson Matthey copper alloy standards

Sample number	Cr		Ga		Ag		Sn		Sb		Pb		Bi	
	S_R	s, %	S_R	s, %	S_R	s, %	S_R	s, %	S_R	s, %	S_R	s, %	S_R	s, %
CA-3	1.8	6	2.2	10	1.9	7	2.6	10	3.3	13	3.4	18	2.0	13
CA-4	1.76	5	1.7	9	2.5	10	2.7	12	4.3	19	2.9	19	2.4	15
CA-6	2.2	6	2.3	8	2.8	9	2.7	8	4.5	17	4.4	21	2.0	12
	Si		Mn		Fe		Co		Ni		Cu			
	S_R	s, %	S_R	s, %	S_R	s, %	S_R	s, %	S_R	s, %	S_R	s, %		
CB-0	1.02	5	1.70	5	1	—	0.88	4	0.75	5	0.79	3		
CB-1	1.1	9	1.85	5	1	—	0.94	7	0.74	4	0.81	3		
	Be		P		Zn		As		Se		Te			
	S_R	s, %	S_R	s, %	S_R	s, %	S_R	s, %	S_R	s, %	S_R	s, %		
CC-1	0.58	8	1.5	13	1.01	6	2.5	15	2.4	14	3.6	10		
CC-3	0.62	9	1.8	11	1.12	8	2.2	11	2.0	12	3.3	9		
CC-5			1.4	15	0.85	7	1.9	16	1.6	15	3.0	14		

Copper samples with standardized platinum content

The BCR has been sponsoring the development of standard reference materials for noble metals. Three of them, *viz.* copper containing 100, 12 and 1.2 ppm platinum, and the "blank" copper were analysed.

First a panoramic analysis was made of the "blank" copper sample by using magnetic scanning. Five scans, each taking 40 min for the total mass range, were recorded. The average concentrations found are listed in Table 8, column 2. They are corrected with the sensitivity coefficients shown in Table 10. In column 3, the results found by Beske[7] by using low-voltage discharge mass-spectrometry are listed. The values between square brackets are not corrected with a sensitivity factor. Column 4 shows the values found by Govaerts *et al.*[8] by neutron-activation analysis.

Table 7. Experimentally determined S_R values for the commercial-purity copper rods from the Canada Centre for Mineral and Energy Technology

Element	SSC-1		SSC-2		SSC-3		SSC-4	
	S_R	s, %	S_R	s, %	S_R	s, %	S_R	s, %
Fe	1	—	1	—	1	—	1	—
Ni	0.67	7	0.70	12	0.60	9	0.63	6
Cu	0.55	5	0.56	6	0.58	4	0.61	4
Zn	1.03	9	0.90	12	0.92	9	0.98	9
As	1.7	16	1.8	14	2.6	12	3.0	9
Se	2.9	19	2.5	17	1.5	17	2.9	11
Ag	1.5	11	1.4	10	1.4	12	1.7	6
Cd	—	—	2.2	15	—	—	2.6	9
Sn	2.5	12	2.3	14	2.1	15	2.4	7
Sb	2.4	19	2.6	21	2.7	21	3.2	16
Te	3.4	15	—	—	—	—	—	—
Pb	2.5	20	2.7	24	2.5	21	3.5	14
Bi	2.0	17	1.9	21	1.7	16	2.0	13

The concentrations of some elements, namely Fe, Ni, Cu, As, Ag, Sb and Pb, are known from independent analysis.[7,8] They could be used for determining the sensitivity coefficients and were therefore studied by use of the more precise peak-switching mode of operation. The sensitivity coefficients obtained are listed in Table 9 and are in good agreement with those listed in Tables 5, 6 and 7.

The three copper samples with a standardized platinum content were also analysed by using peak-switching. The concentrations found were 87 ± 7, 10 ± 1 and 1.0 ± 0.1 ppm, corresponding to sensitivity coefficients of 0.88, 0.87 and 0.85 respectively. The average standard deviation is 10%, which indicates a homogeneous distribution of platinum. It was noted, however, that when measurements were made immediately after etching, values of the platinum concentration twice as high were obtained. The initial results were erratic and decreased to the values given above. These correct values were found when no chemical treatment was carried out or when the electrodes were ground flat with silicon carbide paper

Table 8. Panoramic analysis of the "blank" copper from BCR with magnetic scanning, *ppm**

Element	This work†	Beske[7]§	Element	This work†	Beske[7]§	Govaerts[8]‡
C	[0.19]	[0.4]	Cr	0.80	[3.2]	
N	[16]	8.6	Mn	0.61	0.8	
O	[61]	39	Fe	intern. stand.	6.7	
F	[0.15]	[0.3]	Co	0.37	[0.3]	
Na	[1.2]	[0.4]	Ni	1.4	1.4	
Mg	[0.50]	[0.3]	As	1.4	1.5	1.3
Al	0.28	[0.4]	Ag	10	8.3	7.4
Si	1.4	[8]	Sb	0.39		0.35
S	[12]		Pt	<0.1		
Cl	[0.52]		Pb	2.6	3.3	
Ca	[1.9]		Bi	0.16		

* Values between brackets not corrected with a relative sensitivity coefficient.
† Spark-source mass-spectrometry, electrical detection (magnetic scanning).
§ Low-voltage discharge source mass-spectrometry, photoplate detection.
‡ Instrumental neutron-activation analysis.

Table 9. Experimentally determined S_R values for the "blank" copper from BCR, with Fe as the internal standard

Element	Uncorrected concentration, *ppm*	Relative standard deviation, %	Sensitivity coefficient
Fe	6.7	—	1
Ni	1.4	8	1.00
Cu	85×10^4	6	0.85
As	3.3	15	2.5
Ag	21	11	2.8
Sb	1.1	17	3.2
Pb	8.9	16	2.7

after etching. The erroneous results after chemical etching suggest that platinum may be redeposited onto the etched surface.

Average sensitivity coefficients for the analysis of copper and copper alloys

The errors in the data given in Tables 1–3 differ widely. The standard deviation of the S_R-values was obtained from:

$$s = \frac{ab'}{b}\sqrt{\left(\frac{s_a}{a}\right)^2 + \left(\frac{s_b}{b}\right)^2 + \left(\frac{s_{b'}}{b'}\right)^2}$$

where a refers to the value measured by mass-spectrometry, and b and b' to the certified concentration of the analysed element and the reference element respectively.

The weighted averages of all the relative sensitivity coefficients determined above and their standard deviation were then calculated from

$$\bar{S}_R = \frac{\Sigma(S_{R_i}/s_i^2)}{\Sigma(1/s_i^2)}$$

and

$$s = \frac{\sqrt{N}}{\sqrt{\Sigma(1/s_i^2)}}$$

The results are listed in Table 10. The overall mean relative standard deviation obtained is 15%. This figure is significantly affected by the uncertainties of the certified concentrations of the reference materials, especially those of the SSC-standards. As can be seen from Table 3, the average relative standard deviation for these samples is 20% for the internal standard and 22% for the other elements used.

The relative sensitivity coefficients found here are in good agreement with those found for iron and steel samples,[2] except for manganese and copper which show a significantly higher sensitivity in iron than in copper. The higher sensitivity of manganese in iron samples was also reported by other authors, *e.g.*, by Jaworski and Morrison,[9] who suggested that it may be affected by the strong matrix lines on either side.

A systematic survey for all the elements investigated shows no evidence that the S_R values change with concentration. In all cases the slope of the most probable straight line drawn through the data points does not significantly differ from zero. By way of example, Fig. 2 shows the S_R values for phosphorus, nickel, zinc and arsenic plotted *vs.* their concentration in the samples.

CONCLUSIONS

The relative sensitivity coefficients for 21 elements in copper and copper alloy samples for spark-source mass-spectrometric analysis with magnetic peak-switching varied from 0.63 for beryllium to 3.3 for tellurium and lead. They appeared to be independent of the elemental concentration at widely differing concentration levels and matrix compositions. Except for copper and manganese, they are in good agreement with those determined for iron and steel samples.

The precision of the peak-switching measurements for the samples from Johnson Matthey and the BCR was the same as that found for iron and steel samples in a previous study, *viz.* 10% relative standard deviation. For the copper alloys obtained from the National Bureau of Standards and for the commercial-purity coppers from the Canada Centre for Mineral and Energy Technology a 13% r.s.d. was obtained. With the NBS brass samples this was probably due to the fact that it proved difficult to obtain stable sparking conditions. The Canadian samples seemed less homogeneous.

The overall precision of the experimentally determined relative sensitivity coefficients is 15% r.s.d. compared with 10% for the iron and steel samples. This is mainly due to the larger uncertainties of the certified values of the reference materials used.

Table 10. Weighted average relative sensitivity coefficients for the analysis of copper and copper alloys (Fe: $S_R = 1$).

Element	S_R	Number of reference materials, used N	Element	S_R	Number of reference materials, used, N
Be	0.63 ± 0.08	3	As	2.3 ± 0.6	10
Al	1.3 ± 0.2	2	Se	2.0 ± 0.4	7
Si	0.98 ± 0.08	3	Ag	2.0 ± 0.3	11
P	1.6 ± 0.2	6	Cd	2.4 ± 0.5	4
Cr	1.7 ± 0.2	4	Sn	2.6 ± 0.5	12
Mn	1.5 ± 0.1	7	Sb	3.1 ± 0.7	10
Co	0.86 ± 0.06	3	Te	3.3 ± 0.5	5
Ni	0.72 ± 0.07	10	Pt	0.9 ± 0.2	3
Cu	0.66 ± 0.05	12	Pb	3.3 ± 0.8	13
Zn	1.0 ± 0.1	12	Bi	2.0 ± 0.5	9
Ga	2.0 ± 0.2	3			

Overall mean relative standard deviation: 15%

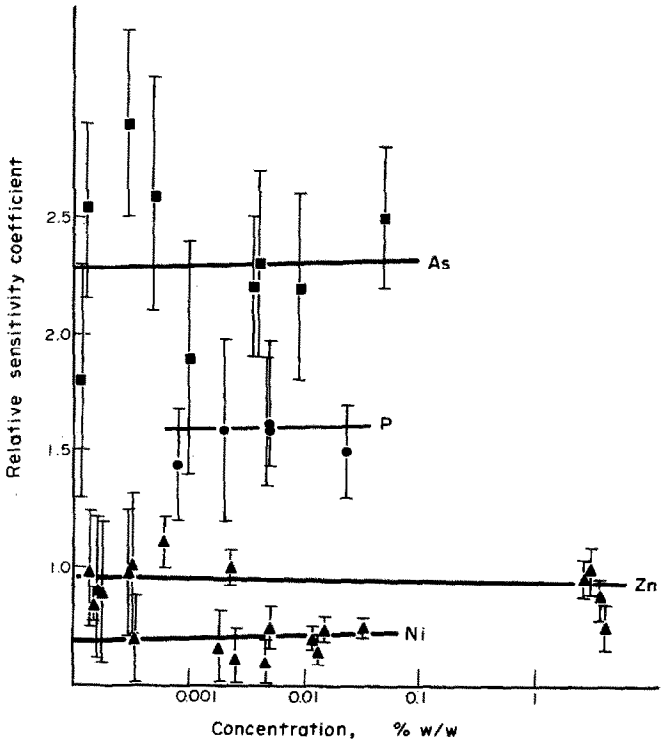

Fig. 2. Effect of concentration on the relative sensitivity coefficients of some elements in copper and copper alloy samples. (The concentration-axis for Zn is displaced by 1 decade to the low concentration side).

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EXTRACTION–SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF GOLD IN COPPER, SILVER, LEAD, BLISTER COPPER, COPPER CONCENTRATE AND ANODE SLIME WITH 4,4′-BIS(DIMETHYLAMINO)-THIOBENZOPHENONE

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Summary—A sensitive spectrophotometric method has been developed for the determination of gold in copper, silver, lead, blister copper, copper concentrate and anode slime. Optimal conditions have been established for the extraction and determination of gold. Gold is extracted as its bromo complex with tri-n-octylamine and determined photometrically with 4,4′-bis(dimethylamino)thiobenzophenone; the absorbance of the organic phase is measured at 540 nm and the apparent molar absorptivity is about 1.2×10^5 l.mole^{-1}.cm^{-1}. As little as 0.1 or 0.2 ppm of gold in these materials can be determined.

Because of the importance of the determination of trace amounts of gold in products from copper metallurgy and related materials, the development of sensitive and reliable methods is desired. In the past, trace amounts of gold in these materials were determined spectrophotometrically with *p*-dimethylaminobenzylidenerhodanine[1–3] or *N*,*N*′-tetramethyl-*o*-tolidine (Tetron);[4,5] these spectrophotometric methods, however, are not sufficiently sensitive (the molar absorptivities are about 10^4 and 10^5 l.mole^{-1}.cm^{-1}, respectively).

The most sensitive spectrophotometric method at present available is that with 4,4′-bis(dimethylamino)thiobenzophenone (thio-Michler's ketone, TMK), which was used by Cheng and Lott[6] (the molar absorptivity is about 1.6×10^5 l.mole^{-1}.cm^{-1}). Lakin and Nakagawa[7] successfully applied the method to the determination of trace amounts of gold in geological materials, after use of ether extraction for the separation of gold from the major constituents. In the present work, a spectrophotometric method using TMK is developed and applied to the determination of trace amounts of gold in copper, silver, lead, blister copper, copper concentrate and anode slime from copper refining. The proposed method involves the separation of gold from the major constituents by solvent extraction with a toluene solution of tri-n-octylamine (TOA) in the presence of hydrobromic acid, and colour development by direct addition of an n-butyl alcohol solution of TMK to the organic phase, followed by shaking with an aqueous buffer solution. The optimal conditions for the extraction and determination of gold are discussed. A method for the separation of interfering elements such as palladium or platinum is described.

EXPERIMENTAL

Reagents

TMK solution. Dissolve 0.01 g of TMK in 100 ml of n-butyl alcohol by stirring with a magnetic stirrer. Store in a dark place. Prepare freshly every one or two days.

TOA solution. Dilute 7 ml of TOA to 100 ml with toluene.

Wash solution A. Dilute 11.6 ml of hydrobromic acid (sp.gr. 1.48) and 108 ml of perchloric acid (sp.gr. 1.55) to 1000 ml with water; this solution is 0.1*M* with respect to hydrobromic acid and 1*M* with respect to perchloric acid.

Wash solution B. Dilute 11.6 ml of hydrobromic acid (sp.gr. 1.48) and 74.6 ml of nitric acid (sp.gr. 1.38) to 1000 ml with water; this solution is 0.1*M* with respect to hydrobromic acid and 1*M* with respect to nitric acid.

Wash solution C. Dissolve 3.7 g of disodium ethylenediamine tetra-acetate (EDTA) in 1000 ml of 1*M* sodium acetate solution and adjust the pH to 5.9–6.1 with hydrochloric acid (1 + 1).

Buffer solution. Adjust the pH of 1*M* sodium acetate to 3.2 with hydrochloric acid (1 + 1).

Standard gold solution. Dissolve 0.500 g of gold metal in 8 ml of *aqua regia* and make up to 500 ml with water. Before use, dilute the solution to an appropriate concentration.

General procedure

Transfer an aliquot (10 μg of Au) of the standard gold solution to a 100-ml separatory funnel. Add hydrobromic acid to give a final concentration of 0.05*M*. Make up to 50 ml with water and extract the gold by shaking with 5.0 ml of the TOA solution for 5 min. Discard the aqueous layer. Wash the organic layer twice with 20-ml portions of wash solution A for 2 min (discard the aqueous layers). Add 5.0 ml of the TMK solution to the organic layer and then shake with 50 ml of the buffer solution for 2 min. Measure the absorbance of the organic layer at 540 nm against the TOA solution or a reagent blank taken through the procedure.

Recommended procedures for the analysis of samples

Copper metal. Decompose 5 g of sample with 5 ml of 6*M* hydrochloric acid and 30 ml of 7*M* nitric acid; heat gently to assist the decomposition. Transfer this solution and a blank (5 ml of 7*M* nitric acid) to separatory funnels. Add 5.0 ml of 0.75*M* hydrobromic acid and make up to 75 ml with water. Shake vigorously with 5.0 ml of the TOA solution for 5 min. Discard the aqueous layer. Wash the organic layer once with 50 ml of wash solution B and then twice with 20-ml portions of wash solution A for 2 min (discard the aqueous layers). Add 5.0 ml of the TMK solution to the organic layer and then shake vigorously with 50 ml of the buffer solution for 2 min. Discard the aqueous layer. After 30 min, measure the absorbance of the organic layer at 540 nm against the TOA solution and correct for the blank.

Blister copper. Decompose 1–2 g of sample with 5 ml of 6*M* hydrochloric acid and 5–10 ml of 7*M* nitric acid; heat gently to assist the decomposition. Transfer the solution together with the silver chloride precipitate formed during decomposition of sample to a 100-ml volumetric flask and dilute to the mark with water. Transfer an aliquot of the supernatant solution (2–10 μg of Au) and a blank (5 ml of 7*M* nitric acid) to separatory funnels. Add 5.0 ml of 0.75*M* hydrobromic acid and make up to 75 ml with water. Then extract with the TOA solution and complete the determination of gold as for copper metal.

Lead metal. Decompose 5 g of sample with 15 ml of 7*M* nitric acid; heat gently to assist the decomposition. Add 10 ml of 6*M* hydrochloric acid and heat on a water-bath for 1 hr. Transfer the solution together with the lead chloride precipitate (formed on the addition of hydrochloric acid) to a 100-ml volumetric flask and dilute to the mark with water. Transfer 50.0 ml of the supernatant solution and a blank (5 ml of 7*M* nitric acid) to separatory funnels. Add 5.0 ml of 0.75*M* hydrobromic acid and make up to 75 ml with water. Then, extract with the TOA solution and complete the determination of gold as for copper metal (when the amount of thallium present is above its tolerance limit, wash the organic layer twice with 50-ml portions of the wash solution C and then once with 20 ml of the wash solution A, instead of washing once with 50 ml of the wash solution B and twice with 20-ml portions of the wash solution A).

Silver metal. Decompose 2 g of sample with 10 ml of 7*M* nitric acid; heat gently to assist the decomposition. Add 23 ml of 6*M* hydrochloric acid and heat on a water-bath for 1 hr. Transfer the solution together with the silver chloride precipitate to a 100-ml volumetric flask and dilute to the mark with water. Transfer 25.0 ml of the supernatant solution and a blank (25.0 ml of 1.2*M* hydrochloric acid) to separatory funnels and apply the ethyl acetate extraction procedure described below. Then extract with the TOA solution and complete the determination as described above.

Copper concentrate. Decompose 5 g of sample with 40 ml of *aqua regia*; heat gently to assist the decomposition. Add 5 ml of saturated bromine water and evaporate nearly to dryness. Add 5 ml of 7*M* nitric acid and 10 ml of 6*M* hydrochloric acid. Boil for several minutes. Transfer the solution together with the residue to a 50-ml volumetric flask and dilute to the mark with water. Transfer 25.0 ml of the supernatant solution and a blank (25 ml of 1.2*M* hydrochloric acid) to separatory funnels and apply the ethyl acetate extraction procedure below. Then extract with the TOA solution and complete the determination as described above.

Anode slime. Decompose 1 g of the sample, previously dried at 250° for 10 hr, with 20 ml of *aqua regia*; heat on a sand-bath to assist the decomposition and evaporate nearly to dryness. Add 10 ml of 7*M* nitric acid and 20 ml of 6*M* hydrochloric acid. Boil for several minutes. Transfer the solution together with the residue to a 100-ml volumetric flask and dilute to the mark with water. Transfer an aliquot (2–10 μg of Au) of the supernatant solution and a blank (25 ml of 1.2*M* hydrochloric acid) to separatory funnels and apply the ethyl acetate extraction procedure below. Then extract with the TOA solution and complete the determination as described above.

Preparation of calibration curves. Transfer portions of the standard gold solution (0–10 μg of Au) to beakers or separatory funnels. Treat these solutions and a blank (water) in parallel with samples by the procedures described above, and measure the relationship between the absorbance and the amounts of gold.

Ethyl acetate extraction procedure. Transfer the sample solution to a separatory funnel. Add hydrochloric acid to give a final concentration of 1.0–1.5*M* and make up to 25 ml with water. Shake twice with 25-ml portions of ethyl acetate for 5 min (discard the aqueous layer). Combine the organic layers and shake for 2 min with 20 ml of 1.2*M* hydrochloric acid saturated with ethyl acetate. Transfer the organic layer to a beaker containing 1 ml of 10% (w/v) sodium chloride solution. Heat on a water-bath to dryness. Add 5 ml of *aqua regia* and heat on a water-bath for about 15 min. Transfer to a separatory funnel. Add 5.0 ml of 0.75*M* hydrobromic acid and make up to 75 ml with water. Then extract with the TOA solution and continue as for copper metal. This procedure separates gold from palladium, platinum *etc.*

RESULTS AND DISCUSSION

Absorption spectra

Figure 1 shows the absorption spectra obtained when gold reacts with various TMK solutions; the absorbances are higher with the alcohol solutions of TMK. No colour developed when a methyl isobutyl ketone solution of TMK was used. The isopropyl alcohol solution gave the highest absorbance, but the

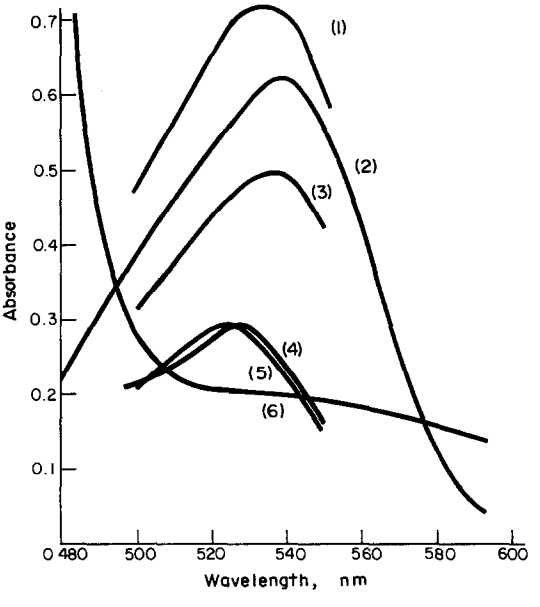

Fig. 1. Absorption spectra. TMK solution used: 5 ml of 0.01% (w/v) solution in (1) isopropyl alcohol; (2), (6) n-butyl alcohol; (3) isoamyl alcohol; (4) toluene; (5) n-butyl acetate. (1)–(5) Au 10 μg (absorbance against corresponding reagent blank); (6) reagent blank (absorbance against the TOA solution).

volume of the organic phase decreased more on shaking with the buffer solution, because of the higher solubility of isopropyl alcohol in the aqueous phase; the n-butyl alcohol solution was therefore adopted. The absorption maximum with the n-butyl alcohol solution is at 540 nm and in good agreement with that (545 nm) for the gold–TMK complex extracted into isoamyl alcohol;[6] this indicates that the reaction between bromoaurate and TMK proceeds in the organic phase in a manner similar to that reported by Cheng and Lott.[6]

Effects of experimental conditions

The optimal conditions for the extraction and determination of gold were investigated by using the general procedure but with variation of one parameter at a time.

An examination of the extraction of gold from 0.01–4*M* hydrobromic acid solutions showed that differences in the absorbances were negligible. A 0.05*M* hydrobromic acid concentration was therefore chosen.

The concentration of TOA in toluene was varied from 1 to 10% (v/v); the absorbance increased gradually as the TOA concentration increased and maximal absorbance was obtained with 6–10% (v/v) solution of TOA in toluene. This increase may be due to an increase in extractability of bromoaurate with increase in the TOA concentration. A 7% solution of TOA was chosen.

The shaking times for the extraction and the washing of the organic layer were varied from 2 to 10 min and from 1 to 5 min, respectively; the absorbances were independent of the shaking time in these ranges, and a 5-min extraction and a 2-min wash were selected.

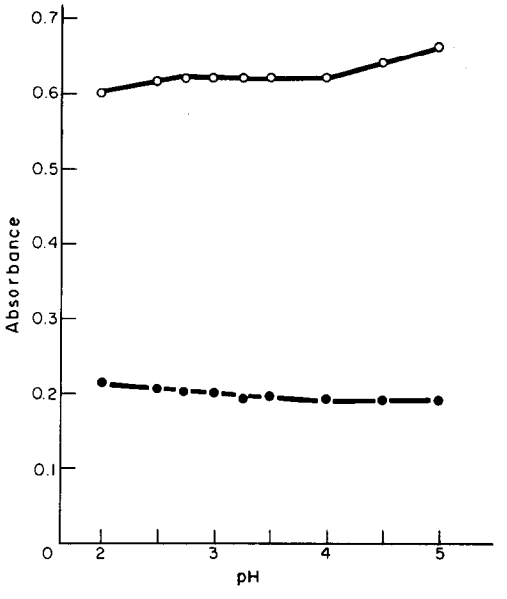

Fig. 2. Effect of pH of the buffer solution. (○) Au 10 μg, against reagent blank; (●) reagent blank, against the TOA solution.

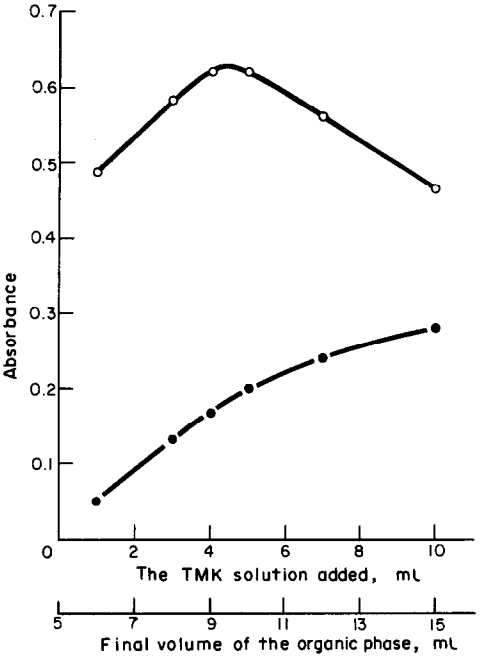

Fig. 3. Effect of amount of TMK solution added. (○) and (●) are as for Fig. 2.

For complete and stable colour development, it was necessary to shake the organic phase with an aqueous buffer solution after direct addition of the TMK solution to the organic (bromoaurate–TOA–toluene) phase; this phenomenon and the higher absorbances obtained with the alcohol solutions of TMK show that a highly polar medium is required for the reaction between bromoaurate and TMK. The absorbance measured against the corresponding reagent blank was independent of the shaking time in the range 1–4 min and of the pH of the buffer solution in the range 2.75–4.00 (Fig. 2). A 2-min shake and a pH of 3.2 were selected.

The amount of TMK solution adding to the organic phase was varied from 1 to 10 ml; maximal absorbance was obtained with 4.5 ml (Fig. 3). The decrease in the absorbance when more than 4.5 ml of TMK solution is used is probably due to a lowering of relative concentration of the gold–TMK complex with an increase in final volume of the organic phase. A 5.0-ml addition was adopted.

The absorbance measured against corresponding reagent blank increased as the TMK concentration in the TMK solution increased (Fig. 4). A 0.01% (w/v) solution of TMK was selected.

The colour faded slightly (by about 4%) during the first 30 min after the completion of colour development but little during the next hour; it is therefore desirable for higher reliability to measure the absorbance after about 30 min.

On the basis of these experimental results, the optimal conditions for the photometric determination of gold were established (the general procedure). Beer's law is obeyed over the range 0–10 μg of gold. The

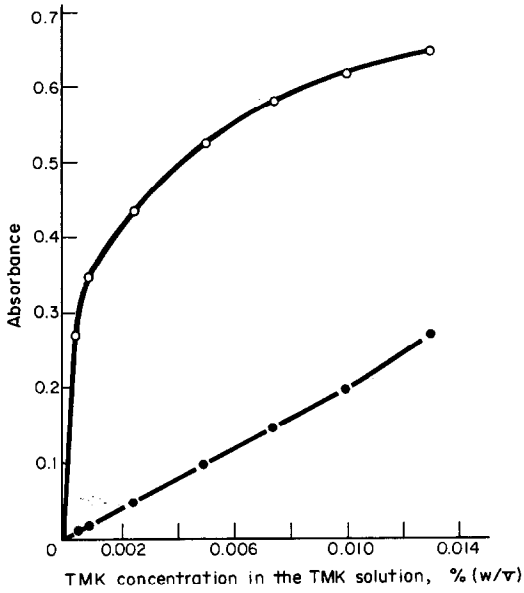

Fig. 4. Effect of TMK concentration in the TMK solution. (○) and (●) are as for Fig. 2.

apparent molar absorptivity at 540 nm is about 1.2×10^5 l.mole^{-1}.cm^{-1}, and the Sandell sensitivity-index is about 1.6×10^{-3} μg/cm^2. The molar absorptivity is lower than that obtained by the TMK–isoamyl alcohol extraction method;[6] the origin of the lower absorptivity is not clear, but is probably the presence of toluene or TOA in the organic phase.

Effects of various acids

It was found that hydrochloric acid up to 3*M*, nitric acid up to 3*M*, phosphoric acid up to 1*M*, or sulphuric acid up to 4*M* did not interfere. Hydrochloric and nitric acids present together in any proportion also did not interfere when their total concentration was below 3*M*.

The concentration of perchloric acid was varied from 0 to 3*M*; the absorbance measured against the corresponding reagent blank decreased gradually as the perchloric acid concentration increased, but the absorbance of the reagent blank measured against the TOA solution was independent of the perchloric acid concentration. The decrease is probably due to a lowering of the extractability of the bromoaurate ion in the presence of perchloric acid. On the other hand, the absorbance did not decrease (gold was not stripped) when the organic layer was washed with a solution 1*M* in perchloric acid (wash solution A), probably because of the high stability of the extracted bromoaurate–TOA complex.

Effects of various elements

There was no interference from 5 g of Pb^{2+}, 10 mg of Al^{3+}, As(III), Be^{2+}, Bi^{3+}, Ca^{2+}, Cd^{2+}, Ce^{4+}, Co^{2+}, Cr^{3+}, Fe^{3+}, Ga^{3+}, Ge(IV), In^{3+}, Mg^{2+}, Mn^{2+}, Mo(VI), Nb^{5+}, Ni^{2+}, Sb(V), Se(IV), Sn^{4+}, Ta^{5+}, Te(VI), Ti^{4+}, V(V), Y^{3+}, Zn^{2+}, Zr^{4+}, or 1 mg of Rh^{3+}, Ru^{3+}, Sb(III) and Tl^+.

Five grams of copper caused a slight positive error; the presence of hydrochloric acid or chloride enhanced the positive error, probably because of the formation of an extractable chloro-complex of copper. This positive error could be eliminated by washing the organic layer once with 50 ml of wash solution B and then twice with 20-ml portions of wash solution A, or twice with 50-ml portions of wash solution C and then once with 20 ml of wash solution A, when the concentration of hydrochloric acid or chloride was below 0.6*M* or 1.2*M* respectively.

One milligram of thallium(III) gave an absorbance equivalent to 1.6 μg of gold; this positive error could be eliminated by washing the organic layer twice with 50-ml portions of wash solution C and then once with 20 ml of wash solution A.

One microgram of palladium(II) and 0.1 mg of platinum(IV) gave absorbances equivalent to 1.3 μg and 0.8 μg of gold, respectively. These positive errors could be eliminated by performing the ethyl acetate extraction procedure employed by Hirano *et al.*[3] for the separation of gold from large amounts of copper; palladium and platinum were not appreciably extracted with ethyl acetate. It was found that, in the ethyl acetate extraction procedure, the addition of sodium chloride to the sample before the evaporation of ethyl acetate (see the recommended procedure) was effective for obtaining higher recovery of gold. In the absence of sodium chloride, lower and variable recoveries were occasionally obtained, probably because of the adsorption of some gold on the wall of the beaker at the time of drying; the effect of sodium chloride is probably due to retention of gold in the solid sodium chloride formed during the heating to dryness. The recovery of 10 μg of gold by the ethyl acetate extraction procedure was 93–95%.

Amounts of 0.1 mg of mercury(II) did not interfere, but 1 mg of mercury(II) gave an absorbance equivalent to 3.7 μg of gold; this positive error could also be eliminated by ethyl acetate extraction. Amounts of 0.1 mg of silver also did not interfere. In the presence of 1 mg of silver, a silver bromide precipitate was formed on the addition of hydrobromic acid, but it had no effect on the absorbance; it is, however, desirable to separate silver before the extraction of gold with TOA.

Analytical results

Gold in copper, silver, lead, blister copper, copper concentrate and anode slime was determined by the proposed method (Table 1); the gold contents in blister copper and anode slime, determined by the proposed method, are in good agreement with those determined by a fire-assay method. As little as 0.5 μg of gold in the sample taken or in the aliquot of the sample solution could be determined and the relative standard deviations (6 variates) in the determination of 1 and 10 ppm (added as standard gold solution) of gold in copper metal were 7.2 and 3.1%, respectively. The amounts of gold added to samples

Table 1. Analytical results for various samples

Sample	Sample taken, *g*	Au added,* *μg*	Total Au found, *μg*	Au content in the sample, *ppm*	Au content determined by fire-assay, *ppm*
Copper metal (V.M.C.)	5.0	0	0.98	0.21	
	5.0	0	1.08		
Copper metal (tough pitch)	5.0	0	0.70	0.14	
	5.0	0	0.70		
Copper metal (electrolytic)	5.0	0	0.54	0.11	
	5.0	0	0.60		
	5.0	5.0*	5.61		
	5.0	5.0*	5.52		
Blister copper	1.0	0	18.3	18	19
	1.0	0	18.0		
	1.0	20*	38.4		
	1.0	20*	37.8		
Blister copper	1.0	0	32.8	33	30
	1.0	0	33.9		
Lead metal	5.0	0	0.00	<0.2	
	5.0	0	0.40		
	5.0	10*	10.04		
	5.0	10*	10.66		
Lead metal	5.0	0	1.06	0.20	
	5.0	0	0.94		
Silver metal	2.0	0	10.36	5.7	
	2.0	0	11.12		
	2.0	20*	31.72		
	2.0	20*	32.20		
Copper concentrate	5.0	0	6.84	1.4	
	5.0	0	7.94		
	5.0	10*	15.70		
	5.0	10*	17.12		
Anode slime	1.0	0	2730	0.27%	0.25%
	1.0	0	2730		

*Gold, in the form of aliquots of standard gold solution, was added to the solid samples before the decomposition.

before the decomposition were recovered quantitatively (Table 1); this shows that no gold is retained in the lead chloride or silver chloride precipitates formed in the sample decomposition step. The slope of the calibration curve was found to vary from run to run, however; to obtain reproducible results, it is necessary to prepare a calibration curve along with each batch of samples analysed.

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VANADIUM(V) AS AN OXIDANT FOR THIOL COMPOUNDS

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Summary—Vanadium(V) is shown to oxidize a number of thiol compounds to the corresponding disulphides. A photometric procedure for the estimation of vanadium(V) in the presence of vanadium (IV) and diverse ions is described. A reinvestigation of the reaction of Se(IV) in 4–8*M* hydrochloric acid with thiosalicylic acid confirms that the Se(IV) acts purely as an oxidant to yield only the corresponding disulphide (RSSR) and not an equimolar mixture of RSSeSR and RSSR.

Studies on the vanadyl ion, VO^{2+}, are of continuing interest in our laboratories,[1] and a method for determining both vanadium(V) and vanadium(IV) in the same solution seems to us to be desirable.

Root[2] analysed mixtures of vanadium(IV) and vanadium(V) spectrophotometrically, but the error was about 5%. Fuller and Ottaway[3] titrated vanadium(IV) photometrically with bromate but did not study interferences. Thiomalic acid has been shown to reduce vanadium(V) instantaneously to vanadium (IV) and the kinetics of this reaction have been studied.[4] Accordingly, a detailed study of the reaction of thiol compounds with vanadium(V) has been undertaken with a view to applying it analytically.

EXPERIMENTAL

Reagents

Vanadium(IV) solutions. Prepared from reagent grade vanadyl sulphate, standardized and freshly diluted before use.

Vanadium(V) solutions. Prepared from ammonium vanadate and vanadium pentoxide, and standardized by permanganate titration after reduction with SO_2.

Buffer solutions. Prepared from 0.1*M* ammonium acetate, 0.1*M* acetic acid, 0.1*M* potassium acetate and 0.1*M* sodium hydroxide.

Freshly prepared aqueous solutions of pure thiomalic acid, thioglycollic acid and thiourea, and an aqueous ethanolic solution of thiosalicylic acid were used.

Procedures

Absorbance measurements were made in matched 1-cm silica cells with a Unicam SP 500 spectrophotometer; the spectra were recorded with a Unicam SP 800 spectrophotometer. Infrared spectra were measured (KBr discs) on a Unicam SP 1200 spectrophotometer.

All polarographic measurements were made on a Sargent model XVI recording polarograph at 27 ± 0.1°. An external saturated calomel electrode was used as reference electrode. The D.M.E. had the following characteristics: $m = 2.01$ mg/sec, $t = 5$ sec (in 2.0*M* potassium nitrate at zero applied potential *vs.* S.C.E.). Oxygen-free nitrogen was used to deaerate the solutions. The half-wave potentials and numbers of electrons involved in the electrode reactions were estimated by the method of Heyrovský and Ilkovič[5] from a plot of E *vs.* $\log i/(i_d - i)$ where i_d = diffusion current.

A Pye model 290 pH-meter with glass and calomel electrodes was used. All photometric titrations were done in 50-ml cells with an EEL titrator (No. 609 filter).

Reactions with thiomalic acid

The absorbance at 775 nm was measured for solutions containing 2 ml of 0.1*M* ammonium vanadate, 2 ml of 0.1*M* thiomalic acid and 2 ml of a 0.1*M* solution of a potentially interfering ion and made up to 20 ml with distilled water. The experiments were repeated with 3 ml of 0.1*M* ammonium vanadate, 3 ml of 0.2*M* thiomalic acid, 1 ml of 0.2*M* vanadyl sulphate and 3 ml of 0.1*M* interferent, made up to 15 ml with distilled water.

Isolation of oxidation products of thiosalicylic acid

Oxidation with lead tetra-acetate. A solution containing 1.54 g of thiosalicylic acid in 40 ml of glacial acetic acid was heated at 49–53° and 2.44 g of lead tetra-acetate were added slowly (2 hr). The mixture was stirred at 50° for a further 2 hr, cooled to 25° and poured into 200 ml of water. The pale yellow solid obtained was filtered off, washed and dried at 80°, then purified by repeated extraction with ether and air-dried (m.p. 286°; found, C 54.6%, H 3.5%, S 20.7%; calculated for $C_{14}H_{10}O_4S_2$, C 54.90%, H 3.27%, S 20.91%).

Oxidation with vanadium(V). A brownish yellow solid of m.p. 290° was obtained by treating an aqueous alcoholic solution of thiosalicylic acid with an excess of ammonium vanadate solution, extracting several times with ether, drying the combined ether extracts with anhydrous Na_2SO_4 and removing the ether. Found, C 54.7%, H 3.6%, S 20.8%; calculated for $C_{14}H_{10}O_4S_2$, C 54.90%, H 3.27%, S 20.91%.

Oxidation with selenium(IV).[6] To 25 ml of a solution prepared by treating 0.1542 g of thiosalicylic acid with 0.3–0.6 ml of 2*M* sodium hydroxide and diluting to 50 ml, were added 50 ml of sodium acetate–hydrochloric acid buffer of pH = 2.3 and 10 ml of a solution of selenium(IV) in conc. hydrochloric acid (prepared by adding 0.0789 g of pure selenium to a mixture containing 10 ml of conc. hydrochloric acid and 2 ml of conc. nitric acid, warming to expel brown fumes and diluting to 50 ml). The solution was extracted with ether, and the ether removed. A brownish yellow solid m.p. 288° was obtained; found, C 54.6%, H 3.8%, S 20.2%; calculated for $C_{14}H_{10}O_4S_2$, C 54.90%, H 3.27%, S 20.91%.

Absorption spectra of the oxidation products

Solutions of all three oxidation products of thiosalicylic acid obtained, all of which have been identified as the disulphide, were prepared by dissolving 0.0152 g of each compound in 0.05–0.10 ml of 2*M* sodium hydroxide and diluting to 50 ml. To 1.50 ml of each solution were added 5 ml of a sodium acetate–hydrochloric acid buffer

(pH = 2.3) and distilled water to make up to 50 ml. These solutions were then each extracted with 20 ml of ethyl acetate and the absorption spectra of the extracts recorded against a solvent blank. A similar experiment was done with 1.50 ml of thiosalicylic acid solution (prepared by dissolving 0.0154 g of thiosalicylic acid in 0.1 ml of 2*M* sodium hydroxide and diluting to 100 ml with distilled water), 5 ml of the pH 2.3 buffer and distilled water to make up to 50 ml, the resulting solution being extracted with 20 ml of ethyl acetate and the absorption spectrum recorded as before.

RESULTS AND DISCUSSION

Photometric titrations

A photometric titration of a solution of vanadium(V) in dilute sulphuric acid with thiomalic acid indicated a reacting ratio of 1:1 ± 0.1, both in presence and absence of vanadium(IV). An attempt to reoxidize the vanadium(IV) by titration with bromate was unsuccessful, probably because of interaction of the bromate with the thiomalic acid oxidation products.

An analytical procedure for the estimation of vanadium(V)

Solutions of vanadium(V) reduced by an excess of thiomalic acid were found to obey Beer's law over a wide range of absorbance values from 0.1 to 0.9 for vanadium contents from 0.5 to 2.5 mg/ml. Table 1 shows that with the amounts of interfering ions used in this study little or no effect is noted both in the presence of comparable amounts of TiO^{2+}, Fe^{3+}, Ni^{2+}, Co^{2+}, Zn^{2+} and in the presence of even larger amounts of UO_2^{2+} and Cd^{2+}. However, interference was noted in the presence of Nb(V), Cr^{3+}, Al^{3+}, Mg^{2+}, Fe^{2+} and F^-.

The vanadium(V) content in a mixture with vanadium(IV) can be estimated from the absorbances at 775 nm before and after treatment with thiomalic acid. Table 2 shows the effect of some diverse ions on this estimation.

Table 1. Interference from diverse ions in the estimation of vanadium(V)*

Vanadium taken, *mg/ml*	Ion added	Amount added, *mg/ml*	Vanadium found *mg/ml*
0.484	UO_2^{2+}	2.380	0.484
0.484	TiO^{2+}	0.480	0.484
0.484	Fe^{3+}	0.560	0.484
0.484	Ni^{2+}	0.585	0.478
0.484	Co^{2+}	0.590	0.478
0.484	Nb^{5+}	0.930	0.509
1.284	Al^{3+}	0.675	1.207
1.284	Fe^{2+}	1.400	1.350
1.284	F^-	0.475	1.146
1.284	Zr^{4+}	2.280	1.284
0.484	Cr^{3+}	0.520	0.509
1.284	Mg^{2+}	0.610	1.256
1.284	Cd^{2+}	2.810	1.299
1.284	Zn^{2+}	1.635	1.275

* Cations were added as their nitrate, sulphate or chloride and anions as their potassium salt.

Table 2. Interference from representative diverse ions in the estimation of vanadium(V) in the presence of vanadium(IV)*

Vanadium taken, *mg/ml*	Ion added	Amount added, *mg/ml*	Vanadium found, *mg/ml*
1.165	UO_2^{2+}	3.570	1.177
1.165	TiO^{2+}	0.715	1.165
1.165	Ni^{2+}	0.885	1.177
1.165	Al^{3+}	0.405	1.146
1.165	Fe^{3+}	0.885	1.165
1.165	F^-	0.285	1.127
1.165	Na^+	0.350	1.165

* Cations were added as their nitrate, sulphate or chloride and anions as their potassium salt.

Reactions of vanadium(V) with other thiol compounds

A solution containing vanadium(V) instantaneously turned blue on the addition of thioglycollic acid, giving λ_{max} at 775 nm, characteristic of vanadium(IV). Photometric titration showed a 1:1 reaction. The reduction was not affected by the presence of vanadium(IV). An equimolar solution of vanadium(V) and thiosalicylic acid turned blue on standing for more than 12 hr, giving the characteristic absorption of VO^{2+} at 775 nm, whereas an equimolar solution of vanadium(V) and thiourea gave no reaction even in 24 hr, but if a tenfold excess of thiourea was used, the solution turned blue after 3 min, with the characteristic λ_{max} at 775 nm.

Nature of the products of oxidation of thiol compounds with vanadium(V)

The oxidation products of the thiol compounds were soluble in water and were found not to react with vanadium(V), nor with Co^{2+} and Cu^{2+}, both of which form brownish purple complexes with thiomalic, thioglycollic and thiosalicylic acids. Aqueous solutions of the oxidation products of the thiol compounds gave negative results in characteristic tests for the –SH group.

A comparison of the infrared spectra of the oxidation products of thiomalic acid, thiosalicylic acid and thiourea with those of the parent compounds showed the following characteristics. The band found at 2520 cm^{-1} for thiomalic acid and at 2500 cm^{-1} for thiosalicylic acid, attributable to the –SH stretching frequency[7] was absent in the oxidation products; a very weak band at 460 cm^{-1} for the oxidation product of thiosalicylic acid may be assigned to the –S–S– stretching frequency, but this band was barely discernible for the oxidation product of thiomalic acid. The infrared spectrum of thiourea had strong bands at 3120 and 3250 cm^{-1} which could be attributed to the –NH stretching frequency, but these bands were not discernible in the spectrum of the oxidation product. A very weak band at 420 cm^{-1} for this oxidation product could be due to the presence of an –S–S– group; the band at 1600 cm^{-1} due

to a –C–N stretching frequency in thiourea shifted to 1680 cm^{-1} for the oxidation product, and this frequency could be assigned to –C=N stretching. These characteristic differences clearly indicate the oxidation of thiol compounds to their disulphides by vanadium(V).

Oxidation products of thiol compounds with other reagents

Lead tetra-acetate[8] is known to oxidize thiosalicylic acid to its disulphide, to give a whitish solid with m.p. 293–295°. Cresser and West[6] report that selenium(IV) forms a complex with thiosalicylic acid at pH 0.5–2.5 with a metal to ligand ratio of 1:3. This complex was said to be characterized by absorption maxima at 268 and 315 nm.

Buděšínský and Svec[9] have investigated the reaction of thiosalicylic acid, RSH, with selenious acid, H_2SeO_3, in 4–8*M* hydrochloric acid and describe the formation of an equimolar mixture of compounds of the type RSSeSR and RSSR. The possible role of selenium(IV) in concentrated hydrochloric acid as a powerful oxidant for dithizone has also been reported.[10]

We therefore oxidized thiosalicylic acid with lead tetra-acetate and selenium(IV) according to the original procedures[6,8] and by vanadium(V) and compared the absorption spectra of identical concentrations of the oxidation products. They were practically identical. A comparison of the infrared spectra of the three oxidation products also showed identical characteristics. These two facts and the similarity of the analyses of the products showed that only one compound was formed, $C_{14}H_{10}O_4S_2$.

The polarograms of equimolar solutions of the oxidation products of thiosalicylic acid obtained by all three methods gave well-defined cathodic waves with identical $E_{\frac{1}{4}}$ values of −0.262 V. The plots of log $i/(i_d - i)$ *vs.* E were linear, showing that the oxidation product undergoes reversible cathodic reduction.[5] Bubbling SO_2 through an aqueous ethanolic solution of the oxidation product of thiosalicylic acid obtained by using selenium(IV) in 6*M* hydrochloric acid according to the methods of Cresser and West[6] and of Buděšínský and Svec[9] gave no precipitation or red colour due to colloidal selenium, showing that the product could not contain any compounds of the type RSSeSR claimed by Buděšínský and Svec. The possibility of selenium(IV) acting purely as an oxidant

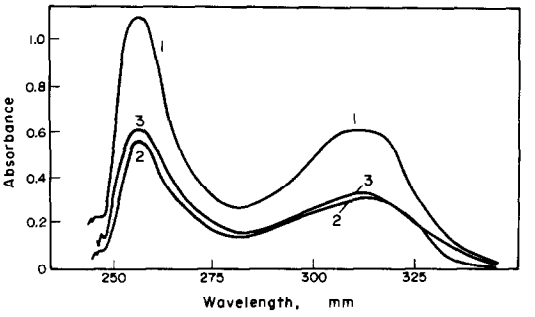

Fig. 1. Absorption spectra of (1) oxidation product of thiosalicylic acid with selenium(IV) in HCl, extracted into ethyl acetate (pH = 1.5, 1.5 × $10^{-5}M$) *vs.* solvent; (2) thiosalicylic acid extracted into ethyl acetate (pH = 1.5, 1.5 × $10^{-5}M$), *vs.* solvent; (3) difference spectrum, (1) *vs.* (2).

seems to have been overlooked by these workers. This is surprising since the redox potential for the system $H_2SeO_3 + 4H^+ + 4e = Se + 3H_2O$ ($E° = 0.74$ V) will be dependent on the hydrogen-ion activity. In concentrated acid, selenium(IV) is a fairly strong oxidant. All the evidence points to the role of selenium (IV) in 6*M* hydrochloric acid as purely oxidative to yield RSSR compounds. The non-existence of the "selenium complex" of thiosalicylic acid does not, of course, invalidate the spectrophotometric method[6] for determining selenium, because it is the oxidation product of thiosalicylic acid which produces the spectrum with λ_{max} at 268 and 315 nm, Fig. 1.

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SHORT COMMUNICATIONS

POLAROGRAPHIC BEHAVIOUR OF SOME *o*-HYDROXYKETOXIMES

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Summary—The polarographic behaviour of three *o*-hydroxyketoximes, $CH_3C_6H_3(OH)CR{=}NOH$, where R = CH_3, C_2H_5 and C_3H_7, has been studied in 5% ethanolic medium, with potassium chloride as supporting electrolyte. A single four-electron reduction wave is obtained which diminishes with increase in pH, being replaced by a new wave in alkaline media. A trough is formed on the limiting-current plateau at higher negative potentials. A mechanism has been proposed for the reduction at the dropping mercury electrode.

This paper describes polarographic investigations on three *o*-hydroxyketoximes, *viz.* 2-hydroxy-5-methylacetophenoneoxime (HMAO), 2-hydroxy-5-methylpropiophenoneoxime (HMPO) and 2-hydroxy-5-methylbutyrophenoneoxime (HMBO).

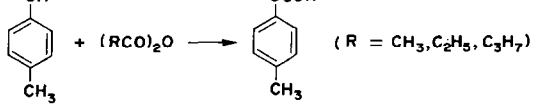
These compounds have been used for spectrophotometric and gravimetric determination[1] of some metal ions. Their metal chelates, studied recently,[2] are of importance as bio-inorganic models. Apart from its analytical nature the present work is aimed towards exploring the behaviour of these compounds at the dropping mercury electrode, as it has direct bearing on their donor properties.

The polarographic behaviour of simple as well as of *N*- and *O*-substituted oximes has been studied by earlier workers.[3–13] The *o*-hydroxyketoximes form a special case for study owing to (*i*) the possible complications that may arise from the intramolecular hydrogen-bonding evidenced by infrared studies[2,14] and (*ii*) the fact that only the phenolic proton is released, while the oxime group remains non-ionized under the experimental conditions.[1]

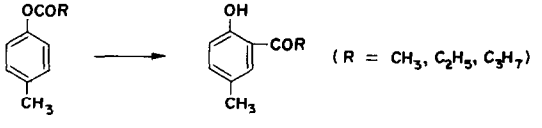
EXPERIMENTAL

Preparation of the oximes

The *p*-methylphenyl esters were first prepared by treatment of *p*-cresol with the corresponding anhydride in the presence of conc. sulphuric acid as catalyst:



The 2-hydroxy-5-methylphenyl ketones were then obtained by the Fries migration reaction:



For preparation of the oximes the phenones were dissolved in ethanol and treated with a solution of hydroxylamine hydrochloride containing sodium acetate, the mole ratio of these reactants being 1:2:3 (phenone:hydroxylamine:acetate). The mixture was heated on a water-bath for about 1 hr, then poured into water. The *o*-hydroxyketoximes were collected and recrystallized from alcohol.

Apparatus

A manual polarograph recommended by Kolthoff was used[15] with a saturated calomel electrode as reference electrode. All potential measurements were made on a Leeds and Northrup potentiometer calibrated with a standard cadmium cell. The capillary used had the following constants: flow-rate (m) = 0.7 mg/sec, drop-time (t) = 1.00 sec, mercury height (h) = 32.5 cm.

Solutions

Ethanolic 0.01*M* solutions of the compounds were prepared. The buffer (McIlvaine) and electrolyte solutions were prepared from reagent grade chemicals.

Techniques

Polarograms were recorded for solutions containing 8.5 ml of buffer, 1.0 ml of supporting electrolyte (1.0*M* potassium chloride) and 0.5 ml of the oxime solution, and deaerated by passage of nitrogen which had been purified by bubbling through vanadous sulphate solution and doubly distilled water. A slow stream of nitrogen was passed above the surface of the solution while the polarograms were recorded. All measurements were made at 20.0 ± 0.1°.

RESULTS AND DISCUSSION

In all three cases a single four-electron reduction wave is obtained in acid and neutral media. A trough on the limiting current plateau is also observed at more negative potentials. In alkaline media, the wave practically disappears and a new wave makes its appearance. The polarograms are typified by the characteristics given in Table 1.

The reducible group is the oxime group. Simple oximes are known to show two waves on the polarographic curve, corresponding to reduction of the acid and base forms of the oxime group; the ratio of the heights of the two waves changes with the pH-value of the solution, in the form of a dissociation curve. Except in 0.65*M* sodium hydroxide, the three *o*-hydroxyketoximes studied here ionize only at the phenolic group.[1] The question of the base form of the oxime group therefore does not arise. With variation in pH, though the compounds will exhibit the acid–base equilibrium involving the phenolic group, only the oxime group will react at the electrode, and then always in its acid form.

Table 1. Characteristics of the polarograms

Acidity	HMAO		HMPO		HMBO	
	i_d*	$E_{1/2}$†	i_d*	$E_{1/2}$†	i_d*	$E_{1/2}$†
1.2*M* HCl	5.60	0.875	5.10	0.870	5.90	0.880
pH 3.00	8.50	0.980	8.70	0.985	8.20	0.970
pH 5.40	6.90	1.150	7.40	1.130	6.90	1.120
pH 6.85	1.90	1.205	2.00	1.210	2.40	1.225
pH 8.27	0.20	1.250	0.24	1.300	0.40	1.250
	0.40	1.050	0.40	1.100	0.24	1.030
pH 10.50	0.24	1.050	0.14	1.04	0.14	1.04
0.65*M* NaOH	—	—	—	—	—	—

* μA.
† V *vs.* S.C.E.

These three compounds therefore show only one wave in acid and neutral media. With increase in pH the diffusion current decreases* in the form of a dissociation curve, as expected from the shift of the equilibrium,

$$CH_3C_6H_3(OH)CR{=}NOH \rightleftharpoons CH_3C_6H_3(O^-)CR{=}NOH$$

In alkaline medium the wave practically disappears, but a new wave makes its appearance which is independent of oxime concentration, but dependent on mercury-column height and seems to be an absorption prewave occurring before the reduction wave of the ionized species, which is not covered in the potential region studied.

The trough on the limiting current plateau observed at higher negative potentials is independent of the addition of various salts and thus resembles that described for chromates.[16] Such an observation is common for several oximes and may be attributed either to the effect of potential on rate and/or equilibrium constants in the vicinity of the electrode, or to decrease (with increase of negative potential) in the concentration of one of the species which take part in the recombination reaction at the electrode surface.

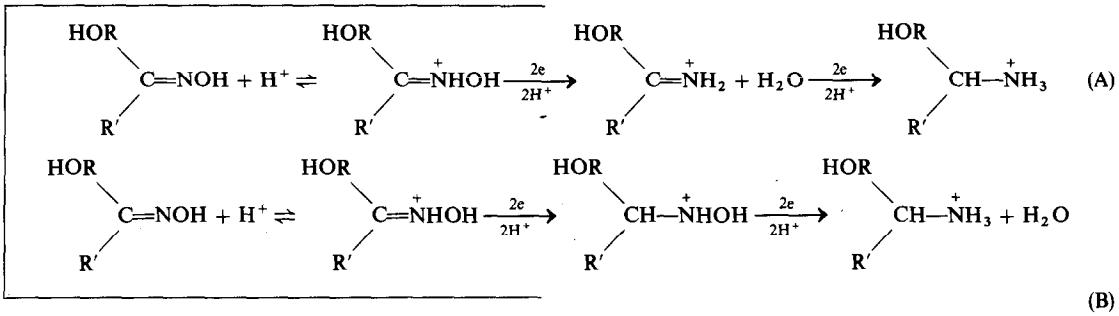
With increasing pH the $E_{\frac{1}{2}}$ shifts to more negative potentials by 50 mV/pH.

Determination of the oximes

The diffusion current was found to be a linear function of oxime concentration in acidic medium. It is also directly proportional to the square root of the height of the mercury column, for both acid and neutral media, indicating a diffusion-controlled electrode reaction. However, only 1.2*M* hydrochloric acid medium, with which the wave is free from the complications of trough formation, is recommended for preparation or analytical purposes.

Mechanism of the electrode process

The four-electron reduction of the compound may follow course A or B, both resulting in the formation of an amine as a final product:



but (B) seems the less likely.[17]

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*It also decreases on fairly strong acidification, presumably because of internal hydrogen-bonding.

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CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—XXVII. INFLUENCE OF MAGNESIUM ON MASKING OF CALCIUM WITH FLUORIDE IN THE DETERMINATION OF MANGANESE

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Summary—Determination of manganese in the presence of calcium and magnesium after their masking with ammonium fluoride was reinvestigated. Normally such a determination gives low results caused by co-precipitation of manganese with calcium fluoride. It has been found that the co-precipitation is highest when magnesium is absent in the solution. With increasing concentration of magnesium ions co-precipitation of manganese decreases and at the ratio Ca:Mg = 0.5–1 is entirely eliminated. An explanation of this phenomenon is discussed.

Ammonium fluoride is very powerful masking agent in complexometry. It forms stable water-soluble complexes with almost all quadri- and tervalent metal ions. In a few cases sparingly soluble salts are formed. For example iron(III) can be masked by precipitation of K_3FeF_6.[1] Ammonium fluoride was proposed more than 20 years ago for masking calcium and magnesium in the determination of zinc.[2] This cannot be considered as true "masking", however, since it depends on precipitation of the insoluble calcium and magnesium fluorides. Other bivalent metals can be determined similarly to zinc,[3] with the exception of manganese. Wehber and Johannsen[4] observed that the results for manganese by direct EDTA titration were always low in the presence of precipitated calcium fluoride. The errors increased with increasing quantity of calcium. This can be attributed to the adsorption of manganese on the surface of the calcium fluoride, since back-titration of an excess of EDTA with manganese solution yields reliable results.[5] Recently Frenzel[6] recommended direct titration of manganese with 0.02–0.1*M* EDTA in 50% ethanol, with Eriochrome Black T as indicator, masking aluminium with triethanolamine, 10–15 mg of iron with 2 g of tartaric acid, and calcium together with magnesium by addition of 2.5 g of ammonium fluoride. He stated that the ethanol decreases the solubility of the calcium fluoride and prevents adsorption of manganese.

Recently we have developed a new method for the determination of calcium in the presence of very large amounts of magnesium.[7] The method could also be used for determination of the sum of Ca + Mn. The problem still to be solved was the direct determination of the manganese. We therefore reinvestigated the well-known masking of calcium and magnesium with ammonium fluoride. Direct EDTA titration of manganese in the presence of precipitated calcium fluoride led—as expected—to results 10–20% lower than the correct value, but the results became closer to the correct value with increasing concentration of magnesium in the solution. Preliminary experiments indicated that at a Ca:Mg ratio in the range 0.5–1 the results were satisfactory. This interesting phenomenon, which had previously escaped the attention of other investigators, is reported in this communication.

EXPERIMENTAL

Reagents

Solutions of EDTA, manganese sulphate and magnesium sulphate (0.05*M*) were prepared by dissolving appropriate amounts of reagent grade salts in 1 litre of redistilled water. Calcium chloride solution (0.05*M*) was prepared by dissolving calcium carbonate in the required amount of hydrochloric acid and diluting to 1 litre with redistilled water. All these solutions were standardized complexometrically.

Further reagents include solid ammonium fluoride, solid hydroxylamine hydrochloride, 50% triethanolamine solution. The indicators were thymolphthalexone and Eriochrome Black T (mixed in 1:100 ratio with potassium nitrate).

Effect of magnesium ions on precipitation of CaF_2

The test solutions were prepared in 250-ml titration flasks by mixing 2–20 ml of 0.05*M* calcium, 2–10 ml of 0.05*M* manganese and 0–40 ml of 0.05*M* magnesium, diluting to 100 ml with redistilled water, adding 1 g of hydroxylamine hydrochloride and 2–4 g of ammonium fluoride and swirling till the added solids had dissolved. After addition of 10 ml of 50% triethanolamine solution and a small amount of thymolphthalexone the solutions were slowly titrated with 0.05*M* EDTA. The consumption of titrant corresponding to the first disappearance of the blue colour was noted. In cases when adsorption of manganese took place the blue colour returned. A small addition of EDTA usually sufficed to complete the titration, *i.e.*, the colour did not reappear within 2–3 min after the final addition of EDTA. Low results were always obtained when an insufficient amount of magnesium was present, even with a 2–3 min delay in the titration at the end-point.

Table 1 gives the two values of EDTA consumption, the first for the first disappearance of the blue colour, the second for the "end" of the titration. The errors in the last column are based on the second values.

We have obtained similar results for the titration of manganese in pH-10 ammonia/ammonium chloride buffer with Eriochrome Black T as indicator. The addition of

Table 1. Determination of manganese after masking of calcium and magnesium with NH_4F

Taken, 0.05*M* solutions, *ml*					Difference	
Mn	Ca	Mg	[Ca]:[Mg]	0.05*M* EDTA, *ml**	*ml*	%
3	0	0		3.12		
3	5	0		2.64–2.68	0.44	14.1
3	5	1	5	2.86–2.90	0.22	7.1
3	5	2	2.5	3.06–3.10	0.02	0.6
3	5	5	1	3.04–3.08	0.04	1.3
3	5	13	0.4	3.12–3.12	0.00	0.0
3	20	3	6.7	2.44–2.56	0.56	17.9
3	20	5	4	2.70–2.76	0.36	11.5
3	20	10	2	3.06–3.12	0.00	0.0
5	0	0	—	5.27		
5	10	0	—	4.16–4.38	0.89	16.9
5	10	5	2	5.24–5.24	0.03	0.6
5	20	5	4	4.60–4.64	0.63	12.0
5	20	10	2	5.18–5.22	0.05	1.0
9	0	0	—	9.50		
9	10	0	—	8.74–8.80	0.70	7.4
9	20	0	—	7.50–7.96	1.54	16.2
9	10	5	2	9.30–9.36	0.14	1.5
9	10	8	1.2	9.40–9.46	0.04	0.4
9	10	10	1	9.44–9.48	0.02	0.2
9	10	40	0.25	9.54	+0.04	+0.4
9	20	10	2	9.20–9.34	0.16	2.1
9	20	16	1.2	9.22–9.40	0.10	1.1
9	20	20	1	9.38–9.48	0.02	0.2

* First value indicates the first disappearance of blue colour, which returns more or less slowly. The second value indicates the "true" end-point at which the blue colour does not reappear during 2–3 min.

ethanol did not prevent the adsorption of manganese in the absence of magnesium ions. For example, for the titration of 5.27 ml of 0.05*M* manganese in the presence of 10 ml of 0.05*M* calcium we used only 4.16–4.25 ml of 0.05*M* EDTA; with 5 ml of 0.05*M* magnesium also present the result was 5.14–5.22 ml of 0.05*M* EDTA.

DISCUSSION

The favourable influence of magnesium ions in diminishing or even eliminating the adsorption capacity of calcium fluoride for manganese ions can be explained by assuming that co-precipitation of MgF_2 with CaF_2 changes the surface activity of the precipitate. Alternatively it is possible to assume that the surface of the CaF_2 is covered with MgF_2 which precipitates slowly and possesses different properties. The first explanation is supported by the fact that the correct titration results are obtained only when calcium and magnesium are precipitated together. When magnesium solution was added to already precipitated calcium fluoride the titrations were unacceptable, giving both low results and a sluggish colour change of the indicator.

The optimum Ca:Mg ratio is not dependent on the amount of manganese present in the solution. This may be taken as a hint at possible formation of a "double" calcium magnesium fluoride although such a compound has never been described in the literature.

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POTENTIOMETRIC APPLICATIONS OF THE RESPONSE OF A SODIUM-SELECTIVE GLASS ELECTRODE TO SILVER

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Summary—The use of a sodium-sensitive glass electrode for the determination of silver ion is demonstrated.

Glass electrodes are normally used for measurements of pH and the activity of alkali-metal ions such as sodium and potassium. The relationship between glass composition and response to specific ions was studied by Lengyel and Blum,[1] and Eisenman *et al.*[2,3] The latter demonstrated that the selectivity of glass electrode membranes is dependent in a systematic way on the glass composition.

In this communication a standard sodium-selective electrode is used as an indicator electrode for the potentiometric titration of silver ions. Although some non-glass ion-selective electrodes can be used as indicators for this titration, the use of glass electrodes for this purpose may come in handy. Glass electrodes are not poisoned by cyanide or sulphides during measurements. On the other hand they might be affected by fluoride and concentrated alkali.

One of the problems with glass electrodes is that none seems to be more selective for metal ions than for hydrogen. It is therefore necessary to raise the pH of the test solution if the metal ion response of the electrode is to be observed. The manufacturers of this particular electrode recommend, for example, that the pH must be 4 units larger than pNa if sodium-ion measurements are to be made.[4]

EXPERIMENTAL

All chemicals used were of analytical reagent grade. A Beckman 39278 glass electrode was studied as a silver-ion sensor. As reference electrode a Beckman 39170 fibre-junction saturated calomel electrode was used. When necessary, ammonium nitrate–agar salt bridges were used. All potential measurements were made with a Beckman Research Model pH meter.

Calibration curves (plots of cell e.m.f. against the logarithm of cation activity in the metal nitrate solutions) were prepared for H^+, Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Ag^+ and Tl^+. The activity coefficients were calculated[5] by using the equation $\log f = 0.51\, z^2\, \mu^{1/2}/(1 + \mu)$.

RESULTS AND DISCUSSION

The slopes of the calibration curves for Na^+, H^+, Ag^+ were close to the theoretical Nernst value. Although the calibration curves for K^+, Rb^+ and Cs^+ were linear, the slopes were too small to be of any use in the potentiometric determination of these ions. Tl^+ gave a non-linear calibration.

pH and selectivity

In order to determine the working pH-range for the electrode, e.m.f. measurements were made in 10^{-1}, 10^{-2} and $10^{-3}M$ silver solutions over a pH range of 1–7. The results indicate that for these silver concentrations the pH has a definite influence on the cell e.m.f., which decreases with increasing pH to a constant value when $a_{Ag^+}/a_{H^+} \geqslant 100$. The manufacturer recommends that for reliable measurements the pH should be at least 3 units larger than the highest pAg. If, however, a set of curves like those described is prepared, it can be seen precisely at which pH values meaningful measurements are still possible.

In the absence of interfering cations the electrode potential is given by $E_1 = E_0 + S\log a_{M^+}$ and in presence of both primary and interfering ions it is $E_2 = E_0 + S\log [a_{M^+} + K_{MN}\, a_{N^+}]$ where E_0 is a constant, S the slope of the calibration curve for the primary ion, a_{M^+} and a_{N^+} the activities of the primary and interfering ions respectively and K_{MN} the selectivity coefficient. With the aid of these equations and the calibration curves obtained in presence of various concentrations of interfering ions, various selectivity coefficients were found by using Moody and Thomas's breaking-point method.[6]

The values obtained were 0.034 for $K_{Ag,H}$, 0.009 for K_{AgNa}, 3.4 for K_{NaH} and 295 for K_{NaAg}. The value for K_{NaH} is much lower than those reported in the literature,[7–9] presumably because our value was determined without addition of buffer or background electrolyte. The value for K_{NaAg} is comparable with those in the literature.[10] It is clear that although the electrode is normally used as a sodium-sensitive glass electrode the selectivity is $Ag^+ > H^+ > Na^+$. This was also quantitatively indicated by Budd.[11]

Analytical use of the electrode

Standard-addition potentiometry.[12] If the sample and the standard solutions are prepared in such a way that the ionic strength is kept high and almost constant, the activity coefficient of the ion in question and the liquid-junction potential do not change appreciably. In order to select a salt which can be used to adjust the ionic strength of solutions to a suitable value, calibration curves for the silver function of the electrode were prepared for 0.10, 0.25, 0.50 and 1.00M magnesium nitrate solutions. The presence of magnesium ions at these concentrations had no influence on the slope of the calibration curves.

As the slope of the calibration curve is used in the calculations this technique can only be applied to silver ion concentrations which fall on the linear part of the curve, *i.e.*, for silver concentrations larger than $10^{-6}M$.

When this method was applied to the determination of small amounts of silver: 0.27, 2.7, 27.0 and 269.7 mg in 25-ml samples kept at constant ionic strength (0.1M magnesium nitrate, error-free results were obtained in all cases.

Sample solutions (25 ml) containing 0.27 mg of silver in the presence of 0.19, 1.59 and 7.62 g of Cu^{2+} or 0.25, 1.0

Table 1. Results and titration conditions for use of a glass electrode as a silver-ion indicator

Ion	Titrant	Amount of ion taken mg	Mean recovery, %	Standard deviation %	Titration conditions
Ag^+	KCl	2.7	99.8	0.4	Mg acetate buffer
		12.0	100.0	0.2	pH 4.7
		28.9	100.0	0.1	
Ag^+	KBr	2.7	99.9	0.5	pH 4.7
		12.0	100.0	0.1	
		28.9	100.0	0.3	
Ag^+	KI	2.7	100.0	0.4	pH 4.7
		12.0	100.0	0.1	
		28.9	99.8	0.2	
Ag^+	thiourea	2.7	101.0	0.1	0.1*M* Mg nitrate
		12.0	99.9	0.3	pH 6.7
		27.0	100.0	0.2	
CN^-	$AgNO_3$	0.65	99.4	0.3	Ammonium acetate buffer
		6.5	100.0	0.0	pH 6.7
$[Fe(CN)_6]^{4-}$	$AgNO_3$	0.13	101.7	8.3	Mg acetate buffer
		0.66	99.9	0.5	pH 4.8
		1.3	100.1	0.2	
		13.2	100.0	0.1	
$[W(CN)_8]^{4-}$	$AgNO_3$	2.5	100.0	1.7	Mg acetate buffer pH 4.7
		4.9	100.6	0.3	
		24.5	100.3	0.2	
$[W(CN)_8]^{3-}$	$AgNO_3$	2.5	106.1	1.0	Ammonium acetate buffer
		4.9	100.4	0.2	pH 6.7
		24.5	99.6	0.3	
$[Mo(CN)_8]^{3-}$	$AgNO_3$	2.5	100.2	0.8	pH 6.7
		10.0	100.1	0.2	
		25.3	100.1	0.2	
$[Mo(CN)_8]^{4-}$	$AgNO_3$	1.9	100.6	0.5	pH 6.7
		15.0	100.3	0.1	
		17.6	100.1	0.1	
Ascorbic acid	$AgNO_3$	22.0	100.0	0.3	Mg acetate buffer
		44.0	100.0	0.2	pH 4.7

and 5.0 g of Tl^+ or 0.20, 1.6 and 7.8 g of Zn^{2+} all gave error-free results when analysed for silver by the standard-addition potentiometric method. In the presence of soluble mercury (I) and (II) salts erroneous results were found.

Titrations. Because the electrode is sensitive to sodium and hydrogen ions as well as to silver ions it is necessary to exclude sodium ions from titration mixtures and to buffer sample solutions at the required pH values. Acetic acid–magnesium acetate buffer solutions are suitable.

In the case of Cl^-, Br^- I^- and thiourea best results were found when these species were used as titrants. For CN^-, $Fe(CN)_6^{4-}$, $W(CN)_8^{3-}$, $W(CN)_8^{4-}$, $Mo(CN)_8^{3-}$ and $Mo(CN)_8^{4-}$ silver nitrate is used as the titrant.

Results and titration conditions are summarized in Table 1.

The results show that these glass electrodes can be used in argentometric titration.

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NORMAL PULSE POLAROGRAPHIC STUDY ON THE EFFECT OF HYDROLYSIS AT AN ELECTRODE, AND THE Mn(II)-CATALYSED REDUCTION OF NITRATE AND NITRITE

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Summary—In neutral unbuffered solutions containing dissolved oxygen, the normal pulse polarograms of certain metal ions [Pb(II), Cd(II), Zn(II), Co(II) and Mn(II)] produce peaks on the limiting plateaux. These peaks reflect the reduction of hydroxide species formed in the vicinity of the electrode. It has been found that $Mn(OH)_2$ formed at the electrode surface exerts a catalytic effect on the reduction of nitrate and nitrite ions, with formation of OH^-.

In normal pulse polarography, potential pulses of gradually increasing amplitude superimposed on a constant initial potential are applied to the electrode. The initial potential is usually chosen in a region where no faradaic process takes place, and normal pulse polarography gives a current–voltage curve similar to that obtained with d.c. polarography. However, when the initial potential chosen is one at which either faradaic or chemical reactions do occur, it can be expected that the resulting polarogram will be different from the conventional d.c. polarogram.

In neutral unbuffered solutions containing dissolved oxygen, the increase in pH in the vicinity of the electrode can lead to hydrolysis of the discharging heavy metal ions. Although the presence of hydrolysed species in the vicinity of the electrode is known,[1] their detailed nature is not. The main reason for this is that the hydroxide species do not give reduction waves in d.c. polarography.

There have been no reports in the literature on the use of normal pulse polarography for investigating these systems. This paper reports on the application of normal pulse polarography to gain further information on the effect of hydrolysis at the electrode, and to evaluate the role of the hydroxide species in the electrode process.

During the course of this investigation, both nitrate and nitrite ions were found to produce a catalytic polarographic wave in the presence of $Mn(OH)_2$ in the vicinity of the electrode. A tentative explanation for the catalytic reaction is also presented.

EXPERIMENTAL

Polarograms were recorded with a PAR (Princeton Applied Research) Polarograph, Model 174. The drop-time of the DME was controlled at 1.0 sec by a Mechanical Drop Time Controller, Model 172-A. Polarograms were recorded on a Riken Denshi *X–Y* Recorder, Model D-8C. The pH-values of the test solutions were measured with a Toa Denpa pH Meter, Model HM-8. The capillary had an $m^{2/3}t^{1/6}$ value of 1.45 $mg^{2/3}.sec^{-1/2}$ in 0.1*M* potassium nitrate and in open circuit. A three-electrode system was used with an external saturated calomel electrode (SCE) as a reference electrode and a platinum wire as auxiliary electrode. The solutions were deoxygenated with nitrogen. All experiments were carried out at 25 ± 0.1°.

All chemicals were of reagent grade and were used without further purification.

RESULTS AND DISCUSSION

The normal pulse polarogram of Mn(II) in neutral unbuffered solutions containing dissolved oxygen consists of two reduction waves, the second of which has a peak. Figure 1(A) shows typical normal pulse polarograms for Mn(II) in 0.1*M* lithium sulphate solution at pH 5.2. Similar peaks have also been observed for Pb(II), Cd(II), Zn(II) and Co(II) under these conditions.

Dissolved oxygen is reduced in two stages at the DME:

1st wave: $O_2 + 2H_2O + 2e = H_2O_2 + 2OH^-$ (from 0 to −0.2 V)

2nd wave: $H_2O_2 + 2e = 2OH^-$ (from −0.8 to −1.2V)

Buffering the solution (at pH 5.2) and removing the dissolved oxygen from the solution causes the second peak to disappear and the first wave to become better defined [Fig. 1(C)]. This result indicates that the second peak is not connected with peroxide formation but with formation of hydroxide ion by reduction of dissolved oxygen. These second peaks may reflect the reduction of the hydroxide species formed in the vicinity of the electrode at the initial potential.

Figure 2 shows the influence of the initial potential on the peak heights. The peaks for Pb(II), Cd(II), Zn(II) and

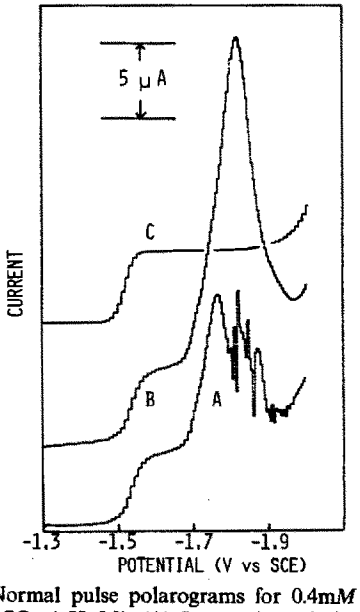

Fig. 1. Normal pulse polarograms for 0.4m*M* Mn(II) in 0.1*M* Li_2SO_4 (pH 5.2). (A) In a quiet solution with dissolved oxygen. (B) In a stirred solution with dissolved oxygen. (C) In the absence of dissolved oxygen. Initial potential; −1.3 V.

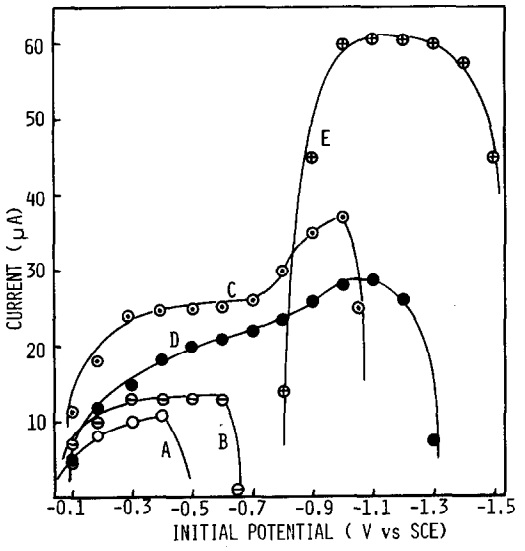

Fig. 2. Effect of initial potential on peak heights for 1m*M* solutions of (A) Pb(II), (B) Cd(II), (C) Zn(II), (D) Co(II) and (E) Mn(II). Supporting electrolyte. (A) 0.1*M* KNO_3, (B) (D) 0.1*M* KCl and (E) 0.1*M* Li_2SO_4. Each solution (pH 5–6) contained dissolved oxygen.

Co(II) started to appear when the initial potential was set at potentials more negative than −0.1 V, while that for Mn(II) was obtained only when the initial potential was set in the range from −0.8 to −1.5 V, where the reduction of hydrogen peroxide takes place. This suggests that in the presence of peroxide, no $Mn(OH)_2$ is formed in the vicinity of the electrode. The significance of the initial potential may thus be interpreted in terms of the oxidation of $Mn(OH)_2$ by peroxide arising from the reduction of dissolved oxygen.

The concentration of hydroxide ion increases in the vicinity of the electrode, because of reduction of the peroxide. Therefore, the peak current for Mn(II) becomes several times as large as that for Pb(II), Cd(II), Zn(II) or Co(II). The sharp drop in the peak current is caused by the direct reduction of each metal ion at the initial potential.

It is well established that adsorption of a depolarizer on the electrode is accompanied by appearance of a peak on the normal pulse polarogram.[2–5] Therefore, these second peaks may be attributed to the adsorption of the hydroxides on the DME.

All the peak currents decreased with increasing concentration of the supporting electrolyte. This effect can be interpreted if it is assumed that coagulation of colloidal hydroxides takes place, the hydroxides in the colloidal state are electroactive, and the flocculated hydroxides cannot form an adsorbed film on the electrode surface.[6]

As shown in Fig. 2, the peak currents reach values of about 10–60 μA. These high currents may arise from the reduction of both adsorbed and colloidal hydroxide species in the vicinity of the electrode.

The effect of hydrogen peroxide on the second peaks was investigated in deoxygenated solutions. For Zn(II), Co(II) and Mn(II), the second peaks appeared when the initial potential was set at potentials more negative than −0.8 V (where the reduction of peroxide takes place). For Cd(II), no second peak was obtained because the aquocation is reduced at potentials where peroxide is reduced to hydroxide and no $Cd(OH)_2$ can be formed at the initial potential. However, in the case of Pb(II), the second peak did appear. According to Strnad, who first observed catalytic waves in the system Pb(II)–H_2O_2 in neutral unbuffered solutions, the catalytic current may be attributed to the oxidation of Pb(II) by peroxide to Pb(IV), which is then rapidly reduced at the electrode.[7] The appearance of the second peak under these conditions indicates that hydroxide is generated in the vicinity of the electrode by the catalytic reaction.

The effect of nitrate and nitrite on the second peak for Mn(II) ion

The presence of nitrate or nitrite caused an increase in the current on the rising portion of the Mn(II) reduction wave in Tast polarography. Typical Tast polarograms are shown in Fig. 3 for 0.4m*M* Mn(II) in 0.1*M* potassium nitrate containing dissolved oxygen (pH 5.5). The shape of the polarogram resembles a polarographic maximum. However, it differs from a maximum in that the height of the wave depends on the concentration of nitrate or nitrite (Fig. 4). The temperature coefficients of the nitrate and the nitrite reduction waves were 3.1 and 3.8 %/deg respectively, indicating that the reaction mechanism is kinetic in nature.

As shown in Fig. 3(C), the catalytic wave disappears either when the solution is buffered (pH 5.5) or when the dissolved oxygen is removed from the solution, and decreases when the concentration of the supporting electrolyte is increased. These results were similar to those observed for the second peak in normal pulse polarography.

In order to check the effect of peroxide and hydroxide on the catalytic wave, a known concentration of hydrogen peroxide was added to the oxygen-free solution: this gave rise to the catalytic wave, but addition of an acetate buffer (pH 5.2) caused this wave to disappear, just as addition of buffer did when dissolved oxygen was present. Therefore, any contribution from peroxide (arising from the reduction of dissolved oxygen) to the catalytic reaction is negligible.

The nitrate catalytic wave was obtained over the pH range 4.0–9.7. This range corresponds to that in which the second peak was obtained in normal pulse polarography, as shown in curves (A) and (B) of Fig. 5. The effect

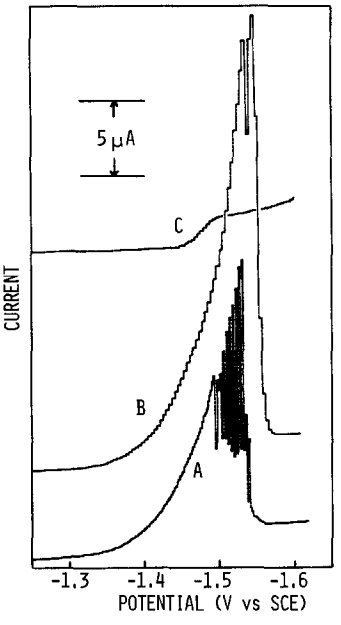

Fig. 3. Tast polarograms for 0.4m*M* Mn(II) in 0.1*M* KNO_3 (pH 5.5) containing dissolved oxygen. (A) In a quiet solution. (B) In a stirred solution. (C) In an acetate buffer solution (pH 5.5).

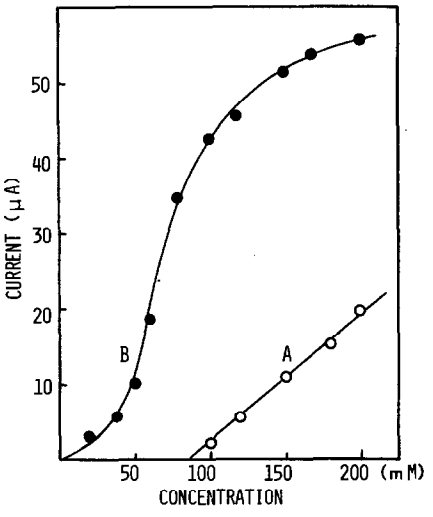

Fig. 4. Catalytic currents as a function of concentration of nitrate or nitrite ion for 0.4m*M* Mn(II) in 0.1*M* Li_2SO_4 containing dissolved oxygen. (A) Nitrate ion. (B) Nitrite ion.

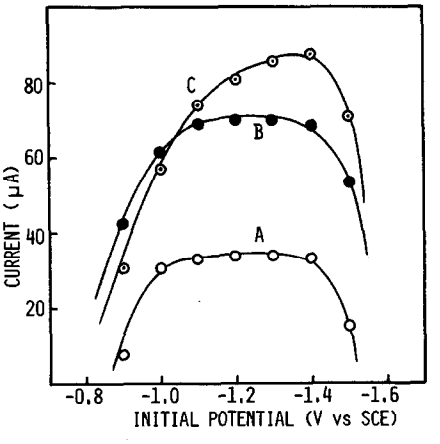

Fig. 6. Relationship between initial potential and height of the second peak in normal pulse polarography. (A) 0.4 m*M* Mn(II) in 0.1*M* Li_2SO_4 containing dissolved oxygen (pH 5.4). (B) Solution (A) with 100m*M* $NaNO_3$ (pH 5.8). (C) Solution (A) with 20m*M* $NaNO_2$ (pH 6.0).

of pH on the nitrite reduction wave is also shown in Fig. 5, in which curve (C) was obtained with Mn(II) present and curve (D) with only nitrite. Even in the absence of Mn(II) the nitrite wave, which was highly irreversible, and had a half-wave potential of −0.95 V, appeared below pH 5.0, while the catalytic wave was observed in the pH range 5.0–9.7. No catalytic reaction was observed in the pH region where nitrite gave a reduction wave at the DME.

Figure 6 displays the relationship between the initial potential and the current of the second peak in normal pulse polarography for 0.4m*M* Mn(II) in 0.1*M* lithium sulphate solution containing dissolved oxygen. When either nitrate or nitrite was added, no variation in the normal pulse polarogram was observed as long as the initial potential was set in the region where no second peak would appear (*i.e.*, more positive than −0.8 V). However, the second peak did increase in the presence of nitrate or of nitrite when the initial potential was set between −0.9 and −1.5 V, indicating that a necessary condition for the catalytic reaction to proceed was the formation of a film of $Mn(OH)_2$ adsorbed on the electrode surface.

The most likely mechanism is that $Mn(OH)_2$ at the electrode surface is oxidized by nitrate (or nitrite) ion to Mn(III) hydroxo-complexes (and/or MnO_2) which will be reduced at the DME, giving rise to the catalytic reduction current. Since many different species exist on the electrode surface during the course of the catalytic reaction, the reaction mechanism will probably be more complex than this.

However, the result in Fig. 6 shows that hydroxide produced as a result of the catalytic reaction is directly related to the formation of $Mn(OH)_2$. This explains the increase in the height of the second peak by the catalytic reaction. The effect of the supporting electrolyte on the catalytic wave in Tast polarography may also be ascribed to the coagulation of colloidal $Mn(OH)_2$.

The catalytic waves of nitrate and nitrite show an irregular alternation of high and low currents in Tast polarography [Fig. 3(A)]. In order to get information on this wave shape, the current–time curves of an individual drop were recorded. The *i–t* curves obtained for the catalytic wave also showed this repetition of high and low currents. Stirring of the solution by means of a magnetic stirrer produced reproducible *i–t* curves for every drop and also eliminated the anomalous behaviour in Tast polarography [Fig. 3(B)].

As shown in Fig. 1(A), the current of the second peak varied irregularly when the capillary of the mechanical drop-time controller was agitated mildly (the amplitude of the drop-release motion can be adjusted in the PAR model). When the solution was stirred, this anomalous behaviour disappeared [Fig. 1(B)]. This result suggests that the production of $Mn(OH)_2$ cannot be reproduced exactly on every drop in a quiet solution, which would explain the anomalous form of the catalytic wave in Tast polarography.

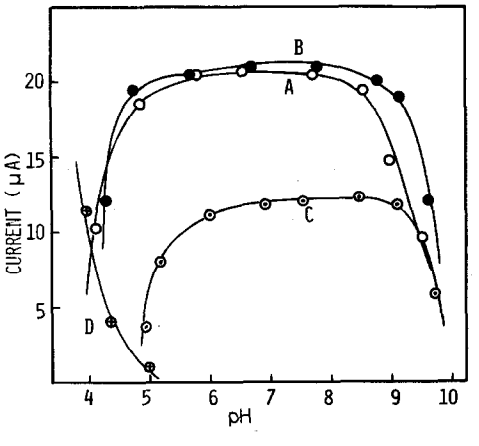

Fig. 5. Effect of pH on the catalytic wave and on the second peak. Normal pulse polarography. (A) 0.4m*M* Mn(II) in 0.1*M* Li_2SO_4 containing dissolved oxygen. Initial potential; −1.2 V. Tast polarography. (B) Solution (A) with 200m*M* $NaNO_3$. (C) Solution (A) with 20 m*M* $NaNO_2$. (D) 20m*M* $NaNO_2$ alone in 0.1*M* Li_2SO_4.

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DETERMINATION OF SILICA IN SILICATES BY FORMATION OF 12-MOLYBDOSILICIC ACID AND REDOX TITRATION OF MOLYBDENUM(III)

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Summary—An indirect titrimetric method for the determination of silica in silicates is described. A boron trioxide–lithium carbonate (10:1) mixture is used as flux and the melt is dissolved in an acidic molybdate solution to form 12-molybdosilicic acid. The yellow complex is extracted with methyl isobutyl ketone (MIBK) and, after removal of the co-extracted molybdate reagent, is decomposed with alkali. The resultant aqueous phase is acidified and passed through a Jones reductor to convert the molybdenum(VI) into molybdenum(III), which is then titrated with potassium permanganate. The method has high precision and accuracy. Phosphorus, titanium, zirconium and vanadium, in amounts that may occur in silicate rocks, do not interfere; at least 5% P_2O_5, 5% TiO_2, 2% ZrO_2 and 0.5% V_2O_5 are permissible. Fluorine (at least 2%) can also be tolerated when lithium metaborate is used as flux.

Indirect amplification methods have been published for the determination of silicon by atomic-absorption spectrometry of the twelve molybdenum atoms associated with each silicon atom in 12-molybdosilicic acid, after its selective extraction into an organic solvent.[1–4]

This paper describes an indirect titrimetric method for the determination of silica in silicates, by formation of 12-molybdosilicic acid, its selective extraction with methyl isobutyl ketone (MIBK), washing of the organic extract with dilute hydrochloric acid to remove excess of molybdate, decomposition of the 12-molybdosilicic acid with dilute ammonia solution and transfer of the molybdenum to the alkaline aqueous phase, acidification with sulphuric acid, reduction to molybdenum(III) in a Jones reductor, then titration with potassium permanganate. A similar procedure has been used by Kirkbright *et al.* for the determination of phosphorus.[5]

EXPERIMENTAL

Reagents

Iron(III) phosphate solution. Prepare 1 litre of solution containing 48.5 g of $NH_4Fe(SO_4)_2 \cdot 12H_2O$, 40 ml of 85% phosphoric acid and 50 ml of concentrated sulphuric acid.

Apparatus

Ultrasonic generator. Operating frequency, 20 kHz; cavitation bath, 16 cm diameter, 10 cm height; power density in the cavitation bath, 2 W/cm^2.

Jones reductor. Prepare and store conventionally.[6] If the reductor has been standing idle, pass 100 ml of sulphuric acid (1 + 19) through it and then a little cold water.

Procedure

Transfer 0.1000–0.1500 g of the finely powdered sample (<200 mesh), containing 50–70 mg of silica, to a 30-ml platinum crucible. Add 1.00 g of boron trioxide and 0.10 g of lithium carbonate and mix intimately with a short glass rod with rounded ends. Heat carefully with a small flame until any water is completely expelled, then cover the crucible and heat with a strong flame (*ca.* 1000°). After fusion for 30 min, allow the crucible to cool to room temperature.

Weigh out 8.0 g of sodium molybdate, $Na_2MoO_4 \cdot 2H_2O$, transfer to a 1000-ml beaker and dissolve in about 700 ml of distilled water. Add, with stirring, 6.0 ml of concentrated hydrochloric acid and then place the crucible in the solution contained in the beaker. Rinse the cover of the crucible into the beaker with distilled water. Put the beaker in the cavitation bath of the ultrasonic generator until the cake becomes detached from the crucible (*ca.* 1 min). Then stir magnetically (Teflon-coated stirrer bar) until the melt dissolves (about 20 min) forming a yellow molybdosilicic acid solution. Remove and rinse the crucible with distilled water. Transfer the yellow solution to a 1000-ml volumetric flask and dilute to volume with distilled water.

Transfer a 50-ml aliquot to a 250-ml separating-funnel and add 16.0 ml of concentrated hydrochloric acid to make the solution about 3*M* in HCl. Then add 75 ml of MIBK and shake for 5 min. Allow adequate time for the layers to separate and transfer the aqueous phase (containing most of the molybdate excess and any unextracted 12-molybdosilicic acid) to a second 250-ml separating funnel, retaining the organic phase in the first one. Rinse the organic phase with a 2–3 ml of water. Add 50 ml of MIBK

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Indirect amplification methods have been published for the determination of silicon by atomic-absorption spectrometry of the twelve molybdenum atoms associated with each silicon atom in 12-molybdosilicic acid, after its selective extraction into an organic solvent.[1–4]

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Jones reductor. Prepare and store conventionally.[6] If the reductor has been standing idle, pass 100 ml of sulphuric acid (1 + 19) through it and then a little cold water.

Procedure

Transfer 0.1000–0.1500 g of the finely powdered sample (<200 mesh), containing 50–70 mg of silica, to a 30-ml platinum crucible. Add 1.00 g of boron trioxide and 0.10 g of lithium carbonate and mix intimately with a short glass rod with rounded ends. Heat carefully with a small flame until any water is completely expelled, then cover the crucible and heat with a strong flame (*ca.* 1000°). After fusion for 30 min, allow the crucible to cool to room temperature.

Weigh out 8.0 g of sodium molybdate, $Na_2MoO_4 \cdot 2H_2O$, transfer to a 1000-ml beaker and dissolve in about 700 ml of distilled water. Add, with stirring, 6.0 ml of concentrated hydrochloric acid and then place the crucible in the solution contained in the beaker. Rinse the cover of the crucible into the beaker with distilled water. Put the beaker in the cavitation bath of the ultrasonic generator until the cake becomes detached from the crucible (*ca.* 1 min). Then stir magnetically (Teflon-coated stirrer bar) until the melt dissolves (about 20 min) forming a yellow molybdosilicic acid solution. Remove and rinse the crucible with distilled water. Transfer the yellow solution to a 1000-ml volumetric flask and dilute to volume with distilled water.

Transfer a 50-ml aliquot to a 250-ml separating-funnel and add 16.0 ml of concentrated hydrochloric acid to make the solution about 3*M* in HCl. Then add 75 ml of MIBK and shake for 5 min. Allow adequate time for the layers to separate and transfer the aqueous phase (containing most of the molybdate excess and any unextracted 12-molybdosilicic acid) to a second 250-ml separating funnel, retaining the organic phase in the first one. Rinse the organic phase with a 2–3 ml of water. Add 50 ml of MIBK

to the second separating-funnel, shake for 5 min and discard the aqueous phase.

Add 25 ml of 1*M* hydrochloric acid to each of the separating-funnels, shake both for 30 sec and allow the layers to separate. Take the first funnel, discard the aqueous phase, and rinse the funnel tip with distilled water (do this after all transfers of aqueous phases). Transfer the aqueous phase from the second funnel to the first. Shake the first funnel for 30 sec and then discard the aqueous phase. Shake the organic phase in the second funnel with 25 ml of 1*M* hydrochloric acid for 30 sec and transfer the aqueous phase to the first funnel. Shake this for 30 sec, allow the layers to separate, and discard the aqueous phase. Transfer the organic phase from the second funnel to the first. Add 30 ml of 1*M* ammonia solution to the funnel and shake for 30 sec. Drain the aqueous phase into a 100-ml beaker. Add another 30 ml of 1*M* ammonium hydroxide, shake for 30 sec, drain the aqueous phase into the beaker and rinse the funnel with distilled water into the beaker.

Add 6 ml of concentrated sulphuric acid to the solution containing the molybdenum. Transfer 35 ml of iron(III) phosphate solution to the receiver of the Jones reductor, and then enough water so that the tip of the reductor dips well beneath the surface of the solution. Draw the cold solution of molybdenum through the reductor. Wash the beaker and reductor successively with 50 ml of sulphuric acid (1 + 19) and then transfer the two 50-ml aliquots of distilled water. Titrate the solution in the receiver with 0.05*N* potassium permanganate.

Make a blank determination, passing successively through the reductor 150 ml of sulphuric acid (1 + 19) and 100 ml of distilled water.

RESULTS AND DISCUSSION

The attack on the sample and the preparation of the solution must ensure the conversion of all silica into the monomeric silicic acid in order to form 12-molybdosilicic acid. A fusion technique employing a boron trioxide–lithium carbonate (10:1) flux was chosen for its speed, simplicity and effectiveness in silicate decomposition as shown in previous studies.[7–9] The dissolution of the cake in an acidic molybdate solution ensures the complete depolymerization of silica and the formation of the 12-molybdosilicic acid. In the dissolution step, sufficient hydrochloric acid is added to lower the pH to 1.3. The correct amount of acid was empirically determined, as the presence of molybdate alters the pH of the solution. The complete formation of the yellow molybdosilicate complex is obtained by the presence of a relatively high excess of molybdate reagent.

An aliquot for analysis should contain no more than 3.5 mg of SiO_2; otherwise the extraction of 12-molybdosilicic acid with the organic solvent is hindered.

Extraction of 12-molybdosilicic acid with MIBK was used to permit the separation of other molybdoheteropoly acids eventually present and also the subsequent removal of the co-extracted molybdate. The extractability of molybdoheteropoly acids in MIBK was studied recently.[10] Molybdosilicic acid has a maximum distribution ratio of approximately 720 from 0.08–4.0*M* hydrochloric acid and thus can be quantitatively extracted over this range. 12-Molybdosilicic acid can be selectively extracted in the presence of molybdophosphoric and molybdoarsenic acids at an acidity $\geqslant 2.5M$ hydrochloric acid. Three washings are needed to remove the excess of molybdate from the extract.

The method was tested with analysed samples (Table 1). The relative errors are less than 0.1%. The six results for the soda feldspar gave a standard deviation of 0.02$_3$%.

Synthetic samples were prepared with a soda feldspar containing 65.49% of SiO_2, to which amounts of the following potentially interfering elements were added: phosphorus, arsenic, titanium, zirconium, vanadium, niobium, tantalum and fluorine. Particular attention was given to phosphorus, titanium, and zirconium because small amounts of these elements may occur in silicate minerals and rocks, and they might be expected to interfere with the method by virtue of their tendency to hydrolyse or form the heteropoly acids.[11–14].

The results obtained with synthetic samples (Table 2) indicate that phosphorus, titanium, zirconium and vana-

Table 1. Results obtained in the determination of silica in silicate standard samples

Sample	Composition, %	SiO_2 found, %	Relative error, %
Soda feldspar (U.S.N.B.S., No. 99)	SiO_2, 68.66; Al_2O_3, 19.06; Fe_2O_3, 0.067; MgO, 0.053; CaO, 0.36; Na_2O, 10.73; K_2O, 0.41; TiO_2, 0.017; P_2O_5, 0.142; MnO, <0.001; BaO, 0.01	68.62 68.60 68.62 68.64 68.60 68.66	−0.06 −0.09 −0.06 −0.03 0.00 −0.09
Plastic clay (U.S.N.B.S., No. 98)	SiO_2, 59.11; Al_2O_3, 25.54; Fe_2O_3, 2.05; TiO_2, 1.43; ZrO_2, 0.041; P_2O_5, 0.08; V_2O_5, 0.025; Cr_2O_3, 0.021; CaO, 0.21; MgO, 0.72; K_2O, 3.17; Na_2O, 0.28; SO_3, 0.07; MnO, 0.005; CuO, 0.009	59.07	−0.07
Flint clay (U.S.N.B.S., No. 97)	SiO_2, 42.87; Al_2O_3, 38.77; Fe_2O_3, 0.98; TiO_2, 2.38; ZrO_2, 0.25; P_2O_5, 0.08; V_2O_5, 0.040; Cr_2O_3, 0.079; CaO, 0.10; MgO, 0.26; K_2O, 0.54; Na_2O, 0.33; SO_3, 0.042; MnO, 0.002; CuO, 0.003	42.83	−0.09
Burst refractory (U.S.N.B.S., No. 76)	SiO_2, 54.69; Al_2O_3, 37.67; Fe_2O_3, 2.38; TiO_2, 2.21; ZrO_2, 0.07; MgO, 0.58; CaO, 0.27; K_2O, 1.37; Na_2O, 0.38; P_2O_5, 0.069; V_2O_5, 0.021	54.64	−0.09

Table 2. Results obtained in the determination of silica in synthetic mixtures prepared with a soda feldspar containing 65.49% of SiO_2

Additions	SiO_2 found, %	Relative error, %
2% TiO_2	65.43	−0.09
5% TiO_2	65.42	−0.11
5% P_2O_5	65.46	−0.05
2% P_2O_5 + 5% TiO_2	65.47	−0.03
5% P_2O_5 + 5% TiO_2	65.46	−0.05
5% P_2O_5 + 5 TiO_2 + 1% ZrO_2	65.46	−0.05
5% P_2O_5 + 5 TiO_2 + 2% ZrO_2	65.41	−0.12
0.5% V_2O_5	65.41	−0.12
1.0% V_2O_5	65.32	−0.26
5% As_2O_5	65.43	−0.09
2% Nb_2O_5	64.34	−1.79
2% Ta_2O_5	65.01	−0.61
2% F (fusion with B_2O_3-Li_2CO_3 10:1)	64.34	−1.76
2% F (fusion with $LiBO_2$)	65.44	−0.08

dium, in amounts that usually occur in silicate rocks, do not interfere: at least 5% P_2O_5, 5% TiO_2, 2% ZrO_2 and 0.5% V_2O_5 are permissible. (The presence of 5% As_2O_5 is also admitted.) Niobium and tantalum interfere. The presence of fluorine yields low results when the sample is fused with boron trioxide–lithium carbonate (10:1) mixture, because some silicon is lost while fluorine volatilizes; but good results are obtained by using a lithium metaborate flux to decompose the sample.

The association of twelve molybdenum atoms with each atom of silicon in 12-molybdosilicic acid and the reduction of the molybdenum(VI) to molybdenum(III) before titration of the latter with standard potassium permanganate gives an amplification factor of 36. Ordinarily, an amplification method is not used for the determination of major constituents, but in this instance it allows the use of a small aliquot and, hence, the separation of interferents by extraction of 12-molybdosilicic acid under selective conditions. The complete analysis can be performed in less than 4 hr.

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RADIOTRACER STUDIES ON ION-SELECTIVE MEMBRANES BASED ON POLY(VINYL CHLORIDE) MATRICES

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Summary—Radiotracer studies with ^{45}Ca, ^{89}Sr and ^{133}Ba have provided evidence that the permeation of magnesium, strontium and barium ions through PVC membranes containing Orion 92-20-02 liquid ion-exchanger is inhibited by their low affinity for the liquid ion-exchanger sites. Experiments with ^{7}Be indicate a strong affinity of the membrane for beryllium ions with corresponding inhibition of permeation. When acid is present in the solution on one side of the membrane, preferential permeation by protons may lead to transport of ions against their concentration gradient in order to maintain the balance of charge.

Previous studies with ^{45}Ca and ^{36}Cl have shown that poly(vinyl chloride) (PVC) membranes containing Orion 92-20-02 liquid ion-exchanger are permselective to counter-cations and that permeation of calcium ions from calcium chloride solutions through the membranes into solutions of the chloride of a Group (II) metal can be explained in terms of solvent extraction and electrode selectivity.[1] An important parameter in the liquid ion-exchanger batch of the earlier study[1] was the quantity $d(C''/C')/dt$ under conditions when the tracer flux was time-independent. Use of this parameter has now been extended to membranes where the calcium ion-exchanger has previously been converted into other forms and a wider range of radioactive tracers is employed.

EXPERIMENTAL

Methods

Membranes were prepared by a standard procedure.[2–4] Experiments involved monitoring the movement of a radiotracer at 35° between two solutions ($10^{-3}M$ metal chlorides) separated by a membrane in an assembly which permitted the solutions to be stirred and also sampled from time to time.[1] Samples of 0.01 ml (0.1 ml for ^{7}Be experiments) were taken from the solutions on each side of the membrane with a Lang-Levy auto-zero micropipette and then spotted onto discs of Whatman No. 1 filter paper 2.1 cm in diameter. The paper discs were placed on a planchette and dried under an infrared lamp, and their activity was measured with a Geiger-Müller mica end-window tube.

The activity in the membrane at the end of each experiment was measured by placing the membrane, sliced off from the supporting PVC tubing, on a planchette under the Geiger-Müller tube in the same position as the filter paper discs.

Liquid ion-exchanger suitable for incorporation into the PVC membrane was prepared from Orion 92-20-02 liquid ion-exchanger (Ca-form): 50 ml of chloroform containing 5 g of the exchanger were shaken with four 50-ml portions of a 0.1 *M* aqueous solution of the appropriate metal chloride. The chloroform was allowed to evaporate at room temperature, leaving the converted exchanger. The beryllium form was truly liquid like the original calcium form, but the barium and strontium forms looked like a half-set jelly, though this did not affect preparation of the membrane.

In a few experiments some hydrochloric acid was added to the $10^{-3}M$ metal chloride solution on one side of the membrane.

Preparation of solutions containing radiotracers

The various experiments involved the use of $10^{-3}M$ solutions of the appropriate metal(II) chloride on both sides of the membrane, with the solution on one side containing the radiotracer, namely, the β-emitting ^{45}Ca and ^{89}Sr and γ-emitting ^{133}Ba and ^{7}Be isotopes.

For the calcium experiments, 0.1 ml of radioactive 0.1*M* calcium chloride solution of activity *ca.* 0.5 mCi/ml was diluted to 10 ml with demineralized water and made up accurately to 50 ml with $10^{-3}M$ calcium chloride.

A $10^{-3}M$ solution of radioactive strontium chloride was prepared by diluting 0.349 ml of 0.287*M* solution of *ca.* 1.42 mCi/ml activity to 100 ml with demineralized water. Ten ml of this solution were accurately diluted to 50 ml with $10^{-3}M$ strontium chloride.

For the barium experiments, 2 ml of radioactive $1.51 \times 10^{-4}M$ barium chloride solution of *ca.* 0.12 mCi/ml activity were added to 10 ml of $1.017 \times 10^{-3}M$ barium chloride.

The radioactive beryllium chloride was supplied as 0.1*M* hydrochloric acid with a beryllium content of less than 0.01 μg/ml. Solid beryllium oxide (1.25 mg/ml) was added to give a 0.05*M* beryllium chloride solution of which 1 ml was accurately diluted to 50 ml with demineralized water to give a solution with an activity of *ca.* 10 μCi/ml. Because of the weak γ-emission, 0.1-ml samples of beryllium chloride solutions were used, but with less frequent sampling than for the other metal(II) chloride experiments.

RESULTS

The results relate to the passage of alkaline-earth metal ions between $10^{-3}M$ solutions of their chlorides separated by a PVC membrane-containing Orion 92-20-02 liquid ion-exchanger in the required form and based on a dialkylphosphate sensor plus phosphonate mediator; one of the solutions, for some of the experiments, was $10^{-2}M$ in hydrochloric acid.

Where migration of radiotracers is observed, it is conveniently represented by $d(C''/C')/dt$ for those conditions where the tracer flux between the initially inactive (tracer concentration, C'') and active (tracer concentration, C') solutions increases linearly with time. The results obtained are presented in Table 1, which also includes some figures for the amount of radiotracer found in the membrane at the end of the experiment. Zero values for $d(C''/C')/dt$ indicate that no measurable amount of tracer appeared on the initially inactive side.

Except for the experiments with ^{7}Be, where the γ-emis-

Table 1. Time-independent $d(C''/C')/dt$ data for PVC membranes containing Orion 92-20-02 liquid ion-exchanger and placed between two alkaline-earth metal chloride solutions

Experiment series no.	Form of exchanger in membrane	Active solution,* $10^{-3}M$	Inactive solution, $10^{-3}M$	$10^7 \times d(C''/C')/dt$ sec^{-1}	Proportion of radiotracer in membrane at end of experiment, %
Membrane composition: 0.40 g of liquid ion-exchanger plus 0.17 g of PVC					
Batch A of Orion 92-20-02 liquid ion-exchanger					
1	Ca	$CaCl_2$	$CaCl_2$	10.8	1.7
2	Be	$BeCl_2$	$BeCl_2$	0	39 Two 72 experiments
3	Sr	$SrCl_2$	$SrCl_2$	0.23	0.5
4	Ba	$BaCl_2$	$BaCl_2$	0	0.4
5	Ca	$SrCl_2$	$SrCl_2$	0	0.3
6	Ca	$BaCl_2$	$BaCl_2$	0	0.7
7	Ca	$BeCl_2$	$BeCl_2$	0	93 Two 94 experiments
8	Ca	$CaCl_2$ in 0.01M HCl	$CaCl_2$	0	0.3
9	Ca	$CaCl_2$	$CaCl_2$ in 0.01M HCl	5.5	0.7
10	Ba	$BaCl_2$ in 0.01M	$BaCl_2$	0	very low ($\ll 0.1$) 0.6
11	Ba	$BaCl_2$	$BaCl_2$ in 0.01M HCl	0	very low ($\ll 0.1$)
12	Ca	$BaCl_2$ in 0.01M HCl	$CaCl_2$	0	
13†	Ca	$CaCl_2$	$CaCl_2$	6.8	not counted
Batch B of Orion 92-20-02 liquid ion-exchanger					
14	Ca	$CaCl_2$	$CaCl_2$	22	3.5
15	Ba	$CaCl_2$	$CaCl_2$	20	2.3
16	Sr	$CaCl_2$	$CaCl_2$	22	2.9

* Labelled with ^{7}Be, ^{45}Ca, ^{89}Sr or ^{133}Ba.
† Membrane composition: 0.35 g of liquid ion-exchanger plus 0.17 g of PVC.

sion was rather weak and the amount of tracer in solution rather small, the figures are means of replicate determinations. By way of illustration the value 10.8×10^{-7} sec^{-1} for $d(C''/C')/dt$ in experiment 1 is the mean of six determinations with a coefficient of variation of 5.4%, and the value of 1.7% for the proportion of radiotracer in the membrane at the end of the experiment has a coefficient of variation of 14.5%. The results are discussed with these limitations borne in mind.

DISCUSSION

The value of $d(C''/C')/dt$ for experiment 1 (10.8×10^{-7} sec^{-1}) is lower than that obtained in the corresponding experiment (18×10^{-7} sec^{-1}, coefficient of variation of 4.8%) in the earlier study.[1] This difference is attributed to the fresh batch of Orion 92-20-02 liquid ion-exchanger employed, which gave a slightly lower calcium-ion concentration of 0.0391 mole/kg in the prepared membrane compared with 0.0434 mole/kg. A further batch of Orion 92-20-02 liquid ion-exchanger used in the later experiments (14–16) of this study gave 22×10^{-7} sec^{-1} for $d(C''/C')/dt$ in the permeation of ^{45}Ca between $10^{-3}M$ calcium chloride solutions (experiment 14).

Although the behaviour of electrodes prepared from membranes made from different batches of ion-exchanger with varying proportions of PVC to ion-exchanger does not change drastically,[3] it has already been noted[1] that in permeation, halving the ion-exchanger:PVC ratio gives a far more than proportionate reduction in $d(C''/C')/dt$, *e.g.*, from 18×10^{-7} to 2.2×10^{-7} sec^{-1}. This trend is confirmed by experiment 13 (Table 1) whereby a 12.5% reduction in the amount of ion-exchanger in the membrane leads to a 37% reduction in $d(C''/C')/dt$.

Previous studies[1] have indicated that permeation of calcium ions through a PVC membrane containing Orion 92-20-02 ion-exchanger into a solution of another alkaline-earth metal chloride is hindered. It has been suggested[1] that magnesium, strontium and barium ions inhibit the migration of calcium ions because their own affinity for the liquid ion-exchanger sites is low. Inhibition by beryllium ions has been attributed[1] to blockage of membrane sites because of the strong affinity of dialkylphosphate for beryllium. Results from the present investigation confirm these trends.

The very short half-lives of magnesium isotopes have prevented their use in these studies, but strontium and barium, although giving near zero values for $d(C''/C')/dt$, produced valuable evidence. Thus, experiments 3–6 indicate there is little or no tendency for strontium or barium ions to pass through the PVC membranes in strontium, barium or calcium form into solutions containing strontium or barium chloride. This inhibition of migration by the low affinity of strontium and barium ions for sites in the liquid ion-exchanger is confirmed by the relatively low proportion of tracer associated with the membrane at the end of the various experiments. The greater relative permeation of calcium ions between calcium chloride and strontium or barium chloride through calcium-form membranes, which is to be expected,[1] can be regarded as due to the higher affinity of calcium ions for the exchanger.

The low affinity of strontium and barium ions for the sites of the PVC-trapped liquid ion-exchanger is also indicated by experiments 14–16. Here calcium ions permeate through barium (experiment 15) and strontium (experiment 16) membranes at about the rate of permeation through calcium membranes (experiment 14).

That beryllium ions have a strong affinity for the ion-exchange sites on the membrane is indicated by experiments 2 and 7, where a high proportion of the tracer was

found on the membrane and little or no tracer appeared in the other solution. For the few experiments conducted, the trend is regular but because of the very low count-rates in these experiments, the possibility of some beryllium ions passing through the membrane into the other solution should not be discounted.

The remaining interesting feature is the effect of acid. Experiments 8, 9 and 12 with calcium membranes should, on the basis of earlier data[1] for $10^{-3}M$ solutions in the absence of acid, give finite values for $d(C''/C')dt$, but this was observed only in experiment 9, and the membranes in experiments 8 and 12 picked up only very small amounts of radioactive calcium. This pattern might be predicted from reports on the transport of ions against their concentration gradients,[5,6] whereby cations will permeate through a membrane into acid solutions containing higher levels of the same cations. The preferential permeation by the proton in one direction is balanced by permeation of the cation in the other direction in order to maintain the balance of charge. It might be assumed that such was the case in experiments 8 and 12, and the assumption would seem to be confirmed by the lower permeation rate in experiment 9 compared to that of experiment 1 where the acid was on the other side of the membrane from that of the tracer.

Experiments 10 and 11 involved only barium ions in the solutions and in the membrane. From what has been said about the low affinity of barium ions for the sites on the membrane, not very much permeation by barium ions would be expected.

Acknowledgements—The authors thank the University of Wales for a Studentship (to AMYJ), the Science Research Council for financial support, and Professor Henry Freiser, University of Arizona, USA and Professor T. P. Hadjiioannou, University of Athens, Greece for valuable discussions made possible by a travel grant from the North Atlantic Treaty Organisation.

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DETERMINATION OF ARSENIC IN HIGH-PURITY COPPER BY FLAMELESS ATOMIC-ABSORPTION SPECTROPHOTOMETRY

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(*Received* 14 *February* 1977. *Accepted* 28 *March* 1977)

Summary—Arsenic is separated from an ammoniacal solution containing 1 g or less of copper(II) by co-precipitation with ferric hydroxide. The precipitate is dissolved in nitric acid, the solution almost neutralized with ammonia, made up to volume and the As determined by flameless atomic-absorption spectrophotometry. Less than 0.5 ppm can be determined.

The routine determination of arsenic in high-purity copper is necessary because of the effect of this impurity on the conductivity. Globule arc-emission spectrography is normally used but is useful only down to a level of *ca.* 2 ppm. Microgram quantities of arsenic can be determined photometrically with silver diethyldithiocarbamate[1] but the method is slow and separation of the arsenic from copper is required. More recent methods involving arsine generation followed by atomic-absorption techniques suffer interference from many ions, including copper.[2] The proposed method, based on a previously described procedure[3], is in use for arsenic contents below 2 ppm and for checking spectrographic results. It involves co-precipitation of the arsenic with ferric hydroxide and its determination in the dissolved precipitate by flameless atomic-absorption spectrophotometry (FAAS).

EXPERIMENTAL

Apparatus

A Varian Model AA4 spectrophotometer with Rank-Hilger slotted-cathode lamp, Model 63 carbon-rod atomizer and an Oxford Instruments 3000-series chart-recorder were used.

Reagents

Ferric nitrate solution, 2%.

Stock solution of arsenic, 1,000 *ppm*. Made by dissolving 1 g of arsenic in 10 ml of conc. nitric acid and diluting to 1 litre with distilled water.

Arsenic solution, 1 *ppm*. Made daily by successive dilutions of the stock solution with distilled water.

Ammonia solution, sp. gr. 0.880.

Nitric acid, sp. gr. 1.42.

Procedure

Standards. To 30-ml portions of distilled water in 100-ml beakers are added 0, 0.5, 1, 2, 3 or 4 ml of a freshly prepared 1-ppm arsenic solution followed by 5 ml of concentrated nitric acid and 1 ml of ferric nitrate solution. Then 10 ml of concentrated ammonia solution are added and the solutions brought briefly to the boil. After settling for 15 min, the precipitates are collected on porosity 3 conical sintered-glass funnels and washed with dilute ammonia

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Table 1. Operating conditions

Operation	Voltage setting	Temperature, °C	Time, sec
Drying	5.5	195	20
Ashing	7	800	12
Atomization	7	2250	3

solution. The funnels are fitted into 125 × 17 mm side-arm filter tubes, the precipitates dissolved in 1 ml of hot concentrated nitric acid and the solutions drawn into the tube, followed by *ca.* 2 ml of water washings. After neutralization of most of the acid with 0.8 ml of concentrated ammonia solution the solutions are transferred to 5-ml volumetric flasks and made up to the mark with water.

Samples. One-gram samples are dissolved in 5 ml of concentrated nitric acid in 100-ml beakers, then made up to *ca.* 30 ml with water; 1 ml of ferric nitrate solution is added to each, followed by 10 ml of concentrated ammonia solution. The solutions are brought briefly to the boil and the same procedure followed as for the standards.

Instrument operation

The instrument settings are shown in Table 1. The wavelength used was 193.7 nm, with a spectral bandwidth of 6.6 Å. A graphite tube is used as furnace in the atomizer work-head and oxygen-free nitrogen as the inert gas. After decontamination of the tube by a preliminary atomization cycle, 5-μl samples are pipetted into the tube and subjected to the cycle conditions given in Table 1. The absorbances are recorded at a chart-speed of 2 cm/min and recorder sensitivity of 2-mV full-scale deflection. For consistent results and long tube-life it is essential that the tube is allowed to cool almost to room temperature before sample injection and for highest accuracy a number of duplicate sample atomizations should be performed, interspersed among the standards.

RESULTS AND DISCUSSION

To find the easiest way of producing reliable standards, 0, 1 and 2 ml of 1-ppm arsenic solution were added to either 30 ml of water or 30 ml of a solution of 1 g of arsenic-free copper in nitric acid and treated as described above. The same amounts were also added to 1 ml of concentrated nitric acid, 0.8 ml of concentrated ammonia solution and 1 ml of ferric nitrate solution and the whole made up to 5 ml. There was no significant difference in the FAAS results for the samples precipitated in the absence and presence of copper. The blanks prepared without precipitation gave slightly lower absorbances than those prepared with a precipitation step, presumably because of the smaller amounts of reagents used. The absorbances of standards prepared without precipitation were correspondingly lower than those of standards made with precipitation but much more erratic; there is no obvious reason for this. Standards prepared as described in the procedure and stored in small glass specimen tubes give reliable results for at least a month.

Table 2. Arsenic standards

As, μg	Absorbance	Relative std. devn., %
0	0.014	7
0.5	0.056	12
1.0	0.096	9
2.0	0.184	9
3.0	0.270	8
4.0	0.340	7

Table 3. Results for spectrographic standards

Standard	This method, *ppm* (sample weight)	Certificate range, *ppm*
BICC 1	0.92	0.92–1.5
BICC 2	2.8	2.8–3
BICC 3	8.4 (0.5 g) 7.5 (0.25 g)	5.3–8.4
BCR	13.5 (0.2 g)	13–15

The operating conditions of the atomizer were chosen to give the most rapid drying consistent with smooth evaporation and a sufficiently high ashing temperature to remove potential interferences without loss of arsenic. High absorption signals are obtained in both the drying and ashing cycles owing to nitrogen oxides and ammonium nitrate fumes respectively. The recommended atomization setting gives a sharp absorption peak and a low background absorption (0.007 absorbance; hydrogen-continuum lamp).

Table 2 shows the absorbances and their relative standard deviations for a set of standards prepared as recommended. The FAAS part of the procedure accounts for most of the error since the standard deviation is similar whether duplicate standards or single standards are used. If the graphite tube is in good condition there is little variation in the standard absorbances from day to day. Deterioration of the tube is indicated by low and erratic results. Concentrated nitric acid solutions cause rapid deterioration of the tube. The partial neutralization with ammonia, as described, results in a much longer tube-life, up to 100 determinations.

Comparison of results obtained by this method for spectrographic standards shows good agreement with the accepted figures (Table 3).

A sample of electrolytic copper from the European Bureau of Standards was also analysed and gave a mean of 1.9 ppm As, standard deviation 0.2 ppm (duplicate precipitations, 5 analyses on each) compared with a range of quoted figures of 1.00–2.9 ppm, mean 1.66 ppm (10 laboratories, 3 techniques).

Interferences

The elements most likely to interfere with the determination are those co-precipitated with ferric hydroxide, namely Bi, Pb, Se, Sn, Te. No interference was observed when combined solutions containing up to 50 μg of each element were added to solutions containing 2 μg of As and co-precipitated with iron. It is unlikely that any of these elements will be present at this level in high-purity copper.

Conclusions

The proposed method is quite simple and the arsenic content of the highest quality commercial copper can be determined on a 1-g sample. The slotted-cathode lamp is recommended for the method as the sensitivity (concentration in solution for 1% absorption) of 0.01 μg/ml for a 5-μl sample injection is almost twice as good as that attained with other hollow-cathode lamps.

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METHOD FOR MULTI-ELEMENT ALPHA-SPECTROMETRY OF ACTINIDES AND ITS APPLICATION TO ENVIRONMENTAL RADIOACTIVITY STUDIES

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Summary—A method is proposed for measuring simultaneously several actinide elements by α-spectrometry. The actinides in sample solutions are sorbed together on an anion-exchange column from a nitric acid–methanol mixture. After simultaneous elution and electroplating on a disc, the actinides are determined by α-spectrometry. Radiochemical yields of the procedure for Th, U, Np, Pu, Am and Cm are better than 50%, all falling within a range of ± 5%. Examples of the application of this method to various marine environmental samples such as sea-water, seaweed and marine sediment are presented.

The key to an accurate determination of actinides, especially of transuranium elements, by α-spectrometry is to obtain a good radiochemical separation of the element of interest from other α-emitters. To eliminate interfering α-emitters before α-spectrometry, radiochemical procedures for actinides normally require rather elaborate separation steps and are time-consuming. It seems possible, however, to employ simpler separation procedures in studies of α-emitting radionuclides around nuclear installations, where elevated levels of man-made radioactivity are encountered and the composition of released radioactive effluents is reasonably well known. Only a few attempts along this line of approach have been made to date. Hodge and Gurney[1] recently presented a simple precipitation method for measuring U, Pu and Am in sea-water by α-spectrometry, though their results were only semiquantitative.

A simple method for group separation of actinides from interferences by a single anion-exchange process, followed by α-spectrometry, has been developed in our laboratory for quantitative determinations of several actinides in sea-water, marine organisms and marine sediments. Despite the obvious limitation of the method, which is incapable of resolving different actinide nuclides having very close α-peaks in the spectrum, it provides simultaneous measurements of several actinides in environmental matrices with good precision and accuracy. The procedure is described in detail in the present paper with examples of measurements on various marine samples.

EXPERIMENTAL

Sample pretreatment

From several litres of acidified sea-water, to which up to ~ 5 dpm of the yield-monitor ^{242}Pu (or ^{244}Cm) had been added, actinides were co-precipitated with mixed hydroxides and carbonates by neutralizing the sea-water with ammonia or sodium hydroxide solution. The precipitate was centrifuged and dissolved in concentrated nitric acid (~ 5 ml).

Up to 10 g of biological material or ~ 2 g of sediment were dried at 105–110° and the yield-monitor was added. After drying again the samples were ashed at 550° overnight. The ash was leached with hot *aqua regia* with addition of a few ml of hydrogen peroxide (30%) to the solution. The residue was centrifuged and actinides were co-precipitated from the solution with iron hydroxide by adding ammonia. The precipitate was centrifuged and dissolved in concentrated nitric acid.

Ion-exchange separation

The acid solution of the actinides obtained was evaporated nearly to dryness and the residue was dissolved in 3 ml of nitric acid. This solution was diluted with ~ 50 ml of methanol with the addition of solid ammonium nitrate, to adjust the concentrations of nitrate to > 1*M* and methanol to 90% v/v in the final solution. A small quantity of solid sodium nitrite was added to convert all the plutonium into the quadrivalent state. An anion-exchange resin column (Dowex 1, X2, 50–100 mesh) 1 × 20 cm was preconditioned by passing 40 ml of 1*M* nitric acid–90% methanol mixture through it. The sample solution was passed through the column at a flow-rate of 1 ml/min. Actinides in the solution were sorbed onto the column. After the column had been washed three times with 20 ml of 1*M* nitric acid–90% methanol mixture, the sorbed actinides were eluted by passing 80 ml of 0.5*M* nitric acid at the same rate of flow as that of the sample solution.

Electro-deposition and α-spectrometry

The eluate was evaporated to neat dryness in a small beaker and the residue dissolved in 1 ml of concentrated sulphuric acid. After heating to fuming the solution was diluted with 4 ml of distilled water. After the addition of 50 μl of 1*M* oxalic acid the solution was partially neutralized with ammonia to pH 2.5 (Thymol Blue as indicator) and transferred to a disposable polyethylene vial with 4 ml of 1% sulphuric acid. The pH was readjusted to 2.5.

The electro-deposition of the actinides on a stainless-steel disc was performed at a current of 1.2 A for 1 hr. Alpha-spectrometry of the actinides electroplated on the disc was carried out with a silicon surface-barrier detector, having a sensitive area of 300 mm^2, connected to a multi-

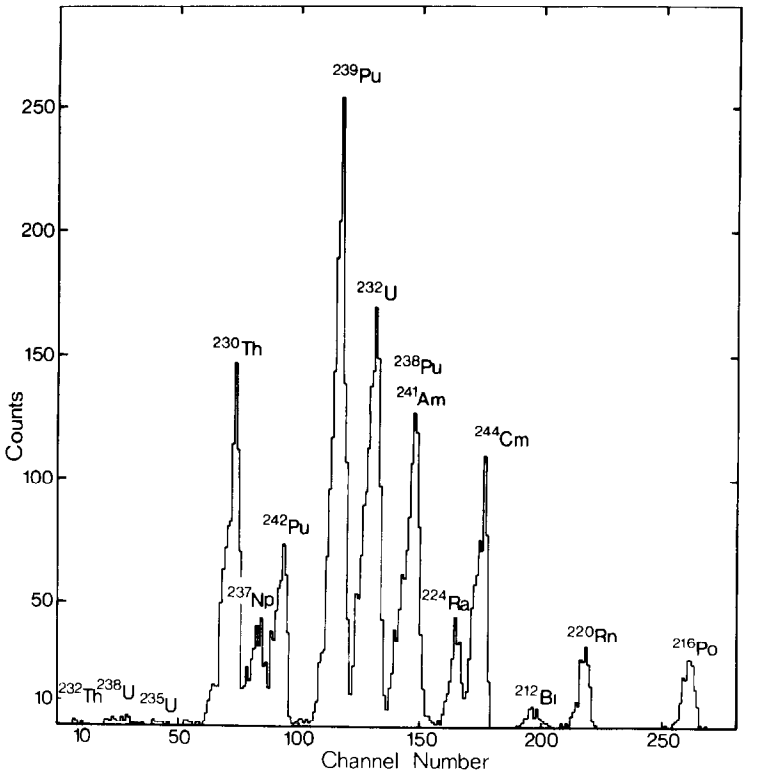

Fig. 1. Alpha-spectrogram of the IAEA seaweed sample AG-I-1 spiked with ^{230}Th, ^{232}U, ^{237}Np, ^{242}Pu and ^{244}Cm (1 g seaweed; 310 min counting; $^{239+240}$Pu was designated as ^{239}Pu).

channel analyser. Resolution was around 35 keV for the 5.15-MeV peak of $^{239+240}$Pu.

RESULTS AND DISCUSSION

Group separation of actinides

The method described above is based on the possibility of quantitatively separating the actinides as a group from the interferences. It was shown by Guseva *et al.*[2] and von Haidvogel *et al.*[3] that sorption of Pu, Am and Cm on anion-exchange resins was substantially increased by adding alcohol to a dilute nitric acid solution. Recently, Holm and Fukai[4] found that other actinides such as Th, U and Np were also strongly sorbed on the anion-exchange resin from 1:9 v/v 1*M* nitric acid–methanol mixture. These findings suggest the possibility of separating actinides from the bulk of various elements which constitute the matrices and from non-actinide radionuclides which might interfere with the measurements. To test the quantitative performance of the group separation, known quantities of ^{230}Th, ^{232}U, ^{237}Np, ^{242}Pu and ^{244}Cm were added to 1 g of the IAEA seaweed sample AG-I-1, the radionuclide composition of which is well known[5,6] and the radiochemical procedures above were applied. An example of the α-spectrograms obtained is given in Fig. 1; the radiochemical yields of the added actinides are compared in Table 1. Figure 1 shows that the α-peaks of the spiked actinides were well resolved from those of the actinides originally occurring in the seaweed and their daughter products (the content of ^{230}Th in the sea-

Table 1. Radiochemical yields of various actinides obtained by the single anion-exchange group separation (relative to the yield of ^{244}Cm as 1.00)

Experiment	Nuclide	Major α-peak, *MeV*	Activity spiked, *dpm*	Counting efficiency, %	No. of counts*	Chemical yield, %	Relative yield
A	^{230}Th	4.68	20	18	730	68 ± 2	1.10 ± 0.06
	^{232}U	5.32	34	18	1198	66 ± 2	1.06 ± 0.06
	^{237}Np	4.79	11	18	369	62 ± 5	1.00 ± 0.09
	^{242}Pu	4.90	12	18	423	65 ± 4	1.05 ± 0.08
	^{244}Cm	5.80	17	18	572	62 ± 3	1.00
B	^{243}Am	5.27	16	26	945	76 ± 2	0.96 ± 0.04
	^{244}Cm	5.80	36	26	2256	79 ± 2	1.00

* Normalized for 300-min counting.

weed was negligible compared to the quantity added as a spike). The radiochemical yields of Th, U, Np, Pu and Am relative to that of Cm (Table 1) agree within a range of $\simeq 10\%$ and can be considered as identical for all the actinides in question. This implies that a single yield determination is sufficient for monitoring the yield of all the actinides concerned. Plutonium-242 is preferable for this purpose, since its α-energy (4.90 MeV) does not interfere with that of the other actinides except for ^{231}Pa, which is normally very low in environmental samples anyway. If samples are not expected to contain ^{244}Cm, ^{244}Cm can also be used, since its α-energy (5.80 MeV) is higher than that of most actinides.

Major interferences

A drawback of the present method is its inability to measure ^{238}Pu and ^{241}Am separately, since the major α-energies of these isotopes (^{238}Pu, 5.48 MeV; ^{241}Am, 5.49 MeV) are too close to be resolved by present α-spectrometry. The major α-energy of ^{228}Th (5.42 MeV) is also close, so that ^{228}Th interferes somewhat. However, since the ^{228}Th reaches a radioactive equilibrium with its daughter, ^{224}Ra (α-energy: 5.68 MeV), about two weeks after the separation and since the Ra originally present in the sample is not recovered by the present procedure, the quantity of ^{228}Th can be estimated by measuring the ingrown ^{224}Ra peak. The α-peaks of ^{224}Ra, ^{212}Bi, ^{220}Rn and ^{216}Po shown in Fig. 1 represent those of short-lived decay products of ^{228}Th, although radioactive equilibria of these daughters with ^{228}Th had not yet been reached.

If the ratio of ^{238}Pu/$^{239+240}$Pu in a sample is known, ^{241}Am in the sample can be estimated by subtracting the ^{238}Pu plus ^{228}Th counts from the α-peak around 5.49 MeV. In general, however, statistics of such an estimation are poor, owing to the manipulations involved.

A similar situation applies to the ^{234}U (major α-energy: 4.77 MeV)–^{237}Np (major α-energy: 4.79 MeV) pair, and also to the ^{231}Pa (major α-energy: 5.00 MeV)–^{242}Pu (major α-energy: 4.90 MeV) pair when ^{242}Pu is used as a group yield-monitor. In most environmental samples, however, the levels of ^{237}Np and ^{231}Pa are very low. Special separation techniques are, in any case, required for the precise measurements of these isotopes.

Since the present procedure involves oven-ashing or evaporating to dryness in a strong acid medium, most of the ^{210}Po is eliminated before the ion-exchange step. The parent of ^{210}Po, ^{210}Pb, however, follows the actinides during the ion-exchange step and is electroplated on the disc. Owing to the decay of ^{210}Pb (β-emitter, half-life 21 y), ^{210}Po (α-energy: 5.30 MeV) will be slowly built up on the disc. The α-peak of ^{210}Po does not interfere with the α-spectrometry of the actinides of interest, except at excessively high ^{210}Pb levels.

Another interference is caused by stable elements, especially by lanthanides, contained in sample matrices. Since lanthanides are not removed by the present procedure, they are electroplated on the discs. In large amounts they cause the quality of the spectra to deteriorate. Thus, the lanthanide content limits the sample size which can be processed successfully. On the basis of our experiences, several kg of sea-water, ~ 20 g of biological material and ~ 3 g of sediments are the maximum sample sizes for successful performances.

APPLICATIONS

Our proposed method was applied to various marine samples known to be contaminated with man-made actinides at levels detectable by routine environmental monitoring. Typical α-spectra obtained for different matrices such as sea-water, seaweed and bottom sediments are presented in Figs. 2, 3 and 4. Concentrations of several actinides estimated on the basis of these spectra are given in Table 2.

The IAEA sea-water (SW-I-3) and seaweed (AG-I-1) samples were collected from the vicinity of a reprocessing plant and the concentrations of various fission and activation products[5] as well as transuranium elements[6] in the samples were already known through intercalibration exercises. The Windscale sediment was collected by the British Radiobiological Laboratory, Lowestoft, U.K., and given to our laboratory for use in biological experiments. Despite the interferences discussed previously, the spectra shown in Figs. 2, 3 and 4 demonstrate resolutions of the α-peaks of the actinides sufficient for their quantification. Since the concentrations of $^{239+240}$Pu and ^{238}Pu were already known, no yield-determinant was added to these samples; instead the quantities of $^{239+240}$Pu computed from the spectra were compared with the known concentrations of $^{239+240}$Pu in the samples to determine the yield. The abundance of transuranium elements relative to the naturally occurring α-emitters such as U and Th varies significantly with the type of sample; transuranium elements. Pu, Am and Cm concentrations are much higher in the seaweed and sediment samples than in the sea-water sample (relative to U). In the sediment sample high ^{230}Th and ^{241}Am concentrations were observed. The high ^{241}Am concentration is believed to be due to the decay of ^{241}Pu deposited in the sediment. Concentrations of ^{241}Am obtained by subtraction of the ^{238}Pu and ^{228}Th activities were compared with those obtained by direct americium separations (Table 2). Although the ^{241}Am concentration obtained in the present work is greater, the agreement with that directly determined is reasonably good, if the increase of ^{241}Am with time, due to the decay of ^{241}Pu, is taken into consideration.

It can be concluded from Table 2 that the accuracy of the determinations by the proposed method is sufficient to follow the geochemical behaviour of various actinides in a contaminated marine environment.

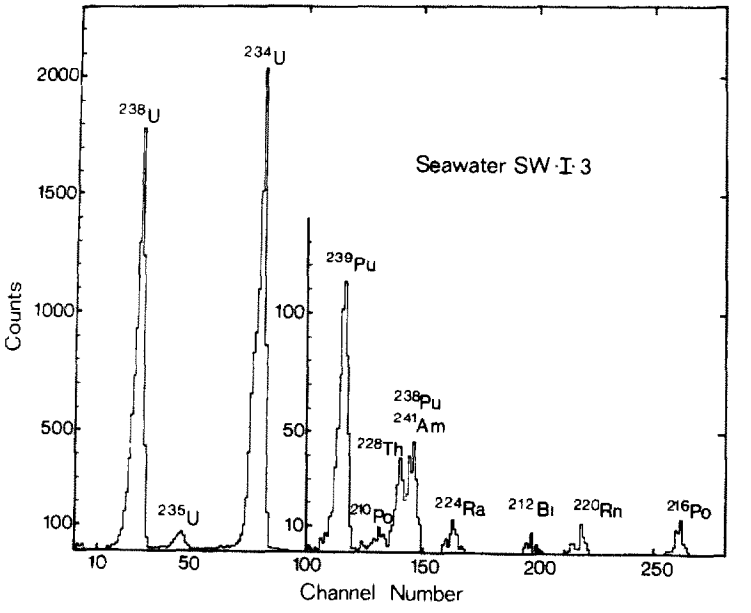

Fig. 2. Alpha-spectrogram of the IAEA sea-water sample SW-I-3. (5.7 kg sea water; 6666 min counting; $^{239+240}$Pu was designated as ^{239}Pu).

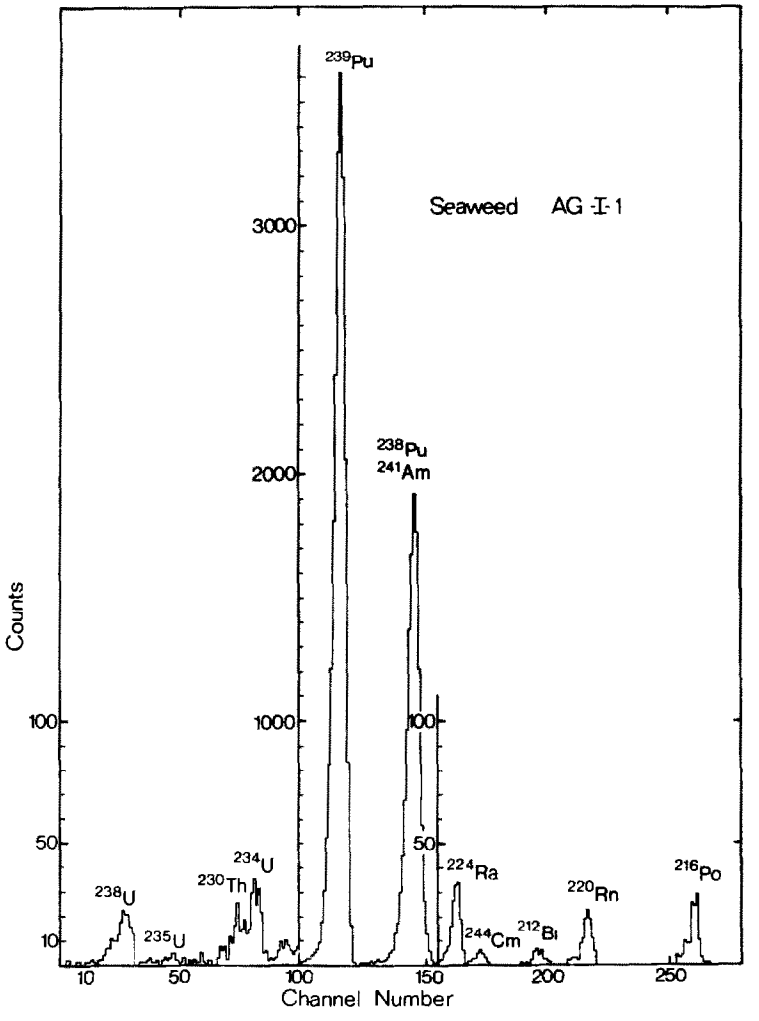

Fig. 3. Alpha-spectrogram of the IAEA seaweed sample AG-I-1 (1.0 g seaweed; 3188 min counting; $^{239+240}$Pu was designated as ^{239}Pu).

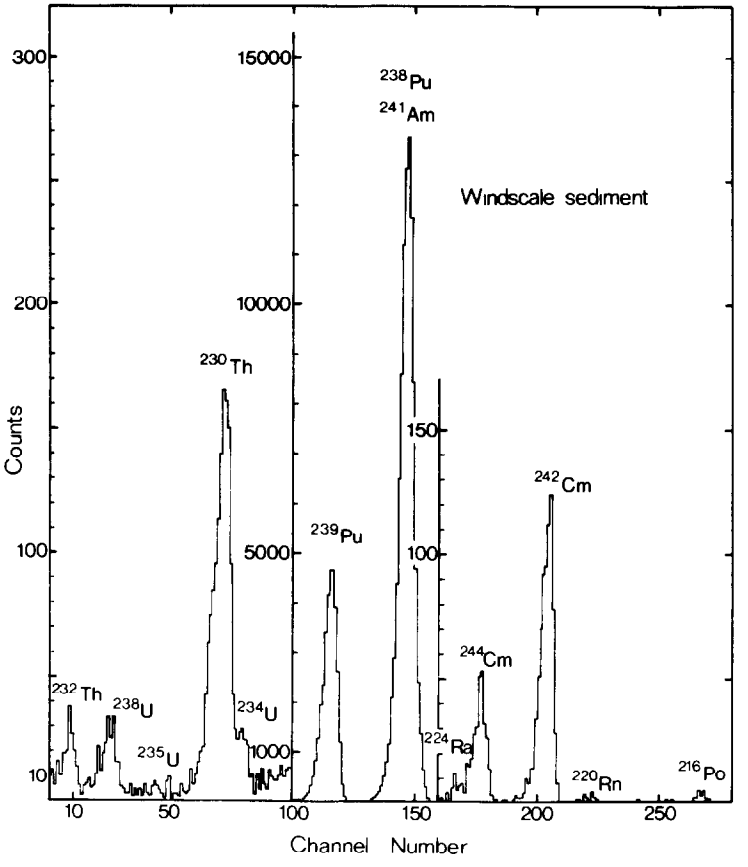

Fig. 4. Alpha-spectrogram of the Windscale sediment (0.6 g sediment; 2609 min counting; $^{239+240}$Pu was designated as ^{239}Pu).

Table 2. Concentrations of actinides in various marine environmental samples contaminated with man-made actinides released from nuclear installations (*pCi/kg*)

Sample	IAEA sea-water SW-I-3	IAEA seaweed AG-I-1	Windscale sediment
Date of collection	March 1972	Oct. 1970	July 1975
Date of analysis	Feb. 1976	Dec. 1975	March 1976
^{232}Th	—	8.0	740
^{238}U	1.5	230	790
^{235}U	0.057	30	150
^{230}Th	—	180	4.4×10^3
^{234}U	1.7	250	—
$^{239+240}$Pu*	0.11§	27×10^3§	110×10^3†
^{238}Pu*	0.018§	3.8×10^3§	26×10^3†
^{241}Am	0.047	9.9×10^3	286×10^3
^{244}Cm	—	30	980
^{242}Cm	—	—	2.8×10^3
^{241}Am (known concentration)	0.034§ (Oct. 1975)	5.9×10^3§ (July 1975)	224×10^3† (Oct. 1975)

* The values were determined in separate measurements. The values for $^{239+240}$Pu were used for determining the radiochemical yield of the group separation.

§ Cited from reference 4.

† Cited from reference 7.

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DETERMINATION OF ACID-SOLUBLE AND TOTAL RHODIUM ON ALUMINA-SUPPORTED CATALYSTS

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Summary—Characterization of alumina-supported catalysts required determination of rhodium by atomic-absorption spectroscopy (AAS). Catalysts were loaded with 0.1–2.0% rhodium chloride and calcined at 400°. Rhodium remaining as the chloride was regarded as the soluble form, while that converted into the oxide or bonded to the alumina was regarded as the bonded form. By selective dissolution procedures, soluble rhodium was leached from the substrate and determined by AAS. Total rhodium was determined after the catalyst had been fused with sodium peroxide. Bonded rhodium can be determined by difference or by analysing leached residue. Optimization of AAS conditions, use of spectroscopic buffer solution and elimination of interelement interferences are discussed.

Alumina-supported rhodium catalysts have been used in a variety of industrial applications. Characterization of the state of the rhodium can assist in improving catalyst performance. Determination of very low rhodium levels can help in finding the minimum amounts of this metal necessary to retain catalytic activity. List *et al.*[1] have reported a method for determining total rhodium at the 2–5% level in alumina catalysts. For this study, catalysts were loaded with aqueous rhodium(III) chloride solution, dried at 100–200°, and subsequently calcined at 400° in an air stream. The resulting catalysts contained 0.05–1.0% rhodium.

Since these calcining conditions were not stringent enough for quantitative conversion of bulk rhodium(III) chloride into rhodium oxide,[2] the possibility of the rhodium existing as two species on the catalysts was investigated. Other authors have shown evidence for two or more rhodium species in catalytic materials. In a recent Russian study, alumina-supported rhodium catalysts were examined after reduction in hydrogen. Magnetic susceptibility and chemisorption techniques were used to indicate the existence of two forms.[3] Other workers have used ESCA (electron spectroscopy for chemical analysis) to examine charcoal-supported rhodium catalysts and provided evidence for the presence of multiple forms of rhodium.[4–6] The previously reported techniques were not applicable to our catalysts for a number of reasons. ESCA evaluation did not prove useful because of the very low concentrations present. Since known rhodium(III) compounds are diamagnetic,[7] application of magnetic susceptibility methods to unreduced catalysts did not appear promising.

Therefore, a method for distinguishing different forms of rhodium at very low concentrations, based on selective dissolution procedures, was investigated. We have previously reported atomic-absorption spectroscopy (AAS) methods for determination of total rhodium in industrial electrochemical surface catalysts.[8] That study indicated that heat-treated rhodium oxide and all other forms of rhodium were quantitatively dissolved by sodium peroxide fusion. Therefore, total rhodium on alumina-supported catalysts was determined by AAS following sodium peroxide fusion. Rhodium chloride was found to be readily soluble in dilute hydrochloric acid. Soluble rhodium was separated from the catalyst by mild leaching before AAS determination.

EXPERIMENTAL

Preparation of rhodium standards

A stock solution was prepared by dissolving hydrated rhodium(III) chloride in distilled water.[8] Working standards for leaching solutions contained 2, 4 and 6 ppm rhodium and were prepared by adding 2, 4 and 6 ml of 50-ppm rhodium solution to 23, 21 and 19 ml respectively of 10% hydrochloric acid plus 25 ml of the spectroscopic buffer solution described earlier.[8,9] Working standards for solutions prepared by fusion contained 2, 4 and 6 ppm rhodium and were matrix-matched for aluminium, zirconium and sodium content of samples.

To simulate (for interference studies), solutions obtained from fusion procedures, a synthetic fusion matrix solution was prepared by mixing 6 ml of 1000 ppm rhodium solution, 25 ml of 10000 ppm zirconium solution, 60 ml of 300 g/l. sodium chloride solution, 70 ml of 10000 ppm aluminium solution and 50 ml of concentrated hydrochloric acid, and diluting to 500 ml with distilled water.

Leach of alumina-supported catalyst

Catalyst pellets were ground to fine powder. Portions of 0.1–0.5 g were weighed to ±0.1 mg in a 50-ml beaker.

Table 1. Selected operating conditions for different solution matrices

Parameters	10% HCl	Spectroscopic buffer	Fusion solution
Air flow, *l/min.*	23.2	23.6	21.6
Acetylene flow, *l/min.*	4.02	4.72	3.68
Height above burner, *nm*	12.5	2.5	7.5
Fuel/air	0.173	0.200	0.170

Ten ml of concentrated hydrochloric acid were added, and the beakers were heated on a steam-bath for 1–2 hr or until the alumina appeared white. After washing and centrifuging 3–5 times, the solutions were diluted to 25 ml with distilled water, followed by addition of 25 ml of spectroscopic buffer solution.

Sodium peroxide fusion of alumina-supported catalyst

Samples of ground alumina (0.5–1.0 g) were mixed with 10.0 g of sodium peroxide and fused in zirconium crucibles for 30 min. The solidified melts were dissolved in water and the solutions acidified with 30 ml of concentrated hydrochloric acid, heated on a boiling water-bath for 1 hr, and diluted to 200 ml in standard flasks with distilled water.

Apparatus

A Perkin-Elmer Model 403 Atomic Absorption Spectrometer was used, with wavelength 343.3 nm, lamp current 15 mA, bandwidth 0.7 nm, and a single-slot 4-in. burner. The preferred flame conditions and observation heights[8] for different solution matrices are shown in Table 1.

Preparation of simulated catalyst

To assess the overall accuracy of the method, it was necessary to synthesize a model catalyst. Pellets of pure α-alumina, supplied by Girdler (T-708), were ground to pass a 200-mesh sieve. Assayed $RhCl_3 \cdot xH_2O$ and reagent-grade Rh_2O_3 (both from Alpha Products) were added dry to the α-alumina and the powder was mixed on a PICA blender mill.

Interference studies

Rhodium solutions (4-ppm) were prepared, containing 4 ppm of another cation; the cations investigated were those found as contaminants of the alumina, or used to enhance the catalytic activity. The absorbance values for each solution were used to calculate the apparent rhodium content. Solutions for interference studies were prepared from Fisher "Certified" atomic-absorption standard solutions.

RESULTS AND DISCUSSION

The two decomposition techniques, leaching and fusion, provided two solutions for AAS analysis. The leach procedure yielded a solution with the simpler matrix, and this determination will be discussed first. Previous work with rhodium indicated that a titanium-based spectroscopic buffer solution provided enhancement and a levelling effect on interelement interferences, but there was a notable burner-height dependence.[8]

The effects of interelement interferences were examined in each solution matrix with each contaminant in binary combination with rhodium. In Fig. 1, the results of the interference study in 10% hydrochloric acid medium are shown. The scattered points clearly indicate that the rhodium determination can be adversely affected by low concentrations of contaminant species. To circumvent the problem, spectroscopic buffer solution can be added, as shown in Fig. 2. All the data points now fall much closer to the expected result. The levelling effect of the spectroscopic buffer was optimized when the fuel-to-oxidant ratio was 0.67, and the burner was 2.5 mm below the light-path.

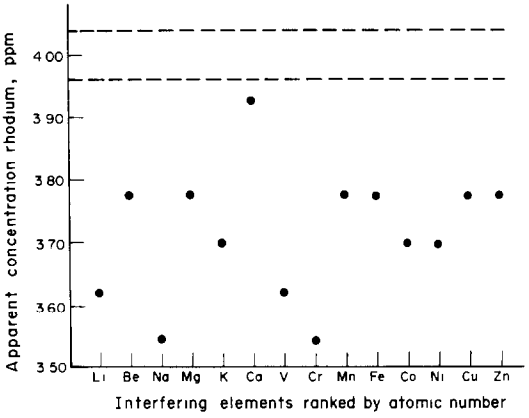

Fig. 1. Rhodium interference study, 10% HCl solution.

Earlier, fourteen other elements were observed to cause severe interferences in 10% hydrochloric acid medium, and these interferences were also levelled with spectroscopic buffer.[8] With proper selection of flame conditions and burner height, and with the use of spectroscopic buffer solution, rhodium in the leached solutions can be determined at the expected precision level. The precision was evaluated at three concentrations in each type of solution matrix, and the results are shown in Table 2.

Determination of rhodium after fusion

Rhodium solutions obtained from the fusion procedure contain aluminium, sodium, zirconium and small amounts of the elements previously discussed

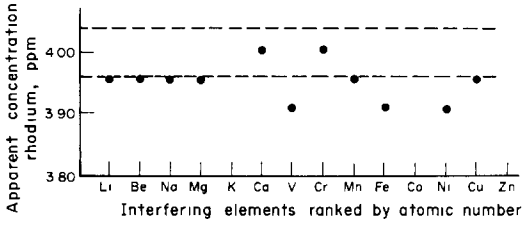

Fig. 2. Rhodium interference study, spectroscopic buffer solution.

Table 2. Precision study—coefficient of variation (%) at various concentrations in different solution matrices (10 variates analysed on separate days)

Rhodium concentration, *ppm*	10% HCl	Spectroscopic buffer	Fusion matrix
2.00	1.9	2.1	1.9
4.00	1.4	1.1	1.6
6.00	1.4	0.5	2.6
Average	1.6	1.2	2.0

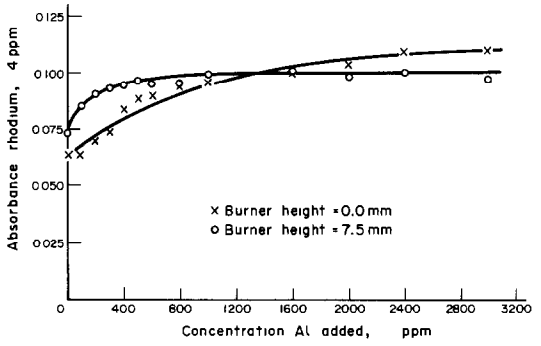

Fig. 3. Effect of varying aluminium concentration.

in the interference studies. List *et al.*[1] reported an enhancing effect on rhodium by aluminium in an air–acetylene flame, but they were not able to incorporate it into an analytical method. Their suggested use of a nitrous oxide–acetylene flame to circumvent the enhancement is satisfactory only if the rhodium levels are high, since the flame exhibits a significantly reduced sensitivity for rhodium. Reinvestigation of the aluminium enhancement indicated that the rhodium absorbance values were greatly affected by the height of observation in the flame. Solutions of 4 ppm rhodium containing various amounts of aluminium were examined at various heights in the acetylene–air flame. The enhancement was observed, but appeared useless because of the continuing increase in absorbance with increasing aluminium content when the light-path was immediately above the burner slot. With the light-path 7.5 mm higher in the flame, however, the absorbance levelled off when the aluminium concentration exceeded 1000 ppm (Fig. 3).

There are a number of variables that affect the composition of a fusion solution: the amount of alumina fused, quantity of sodium peroxide used, size and texture of zirconium crucible, *etc.* In general, it was desired to use a single set of standards for all sample solutions, even if the fusion solutions were diluted. In order to use a single set of matrix-matched standards, it was necessary to examine the effect of increasing contaminant levels. A 4-ppm rhodium solution was doped with increasing aliquots of the previously described synthetic fusion matrix solution and the apparent rhodium content measured (Fig. 4). The absorbance became effectively constant when at least 4 ml of synthetic fusion matrix solution was added. It was concluded that samples requiring high accuracy must have standards closely matched to the fusion matrix, but, in general, when a 3–4% error can be tolerated, a single set of standards is sufficient. The results of the interelement interference study with enough synthetic fusion matrix solution added are shown in Fig. 5. The precision band was set at $\pm 1.5\%$ coefficient of variation, on the basis of the precision study. Only magnesium, manganese and nickel had sufficient effect to bring the absorbance outside the precision band.

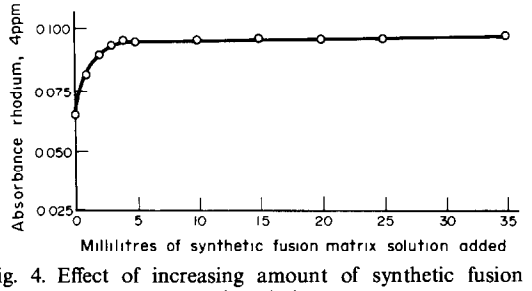

Fig. 4. Effect of increasing amount of synthetic fusion matrix solution.

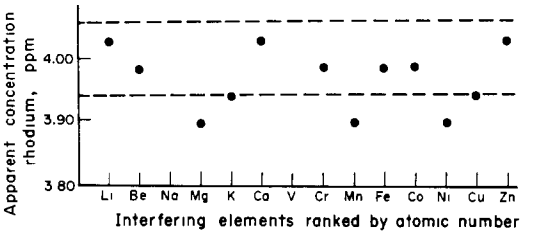

Fig. 5. Rhodium interference study, synthetic fusion matrix solution.

To analyse catalysts with very low rhodium levels, calibration curves for 2–6 ppm were needed. Table 3

Table 3. Comparison of absorbance values of various standard calibration curves

Rh, *ppm*	10% HCl matrix	Spectroscopic buffer matrix	Fusion solution matrix
2.00	0.028	0.052	0.060
4.00	0.049	0.102	0.110
6.00	0.068	0.150	0.156
Blank	0.000	0.001	0.001

Table 4. Recovery of soluble, total and bonded rhodium from spiked alumina

Sample	% Soluble Rh ($RhCl_3$) Theoretical	% Soluble Rh ($RhCl_3$) Average recovery, %	% Bonded Rh (Rh_2O_3) Theoretical	% Bonded Rh (Rh_2O_3) Average recovery, %	% Total Rh Theoretical	% Total Rh Average recovery, %
1	0.029	94	0.057	98	0.086	100
2	0.065	100*	0.118	—	0.183	75*
3	0.075	101*	0.137	102*	0.212	82*
4	0.227	106	0.397	115	0.624	105
5	0.247	100	0.464	87	0.711	104
6	0.433	91	0.849	99	1.282	95
7	0.650	96	1.087	111	1.737	101
Average		98		102		95

* Single determination.

Table 5. Comparison of fresh and used catalysts

Sample	Soluble Rh (S), %	Total Rh (T), %	S/T
1F	0.019	0.020	0.95
1U	0.010	0.020	0.50
2F	0.020	0.045	0.44
2U	0.013	0.036	0.36
3F	0.028	0.033	0.85
3U	0.017	0.034	0.50
4F	0.034	0.052	0.65
4U	0.021	0.054	0.39
5F	0.025	0.037	0.68
5U	0.022	0.040	0.55

shows a comparison of representative calibration data for the different solution matrices used. Least-squares fitting of second-degree equations to the calibration lines[10] showed that the spectroscopic buffer solution standards fit a second-degree equation better than synthetic fusion matrix solution standards do. This supports the general observation that the noise level is higher for the synthetic fusion matrix solution.

To assess the accuracy of the procedures, simulated catalysts were analysed for soluble, bonded and total rhodium. To obtain the bonded rhodium, the residue from the acid leach procedure was analysed, following sodium peroxide fusion. Theoretical values were calculated from the amounts of $RhCl_3 \cdot xH_2O$ and Rh_2O_3 used in preparing the synthetic samples. Duplicate determinations were done for each sample and the results are shown in Table 4. Average recoveries of acid-soluble and total rhodium from simulated catalysts were 98 and 95%, respectively. When large amounts of soluble rhodium were present, additional washings were necessary.

Analytical results for actual catalyst samples are shown in Table 5. Fresh (F) and used (U) samples of different batches were analysed. The results indicated that after catalysts were used in a strongly oxidizing environment, the amount of soluble rhodium present decreased. Ratios of soluble (S) to total (T) rhodium on fresh and used catalysts decreased in all cases. In some instances, total rhodium on a set of fresh and used samples was not equivalent. This might be a result of catalyst inhomogenity, sampling error, or loss of substrate due to catalyst wear.

Since instrumental techniques such as ESCA and X-ray diffraction are not generally applicable to such low concentrations of rhodium, the method presented provides a simple technique for monitoring very low levels of rhodium on catalyst supports. Additional information on the form of rhodium present can be obtained by selecting the appropriate dissolution technique.

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SOLVENT COMPOSITION EFFECTS IN THE CHROMATOGRAPHY OF AROMATIC NITRO-COMPOUNDS ON THIN LAYERS OF ALUMINA

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Summary—The relationship between the R_M-value and the concentration of the polar solvent in the mobile phase was investigated for a number of nitro-derivatives of benzene, naphthalene and biphenyl. In accordance with a molecular model of adsorption, linear R_M *vs.* log X_S plots were obtained (X_S is the mole fraction of the polar solvent). The effect of the number of nitro-groups and their position in the aromatic ring on adsorption was investigated.

In recent years a mechanistic model of liquid–solid chromatography has been proposed, the experimental verification being based on the analysis of R_M (log k' *vs.* solvent composition relationships[1–6] analogous to the dilution method applied in the analysis of complex formation, ion-exchange, solvation and other equilibria[7] (k' is the "capacity ratio"[8]). The advantages of this approach lie in the frequent use of mixed mobile phases composed of a polar solvent and a non-polar diluent; k' *vs.* composition relationships (determined for isocratic systems) are also a necessary starting point for the optimization theory of gradient elution chromatography.[8]

In the present study the model is used to analyse the behaviour of aromatic nitro-compounds chromatographed on thin layers of alumina.

The compounds belong to an interesting group owing to the properties of the nitro-substituent which exerts a strong mesomeric ($-M$) effect, causing electron-density shifts and polar conjugation. The consequences of these effects are increased acidity of the phenol and carboxyl groups, decreased basicity of amino-groups, and large dipole moments that are greater than those predicted.[9] The position and number of the nitro-groups should thus influence the adsorption behaviour; further effects are caused by additional aromatic rings in conjugated and condensed systems (biphenyl and naphthalene derivatives, respectively).

The investigations are related to an analogous study of nitro-compounds chromatographed on thin layers of silica[10] and Florisil,[11] in which the effect of the number and position of nitro-groups on the slope of R_M *vs.* log X_S plots was analysed (X_S = mole fraction of polar solvent S in cyclohexane as diluent). Differentiated slopes for nitro-compounds and anomalously large molecular areas were reported by Snyder,[12] who interpreted the apparent increase of the projection areas in terms of the localized adsorption of nitro-groups on the strong adsorption sites of silica.

The investigations have also a practical analytical aspect, since TLC data can be utilized to choose solvent–adsorbent systems suitable for the preparative column chromatography of mixtures of nitro-compounds, obtained as intermediates in organic syntheses. In the nitration of 1-nitronaphthalene[13] a number of isomers are formed in addition to the main product, including the 1,8- and 1,5-dinitronaphthalenes which are difficult to separate by classical methods.

EXPERIMENTAL

Aromatic nitro-compounds listed in Table 1 were chromatographed on thin layers of alumina (aluminium oxide GF_{254}, Merck, Darmstadt, FGR). Glass plates were covered with 0.25-mm thick layers of the adsorbent, mixed with water in 4:5 ratio, dried in air for 30 min and then activated for 1 hr at 80° and then 2 hr at 135°. The solutes were spotted as 0.5% solutions in benzene (2 μl). The plates were developed in glass tanks, 7 × 14 × 25 cm after conditioning for 30 min. The spots were located under ultraviolet light or by spraying with Ehrlich reagent (ethanolic 1% solution of *p*-dimethylaminobenzaldehyde) after reduction of the nitro-compounds with a 0.7% solution of tin(II) chloride in hydrochloric acid. Solutions of polar solvents (S) in cyclohexane were used for development. All solvents were purified and dried with 5A molecular sieve before use.

The experimental results (averages from 4–6 runs) are illustrated in Figs. 1–5 as plots of R_M *vs.* log X_S for systems of cyclohexane solutions of methyl ethyl ketone or chloroform and heptane solutions of benzene. The data for the remaining systems investigated (cyclohexane solutions of ethyl acetate, di-isopropyl ether or nitropropane) are presented in Table 1 as the coefficients of the linear plots

$$R_M = \text{const} - n \log X_S \qquad (1)$$

together with the correlation coefficient r_k.

Some of the compounds were synthesized in the course of the investigations (e.g., the mono- and dinitro derivatives of biphenyl,[14,15] 1-nitronaphthalene, 1,5- and 1,8-dinitronaphthalenes[16]). The derivatives of biphenyl were rela-

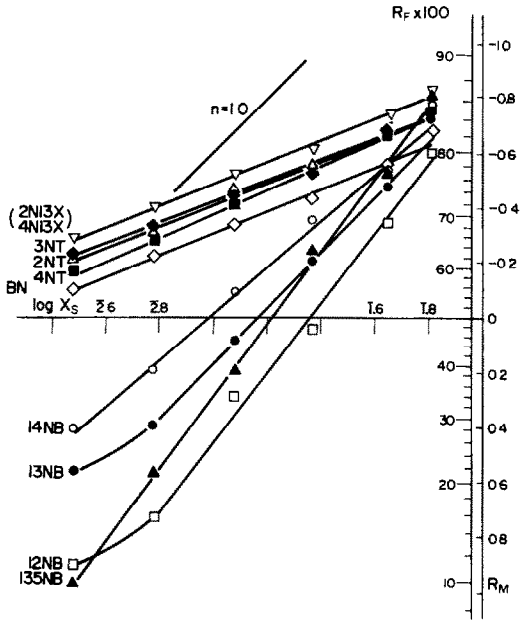

Fig. 1. The R_M *vs* log X_S plots of some nitro-derivatives of benzene and naphthalene. Polar solvent: methyl ethyl ketone. Diluent: cyclohexane. (For notation of solutes see Table 1.)

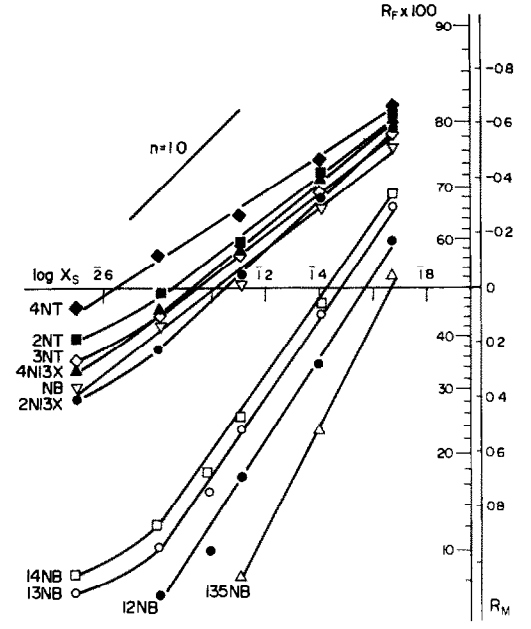

Fig. 3. The R_M *vs.* log X_S plots of some nitro-derivatives of benzene and naphthalene. Polar solvent: chloroform. Diluent: cyclohexane.

tively pure and required only crystallization; on the other hand, the nitration of 1-nitronaphthalene resulted in the formation of a mixture of dinitronaphthalenes, as illustrated by the chromatogram in Fig. 6. To identify the main products, the 1,5- and 1,8-isomers, the crude product was separated chromatographically with the system alumina–40% chloroform in cyclohexane. The zones were located under ultraviolet light, scraped off and eluted with ethanol. The compounds were identified from their melting points and by reduction and chromatography of the naphthylamines in parallel with standard samples. Larger amounts of the compounds were obtained by using a dry-packed column of 20 g of alumina (aluminium oxide—Schuchardt, Munich, FGR) developed with a 20% solution of chloroform in cyclohexane.

RESULTS AND DISCUSSION

The chromatographic results presented in Figs. 1–5 and Table 1 indicate that the solutes can be classified, with respect to their adsorption affinities, into three groups.

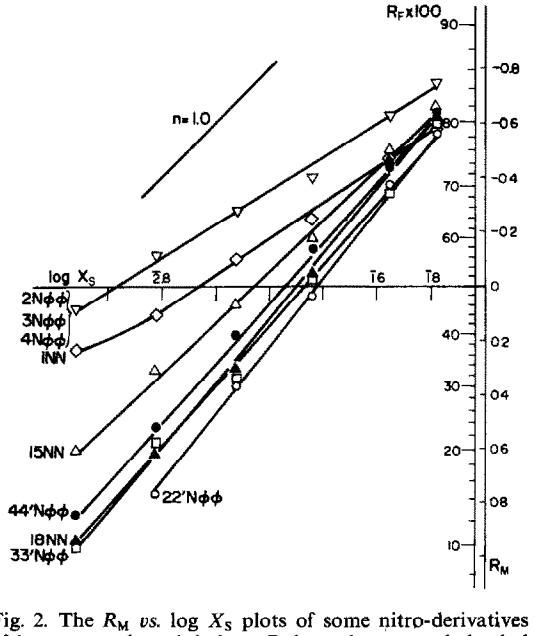

Fig. 2. The R_M *vs.* log X_S plots of some nitro-derivatives of benzene and naphthalene. Polar solvent: methyl ethyl ketone. Diluent: cyclohexane.

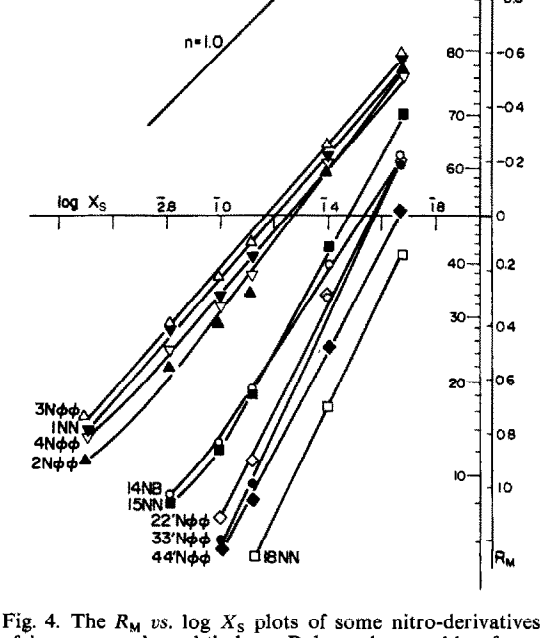

Fig. 4. The R_M *vs.* log X_S plots of some nitro-derivatives of benzene and naphthalene. Polar solvent: chloroform. Diluent: cyclohexane.

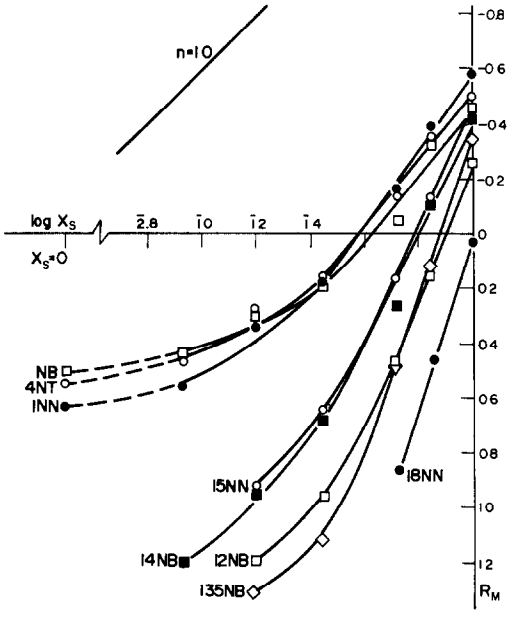

Fig. 5. The R_M *vs.* log X_S plots of some nitro-derivatives of benzene and naphthalene. Polar solvent: benzene. Diluent: heptane.

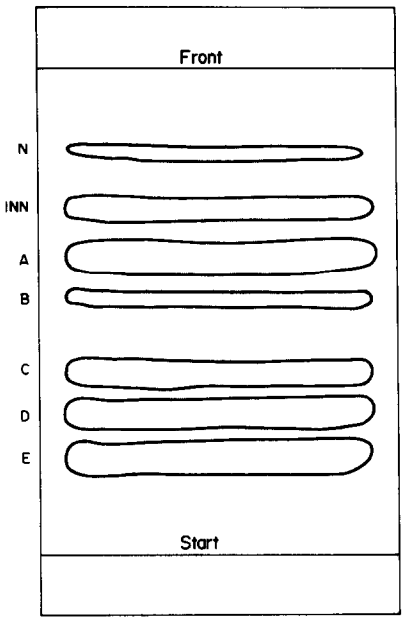

Fig. 6. Thin-layer chromatogram of the products of nitration of 1-nitronaphthalene. Mobile phase: 40% v/v solution of chloroform in cyclohexane. N—naphthalene; 1NN—1-nitronaphthalene; A, C—zones identified as 1,5-dinitronaphthalene and 1,8-dinitronaphthalene, respectively; B, D, E—zones of unidentified nitronaphthalenes.

1. Mononitroderivatives of benzene, toluene and xylene are weakly adsorbed compounds and the differences in their R_F values at low concentrations of the polar solvent are small. For 2.5% methyl ethyl ketone the R_F values are 0.66 for both nitroxylenes, 0.63 for 3-nitrotoluene and 0.62 for 2-nitrotoluene, Fig. 1. The lines merge at higher concentrations of the polar solvent. The R_F values are more differentiated for the di-isopropyl ether and 1-nitropropane systems, with some changes in the sequence of mononitro derivatives of benzene (*cf.* Table 1 where the absolute values of the linear constant decrease in the order: 2N13X, 4N13X, 2NT, 3NT, 4NT). It can be presumed that the influence of the *ortho*-methyl group is due to steric hindrance (increased

Table 1. Linearity constants calculated by the least-squares method from the equation: R_M = const − n log X_S [X_S = mole fraction of the polar solvent (S) in cyclohexane]*

		Polar solvents (S)					
		Ethyl acetate		Di-isopropyl ether		1-Nitropropane	
Solute	Abbreviation.	const	n	const	n	const	n
Nitrobenzene	NB	−0.61	0.48	−0.40	0.43	−0.85	0.58
2-Nitrotoluene	2NT	−0.66	0.39	−0.51	0.40	−0.92	0.61
3-Nitrotoluene	3NT	−0.77	0.48	−0.49	0.39	−0.91	0.61
4-Nitrotoluene	4NT	−0.77	0.52	−0.47	0.41	−0.91	0.61
2-Nitro-1,3-xylene	2N13X	−0.75	0.40	−0.60	0.36	−0.97	0.57
4-Nitro-1,3-xylene	4N13x	−0.75	0.40	−0.55	0.39	−0.94	0.58
2-Nitrobiphenyl	2NØØ	−0.85	0.61	−0.57	0.58	−1.01	0.77
3-Nitrobiphenyl	3NØØ	−0.98	0.64	−0.57	0.53	−1.00	0.70
4-Nitrobiphenyl	4NØØ	−0.83	0.61	−0.55	0.59	−1.01	0.78
1-Nitronaphthalene	1NN	−0.62	0.57	−0.39	0.47	−0.91	0.67
1,2-Dinitrobenzene	12NB	−0.52	1.22	+0.25	0.80	−0.83	1.23
1,3-Dinitrobenzene	13NB	−0.67	1.01	+0.02	0.75	−0.59	1.18
1,4-Dinitrobenzene	14NB	−0.81	0.93	−0.21	0.81	−0.94	1.15
1,3,5-Trinitrobenzene	135NB	−0.94	1.33	+0.34	1.08	−0.58	1.51
2,2′-Dinitrobiphenyl	22′NØØ	−0.74	1.14	−0.04	0.85	−0.99	1.43
3,3′-Dinitrobiphenyl	33′ØØ	−0.73	1.15	−0.12	0.86	−1.00	1.40
4,4′-Dinitrobiphenyl	44′ØØ	—	—	+0.01	0.88	−1.11	1.55
1,8-Dinitronaphthalene	18NN	−0.95	1.27	+0.58	0.95	−0.80	1.54
1,5-Dinitronaphthalene	15NN	−0.82	0.98	−0.27	0.84	−0.84	1.01

* The correlation coefficient of the lines (r_k) was for most cases in the range 0.933–1.00

R_F values), but the effect is not observed for the ethyl acetate, methyl ethyl ketone and chloroform systems. For the last-named polar solvent the sequence of spots is quite different (*cf.* Fig. 3, where for 5% chloroform the R_F value of 2-nitrotoluene, 0.49, is intermediate between those of the *meta*- and *para*-isomers, 0.44 and 0.56, respectively). This behaviour is probably caused by the proton-donor properties of chloroform and the competitive solvation of the nitro-group or hyperconjugation. According to Ingold[9] the nitro-group causes hyperconjugation in addition to inductive polarization of the aromatic system. The effects are stronger for 4-nitrotoluene ($+M$ effect of the methyl-group and $-M$ effect of the nitro-group). Apparently stronger solvation of 4-nitrotoluene by chloroform is reflected by the higher (absolute) slope of the R_M *vs.* log X (chloroform) plot.

2. The second group of solutes is formed by the mononitro-derivatives of biphenyl and naphthalene which have higher slopes than those of the first group of compounds, although they do not show greater differences in their adsorption affinities, especially at higher concentrations of the polar solvent. Dilution of the polar solvent causes decrease of the R_F values, greater than for benzene derivatives (increased values of the absolute slope, n). Increase of molecular size often reduces the adsorption affinity; in the case of biphenyl and naphthalene derivatives the effect is apparently counteracted by the greater polarizability of the aromatic systems and favourable increase of electron-donor properties of the nitro-groups.

3. The third group contains dinitro-derivatives of benzene, naphthalene and biphenyl; their slopes are approximately twice those of the mononitro-compounds. The slopes are somewhat higher for chloroform systems and highest for benzene systems (*ca.* 2.0 or more). Dinitro-compounds are more strongly adsorbed, the increase of adsorption affinity being dependent on the number and positions of the nitro-groups (*cf.* 1,3- and 1,3,5-trinitrobenzene in Figs. 1 and 3). The strongest adsorption was observed for 1,2-dinitrobenzene and 1,8-dinitronaphthalene, which also show the highest slopes of the R_M *vs.* log X_S lines (Figs. 1–5). The adsorption behaviour of 1,2-dinitrobenzene on silica has also been reported by Fishbein [17] and Gołkiewicz.[10] Snyder,[18] while discussing the effect of vicinal groups on adsorption, assumed that stronger adsorption may be due to formation of chelates with the active sites. Vicinal nitro-groups in 1,2-dinitrobenzene and the closely spaced groups of 1,8-dinitronaphthalene are capable of simultaneous interaction with active sites of the Lewis acid type on the surface of the alumina (or hydrogen-bonding with surface hydroxyl groups). The two nitro-groups in 1,8-dinitronaphthalene cannot lie in the plane of the condensed rings since even the 8-hydrogen atom in 1-nitronaphthalene forces the nitro-group out of the plane.[19] This effect favours the simultaneous interaction with the adsorbent surface (called by Klemm "anchoring interactions"[20]) as in the case of vicinal polar groups.[21] Solutes with two polar groups in the vicinal (or closely spaced) positions require less area on the adsorbent surface and are thus more easily accommodated among the adsorbed solvent molecules and displace a lower (average) number of the molecules of the polar solvent.

The slopes for the mononitro-compounds are lower than the theoretical unit value; however, it follows from Snyder's data[12] that the adsorption energy (S^0) of the nitro-group in aromatic compounds ($S^0 = 2.75$) is considerably lower than that of the polar groups of the solvent used (5.0 for a carbonyl-group in esters and ketones, 5.4 for an aliphatic nitro-group and 3.5 for an ether oxygen) so that the condition[1] that $K_{AZ} \gg K_{AS}$ is not fulfilled. The solute molecules are displaced from a surface already at low X_S values and the left-hand sides of the R_M *vs.* log X_S lines are higher, with a resulting decrease of the slopes. The slopes are higher for chloroform (which is relatively weakly adsorbed on alumina and can solvate the nitro group) and especially for benzene, the weakest solvent investigated (solvent strength[12] $\epsilon^0 = 0.32$), for which the R_M *vs.* log X_S plot becomes much steeper above 20% (*ca.* 3 M) concentration.

For di- and trinitro-compounds which are strongly adsorbed from dilute solutions of the polar solvents, the slopes are correspondingly higher, presumably because of varying contributions from two-point and even three-point adsorption, depending on the adsorption energy of the solvent. The relatively low adsorption energy of the nitro-group should enhance one-point vertical adsorption of the nitro-compounds from solutions in electron-donor solvents, since flat adsorption would require the removal of additional solvent molecules, with unfavourable balance of energy terms.

The molecular interpretation of the relationships requires further investigation since the polar systems studied are very complex from the thermodynamic point of view. Phenomena specific to the TLC technique, such as changes in activity, gradient effects, and condensation of solvent vapours from the tank atmosphere (which can be accounted for by use of the correction factor ξ)[22] introduce additional deformations of the relationships, especially in the range of the higher R_F values. On the other hand, the experimental results indicate that the equation derived by Soczewiński for silica [equation (1)] is also applicable to alumina, although the slope n may have a more complex sense than the simple ratio of mutually displaced solute and solvent molecules. The experimental data can also be utilized in the separation of isomers in preparative and analytical column chromatography.

Acknowledgement—The authors wish to express their gratitude to Prof. Edward Soczewiński for valuable discussions.

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OXIDATION OF SULPHIDE MINERALS—III
DETERMINATION OF SULPHATE AND THIOSULPHATE IN OXIDISED SULPHIDE MINERALS

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Summary—A method has been developed to determine sulphate and thiosulphate in small amounts of the oxidation products of sulphide minerals. The sample is treated with ammonium sulphide solution to promote ion-exchange between sulphide ion and the sulphur-bearing anions of the oxidation products. Sulphate is determined alone and then all other sulphoxy anions are oxidized to sulphate and determined as such. The non-sulphate anions are reported as thiosulphate. The relative error is about 10% or less for 2 mg or more of sulphoxy anion. Although this method does not yield exact results with respect to sulphite or polythionates, a clearer understanding of the oxidation of sulphide minerals is now available.

To understand fully the air oxidation of sulphide minerals and ores, it is necessary to determine the products of oxidation. A method is available to determine ferrous and ferric iron in the oxidation products of pyrrhotite, pyrite and chalcopyrite,[1] and lead, zinc and copper in those of galena, sphalerite and chalcocite, respectively.[2] Although elemental sulphur and sulphate[3] are known to be oxidation products of several sulphide minerals, the formation of partially oxidized sulphur anions such as sulphite, thiosulphate, *etc.*, may also be possible. Indeed for galena, it has not yet been decided whether $PbSO_4$[4] or PbS_2O_3[5] is formed.

This laboratory is currently investigating the air oxidation of several of the more common sulphide minerals, *e.g.*, pyrrhotite, pyrite, galena, sphalerite, and has found it necessary to develop a method to determine small amounts of sulphate and sulphoxy anions (*i.e.*, partially oxidized sulphur anions[6]) in these minerals. The sulphur anions are separated from the mineral by ion-exchange treatment of the mineral with an ammonium sulphide solution. Previous workers[7,8] have used sodium sulphide solution to prepare "clean" galena surfaces but have not extended this procedure to analytical application. Freshly prepared ammonium sulphide was used in this study in order to avoid, as much as possible, the introduction of the small amounts of sulphoxy anions always present in sodium sulphide.[9] The subsequent determination of sulphate and sulphoxy anions involves the introduction of correction factors for incomplete recovery. Correction factors are often used in chemical phase analysis and errors up to 20% are commonly associated with such methods.[10,11]

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* Containing an amount of Cd^{2+} equivalent to 110% of the sulphide found in the ammonium sulphide solution.

Although the proposed method does not yield exact results for the sulphoxy anions formed during oxidation of a sulphide mineral, it nevertheless does give a clearer picture of which ones are produced and, in conjunction with the methods for determining the metal in the oxidation products,[1,2] permits the calculation of such parameters as extent of oxidation or gain in oxygen to a much more realistic degree than was possible previously.

EXPERIMENTAL

Reagents

All chemicals were analytical grade. The hydrogen sulphide (Fisher Scientific Co.) was C. P. grade.

Sodium thiosulphate solution. $Na_2S_2O_3.5H_2O$ (22.7 g) and Na_2CO_3 (0.2 g) dissolved in water and the solution diluted to 2 litres with deaerated water.

Barium solution, 1000 mg/l. Prepared with $BaCl_2.2H_2O$.

Sulphate solution, 1000 mg/l. Prepared with Na_2SO_4.

Potassium solution, 50.0 g/l. Prepared with KCl.

Ammonium sulphide solution. Prepared fresh for immediate use. Hydrogen sulphide is bubbled through a stirred mixture of 900 ml of water and 28 ml of conc. ammonia solution in a 1-litre three-necked flask for 3 min at the rate of approximately one bubble per second. The flask is then kept sealed except when portions of the solution are to be taken out. The sulphide content of this solution is determined by titration of a 25-ml aliquot with KIO_3–KI solution, with starch as indicator.

Procedure for sulphide minerals

A 100-ml portion of ammonium sulphide solution is transferred to a 250-ml "Nalgene" bottle for each mineral sample. After the addition of a weighed amount of the mineral (0.3–2 g), 3 g of boric acid and 2.00 ml of the sodium sulphate solution, the bottle is tightly capped and stirred vigorously for 5 min. An appropriate portion of ammoniacal cadmium chloride* is added to each bottle, the contents of which are then stirred for 5 min and allowed to settle for 30 min. The supernatant liquid is carefully decanted from the bulk of the CdS precipitate and

filtered through a Whatman No. 42 paper containing approximately 1 g of filter paper pulp. The filtrate is retained for the determination of sulphate and sulphoxy anions in the sulphide minerals.

A blank determination is run simultaneously to allow for impurities in the H_2S or possible oxidation of the ammonium sulphide.

Determination of sulphate

For each sample and the blank, a 25-ml aliquot of the filtrate is transferred to a 150-ml beaker. After adjustment of the pH to 1.0 ± 0.5, the samples are boiled for 10–15 min to ensure the decomposition of sulphite and thiosulphate if present. The solutions are cooled to room temperature, the pH of each is adjusted to 3.5 ± 0.5, and the solutions are transferred to 250-ml volumetric flasks. Ten ml of the barium solution are added to each flask, and the flasks are heated on a steam-bath for 2 hr. Ten ml of potassium solution (to give a final potassium concentration of 2000 mg/l.) and 125 ml of methanol are added and the solutions made up to slightly below the mark with water. After cooling to room temperature (because of the heat generated on mixing methanol and water), the solutions are made up to volume and a portion is filtered through a Whatman No. 42 paper. The concentration of unprecipitated barium in the filtrate is then determined and the sulphate in the sample is calculated.

The unprecipitated barium is determined by flame emission at 553.2 nm in the acetylene–nitrous oxide flame (a Varian Techtron AA 6 Spectrophotometer was used in our work). The emission intensity of the samples and the blank is compared with that of a series of standard barium solutions having a composition very similar to the samples. Our calibration curve obtained was slightly non-linear and for convenience a computer and a quadratic multi-regression equation were used to calculate the barium concentrations.

Determination of sulphoxy anions

For each sample and the blank, a 25-ml aliquot of filtrate from the ammonium sulphide step is transferred to a 150-ml beaker. After adjustment of the pH to 1.0 ± 0.5, 1.0 ml of hydrogen peroxide is added to each and the solutions are boiled for 10–15 min to ensure the oxidation of sulphoxy anions to sulphate, then cooled to room temperature; the pH is adjusted to 3.5 ± 0.5 and the total sulphate is determined by the procedure given above for sulphate. The sulphate arising from the sulphoxy anions is the difference between total sulphate and the sulphate in the sample.

The amount of sulphate obtained from the sulphoxy anions does not give any information about the nature of these anions but does permit calculation of the number of moles of mineral sulphide that have been transformed into sulphate and sulphoxy anions respectively.

RESULTS AND DISCUSSION

Control of pH

It was found that even with the use of a flowmeter and constant rate of stirring, the ammonium sulphide solution could not be prepared with a reproducibility better than 15% with respect to sulphide. To minimize the resultant variation in the pH of this solution from one preparation to another, the 100-ml of ammonium sulphide solution used per sample was buffered with 3 g of boric acid. The boric acid concentration was then approximately 10 times that of the sulphide and maintained the pH at 9.6.

Recovery of sulphoxy anions

Because of the potential loss of sulphoxy anions by adsorption on the CdS, the recovery of known amounts of sulphoxy anions by the proposed method was determined. This study was performed only for sulphate and thiosulphate. Any polythionate that is present as an oxidation product of a mineral would react with sulphide to form thiosulphate and elemental sulphur.[12] We experienced appreciable difficulty in the transfer of small amounts of sulphite (1–10 mg) because of rapid oxidation of this species. It was feared that this would cause suspect recovery data and it was therefore assumed that sulphite behaves similarly to sulphate and thiosulphate with respect to adsorption on CdS. In any case, any small differences in the recovery of sulphite and thiosulphate because of this phenomenon would probably be less than the reproducibility of the proposed method and thus be concealed.

It should be noted that the 2.00-ml aliquot of sodium sulphate solution was not added in the tests described below to determine the recovery of sulphate and thiosulphate.

Recovery of sulphate. The recovery of sulphate by the proposed method was determined with known additions of sodium sulphate solution in place of the mineral sample. The results are summarized in Table 1 and demonstrate that sulphate can be recovered with an error of 2–7%, depending on the amount present and with a reproducibility of 2–3%.

Recovery of thiosulphate. The recovery of thiosulphate was determined with the use of known additions of standard sodium thiosulphate solution in place of the mineral sample. The results are shown in Table 2. The thiosulphate was, of course, oxidized and determined as sulphate, and the values for "thiosulphate found" in Table 2 were calculated from the total sulphate; "sulphate found" refers to sulphate in the test solutions before chemical oxidation of the thiosulphate and indicates that there is some oxidation of thiosulphate during the execution of the proposed method up to the stage at which thiosulphate is determined.

The results in Table 2 show that the reproducibility of the recovery of 1 mg or more of thiosulphate is similar to that of sulphate (Table 1). The non-quantitative recovery, however, necessitates the introduction of a correction term that must be applied to the experimentally determined value of thiosulphate to give the "true" value. The data in Table 2 can be

Table 1. Recovery of sulphate

Sulphate added, *mg*	Sulphate found, *mg*	No. of detns.
1.00	$0.9_2 \pm 0.0_3$	5
2.50	2.6 ± 0.1	5
5.00	4.8 ± 0.1	6
10.00	10.2 ± 0.2	6

Table 2. Recovery of thiosulphate

Thiosulphate added, *mg*	Sulphate found, *mg*	Thiosulphate found, *mg*	No. of detns.
0.53	0.3 ± 0.1	0.3 ± 0.1	5
1.07	0.5 ± 0.2	0.7 ± 0.1	5
2.67	0.5 ± 0.1	2.2 ± 0.1	5
5.34	0.7 ± 0.2	4.7 ± 0.2	6
10.67	0.7 ± 0.4	9.8 ± 0.1	6

employed to devise a correction curve for the range of thiosulphate studied, such that the "true" thiosulphate value of a sample can be readily obtained graphically or by calculation from the experimentally determined thiosulphate value.

The oxidation of thiosulphate to sulphate during the procedure up to the chemical oxidation of thiosulphate has, of course, little effect on the reproducibility or accuracy of the determination of thiosulphate in the sample because the thiosulphate is oxidized to sulphate and determined as such. This initial partial oxidation to sulphate is, however, important in the case of oxidized mineral samples where both sulphate and thiosulphate are present, because unless the appropriate correction is made the sulphate value obtained will be high. Again, the data in Table 2 (for sulphate found) can be used to correct the experimentally determined value to give the "true" value whenever thiosulphate is also present. It must be pointed out that this correction of experimentally determined sulphate values will result in making the reproducibility of the sulphate value for the sample no better than that of the correction (Table 2). The extent of this lowering in reproducibility will, of course, depend on the amount of sulphate in the mineral sample.

It should be stressed here that the thiosulphate is given by the difference between the "natural" sulphate and the total sulphate, and therefore has contributory errors from both determinations. This must be taken into account when the amount of sulphate is much greater than that of thiosulphate, because the value for the latter would be a small difference between two rather similar numbers.

Recovery of sulphoxy anions from mineral samples

Effect of reaction time. The effect of varying the reaction time with the ammonium sulphide solution was determined with a pyrite sample known to be highly oxidized. A blank was run with each sample. The results are shown in Table 3, where "total sulphate" refers to the sulphate found after chemical oxidation of the thiosulphate. These results show that the reaction time has no significant effect on the recovery of total sulphate, *i.e.*, sulphate + thiosulphate, from pyrite. The recovery of sulphate, however, does increase with an increase in the reaction time; this, of course, signifies increasing oxidation of thiosulphate and it is apparent that there is no advantage in the use of a reaction time greater than 5 min.

Table 3. Effect of reaction period

Time, *min*	Amount found, *mg/g* of pyrite Sulphate	Total sulphate	Thiosulphate*
5	84.7	100	8.9
10	89.5	102	7.9
15	85.1	101	9.3
30	89.0	109	11.7
45	93.0	101	4.5
60	96.0	100	2.3

* Given by (Total sulphate − sulphate) × ½ × Eq. wt. of thiosulphate/Eq. wt. of sulphate.

Table 4. Recovery of sulphate in presence of pyrite

Sulphate added, *mg*	Sulphate found, *mg*
1.00	0.9 ± 0.3*
2.50	2.6 ± 0.2
5.00	5.0 ± 0.1
10.00	9.7 ± 0.3

* Duplicate determinations.

Recovery of added sulphoxy anions. Table 4 summarizes the results for recovery of known additions of sodium sulphate solution in the presence of ~ 0.32 g of pyrite. The blank was pyrite only. A comparison of Tables 1 and 4 shows that the recovery of added sulphate remains essentially the same whether a sulphide mineral is present or not. The reproducibility is somewhat poorer when a sulphide mineral is present but is still good enough for the method to be analytically useful.

The recovery of added thiosulphate (1.07 and 5.34 mg) was determined for several sulphide minerals but only the total sulphate after chemical oxidation of the thiosulphate was determined. The results given in Table 5 indicate that the recovery is essentially unaffected by the presence of sulphide minerals (within the reproducibility expected).

The amount of sulphate formed by oxidation of thiosulphate before the deliberate chemical oxidation of the latter was determined for various amounts of thiosulphate in presence of pyrite (~ 0.32 g). The results are shown in Table 6. A comparison of Tables 2 and 6 shows that the oxidation of thiosulphate before the chemical oxidation is essentially unaffected by the presence of mineral sulphides. It is possible, therefore, to correct the experimentally determined

Table 5. Recovery of thiosulphate in presence of sulphide minerals

Mineral	Thiosulphate recovered, *mg* (Taken, 1.07 mg)	(Taken, 5.34 mg)
—	0.7	4.7 ± 0.2
Pyrite	0.8	4.9
Pyrrhotite	0.9	5.0
Chalcopyrite	0.7	4.5
Sphalerite	1.0	4.9
Galena	0.8	4.7
Chalcocite	1.1	5.1

Table 6. Oxidation of thiosulphate to sulphate

Thiosulphate added, *mg*	Sulphate found, *mg*
0.53	0.3 ± 0.2*
1.07	0.6 ± 0.2
5.34	0.7 ± 0.2
10.67	0.9 ± 0.3

* Duplicate determinations.

sulphate value to give the "true" sulphate in a mineral sample in which both sulphate and thiosulphate are present.

The data in Tables 1–6 show that the reproducibility does not vary much with the amount of sulphate or thiosulphate found. Accordingly, it was decided to add 2.00 mg of sulphate to all mineral samples to ensure the presence of enough sulphoxy anion for the reproducibility to be 10% or better.

Calculation of sulphate and thiosulphate content

The following procedure is used to calculate the sulphate and thiosulphate content of the mineral samples after the appropriate experimental results have been corrected for sulphate and thiosulphate in the blank. For convenience, the terms SO_4, TSO_4 and $SO_4(Ox)$ are used to denote the sulphate content before the deliberate chemical oxidation of thiosulphate, the total sulphate after thiosulphate oxidation and the sulphate derived from the oxidation of thiosulphate before the chemical oxidation.

(1) The sulphate from the chemical oxidation of thiosulphate is given by $TSO_4 - SO_4$.

(2) The "true" thiosulphate is determined graphically (data in Table 2) from $TSO_4 - SO_4$ and multiplication by the factor 0.583.

(3) The value of $SO_4(Ox)$ corresponding to $TSO_4 - SO_4$ is also read graphically and the "true" sulphate is given by $SO_4 - SO_4(Ox)$.

Some exemplary results are shown in Table 7. A comparison of the sulphate or expected total sulphate value determined by the proposed method with the sulphate determined by complete dissolution of the sample in 6*M* hydrochloric acid with a flow of nitrogen to remove H_2S clearly indicates that the proposed method gives reasonable values. It is not valid to seek complete agreement between the values for the two methods, because the total dissolution technique will only in rare and fortuitous instances give the true sulphate but will in general give sulphate plus some or all of the thiosulphate (determined as sulphate) for iron sulphide minerals. Any Fe(III) present can react with thiosulphate to form tetrathionate, which can co-precipitate with $BaSO_4$ in 50% methanol medium. Moreover, thiosulphate decomposes to sulphur and sulphite in acidic media and Fe(III) will oxidize sulphite to dithionate.

Interpretation of results

A comparison of the true sulphate and total sulphate values for a mineral sample will give the ratio of sulphide atoms that have been fully oxidized to sulphate to those that have been only partially oxidized to sulphite and thiosulphate. Sulphide atoms that have been oxidized to polythionates other than tetrathionates will not be correctly accounted for, because of the reaction[12]

$$S_xO_6^{2-} + S^{2-} \rightarrow 2S_2O_3^{2-} + (x-3)S \xrightarrow{O_2} 4SO_4^{2-}.$$

The elemental sulphur is, of course, filtered off with the CdS. As is readily observed, the value obtained for sulphide atoms oxidized to polythionates will be somewhat high if trithionate ($x = 3$) is formed but somewhat low if polythionates with $x > 4$ are formed.

Moreover, the potential complexity of the mixture of sulphoxy anions that could be formed during oxidation would result in an error in calculating the gain in oxygen during the oxidation of a sample. Each ion of sulphate requires a gain of 4 atoms of oxygen; this presents no problem in calculation. Similarly, polythionates present no calculation problem because each polythionate (6 oxygen atoms) reacts with S^{2-} to give 2 thiosulphate ions which together contain 6 oxygen atoms. For sulphite, however, a low gain in oxygen per sulphite ion would be registered because the proposed method would assume 2 sulphite ions (6 oxygen atoms) to be one thiosulphate ion (3 oxygen atoms).

Despite the error inherent in the interpretation of the data by the proposed method, the understanding of the nature of the oxidation of sulphide minerals

Table 7. Calculation of sulphate and thiosulphate in sulphide minerals

Mineral	Wt., *g*	SO_4, *mg*	TSO_4, *mg*	$TSO_4(C)$, *mg*	$SO_4(Ox)$, *mg*	SO_4^{2-}, *mg/g*	$S_2O_3^{2-}$, *mg/g*	Expected total SO_4^{2-}, *mg/g*	SO_4^{2-} by T.D.,* *mg/g*
Pyrite (a)	1.8561	2.26	4.24	2.40	0.5	0.9	0.8	2.3	0.7
Pyrite (b)	0.3460	3.97	5.50	1.92	0.5	10.0	3.2	15.5	13.7
Pyrrhotite (a)	1.9478	1.20	2.71	1.90	0.5	0.4	0.6	1.4	0.5
Pyrrhotite (b)	0.4002	2.91	4.48	1.96	0.5	6.0	2.9	11.0	12.9
Chalcopyrite	0.6314	2.06	3.36	1.67	0.4	2.6	1.5	5.2	4.2
Pyrite†	0.1590	13.42	15.93	2.91	0.5	81.3	10.7	99.6	103

* Total dissolution.

† Pyrite (Table 3) at 5 min reaction time.

has been improved. Moreover, if the proposed method could be extended to much higher amounts of sulphoxy anions, the established methods[13] for determining individual sulphoxy species in a mixture might be applicable.

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SHORT COMMUNICATIONS

TITRIMETRIC MICRODETERMINATION OF INORGANIC OR ORGANIC MERCURY BY AMPLIFICATION REACTIONS

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Summary—A simple titrimetric method for estimation of 0.05–7 mg of Hg(II) is presented. The acidic sample solution is treated with a measured and excessive amount of iodide, then mercuric iodide is extracted at pH 2–3.5, and the unreacted iodide is determined iodometrically after 6- or 36-fold amplification by use of bromine water for oxidation of iodide to iodate. Periodate oxidation of excess of iodide gives 24-fold amplification. The coefficient of variation does not usually exceed 1% for above 1 mg of mercury but increases to 4% at the 0.05-mg level. The 6-fold amplification method is used for microdetermination of organically bound mercury following oxygen-flask combustion. The average absolute error for 10 determinations (3 compounds) amounted to ±0.6%; one determination takes less than one hour.

Classical and instrumental methods are available for the determination of mercury, which is a serious pollutant and poison.[1,2] However, some of the instrumental methods[2–5] are sensitive to light and temperature, whilst others require activation sources. The British and U.S. Pharmacopoeia method based on thiocyanate titration requires rather a large sample. A titrimetric determination of as little as 100 μg of mercury(II) has been reported, based on the addition of an excess of standard L-ascorbic acid[6] solution to a mercuric chloride solution to precipitate mercurous chloride, followed by titration of the unreacted ascorbic acid with *N*-bromosuccinimide.

In order to develop a cheap, reliable and sensitive method we have investigated the combination of a titrimetric procedure with an amplification reaction for determination of mercury(II), based on the reaction between Hg(II) and excess of iodide; the mercuric iodide is extracted into ether, and the unreacted iodide is determined by the Leipert amplification procedure with either 6-fold or 36-fold amplification.[7]

Alternatively, the excess of iodide is oxidized by periodate,[8]

$$I \mp 3IO_4^- \rightarrow 4IO_3^-$$

the excess of periodate is masked with molybdate[9] and the iodate formed is reacted with iodide to give 24-fold amplification.

EXPERIMENTAL

Reagents

All reagents used were of analytical or microanalytical reagent grade and doubly distilled water was always used.

Potassium iodide solution (I^- 1 mg/ml).

Sodium thiosulphate solutions, 0.01, 0.02, and 0.04 *M*.

Mercuric nitrate solutions (Hg 0.6 and 1.5 mg/ml). In 0.03*M* nitric acid.

Mercuric chloride solution (Hg 1 mg/ml). In 0.03 *M* nitric acid.

Mercuric sulphate solution (Hg 1 mg/ml). In 0.03 *M* nitric acid. The mercury(II) solutions were standardized against known weights of sodium chloride, with diphenylcarbazone as indicator.[10]

Sodium hydrogen sulphite solution, 1%.

Potassium periodate solution, 0.01*M*. Dissolve 1.75 g of the salt in 500 ml of water, add 3 ml of saturated borax solution and store in a dark glass bottle.[8] Prepare fresh as required.

Ammonium molybdate solution, 25%. Freshly prepared.

Acetate buffer solution, pH 2.2.

Formic acid solution, 80%.

Procedure

In a 50-ml separating funnel, place a suitable volume (0.1–5 ml) of Hg(II) solution (0.06–7 mg of Hg), followed by 0.4–10 ml of potassium iodide solution (0.4–10 mg of I^-), and then water. Consult Table 1 for the relative volumes and concentrations. The pH value of the aqueous layer should be 2–3.5. Add the corresponding volume of diethyl ether. Extract by shaking for 30–40 sec then let the solution stand for 3–5 min. Transfer the aqueous layer into a 100-ml conical flask, then treat by one of the following methods. Run a blank determination.

6-Fold amplification. To the iodide solution, add 2 ml of saturated bromine water. Stopper the flask and stir the solution for 10 min. Destroy excess of bromine by addition of 1 ml of formic acid solution and stirring for 5 min. Add 5 ml of 2*N* sulphuric acid and about 0.5 g of potassium iodide, and determine the liberated iodine with 0.02*M* thiosulphate in the usual way.

36-Fold amplification. Transfer the iodine solution, formed as above, to a 100-ml separating funnel. Extract the iodine with two 25-ml portions of benzene. Collect the extracts in another funnel. Wash the combined extract with 5 ml of water to remove any iodide carried over. Shake the iodine solution with 10 ml of water containing 0.5 ml of sodium hydrogen sulphite solution to reduce iodine to iodide. Transfer the aqueous (lower) layer, containing the iodide, to a 50-ml conical flask and oxidize it with bromine water. Continue as described for the 6-fold method. Titrate the liberated iodine with 0.01*M* thiosulphate. For this method the amount of mercury taken should be less than 0.25 mg.

24-Fold amplification. To the iodide solution, add 10 ml of periodate solution. Stopper and allow the reaction mix-

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Table 1. Amounts of reagents used for different mercury concentrations

Range of mercury, *mg*	KI solution, *ml*	Final vol. of aqueous phase, *ml*	Vol. of organic phase, *ml*
0.06–0.25	0.4	12	6
0.5–4	6		
4.5–7	10	24	12

ture to stand for 10 min at room temperature, then place the flask in a boiling water-bath for 30 min for complete oxidation. Cool, add 10 ml of ammonium molybdate solution and 5 ml of pH-2.2 acetate buffer. Add 0.5 g of potassium iodide; stopper the flask and set aside for 10 min. Titrate the liberated iodine with 0.04*M* thiosulphate.

If there is less than 6 mg of iodide use 10 ml of periodate solution; for 8–10 mg use 15 ml of periodate.

Analysis of organomercurial compounds by 6-fold amplification. Combust 3–6 mg of sample by the oxygen-flask method,[11] absorbing the combustion products in 5 ml of saturated bromine water. Rinse the stopper with 2–3 ml of water. Remove excess of bromine by boiling for 5 min (to avoid oxidation of the iodide subsequently added). Cool, and introduce 0.25 ml of 0.1*M* nitric acid. Transfer quantitatively to a 50-ml separating funnel with 3–4 ml of water. Add 6 ml of potassium iodide solution (the volume of the aqueous layer should be *ca.* 12 ml and the pH value 2–3.5). Extract with 6 ml of diethyl ether and proceed as for inorganic mercury.

RESULTS AND DISCUSSION

Under the experimental conditions used, the mercury is extracted as HgI_2. This has been proved experimentally by allowing solutions of mercury(II) and iodide in a 1:4 ratio to react, then extracting the solution with ether and determining the residual iodide in the aqueous layer. The amount of iodide remaining corresponded to HgI_2 being extracted. Atomic-absorption spectrometry showed that all the mercury was extracted.

To attain complete extraction, the ether–water volume ratio was always 1:2 (see Table1) and the pH value of the aqueous layer was 2–3.5. Solutions of higher pH gave rise to high results; those with pH values lower than 2 gave low metal recoveries.

The three amplification methods gave satisfactory results, the recovery ranging from 98.8 to 99.8% for the 6-fold method (0.15–7.0 mg of mercury), from 98.8 to 101.8 for the 36-fold method (0.04–0.25 mg), and from 99.4 to 99.9% for the 24-fold method (0.15–7.0 mg). The recoveries were 2–3% high for lower amounts of mercury. However, the 6-fold amplification method seems simpler and less time-consuming than the others; one determination takes *ca.* 30 min. The coefficients of variation for the 6-fold amplification method were 3.9, 0.9 and 0.5% for 0.06, 1.5, and 7 mg of mercury respectively (5 replicates). The 6- and 24-fold amplification methods can be used to determine 0.05–7 mg of mercury. The 36-fold amplification method is applicable for the determination of 0.05–0.25 mg of mercury; higher amounts of metal can be determined provided the unreacted iodide does not exceed 0.4 mg, which after oxidation to iodate liberates an amount of iodine extractable with two 25-ml portions of benzene. More iodine requires larger volumes of benzene. The coefficients of variation for 0.04, 0.12, and 0.25 mg of mercury were 4.6, 1.2, and 1.0%, respectively (5 replicates).

Table 2. Microdetermination of mercury in organomercurial compounds

Compound	Sample wt. *mg*	Mercury, % Theory	Mercury, % Found	Coeff. of variation, %
Phenylmercury(II) acetate	3.075	59.52	60.1	0.6
	4.129		58.9	
	4.885		59.3	
	5.220		59.6	
Methylmercury(II) bromide	2.833	67.87	68.2	0.8
	3.767		66.8	
	5.024		67.6	
Mercury(II) acetate	3.265	62.94	64.5	1.2
	5.664		63.6	
	6.976		62.7	

For the 24-fold amplification, the excess of iodide was oxidized with periodate in borate buffer at pH 7 as recommended by Belcher *et al.*,[8] who described the determination of 10–200 μg of iodide. It was found that up to 10 mg of iodide can be oxidized quantitatively with 15 ml of 0.015 *M* periodate. The unused periodate is masked by molybdate[9] at pH 3–3.5; 10 ml of 25% molybdate solution did not affect the final determination. The coefficients of variation were 3.1, 1.3, and 0.9% for 0.06, 1.5, and 7 mg of mercury, respectively (5 replicates).

Metals which form ether-soluble complexes or insoluble compounds with iodide, or oxidize iodide to iodine, are expected to interfere.

The method has been applied to the microdetermination of mercury in organomercurial compounds following oxygen-flask combustion (Table 2). It can determine as little as 40 μg of mercury in 12 ml of solution, which compares favourably with the detection limit of 100 μg for the ascorbic acid method[6].

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INDIRECT DETERMINATION OF NITROGLYCERINE BY BIAMPEROMETRIC TITRIMETRY

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Summary—A procedure is described for the determination of nitroglycerine in propellant samples by biamperometric titrimetry. The method is simple, avoids the use of expensive instruments, and is free from interferences other than those occurring in the classical techniques. The accuracy and precision are equal to those of existing methods. The reduction and titration steps are performed in the specially designed flask.

The quantitative determination of nitroglycerine in propellant samples has received considerable attention. Many analytical methods have been applied such as polarography,[1] infrared spectrophotometry,[2–4] gas chromatography.[5,6] While each of these methods offers some advantages, they all require expensive instruments. Titrimetric procedures[7,8] are also applicable, but they have some practical disadvantages: for instance, titanium(III) needs daily restandardization because of its instability and, furthermore, some materials such as 2-nitrodiphenylamine (2-NDPA), impart an intense colour to the sample solutions, necessitating potentiometric detection of the end-point.

Nitroglycerine (NG) is frequently determined in this laboratory by the method of Lambert and DuBois.[9] Although the procedure is quite satisfactory, it requires pH adjustment before the titration, and the use of a potential-recording device.

The importance of the titrimetric procedure in routine analysis has stimulated considerable interest in the development of methods with reduced instrumental requirements and a minimum of operational steps whenever possible. The biamperometric method of end-point detection has very simple instrumental requirements. Devices for performing "dead-stop" titrimetry with the aid of a pH-meter have been reported[10] and the construction of a simple LED circuit for amperometric end-point detection has recently been published.[11]

The purpose of the present work was to develop a titrimetric procedure with few instrumental requirements and a minimum of operational steps. A new device for performing the reduction and titration steps will be described in this paper.

EXPERIMENTAL

Apparatus

Both reduction and titration were carried out in a 200-ml cylindrical vessel (shown as *a* in Fig. 1) with a flat bottom and a stoppered side-arm. Into the standard ST 50/50 ground-glass neck was fitted an intermediate reducing joint *b* provided with a gas-inlet tube. This intermediate joint carried a water-cooled reflux condenser *c* during the reduction stage, and then the "titration-head" *c* during the titration. The "titration-head" *d* held the titrant delivery tube, the nitrogen outlet and the separatory funnel through which the potassium iodide solution was added.

Twin platinum electrodes were introduced through the side-arm of the vessel for following the biamperometric titration. They were rinsed frequently between determinations, and were cleaned by being kept for some hours in concentrated nitric acid.

For the sake of convenience, an automatic titrator—Radiometer Model TTTld—synchronized by means of a Model MNV1 magnetic valve, was employed for controlling the titration process, but simpler equipment may be used.

Reagents

All solutions were prepared with glass-distilled water and all chemicals used were of analytical-reagent grade.

A 0.7*M* ferrous ammonium sulphate solution was prepared by dissolving 137.3 g of $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ in a mixture of 35 ml of concentrated sulphuric and 35 ml of distilled water, and then diluting to 500 ml. This solution was kept under a layer of light petroleum.

The thiosulphate solutions were standardized with potassium dichromate.

The NG was propellant-production grade, and was purified according to the literature.[12]

Sample preparation

Samples were obtained either by extracting with methylene chloride in a Soxhlet extractor[13] or by refluxing with 68% w/w acetic acid.[14]

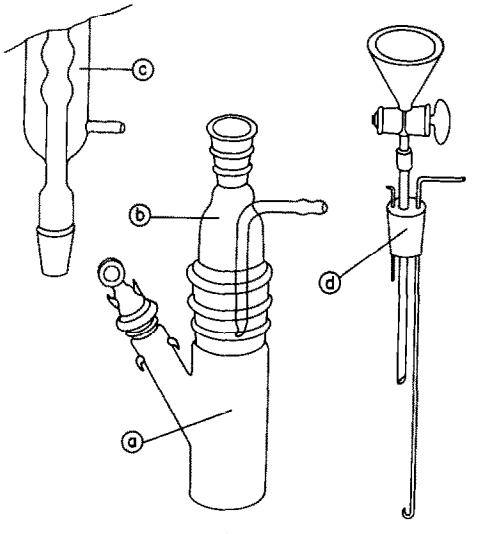

Fig. 1.

Procedure

Dissolve the extract from an accurately known amount of propellant in 50 ml of 68% w/w acetic acid. This sample should contain 0.09–0.10 g of NG. Transfer it to the reduction–titration vessel, add 25 ml of hydrochloric acid (1 + 1) and a few antibumping granules, attach the intermediate reducing joint *b* and allow the nitrogen to flow gently for 5 min to displace the air in the flask.

Add 10 ml of the ferrous ammonium sulphate solution through the side-arm and replace the stopper. Fit the reflux condenser *c* and boil the solution gently on a heating mantle for about 15 min (as the reaction proceeds the colour of the solution will turn from yellow to reddish-brown and back to yellow).

Remove the apparatus from the heating mantle without disconnecting the condenser, increase the flow of nitrogen and immerse the vessel in a cold-water bath till the solution is at about room temperature.

Replace the condenser by the "titration-head" *d*. Introduce a magnetic stirring bar and the twin platinum electrodes through the side-arm of the vessel. Add 50 ml of 10% potassium iodide solution from the separatory funnel. Titrate the liberated iodine slowly with 0.1*M* sodium thiosulphate, using magnetic stirring and flushing nitrogen through the vessel. Run a blank on the same amounts of reagents, at the same time as the determination, including all steps. Adjust the flow of titrant so that the volume used for the blank titration will be delivered in approximately the same time as that for the sample titration.

RESULTS

Standard samples were prepared and analysed to establish the validity of the technique. The results are shown in Table 1. The relative standard deviation of 0.4% (7 determinations) is considered satisfactory.

Interferences

Materials always present along with NG in modern propellant formulations include stabilizers and plasticizers which are also extractable into methylene chloride or 68% w/w acetic acid.

Varying amounts of ethyl centralite (*N,N'*-diethyl-*N,N'*-diphenylurea), diethyl phthalate and dibutyl phthalate as representative materials caused no interference at the typical levels at which they are found in rocket propellant compositions. The additions were made to aliquots of a solution of NG in 68% w/w acetic acid.

The 2-nitrodiphenylamine (2-NDPA) caused a positive error (as found by Lambert and Dubois[9]) which was eliminated by adding to the blank determination the estimated amount of 2-NDPA.[15,16]

Table 1. Titration of nitroglycerine

NG taken, *mg*	NG found, *mg*
103.2	102.9
96.6	96.4
101.2	100.5
104.0	103.3
100.3	100.5
102.2	101.5

The NG content of samples from different propellant formulations was determined by the procedure described and also by the EDTA method[9] and the dichromate method.[17] Agreement of the results was acceptable.

DISCUSSION

The initial step of this procedure, involving the reduction of nitrate groups with an appropriate excess of iron(II), is almost identical to that of the EDTA method of Lambert and Dubois.[9] The several modifications in the design of the reduction vessel and the change of the method used for the determination of iron(III) formed in the NG reduction were introduced in order to reduce the number of operational steps (thus reducing the blank value) and to avoid the use of a potential-recording device. Use of the proposed reduction–titration vessel eliminates the transfer of the solution after the reduction step. It is also unnecessary to adjust the pH before titration, thus avoiding the use of glass and calomel electrodes. The end-point can be detected with the LED circuit—somewhat modified—or any other suitable device.[18,19] Karl Fischer titrators, often employed in chemical laboratories dealing with solid propellants, may also be adapted for the titration.

The method is applicable to the determination of NG in the absence of any materials capable of reacting with iron(II) or iron(III), potassium iodide or thiosulphate. Thus, interferences from materials present in propellant formulations would be, at the most, the same as for the EDTA or the classical Becker and Shaefer methods.[7]

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NEW CHROMOGENS OF THE FERROIN TYPE—VIII

SOME DI- AND TRISUBSTITUTED 1,2,4-TRIAZINES, 3-SUBSTITUTED-9*H*-INDENO[1,2-*e*]-1,2,4-TRIAZIN-9-ONES, AND DI- AND TRISUBSTITUTED 1,2,4-TRIAZOLINES

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Summary—Thirty-six new ferroin compounds have been investigated as possible chelation regents for the colorimetric detection and determination of trace amounts of iron(II), copper(I), and cobalt(II). Spectral data, solution conditions favourable for chelate formation, and other data are reported. The results reveal that incorporation of triazoline heterocycles in ferroin chromophore groupings generally leads to poor chromogenic properties, except with respect to cobalt. Triazine groups, however, can give rise to superior properties. The most sensitive iron(II) chromogen of the ferroin type found to date and a promising new cobalt chromogen are described.

Previous investigations reported in this series of communications have revealed that certain substituted 1,2,4-triazine derivatives which possess the ferroin group exhibit interesting and analytically promising chromogenic properties. For example, some of the most sensitive chromogenic reagents for iron developed to date are among this class of compounds. Included in this category are 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine (commonly referred to as PDT),[1–4] 3-(4-phenyl-2-pyridyl)-5,6-diphenyl-1,2,4-triazine (PPDT),[1,2,5] 2,4 bis(5,6-diphenyl-1,2,4-triazin-3-yl)pyridine (2,4-BDTP),[6,7] and their water-soluble sulphonated derivatives Ferrozine,[8] PPDT[9] and 2,4-BDTPS.[9]

Case, who first synthesized these compounds, has developed further syntheses and made[10–12] several new triazine derivatives for us to test for analytical utility. This note reports the results of our evaluation of these and a number of new triazoline derivatives of the ferroin type, also recently synthesized by Case.[10–12]

The new compounds are listed below; the structures and other details can be found in the publications by Case.[10–12]

3-Substituted-5-phenyl-1,2,4-triazines

	Substitutents
I	3-(4-Methyl-2-pyridyl)
II	3-(4-Phenyl-2-pyridyl)
III	3-[2-(1,10-Phenanthrolyl)]
IV	3-[6-(2,2′-Bipyridyl)]

3,5,6-Trisubstituted-1,2,4-triazines

	Substituents
V	3-(Pyrazyl)-5,6-dimethyl
VI	3-(3-Pyridazyl)-5,6-dimethyl
VII	3-(4-Pyrimidyl)-5,6-dimethyl
VIII	3-[6-(2,2′-Bipyridyl)]-5,6-dimethyl
IX	3-(4-Methyl-2-pyridyl)-5-phenyl-6-benzoyl
X	3-(4-Phenyl-2-pyridyl)-5-phenyl-6-benzoyl
XI	3-[6-(2,2′-Bipyridyl)]-5-phenyl-6-benzoyl
XII	3-[2(1,10-Phenanthrolyl)]-5-phenyl-6-benzoyl
XIII	3-(2-Thiazolyl)-5-phenyl-6-benzoyl
XIV	3-(4-Pyrimidyl)-1,2,4-triazino[5,6-f] [4,7]phenanthroline

3-Substituted-9H-indeno[1,2-e]-1,2,4-triazin-9-ones

	Substituents
XV	3-(4-Methyl-2-pyridyl)
XVI	3-(4-Phenyl-2-pyridyl)
XVII	3-[6-(2,2′-Bipyridyl)]
XVIII	3-[2-(1,10-Phenanthrolyl)]
XIX	3-(2-Thiazolyl)

3,5-Disubstituted-Δ²-1,2,4-triazolines

	Substituents
XX	3-Pyrazyl-5-phenyl
XXI	3-Pyrazyl-5-(2-pyridyl)
XXII	3-(3-Pyridazyl)-5-phenyl
XXIII	3-(3-Pyridazyl)-5-(2-pyridyl)
XXIV	3-(4-Pyrimidyl)-5-phenyl
XXV	3-(4-Pyrimidyl)-5-(2-pyridyl)
XXVI	3-[6-(2,2′-Bipyridyl)]-5-phenyl
XXVII	3-[6-(2,2′-Bipyridyl)]-5-(2-pyridyl)

5,5,3-Trisubstituted-Δ²-1,2,4-triazoline

	Substituents
XXVIII	5-Methyl-5-phenyl-3-(4-methyl-2-pyridyl)
XXIX	5-Methyl-5-phenyl-3-(4-phenyl-2-pyridyl)
XXX	5-Methyl-5-phenyl-3-[2-(1,10-phenanthrolyl)]
XXXI	5-Methyl-5-(2-pyridyl)-3-(2-pyridyl)
XXXII	5-Methyl-5-(2-pyridyl)-3-(4-methyl-2-pyridyl)
XXXIII	5-Methyl-5-(2-pyridyl)-3-(4-phenyl-2-pyridyl)
XXXIV	5-Methyl-5-(2-pyridyl)-3-[2-(1,10-phenanthrolyl)
XXXV	5-Methyl-5-(2-pyridyl)-3-[6-(2,2′-bipyridyl)]
XXXVI	5-Phenyl-5-(2-pyridyl)-3-[2-(1,10-phenanthrolyl)]

EXPERIMENTAL

Standard solutions, buffers, reagents, and procedures used in this investigation are those used previously.[13] Spectra were recorded with a Cary Model 14 spectrophotometer and corrected for absorbance due to reagent blanks. Ligand:metal ratios of the chelates were determined spectrophotometrically by the mole-ratio method.[14,15] The free ligands are all pale yellow.

RESULTS AND DISCUSSION

Iron(II) chelates

All the compounds form iron(II) chelates, generally with maximum colour formation over the pH range 5–8. Chelation occurs over a much broader range of pH with many of them but not necessarily with production of maximum colour. Compounds V and VIII are exceptional in this regard as they complex iron(II) at unusually low pH; VIII chelates iron(II) even in 4*M* hydrochloric acid, and shows promise as a reagent for iron in strong acids, even though the sensitivity is not particularly high. The stabilities of the iron(II) chelates of V–VIII probably derive from the methyl substituents in their triazine moities which, by their strong electron-donor character, enhance the electron density on the nitrogen donor atoms, thereby contributing to the strength of the chelate rings. The broadest pH ranges of complexation occur with derivatives XV–XVIII (pH 1–13) and I–IV (pH 3–12), and the narrowest with XX–XXV (pH 5–8).

The curve-matching mole-ratio technique of Chriswell and Schilt[15] was used to determine the compositions of certain chelates selected because of the unusual structure of the reagent or the possibility of its acting as either a bidentate or a terdentate ligand. The results are compiled in Table 1. As expected, I and II act as bidentate ligands and III and IV as terdentate ligands. All four chelates have high stability. The structures of compounds XXI, XXIII, XXV, XXVII and XXXI suggest that they could behave as either bi- or terdentate ligands. The results indicate only XXVII forms a bis-chelate with iron(II), and even then only weakly. The other four act as weak bidentate ligands to form relatively weak tris-chelates. Compound XIV proved to be a relatively weak terdentate ligand for iron(II), which is surprising in view of its several possible modes of chelation. It is curious that the bidentate mode (involving the 4-phenanthroline and 2-triazine nitrogen atoms), which would ordinarily be expected to give a strong chelate, is ignored in favour of the terdentate mode which gives quite a weak chelate. Apparently the pyrimidyl nitrogen does not co-ordinate strongly to iron(II) but if it does not co-ordinate, then the pyrimidyl group can sterically hinder the formation of a tris-chelate. Thus the pyrimidyl group of XIV would lead to poor stability in either case, but especially for the tris-chelate. (In VII this effect will presumably offset the effect of the methyl groups.)

Compound II is the most sensitive iron chromogen of its type so far found. We are studying it further to develop

Table 1. Properties of the iron(II) chelates

Chromogen	Colour	λ, *nm*	ϵ, $l.mole^{-1}.cm^{-1}$	Solvent*	Fe:L ratio	Remarks†
I	Violet	560	2.98×10^4	b	1:3	4
II	Violet	560	3.48×10^4	b	1:3	4
III	Violet	604	1.48×10^4	c	1:2	
IV	Violet	583	1.45×10^4	c	1:2	
V	Red	521	1.41×10^4	a	—	1
VI	Orange	512	1.53×10^4	a	—	
VII	Red	530	9.9×10^3	a	—	1
VIII	Violet	555	9.9×10^3	a	—	
IX	Purple	572	2.34×10^4	b	—	4
X	Blue	573	2.68×10^4	b	—	4
XI	Blue	608	1.12×10^4	b	—	4
XII	Purple	623	9.9×10^3	b	—	4
XIII	Yellow	562	5.2×10^3	b	—	
XIV	Blue	582	2.24×10^4	b	1:2	1,2
XV	Blue	585	2.49×10^4	b	—	
XVI	Blue	581	2.89×10^4	c	—	
XVII	Violet	600	1.18×10^4	b	—	
XVIII	Violet	520	8.7×10^3	c	—	
XIX	Green	583	6.0×10^3	b	—	4
XX	Red	530	7.4×10^3	a	—	1
XXI	Red	512	7.2×10^3	a	1:3	1,2
XXII	Red	524	1.23×10^4	a	—	
XXIII	Red	514	9.4×10^3	a	1:3	1,2
XXIV	Red	530	3.0×10^3	a	—	1,3
XXV	Red	510	7.1×10^3	a	1:3	1,2,3
XXVI	Purple	548	9.2×10^3	a	—	4
XXVII	Purple	551	9.0×10^3	a	1:2	
XXVIII	Orange	493	8.0×10^3	b	—	1,3,4
XXIX	Red	526	1.46×10^4	b	—	3
XXX	Purple	555	1.35×10^4	b	—	3
XXXI	Purple	484	6.9×10^3	b	1:3	2,3
XXXII	Purple	490	6.7×10^3	b	—	3
XXXIII	Brown	484	7.7×10^3	b	—	3,4
XXXIV	Brown	495	1.00×10^4	b	—	1,3
XXXV	Purple	550	8.9×10^3	b	—	3
XXXVI	Purple	515	4.2×10^3	b	—	3

* a, Water (pH 7). b, Ethanol and water (pH 7). c, Dimethylformamide and water (pH 7).

† 1, Beer's law not followed unless very large excess of chromogen is present. 2, Mole-ratio plot exhibits extreme curvature, indicating weak complex. 3, Poor colour stability on aging. 4, Quantitatively extractable into isoamyl alcohol.

Table 2. Properties of the copper(I) and cobalt(II) chelates

Chromogen	Copper(I) Colour	λ, nm	ϵ, $l.mole^{-1}.cm^{-1}$	Cobalt(II) Colour	λ, nm	ϵ, $l.\ mole^{-1}.cm^{-1}$
I	Orange	495	8.9×10^3	Orange	525	1.36×10^3
II	Orange	495	1.05×10^4	Colourless	—	—
III	Yellow	440	3.6×10^3	Orange	555	1.85×10^3
IV	Yellow	450	4.6×10^3	Purple	545	3.35×10^3
VI	Gold	455	9.3×10^3	Colourless	—	—
VIII	Brown	425	3.7×10^3	Orange	514	1.83×10^3
IX	Brown	490	5.9×10^3	Red	525*	120
X	Red	497	6.4×10^3	Orange	525*	140
XIV	Brown	522	8.0×10^3	Brown	550	3.5×10^3
XV	Brown	481	7.0×10^3	Yellow	450*	280
XVI	Yellow	493	9.3×10^3	Yellow	450*	580
XXI	Pale yellow	—	—	Orange	424	1.04×10^4

* Wavelength not a maximum but at side of band just before reagent blank absorbance becomes appreciable.

practical applications and to prepare a water-soluble sulphonated derivative for more convenient use. The compounds I, IX, X, XV and XVI are also promising as sensitive iron reagents, but less so than II. II has the PPDT structure without the phenyl substituent in the 6-triazine position. The molar absorptivity of its iron(II) chelate (3.48×10^4 l.mole^{-1}.cm^{-1}) is considerably greater than that of the PPDT chelate (2.87×10^4) which appears to contradict the empirical rule that phenyl substituents generally give rise to enhanced absorptivities for ferroin chelates. This may be because two adjacent phenyl substituents (such as the 5,6-diphenyl groups in PPDT) tend to cause loss of the co-planarity essential for π-electron delocalization and concomitant high absorptivity. Another example may be provided by II and X, where X differs from II only in having a benzoyl moiety in the 6-triazine position adjacent to the 5-phenyl group, yet the absorptivity of its iron(II) chelate is appreciably less than that of the II complex.

Triazolines XX–XXVI are without special merit as chromogenic reagents for iron, the molar absorptivities are lower than those for most ferroin chelates, the complexes are weak and the colours tend to fade or change with time.

Cobalt(II) chelates

All the compounds gave evidence of forming cobalt(II) complexes, generally over the pH range 3–11, but only a few gave an appreciable change in spectrum in doing so. Most of the exceptions are listed in Table 2. Outstanding is XXI, which is remarkably sensitive for cobalt (optimum pH range 5–12), and merits further attention. The absorbance obeys Beer's law.

Triazolines XXIII and XXV behave similarly to XXI but their cobalt(II) systems do not follow Beer's law unless a large excess of chromogen is employed.

Copper(I) chelates

All the compounds gave copper(I) chelates, with colour formation (yellow or brown) favoured generally between pH 4 and 9. None of the triazolines, however, proved particularly effective as copper chromogens. The colours and spectra of their copper chelates closely resembled those of the free ligands, and colour fading was common.

Table 2 includes spectral data for only the more interesting copper(I) chelates, *i.e.*, those with molar absorptivities greater than 3.0×10^3 l.mole^{-1}.cm^{-1} or with ligands that form intensely coloured iron(II) or cobalt(II) chelates. As might be expected, II proved to be a highly sensitive reagent for copper as well as for iron, but it is not as sensitive as 2,4-BDTP. Further study of II is nevertheless merited and should result in practical application for simultaneous determination of trace amounts of iron and copper.

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A POLAROGRAPHIC STUDY OF THE PYRIDINE–COPPER–CHLORIDE COMPLEXES IN METHANOL AND DETERMINATION OF THE STABILITY CONSTANTS

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Summary—Copper(I) chloride has been shown to form two complexes with pyridine in anhydrous methanol, CuClPy and $CuClPy_2$. Formation constants have been determined and found to be $\log K_1 = 7.8 \pm 0.3$ and $\log K_2 = 9.45 \pm 0.3$. The role of the complexes in the catalytic oxidation of xylenol is discussed.

We have been engaged for several years in a study of the oxidation of xylenol by gaseous oxygen in the presence of a pyridine–copper chloride catalyst: the oxidative coupling yields quinones and polymers.[1] The pyridine plays an important role in determining the rate and orientation (C–C or C–O) of the coupling.[2] Several forms of the catalyst may exist with different ratios of co-ordinated pyridine to copper, depending on the experimental conditions (concentrations, solvent, temperature, *etc.*) and the oxidation state of the copper. The oxidized solid compound contains pyridine and copper in a 1:1 ratio;[3] the exact ratio has not been found for either the oxidized or the reduced form in solution, in spite of ultraviolet and infrared spectroscopic studies.[4]

A survey of the literature leads to various conclusions. Jardine suggested that the number of ligand molecules varied from one to four but was seldom two or three for complexes of copper(I).[5] A number of labile complexes with halides and aliphatic amines[6–8] or ammonia[9] have a 1:1 stoichiometry. On the whole, the stability increases with the molecular weight of the amine.[10–15] Though of the halides, bromide and iodide form the more stable ternary copper–pyridine complexes, a white, solid 1:1 complex of CuCl and pyridine has been prepared by exchange for another amine Oxidation of this compound leads to the well defined $CuCl_2Py_2$ [16,17] The role of the solvent in these reactions has been investigated through studies on solvation by acetonitrile[18] and by methanol[19–22]—solvents of interest for the oxidative coupling. The behaviour in methanol is similar to that in water: CuCl disproportionates into $CuCl_2$ and copper metal.[22]

This paper describes the results of a polarographic study of the reduced state of the complex, intended to give values for the equilibrium constants and the corresponding concentrations of the various species related to CuCl under the conditions of interest. These may be of interest for an understanding of the reoxidation to an active form rather than to $CuCl_2Py_2$ which is inactive. The solvent is methanol

EXPERIMENTAL

A Princeton Applied Research Polarographic Analyser Model 174 equipped with a drop-timer system was used with a SEFRAM TRP X–Y recorder. A methanolic saturated calomel electrode was used as the reference electrode.

Methanol and pyridine were dried over molecular sieve UC 3A. The copper(I) chloride was prepared by reduction

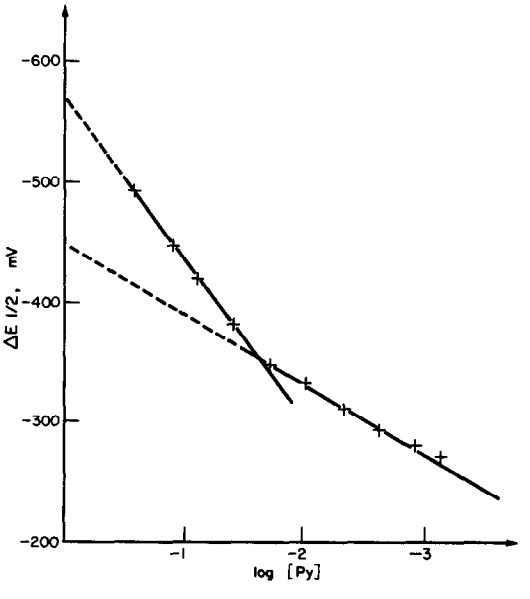


Fig. 1. Variation of the half-wave potential with respect to standard potential in absence of pyridine, with the concentration of pyridine. Methanol solvent—$[Li ClO_4] = 10^{-1}M$; $[CuCl] = 10^{-4}M$.

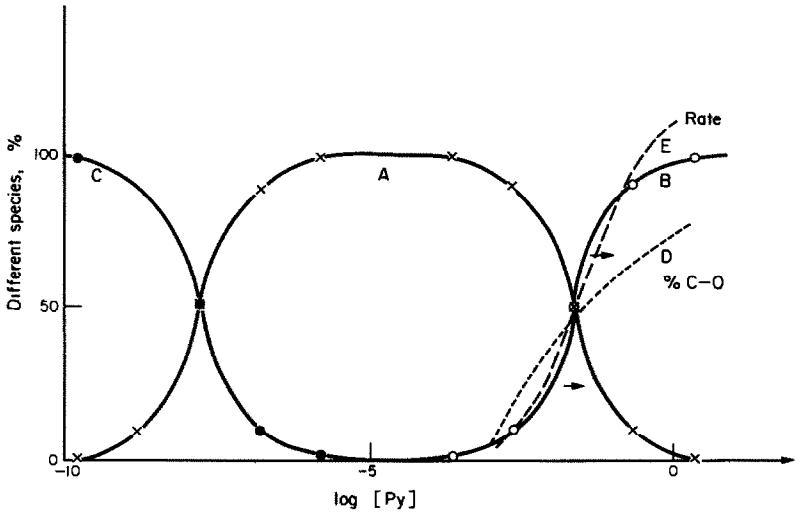


Fig. 2. Relative concentrations of the three forms of CuCl as a function of the concentration of free pyridine. × CuClPy (A), ○ $CuClPy_2$ (B), ● CuCl (C); (D) and (E), are degree of C–O bonding (%) and rate of oxygen absorption respectively and are from ref. 2.

and drying as previously described,[3] and was used as a $10^{-4}M$ solution in dry methanol. Two supporting electrolytes, both 0.1*M*, were used: sodium and lithium perchlorate.

The numerical results were evaluated by Lingane's method,[23] in which the shift in half-wave potential $E_{1/2}$ on going from the uncomplexed species to the complexed form as ligand is added, is plotted against the logarithm of the free ligand concentration. For a one-electron transfer at 20°C.

$$\Delta E_{\frac{1}{2}} = E_{\frac{1}{2}(\text{free})} - E_{\frac{1}{2}(\text{compl.})} = 0.058\,\{\log \beta_p + p \log [\text{Py}]\} \quad (1)$$

where p is the number of ligands attached to the metal ion, and

$$\beta_p = [\text{CuCl}\cdot \text{Py}_p]/[\text{CuCl}][\text{Py}]^p$$

A plot of $E_{1/2}$ *vs.* log [Py] is, according to (1), a straight line with a slope of $0.058p$ with an intercept of $0.058 \log \beta_p$. When a series of complexes exists, with increasing number of ligands co-ordinated to the metal, the plot may consist of a series of linear segments each with a slope corresponding to a different value of p, though more often there is a smooth curve when the successive equilibria overlap.

As pyridine itself gives rise to a wave at the dropping mercury electrode, and as this wave is close to that of the complex, we used differential pulse polarography, which gives peaks which are more easily resolved than successive waves are. The peak-height is proportional to the concentration of the active species and the location of the maximum corresponds to the $E_{1/2}$.

RESULTS

Measurements were made in both electrolytes, in methanol. Figure 1 shows the plot of $E_{\frac{1}{2}}$ *vs.* log[Py]. The slopes of the linear segments, calculated by a least-squares procedure, are 58 ± 10 mV and 110 ± 10 mV per log unit, which correspond to p-values of one (for low pyridine concentrations) and two (for higher concentrations). Since CuCl disproportionates in methanol, as it does in water, the $E_{\frac{1}{2}}$-value cannot be determined in the absence of pyridine, but a value for the standard potential of the Cu(I)/Cu couple in methanol has been calculated[22] from measurements on related systems and is quoted as +0.26 V *vs.* the saturated methanolic calomel electrode. From this figure and the data shown in Fig. 1, values for the formation constants were calculated to be $\log \beta_1 = 7.8 \pm 0.3$ and $\log \beta_2 = 9.45 \pm 0.3$

These constants were then used to calculate the distribution of the species as a function of the pyridine concentration from the following equations. The results are plotted in Fig. 2.

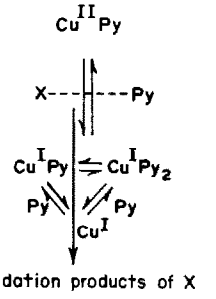
$$\%\,\text{CuCl} = 100/(1 + 10^{7.8}[\text{Py}] + 10^{9.45}[\text{Py}]^2)$$

$$\%\,\text{CuClPy} = 100/(1 + 10^{-7.8}[\text{Py}]^{-1} + 10^{1.65}[\text{Py}])$$

$$\%\,\text{CuClPy}_2 = 100/(1 + 10^{-1.65}[\text{Py}]^{-1} + 10^{-9.45}[\text{Py}]^{-2})$$

During the oxidation of xylenol, when no additional pyridine is present above that exchanged between the catalyst and the medium,[3] the copper species are likely to be CuCl and CuClPy. The oxidation is slow and yields quinones. Under the usual conditions of polymer synthesis, the pyridine concentration lies between 0.1 and 1*M*, and the rate of polymerization is highest for Py:Cu ratios between 10 and 100, with a xylenol:copper ratio of about 50. It must be remembered that xylenol is also associated with the pyridine[24] so that the concentration of free pyridine is diminished. Consequently the calculated curves should be displaced as indicated by the arrows in Fig. 2, the extent of the shift depending on the various concentrations. One can conclude that over the range of concentrations used for the oxidation, there exists a mixture of CuClPy and $CuClPy_2$.

We have superimposed on Fig. 2 the curves representing the rate of coupling **R** and the degree (%) of C–O bond formation **D**,[2] the slopes of which are similar to that of the distribution of the $CuClPy_2$ species; this would seem to increase the reoxidation rate for the complex, which is a rate-limiting step in the sequence of reactions. As far as the orientation is concerned, we have obtained other results which indicate that the main effect is one of pH.[25] The various reactions and equilibria can be depicted by the following diagram:



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DETERMINATION OF TRACE AMOUNTS OF ZIRCONIUM IN SILICATES BY CATION-EXCHANGE CHROMATOGRAPHY AND SPECTROPHOTOMETRY WITH XYLENOL ORANGE

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Summary—An ion-exchange scheme and colorimetric determination with Xylenol Orange are used for estimating traces of zirconium in silicate rocks.

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Several organic reagents have been utilized for the photometric determination of zirconium, and the general principles on which they are based have been given by Kuznetsov[7–9] and others.[10–16] The most sensitive and also most selective reagents are Xylenol Orange, Arsenazo III, Methylthymol Blue, chloranilic acid, Pyrocatechol Violet, and certain other reagents, which form comparatively stable zirconium complexes having a colour intensity little affected by slight variations in acidity. Like Elinson and Petrov[17] we regard Xylenol Orange as the best colorimetric reagent for zirconium. Although there are many papers on colorimetric determination of zirconium, relatively few deal with trace levels in rocks and minerals.[18–24]

Xylenol Orange reacts with zirconium to form a 1:1 coloured complex in acid solutions. The absorption maximum of the complex is at 535–540 nm, that of the reagent is at 440 nm. The maximum colour intensity is obtained at a concentration of 0.8*M* hydrochloric or perchloric acid. Fluoride, phosphate, chromate, citrate, tartrate, iron(III), molybdenum(VI), niobium and tantalum interfere.

Because these interfering elements are always present in common silicate rocks and because (in our opinion) the high content of iron(III) present cannot be completely masked by the usual reducing agents, we think it necessary to separate the zirconium traces from the silicate matrix. Meyrowitz[20] dealt with the interference of titanium and niobium by matching the sample and calibration

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DETERMINATION OF TRACE AMOUNTS OF ZIRCONIUM IN SILICATES BY CATION-EXCHANGE CHROMATOGRAPHY AND SPECTROPHOTOMETRY WITH XYLENOL ORANGE

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Because these interfering elements are always present in common silicate rocks and because (in our opinion) the high content of iron(III) present cannot be completely masked by the usual reducing agents, we think it necessary to separate the zirconium traces from the silicate matrix. Meyrowitz[20] dealt with the interference of titanium and niobium by matching the sample and calibration

standards for concentration of these elements, but this is inconvenient because the composition of each sample has to be known and a calibration curve made for each sample. Culkin and Riley[19] separated traces of zirconium, hafnium, cerium and thorium by extraction with tri-n-butyl phosphate and cation-exchange; zirconium was eluted with oxalic acid. Strelow *et al.*[22] separated zirconium from the silicate matrix of some standard rocks by cation-exchange, eluting zirconium and titanium with a sulphuric acid–hydrogen peroxide solution and then separating the zirconium on another ion-exchange column. They dissolved the sample in HF–HCl–$HClO_4$ mixture; only the W-1 (diabase) sample was dissolved completely. The recovery of zirconium was erratic and low for the other rock samples: in the case of S-1 (syenite) about 70% of the zirconium remained in the insoluble residue. When this residue was treated with a phosphoric acid mixture and, after dissolution, passed through a separate column, a large part of the zirconium appeared in the initial fractions. Part of the zirconium therefore seems to form an insoluble colloidal phosphate which is uncharged and passes through the column.

To achieve complete dissolution of the sample, the combination of a sodium peroxide fusion with a hydrogen peroxide–hydrochloric acid leach appears to be the most powerful solubilization technique, especially since zirconium may be present in rocks not as zirconia and zircon but as a vicarious substituent for other elements in high-melting minerals such as spinel, which is decomposed easily only by this dissolution technique. We separate the silicate matrix and the interfering elements (iron, niobium, titanium and molybdenum) by ion-exchange chromatography on Dowex 50 × 8 and elute the interfering elements with hydrochloric acid and ethanol as described previously.[25,26] The large amounts of nickel and sodium derived from the crucible and the reagents are also separated because they are eluted with the silicate matrix.

To avoid the use of another ion-exchange column as described by Strelow *et al.*[22] we elute zirconium with oxalic acid as suggested by Culkin and Riley.[19] The oxalic acid, which inhibits formation of the zirconium–Xylenol Orange complex, is destroyed by fuming with perchloric acid. Cheng's method[27] is used for the colorimetric determination. The use of sulphuric acid is avoided, with a view to determination of barium, which remains on the column after the elution with oxalic acid.

EXPERIMENTAL

Reagents

Hydrochloric acid (0.6M)–hydrogen peroxide (0.15%).

Hydrochloric acid (3M)–ethanol (20%).

Oxalic acid solution, 0.1M.

Hydrochloric acid, 6M.

Xylenol Orange solution, 0.03%.

Zirconium standard solution, 100 ppm. Weigh 67.5 mg of pure zirconium dioxide about 1.5 g of sodium peroxide and mix. Add another 1.5 g of sodium peroxide as a thin layer over the sample. Fuse on an asbestos board over a bunsen burner to a black liquid melt. Let the crucible cool, clean the outside with hot 6*M* hydrochloric acid, place it in a large beaker, and carefully add 0.6*M* hydrochloric acid–0.15% hydrogen peroxide mixture to obtain a clear solution. Use the mixture to rinse the crucible and dilute the solution to volume in a 250-ml standard flask.

N-Phenylbenzohydroxamic acid solution (NPBHA), 1%. Dissolve 1 g of NPBHA in 50 ml of pure ethanol (95%). Add water dropwise, with mixing, until the volume is 100 ml. Filter through a medium filter. Prepare just before use.

Wash solution saturated with NPBHA. Add 0.5 g of NPBHA to 500 ml of water, heat until dissolved and let stand at room temperature overnight. Filter through a medium filter. Prepare the day before use.

Silver nitrate solution, 10%.

Standardization of the zirconium solution. Transfer 50 ml of the zirconium solution to a 100-ml beaker, heat to about 60°, add 10 ml of 1% NPBHA solution dropwise with constant stirring, let stand overnight on a hot-air bath (60°), filter off hot on medium paper. Test for complete precipitation by adding 1 ml of NPBHA solution to the filtrate. Wash with saturated NPBHA solution until a negative test for chloride is obtained. Dry the filter in a platinum crucible at 110°, cover the crucible and place it in an electric furnace at 900° for 1 hr, cool and weigh the ZrO_2.

Column packing. Fill a borosilicate glass tube (22-mm bore, with fused-in porosity-3 glass sinter and a burette tap at the bottom) with Dowex 50W × 8 resin (200–400 mesh, H^+-form) to give a column height of 18 cm, and wash it with 300 ml of 3*M* hydrochloric acid. Wash with water until free from acid reaction. Adjust the flow-rate to 3.0 ± 0.5 ml/min. Pretreat the column with 30 ml of 0.6*M* hydrochloric acid–0.15% hydrogen peroxide solution.

Analytical procedure

Weigh out 0.3000 ± 0.001 g of finely powdered (130 mesh) sample in a pure nickel crucible. Proceed as for the preparation of the standard zirconium solution to obtain a clear solution. Pass the sample solution through the ion-exchange column, and wash with 50 ml of 0.6*M* hydrochloric acid–0.15% hydrogen peroxide mixture. Pass 250 ml of 3*M* hydrochloric acid–20% ethanol solution through the column to separate the silicate matrix. Wash the column with water until free from acid reaction. Pass 100 ml of 0.1*M* oxalic acid through the column and collect in a 150-ml Teflon beaker. Add 25 ml of perchloric acid and evaporate slowly to 2 ml or less. Transfer to a 25 ml standard flask by Eppendorf micropipette, and add perchloric acid, if necessary, to give a total volume of 2.00 ml. Dilute with water to about 20 ml. Add 2 ml of Xylenol Orange solution, dilute to volume and measure the absorbance at 535 nm, in 2-cm cells, after 2 hr.

Table 1. Zirconium content (*ppm*) of rock and mineral standard samples

Sample	Mean	Std devn.	Flanagan's range[29]	Flanagan's recommended value[32]	Abbey's usable value[33]	Carmichael's colorimetric value[31]
G-2	290	22	250–400	300	300	290
GSP-I	515	31	323–685	500	0.07*	533
AGV-I	210	21	186–315	225	220	195
UB-N	90	12	8–100[30]	—	—	—
FK-N	15	4.7	—	—	—	—
GS-N	245	17	—	—	—	—

* As % ZrO_2.

RESULTS AND CONCLUSIONS

To assess the reproducibility of the method, the separation was performed on a synthetic sample, containing major and trace elements as described previously.[26,28] In six aliquots, each containing 200 μg of zirconium; the amount found was 200 ± 7 μg.

Eight determinations performed on international standard rock samples (G-2, GSP-1, AGB-1, U.S. Geological Survey; UB-N, FK-N, GS-N, Association Nationale de la Recherche Technique) gave the results shown in Table 1, which are generally in the ranges reported by Flanagan[29] and De la Roche and Govindaraju.[30] FK-N and GS-N are new standards and no results are available. Only Carmichael's results[31] were obtained by a colorimetric method; the others were obtained by other instrumental methods. Our results are in good agreement with Carmichael's.

Blank runs gave negligible absorbance.

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DETERMINATION OF CALCIUM IN CEMENT BY FLAME-EMISSION SPECTROMETRY WITH STRONTIUM AS INTERNAL STANDARD

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The determination of calcium by oxygen/acetylene flame emission with a turbulent-flame burner gives very scattered results even in the presence of 8-hydroxyquinoline or phenol, which considerably reduce the interelement effects without, however, attenuating the scatter of the values obtained.[3–5] The same determination by emission with an air/acetylene or nitrous oxide/acetylene flame with a laminar-flow burner also shows a scattering of results greater than that given by atomic-absorption spectrometry.

It is known that in arc or spark spectrometry, it has been possible to reduce considerably the fluctuations in the determination of various elements by measuring not only the intensity of the spectral line of the element to be determined but also the *ratio of the intensity* of this spectral line to that of another element used as an internal standard. For this reason, with an apparatus designed for flame-emission spectrometry with an internal standard, we thought it would be of interest to examine the flame-emission possibilities of this method.

EXPERIMENTAL

Apparatus and procedures

The spectrometer used is the IL 453, of double-beam and double-channel type with a grating for each channel, these two gratings having different characteristics. This in-

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EXPERIMENTAL

Apparatus and procedures

The spectrometer used is the IL 453, of double-beam and double-channel type with a grating for each channel, these two gratings having different characteristics. This in-

strument can operate either in the absorption or the flame-emission mode and is equipped with a counting system making it possible to work directly in terms of concentration or by the internal standard technique.

Choice of internal standard

For determinations by this technique, it is not every element that may be used as an internal standard. If the intensities of the spectral lines of the element to be analysed and of the internal standard are to vary as concomitantly as possible, these two elements must meet certain well-defined conditions, investigated by Feldman,[6] and by Smith *et al.*[7–9]

They must emit in the same flame, have the same behaviour in the same flame, undergo the same interferences, and have similar chemical properties and vaporization/atomization rates.

In addition, the measured lines must be of the same type (neutral atom line or ionized atom line) and have similar excitation potentials and be spectrally similar so that the flame background spectrum is the same for both.

Strontium can play this part with respect to calcium, as already indicated by Feldman.[6] Both being in the same group of the Periodic Table, they have similar physical and chemical properties and the same valence. Finally, the excitation potentials of the spectral lines measured are similar: 2.9 eV for the calcium line at 422.6 nm and 2.7 eV for the strontium line at 460.7 nm.

Measurement technique

The signals corresponding to the calcium line at 422.6 nm and strontium at 460.7 nm are measured on channels A and B respectively. In direct emission, the signal from channel A is compared automatically with a fixed reference of 4 V (according to the design of the apparatus). When the channel A signal is measured relative to that from channel B, this reference is replaced by the signal corresponding to the emission from the internal standard, and this signal (which must be about 4 V) is amplified if necessary. Integration of the ratio of the signals from channel A and channel B is performed automatically in 20 sec. The air/acetylene or nitrous oxide/acetylene flame is used, the different instrumental parameters and the stoichiometry of the flame being optimized so as to give the best sensitivity and stability for calcium.

Reagents

Dissolution of cement. Dissolve 1 g of cement in 0.2*M* hydrochloric acid, filter off the insoluble residue and make up to 500 ml. Then dilute this solution 200-fold for the measurements.

Calcium solution. Dissolve, in hydrochloric acid, enough calcium carbonate previously dried at 105° to constant weight to give a CaO concentration of 1 g/l. The determination range is between 5 and 7 μg/ml.

Strontium solution. Dissolve, in hydrochloric acid, enough strontium carbonate (dried at 105°) to give a strontium concentration of 1 g/l. The amount of strontium added to the standard and sample solutions is imposed by the sensitivity of channel B of the spectrometer and is adjusted so as to be within satisfactory stability limits on this channel.

Lanthanum solution. Dissolve 58 g of La_2O_3 in 250 ml of concentrated hydrochloric acid and dilute to 1000 ml. The amount of lanthanum to be added to the standard and sample solutions is determined experimentally.

The calibration solution contains 700 μg of strontium, 5100 μg of lanthanum and 5 μg of CaO per ml. The solutions to be analysed contain 700 μg of strontium, 5100 μg of lanthanum and 5–7 μg of CaO from the cement, per ml. All the reagents used must be pure for analysis.

RESULTS AND DISCUSSION

We first examined whether direct emission, with an air/acetylene or nitrous oxide/acetylene flame, made it possible to obtain, for the determination of calcium in cement, values similar to those obtained by complexometric titration with EGTA (reference values) or by atomic-absorption spectrometry. We found that the results were systematically low by 10–20%. The addition of lanthanum to inhibit interference by aluminium and iron did not improve the results. Direct emission with these flames, but in the presence of strontium, led to results closer to the reference values but still 2–4% low and the improvement in the results was closely related to the stoichiometry of the flame, especially with air/acetylene.

Tests with a nitrous oxide/acetylene flame indicate that the use of this flame is not suitable for the determination of high calcium contents owing to the greater sensitivity for the emission of this element. On the other hand, it offers an advantage due to the reduction in the interference from aluminium and iron. Also the emission of a given amount of strontium in this flame is proportional to the concomitant calcium content. Consequently, the amount of strontium must be adjusted in accordance with the amount of calcium present in each case, thus making the determination very tedious.

We therefore attempted to use lanthanum both as a releasing agent and as an internal standard, but unfortunately lanthanum gives rise to the same phenomenon as strontium in the nitrous oxide/acetylene flame. If use is made of the four least sensitive spectral lines for lanthanum (394.9, 398.8, 447.1, 360.2 nm), excessively high amounts of this element must be used, and if the most sensitive lines are used (560.2, 566.0 and 442.0 nm), the lanthanum emission is dependent on the amount of calcium present. However, for the line at 360.2 nm, this phenomenon is clearly attenuated.

It is likely that this effect also occurs in the air/acetylene flame with lanthanum and strontium but to a much lower degree, thereby allowing advantageous use of this flame.

With strontium as an internal standard, in an air/acetylene flame, the calcium values are better and more reproducible than those obtained by direct flame-emission determination in the presence of strontium, but are still low. Further, if both lanthanum and strontium are used (as releasing agent and internal standard respectively) correct calcium results are obtained and much improved reproducibility compared with that of direct emission in the presence of lanthanum or strontium. A set of 11 replicate determinations gave a mean of 65.3%, range ±0.3%; reference analysis of the set by complexometric titration gave a mean of 65.2%, range ±0.2%.

The reproducibility of this last method was examined by carrying out series of seven measurements at intervals of 2 months. The values showed good regularity, since a difference of only 0.3% was found in the average values obtained: 65.0, 65.1, 65.2 and 65.3% with ranges of ±0.3, ±0.2, ±0.2 and ±0.3%. The range of all 32 values was 0.9% (minimum value 64.7% and maximum value 65.6%). These figures are comparable to those obtainable by complexometric titration with EGTA and by atomic-absorption or X-ray fluorescence spectrometry.

We also investigated whether the lanthanum could be replaced by oxine or phenol when an air/acetylene flame is used with a laminar-flow burner. Both produced a releasing effect, but it was not as great as that of lanthanum; it was also found that the combined action of effect of strontium and oxine or strontium and phenol was less than that of the strontium–lanthanum combination.[10]

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NON-AQUEOUS REDOX DETERMINATION OF ASCORBIC ACID WITH COPPER (II)

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(*Received* 22 *October* 1976, *Revised* 7 *April* 1976. *Accepted* 19 *May* 1977)

Summary—Hydrated copper (II) perchlorate (in acetonitrile) has been used for the direct visual and potentiometric determination of ascorbic acid in acetic acid–acetonitrile media. Diphenylamine and diphenylbenzidine are suitable indicators. A bright platinum wire is used as indicator electrode and a modified calomel or an antimony electrode as reference electrode for the potentiometric titration. Ascorbic acid is oxidized to dehydroascorbic acid. The proposed method is simple, accurate and reliable. The reverse titration also works well.

Copper(II) in acetonitrile has been found to be a powerful oxidizing agent possessing good stability. The formal reduction potential for the copper(II)–(I) couple is +0.798 V *vs.* a silver–0.01*M* silver nitrate reference electrode.[1] This high value is caused by the large solvation energy for copper(I) in acetonitrile, which raises the potential of the copper(II)–(I) couple and lowers that of the copper(I)–(0) couple such that a difference of more than 1.5 V exists between the two. Kratochvil *et al.* [2–5] used acetonitrile solutions of hydrated and anhydrous copper(II) perchlorate for the oxidimetric determination of tetrabutylammonium iodide, thioureas, arylamines and ferrocenes by potentiometric titration, using a platinum wire indicator electrode and a silver–0.01*M* silver nitrate (in acetonitrile) reference electrode. Mruthyunjaya and Murthy[6] have employed copper(II) nitrate and perchlorate solutions for the potentiometric titration of a copper(I)–thiourea complex, potassium ethyl xanthate, thiourea, copper(I) iodide, sodium iodide and tetra-alkylammonium iodide, using a glass and platinum electrode assembly. The same authors[7] have studied anion effects on redox determination with copper(II) in acetonitrile medium. Verma and Kumar[8] have described the use of copper(II) nitrate for the visual and potentiometric determination of xanthates and organotrithiocarbonates in acetonitrile medium.

The determination of copper(II) with ascorbic acid in aqueous solution was studied by Erdey and Siposs.[9] The instability of copper(I) in aqueous solutions and its susceptibility to aerial oxidation were the main difficulties described in the analysis. It was recommended that they should be avoided by the addition of a complexing agent (KSCN, KBr or NaCl) before the titration, and the passage of carbon dioxide during the titration. The titration was done in acetate-buffered aqueous medium with 2,6-dichlorophenolindophenol as indicator, which worked only when added near the end-point. An indicator correction was applied.

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The determination of ascorbic acid with copper(II) in non-aqueous media does not appear to have been attempted so far. The present communication reports the use of hydrated copper(II) perchlorate (in acetonitrile) for the direct visual or potentiometric determination of ascorbic acid in acetic acid–acetonitrile media. The use of an acetonitrile solution of copper (II) as a redox reagent has the advantage that the resulting copper(I) is stabilized by solvation with the acetonitrile[10] and that there is therefore little risk of aerial oxidation. Diphenylamine and diphenylbenzidine have been found to be excellent indicators. The potentiometric titrations have been performed with a bright platinum wire as indicator electrode and a modified calomel or an antimony electrode as reference electrode.

Ascorbic acid is oxidized to dehydroascorbic acid under these conditions. The reverse titration is equally feasible. The proposed method for the determination of ascorbic acid with copper(II) and *vice versa* in acetic acid–acetonitrile media is simple, accurate and reliable. It is free from the difficulties which are encountered in aqueous medium.

EXPERIMENTAL

Apparatus

Potentiometric titrations were performed with a Toshniwal-CLO6A potentiometer, and a bright platinum wire as indicator electrode and modified calomel (saturated methanolic potassium chloride solution instead of aqueous) or antimony electrode as reference electrode. The solutions were stirred with a magnetic stirrer.

Reagents

Acetonitrile. Distilled twice from phosphorus pentoxide (5 g/l.).

Acetic acid. Distilled twice from chromium trioxide.

Hydrated copper(II) perchlorate, 0.05N in acetonitrile. The solid compound was prepared[4] by adding a slight excess of 60% perchloric acid to a suspension of copper carbonate in water. The solution was boiled to eliminate

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carbon dioxide. The crystalline compound separated on cooling, and was dried under vacuum. A standard solution was prepared by dissolving a little more than the calculated amount of the dry solid in acetonitrile and standardizing it iodometrically in aqueous acidic medium.

Ascorbic acid. A known weight was dissolved in the minimum quantity of warm acetic acid. The solution was left to attain room temperature, then diluted with acetonitrile to a known volume and aliquots were taken for analysis. Several aliquots were checked for ascorbic acid content by a published method.[11] The standard (0.05*N*) ascorbic acid solution in acetic acid–acetonitrile for the determination of copper(II) was prepared in a similar manner.

Indicator solutions. Diphenylamine and diphenylbenzidine solutions in acetonitrile, 0.1% and 0.05% respectively.

Procedure

Aliquots of ascorbic acid in acetic acid–acetonitrile medium were transferred to dry titration vessels and diluted with 25–30 ml of acetonitrile. For visual titrations, 2–3 drops of indicator solution were added, the solution was cooled to room temperature (~20°) and titrated with standard (0.05*N*) hydrated copper(II) perchlorate solution (in acetonitrile) from a microburette provided with a guard tube to protect the titrant from atmospheric moisture. The end-point was signalled by appearance of a blue colour. Aliquots of copper(II) in acetonitrile were titrated with standard (0.05*N*) ascorbic acid solution (in acetic acid–acetonitrile), the same indicators being used. The end-point was marked by disappearance of the blue colour.

Table 1. Determination of ascorbic acid with hydrated copper(II) perchlorate (0.05*N*) and *vice versa* in acetic acid–acetonitrile media

	Found*, *mg*			
	Visual method		Potentiometric method	
Taken, *mg*	mean	s.d.	mean	s.d.
Ascorbic acid				
9.00	8.95	0.05	9.02	0.04
43.00	42.84	0.10	42.88	0.08
Copper(II)				
6.40	6.42	0.02	6.41	0.02
25.60	25.70	0.04	25.66	0.04

* Mean of ten determinations.

RESULTS AND DISCUSSION

Some results are recorded in Table 1. Since the results obtained by potentiometric titration were essentially the same for both types of reference electrode, but only those for the calomel electrode system are recorded in the table.

Diphenylamine and diphenylbenzidine have been found excellent indicators for the titration, done in either direction. When ascorbic acid is titrated with copper(II), the solution is colourless to start with, becomes light yellow, and changes sharply to blue at the end-point. In the reverse titration, the initial blue colour changes sharply to light yellow at the end-point.

In the potentiometric titrations, the potentials attained stable values immediately on addition of each portion of oxidant. A sharp change in potential of 250–400 mV (antimony reference electrode) and 200–250 mV (modified calomel reference electrode) per 0.05 ml of 0.05*N* titrant was observed at the equivalence point. In the titrations of ascorbic acid with copper(II) the potentials of the inflection points were 80–200 mV (antimony electrode) and 450–550 mV (calomel), and for copper(II) titrated with ascorbic acid they were 500–600 mV and 480–560 mV respectively.

Glucose, fructose, maltose, formic acid and benzoic acid do not interfere when present in amounts up to 25 mg. Oxalic acid, phenylhydrazine, *N,N*-dimethylhydrazine, thiourea, xanthates, dithiocarbamates and organotrithiocarbonates, however, do interfere.

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EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF THALLIUM(III) WITH THIOTHENOYLTRIFLUOROACETONE

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Summary—A procedure is described for the extractive photometric determination of thallium(III) with thiothenoyltrifluoroacetone in carbon tetrachloride. Thallium(III) is extracted quantitatively at pH 4–5 and the bright yellow extract obeys Beer's law over the Tl(III) concentration range 2.5–17.5 μg/ml, at 440 nm. Thallium(III) can be determined in the presence of a large number of cations and anions.

Thiothenoyltrifluoroacetone has been used as extraction and colorimetric reagent for transition elements.[1–3] This paper describes systematic studies on its use for solvent extraction of thallium(III).

Spectrophotometric determination of Tl(III) with various chelating agents and dyes has been reviewed.[4,5] The methods based on PAR,[6,7] Xylenol Orange,[8] 3-hydroxy-1,3-diphenyltriazine,[9] Methyl Violet[10] and *p*-phenetidine[11] suffer from several interferences, and some of them are also less sensitive. The thiosalicylamide method[12] has low tolerance limits, and the TTA,[13] Xylenol Orange[8] and *p*-aminophenol[14] methods require 20–30 min for complete colour development. The proposed method is comparatively simple, sensitive, and affords separation and simultaneous spectrophotometric determination of microamounts of Tl(III) in presence of a large number of foreign ions. The method is also rapid, requiring only 15–20 min.

EXPERIMENTAL

Reagents

Thiothenoyltrifluoroacetone. Prepared as described by Berg and Reed,[15] and used as a $4 \times 10^{-4}M$ solution in carbon tetrachloride.

Stock thallium solution. Prepared by dissolving 6.5 g of thallous nitrate in 500 ml of distilled water, standardized gravimetrically by the chromate method[16] and diluted to give a concentration of 50 μg/ml.

Buffer solution, pH 4.4. Prepared by dissolving 13.7 g of sodium acetate and 6 ml of glacial acetic acid in 100 ml of water.

Procedure

An aliquot of solution containing about 100 μg of thallium was first oxidized by heating with a few drops of bromine water and then mixed with 10 ml of pH 4.4 buffer solution. After dilution to 20 ml with distilled water, the solution was transferred to a separating funnel and shaken for 30 sec with 10 ml of $4 \times 10^{-4}M$ reagent solution. The layers were allowed to separate and the absorbance of the yellow thallium chelate in the organic phase was measured at 440 nm against a reagent blank prepared in an identical manner. The amount of thallium was computed from the calibration curve.

RESULTS AND DISCUSSION

The absorption spectra of the reagent and of the Tl(III)–STTA complex (100 μg of Tl) extracted at pH 4.4 with reagent solutions of different concentrations are shown in Fig. 1. They show that λ_{max} for the complex is at 440 nm when the complex is extracted with $1–6 \times 10^{-4}M$ reagent. With higher reagent concentrations λ_{max} could not be established but the difference in absorbance between the complex and the reagent blank appears to be maximal at 440–450 nm. The system conforms to Beer's law over the thallium concentration range 2.5–17.5 μg/ml at 440 and 450 nm. The molar absorptivity is 0.8×10^4 l. mole^{-1}.cm^{-1} at 440 nm. The colour remains stable for 15 min. The extraction is quantitative at pH 4–5 (Fig. 2), and an acetate buffer of pH 4.4 is recommended. A single extraction with 10 ml of $4 \times 10^{-4}M$ reagent was found to be quantitative. There is no advantage in using a greater volume of reagent at this concentration, and extraction is incomplete with more dilute solutions.

For quantitative extraction 0.5 min shaking is adequate. Prolonged shaking has an adverse effect on the extraction.

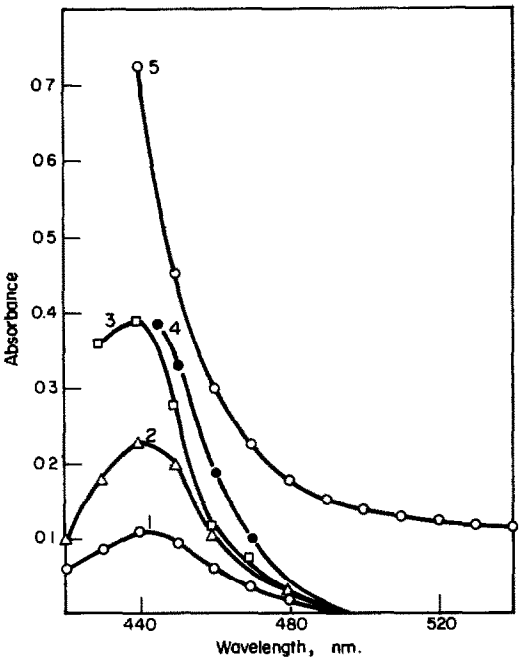

Fig. 1. Absorption spectra of Tl(III)-STTA complex measured against reagent blank, with varying reagent concentrations. 1—$1 \times 10^{-4}M$ STTA; 2—$2.5 \times 10^{-4}M$ STTA; 3—$4.0 \times 10^{-4}M$ STTA; 4—$1.0 \times 10^{-3}M$ STTA; 5-reagent ($4 \times 10^{-4}M$) *vs.* CCl_4.

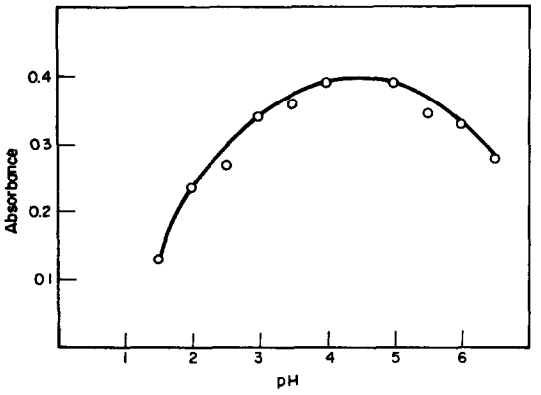

Fig. 2.

Table 1. Effect of diverse ions [Tl(III) = 50 μg, pH 4.4 acetate buffer, STTA = $4 \times 10^{-4}M$ in CCl_4]

Foreign ion	Tolerance limit, *mg*	Foreign ion	Tolerance limit, *mg*
Ag(I)	10	Se(IV)	10
Pb(II)	5	Te(IV)	10
Sn(II)	none	*Au(III)	1
Zn(II)	5	Ce(III)	10
Al(III)	10	Sb(III)	5
*Cu(II)	3	$EDTA^{4-}$	none
Bi(III)	10	Thiocyanate	8
Co(II)	none	Fluoride	8
Fe(III)	5	Phosphate	8
Mn(II)	10	Citrate	8
V(V)	10	Ascorbate	none
Cd(II)	5	Tartrate	8
*Hg(II)	5	Oxalate	8
In(III)	5	Bromide	5
Cr(III)	5	Cyanide	25
Mo(VI)	10	Thiourea	none
W(VI)	10		
U(VI)	0.1		

* Masked with cyanide.

An interference study showed that of the ions tested (Table 1), only Sn(II), Co(II), EDTA, ascorbate and thiourea seriously affect the extraction and determination of thallium(III). Ions such as Cu(II), Hg(II) and Au(III) can be masked with cyanide.

The method has fairly good precision, the relative standard deviation being 1–2%. Analysis of a series of synthetic mixtures gave mean errors of less than 1%.

A log–log plot of distribution coefficient vs. $[STTA]_{org}$ at fixed pH gave a slope of 1.96, indicating a molar ratio of 1:2 for the reaction of thallium and STTA. As thallium(I) is not extracted, it is concluded that a positively charged complex is formed, which is extracted as an ion-pair with one of the anionic species present, probably acetate.

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LIQUID–LIQUID EXTRACTION OF MOLYBDENUM THIOCYANATE WITH HEXAMETHYL PHOSPHORTRIAMIDE AND DIRECT SPECTROPHOTOMETRIC DETERMINATION IN THE ORGANIC PHASE

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Summary—A sensitive and selective method for estimation of trace molybdenum with fairly common reagents has been developed. The Mo–thiocyanate complex is extracted with hexamethyl phosphortriamide and chloroform from 0.75–1.5*M* hydrochloric acid. The molar absorptivity is 1.76×10^4 $l.mole^{-1}.cm^{-1}$. The system obeys Beer's law at 460 nm over the molybdenum concentration range 0.75–5 ppm. The method is simple, rapid, and requires no additional reducing agent. It is generally free from interference by most of the metals commonly associated with molybdenum, including rhenium. Molybdenum in alloy steel has been successfully determined.

Minute amounts of molybdenum have generally been determined by colorimetric methods. Of the standard methods, the thiocyanate–stannous chloride method,[1] because of its high sensitivity and selectivity, is said to be superior. The thiocyanate–cuprous chloride method[2] in acetone–water medium has high sensitivity, but its main drawbacks are that the original volume of the sample solution must not exceed a few ml and iron cannot be present in more than minute amounts. The molybdenum–thiocyanate complex has been extracted with *N*-benzylaniline,[3] tribenzylamine,[4,5] tributyl phosphate,[6,7] tetraphenylarsonium chloride,[8,9] tetraphenylphosphonium chloride,[9] and monoethyl α-anilinobenzylphosphonate.[10]

The method described here utilizes the solvent extraction of the mixed complex with thiocyanate and hexamethyl phosphortriamide (HMPA) into chloroform and avoids the use of $SnCl_2$ or Cu_2Cl_2 as the reducing agent. The method has been applied successfully in the determination of small amounts of molybdenum in alloy steel.

EXPERIMENTAL

Molybdenum standard solution

Dissolve analytical-grade ammonium molybdate in dilute ammonia solution, dilute to known volume with distilled water and standardize by the oxine method.[11] Dilute the standard solution to obtain the desired concentrations (*e.g.*, 0.01 mg/ml).

General procedure

To the sample solution (containing 25–125 μg of molybdenum) in a 100-ml beaker add 400 mg of ammonium thiocyanate and adjust the acidity to 1.0*M* in hydrochloric acid. Add 1 ml of HMPA and heat the solution on a boiling water-bath for about 15 min, cool, transfer to a separatory funnel and extract with three 5-ml portions of chloroform. Combine the extracts in a 25-ml standard flask and made up to volume with chloroform. Prepare a reagent blank under identical conditions. Measure the absorbance at 460 nm.

RESULTS AND DISCUSSION

The absorption spectrum is shown in Fig. 1. The system obeys Beer's law over the range 0.5–6 ppm (in the chloroform solution). The optimum concentration range (according to Ringbom[12]) is 0.75–5 ppm. The molar absorptivity is 1.76×10^4 $l.mole^{-1}.cm^{-1}$.

Optimal conditions

The absorbance reaches its maximum after the reaction mixture has been warmed for at least 15 min, and remains constant for at least 24 hr. There is no colour development at pH 2–6. The absorbance reaches a maximum at a hydrochloric acid concentration of 0.75–1.5*M* and decreases again at higher acidity.

With only 25 mg of ammonium thiocyanate there is no colour, but with increasing amount of thiocyanate the absorbance increases, becoming constant with 250 mg or more. Therefore 400 mg was chosen.

The amount of HMPA can be varied from 0.5 to 2 ml without effect on the absorbance.

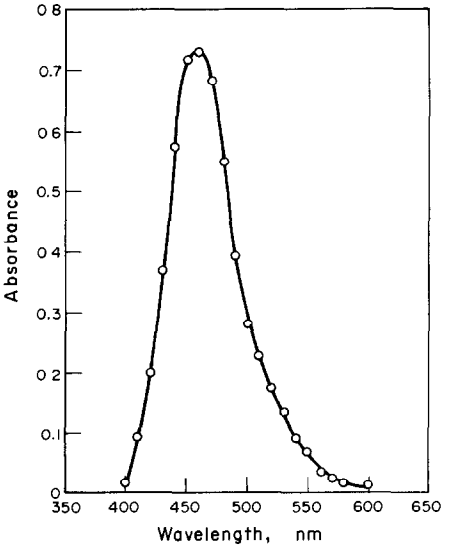

Fig. 1. Absorbance spectrum of molybdenum complex (4 ppm Mo) in chloroform medium.

Interferences

Solutions containing 50 μg of molybdenum were mixed with solutions containing various ions and the procedure was applied. It was found that no interference was caused by 1 mg of uranium(VI), vanadium(V), vanadium(IV), tantalum or zirconium, 500 μg of rhenium(VII), 1 g of hydroxylamine hydrochloride, 500 mg of tartaric acid or ascorbic acid, 5 ml of 0.1*M* EDTA or 450 mg of sodium fluoride. Niobium and titanium (1 mg) were masked with sodium fluoride. Copper(II) could be easily masked with thiourea. For rhenium(VII), 500 μg is the maximum amount tolerable. Tungsten lowers the absorbance, but this effect can easily be overcome by adding a large excess of ammonium thiocyanate (an extra 1.5 g).

Iron also interferes, but is dealt with by oxidizing it with conc. nitric acid, and extracting it as the thiocyanate with tri-n-butyl phosphate (TBP) at pH 2–3 before the addition of the HMPA.

Estimation of molybdenum in alloy steel

A 100-mg sample is dissolved in nitric acid (1 + 1) on a hot-plate, and the solution is evaporated to small volume and cooled; 1 ml of conc. sulphuric acid is added and heated to fumes to drive off the nitric acid. The residue is cooled and then heated with about 50 ml of water to dissolve the soluble salts, any insoluble matter is filtered off and the solution is made up to 100 ml with distilled water in a standard flask. A 20-ml aliquot is taken, evaporated to small volume and adjusted to about pH 2.5 after addition of ammonium thiocyanate. The iron is then extracted with three portions of TBP. The acidity of the aqueous phase is adjusted to about 0.8*M* hydrochloric acid and the molybdenum is determined as already described.

For the Bureau of Analysed Samples alloy steel 60b the molybdenum found was 0.420, 0.426, 0.422% (certificate value 0.43%.

Acknowledgement—This work was financed by C.S.I.R. (India) by awarding a scholarship to one of us (M.M.) for whom it is a pleasure to thank the scholarship-awarding authority.

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DEVELOPMENT APPARATUS FOR THIN-LAYER GEL CHROMATOGRAPHY IN ORGANIC SOLVENT SYSTEMS

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(*Received* 10 *May* 1977, *Accepted* 13 *May* 1977)

Summary—An apparatus is devised for development of thin-layer gel chromatograms, which is easy to handle and gives reproducible results even with volatile organic solvent systems. The print technique with a silicone-treated paper can facilitate detection of the samples chromatographed.

Determann[1] and Johanson and Rymo[2] first described thin-layer gel chromatography (TLGC) in 1962. Since then TLGC has been utilized by many investigators, mainly for rapid separation of proteins and/or the estimation of their molecular weights.[3–5] Separations of dyes,[6] polymers[7] and inorganic substances[8–11] have also been reported. A rapid characterization of synthesized gel networks by use of dyed protein standards has recently been presented.[12]

The separations cited above, however, have been carried out exclusively in aqueous media. Except for the separation of polymers on a rigid inorganic gel, *e.g.*, silica gel, [13,14] little information is available on TLGC in organic solvent systems.[15] Apparatus which will give reproducible results for TLGC, in organic solvent media, does not seem to have been devised. This seems to be due to methodological difficulties caused by the high volatility of many of the organic solvents used.

We have devised a development apparatus for TLGC, which can be easily handled and gives reproducible results even with volatile organic solvent systems.

Preparation of gel plates

An appropriate amount of swollen gel is slurried with a slight excess of solvent and spread on glass plates (20 × 20 cm) with a conventional applicator (Yamato Scientific Co., Tokyo, Japan). Rapid evaporation of the solvent during this step makes it impossible to prepare many plates at a time. In this work, therefore, two uniform gel layer (thickness 250–750 μm) plates are quickly made from each batch of the slurried gel. Then, a 5-mm width of the gel layer is scraped off on two opposite edges. Before the gel becomes thoroughly dry, the plate is set up in the development apparatus as described below.

Interferences

Solutions containing 50 μg of molybdenum were mixed with solutions containing various ions and the procedure was applied. It was found that no interference was caused by 1 mg of uranium(VI), vanadium(V), vanadium(IV), tantalum or zirconium, 500 μg of rhenium(VII), 1 g of hydroxylamine hydrochloride, 500 mg of tartaric acid or ascorbic acid, 5 ml of 0.1*M* EDTA or 450 mg of sodium fluoride. Niobium and titanium (1 mg) were masked with sodium fluoride. Copper(II) could be easily masked with thiourea. For rhenium(VII), 500 μg is the maximum amount tolerable. Tungsten lowers the absorbance, but this effect can easily be overcome by adding a large excess of ammonium thiocyanate (an extra 1.5 g).

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We have devised a development apparatus for TLGC, which can be easily handled and gives reproducible results even with volatile organic solvent systems.

Preparation of gel plates

An appropriate amount of swollen gel is slurried with a slight excess of solvent and spread on glass plates (20 × 20 cm) with a conventional applicator (Yamato Scientific Co., Tokyo, Japan). Rapid evaporation of the solvent during this step makes it impossible to prepare many plates at a time. In this work, therefore, two uniform gel layer (thickness 250–750 μm) plates are quickly made from each batch of the slurried gel. Then, a 5-mm width of the gel layer is scraped off on two opposite edges. Before the gel becomes thoroughly dry, the plate is set up in the development apparatus as described below.

Development apparatus

The apparatus used for development is shown in Fig. 1. The upper and lower edges of the gel plate are connected to the solvent reservoirs (2) with filter-paper bridges (1). Then a glass cover plate (4) fitted with slit Teflon tubes (6) at both ends but without any adhesive (see Fig. 1*b*) is clamped over the gel plate. The sides of the gel layer which come into contact with the Teflon tubes are those that have been scraped as described above. To ensure good contact of the paper wicks with the gel layer, it is advisable to fold them as shown in Fig. 1*c*. Silicone-treated paper, Whatman Chromatography Paper ST 81 (Balston Ltd., Springfield Mill, Maidstone, Kent, England) is preferred because of its higher power of imbibition for organic solvents. The sample solutions are applied to the gel plate by micropipette through the holes (3 mm in diameter) drilled in the top plate,[15] and these holes are closed with small pieces of glass plate.

With this arrangement, the leakage of solvent vapour from the air-space over the gel surface can be nearly completely prevented, and the time needed for pre-equilibration can be shortened. However, the samples tend to migrate toward the side of the gel plate during the development, probably because of the loss of solvent vapour at the sides of the gel layer and/or the differential evaporation of the solvent at the sides of the paper wicks. Therefore the whole arrangement should be placed in another closed chamber so that this undesirable migration of samples can be completely prevented. Samples are then applied through holes drilled in the cover glass (5) of the outer chamber so that they register with the holes in the inner top plate (4); these holes are similarly closed with small pieces of glass plate and it is then unnecessary to close the holes in the inner top plate. Development can be achieved by inclining this chamber at a suitable angle.

Preparation of replicas

In TLGC, the wet gel layer is extremely fragile and difficult to handle, so sample detection is best accomplished on paper replicas. The replica may then be handled like an ordinary paper chromatogram.

With volatile organic solvent systems, however, when a strip of dry filter paper is placed on the wet gel layer immediately after the development, the samples cannot be printed, because of the rapid evaporation of solvent from the gel layer. Thus we adopted the print technique using a filter paper impregnated with the developer, and found that it was quite successful, particularly with silicone-treated filter paper. The following procedure is recommended. First the pair of plates is taken out of the chamber, and the top plate is removed. Then a silicone-treated paper, which has been impregnated with the solvent used as the developer, is quickly brought into contact with the wet gel layer and allowed to stand for a few minutes. When the solvent has evaporated from the filter paper, most of the sample will be found on the filter paper. Compared with common filter papers, the silicone-treated paper permits surer printing of the samples and precludes all chance of disturbing the shapes of the zones.

Various metal β-diketonates were successfully developed on Styragel 60A (polystyrene–divinylbenzene copolymer, particle size $<37\ \mu m$, Waters Associates Inc., Milford, Mass., U.S.A.) with *p*-dioxan or benzene, according to the procedure described above. The β-diketonates could be detected on the paper replicas as dark spots under ultraviolet light. Standard polystyrene (m.w. 2×10^5, Pressure Chemical Co., Pittsburgh, Pa., U.S.A.), which is completely excluded from the network of Styragel 60A, was used as an internal standard. The polystyrene was visualized as red spots on paper replicas by spraying with 20% (w/v) antimony pentachloride solution in carbon tetrachloride and heating gently over a hot-plate. When *p*-dioxan was used for development of 250-μm Styragel 60A plates inclined at 30–40°, the average R_f value (7 developments) and standard deviation for tris(acetylacetonato)cobalt(III) were 0.66 and 0.01, respectively.

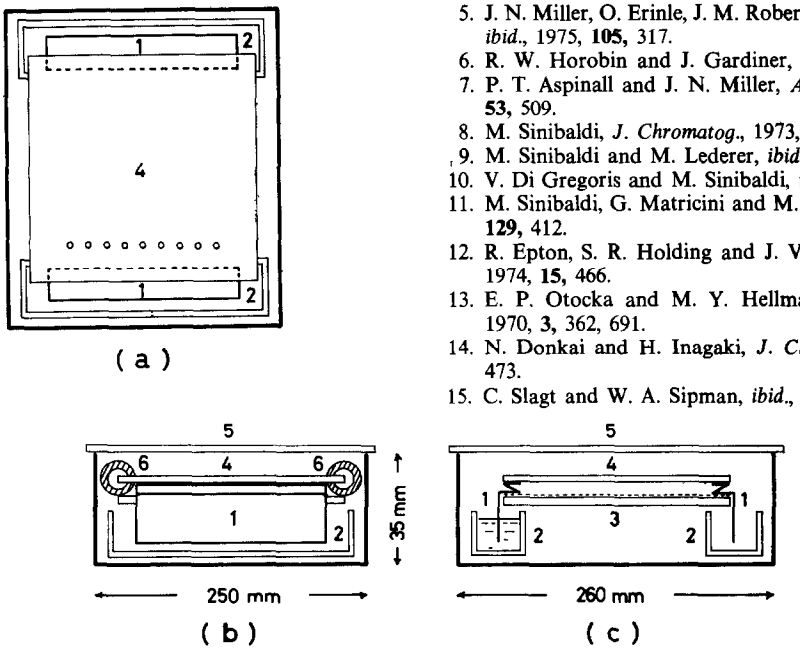

Fig. 1. Development apparatus for thin-layer gel chromatography with volatile organic solvent systems. (*a*) Top view; (*b*) front view; (*c*) side view; 1—silicone-treated filter paper; 2—solvent reservoir; 3—gel plate; 4—inner top plate; 5—outer cover plate; 6—slit Teflon tube.

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DETERMINATION OF MAGNESIUM AT TRACE LEVELS BY ISOTOPE DILUTION

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Summary—A mass spectrometric method for the isotopic analysis of magnesium and its determination at low concentrations in the presence of an excess of other elements is described. The lowest level at which magnesium was determined was 1 ppm with a precision and error ±1%.

An accurate method for the determination of magnesium at low concentrations in the presence of an excess of other elements became necessary when the element was proposed as a tracer for the input accountability of plutonium in fuel-reprocessing plants.[1,2] A number of techniques, including gravimetry, titrimetry, spectrophotometry and emission spectrography, have been used for the determination of magnesium,[3,4] but they do not have the accuracy or the sensitivity required for this application. Because isotope dilution analysis offers high sensitivity, selectivity and accuracy in such measurements,[5,6] the mass spectrometric method was developed for the accurate determination of trace levels of magnesium. This has made it possible to use the magnesium tracer technique for the determination of the total amount of plutonium in the accountability tanks of reprocessing plants and to check the volume calibration of these tanks with an error of less than 1%.[2]

In isotope dilution analysis, the concentration of an element is determined by increasing the relative abundance of one of its isotopes by adding a known amount of this element enriched in this isotope (spike) and measuring the increased abundance. If R^S, R^{Sp} and R^M are the relative abundances of two isotopes in the sample (S), spike (Sp) and mixture (M) respectively, then the concentration of the element in the sample is given by

$$C_S = \frac{C_{Sp} \cdot W_{Sp}}{W_S \cdot R^{Sp}} \cdot \left(\frac{R^{Sp} - R^M}{R^M - R^S}\right) \cdot \frac{\sum_i R_i^S(\mathrm{Mg}) M_i^S(\mathrm{Mg})}{\sum_i R_i^{Sp}(\mathrm{Mg}) M_i^{Sp}(\mathrm{Mg})} \quad (1)$$

where C is concentration, W is weight and the summation is over all the isotopes of the element (in this case magnesium).

There are several reports on the determination of the isotopic composition of magnesium. The pioneering work of Dempster[7] and that of White and Cameron,[8] whose results are often accepted as the best estimates for the isotopic abundances in natural magnesium, was done with use of electron-impact ion sources, but this is not suitable for the present purpose as the magnesium would have to be converted into the gaseous state. If a thermionic source is used isotope fractionation becomes a serious problem,[9] and erroneous conclusions on the variation of isotopic abundances in natural magnesium have been arrived at because of the fractionation effects.[10] Some workers have used binding agents such as uranyl nitrate, beryllium oxide and amorphous carbon for loading magnesium on the filaments.[9–11] The National Bureau of Standards has standardized a method for the isotope abundance measurement of magnesium, using uranyl nitrate as a binding agent,[12] and reported that strict control of filament temperatures was necessary to minimize the effects of isotope fractionation.

In the present work, we have used a thermionic source. Significant fractionation was observed when magnesium was analysed by loading the sample on the filament in the nitrate form. This prompted a search for a compound which would give rise to negligible fractionation effects. Magnesium chloride was found to be suitable. This paper reports the standardization of the conditions for the isotopic analysis of magnesium and the procedure for the measurement of magnesium concentration down to the ppm level.

EXPERIMENTAL

The instrument used was a Varian MAT CH-5 mass spectrometer with a thermionic source. It had a resolution of 425 (on 10% valley definition) measured at around mass 238 and an abundance sensitivity of 10^5. Rhenium ribbons (0.04 × 0.7 × 8 mm) were used as sample and ionization filaments.

Isotopic analysis

A drop of the magnesium solution in suitable chemical form (chloride in most of this work) was taken on a Teflon sheet, evaporated to very small volume, transferred by means of a capillary onto the sample filament of a prebaked double-filament assembly and evaporated to dryness. The filament assembly was introduced into the mass spectrometer and the isotope abundance measured after adjustment of the temperatures of the vaporizing and ionizing filaments. The heating pattern depended on the chemical nature of the sample. The procedure for analysing magnesium in the chloride form is as follows.

Time from start, *min*	Operation
0–2	The ionizing-filament current is set at about 2 A.
2–15	The ionizing-filament current is increased slowly stepwise to about 5 A.
15–20	The Re^+ signal is found and focused. If this signal (for mass number 187) is greater or less than 10 mV (at SEM gain = 5×10^4 and grid-leak resistance = 10^7 ohm, *i.e.*, an ion-current of 2×10^{-14} A), the ionizing-filament current is readjusted to give a 10-mV signal for $^{187}Re^+$.
20–30	The sample filament is heated with a current of 1 A and the Mg^+ signal is found and focused. Initially the signal decays and then becomes almost steady.

30 onwards Data recording begins. If the signal is less than 30 mV (*i.e.*, 6×10^{-14} A), the sample-filament current is further increased and data recorded as soon as a steady ion-current is obtained.

Concentration measurement using the isotope dilution technique

The concentration of magnesium in demineralized water, commercial nitric acid and nuclear grade uranium oxide was determined. In each case a weighed portion of sample solution was taken (UO_2 was first dissolved in acid) and mixed with a suitable weight of the ^{26}Mg-enriched spike solution, which had already been calibrated. The mixed solution was evaporated to dryness and converted into the chloride form by repeated evaporation with 8*M* hydrochloric acid. Magnesium was separated from most of the impurities by passing the solution through an anion-exchange column (Dowex 1 × 8, 200–400 mesh); the magnesium appeared in the eluate and was collected in a clean glass vial, evaporated to dryness and dissolved in 0.5–1*M* hydrochloric acid for mass spectrometric analysis.

To avoid contamination the acids and water used were doubly distilled in quartz, the glassware was leached with nitric acid and the filaments were prebaked in vacuum.

RESULTS AND DISCUSSION

Isotope abundance measurements

Isotopic analysis of magnesium as the nitrate. Mass spectrometric analysis of magnesium was carried out several times with the sample loaded in the nitrate form and the sample size (20–30 μg of Mg), sample composition (pure magnesium nitrate) and acidity of the loading solution (about 0.5*M* nitric acid) were kept constant. The ionizing filament was heated with a current of 5–6 A (adjusted to give the same peak height for Re^+ ions) and the sample-filament current varied from 1.5 to 2.5 A. However, significant isotope fractionation occurred and it was not possible to find a filament current that would give reproducible results.

Choice of a suitable magnesium compound for isotopic analysis. A search was made for a more suitable magnesium compound than the nitrate. Magnesium nitrate decomposes at around 600 K to magnesium oxide which has a melting point of 3073 K and hence would have to be heated to very high temperatures to give sufficient vapour pressure at the ionizing filament.[13] Isotope fractionation is enhanced at such high temperatures. The carbonate and sulphate also decompose to the oxide at relatively low temperatures. Magnesium chloride, however, has a relatively low melting point and a vapour pressure of 10^{-4} atm at 1000 K.[14] The comparatively low evaporation temperature and high molecular weight of the species evaporated both minimize isotope fractionation. Hence magnesium chloride was chosen as a suitable compound.

Isotopic analysis of magnesium as the chloride. A sample size of 10–20 μg of magnesium was found to be optimal. It was observed that magnesium ions could be obtained in many cases by heating only the ionization filament. However, the procedure finally adopted consisted of heating the ionizing filament with a current of 5–6 A (the temperature being adjusted by monitoring the Re^+ signal) with the sample-filament current varied from 1.2 to 1.8 A. This gave good reproducibility and no detectable isotope fractionation was observed with sample filament currents up to 1.8 A. Typical results are given in Tables 1 and 2. As can be seen from Table 1, there is no significant variation in ^{26}Mg/^{24}Mg isotope ratios as the sample filament temperature is varied within a reasonable range, thus making it possible to obtain reproducible results. Table 2 shows that more reproducible values can be obtained by loading as the chloride than as the nitrate. The results obtained for the isotopic composition of natural magnesium were $^{25}Mg/^{24}Mg = 0.1247$ and $^{26}Mg/^{24}Mg = 0.1352$, the relative standard deviation being about 0.5% in both cases.

Mass discrimination factor (mdf). The absolute isotope ratios are obtained from the observed values by applying a correction factor called the mass discrimination factor (mdf) which is usually determined by analysing isotopic standards. As no isotopic standard for magnesium was readily available, the overall mass discrimination was determined by analysing natural magnesium samples. The ^{26}Mg/^{24}Mg ratio was used for calculating the mdf, as the use of two isotopes with the greatest mass separation gives the maximum sensitivity for determination of the bias. The overall mdf per mass unit was found to be 1.0157 ± 0.0015. That this bias is essentially due to the use of an electron multiplier was confirmed by comparison with results obtained with a Faraday-cup detector, from which little bias is expected. It was found that the electron multiplier

Table 2. Comparison of ^{26}Mg/^{24}Mg isotope ratios obtained with sample loaded in the nitrate and chloride forms

Sample	^{26}Mg/^{24}Mg ratio	
	Magnesium nitrate	Magnesium chloride
1	0.8431	0.8472
	0.8405	0.8457
	0.8535	0.8455
	0.8596	—
2	0.6901	0.6743
	0.6901	0.6754
3	1.1855	1.1445
	1.1903	1.1411
4	0.1355	0.1354
	0.1376	0.1359
	0.1392	0.1354

* 1, 2 and 3 are synthetic samples, 4 is a natural magnesium sample.

Table 1. Variation in ^{26}Mg/^{24}Mg isotope ratio with sample-filament temperature (magnesium loaded as chloride)

Sample-filament current A	^{26}Mg/^{24}Mg ratio		
	Sample 1	Sample 2	Sample 3
1.2	1.807 ± 0.008	—	1.701 ± 0.009
1.3	1.819 ± 0.009	—	—
1.4	1.819 ± 0.008	—	1.703 ± 0.012
1.5	—	1.836 ± 0.008	1.710 ± 0.009
1.6	1.822 ± 0.010	1.846 ± 0.009	—
1.7	1.800 ± 0.010	1.848 ± 0.006	1.719 ± 0.007
1.8	1.802 ± 0.005	1.846 ± 0.008	—

gave a value which was 1.0282 ± 0.0064 times that obtained with the Faraday cup, giving 1.0141 ± 0.0032 as the mdf per mass unit. This value is close enough to the observed mdf; hence there can be no doubt that isotope fractionation effects are negligible. Moreover, in concentration measurement the mass discrimination factor is cancelled because spike calibration is also carried out by isotope dilution. When the variation in the isotopic composition of different natural magnesium samples is studied, the mdf is not important.

Table 3. Estimation of magnesium in various samples

Sample	Mean value, *ppm*	Estimated error, %	RSD, %
Demineralized water	6.34	0.8	0.7
Nitric acid (commercial grade)	1.16	0.6	1.0
Uranium (U_3O_8)	3.30	0.6	0.9

CONCENTRATION MEASUREMENTS

Results on the concentration measurement of magnesium in various samples are given in Table 3. The errors arise from uncertainty in the isotope ratio measurement and in the measurement of portions of sample and spike solution used. In the isotope ratio measurement, there can be random and systematic errors. The systematic errors arising from isotope fractionation and mass discrimination were shown above to be negligible. The error in measurement of fractions used for isotope dilution was negligible (less than 0.1%) since the fractions were weighed. The total error stated is based on error propagation and equation (1). The precision is also given, as the relative standard deviation (RSD). The lowest level of magnesium estimated in the present work was 1 ppm (precision and accuracy $\pm$ 1%). The method is, however, much more sensitive and should be able to determine magnesium at levels down to 1 part in 10^{12} (this is an estimate based on the lowest signal which can be detected above background). The sensitivity, precision and accuracy may be compared with the sensitivity of 0.1 ppm and precision of about 10% at the 1-ppm level in spectrographic measurements.[15,16]

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THE REACTIONS OF PENTACYANOFERRATE(II) IONS—IV SPECTROPHOTOMETRIC STUDY, DETECTION AND DETERMINATION OF TOXOGONINE

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Summary—The interaction of Toxogonine with ammine- and nitrosyl-pentacyanoferrate(II) ions has been studied spectrophotometrically under different reaction conditions. The same reactions were the basis for specific spot-tests and new simple and rapid spectrophotometric methods for the determination of Toxogonine in the range 15–85 or 15–150 μg/ml. From the calibration curves the molar absorptivities of the complexes were calculated and the proposed methods tested for the determination of Toxogonine in pharmaceutical preparations.

In previous papers[1–3] reports were given on the reactions between some mono quaternary pyridinium aldoximes and aquo-, ammine- and nitrosyl-pentacyanoferrate(II) ions, abbreviated here as AqPF, AmPF and NP respectively, which result in coloured, water-soluble oximatopentacyanoferrate(II) complexes. Because many of the oximes examined are effective re-activators for cholinesterase that has been inhibited by organophosphorus compounds (esters of phosphoric acid, insecticides, nerve gases)[4–6] the same reactions were used for analytical applications.[7]

The bis quaternary pyridinium aldoximes are also used as good re-activators of inhibited cholinesterase in human therapy.[8] Among them the most successful in treatment of man is 1,1-oxydimethylene-bis-4-pyridinium aldoxime dichloride, also known as Toxogonine, Obidoxime or LüH6.[9,10] Therefore it was of interest to examine the reactions of Toxogonine with pentacyanoferrate(II) ions. This was done here with AmPF and NP, and had earlier been done with AqPF.[11] In this paper we report on the nature of the complexes produced and the optimum conditions for their production. We also propose a rapid, simple and accurate method of determining Toxogonine spectrophotometrically with AmPF and NP, which have the advantage over AqPF of being commercially available. The procedures are applied to the detection and determination of Toxogonine in pharmaceutical preparations.

EXPERIMENTAL

Reagents

All reagents were of analytical-reagent grade. Redistilled water was used throughout.

The Britton–Robinson buffers[12] of pH 6.06 and 11.7 were prepared by mixing 100 ml of a 0.04*M* mixture of phosphoric, boric and acetic acids with 42.5 and 100.8 ml of 0.2*M* sodium hydroxide respectively.

$Na_3Fe(CN)_5NH_3 \cdot 3H_2O$ solution (AmPF), 0.02*M*, was prepared from a Touzart-Matignon reagent. The solution was used after standing for 10–15 min.

$Na_2Fe(CN)_5NO \cdot 2H_2O$ solution (NP), 0.02*M* was prepared from a Kemika (Zagreb) reagent. The solution remains stable for a few days if kept in the dark.

The stock solution of Toxogonine was prepared from the Merck reagent by dissolving the weighed quantity in water. It remains stable for several days. More dilute solutions were obtained by appropriate dilution with water.

The solutions of the injections (Merck) containing Toxogonine were prepared so that 1 ml of the sample solution contained about 150 μg of Toxogonine.

Determination procedures

A. To 2 ml of Britton–Robinson buffer of pH 6.06, add 1 ml of the sample solution containing 15–85 μg of Toxogonine, 1 ml of water and 1 ml of 0.02*M* AmPF. Mix the solution well and measure the absorbance at 610 nm against a reagent blank after about 5 min.

B. To 1 ml of 0.35*M* sodium hydroxide add 1 ml of 0.02*M* NP solution, mix well and after 10 min add 1 ml of the sample solution containing 15–150 μg of Toxogonine, and 2 ml of water. Mix the solution again and after 5 min measure the absorbance at 615 nm against a reagent blank.

Detection procedures (spot tests)

A. To 1 drop (0.05 ml) of Britton–Robinson buffer of pH 6.06 add 1 drop of the Toxogonine solution and 1 drop of 0.02*M* AmPF. Compare the colour with a reagent blank after 5 min. It is possible to identify 1.25 μg of Toxogonine in the reaction mixture (0.15 ml).

B. To 1 drop of 0.02*M* NP add 1 drop of 0.35*M* sodium hydroxide, mix the solution and let it stand for 10 min. Add 1 drop of Toxogonine solution and compare the colour with a reagent blank 5 min after mixing. Buffer is not necessary, because of the high pH (~12). The limit of identification is again 1.25 μg of Toxogonine in the reaction mixture.

RESULTS AND DISCUSSION

Characteristics and optimum conditions of complex formation

When Toxogonine is added to the aqueous AmPF solution or to a strongly alkaline NP solution it forms a blue complex, the absorption spectra of which have maxima at 610 and 615 nm respectively (Fig. 1). The complexes form quickly but remain stable for only a short while (Fig. 2) so the absorbances should be measured at a definite time after the reagents are mixed.

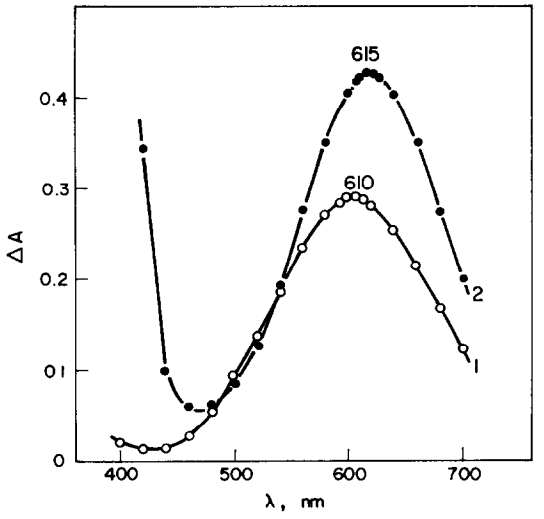

Fig. 1. Absorption spectra of the complexes measured against the reagent blank. *1*–Toxogonine–AmPF 1 × $10^{-4}M$ measured 5 min after mixing. pH = 6.17, I = 0.05, T = 24°C. *2*–Toxogonine–NP 2 × $10^{-4}M$ measured 5 min after mixing. pH = 12, I = 0.1, T = 24°C.

Formation and the stability of the complex depend on the temperature, the ionic strength, and especially on the pH value of the medium. Room temperature (20–25°) is the most convenient. High temperatures cause disintegration of the pentacyanide reagent.[13] Increased ionic strength decreases the absorbance, but the quantity of complex formed is independent of the kind of electrolyte added.

Figure 3 shows that a large excess of reagent is necessary, and that with AmPF the absorbance is markedly dependent on the molar ratio of the reactants, whereas with NP it is constant if the [NP]/[Toxogonine] ratio exceeds about 60.

Formation of the AmPF complex is optimal at pH 7–8 (Fig. 4). The absorption maximum like that for the AqPF complex[11] does not depend much on the pH of the medium, but at somewhat higher pH values shifts bathochromically from 610 to 615 nm. In alkaline medium, the complex forms faster but also decomposes faster. The NP

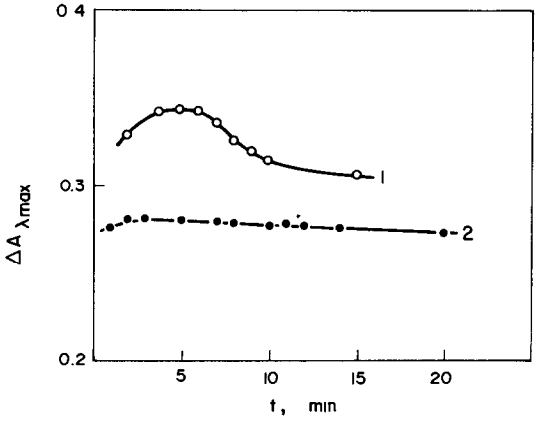

Fig. 2. Variation of the absorbance as a function of time for the complexes. *1*–Toxogonine 2.5 × $10^{-5}M$, AmPF 4 × 10^{-3}M, T = 22°C, pH = 6.99. *2*–Toxogonine 2.5 × $10^{-5}M$, NP 4 × $10^{-3}M$, T = 21°C, pH ~ 12. Absorbances measured against reagent blanks.

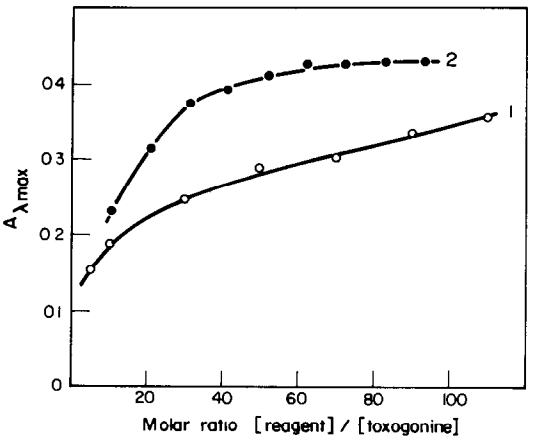

Fig. 3. Effect of the amount of AmPF and NP on the complex formation. Absorbance measured against water. *1*–AmPF 1.26 × 10^{-4}–27.6 × $10^{-4}M$, Toxogonine 2.5 × $10^{-5}M$, pH = 6.2–6.8, T = 24°C. *2*–NP 5.2 × 10^{-4}–46.8 × $10^{-4}M$, Toxogonine 5 × $10^{-5}M$, pH = 11.88–12.2, T = 28°C.

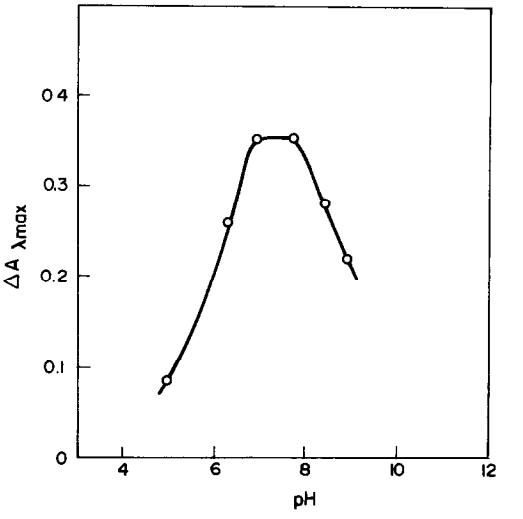

Fig. 4. Effect of pH on the AmPF complex formation. Toxogonine 2.5 × $10^{-5}M$, AmPF 4 × $10^{-3}M$, T = 21°C. Absorbances measured against appropriate blanks.

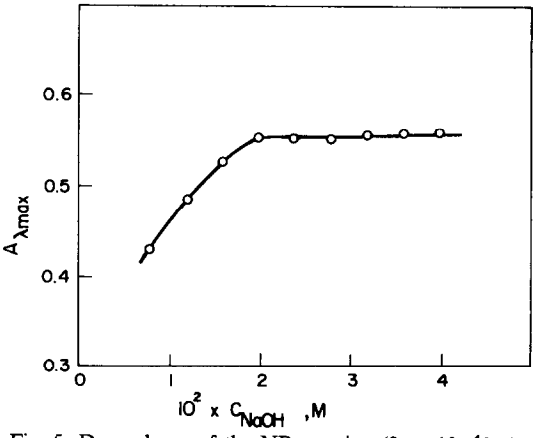

Fig. 5. Dependence of the NP reaction (2 × $10^{-4}M$) on NaOH concentration. Absorbance measured against water 5 min after mixing. I = 0.1, T = 23°C.

Table 1. Precision of the determination of Toxogonine

Taken, μg	ΔA*	Found†, μg	Standard deviation, μg	Rel. std. devn.,%	No. of detns.
Procedure A (AmPF as reagent)					
28.74	0.228	29.6	1.2	4.1	10
57.48	0.437	56.8	2.1	3.8	9
86.22	0.644	83.7	4.0	4.8	10
Procedure B (NP as reagent)					
28.74	0.176	28.4	1.9	6.5	6
57.48	0.342	56.5	2.9	5.2	7
86.22	0.521	86.5	4.3	5.0	8

* ΔA = absorbance measured at λ_{max} against a reagent blank.
† Calculated by means of calibration equations.

Table 2. Determination of Toxogonine in injections

Preparation	Found g/amp.	Average with 95% confidence limit* g/amp.	Standard deviation, %
Ampoules of Toxogonine "Merck", 0.250 g/amp.	Procedure A 0.257 0.260 0.262	0.259 ± 0.0065	1.0
	Procedure B 0.277 0.275 0.271	0.274 ± 0.0076	1.1

* Calculated by means of Student's *t*.

complex forms only at pH >10. The absorbance is maximal at pH > 11.7 which necessitates an adequate excess of base (Fig. 5). It should be pointed out that the buffer pH of 6.06 is used with AmPF as reagent, because owing to the large excess of AmPF, the pH of the final reaction mixture is 7, *i.e.*, the optimum value.

These studies prove that the reactions can be successfully used for detection and determination of microquantities of Toxogonine. A quantity of 1.25 μg of Toxogonine can be visually identified by the blue colour produced in 1 drop of sample. Beer's law is obeyed over the whole measurement range for the NP complex and up to an absorbance of 0.65 for the AmPF complex. The optimal Toxogonine concentration range for both reagents is from 30 to 60 μg/ml.

The molar absorptivities calculated from the calibration curves are 1.39×10^4 $l.mole^{-1}.cm^{-1}$ for the AmPF complex and 1.08×10^4 for the NP complex.

The results (Table 1) of precision tests show that the standard deviations are minimal when the absorbance is about 0.4. The error of the average in that case is not more than 2%, but the relative standard deviation is about 4%.

The methods have been used for the determination of Toxogonine in injections. The results given in Tables 2 and 3 are satisfactory. Procedure *A* is somewhat more precise and simple because of the higher stability of the solutions. The small quantities of atropine in the injection solutions do not interfere. From the literature[14,15] it is known that a number of pyridine derivatives without the oxime grouping also develop a colour with AmPF under somewhat similar conditions. These substances are not present in the injections and do not interfere in the analysis.

Composition and structure of the complex, and reaction mechanism

The composition of the complex was determined by the method of continuous variations[16] and the slope-ratio method.[17] For both reagents a molar ratio of 1:1 was found although Toxogonine has two oxime groups.

Table 3. Recovery of Toxogonine from injection solutions (Merck)

In sample	Added	Total	Toxogonine, μg Found*	Recovery, %	Mean recovery, %
Procedure A					
28.74	—	28.74	29.7	103.4	
28.74	14.37	43.11	44.0	102.0	101.4
28.74	28.74	57.48	56.8	98.8	
Procedure B					
43.11	—	43.11	46.6	108.2	
43.11	14.37	57.48	60.5	105.3	105.8
43.11	28.74	71.85	74.6	103.8	

* Average of 5–7 samples, calculated by means of calibration equations

The complexes were shown to be anionic by treatment with a strong anion-exchange resin (Merck III), at pH 7. The colour was transferred to the resin from the solution.

According to our earlier work[1–3] and other literature data[1,8] it can be supposed that the $[Fe(CN)_5TOXO]^{n-}$ complex is formed with both reagents. The reactions probably take place through AqPF, which is formed as an intermediate in aqueous AmPF solutions and alkaline NP solutions. The reaction is of substitutional type, replacement of the H_2O ligand by Toxogonine producing the blue negatively-charged complex. Works on isolation of the reaction products and confirmation of the proposed mechanism is still going on.

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DEVELOPMENT AND PUBLICATION OF NEW POLAROGRAPHIC AND RELATED METHODS OF ANALYSIS

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Summary—A review is made of the factors that should be investigated in the development of new polarographic methods of analysis. Recommendations are made concerning the preparation for publication of the results of such investigations.

The authors of the preceding papers in this series formulated considerations that should be taken into account in developing new and reliable spectrophotometric,[1] gravimetric,[2] and other[3–6] methods of analysis and investigation, and in preparing descriptions of them for publication. A similar treatment of polarographic and related electrochemical methods is warranted by their increasing importance as analytical tools. This paper is similar to its predecessors in purpose and structure, but differs from them in that it deals not with a single technique but with several, although these are all related to or derived from classical d.c. polarography. To have limited the paper to "classical" polarography would have led to a severe misrepresentation of the analytical significance of these newer techniques.

In the course of a recent survey[7] of the fundamental electrochemical data on 2015 organic, organometallic, and biochemically important substances (the data being obtained by approximately 50 of the electroanalytical techniques listed in a comprehensive summary[8] of the field), we found that approximately 80% of the information published between 1960 and 1971 came from classical d.c. polarography. We shall therefore stress d.c. polarography in this paper, but will also discuss linear-sweep polarography, differential pulse polarography, stripping methods and, but more briefly, cyclic triangular-wave voltammetry.

HISTORICAL

For many years most of the analytical applications of polarography were to determination of metal ions and a few other inorganic species such as oxygen and nitrate ion; determinations of organic substances were much less common and gained ground only slowly. The advent of atomic-absorption spectroscopy, because of its simplicity, made the future of analytical inorganic polarography seem rather unpromising, but with the increasing interest in high sensitivity for environmental and pollution studies, polarography has come to be more widely used again. This is mainly due to two developments, one (in our opinion the most useful in practical analysis) being the introduction of differential pulse polarography[9] and the other the stripping techniques.[10–15] Together with the commercial availability of reliable but relatively simple and inexpensive instruments, these developments have extended into the region of true trace analysis the lower limit of the range of concentrations over which polarography and allied techniques can be applied. Polarographic methods have become, in many cases, comparable or even superior to atomic-absorption spectroscopy in sensitivity, selectivity, and reliability. Consequently industrial and other laboratories have begun to return to the use of polarographic methods to analyse alloys, pharmaceuticals, foods, polymers, and petrochemicals, *etc.*, for traces of metals.

The trend has not been for the polarographic methods to replace atomic-absorption spectroscopy, but rather for the two techniques to be considered as complementary, the analyst choosing whichever seems to be more advantageous for each particular problem. Another factor that has contributed to the decided increase in the importance of polarography is the growing realization of its applicability in organic analysis, especially in the pharmaceutical industry. Other possibilities, particularly in environmental trace analysis, remain to be explored.

FUNDAMENTALS

As with most other techniques, polarographic methods can be developed purely empirically. In a simple case this might involve recording current–voltage curves of the substance to be determined in a few supporting electrolytes picked more or less haphazardly, finding that one of these curves shows a well-developed wave without interference from other substances expected to occur in the sample, and

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using these observations for analytical purposes in straightforward fashion.

Considerations of time or money may force the analyst to adopt such an approach, if only a very small number of non-routine samples is in question. However, a method so devised should not be offered for publication*, because it is unlikely that the optimum conditions would have been arrived at by chance.

The rational development of a polarographic method certainly requires knowledge of at least the general outlines of the course of the electrode process. It is necessary to know which species is reduced or oxidized at the indicator electrode, how many electrons are involved in the process, what chemical reactions accompany the electron-transfer steps, and the nature of the product finally formed.

For purely analytical purposes, however, it is not necessary to obtain as much understanding of the details of an electrode process as would be needed in a fundamental electrochemical study or even in a theoretical study of the effects of structure on electrochemical behaviour. In the following section we shall describe the information that is needed in developing an analytical method and the ways in which it may be obtained.

THE ELECTRODE PROCESS

The course of an electrode process depends not only on the nature of the electroactive substance, but also on the medium in which it is dissolved. The presence and concentrations of complexing agents, the pH, the identity of the solvent and sometimes the supporting electrolyte and the presence of a surface-active agent can all influence the course of an electrode process. To find such effects, elucidate the electrode process, and choose the best conditions for an analysis, it is necessary to observe the effect of varying the concentration of each component of the medium.

There are three common situations. In one, the literature describes the course of the electrode process for the substance of interest in a medium and under conditions that seem to be suitable for carrying out the analysis. In the second, the course of the electrode process has been described either for the substance of interest in media that are not well suited to analysis of the particular material, or for a structurally related substance in a medium that seems suitable. In the third, neither the substance to be determined nor any other substance closely related to it has been studied at all. In the first situation a brief check of the literature usually suffices; in the third an electrochemical study is unavoidable. The second situation involves the principle of analogy, which can be a very powerful working tool, but has limitations which must be recognized.

In the periodic table there are several groups of elements with members which display more or less analogous inorganic polarographic behaviour. The analogies are strong for the alkaline earths and the halides, but much less so for groups such as V, Nb, Ta, or Al, Ga, In, Tl. The identity of the ligand(s) in complexing media or complexes inert toward substitution may also be important: the complexes of nickel(II) with various amines behave in very similar ways, but the behaviours of ferricyanide and nitroprusside have little in common although both contain iron.

In organic polarography the use of analogy has similar limitations. Knowing how organic bromides behave, it is possible to make useful predictions about the behaviour of structurally related chlorides or iodides. Some nitro compounds behave similarly to the corresponding nitroso compounds, and the reductions of some aldehydes resemble those of some ketones. But when we try to apply the principle of analogy to wider groups of organic compounds it is unusual to find useful similarities.

It was once assumed that all compounds containing a given functional group will behave in the same general way, giving the same number of waves corresponding to identical numbers of electrons and changing in the same ways with change in the pH or any other experimental condition. We now know that, although such a generalization does seem to apply to a few classes of compounds (such as thiols and semicarbazones), usually the majority of compounds bearing a given functional group behave in much the same way, but there are some that behave quite differently. For example, nitrobenzenes, nitronaphthalenes, and nitrothiophenes behave similarly regardless of whether they are unsubstituted or bear such substituents as methyl, methoxyl or carboxyl groups, or halogen atoms; but *o*- and *p*-nitroanilines, nitrophenols, and *p*-nitrobenzenes show different reduction mechanisms. The reductions of a few functional groups show even more pronounced dependence on structure: benzonitriles can be reduced in four different ways, depending on the nature of the substituent. Fortunately such cases are rare.

Expectations based on analogy should always be checked experimentally during the development of an analytical procedure.

That the literature already contains the information needed in developing an analytical method is more likely for inorganic than organic polarography for two reasons. The number of simple inorganic ions is far smaller than the number of organic substances and even allowing for different oxidation states and different supporting electrolytes, the field of study is less broad than in organic polarography, and explorations of it have been correspondingly more intensive. Thus some seventy more or less standard supporting electrolytes are used in aqueous medium, and the behaviour of most common metal ions has been sur-

* Except perhaps as a short note to make the existence of the method known so that it may be developed if of sufficient interest [Ed.].

veyed for each of them, giving the inorganic analyst a wealth of data. Of course much is still unknown: the behaviour of many substances (such as sulphur dioxide) is only incompletely understood despite much research, some compounds have been investigated only slightly, and large areas (such as the behaviours of some less familiar inert complexes) have hardly been touched at all. Furthermore, the data available do not always readily suggest ways of dealing with complex mixtures or, for example, of analysing samples containing high concentrations of hydrofluoric acid, for which the number of reference values is very limited. More may be accomplished by using mixtures of complexing agents than the data for the individual ligands suggest to the neophyte, and further possibilities are provided by use of anhydrous or mixed solvents, to which much less attention has been paid than they deserve.

For the majority of common organic compounds, information is available on suitable analytical conditions and the reaction mechanisms under those conditions. Most analytical applications involve aqueous solutions or mixed solvents containing water. As in inorganic analysis, other constituents of the sample sometimes make it impossible to use a medium described in the literature. Those developing organic analytical methods are often confronted by a wider variety of choices (*e.g.*, of the solvent, the buffer system, and the concentration of buffer to be used to attain a desired pH) among which decisions are to be made.

Because of the greater possible variability in the composition of the supporting electrolyte and solvent, the coverage of the behaviour of even the most frequently studied organic substances is less complete than that for the common inorganic ions. Because of the wide variation in structure of organic compounds, together with the fact that whole classes of even common organic compounds have been studied only superficially if at all, it is understandable that additional or preliminary experiments are needed more often for organic than for inorganic analyses.

The use of non-aqueous solvents deserves more attention from analytical electrochemists. Theoretical studies on such media have been carried out both for inorganic and for organic species, but practical analytical methods are very few. The chief reason for using such solvents is not that they increase the solubility of the determinand and the other substances present in the sample, for at the level used in polarographic studies (10^{-4}–$10^{-5}M$) most inorganic and organic species are sufficiently soluble in water or in mixed solvents containing water. It is rather that they can prevent undesirable reactions that would occur in the presence of water, such as the hydrolysis and hydration of inorganic species, or hydration and proton-transfer reactions accompanying electrolysis of organic compounds. Unfortunately, this advantage is only incompletely realized in wet solvents: even 0.001% w/v of water corresponds to a concentration of $5 \times 10^{-4}M$, which is likely to be so much larger than the concentration of the electroactive substance that these undesirable processes may still be both fairly fast and fairly complete. Progress would be greatly facilitated if better procedures for determining traces of water in—and removing them from—organic solvents were available. The problems associated with the limited solubility of dissociated supporting electrolytes and with the control of acidity at the electrode surface in such media will become easier to solve when our knowledge of chemistry in non-aqueous media is based on safer foundations.

A similar state of affairs has arisen from the proliferation, during the last 15 years or so, of other techniques related to polarography. When these are applied to compounds having polarographic behaviour that is thoroughly known and well understood, they can yield confirmation, supplementation, or contradiction of prior beliefs, and either added certainty or new enlightenment is bound to result. By itself, however, each such technique provides information of limited value to the prospective user of a different technique, for differences of time-scales, mass-transport regimes, degrees of accumulation of adsorbed materials at the surface of the indicator electrode, and other conditions are all too likely to be involved. Useful though all these differences undoubtedly are in providing new points of view from which features of the electrode process can be detected and studied even when they might be missed by d.c. polarography alone, they often render the data secured by these techniques extraordinarily difficult to translate into polarographic terms. A striking example arises in the reduction of 1-nitroso-2-naphthol.[16,17] Streuli and Cooke,[18] using stationary mercury-pool voltammetry, found this compound to have a half-wave potential of −0.80 V *vs.* S.C.E. in an aqueous ammoniacal buffer of pH 9. Its polarographic half-wave potential, obtained with the dropping-mercury electrode in exactly the same supporting electrolyte, is −0.27 V.[11,12] If it were the only one available, the polarographic value might either confuse or mislead an analyst attempting to devise a voltammetric or coulometric method for determination of this compound, or of another compound in its presence.

Similarly, it cannot be assumed—as it sometimes is—that knowing the shape of a d.c. polarographic curve and the optimum conditions for performing an analysis by d.c. polarography makes it possible to predict the wave-shape and optimum conditions for an analysis by a linear-sweep method. In some simple cases these two kinds of curve are closely analogous, but often their shapes, and even the mechanisms of the underlying processes, are different. This is due not only to the difference in the rates of voltage-scanning, but also to the fact that d.c. polarography is virtually a potentiostatic technique where the current measured at any one potential is unaffected by electrochemical processes responsible for portions of the curve that have already been recorded. In a rapid-

scanning technique, however, the surface of the electrode and the composition of the solution surrounding the electrode can be altered by products formed at an earlier stage of the potential scan, and those products can interact with other species in the solution and with the products of other reactions that occur at later stages.

Similarly, information obtained by d.c. polarography cannot be directly used for prediction of shapes of a.c. polarographic or pulse polarographic curves, as the latter are often more affected by adsorption and depend on the rate and transfer coefficient of the electrode process. This limitation works also in the opposite direction.

Of course it is important to have data secured by techniques other than polarography; without them definitive assessments of the utility (or the lack of it) of these techniques can hardly be made. Further, a polarographic study of a new compound should be supplemented by other techniques for the sake of the added enlightenment these so often yield. It is also useful and worthwhile to employ other techniques for studying compounds about which polarographic information is available and is believed to be reliable. Likewise, an investigator applying another technique to a compound for which polarographic data are non-existent, incomplete, or of dubious validity should certainly accompany his work with a careful, even though brief, polarographic investigation under closely comparable conditions. He can then compare the polarographic and other data on the compound he studies, and so contribute to the full appreciation of the characteristics, advantages, and limitations of the electroanalytical techniques he uses. Finally, he makes it possible for other chemists to compare their data with his.

GENERAL PROCEDURE

Preliminary experiments

Because reliable information on polarographic behaviour is less often available in organic than in inorganic analysis, the investigation of an organic compound is described here. First a stock solution of the compound is made and the current–voltage curves in a few selected electrolytes are recorded.

It is convenient (if possible) to make a 0.01M stock solution, using the most appropriate solvent, *i.e.*, water if possible (unless an anhydrous medium is to be used in the electrochemical work), and otherwise ethanol, dimethylformamide, dimethylsulphoxide or acetonitrile. If such a stock solution is diluted to $2 \times 10^{-4}M$ with a solution of supporting electrolyte in a solvent different from that used for the stock solution, only 2% of "stock" solvent will be present in the resulting mixture. In most cases no harm will result from the presence of as much as about 5% of the stock-solution solvent, but if an anhydrous solution (*i.e.*, one containing less than 0.01% of water) is to be used, the stock solution must not contain more than 0.5% of water. If, however, a stock solution more concentrated than 0.001M cannot be prepared conveniently, the analyst should remember that the properties of the solvent may change as more stock solution is added to it, and this may lead to fictitious variations of various parameters, such as that of i_l/c with concentration. It is best to prepare all test solutions so that they have virtually identical compositions.

When the solvent or solvent mixture used is aqueous, the following supporting electrolytes are recommended for the preliminary investigations: 0.1M sulphuric acid, acetate buffer of pH 4.7, phosphate buffer of pH 6.8, borate buffer of pH 9.3, and 0.1M sodium hydroxide. The buffers should preferably have ionic strengths close to 0.1M. These five solutions conveniently cover the most frequently studied range of pH-values. If an anhydrous solvent is necessary, however, lithium or tetra-alkylammonium salts must be used and there is no practical general way of controlling the acidity.

The current–potential curves of the $2 \times 10^{-4}M$ solutions in the selected supporting electrolytes are recorded and the number, heights and shapes of the waves, and the effects of pH on the wave-heights and half-wave potentials observed. It is best to deaerate the supporting electrolyte, add an aliquot of the stock solution, deaerate briefly, and record the curve. This procedure minimizes the effect of volatility and any slow chemical interaction between the substance being studied and the supporting electrolyte.

The limiting diffusion currents in $2 \times 10^{-4}M$ solutions of most organic compounds are between about 1 and 5 μA, when capillaries having normal characteristics are employed. A limiting current much smaller than this may be a kinetic current or due to an impurity in the sample; one that is much larger may be a catalytic current. These possibilities may be tested by applying techniques described in detail elsewhere.[19–21]

The appearance of only one wave on a polarogram indicates that a single electrode process is involved, but when two or more waves appear they may originate in several different ways. These include successive reduction of oxidation, competitive reduction or oxidation of two or more species in chemical equilibrium, intermediate reactions involving the primary product or products of electrolysis, reduction or oxidation of both dissolved and adsorbed species, or the presence of an impurity. To distinguish among these, use is made of the dependence of the wave-height ratios on the pH, the concentration of the electroactive substance, and the composition of the solvent. The products formed in prolonged electrolyses on the plateaus of the different waves should also be identified. Linear-sweep polarography and cyclic triangular-wave polarography have proved to be the techniques most useful in studying chemical reactions

occurring between electron-transfer steps, and electron-spin resonance spectroscopy has been shown to be most useful for studying radicals and radical ions formed electrolytically.

The shapes of polarographic waves are governed by the kinetics of electron transfer and are of little interest in analytical applications, except for the difficulty involved in measuring the limiting current for very drawn-out waves such as those obtained with some organic halogen compounds and peroxides.

Detailed investigations

The effects of pH on wave-heights and half-wave potentials are of great practical importance. They are due to the proton-transfer steps that accompany the reductions or oxidations of almost all organic compounds. For a few of these the electron-transfer steps, the last one of which is totally irreversible, precede all the proton-transfer steps. Such compounds, which include the alkyl halides, have wave-heights and half-wave potentials that are independent of pH. but this is the exception, not the rule.

When preliminary investigation indicates that the height or half-wave potential of the wave depends on pH, a more detailed investigation must be made. The pH range to be covered may extend as far as the acidity of concentrated sulphuric acid on the one side and the alkalinity of 10*M* sodium hydroxide on the other. Over the ordinary range from pH 2 to 12, simple buffers should be used: universal buffers, such as Britton-Robinson buffers, should be used only for initial studies. Simple buffers minimize any complications caused by interactions of their components with the compound being studied; they are also easier to prepare and their purities can be more easily controlled.

The proton-transfer reactions that cause polarographic waves to be pH-dependent may either precede the first electron-transfer step or occur between successive electron-transfer steps. For either the first wave or one of the following waves a dependence of wave-height, half-wave potential, or both, on pH is then observed, and its correct interpretation can provide information about the nature of the species participating in the first electron-transfer step or about the transformation of the primary electrolysis product into another species that undergoes further reduction or oxidation. Details have been published elsewhere.[22–25] Tautomeric and hydration–dehydration equilibria are included in the group of processes that involve acid–base reactions and give rise to such dependences on pH.

Acid–base equilibria are affected by the introduction of organic solvents, often to such an extent that though virtually instantaneous and complete in one solvent, they do not seem to occur at all in another. This is especially important with systems in which such reactions are interposed between successive electron-transfer steps: the use of an anhydrous aprotic solvent can sometimes eliminate consecutive reduction steps and thus yield polarograms that are simpler and therefore of greater analytical utility. The use of organic solvents can also cause a tautomeric or hydration–dehydration equilibrium to shift so as to favour the analytically important form. However, these advantages may be counterbalanced by complexities caused by radicals or radical ions formed in these non-aqueous media or by the presence of unexpected proton-donors, including the electroactive species.[26]

To evaluate the number of electrons transferred the simplest technique is by comparison of the responses, under the same conditions, from equimolar solutions of the compound of interest and of other compounds of similar molecular size. In d.c. polarography or hydrodynamic voltammetry the wave-height is used, in chronopotentiometry the transition time, and so on. All the processes in the systems thus compared must be diffusion-controlled, and the values of n for the reference compounds must be known. It is wise to use at least two or three different reference compounds; if only one is selected it may be impure or exhibit atypical behaviour under the conditions employed. We shall use the term "voltammetric n-value" to denote a value of n obtained from such comparisons.

Coulometric procedures for evaluating n are more sophisticated, and also appear to be much more reliable because they do not involve the assumption, implicit in the comparison techniques, that the diffusion coefficients of different species are the same. We shall emphasize the errors that may result (and often have resulted) from misunderstanding the relation between voltammetric and coulometric n-values.

Dropping-electrode coulometry, in which a small volume (1 ml or less) of the solution being investigated is electrolysed for a long time with a dropping-mercury electrode kept at some potential on the plateau of the wave of interest, seems simple, but much experience is required before reproducible results can be obtained with it. Coulometry at controlled potential with a stirred mercury-pool electrode is far more precise: the literature contains many examples showing that relative standard deviations as small as a few tenths or even hundredths of a per cent can be obtained. For the present purpose, however, high precision is of limited value, because a reliable decision between integral values of n is usually all that is required, and the choice between these techniques should not be made on the basis of their precisions alone.

Because dropping-electrode and stirred-pool coulometry involve different time scales, different mass-transfer regimes, and different extents of adsorption, they sometimes yield different values of n even with the same concentration of electroactive substance in the same supporting electrolyte. The coulometric values may agree with each other but differ from the voltammetric one. If, for example, an electrode reac-

tion occurs by the ECE* mechanism

$$\begin{array}{rcl} O + n_1e & \rightarrow & I \\ I & \rightarrow & J \\ J + n_2e & \rightarrow & P \end{array} \qquad (1)$$

and if the transformation of I into J is fairly slow, the voltammetric n-value is likely to be indistinguishable from n_1. In the much longer time required by any coulometric procedure, an appreciable fraction of the first intermediate I will be transformed into the electroactive species J and then further reduced to the final product P. Stirred-pool coulometry will result in reduction of all of the J, and will yield an n-value equal to $n_1 + n_2$. In dropping-electrode coulometry some of the J will escape reduction and the n-value will lie between n_1 and $n_1 + n_2$.

Detailed studies have been made of the behaviour of this and many other mechanisms, but are not very relevant to practical analysis. What is important is that *both* a voltammetric and a coulometric n-value *must* be obtained in the course of any electrochemical investigation. When they do not agree, a correct elucidation of the process must include an explanation of the discrepancy between them. Statements like "Coulometric experiments showed that the value of n is 4.02, and therefore the process must be..." have no place in the literature.

One advantage of stirred-pool coulometry in determining n is that it is much faster than dropping-electrode coulometry; another is that it yields enough of the product(s) to facilitate identification (this can also be done by prolonged electrolysis with a dropping electrode or other voltammetric electrode). Sensitive identification techniques are required in any case: absorption spectroscopy (especially in the ultraviolet), chromatography (paper, thin-layer, or gas–liquid with an ionization detector), polarography, potentiometry and other techniques for determining pK-values, and sensitive colour-forming reactions have proved the most useful.

Because coulometry with a voltammetric indicator electrode is intimately related to voltammetry with the same electrode, it will usually be dropping-electrode coulometry that yields n-values most directly comparable with those from polarographic data. The material from which the coulometric working electrode is made must certainly be the same as that used for the voltammetric indicator electrode. Whether the greater precision attainable by exhaustive (*e.g.*, stirred-pool) coulometry is an advantage or a drawback is a question that the experimenter must decide for himself. It makes side- and competing reactions harder to overlook, thus leading to fuller understanding of the process, but may obscure the basic nature of the process by yielding an excess of subsidiary information before the experimenter is ready to deal with it.

For compounds that give two or more waves corresponding to successive electron-transfer steps, it suffices to evaluate n for one of the waves. The other n-values can then be estimated by assuming them to be proportional to the limiting currents, provided it is proved that the latter are diffusion-controlled and that their ratios are independent of experimental conditions over a wide range.

Similar approaches serve when linear-sweep or cyclic voltammetry (or polarography) is used. These techniques provide the investigator with an additional variable, the rate of voltage scanning, which gives rise to some useful diagnostic criteria, but at the expense of two sacrifices. One is that the capillary characteristics, which in polarography can be varied to distinguish between rate-, adsorption-, and diffusion-controlled currents, can no longer be used for this purpose. The other is that the peak-current obtained in single-sweep and cyclic voltammetry often depends on the rate of the heterogeneous process, the value of the transfer coefficient, and on the number of electrons consumed in the rate-determining step and any faster steps that precede it. Only when the electrode process exhibits Nernstian behaviour is the peak-current governed only by the factors (including the scan-rate, the rate of mass transport by diffusion or some other mechanism and the overall n-value) that govern the wave-height in polarography. Hence it is generally not possible to deduce the ratio of two n-values from the ratio of two voltammetric peak heights. In addition, as pointed out above, the products formed at one potential can affect the current at another potential, particularly when they are adsorbed. All this means that the voltammetric techniques have both advantages and disadvantages *vis à vis* polarography for the elucidation of electrode processes. Only for consecutive processes do cyclic voltammetry and other cyclic techniques offer additional information, and even then a better insight into the electrode process can be gained by using both polarography and cyclic voltammetry.

The analytical utility of linear-sweep and cyclic voltammetry has often been overestimated. The chief limitation is one that was evident[27–29] even before attempts to apply these techniques to analytical problems had become numerous, namely that the peak-current for any non-Nernstian process depends on the value of αn_a for that process. Substantial variations of αn_a can often result from the unexpected presence of a trace of surface-active material, or from variations in the concentration of such a material. Surface-active substances are ubiquitous in organic electrochemistry, in the reagent-grade chemicals from which supporting electrolytes are prepared, and even in water purified by distillation (to say nothing of water obtained from mixed-bed ion-exchangers): Bauer[30] has shown how much their effects have been underestimated in a different connection. This means that the peak-height often depends on factors (including the concentration of the determinand) that the

* ECE = electrode reaction followed by chemical reaction, followed by electrode reaction.

analyst cannot reproduce or control. There is no question that linear-sweep and cyclic voltammetry are useful for determinations of substances that yield Nernstian response, but the effects mentioned constitute a very severe limitation.

The analytical applications of linear-sweep and cyclic voltammetry are further hindered by problems of overlap of peaks. Data-handling techniques are available that provide a complete analysis of two very closely overlapping polarographic waves in only a few seconds of computer time,[31] but their application to the analogous problem of overlapping peaks in linear-sweep and cyclic voltammetry is far more difficult because formidable equations would be required to describe the peaks and empirical descriptions do not suffice.[32] When two processes occur at nearly equal potentials, they are more obvious on a linear-sweep or cyclic voltammogram than on a d.c. polarogram. Consequently linear-sweep and cyclic voltammetry are more useful than d.c. polarography for detection and identification, but in our opinion they have very little, if any, advantage over polarography in quantitative analysis in this situation. Their quantitative use is therefore largely restricted to the analysis of samples that contain only a single electroactive species, or two or more electroactive species if the peak-potential for the substance of interest differs substantially from the peak-potentials of all the others.

Differential pulse polarography has much more promise as an analytical technique. As yet its use has been limited by the incompleteness of our understanding of the ways in which the curves obtained reflect the details of electrode processes. Provided that the experimental variables peculiar to the differential pulse technique—the drop-time, the rate of voltage-scan, the pulse-amplitude, the delay-time and the width of the sampling interval—are kept constant, investigations may be made in the same way as for d.c. polarography.

APPLICABILITY

The reproducibility of a polarographic determination is usually about 2–3%.* Hence polarography is only rarely useful for determining the main component of a sample. Other electroanalytical techniques, notably coulometric titration and controlled-potential coulometry, are far better adapted to such analyses because they decrease the number of experimental variables that have to be measured or controlled and therefore simplify the attainment of high accuracy and precision. It can be recommended for analyses of such samples only if no other method is available; if other methods are more tedious or expensive or less reliable or selective than polarography; or if it is essential to obtain an approximate result in the least possible time. When many samples have to be analysed quickly, it may be advantageous to use an oscilloscopic technique, such as linear-sweep or cyclic voltammetry or oscillopolarography, although it does *not* follow that because roughly 10 minutes are required to record a complete polarogram,† 10 minutes or more will be needed to analyse a single sample by d.c. polarography. When only a single substance is to be determined, it is never necessary to record the entire curve: only the wave of interest is needed. For such purposes it is easy to set up apparatus that includes two or more cells and a single polarograph, so that one solution is being deaerated while the curve for another is being recorded.

It is sometimes even possible to measure the limiting current at only a single potential, but we do not recommend this to the inexperienced. The dangers are similar to those in colorimetric analysis in which the absorbance is measured at only a single wavelength: the blank may vary from sample to sample, and some samples may contain unexpected foreign components that affect the measured signal. Such unsuspected contaminants would often be revealed if the whole current–potential (or absorption) curve were inspected. If such dangers have been carefully considered and adjudged to be negligible, however, these two expedients together can enable the chemist to perform polarographic analyses at a rate difficult to approach by any other technique. For example, they once enabled one of us[36] to analyse some thousands of samples of silver-plating wastes for five elements (silver, copper, cadmium, nickel, and zinc) at a steady rate of 30–35 samples (150–175 individual results) per hour, including the preparation of the samples and the computation of the results. It is particularly in situations where several substances have to be determined in each sample that polarography may be very much superior in speed and convenience to any other technique.

Considerable speed can be achieved even when portions of current–potential curves are recorded. Thus it was found possible to analyse polarographically 14–16 samples of fruit or vegetables per hour for ascorbic acid, including preparation of samples containing glutathione and evaluation of the results.[37]

When only a single constituent of the sample is to be determined, polarography is at its best if the content of that constituent in the sample lies between 20% and 0.1 ppm. Toward the lower end of this range the superior sensitivity and limit of detection of differential pulse polarography make it the technique of

* There are those who believe that this reflects some inherent limitation of d.c. polarography, and that some newer techniques are so far superior to it that they enable an accuracy and precision of the error of ±0.1% to be obtained by skilled operators. Actually, this accuracy and precision were being achieved in the analysis of technical materials by d.c. polarography three decades ago,[33,34] and would be even easier to obtain nowadays.[35]

† The word "polarogram" is used in two different senses: in the U.S. it is generally used to denote a single current–potential curve, but in some European countries it denotes a set of such curves, usually for a group of solutions of related composition, recorded on one sheet of paper. Here we intend the first of these meanings.

choice. The time required for a single analysis is practically the same over the whole range of concentration, typically 1–3 min for a single constituent once the solution has been prepared. The relative error of d.c. polarography is about 3% at the 0.01–20% level; if differential pulse polarography is used to analyse samples containing 0.0001–0.01% of the substance being determined, the relative error is typically about 5%. The limit of detection by d.c. polarography is about the same as that for most spectrophotometric methods; for differential pulse polarography it is about two orders of magnitude lower, and is below that of neutron-activation analysis for lead and a few other elements.

The limit of detection by the differential pulse technique can be further improved by combining it with stripping analysis. Such procedures employ hanging mercury-drop or mercury-coated carbon electrodes. and are as yet restricted to metals that form amalgams and to anions that form slightly soluble compounds with mercury. The metal (or anion) is first accumulated in (or on the surface of) the electrode by pre-electrolysis for a definite period of time, and the metal (or mercury salt) is then stripped from the electrode by anodic (or cathodic) dissolution. The analysis is based on the current–potential curve for the dissolution process. Concentrations in the parts per milliard (ppM) range can be determined in this way, and the limit of detection may correspond to a concentration of $10^{-9}M$ or even lower in the solution from which the metal or anion is deposited.

In practical analysis the lowest molar concentration of a substance that can be determined by d.c. polarography is usually about $5 \times 10^{-6}/n$ if the wave is diffusion-controlled, n being the number of electrons (per ion or molecule of the electroactive species) involved. If the substance gives rise to a catalytic wave it may be determined at much lower concentrations. Thus the limit of detection of cobalamin in buffered media is about $10^{-8}M$, and that of vanadium(V) in the presence of a large excess of hydrogen peroxide may be as low as $10^{-9}M$.

The selectivity of polarographic methods is of particular importance. Whenever only a single measurement is made, the analyst cannot be sure that no substance other than the one being determined is contributing to the measured response. For example, an absorbance that will be interpreted as being proportional to the concentration of one substance in a solution may contain a contribution from another constituent having an absorption band some tens of nanometres away. It is true that a similar problem can arise in polarographic analyses in which the current is measured at only a single value of the applied potential; it is also true that the problem can be solved, or at least recognized, in spectrophotometry by recording the entire spectrum (or at least enough of it to provide assurance that no other substance is absorbing significantly within the range of wavelengths that is of interest). Nevertheless, the great majority of spectrophotometric analyses are based on the measurement of a single absorbance whereas the great majority of polarographic ones are made by recording the entire wave. The unexpected presence of an interfering substance cannot escape notice in polarographic analyses as often as it can in analyses performed by many other techniques.

The problem of chemical interference needs no discussion here; it arises in every branch of chemical analysis. We confine the discussion to interference by overlapping instrumental response or other complications in measurement.

Interferences caused by inadequate resolution

In d.c. polarography it is often possible to determine two electro-reducible (or -oxidizable) substances from a single polarogram, if the difference between their half-wave potentials is as small as 0.1 V. In differential pulse polarography the corresponding figure is about 0.05 V difference between summit-potentials. These are traditional criteria, and depend to some extent on the slopes and relative heights of the waves. Under very special and admittedly extreme conditions it is even possible to analyse a mixture containing two components with half-wave potentials which differ by only a few mV.[31] Since the resolution often depends on the medium employed, the selection of the supporting electrolyte is frequently a crucial factor. A classical example is the analysis of a mixture of lead(II) and thallium(I). In non-complexing media the half-wave potentials of both are close to -0.45 V *vs.* S.C.E., and the polarogram of a mixture can be resolved only by non-linear regression analysis or with the aid of very precise measurements with solutions of known concentrations. In moderately concentrated sodium hydroxide solution, however, the wave of lead(II) shifts toward more negative potentials because of the formation of $Pb(OH)_3^-$, while that of thallium(I) is virtually unaffected because there is no hydroxo-thallium(I) complex of appreciable strength. This permits the determination of thallium(I) in the presence of a large excess of lead. Many different complexing agents have now been investigated as supporting electrolytes, and there are many possibilities of combining several complexing or reducing agents to mask some metal ions while permitting waves to be obtained for others. Hence there are few situations in which a metal ion has to be determined in the presence of a limited number of others, of known identities, that are not easy to deal with. In organic analysis the possibilities of differential complexation are less numerous, but it is still often possible to achieve satisfactory resolution of overlapping waves by varying the composition or identity of the solvent, the nature and pH of the buffer, and the ionic strength.

Interferences caused by prior waves

If the resolution is good, the ease of determination depends on the order in which the waves appear. If

the wave of interest is the one that occurs at the less negative potential if both waves are cathodic (or at the more negative potential if both waves are anodic), the determination is easy even when much higher concentrations of the substances responsible for the other waves are present. If it is not, no more than about a tenfold molar ratio of the interfering substance can be tolerated in d.c. polarography. There are several general solutions to this problem. The easiest is to change the supporting electrolyte so that the order in which the waves appear is reversed. This is less often possible in organic than in inorganic analysis. Much more generally applicable is reduction (or oxidation) of most of the interfering substance by controlled-potential electrolysis before the polarogram is recorded. In this way one of us was able[38] to determine 0.1 ppm of nickel or zinc in copper or a copper salt, and the limit was set by the limit of detection of d.c. polarography, which was used to analyse the solutions after removal of copper by controlled-potential electro-deposition; by means of anodic stripping voltammetry it should be possible to determine 0.1 ppM of zinc in such samples. In this example the interfering substance is removed from the solution, but of course it might equally well be reduced (or oxidized) to give a species that remains in the solution but is innocuous. If this is done, it is essential to make sure that the reduced form (supposing both waves to be cathodic) of the interfering substance does not consume the substance of interest by a slow chemical reaction in the bulk of the solution. Sometimes the reduction (or oxidation) can be effected chemically, as for example when copper(II) is reduced by cyanide in determining nickel in copper-base alloys[41] or when iron(III) is reduced by hydroxylamine in determining copper in aluminium alloys containing substantial amounts of iron.[42] Although chemical treatment is faster and easier than controlled-potential electrolysis, it necessitates making sure that no ill effect can result from the presence of the excess of reagent or the product obtained from it. Other techniques of separation, such as distillation, extraction, or a chromatographic method, can also be used, but almost always involve more manipulation and attention from the analyst. Finally, it is often advantageous to use another technique instead of d.c. polarography. Those curves that are, or resemble, derivatives of d.c. polarographic waves are particularly useful. One such technique is differential pulse polarography, in which the current decreases almost to the background level after a summit* has been passed. The response due to the large excess of interfering substance therefore decays considerably before the summit of interest begins, and a separation of 0.2 or 0.3 V between the summit potentials suffices to permit the determination of traces of the substance sought.

Systematic errors

In a polarographic method of analysis, systematic errors may arise in preparing the test solution, in recording the curve, and in the measurement and interpretation of the limiting, peak, or summit current. Systematic errors belonging to the first group are generally chemical and are not discussed here. Errors arising during the polarographic manipulations include those caused by interaction with metallic mercury or the metal of an internal reference electrode, by loss of a volatile compound into the stream of gas used for deaeration, and by problems associated with the use of a reference electrode. Cells with separate reference electrodes are unquestionably superior for investigative work, but in routine work they involve the danger that the sample solution will react with the reference electrolyte or with an agar bridge or that adsorption onto a glass, porcelain, or plastic diaphragm will occur. There are many polarographers who prefer to obviate these dangers by using a mercury pool, silver–silver chloride, graphite, or other internal reference electrode in direct contact with the solution being analysed, but others are more fearful of the errors (due to reaction with mercury or silver, solubility of silver chloride, *etc.*) to which these electrodes themselves can give rise, and the choice becomes a matter of taste. In any event, a cell used for routine analysis should be simple and have few crevices, be easy to wash, rinse, and dry, and allow deaeration of one solution while the curve for another is being recorded. For example, the cell designed by Novák[39] meets these desiderata, but most commercially produced cells fail to do so in one or more respects.

The interpretation of the recorded curve may be an important source of systematic error. There are two different problems: the method of measuring the current, and the design of the standardization procedure. Many ways of measuring wave-heights are described in the literature, and choosing among them is often difficult for the novice. That they can give different values of the limiting current, especially if the wave is ill-defined, is immaterial: what is really wanted is the ratio of the limiting current for the unknown solution to that for a standard solution (or to the average of the ratio of limiting current i_l to concentration c for a number of standards). As long as some simple principles are followed—for example,

* A forthcoming recommendation of Commission V.5 on Electroanalytical Chemistry of the International Union of Pure and Applied Chemistry is that the terms "peak" and "summit" be distinguished, the former being applied to curves like those obtained in linear-sweep, triangular-wave, and cyclic voltammetry and the latter to curves like those obtained in a.c. and differential pulse polarography. Although in all these techniques the current or other signal passes through a maximum value when the applied emf is varied, it does so for quite different reasons. As a general guide it may be said that a summit potential is identical, or nearly identical, with the corresponding half-wave potential in d.c. polarography, while a peak potential is not, and that a summit is symmetrical, or nearly so, while a peak is not.

the wave height must be measured parallel to the current axis rather than at an angle to it, and correction for the residual current must be made—there is not much difference between the final results obtained by different techniques of measurement. The reliability of the final result (*i.e.*, the concentration of the electroactive substance) depends on the nature of the wave. If the wave is well-developed, is preceded by a linear portion of the residual-current curve, and has its plateau parallel to that portion of the residual-current curve, it is not difficult to obtain a value of the limiting current that is accurate and precise to $\pm 1\%$. With an ill-developed drawn-out wave that is closely followed by another wave or by the final current rise, or deformed by adsorption or mechanistic complications, the precision may be as poor as $\pm 10\%$, or even worse.

The oscillations on polarographic waves are sometimes considered to be a nuisance, but actually provide an invaluable indication that the dropping electrode is functioning properly and also indicate the occurrence of unusual phenomena such as adsorption. Measurement of the mid-points of the oscillations is superior, if the recording system is properly damped, to measurement of either their maxima or their minima.

Correction for the blank (residual) current, is essential. Frequently it can be measured in a separate experiment with a solution that contains the supporting electrolyte and all the components of the sample except the one being determined. Point-by-point subtraction of this curve from the curve for the sample is often considered to yield the optimum result, but entails an assumption that is too often ignored, namely that the residual current is unaffected by the substance being determined. The assumption usually seems justifiable for inorganic substances, though exceptions could be cited, but is less frequently so for organic substances because these, and their reduction or oxidation products, are more often strongly adsorbed onto the surface of the electrode. Adsorption affects the capacitance of the electrical double-layer, and consequently alters the residual current; partial or complete coverage of the electrode surface may cause i_l/c to deviate from constancy. Data obtained with known solutions under exactly the same conditions enable appropriate corrections to be made in this situation. However, it is sometimes impossible to prepare or obtain a solution having exactly the same composition as the sample but containing none of the substance to be determined, as in the analysis of a biological material containing many unknown components.

When such difficulties arise, it is sometimes better to correct for the residual current by extrapolating the portion of the recorded curve that precedes the wave of interest than to rely on a separately recorded residual-current curve. If the wave of interest is not too closely followed by another wave or by the final current rise, and if a linear extrapolation can be made over a short range of potentials, it is rare for substantial error to result. If the extrapolation must be nonlinear, curve-fitting is the best approach.[31]

Finally, the accuracy of a polarographic method depends on the calibration procedure employed. There are two kinds of calibration procedures: (1) the use of a calibration curve, previously obtained with a number of known solutions covering the range of concentrations that is of interest, and (2) those in which calibration and analysis are carried out together.

The calibration-curve method involves adding various known amounts of the substance of interest to a supporting electrolyte containing the other components of the samples to be analysed. All of the conditions—the height of the mercury column, the position of the capillary, the temperature, *etc.*—must be exactly the same for the calibration as for the analyses. A new calibration curve is needed whenever the dropping electrode is changed, but only a wave-height is used in performing a single analysis. The method is best suited to the routine analysis of large numbers of similar samples.

For simultaneous calibration and analysis, the standard-addition and pilot-ion (internal-standard) methods are the most useful. In one standard-addition method, a known volume of a standard solution of the substance being determined is added to the test solution (of known volume) after its polarogram has been recorded, and a second polarogram is recorded. This can then be—but rarely is—repeated with further additions of standard. Alternatively, the standard solution is added to a test sample before any analytical operations are begun, and this "spiked" sample is analysed in parallel with an unspiked sample. It is assumed that the relative errors arising during the sample preparation (which may be due to such processes as co-precipitation, adsorption, and volatilization) will be the same for both samples. In both these variations of the standard-addition method, the value of i_l/c is, in effect, obtained from the differences between the limiting currents and concentrations for the two curves. In pilot-ion methods a known amount of a substance, which must be known to be absent from the sample and to give a well-developed wave that does not overlap any wave on the polarogram of the sample, is added to each solution before its polarogram is recorded, and the amount of the substance being determined is obtained from the ratio of the height of its wave to that of the wave of the substance added. Usually the pilot-substance is chosen in such a way that its wave precedes the wave of the component to be determined.

These methods have advantages and disadvantages. They eliminate, or at least greatly decrease, the effects of a number of sources of experimental error, including variations of the capillary characteristics, the temperature, and the viscosity of the solution. They consequently free the analyst from the necessity of measuring or controlling these, and greatly simplify

practical analyses. When the pilot-ion method is used it is even unnecessary to dilute the solution to known volume. However, there will be some loss of precision and accuracy. In standard-addition methods the precision will be lower unless the value of i_1/c is based on more data than would be used for constructing a calibration curve, and the accuracy will be poor if the wave height is not exactly proportional to concentration.* A graph of current *vs.* concentration of standard added will serve to test the latter point, provided that enough additions are made and that they are sufficiently well spaced. There are standard-addition methods in which that proportionality is not assumed,[40] but they are known to few analysts and are virtually unused. In pilot-ion methods the ratio of the values of i_1/c for the substance being determined and the added substance is needed in the calculations and can be very reliably established under conditions closely similar to (though not necessarily exactly identical with) those used in the analyses, but each of the wave-heights obtained in analysing an unknown solution contributes some uncertainty to the result. The standard addition and pilot-ion methods are most useful when there are only a few samples to be analysed at a time or when, as in the analysis of a biological or other complex sample, it is impossible to obtain a blank that is free from the substance being determined.

PREPARATION OF A PAPER FOR PUBLICATION

A successful method or procedure for polarographic analysis should be submitted for publication if it can be shown to be superior to existing methods for the same problem and to have *useful* application. The presentation will differ greatly from one method or procedure to another: for example, a general method for the determination of an element, in which it is isolated from any other elements that accompany it and is finally determined in a nearly pure solution, should be described in quite a different way from a procedure for the determination of an organic substance in a particular kind of sample, either without separation or with separations designed to remove the particular interfering substances present. However, there is some information that should be included in every serious polarographic publication because it is essential to everyone who is concerned with the electrochemical behaviour of the species investigated. Many of the following precepts seem obvious, and some are almost trivial, but all are repeatedly ignored, much to the detriment both of fundamental knowledge and of the probability that an author's success with the method can be reproduced by others.

1. Compounds investigated. The systematic names of the compounds studied should be given, following the I.U.P.A.C.[43] or American Chemical Society recommendations[44] (except where trivial names are allowed and are more convenient). For even moderately complicated organic compounds, structural formulas should also be given, to avoid possible misunderstanding. Line-notation systems, like that of Wiswesser (WLN),[45] are becoming more useful and important, and are worth inclusion, as are the *Chemical Abstracts* Registry Numbers. If a trivial or abbreviated name is used, the correct name should be given in parentheses. There is no excuse for the use of acronyms: we have seen "AN" used to denote either 1-naphthol or acetonitrile, and "DMF" used for 2-(diethoxymethyl)furan or *N*,*N*-dimethylformamide. Information about the purity (such as a melting or boiling point or an assay value) should be given: to say that a compound was of the "highest available purity" is meaningless. On the other hand, a defined grade of purity, such as "analytical reagent grade" is acceptable. Naming the commercial source is not obligatory, though it may be useful.

2. Solvent. The composition of the solvent should be clearly stated and an indication of its purity should be given. For water the methods of purification (distillation or ion-exchange) and storage should be stated, and some details about them should be specified, such as the nature of the still or resin and of the storage container employed, and information on whether carbon dioxide was excluded or removed, and how. For a non-aqueous solvent the concentration of water is often of paramount importance, and should therefore be given together with an indication of how it was estimated. The grade of purity of the solvent should be indicated, though we wonder what, for example, the designation "spectroquality" in a 1975 paper can be expected to mean to a reader in 1985 or 1995. For mixed solvents the proportions should be given, and it must be stated whether these are by weight or by volume and, if by volume, whether the proportions were measured before or after mixing: a mixture of 50 ml of ethanol with 50 ml of water is not the same as one prepared by adding water to 50 ml of ethanol until the total volume becomes 100 ml, but either is likely to be called "50% v/v ethanol".

3. Supporting electrolytes. The composition of each supporting electrolyte must be given, together with the purity of each of its components. The name and concentration of each acid, base, or salt should be clearly given, the concentration being specified in a manner that indicates the accuracy of measurement. Buffers should not be identified by name (*e.g.*, Britton-Robinson, Clark-Lubs, McIlvaine, *etc.*) unless, like

* It should be, but unfortunately is not, unnecessary to point out what this means. If y is proportional to x, a plot of y against x is a straight line passing through the origin: this is expressed by the relation $y = bx$. It is becoming regrettably more common to say that y is proportional to x if such a plot is linear, regardless of whether it passes through the origin (that is, if $y = a + bx$ and a has some finite value): this is erroneous. The statement "y is proportional to x" should be used only when y/x is constant and independent of x. If $y = a + bx$ and the value of a is finite, y/x will vary with x, and this relationship should be described by saying that "y is a linear function of x."

those cited here, they are so commonly used that the reader cannot encounter difficulty in finding their compositions. Specifications such as "buffer of pH 4.7" are completely useless, because the polarographic behaviour of a compound can vary from one buffer to another even though the pH is the same; statements such as "0.1*M* acetate buffer, pH 4.7" are also to be deprecated because it is not made clear whether the concentration of the anion or the sum of the concentrations of the components is referred to. In studies in which the pH is varied, it is important to state whether the variation was accomplished by changing the concentration of the acidic component of the buffer, the concentration of the basic form, or both, for wave-heights and half-wave potentials are often easier to correlate with pH when one of these two concentrations is kept constant. The value of the pH (or other acidity function) of the final solution should be given. If the solvent is a mixture of water and an organic liquid, it is important to state whether the pH is that of an aqueous buffer to which the organic solvent was then added, or that measured in the mixed solvent; if it is the latter, there should also be a description of how the glass electrode was conditioned and standardized, if one was used. The certainty with which the pH was known should also be stated. It is useless to say merely that polarograms were recorded in "neutral" or "slightly acidic" solutions. If a complexing agent is used, it should be identified (preferably by name, not acronym), and its concentration, the concentration of the acid or base used to control the pH in the reaction medium, and the nature of any neutral salt used for adjustment of ionic strength, should all be given.

Often only a portion of the data is given. The pH-values selected for publication should then cover the whole range investigated at more or less regular intervals, with more detailed information for that range in which the measured quantity, or its rate of variation, undergoes a change. Intervals as large as 2 or 3 pH-units suffice for portions of the range in which changes are small or regular, but may need to be as small as 0.2 or 0.3 pH-unit in portions where sudden changes occur.

The importance of the ionic strength to some electrode processes, and the role of the cations or anions of some neutral salts, were discovered many years ago[46–48] and are coming to be more widely recognized. The identity and concentration of every neutral salt added to a supporting electrolyte should be clearly stated. This is especially essential with tetraalkylammonium salts, the cations of which can be involved in adsorption, ion-pair and complex formation, or double-layer phenomena, and can also influence the structure of water. The ionic strength is generally best kept to 0.1*M* or below, unless there is a specific reason for using a higher value.

Surface-active agents added as maximum suppressors or for any other purpose should be identified by chemical name and structural formula, and the approximate molecular weight should be given if possible. The concentrations of such materials must also be specified.

4. Temperature. The temperature at which the data were obtained and the range over which it varied should be stated. Geographic and seasonal variations render the words "room temperature" meaningless.

5. Technique employed. Most authors do name the techniques they use, but nomenclature has not been uniform and a term such as "oscillographic polarography," which different authors have used to denote very different techniques, puts the reader to the trouble of trying to infer from the context and figures what has actually been done. Adherence to the nomenclature recommended[8] by I.U.P.A.C. is strongly urged on authors and editors, even though new terms will continue to be coined as new techniques are developed. The adjectives "derivative" and "differential" have caused much confusion in the past, and the I.U.P.A.C. recommendation is that "derivative" be confined to the measurement, recording, or observation of di/dt, di/dE, or a similar quantity while "differential" is used only to denote the measurement, recording, or observation of a difference between two currents, potentials, or other signals. Thus, for example, derivative chronopotentiometry deals with the variation of dE/dt with time, whereas differential chronopotentiometry would deal with the time-dependence of the difference between the potentials of two chronopotentiometric indicator electrodes.

6. Electrodes. The material from which the indicator electrode is made (mercury, platinum, graphite, *etc.*), its physical form (wire, disc, sphere, *etc.*), and the mode in which it is used (stationary, rotating, vibrating, *etc.*) should all be specified and characterized. The grade or purity of the material should be given, and for solid electrodes these should be accompanied by detailed descriptions of the pretreatment or conditioning employed. For electrodes having fixed surfaces the geometry and dimensions should be given, as should an estimate of the roughness factors for solid electrodes, if possible. For dropping electrodes the rate of flow of mercury m or the drop-mass mt_1 should be stated together with the drop-time t_1 and there should be a description of the conditions under which they were measured.

If values of m and t_1 are to be used only for rough characterization of the capillary, the value of t_1 may be measured in, say, 1*M* potassium chloride at an arbitrarily chosen potential such as 0.0 V, and that of m may be measured by weighing the mercury that flows from the capillary tip into a previously weighed amount of mercury during some measured period of time. Deviations from traditional practice, such as the use of a bent or tapered capillary or of enforced mechanical detachment of the drop, should be clearly stated. It is often helpful in interpreting the data to know whether the capillary was atypical in average radius or length; the radius of the capillary lumen at its tip can be judged from the value of mt_1, but

mention should also be made of the approximate height of the mercury column above the capillary tip. For rotated or vibrated electrodes mechanical details such as the angular rate of rotation or the frequency and amplitude of vibration are essential.

The nature of the reference electrode must also be specified, and the specification should include both the nature and concentration of the electrolyte employed and the identity or composition of the solvent. In describing a study carried out with acetonitrile as the solvent, for example, it does not suffice to say that a saturated calomel electrode was used: to some readers this may signify the common aqueous calomel electrode made with saturated potassium chloride, while to others it may suggest an electrode such as $Hg/Hg_2Cl_2(s)$, LiCl(s), $CH_3CN(l)$. When an internal reference substance (such as biphenylchromium ferrocene, or ferricinium ion) is used in measurements in non-aqueous systems, it is essential to measure and report the characteristic potential of that substance with respect to some standard reference electrode, preferably the saturated (potassium chloride) aqueous calomel electrode. The literature is all too full of cases in which one investigator has reported half-wave potentials with respect to one reference electrode, another has reported others with respect to a different one, and neither has provided any basis for comparison of the values.

7. Apparatus. The electrical apparatus should be described in enough detail to enable the reader to identify it, if it is a commercial instrument, or to assess its performance and reliability if it was constructed in the author's laboratory. Calibration of instruments is certainly less common than it used to be, and is probably less common than it should be.

The cell should also be identified or, if its design differs from familiar ones, described and depicted. The manner in which the solution of the sample is connected with the electrolyte in the reference electrode (liquid junction, agar bridge, porous or fritted glass separator, *etc.*) is of special interest. The technique of deaeration should be described and, for prolonged experiments, so should the way in which the solution is guarded against atmospheric oxygen; the purity of any inert gas used should be stated, together with information about any purification necessary. If correction is made for the *iR* drop, the method adopted for evaluating the resistance should be mentioned; if a three-electrode cell is employed, the placement of the auxiliary and reference electrodes should be described.

8. Experimental parameters. The concentration of the electroactive substance employed in a mechanistic study must not be omitted; in an analytical paper there should be information about the range of concentrations investigated, even if the measured signal is not proportional to concentration over the whole of this range. Certain other information is also necessary but depends on the technique employed. It includes the range of current densities employed in chronopotentiometry; the scan-rate and the boundaries of the range of applied emf investigated in linear-sweep, triangular-wave, or cyclic voltammetry; the frequency of the sinusoidal applied signal in a.c. techniques; the durations of the pulse and the sampling interval in pulse methods; some indication of the efficiency of stirring, such as the value of the mass-transfer constant obtained for a common reference substance under conditions as nearly identical as possible, in stirred-pool and other convective techniques, and so on. No matter how precious space in journals is or becomes, it makes no sense to publish data without giving the reader enough information to enable him to interpret or reproduce them.

9. Reported values. A paper aimed primarily at elucidating the course of the electrode process must include information about how wave-heights and half-wave potentials depend on the composition of the medium (pH, ionic strength, concentrations of buffer components, complexing agents, and surface-active materials, *etc.*). The dependences of derived quantities—such as heterogeneous and homogeneous rate constants, values of αn_a, slopes of log plots, and the like—are often also needed for documentation of the conclusions presented. In opposition to some editorial policies, we strongly recommend that all such dependences be presented in both graphical and tabular forms: the graphs to provide qualitative descriptions that are easy to assimilate, and the tables to permit detailed numerical examination.* If possible, each graph should contain both a "theoretical" or calculated curve, corresponding to the scheme proposed and the rate and equilibrium constants evaluated, and the experimental points. When this is done, the reader is enabled to judge for himself how closely the proposed interpretation corresponds to the observed facts. Such figures can be relatively small, if they are accompanied by tabular data, because the reader need not attempt to reconstruct the numerical values from them. The omission of tabulated data, on the other hand, hinders future collections, comparisons, and interpretations; figures are of little help for these purposes because reading values from them is both tedious and imprecise. It might be thought unnecessary to warn against failure to label the axes of graphs or to specify the units of numbers given in tables, but it is not.

A paper on polarographic analysis should contain at least one original curve, and preferably a family of curves illustrating the effect of pH, of the nature or concentration of a complexing agent, of solvent composition, or of a chemical or physical operation, or comparing the responses obtained with different compounds. Such figures add to the cost of printing a paper, but they show details—such as a change in the shapes of the oscillations corresponding to individual drops, or the presence of a wave that the author

* See, however, the exceptions named in the second paragraph below this one.

did not notice or discuss—that may be invaluable to a future reader even though the author did not consider them to be important.

It is not, however, necessary or desirable to include tables or figures (especially original curves) to illustrate common dependences, such as proportionality of wave-height or peak-height to concentration or to square-root of the height of the mercury column, or a linear variation of $\log[i/(i_d - i)]$ with potential. Such dependences can be adequately described in the text. They should preferably be accompanied by values of the slope and standard deviation. Only when such plots have unusual forms do they deserve presentation as illustrations.

Theoretical sections of papers should describe the assumptions made, give all the mathematical expressions used, and indicate which parameters were assumed to be constant, large, small, or negligible. The way in which the data were processed to permit comparison with theory should be clearly described. The experimental data and values of the physical constants used in such comparisons should be clearly identified together with their sources.

Papers on analytical methods should also include detailed information about the range of concentration over which the measured response is proportional to concentration, together with values of the constant of proportionality (the sensitivity), the standard deviation, and the limit of detection (which depends on the sensitivity and also on the precision with which corrections for the residual or other background current can be made). They should further include information about those substances that are likely to be found in analytical samples to which the method is applicable and were found to interfere or to be innocuous; for those found to interfere, clear statements about the nature and magnitude of the interference should be included.

Papers on polarographic analysis sometimes present numerical information in addition to that already mentioned. This may include the slopes of plots of half-wave potential against pH or, for a group of structurally related compounds, against the Hammett substituent-constant σ_x; the values of diffusion-current constants or of $E_{3/4} - E_{1/4}$ in polarography or $E_{3\tau/4} - E_{\tau/4}$ in chronopotentiometry; the values of αn_a and k_s; and many more. All of these should be presented in tabular form wherever possible.

10. Reaction mechanism. When a study has included the elucidation of the course or mechanism of the electrode process, this should be clearly depicted by an equation or scheme, and *all* of the observations related to the mechanism should be described, regardless of whether or not they appear to bear on its correctness. Mechanisms that cannot be definitely ruled out should also be given whenever possible.

11. Applications. In an analytical study it is essential to say clearly what kinds of samples were successfully analysed by the procedure proposed, and to give information about the natures and proportions of all other substances known to be or likely to be present in those samples. Other kinds of samples to which the procedure should be—but is not definitely known to be—applicable should be briefly indicated.

12. Reliability. There is not much agreement about how the reliability of an analytical procedure should be described. In large part this is because the evidence that is available and wanted depends on the scope of the procedure and on the variety of the different samples to which it has been applied. There are three major possibilities. One is that the procedure has been designed and used for the routine analysis of a particular kind of sample having a composition which varies only within quite narrow limits. Here it is possible to analyse a relatively large number of samples by the procedure proposed and also by an umpire method and to give a reliable statistical evaluation of the results. This is not a common situation, and despite the undoubted value of the statistical treatment it is also not a very interesting one, for it is not probable that many readers will be concerned with the analyses of samples exactly comparable to those described.

The other extreme is that in which the newly described procedure is presented as being specific for the substance sought and in which this claim is supported by the results of analyses of a great many different samples having widely divergent compositions. It is not often, in such situations, that enough portions of any one sample will have been analysed to permit a really thorough statistical analysis of the results. Nor would it be likely that a single umpire method would be available to serve for comparisons over a very wide range of sample compositions, and the analysis of intersample variability would probably then be hampered by uncertainty about the relative reliabilities of the different methods chosen. This is also not a common situation, for few procedures are as widely applicable as the ones we imagine here, but it would be hard to propose an approach much better suited to illustrating both the reliability and the scope of a very versatile method than the inclusion of a table giving the "known" composition of each sample (with an indication of how the content of the substance determined was found, except for National Bureau of Standards and other widely available reference materials for which such information is available elsewhere) together with the one determined. For a few of the samples enough replicate results should be obtained to provide reasonably reliable estimates of the standard errors. Those who stigmatize such tables as pedestrian may be ignored as being jealous that their own procedures are not so broadly applicable as to deserve such treatment. Editorial care should be exerted to deny the space that such treatment consumes except where the versatility of a procedure justifies it.

Most procedures fall somewhere between these extremes. They are sufficiently versatile that they must be applied to a fairly large number of samples in

order to prove that they are as widely useful as they are said to be. However, they are not so versatile that an impossibly large number of different kinds of samples would have to be analysed to provide such proof. Two points must be kept in mind above all others: (1) there must be enough replicate analyses of some samples to enable the reader to form a fair estimate of the precision of the procedure and of whether and how that precision depends on the nature of the sample; (2) no polarographic (or any other) analytical result should be given unless it is accompanied by one obtained by a different procedure so that the reader can form an estimate of the accuracy of the procedure proposed (except, of course, in cases where no other suitable procedure exists). The second of these precepts is often violated, especially by manufacturers of apparatus, although the manufacturers of polarographic apparatus are by no means the only ones who are guilty in this respect. It may perhaps suffice to point out that a curve signifying the presence of, say, 0.1 ppM of lead in tap water, about which the reader can know nothing and have no idea whether that figure is within two orders of magnitude of the truth, can scarcely be expected to impress or convince any serious scientist.

Pride of invention is a human characteristic and analytical chemists are not immune to it. Unfortunately it may be badly flawed by the grumbling of those who study the published description of a procedure, apply it to their own samples, and obtain inaccurate or imprecise results despite their best efforts to adhere to the directions given. It is only to be expected that this will happen whenever the author is more skilful and meticulous than the would-be user. Too often, however, the problem is that vital conditions, cautions, and points of technique have been omitted. The author who is concerned to avoid such problems can best do so by giving a copy of the manuscript to a colleague or technician—preferably one who has not previously been involved in the development of the procedure—along with one or two representative samples and a request that the procedure be used to analyse them. If the results can be considered acceptable in view of the claims that are made for the procedure, the manuscript is ready to be submitted for publication. Otherwise the cause of the discrepancy should be identified and the manuscript should be changed accordingly.

On the basis of all these comparisons a realistic assessment of the value of the proposed procedure should be given and should take into account its scope, accuracy, precision, sensitivity, speed, cost, selectivity, ease of execution, and feasibility in the hands of its prospective users.

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UNTERSUCHUNGEN ZUR ATOMSPEKTROSKOPISCHEN SPURENANALYSE IN $A^{III}B^{V}$-HALBLEITER-MIKROPROBEN—I

VERDAMPFBARKEIT UND UNSPEZIFISCHE ABSORPTION VON $A^{III}B^{V}$-VERBINDUNGEN UND IHREN KOMPONENTEN IN DER GRAPHITROHRKÜVETTE

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Zusammenfassung—Die Verdampfung der Matrices Ga^{3+}, In^{3+}, PO_4^{3-}, AsO_4^{3-}, Ga^{3+}/AsO_4^{3-}, Ga^{3+}/PO_4^{3-} und In^{3+}/AsO_4^{3-} in salz- und salpetersaurem Medium wurde durch Messung der unspezifischen Absorption in einer Graphitrohrküvette mit einer Kontinuumlichtquelle bei 250 nm untersucht. Die maximale unspezifische Absorption wurde für die Veraschungs- und Atomisierungsphase in Abhängigkeit von der Veraschungstemperatur dargestellt. Aus den Resultaten können Veraschungstemperaturen für analytische Bestimmungen abgeleitet werden. Der Mechanismus der Verdampfung der Substanzen wurde durch Extinktions–Zeit-Kurven untersucht. Absorptionsspektren der Matrices und der reinen Säuren HCl und HNO_3 wurden bei unterschiedlichen Veraschungs- und Atomisierungstemperaturen zwischen 190 und 330 nm in der Graphitrohrküvette aufgenommen. Die InCl- und GaCl-Banden des C-Systems und neue Banden der GaO- und InO-Moleküle wurden gefunden. Die PO-Bande bei 246 nm wurde nachgewiesen. Die Resultate werden ausführlich diskutiert. Sie können verwendet werden für thermische Fraktionierungen und für die Untergrundkompensation nach der Zweilinienmethode in der Spurenanalyse der elektrothermischen AAS.

Für die analytische Bestimmung von Spuren- und Dotierungselementen in $A^{III}B^{V}$-Verbindungen (GaP, GaAs, InAs) durch AAS, die ohne Matrixabtrennung durchgeführt werden sollten, ist die Untersuchung der Verdampfung und der unspezifischen Absorption der $A^{III}B^{V}$-Matrices erforderlich. Dabei ist zu berücksichtigen, daß zur Erzielung einer guten relativen Nachweisgrenze für die Spuren möglichst hohe Matrixmengen eingesetzt werden müssen. Diese Matrixmengen können bei Einsatz der AAS mit elektrothermischer Atomisierung in der Graphitrohrküvette folgende Störungen hervorrufen.

(1) *Verdampfungsbeeinflussung der Spuren durch die Matrix.* Es kann eine Verdampfungsbehinderung, z.B. durch Bildung schwer verdampfbarer Doppeloxide, Arsenate oder Phosphate oder eine Verdampfungsbeschleunigung, z.B. durch Bildung leicht verdampfbarer Chloride vorliegen.

(2) Beeinflussung der Teilchenzusammensetzung im Plasma. Vor allem durch die anionischen Bestandteile der Matrix können sich bei gleichzeitiger Verdampfung von Matrix und Spur Radikale im Plasma bilden, die zu einer Reduzierung der Atomkonzentration im Plasma führen (z.B. CdCl in Gegenwart von Cl).

(3) *Spektrale Störungen durch die Matrix.* Die Matrix kann durch unspezifische Absorption (Streuung und Molekülabsorption) die Messung der spezifischen Atomabsorption erheblich stören oder auch unmöglich machen.

Über Atombildungsprozesse von Spurenelementen in der Graphitrohrküvette und deren Beeinflussung im Sinne der in den Punkten (1) und (2) angegebenen Störungen sind einige Mitteilungen in der Literatur erschienen.[1–9] Diese behandeln jedoch nicht die hier eingesetzten Matrices. Als Voraussetzung für die angestrebten, fraktionierten thermischen Spur–Matrix- bzw. Matrix–Spur-Trennungen wird in dieser Arbeit über das Verdampfungsverhalten der $A^{III}B^{V}$-Matrices in der Graphitrohrküvette berichtet.

Betrachtungen über spektrale Störungen durch Matrices wurden vor allem von Massmann und Mitarbeitern[1,7] angestellt, wobei besonders auf nichtkompensierbare Einflüsse durch die Feinstruktur von Molekülbanden hingewiesen wird. Untersuchungen über die unspezifische Absorption von Alkalihalogenid-Matrices wurden von Culver und Surles durchgeführt.[10] Über spektrale Störungen durch $A^{III}B^{V}$-Matrices wurde bisher nicht berichtet. Störungen dieser Art wurden jedoch in einigen Fällen bei der Atomisierung durch Flammen festgestellt. Höhn und Jackwerth[11] berichten über die Störung der Au-AAS durch die InCl-Absorption. Informationen über die InCl-Molekülabsorption in Flammen wurden auch von anderen Autoren gegeben.[12–16] Im 2. Teil dieser Arbeit wird über die spektralen Störungen, die bei Verdampfung der genannten Matrices in der Graphitrohrküvette auftreten, berichtet.

EXPERIMENTELLER TEIL

Apparatives

Spektrometer. Zweikanal-AAS-Gerät Typ 811, Jarrell-Ash, U.S.A.

Atomisator. Graphitrohrküvette Typ 1268, Beckman, U.S.A.

Lichtquelle. H_2-HKL, Jarrell-Ash, U.S.A.

Substanzen

Die Auflösung der $A^{III}B^{V}$-Verbindungen GaP, GaAs und InAs ist im sauren Medium durch Oxydation möglich. Gebräuchlichtes Lösungsmittel ist eine 1:1 Mischung von konzentrierter Salzäure und Salpetersäure. Durch Nachbehandlung der Lösungen kann entweder ein reines Cl^-- oder NO_3^--Medium erzielt werden. Die Oxydationsprodukte beim oxydativen Lösen sind: Me^{3+} (Me = Ga, In) und XO_4^{3-} (X = P,As). Aus diesem Grund wurden folgende Lösungen für die Untersuchungen eingesetzt: Konzentrierte Salzsäure und Salpetersäure Suprapur (Merck), auch 1*M* Lösungen durch Verdünnung mit bidestilliertem Wasser; AsO_4^{3-}/1*N* HCl, aus 6-Neuner As, VEB Mansfeld-Kombinat, DDR PO_4^{3-}/1*N* HCl, aus H_3PO_4 (conz.) z.A; In^{3+}/1*N* HCl und In^{3+}/1*N* HNO_3, aus 6-Neuner In, VEB Mansfeld-Kombinat, DDR; Ga^{3+}/1*N* HCl und Ga^{3+}/1*N* HNO_3, aus 6-Neuner Ga, VEB Mansfeld-Kombinat, DDR; In^{3+}/AsO_4^{3-}/1*N* HCl und In^{3+}/AsO_4^{3-}/1*N* HNO_3; Ga^{3+}/AsO_4^{3-}/1*N* HCl und Ga^{3+}/AsO_4^{3-}/1*N* HNO_3; Ga^{3+}/PO_4^{3-}/1*N* HCl und Ga^{3+}/PO_4^{3-}/1*N* HNO_3.

Allgemeine Arbeitsweise

Jeweils 0,01 ml der obigen Lösungen (Absolutmengen der Matrices zwischen 0,01 und 0,1 mg) wurden in die Graphitrohrküvette gegeben. Die Veraschungstemperatur wurde zwischen 500° und 2080° variiert. Die Atomisierungstemperatur lag bei 3300° (Maximalwert der Apparatur). Diese Temperaturwerte entsprechen den Angaben des Herstellers. Es wurden keine Temperaturbestimmungen mit einer unabhängigen Meßmethode durchgeführt. In diesem Sinne sind alle in dieser Arbeit angegebenen Temperaturwerte der Graphitrohrküvette zu betrachten. Die elektrothermische Aufheizung der Graphitrohrküvette erfolgte durch Anlegen einer konstanten Spannung. Der Anstieg der Temperatur in der jeweiligen Phase wurde bei der Diskussion nur qualitativ berücksichtigt.

Die Untersuchung der Verdampfung erfolgte durch Messung der unspezifischen Absorption bei 250 nm. Die spektralen Effekte wurden im Gebiet zwischen 190 und 330 nm ermittelt.

RESULTATE UND DISKUSSION

Untersuchungen zur Temperaturabhängigkeit der Verdampfung

In den Abb. 1 und 2 ist die maximale unspezifische Absorption, die während der Veraschungsphase bei den angegebenen Temperaturen (Teil *a* der Abbildungen) und während der jeweils nachfolgenden Atomisierungsphase bei der maximalen Atomisierungstemperatur auftritt, in Abhängigkeit von der Veraschungstemperatur dargestellt.

Aus der Abb. 1, Teil *a*, ist zu entnehmen, daß die Verdampfung von AsO_4^{3-}, PO_4^{3-} und In^{3+}/HCl bei 500 bis 600°, von In^{3+}/HNO_3 bei 1200° und von Ga^{3+}/HCl oder /HNO_3 bei 1500 bis 1600° beginnt. Mit zunehmender Temperatur wird die Verdampfung in der Veraschungsphase stärker. Eine Aussage über das jeweilige Ausmaß der Verdampfung in der Veraschungsphase ist aus dem Teil *b* der Abbildungen zu entnehmen. Daraus geht hervor, daß die AsO_3^{3-}-Rückstände in einer Veraschungsphase von 25 s bei 1800° vollständig verdampften. Die Rückstände der anderen Substanzen verdampfen in einer Veraschungsphase von 25 s bei 2080° fast vollständig.

Die Ergebnisse für die komplexen Matrices weisen einen Verdampfungsbeginn von In^{3+}/AsO_4^{3-} in 1*M* HCl oder 1*M* HNO_3 bei 1000° und von Ga^{3+}/AsO_4^{3-} bzw. Ga^{3+}/PO_4^{3-} in 1*M* HCl oder 1*M* HNO_3 bei 1600° aus (Abb. 2, Teil *a*). Daraus ist zu entnehmen, daß durch die Bildung von $InAsO_4$, $GaAsO_4$ und $GaPO_4$ während der Trocknungsphase eine wesentliche thermische Stabilisierung der Anionen erfolgt. Hinsichtlich der Vollständigkeit der Verdampfung ergeben sich etwa die gleichen Verhältnisse wie bei den Einzelkomponenten (Abb. 2, Teil *b*).

Da mit Hilfe der Untergrundkompensation im allgemeinen unspezifische Absorptionen bis zu einer Extinktion von 0,5 (Abszissenparallele in den Abb. 1 und 2) ohne wesentlichen Nachteil für die Messung der spezifischen Atomabsorption kompensiert werden können, sind die Temperaturen, die bei der Kreuzung der Kurven mit der Abszissenparallele ablesbar sind, für analytische Spurenbestimmungen von Interesse. Rückschlüsse auf die eigentlich erforderlichen Veraschungstemperaturen sind möglich: AsO_4^{3-}–500°, In^{3+} in HCl oder HNO_3 und PO_4^{3-}–1500 bis 1600°, Ga^{3+} in HCl oder HNO_3–1800°, In^{3+}/AsO_4^{3-}–1500°, Ga^{3+}/AsO_4^{3-} oder /PO_4^{3-} 1700–1800°. Eindeutige Fest-

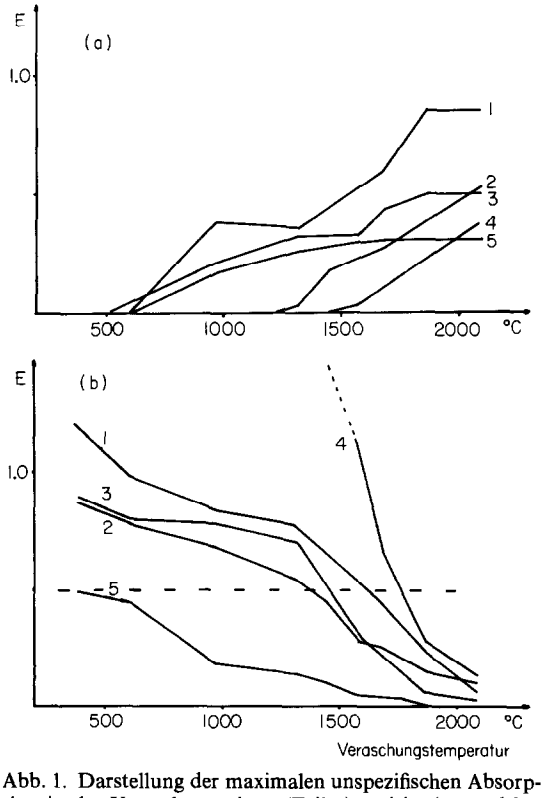

Abb. 1. Darstellung der maximalen unspezifischen Absorption in der Veraschungsphase (Teil *a*) und in der nachfolgenden Atomisierungsphase (Teil *b*) in Abhängigkeit von der Veraschungstemperatur. Veraschungsphase 25 s; Wellenlänge 250 nm; Atomisierungsphase 10 s; 3300°C. Kurve 1: 0,1 mg P als PO_4^{3-}; Kurve 2: 0,1 mg In^{3+}/1*M* HNO_3; Kurve 3: 0,1 mg In^{3+}/1*M*HCl; Kurve 4: 0,01 mg Ga^{3+}/1*M* HNO_3 oder 1*M*HCl, Kurve 5: 0,1 mg As als AsO_4^{3-}.

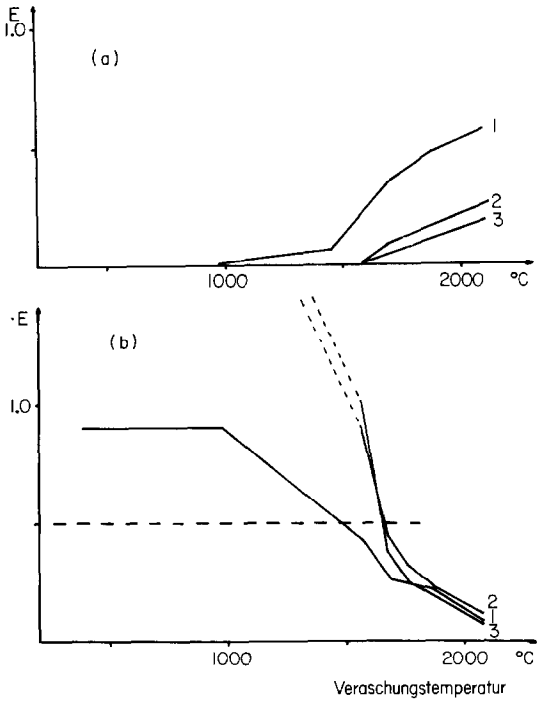

Abb. 2. Darstellung der maximalen unspezifischen Absorption in der Veraschungsphase (Teil *a*) und in der nachfolgenden Atomisierungsphase (Teil *b*) in Abhängigkeit von der Veraschungstemperatur. Veraschungsphase 25 s; Wellenlänge 250 nm; Atomisierungsphase 10 s; 3300°C. Kurve 1: 0,1 mg InAs als $In^{3+}/AsO_4^{3-}/1M$ HCl; Kurve 2: 0,01 mg GaAs als $Ga^{3+}/ASO_4^{3-}/1M$ HCl; Kurve 3: 0,01 mg GaP als $Ga^{3+}/PO_4^{3-}/1M$ HCl.

legungen für thermische Spur–Matrix- oder Matrix–Spur-Trennungen sind aus diesen Ergebnissen jedoch noch nicht möglich, da einesteils der zeitliche Verlauf der Verdampfung und andererseits die Abhängigkeit der unspezifischen Absorption von der Wellenlänge berücksichtigt werden müssen.

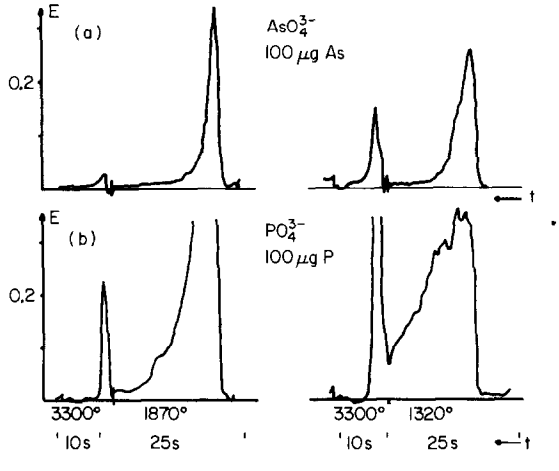

Abb. 3. Verdampfungskurven für AsO_4^{3-} und PO_4^{3-} bei unterschiedlichen Veraschungstemperaturen. Veraschungsphase 25 s; Wellenlänge 250 nm; Atomisierungsphase 10 s. Zeitverlauf: von rechts nach links.

Untersuchung des zeitlichen Ablaufs der Verdampfung

In den Abb. 3–5 sind ausgewählte Beispiele für den zeitlichen Verlauf der Verdampfung dargestellt.

Aus der Abb. 3 ist ersichtlich, daß die in der Trocknungsphase entstandenen Rückstände des AsO_4^{3-} relativ glatt, die des PO_4^{3-} jedoch sehr schleppend verdampfen. Obwohl die unspezifische Absorption auch im Fall des PO_4^{3-} bei einer Veraschungstemperatur von 1870° nahezu auf den Extinktionswert = 0 zurückgeht, ergibt sich ein erhebliches Restsignal in der Atomisierungsphase. Dieses Ergebnis ist nur mit einer intensiveren Bindung des PO_4^{3-} am Graphit zu erklären. Es ist bekannt daß Graphit mit H_3PO_4, aber nicht mit H_3AsO_4 Verbindungen bildet.[17]

In der Abb. 4 sind die Verdampfungskurven des Ga^{3+} und In^{3+} in salz- und salpetersaurem Medium dargestellt. Unterschiede zwischen den beiden Medien ergeben sich nur für In. Im salzsauren Medium ergibt sich bei verhältnismäßig niedrigen Temperaturen eine intensive unspezifische Absorption, die u.E. auf $InCl_3$ (Sublimationspunkt 498°) zurückzuführen ist. In Gegenwart von Ga^{3+} entstehen beim Trocknungsprozeß offensichtlich nur Hydrolyseprodukte, denn $GaCl_3$ (Siedepunkt 201°) müßte sonst ebenfalls ein intensives Signal hervorrufen.

Da bei bestimmten Temperaturen der Veraschungsphase (1580 und 2080°) in Gegenwart von In^{3+}/HCl zwei getrennte unspezifische Signale auftreten, müssen Konkurrenzreaktionen während der Veraschungsphase verlaufen, deren Relation weitgehend vom Temperaturanstieg bestimmt wird. Diese Konkurrenzreaktionen sind nach unserer Auffassung: Sublimation von $InCl_3$ und thermische Zersetzung bzw.

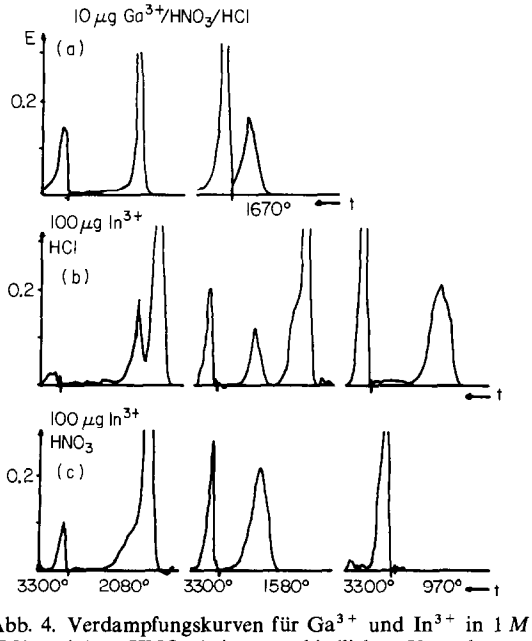

Abb. 4. Verdampfungskurven für Ga^{3+} und In^{3+} in 1 *M* HCl und 1 *M* HNO_3 bei unterschiedlichen Veraschungstemperaturen. Veraschungsphase 25 s; Wellenlänge 250 nm; Atomisierungsphase 10 s. Zeitverlauf von rechts nach links.

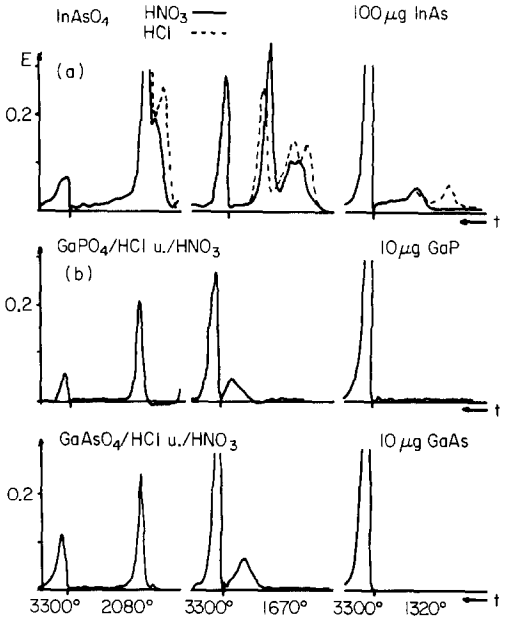

Abb. 5. Verdampfungskurven für $InAsO_4$, $GaPO_4$ und $GaAsO_4$ in 1*M* HCl und 1*M* HNO_3 bei unterschiedlichen Veraschungstemperaturen. Veraschungsphase: 25 s, Wellenlänge: 250 nm, Atomisierungsphase: 10 s, Zeitverlauf von rechts nach links.

Hydrolyse des $InCl_3$ zu schwerer verdampfbaren basischen Produkten bzw. Oxiden.

Der jeweils zweite Peak in der Veraschungsphase für In^{3+}/HCl entspricht dem Peak, der auch in der Veraschungsphase der salpetersauren Lösungen des In^{3+} auftritt. Er ist auch vergleichbar mit dem unspezifischen Absorptionssignal, das in Gegenwart von Ga^{3+} in salz- und salpetersaurem Medium gemessen wird. Da die beiden Endprodukte der Hydrolyse In_2O_3 und Ga_2O_3 bei diesen Temperaturen noch nicht verdampfbar sind, müssen Reaktionen der Hydrolyseprodukte mit dem Kohlenstoff zu leichter verdampfbaren Verbindungen stattfinden (vgl. Zitat. 3). Mögliche Reduktionsprodukte sind: In_2O (Sublimation bei 700°), InO, Ga_2O (Sublimation im Vakuum bei 500° vgl. Citat. 17) und GaO. Bestimmend für das unspezifische Signal ist dabei die temperaturabhängige Geschwindigkeit der Reduktion. Wie im nächsten Abschnitt gezeigt wird, treten auch die Moleküle InCl (Siedepunkt 608°) und GaCl (Siedepunkt >800°) in Gegenwart von HCl im Plasma auf.

Die Abb. 5 zeigt die Ergebnisse für die komplex zusammengesetzten Matrices. Geringe Unterschiede zwischen salz- und salpetersaurem Medium ergeben sich wiederum nur für In^{3+}/AsO_4^{3-}. Weiterhin ist durch Vergleich der Abbildungen 3 und 5 festzustellen, daß die Anionen PO_4^{3-} und AsO_4^{3-} durch die Kationen Ga^{3+} und In^{3+} thermisch stabilisiert werden.

Die Abb. 4 und 5 zeigen weiterhin, daß trotz Rückgang des Signals in der Veraschungsphase auf einen Extinktionswert von nahezu 0 in der Atomisierungsphase ein Restsignal auftritt. Auch hierfür müssen zwei parallel verlaufende Reaktionen verantwortlich sein. Folgende Reaktionen sind möglich: 1. Reduktion der Hydrolyse- bzw. Zersetzungsprodukte durch Kohlenstoff (verantwortlich für Signal während der Veraschungsphase) und 2. Überführung der Hydrolyse- und Zersetzungsprodukte in thermisch stabiles Ga_2O_3, und In_2O_3 mit nachfolgender Verdampfung in der Atomisierungsphase.

Die Tatsache, daß unterschiedliche Matrixmengen des Ga und In bei 250 nm vergleichbare Signale hervorrufen, deutet bereits darauf hin, daß eine spektrale Abhängigkeit der unspezifischen Absorption vorliegt, die wegen ihrer Bedeutung für analytische Spurenbestimmungen im nächsten Abschnitt untersucht wird.

Untersuchung der spektralen Störungen in Abhängigkeit vom Wellenlängengebiet

Neben der Rayleigh-Streuung, die mit abnehmender Wellenlänge stark zunimmt, kann beim Vorliegen von Molekülen oder Radikalen im Plasma Bandenabsorption auftreten.

In Gegenwart der von uns eingesetzten Matrices sind wegen ihrer Stabilität folgende Moleküle bzw. Radikale im Plasma zu erwarten: AsO (4,9 eV), As_2 (3,96 eV). PO (6 eV), GaO (2,5 eV), GaCl (4 eV), InO (3,3 eV), InCl (4,5 eV). [15,18]

Im interessierenden Spektralgebiet zwischen 190 und 330 nm wurden zur Untersuchung der spektralen Störungen Absorptionsspektren aufgenommen. Die Messung erfolgte diskontinuierlich. Es wurden in Abhängigkeit von den auftretenden Störungen die Wellenlängendifferenzen der einzelnen Meßpunkte variiert (0,1 bis 5 nm). In den Abb. 6–9 sind die Ergebnisse für ausgewählte thermische Bedingungen dargestellt.

Die Abb. 6 zeigt die Spektren der reinen Säuren und der anionischen Komponenten AsO_4^{3-}/HCl und PO_4^{3-}/HCl. Für Salzsäure und Salpetersäure ist nur das Spektrum, welches in der Atomisierungsphase vermessen wurde, dargestellt. Erst unterhalb von 200 nm wird eine nennenswerte Extinktion gemessen, die hauptsächlich von Teilchen des Probeträgers verursacht wird (Streulicht). In Gegenwart von Salpetersäure wurde eine schmale Bande bei 214,5 nm (Maximum), die Störungen bei der Te-AAS bewirkt, gefunden. Die Ursache dieser Bande, die nur in der Atomisierungsphase entsteht, und auch noch nach einer Veraschungsphase von 10 s bei 970° vorhanden ist, konnte nicht eindeutig geklärt werden. Es wird angenommen, daß durch die Einwirkung von Salpetersäure auf Graphit, dieser z. T. in Graphitoxid oder eine ähnliche, sauerstoffärmere Verbindung überführt wird, welche erst bei hohen Temperaturen vollständig zerstört wird. Danach könnte diese Band durch CO hervorgerufen werden. Eine CO-Bande bei 215 nm ($X^1\Sigma^+ 12 \rightarrow A^1\Pi$ 4, 2,97–8,7 eV) wird beschrieben.[19] Es besteht allerdings auch die Möglichkeit, daß diese Absorption durch ein Zersetzungsprodukt der Salpetersäure verursacht wird. Das würde bedeuten, daß Verbindungen der Salpetersäure bzw. von deren

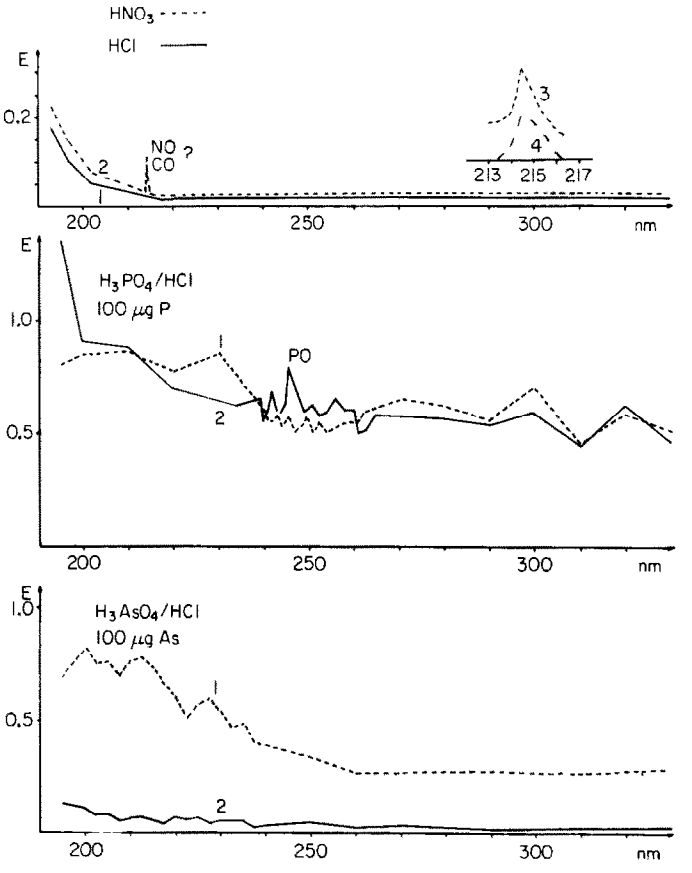

Abb. 6. Absorptionsspektren bei Verdampfung in der Graphitrohrküvette Bild *a*: Maximale Extinktion in der Atomisierungsphase bei 3150°C. Vorhergehende Veraschungsphase: 10 s, 380°C, Kurve 1: 1*N* HCl, Kurve 2 und 3: 1*N* HNO_3. Vorhergehende Veraschungsphase: 10 s, 970°C, Kurve 4: 1*N* HNO_3, Bilder *b* und *c*: Maximale Extinktionen in der Veraschungs- und der nachfolgenden Atomisierungsphase Veraschungsphase: 25 s, 1320°C, Kurven 1. Atomisierungsphase: 10 s, 3300°C, Kurven 2.

Zersetzungsprodukten mit Graphit existieren, die bei 970° noch nicht vollständig zerstört werden.

In Gegenwart von H_3PO_4 ist die unspezifische Absorption erheblich größer. Außerdem ist eine Abhängigkeit der Extinktion von der Wellenlänge über den gesamten, vermessenen Spektralbereich erkennbar. Die PO-Banden bei 246 nm ($X^2\Pi_r \rightarrow B^2\Sigma^+$ 0,0; $X^2\Pi_r \rightarrow B^1\,^2\Sigma$ 0,0; $X^2\Pi_r \rightarrow B''\,^2\Pi$ 0,0), die laut[20,21] in Emission auftreten können, sind in Absorption nachgewiesen worden (vgl. Zitat. 13). Die schleppende Verdampfung des Phosphates (s.o.) wird auch durch die Tatsache unterstrichen, daß unter den gewählten Bedingungen in der Veraschungs- und Atomisierungsphase nahezu die gleichen Extinktionswerte auftreten.

In Gegenwart von H_3AsO_4 treten breite Banden unterhalb von 250 nm in der Veraschungsphase auf, die möglicherweise dem As_2- oder AsO-Molekül zuzuordnen sind. Die kurzwelligsten Banden für As_2 reichen bis zu 224 nm ($X^1\Sigma^+{}_g \rightarrow A^1\Sigma^+{}_u$; $X^1\Sigma^+{}_g \rightarrow B$) und für AsO bis zu 235 nm ($X_2\Pi \rightarrow B^2\Sigma^+$; $X^2\Pi \rightarrow C^2\Delta$; $X^2\Pi \rightarrow D^2\Sigma^-$).[21] Infolge der schnellen Verdampfung der AsO_4^{3-}-Rückstände während der Veraschungsphase tritt in der Atomisierungsphase kaum noch unspezifische Absorption auf.

Die Abb. 7 zeigt die Spektren, die bei der Verdampfung von In^{3+}-Rückständen aus salz- und salpetersaurem Medium auftreten. In beiden Medien wurden sehr strukturierte Spektren gefunden. Ähnliche Ergebnisse erzielten Haraguchi und Fuwa[12–14] und Nakahara und Musha[16] bei der Untersuchung der InCl-Molekülabsorption in Flammen.

Die Bande zwischen 265 und 270 nm kann eindeutig dem InCl-Molekül zugeordnet werden (vgl. Zitat. 12). Sie entspricht dem Übergang $X^1\Sigma^+ \rightarrow C^1\Pi_1$, für den Miescher und Wehrli[22] (vgl. Zitat. 21) ein Gebiet von 263 bis 300 nm angegeben haben. In Übereinstimmung mit Zitat 12 sind wir der Auffassung, daß die InCl-Bande nicht in diesem ganzen Spektralgebiet auftritt. Beim Vergleich der in salz- und salpetersaurem Medium aufgenommenen Spektren ist zu sehen, daß auch im salpetersauren Medium zwischen 270 und 300 nm eine breite Bande auftritt, die nicht dem InCl-Molekül zugeordnet werden kann. Es ist anzunehmen, daß diese Bande, die im HCl-Medium mit der InCl-Bande überlappt, vom InO-Molekül ver-

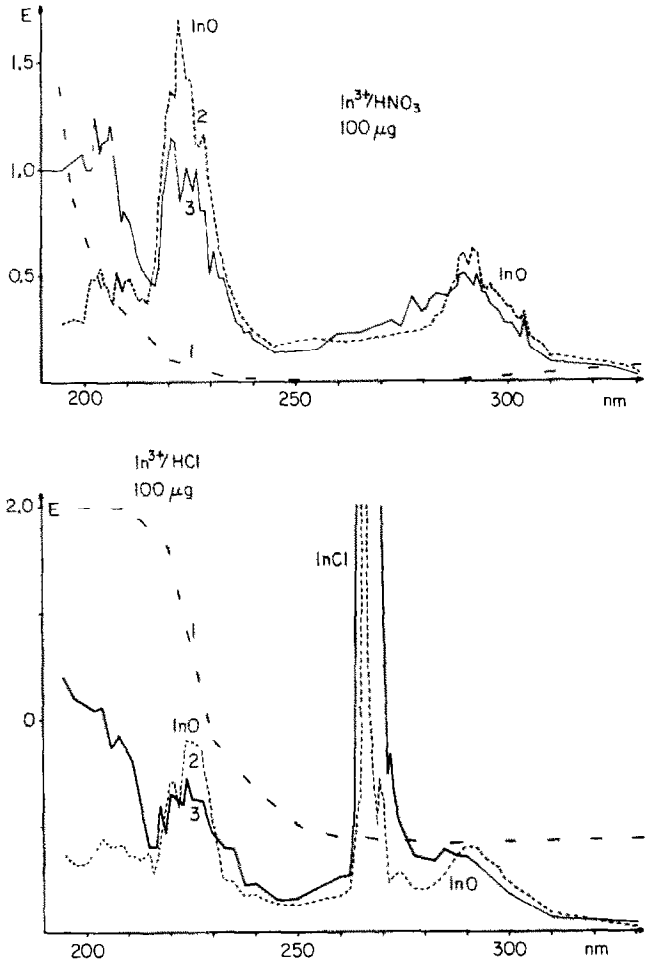

Abb. 7. Absorptionsspektren bei Verdampfung in der Graphitrohrküvette für In^{3+} in 1*N* HNO_3 und 1*N* HCl. Veraschungsphase: 25 s, 1680°C, Atomisierungsphase: 10 s, 3300°C. Kurven 1: Beginn der Veraschungsphase (etwa 500°C), Kurven 2: Hauptpeak der Veraschungsphase, Kurven 3: Atomisierungsphase.

ursacht wird. Wegen der Gleichartigkeit der Relationen, die in der Veraschungs- und Atomisierungsphase vermessen wurden, ist zu schlußfolgern, daß auch die Bande zwischen 215 und 240 nm dem InO-Molekül zuzuordnen ist. In der Literatur sind bisher keine InO-Banden in diesem Spektralgebiet beschrieben worden. Daß diese Banden nicht durch In-freie stickstoffhaltige Zersetzungsprodukte verursacht werden, ist durch Vergleich der Abb. 7 und 8 eindeutig erkennbar (Ähnlichkeit der beiden Spektren trotz der Wellenlängenverschiebung).

Interessant sind auch die für InCl und InO in der Veraschungs- und Atomisierungsphase gemessenen Maximalextinktionen. Die InO-Banden sind in der Veraschungsphase, die InCl-Bande in der Atomisierungsphase intensiver. Einerseits ist das auf die stärkere reduzierende Wirkung des Kohlenstoffs bei höheren Temperaturen zurückzuführen und zum anderen ist das InCl-Molekül (D_E 4,5 eV) thermisch stabiler als das InO-Molekül (D_E 3,3 eV).

Die Wellenlängenabhängigkeit der am Anfang in der Veraschungsphase besonders im salzsauren Medium auftretenden Peaks (Temperatur zu diesem Zeitpunkt etwa 500°), vgl. *a*., Abb. 4) ist in der Kurve 1 der Abb. 7 dargestellt. Es ist keine Bandenstruktur erkennbar. Das bedeutet, daß diese "Absorptionserscheinung" durch Streuung hervorgerufen wird, die auf kondensiertes $InCl_3$ zurückzuführen ist (s.o.). Damit wird die gegebene Erklärung für den Verdampfungsablauf unterstrichen. Im salpetersauren Medium tritt eine ähnliche Streuung erst unterhalb von 240 nm auf.

Die Abb. 8 zeigt die Spektren, die bei der Verdampfung des Ga^{3+} aus salz- und salpetersaurem Medium erhalten wurden. Die intensive Bande zwischen 242 und 250 nm, die im salzsauren Medium auftritt, wird vom GaCl-Molekül hervorgerufen (Bandensystem C: $X^1\Sigma^+ \rightarrow C^1\Pi_1$; vgl. Zitate 18,20,21,23). In der Literatur wird ein Bandengebiet zwischen 242 und 270 nm angegeben. Durch Vergleich der Ergebnisse für das salz- und salpetersaure Medium ist in Analogie zu den Erscheinungen beim In zu schlußfolgern, daß auch beim Ga zwei Banden existieren. Die im salpetersauren Medium auftretende Bande zwischen

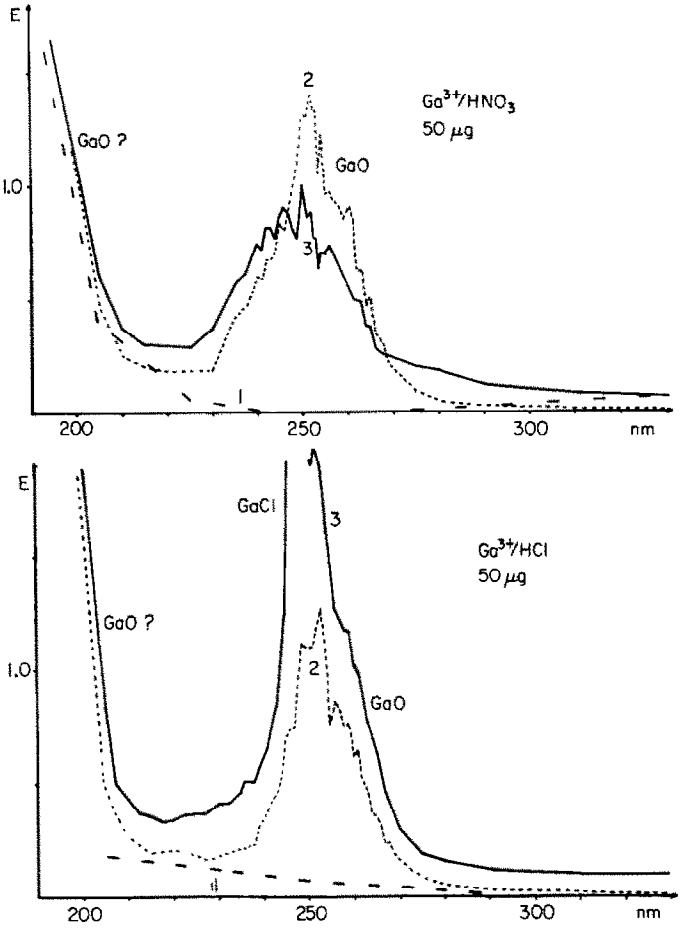

Abb. 8. Absorptionsspektren bei Verdampfung in der Graphitrohrküvette für Ga^{3+} in 1*N* HNO_3 und 1*N* HCl. Veraschungsphase: 25 s, 1760°C, Atomisierungsphase: 10 s, 3300°C. Kurven 1: Beginn der Veraschungsphase (etwa 500°C), Kurven 2: Hauptpeak der Veraschungsphase, Kurven, 3: Atomisierungsphase

235 und 270 nm wird demzufolge vom GaO-Moleküle verursacht. Außerdem wird unterhalb von 210 nm eine extrem starke Zunahme der Extinktion beobachtet. Es ist anzunehmen, daß es sich dabei um die langwellige Flanke der zweiten GaO-Bande (vgl. Abb. 7) handelt. Eine solche Bande ist in Analogie zum In zu erwarten, da alle Ga-Banden wegen des gegenüber In kleineren Atomradius des Ga nach kürzeren Wellenlängen verschoben sind. Eine eindeutige Identifizierung war nicht möglich, weil Messungen unterhalb von 190 nm mit der gegebenen Apparatur nicht möglich waren.

Weiterhin ist festzustellen, daß die GaCl-Bande eigentlich nur während der Atomisierungsphase auftritt, d.h. Ga^{3+} wird gegenüber In^{3+} erst bei höheren Temperaturen zum Ga^{+} reduziert. Die Streuung zu Beginn der Veraschungsphase ist weit geringer als beim In (Kurve 1 der Abb. 8). Daraus ist abzuleiten, daß eine Verdampfung von $GaCl_3$ nur in sehr geringem Umfang auftritt.

In der Abb. 9 sind die Absorptionsspektren der komplex zusammengesetzten Matrices In^{3+}/AsO_4^{3-}, Ga^{3+}/AsO_4^{3-} und Ga^{3+}/PO_4^{3-} in salzsaurem Medium dargestellt. Diese Spektren zeigen im wesentlichen die Struktur der Spektren der Einzelkomponenten im salzsauren Medium (vgl. Abb. 6–8).

Auffällig ist die gegenüber In^{3+}/HCl und In^{3+}/HNO_3 starke Zunahme der InO-Banden während der Veraschungsphase (Kurve 2 der Abb. 9). Bei Trocknung der komplex zusammengesetzten Lösungen entsteht neben InOCl, $InCl_3$ hauptsächlich $InAsO_4$. Bei der Zersetzung des $InAsO_4$, die während der Veraschungsphase erfolgt, liegt das In in aktivierter Form vor und ist leichter zu reduzieren als in reinem salz- oder salpetersauren Medium. Auffällig ist, daß ähnliche Erscheinungen beim Ga nicht beobachtet werden. Auf Grund der geringeren Basizität und der größeren thermischen Stabilität der Oxide des Ga ist anzunehmen, daß die Gegenwart von AsO_4^{3-} und PO_4^{3-} nur geringe Unterschiede des Verdampfungsablaufs der Ga-Spezies bewirken.

Aus den Darlegungen geht hervor, daß bei der Verdampfung der untersuchten Substanzen in der Graphitrohrküvette erhebliche spektrale Störungen auftreten, die, wenn sie nicht berücksichtigt werden, leicht zu systematischen Fehlern bei der Bestimmung

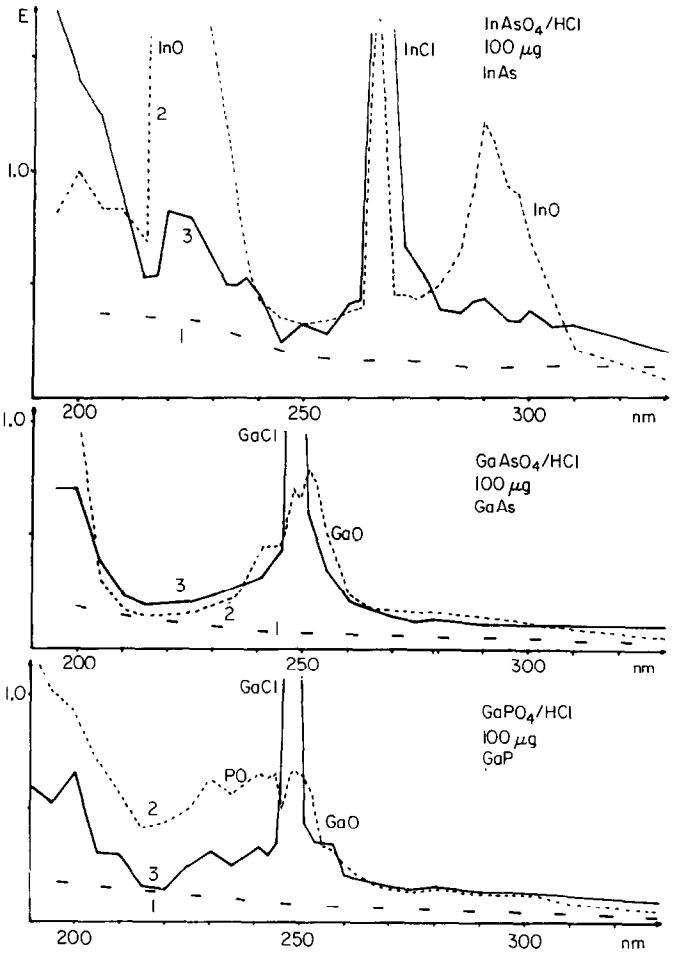

Abb. 9. Absorptionsspektren bei Verdampfung in der Graphitrohrküvette für $InAsO_4$, $GaAsO_4$ und $GaPO_4$ in 1*N* HCl. Veraschungsphase: 25 s, 1680°C ($InAsO_4$), 25 s, 1760°C ($GaAsO_4^4$, $GaPO_4$), Atomisierungsphase: 10 s, 3300°C. Kurven 1: Beginn der Veraschungsphase (etwa 500°C), Kurven 2: Hauptpeak der Veraschungsphase, Kurven 3: Atomisierungsphase.

von Spuren in diesen Matrices durch AAS führen können.

Besonders bei Verwendung der Untergrundkompensation nach der Zweilinienmethode, deren Vorteil in der gleichzeitigen Messung besteht, sind in Abhängigkeit vom jeweiligen Spurenelement diese spektralen Störungen bei der Wahl der unspezifischen Linie zu berücksichtigen (z.B. spezifische AAS tritt im Flankengebiet einer Bande auf). Eine weitere Schlußfolgerung, die aus den Darlegungen gezogen werden kann, ist: Atomabsorptionsspektralphotometer sind in Verbindung mit der Graphitrohrküvette für die Untersuchung von Banden geeignet. Über derartige Untersuchungen, die auch einen wichtigen analytischen Aspekt haben, wird in Kürze berichtet.

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Summary—The evaporation of the species Ga^{3+}, In^{3+}, PO_4^{3-}, AsO_4^{3-}, Ga^{3+}/AsO_4^{3-}, Ga^{3+}/PO_4^{3-} and In^{3+}/AsO_4^{3-} in HCl and HNO_3 medium was investigated by measurement of the non-specific absorption at 250 nm, in a graphite cuvette, with a continuum light source. The maximum of the non-specific absorption is given for the ashing and atomizing phases as a function of the ashing temperatures. Ashing temperatures for analytical determinations can be derived from the results. The mechanisms of evaporation of the substances were investigated by means of extinction–time curves. Absorption spectra of the matrices and of the pure acids used were measured between 190 and 330 nm in the graphite cuvette at different ashing and atomizing temperatures. The InCl- and GaCl-bands of the C-system and new bands of GaO- and InO-molecules were found. The PO-band at 246 nm was detected. The results are discussed and can be applied for thermal fractionation and for background correction by the two-line method in trace analysis by electrothermal AAS.

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UNTERSUCHUNGEN ZUR ATOMSPEKTROSKOPISCHEN SPURENANALYSE IN $A^{III}B^{V}$-HALBLEITER-MIKROPROBEN—II*

UNTERSUCHUNGEN ZUR BESTIMMUNG VON Ga-SPUREN IN In UND InAs UND VON In-SPUREN IN Ga, GaAs UND GaP DURCH AAS MIT ELEKTROTHERMISCHER ATOMISIERUNG

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Zusammenfassung—Es wird die Bestimmung von Ga-Spuren in In, P, As und InAs und von In-Spuren in Ga, P, As, GaAs und GaP beschrieben. Der Verdampfungsmechanismus wird in Abhängigkeit vom Medium (HCl oder HNO_3) diskutiert. Salpetersaures Medium wird für die analytischen Bestimmungen empfohlen. Die Verdampfung der Spuren und Matrices wird durch Extinktions–Zeit-Kurven untersucht. Es wird gezeigt, daß eine thermische Fraktionierung der AsO_4^{3-}- und PO_4^{3-}-Matrices und Ga- und In-Spuren in der Veraschungsphase möglich ist. Im Fall der Ga-AAS ist eine thermische Fraktionierung der Matrices (In^{3+}, In^{3+}/AsO_4^{3-}) und der Spur in der Atomisierungsphase möglich. Die thermische Fraktionierung der Indium-Spuren und der Matrices (Ga^{3+}, Ga^{3+}/AsO_4^{3-}, Ga^{3+}/PO_4^{3-}) ist nicht möglich. Die Resultate und die Ursachen der unspezifischen Absorption werden diskutiert. Die analytischen Ergebnisse sind: absolute Nachweisgrenzen: Ga 45 pg, In 35 pg. Die relativen Nachweisgrenzen bezogen auf 0,1 mg liegen bei etwa 1 ppm.

$A^{III}B^{V}$-Verbindungen entsprechender Zusammensetzung können wegen des gemeinsamen Vorkommens und der ähnlichen chemischen Eigenschaften der Elemente Gallium und Indium Spurenverunreinigungen der jeweils anderen A^{III}-Komponente enthalten. Außerdem werden zur Erzielung bestimmter elektrischer und optoelektronischer Eigenschaften gemischte Halbleiter des Typs $Ga_xIn_{1-x}X$ (X = As,P) hergestellt. Die analytische Bestimmung von Ga- und In-Spuren ist deshalb zur Charakterisierung der $A^{III}B^{V}$-Verbindungen erforderlich. Außerdem ist die Kontrolle der zur Herstellung der Halbleiter verwendeten Metalle Ga und In auf Spurenverunreinigungen an In und Ga notwendig.

Da die auf dem Wege der Gasphasen- oder Flüssigphasenepitaxie hergestellten $A^{III}B^{V}$-Halbleiter nur eine geringe Masse haben, ergibt sich das Problem der Bestimmung von Spuren in Mikroproben (< 1 mg). Für die Lösung dieses Problems schien die AAS mit elektrothermischer Atomisierung wegen ihres Nachweisvermögens, ihrer Selektivität und Schnelligkeit am geeignetsten, wenn es gelingt, den Einfluß der Matrices auf die Bestimmung der Spuren zu reduzieren. Durch Untersuchung der unspezifischen Absorption und der Verdampfung zum Zweck einer thermischen Spur–Matrix-Fraktionierung sollten die analytischen Bestimmungen optimiert werden.

Bisher wurden Bestimmungen des Galliums[1–4] und des Indiums[2,5,6] bei Einsatz der AAS vor allem unter Anwendung der Atomisierung in Flammen unterschiedlicher Art durchgeführt. Störungen der Bestimmungen treten durch Radikalbildung[7–9] (vgl. Mitteilung I[10]) und Ionisation[11] auf. Zur vollständigen Zerstörung der Radikale ist eine heiße Flamme günstiger.[2] Die in diesen Flammen zunehmende Ionisation wird durch Zusatz leicht ionisierbarer Cäsium- oder Kaliumsalze,[11] die den Elektronendruck im Plasma erhöhen, zurückgedrängt.

Die besten Nachweisgrenzen liegen bei 0,07 μg/ml für Ga[4] und 0,05 μg/ml für In.[5] Für die Spurenanalyse in Mikroproben ist die Flammentechnik somit wenig geeignet.

Über Spurenbestimmungen in Mikroproben gibt es nur wenige Mitteilungen. Prudnikow[12] setzte die Impulsverdampfung mit Flammen für Ga und In ein. Er erreichte Nachweisgrenzen von einigen Nanogramm. Mit der Injektionsmethode nach Sebastiani erzielte Jackwerth[13] eine Nachweisgrenze von 24 ng In. Langmyhr[14] erreichte mit der induktiv beheizten Graphitrohrküvette Nachweisgrenzen von 2,5 ng für Gallium und 0,29 ng für Indium. Vor kurzem berichteten Pelosi und Attolini[15] über die Spurenbestimmung des Ga in $ZnInS_2$. Sie konnten bei einem Probeeinsatz von 10–30 mg bis zu 300 ppm Ga bestimmen. Die absolute Nachweisgrenze im wäßrigen Medium war 0,5 ng bzw. in Chloroform 5 ng. Ohta und Suzuki[16] setzten für die Atomisierung des Galliums einen Metallrohratomisator ein. Regan und Warren[17] berichten über eine Empfindlichkeitsverbesserung der Ga-Bestimmung in der Graphitrohrküvette durch Ascorbinsäure. Systematische Untersuchungen wurden bisher noch nicht durchgeführt.

* Mitteilung I—*Talanta*, 1977, **24**, 725.

EXPERIMENTELLER TEIL

Apparatives

Spektrometer: Zweikanal-AAS-Gerät Typ 811, Jarrell-Ash, U.S.A.

Atomisator: Graphitrohrküvette Typ 1268, Beckman, U.S.A.

Apparative Bedingungen

Lichtquellen: Ga-HKL, Jarrell-Ash, U.S.A. 5 mA, spektrale Bandbreite 0,1 nm, λ = 294,4 nm In-HKL, Jarrell-Ash, U.S.A. 10 mA, spektrale Bandbreite 0,2 nm, λ = 303,9 nm.

Die beiden gewählten Linien besaßen in Übereinstimmung mit[1] die besten Empfindlichkeiten. Außerdem wurden getestet: Gallium 287,4 nm und Indium 325,6 nm.

Untergrundkompensation

Die Untergrundkompensation erfolgte nach der Zweilinienmethode. Sowohl die Ga-HKL als auch die In-HKL emittierten keine intensiven, unspezifischen Linien in der Nähe der spezifischen Absorptionslinien. Es wurden deshalb andere Lichtquellen auf ihre Verwendbarkeit getestet. Folgende optimale Varianten wurden benutzt. Untergrundkompensation bei Ga-Bestimmungen: Pd-HKL, Jarrell-Ash, 20 mA, spektrale Bandbreite 0,1 nm, λ = 292,5 nm.

Untergrundkompensation bei In-Bestimmungen: Co-HKL, Beckman, 10 mA, spektrale Bandbreite 0,2 nm, λ = 304,4 nm.

Elementkonstanten

Gallium: Ionisierungspotential 6,0 eV; Siedepunkt 2237°; Grundzustand: $4p\ ^2P_{1/2}$. Übergang bei 294,4 nm: $4p\ ^2P_{3/2}$ (E_a = 0,1 eV) → $4d\ ^2D_{3/2,5/2}$ (E_a = 4,3 eV).

Indium: Ionisierungspotential 5,8 eV; Siedepunkt 2000° Übergang bei 303,9 nm: $5p\ ^2P_{1/2}$ (Grundzustand) → $5d\ ^2D_{3/2}$ (E_a = 4,08 eV)

Lösungen

Durch Auflösen von 6-Neuner Indium bzw. Gallium (VEB Mansfeld-Kombinat, DDR) in konzentrierter Salz- oder Salpetersäure (suprapur, Merck) wurden die Stammlösungen, die 1 mg/ml 1*N* Säure enthielten, hergestellt.

Da die oxydative Lösung der genannten $A^{III}B^{V}$-Verbindungen zu Ga^{3+}-, In^{3+}-, AsO_4^{3-}- und PO_4^{3-}-Ionen führt, wurden zur Untersuchung des Matrixeinflusses konzentrierte Stammlösungen dieser Ionen (200 mg/ml, bezogen auf Ga, In, As, P) hergestellt, die zur Simulierung von gelösten $A^{III}B^{V}$-Verbindungen entsprechend gemischt und verdünnt wurden.

Allgemeine Arbeitsweise

Lösungsvolumina von 0,01 ml, die die Spuren und Matrices in entsprechenden Konzentrationen enthielten, wurden in die Graphitrohrküvette gegeben, getrocknet, verascht und atomisiert.

UNTERSUCHUNG UND OPTIMIERUNG DER VERDAMPFUNG DER SPUREN UND MATRICES

Einfluß des Mediums

Es wurden Untersuchungen in 1*N* salz- und salpetersaurem Medium durchgeführt. Die Gegenwart von Salzsäure führte gegenüber Salpetersäure zu erheblichen Signaldepressionen (vgl. Tabelle 1). Diese Signaldepressionen sind auf die Bildung der stabilen GaCl- und InCl-Moleküle zurückzuführen. Auch bei Flammenatomisierung wird über derartige Depressionen berichtet, die jedoch bei weitem nicht das hier gefundene Ausmaß erreichen. Das ist auf die unterschiedlichen Plasmaeigenschaften und auf den unterschiedlichen Verdampfungsmechanismus zurückzuführen. Bei der elektrothermischen Verdampfung in der Graphitrohrküvette führt die Reduktionswirkung des Kohlenstoffs bei verhältnismäßig niedrigen Temperaturen zur Bildung der leicht flüchtigen GaCl- und InCl-Moleküle. Infolge des fallenden Temperaturgradienten zwischen Probeträger und Plasma dissoziieren diese Teilchen im Plasma kaum noch. Die Restatomabsorption wird von den Ga- bzw. In-Atomen hervorgerufen, die bereits die Probeträgeroberfläche als Atome verlassen. Im Gegensatz dazu herrscht bei der Flammenatomisierung in der reaktionsfreien Zone der Flammen nahezu thermisches Gleichgewicht. Die vorliegende Temperatur führt zu einer vollständigeren Dissoziation der GaCl- bzw. InCl-Moleküle.

Aus diesen Gründen ist für die Bestimmung von Gallium- und Indium-Spuren bei Anwedung der elektrothermischen Atomisierung nur salpetersaures Medium zu empfehlen.

Weiterhin wurde festgestellt, daß die höchsten Extinktionswerte bei den maximalen Atomisierungstemperaturen der Apparatur (nach Angaben des Herstellers: 3300°) erreicht werden. Da die Verdampfung des Indium und Gallium schon bei erheblich niedrigeren Temperaturen (1000–1600°) einsetzt (vgl. Mitteilung I[10]) kann geschlußfolgert werden, daß die hohe Temperatur über die effektivste Zerstörung der GaO-, InO-, bzw in Gegenwart von Chloridionen auch GaCl- und InCl-Moleküle sowohl auf der Oberfläche des Probetragers als auch zum Teil noch im Plasma zur optimalen Atomkonzentration im Plasma führt.

Einfluß der Matrices auf die Ga-AAS

Die Untersuchung der Verdampfung und unspezifischen Absorption erfolgte durch Messung der Extinktion in Abhängigkeit von der Zeit bei unterschiedlichen thermischen Bedingungen. Es wurde festgestellt, daß auch in Gegenwart von Matrices die maximale Atomisierungstemperatur in der Atomisierungsphase (10 sec) zu den besten Extinktionen führte, so daß diese Bedingung für die analytischen Untersuchungen angewandt wurde.

In der Abb. 1 sind die Extinktions–Zeit-Kurven in Gegenwart von PO_4^{3-}-und AsO_4^{3-}-Ionen für ausgewählte thermische Bedingungen der Veraschungs- und Atomisierungsphase dargestellt. Aus der Abb. 1 ist ersichtlich, daß eine thermische Matrix–Spur-Tren-

Tabelle 1. Reziproke Empfindlichkeiten für die AAS des Ga und In in 1*N* HCl und 1*N* HNO_3

Element	Reziproke Empfindlichkeiten *pg*/0,01 *Extinktion* HCl	HNO_3
Ga	150	45
In	350	35

nung in Gegenwart von AsO_4^{3-}-Ionen vollständig, in Gegenwart von PO_4^{3-}-Ionen fast vollständig erfolgt. Eine Erhöhung der Veraschungstemperatur zur besseren Abtrennung der PO_4^{3-}-Ionen ist nicht möglich, weil dann bereits Galliumverluste auftreten. Bild *d* der Abb. 1 zeigt deutlich, daß bei Anwendung der Untergrundkompensation einwandfreie, spezifische Signale erhalten werden, so daß analytische Bestimmungen in Gegenwart hoher Matrixkonzentrationen möglich sind.

In der Abb. 2 sind die Extinktions–Zeit-Kurven in Gegenwart von Indium und Indiumarsenid (als $InAsO_4$) für die Atomisierungsphase bei ausgewählten thermischen Bedingungen der Veraschungs- und Atomisierungsphase dargestellt.

Die Bilder *a–c* zeigen, daß zu Beginn der Atomisierungsphase nach einer Veraschungsphase von 25 sec noch ein starkes unspezifisches Signal infolge der Verdampfung der Matrix erhalten wird. Die spezifischen Gallium-AA-Signale entstehen entsprechend dem höheren Siedepunkt des Galliums als Flanken nach den unspezifischen Signalen, d.h. eine thermische Matrixabtrennung ist nur bedingt möglich. Eine Erhöhung der Veraschungstemperatur auf 1570° (Bild *b*) verbessert diese Trennung, weil bereits in der Veraschungsphase ein Teil des Indiums verdampft. Allerdings treten dabei auch erhebliche Galliumverluste auf

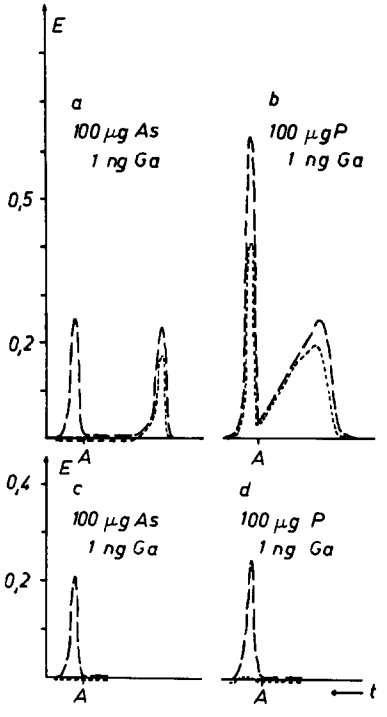

Abb. 1. Extinktions–Zeit-Kurven für die Ga-AAS in Gegenwart von AsO_4^{3-}- und PO_4^{3-}-Ionen. Thermische Bedingungen: Veraschung 25 sec, 1320°, Atomisierung 10 sec, 3300° (Beginn bei A). Schreibergeschwindigkeit: 120 mm/min. Bilder *a* und *b*: —— Gesamtabsorption (Kanal A) ---- unspezifische Absorption (Kanal B) Bilder *c* und *d*: —— Spezifische Absorption (1 ng Ga) (Kanal A – B) ---- Spezifische Absorption (0 ng Ga) (Kanal A – B)

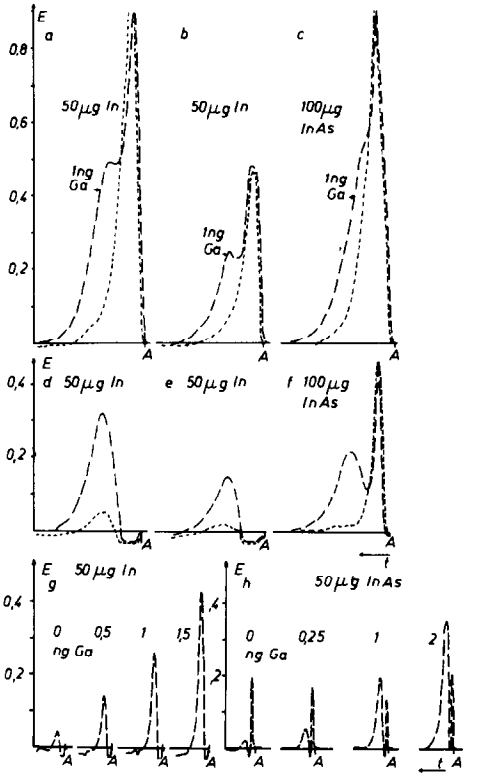

Abb 2. Extinktions–Zeit-Kurven für die Ga-AAS in Gegenwart von In^{3+}-und In^{3+}/AsO_4^{3-}-Ionen. Thermische Bedingungen: Bilder *a, c, d, f–h*: Veraschung 25 sec, 1320°, Atomisierung 10 sec, 3300° Bilder *b, e*: Veraschung 25 sec, 1570°, Atomisierung 10 sec, 3300° (Beginn bei A). Schreibergeschwindigkeit: Bilder *a–f*: 600 mm/min Bilder *g, h*: 120 mm/min Bilder *a–c*: —— Gesamtabsorption (Kanal A) ---- unspezifische Absorption (Kanal B) Bilder *d–h*: —— Spezifische Absorption (1 ng Ga) (Kanal A – B) ---- Spezifische Absorption (0 ng Ga) (Kanal A – B)

(Vergleich zwischen den Bildern *a* und *b* bzw. *d* und *e*).

Die Bilder *d–f* der Abb. 2 zeigen Signale, die bei Anwendung der Untergrundkompensation nach der Zweilinienmethode erhalten wurden. In Gegenwart von Indium ist in der Anfangsphase der Atomisierung eine "unspezifische Emission" ($E_{\text{Kanal A}} - E_{\text{Kanal B}}$ = negativ) (Bild *d,e*) und in Gegenwart von $InAsO_4$ eine nicht vollständig kompensierte unspezifische Absorption (Bild *f*) zu erkennen.

Die Hauptursache für die starke unspezifische Absorption ist eine Bande des InO-Moleküls (270–310 nm, Maximum bei 290 nm, vgl. Mitteilung I[10]). In Gegenwart von $InAsO_4$ sind auch As-Spezies (Lichtstreuung) für diese unspezifische Absorption verantwortlich, weil während der Veraschungsphase infolge der thermischen Stabilisierung des AsO_4^{3-} als $InAsO_4$ keine As-Spezies verdampfen. Diese Lichtstreuung durch As-Spezies ist auch verantwortlich für die nicht vollständige Kompensation. Die "negative Extinktion", die vor allem in Gegenwart von Indium, aber wie aus dem Bild *h* ersichtlich ist, auch als Zwischenphase (nach der Verdampfung des Hauptteils der As-Spezies) in Gegenwart von $InAsO_4$ auftritt, ist auf

das verwendete Kompensationsverfahren zurückzuführen. Die InO-Bande (Max. 290 nm) zeigt bei 294,4 nm eine etwas niedrigere Absorption als bei 292,5 nm (Linien entsprechend Kanal A und Kanal B). Die Bilder *g* und *h* der Abb. 2 zeigen, daß in Gegenwart von 0,05 mg Indium und auch $InAsO_4$ (0,05 mg InAs) eine einwandfreie Bestimmung von Galliumspuren möglich ist. Allerdings ist zu sehen, daß die Gegenwart von $InAsO_4$ zu einer geringen Depression der spezifischen Ga-AAS führt. Letzteres wird auf den Verdampfungsmechanismus zurückgeführt. In Gegenwart des $InAsO_4$ setzt am Anfang der Atomisierungsphase die Zersetzung dieser Substanz unter Abspaltung von As-Spezies ein. Durch diese Auflockerung der Matrix werden auch Gallium-Teilchen mitgerissen. Zum anderen ist der Partialdruck des Sauerstoffs in der Atomisierungsphase in Gegenwart von AsO_4^{3-} größer, so daß sich die Bildung von GaO-Molekülen nachteilig auf die Ga-Atomkonzentration auswirkt.

Einfluß der Matrices auf die In-AAS

Die Gegenwart von PO_4^{3-}- und AsO_4^{3-}-Ionen führt zu den gleichen Ergebnissen wie bei der Ga-AAS, d.h. die thermische Abtrennung des AsO_4^{3-} erfolgt während einer Veraschungsphase von 25 sec (1320°) vollständig, die des PO_4^{3-} nur unvollständig. Die Untergrundkompensation ermöglicht jedoch in beiden Fällen analytische Messungen in Gegenwart von 0,1 mg As bzw. P.

Die Extinktions-Zeit-Kurven in Gegenwart der Matrices Gallium, $GaPO_4$ und $GaAsO_4$ sind in der Abb. 3 dargestellt. Aus den Bildern *a–c* ist zu entnehmen, daß die unspezifische Absorption, die durch Ga-Spezies hervorgeufen wird, nur sehr klein ist. Sie ist vollständig zu kompensieren (Bilder *d–f*). Eine thermische Fraktionierung, wie sie bei der Ga-AAS gefunden wurde, konnte nicht festgestellt werden. Das läßt den allgemeinen Schluß zu, daß thermische Trennungen, bei denen die Matrix leichter flüchtig ist, besser ablaufen als im ungekehrten Fall.

Die Bilder *g–k* zeigen den Einfluß der komplex zusammengesetzten Matrices. Wiederum wurde festgestellt, daß PO_4^{3-}- und AsO_4^{3-}-Ionen als $GaPO_4$ bzw. $GaAsO_4$ stabilisiert werden. Sie verdampfen nicht mehr während der Veraschungs- sondern erst zu Beginn der Atomisierungsphase. Dies führt zu einer starken Steigerung der unspezifischen Absorption (Bilder *g–h*), die jedoch kompensiert werden kann (Bilder *i–k*).

Vergleicht man die Signalhöhen miteinander, so stellt man eine stark depressive Wirkung des reinen Galliums fest. Eine Auswertung der Peakflächen führte zu keiner Verbesserung dieses Ergebnisses. Eine befriedigende Erklärung kann hierfür nicht gegeben werden. Es ist jedoch wahrscheinlich, daß die Ursache in einer verschleppten Verdampfung der In-Spuren infolge der Gegenwart von Ga_2O_3 zu suchen ist.

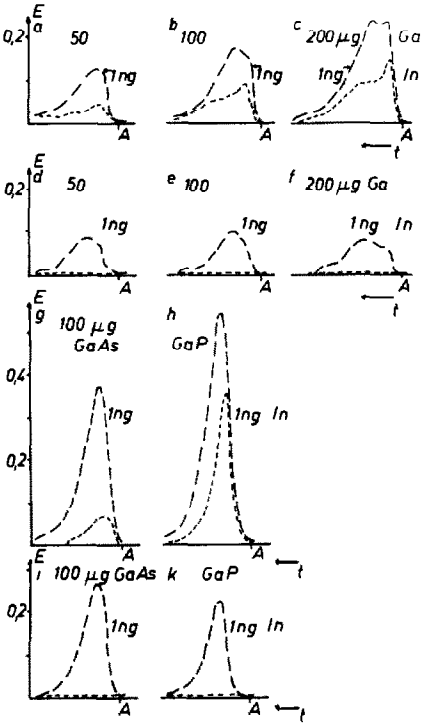

Abb 3. Extinktions–Zeit-Kurven für die In-AAS in Gegenwart von Ga^{3+}- und Ga^{3+}/AsO_4^{3-}- und Ga^{3+}/PO_4^{3-}-Ionen. Thermische Bedingungen: Veraschung 25 sec, 1320°, Atomisierung 10 sec, 3300° (Beginn bei A). Schreibergeschwindigkeit: 600 mm/min Bilder *a–c, g, h*: —— Gesamtabsorption (Kanal A) ---- unspezifische Absorption (Kanal B) Bilder *d–f, i, k*: —— Spezifische Absorption (1 ng In) (Kanal A – B) ---- Spezifische Absorption (0 ng In) (Kanal A – B)

ANALYTISCHE ERGEBNISSE

Die Ergebnisse der analytischen Bestimmungen des Galliums und des Indiums sind in den Tabelle 2 und 3 dargestellt. Im Vergleich zu den bisher bekannten wurde durch die Optimierung der Galliumbestimmung in rein salpetersaurer Lösung eine Verbesserung der Nachweisgrenze um eine Zehnerpotenz erzielt. (vgl. Zitat 15). Auch für die In-AAS konnte durch die Optimierung die Nachweisgrenze um den Faktor 10 verbessert werden (vgl. Zitat 14). Die Bestimmungen in Gegenwart der Matrices ergaben in beiden Fällen sehr gute relative Nachweisgrenzen (meisssens < 1 ppm) bei einem Probeeinsatz von nur 0,05–0,2 mg. Letzteres bedeutet, daß etwa die fünffache Menge an Probe zur Verfügung stehen muß, so daß sich ein Probevolumen von 0,05 ml ergibt. Mit einer solchen Lösung können 3–5 Messungen durchgeführt werden.

Die ausgearbeiteten Bestimmungsmethoden wurden auf Spurenbestimmungen in den entsprechenden Materialien angewandt (vgl. Tab. 4). Die Richtigkeit der Werte wurde durch Vergleich der Werte, die aus den Eichkurven erhalten wurden, mit Werten, die nach der Additionsmethode erhalten wurden, überprüft.

Tabelle 2. Ergebnisse der Ga-AAS bei Anwendung der Graphitrohrküvette

Matrix*, *µg/0,01 ml*	Reziproke Empfindlichkeit, *pg/0,01 E*†	Konzentrationsbereich, *pg/0,01 ml*	Relative Nachweisgrenzen 3*s*-Kriterium, *ppm*	*Atome/cm³*
—	45	50–2000	0,005	—
100 P	100	100–2000	2	—
200 P	50	50–2000	0,5	—
100 In	100	100–2000	0,6	—
50 InAs	60	60–2000	0,6	$2{,}9 \cdot 10^{16}$

* Medium: 1 *M* HNO_3.
† *E* = Extinktion.

Tabelle 3. Ergebnisse der In-AAS bei Anwendung der Graphitrohrküvette

Matrix*, *µ/g/0,01 ml*	Reziproke Empfindlichkeit, *pg/0,01 E*†	Konzentrationsbereich, *pg/0,01 ml*	Relative Nachweisgrenzen 3*s*-Kriterium, *ppm*	*Atome/cm³*
—	35	35–2000	0,005	—
100 P	70	70–2000	1	—
200 As	35	35–2000	0,25	—
100 Ga	270	270–2000	2,4	—
100 GaP	55	55–1500	0,5	$1{,}1 \cdot 10^{16}$
100 GaAs	55	55–2000	0,5	$1{,}5 \cdot 10^{16}$

* Medium: 1*M* HNO_3.
† *E* = Extinktion

Tabelle 4. Ergebnisse der Spurenbestimmung in realen Proben

Matrix	Spur	Gehalt nach Eichkurvenverfahren, *ppm*	Additionsverfahren, *ppm*
Ga	In	$3{,}7 \pm 0{,}5$	$3{,}9 \pm 0{,}4$
GaP	In	$0{,}9 \pm 0{,}2$	$1{,}0 \pm 0{,}2$
GaAs	In	$0{,}6 \pm -0{,}2$	$0{,}8 \pm 0{,}2$
InAs	Ga	$1{,}0 \pm 0{,}2$	$1{,}1 \pm 0{,}1$

Probemenge: 0,5–1 mg

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Summary—The atomic-absorption determination of traces of Ga in In, P, As and InAs and of traces of In in Ga, P, As, GaAs and GaP is described. The mechanism of the evaporation of the trace element according to the medium used (HCl or HNO_3) is discussed. Nitric acid medium is recommended for analytical determinations. The evaporation of the trace elements and matrices was investigated by means of absorbance *vs.* time curves. It is shown that a thermal fractionation of AsO_4^{3-} and PO_4^{3-} matrices and Ga and In traces is possible in the ashing step. In the case of Ga the thermal fractionation of the matrices (In^{3+}, In^{3+}/AsO_4^{3-}) from the trace element is possible in the atomization step. The thermal fractionation of In traces from the matrices (Ga^{3+}, Ga^{3+}/AsO_4^{3-}, Ga^{3+}/PO_4^{3-}) is impossible. The results and the reasons for the non-specific absorption are discussed. The absolute detection limits are Ga 45 pg, In 35 pg. The relative detection limits are ~ 1 ppm in a 0.1 mg sample.

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QUANTITATIVE ION-EXCHANGE SEPARATION OF SUBMICROGRAM AMOUNTS OF IRON FROM PHOSPHATE MEDIUM

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Summary—Radiotracer techniques were used to investigate the separation and recovery of submicrogram amounts of iron from major amounts of phosphate resulting from the hydrolysis of phosphorus oxychloride. Iron is retained quantitatively by the column under conditions permitting the efficient elution of phosphate species with 5.0*M* hydrochloric acid. Iron is then recovered by elution with 0.15*M* hydrochloric acid–1% hydrazine solution. Precise separations of 10–125 ng of iron with recoveries of 95% or better are reported.

In the chemical vapour deposition (CVD) preparation of low-loss optical fibres, it is customary to use high-purity reagents to minimize absorption due to transition metal impurities. To the expanding list of important CVD reagents, phosphorus oxychloride ($POCl_3$) has recently been added. An expensive high-purity commercial reagent and a more economic ultrapure product obtained by a laboratory purification of reagent-grade material are available. In the characterization of these reagents it was especially required to have reliable methods for determining iron, one of the most prevalent and difficult impurities to remove. Because of interference by phosphate, ultratraces of iron can usually only be determined quantitatively after a preliminary separation. An alternative to the procedure of Kuzmin *et al.*[2] (separation of iron from a phosphate medium by extraction with 8-hydroxyquinoline in chloroform and determination by emission spectroscopy) was needed for the quantitative separation and recovery of submicrogram amounts of iron from a highly acidic medium, because of the comparatively high levels of iron in the 8-hydroxyquinoline.

EXPERIMENTAL

Reagents

Hydrochloric acid (5*M*) prepared from reagent-grade acid was purified by passage through a column of Amberlite IR 400 anion-exchange resin to remove $[FeCl_4]^-$. "Ultrex" hydrochloric acid (J. T. Baker) and a stock quality purified by sub-boiling distillation were also used in various experiments. Phosphorus pentoxide (P_2O_5) ("Ultrex", J. T. Baker), practical grade $POCl_3$, reagent grade hydrazine (NH_2NH_2), and demineralized water, which was subsequently distilled in an all-quartz apparatus, were also used.

One litre of 0.15*M* hydrochloric acid–1% hydrazine reagent was prepared by neutralizing (to pH 6–7) 10 ml of hydrazine with 63 ml of pure 5·0*M* hydrochloric acid. A sufficient volume of 12.5*M* hydrochloric acid, purified by sub-boiling distillation, was then added so that a final hydrochloric acid concentration of 0.15*M* was obtained on diluting the mixture to 1 litre.

Procedures

Preparation of ion-exchange columns. Seven quartz columns (1.3 × 38.1 cm) with Teflon stop-cocks and fritted quartz disks were heated in nitric acid (1 + 1) overnight and rinsed thoroughly with pure water. These columns had also previously been used in other experiments in which they were repeatedly soaked in hot 0.1*M* EDTA at a pH of 8.0. The clean columns were filled to a height of 10 cm with an aqueous slurry of Amberlite IR 400 (40–60 mesh) resin, a strongly basic quarternary ammonium anion-exchange resin in the chloride form. A small pad of quartz wool (~1 cm) ("Spectrosil" grade) was placed between the resin and the quartz frit and also at the top of the resin column. Each resin bed was then purified by passage of 100 ml of nitric acid (1 + 1), followed by 50 ml of purified 5.0*M* hydrochloric acid. While this study was in progress, it was found that a subsequent elution of the column with 30.0 ml of 0.15*M* hydrochloric acid–1% hydrazine solution followed by elution with 50.0 ml of pure 5.0*M* hydrochloric acid provided the ultimate procedure for purifying the ion-exchange resin with respect to iron.

Hydrolysis of phosphorus oxychloride. A 100-ml sample of reagent-grade phosphorus oxychloride was pipetted dropwise into 300 ml of pure water in a 1000-ml Pyrex beaker, placed on a hot-plate fitted with a magnetic stirrer. After the addition of each 2.0-ml portion of $POCl_3$, the solution was allowed to react while being vigorously stirred. The exothermic reaction proceeded very slowly at first, but occurred instantaneously after approximately 25 ml of the reagent had been added. Once the hydrolysis was well under way, the temperature of the mixture rose sharply and had to be maintained at 40–50° to prevent excessive loss of hydrogen chloride vapours. The mixture was then diluted in a volumetric flask to a final volume of 500 ml. During this procedure no extra precautions were

taken to prevent loss of $POCl_3$ as the vapour. In a subsequent paper, the quantitative determination of iron in $POCl_3$ and also experimental procedures for the quantitative hydrolysis of the reagent will be described.

A high-purity synthetic hydrolysed $POCl_3$ solution (250 ml) was also prepared, as follows. Phosphorus pentoxide (38.68 g) was weighed in a dry-box (argon atmosphere) and then transferred in a plastic bag to a fume hood. A 1000-ml precleaned Teflon beaker was then placed in a large polyethylene bag, 50 ml of pure water were added, and small portions of the P_2O_5 were added until all of the solid was dissolved. The beaker in which the solid P_2O_5 was initially contained and also the walls of the beaker containing the solution were rinsed with water from a wash-bottle. Hydrochloric acid (10.3*M*, purified by sub-boiling distillation, 162.6 ml) was added to a 250-ml volumetric flask, then the mixture in the beaker was quantitatively transferred to the flask, and the whole diluted to volume with pure water. The resulting solution was filtered through high-purity quartz wool ("Suprasil", washed with hydrochloric acid) in a separatory funnel to remove carbonaceous particles. The final solution, which contained phosphoric and hydrochloric acids at 2.18 and 6.72*M* concentrations respectively, was stored in a tightly capped Teflon (FEP) bottle.

Iron carrier and tracer solutions. Iron carrier solution (10 ml, 1000 μg/ml) was evaporated to near dryness in a 100-ml beaker after the addition of 2.0 ml of 30% hydrogen peroxide, then quantitatively transferred with 5.0*M* hydrochloric acid to a 10-ml volumetric flask and diluted to volume with the 5.0*M* acid.

^{59}Fe tracer (New England Nuclear) was mixed with 1.0 ml of 30% hydrogen peroxide, and with sufficient concentrated hydrochloric acid to give 5.0 ml of solution 5.0*M* in hydrochloric acid. The tracer solution was then heated to boiling in a 100-ml Teflon beaker on a hot-plate located in a radiochemical hood. ^{60}Co impurity and Fe^{2+} were then removed from the oxidized tracer by ion-exchange chromatography (see procedure below for ion-exchange separation).* The eluate containing $^{59}Fe^{3+}$ (in 0.15*M* hydrochloric acid) was evaporated in a Teflon beaker to near dryness and then diluted with 5.0*M* hydrochloric acid to a final volume of ≤ 5.0 ml. A large Pyrex beaker (1000-ml) inverted over the smaller Teflon one (100 ml) prevented contamination of the hood with ^{59}Fe. Both carrier and tracer solutions were freshly reoxidized before use in experiments requiring the minimum amount of Fe^{2+}.

Throughout these experiments precautions were specially taken to minimize introduction of iron contamination during the studies with submicrogram amounts. The reagents, the sublimed P_2O_5 and sub-boiling-distillation hydrochloric acid, typically had iron concentrations of <20 ng/g and 3 ng/g respectively. The amount of iron carrier introduced by adding the high specific activity isotope (15 Ci/g) was estimated to be less than 10 ng. Spot-test comparisons with known aqueous solutions of iron were performed. Iron contamination from the ion-exchange resin was judged to be negligible, since the columns were prepurified before use with the 0.15*M* hydrochloric acid–1% hydrazine eluent. This eluent was found to remove all isotopically labelled ^{59}Fe from a column. Thus it is not likely that exchangeable iron contamination from the prepurified columns subsequently contaminated the samples that were chromatographed. Although quantitative measurements of iron in blanks for the separation procedures were not attempted during these investigations, which were made to establish the exchange behaviour of ultratrace iron, reagents and solutions that contained no phosphate were tested for iron by a semiquantitative carbon-rod atomic-absorption procedure. Total iron in the acids, hydrazine reagents and eluates was below the detection limit of 5 ng/ml.

Elution of $^{32}PO_4^{3-}$ and $^{59}Fe^{3+}$. Portions of either hydrolysed reagent-grade $POCl_3$ or synthetically prepared high-purity solutions (usually 50 ml) were doped with 0.1–0.5 ml of solutions of $NaH_2{}^{32}PO_4$ (New England Nuclear Corp.) in water or $^{59}Fe^{3+}$ in 5.0*M* hydrochloric acid. Enough of each isotope was added to give a count rate of $\geq 10^4$ counts in collected fractions during a period of 5 min or less.

Measured aliquots (2.0–20.0 ml) of the tagged solutions were passed through an ion-exchange column as described above. Following the sorption of the sample onto the column, the section of the quartz tube above the resin (~12 cm) was rinsed with four 3-ml portions of 5.0*M* hydrochloric acid added from a polyethylene wash-bottle, the solution being allowed to fall to the level of the top of the resin after each rinse. The first eluent, 5.0*M* hydrochloric acid, was then added to the reservoir and its level in the column maintained by continuous addition from a separatory funnel during the elution. The eluate was collected automatically in polystyrene test-tubes in a Beckman Model 132 fraction-collector.

For elution of ^{32}P species 4.0-ml fractions were collected. Equal aliquots (100 μl) of each fraction were added to 15.0 ml of liquid scintillation solution, Scintisol-C, thoroughly mixed by shaking in capped glass scintillation vials, and counted for 2 min in a Beckman LS-230 liquid scintillation system.

For the separation of ^{59}Fe from the phosphate–chloride medium it was first necessary to elute with enough 5.0*M* hydrochloric acid for complete removal of species containing phosphorus. Iron was then eluted by passage of 0.15*M* hydrochloric acid either alone or containing 1% of hydrazine. Fractions (4.0 ml) were collected in polystyrene test-tubes and counted either in a well-type (3 × 3 in.) sodium iodide detector with appropriate amplifiers, single-channel analyser and scaler, or with a Northern 1024 multichannel analyser. The latter was used for measuring the γ-ray activity from the most active fractions. Qualitative elution profiles were constructed by plotting the gamma or beta activity of each fraction against the total volume of eluate collected. The wide range of activity levels resulted in dead-lines ranging from 0 to 90% for the least and most intense γ-emitting fractions respectively. Thus, plots of γ-ray activity *vs.* total volume of eluate were used only to determine the volume of eluate required for complete elution of iron. Where quantitative rather than qualitative assessments were made from counting data, samples were diluted before counting, to minimize dead-times.

Quantitative investigations of the retention and recovery of iron and phosphate during ion-exchange separations were performed as described below. Samples of hydrolysed $POCl_3$ containing $^{59}Fe^{3+}$ were applied to three columns and eluted as already described, with 70.0 ml of 5.0*M* hydrochloric acid. The eluates were collected in 100-ml volumetric flasks and diluted to volume with 5.0*M* hydrochloric acid. The iron was then eluted (with 0.15*M* hydrochloric acid or 0.15*M* hydrochloric acid–1% hydrazine and the appropriate volumes of eluate were collected in volumetric flasks and diluted to known volumes.

Ten ml of each diluted eluate were pipetted into glass vials and counted with a well-type NaI(Tl) detector. In counting the original sample, it was necessary to dilute suitable aliquots to 10 ml to avoid excessively large relative dead-times. In most cases an aliquot of each initial sample was selected so that its dead-time, registered on the Northern PHA, matched that for the eluate within ~2% absolute dead-times. For example, the dead-times registered during five experiments, each of which involved three independent

* Failure to oxidize all Fe^{2+} with peroxide may be due to catalytic decomposition of the peroxide by the Haber–Weiss mechanism being complete before all the Fe^{2+} has reacted.

ion-exchange separations of iron, and the corresponding values (in brackets) for the original samples were: (*i*) 13, 13, 13 (11); (*ii*) 8, 8, 8 (12); (*iii*) 11,11, –, (11); (*iv*) 10, 10, 10, (11); (*v*) 10, 10, 10, (11)% [the third sample for experiment (*iii*) was lost by accident].

The efficiency of the removal of phosphate from the iron fraction was determined quantitatively in a manner similar to that described for iron. Samples undoped with tracer were chromatographed and aliquots of the eluates with 5.0*M* hydrochloric acid and 0.15*M* hydrochloric acid–1% hydrazine were analysed for phosphate by gravimetric and spectrophotometric methods respectively.

Upon hydrolysis of $POCl_3$ with an excess of water a highly acidic medium is produced in which iron would be present predominantly as $[FeCl_4]^-$. Complexation by phosphate as $[FeH_{3-x}PO_4]^{(3-x)+}$, where x is 1–3 is also possible. However, the hydrolysis conditions can be selected so that the iron is predominantly in the form $[FeCl_4]^-$ which is readily formed in $\geq 4.0M$ hydrochloric acid. Exchange of $[FeCl_3]^-$ ions for Cl^- on R^+Cl^-, a strongly basic anion-exchange resin, Amberlite IR 400, should be possible. Quantitative uptake of iron by anion-exchange from the phosphate–chloride medium cannot be accomplished if reactions that generate cationic or neutral species of iron, for example reactions yielding $[FeH_{3-x}PO_4]^{(3-x)+}$, are significant. The presence of significant amounts of bivalent iron following hydrolysis must also be precluded.

Separation of extremely small amounts ($<1\ \mu g$) of iron from phosphorus-containing species may be complicated by simultaneous exchange of anionic forms of phosphoric acid for chloride ions on the resin. Displacement of these $[H_{3-x}PO^4]^{x-}$ species from the resin, while $[FeCl_4]^-$ is retained, should be possible by elution with hydrochloric acid ($\geq 5.0M$), in which phosphate should be largely in the form of undissociated H_3PO_4.

Iron retained by the resin can then be recovered by eluting the resin with a solution $\sim 0.5M$ in acid.[4] An alternative approach, removing phosphate by column chromatography under conditions allowing the elution of iron, was considered but not attempted. Available selective column materials used previously by others to remove phosphate did not have sufficient capacity to retain the amounts of phosphate produced by hydrolysing samples of $POCl_3$.[5,6]

RESULTS AND DISCUSSION

Elution profiles of $H_{3-x}PO_4^{x-}$ *and iron*

Upon hydrolysis of $POCl_3$ with water (1:4 by volume and diluting the resulting mixture to five times the original volume of $POCl_3$) a solution is obtained in which the phosphoric acid is only $\sim 0.1\%$ dissociated. Aliquots of such a solution were spiked with $H_3{}^{32}PO_4$ and eluted through a 10-cm resin bed of Amberlite IR 400 under conditions that were preselected to be adequate for the retention of iron. Monitoring the elution of a 20-ml sample by liquid scintillation counting showed that 60 ml of 5.0*M* hydrochloric acid were adequate for eluting phosphorus species (see Fig. 1). When a 3.0-cm column of resin was used this volume was reduced to 45 ml.

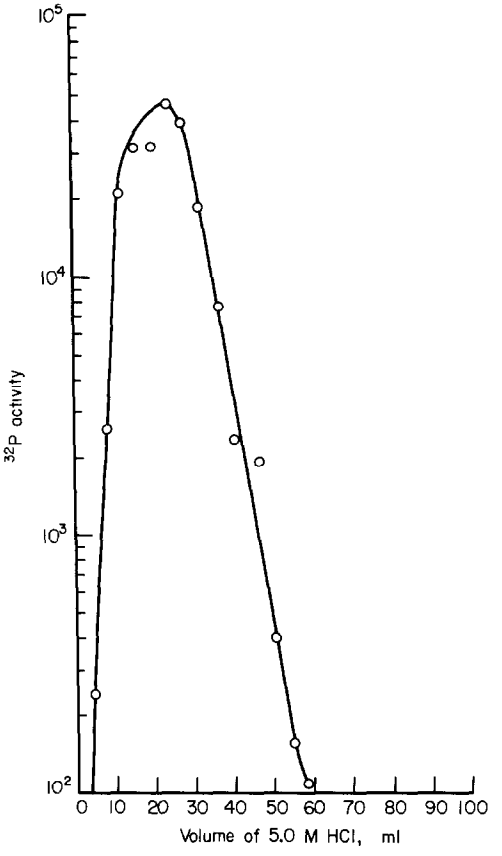

Fig. 1. Elution of phosphorus species from a column of Amberlite IR 400 with 5·0*M* HCl, 10-cm resin bed, flow-rate 1 ml/min.

The loss of iron from the column during the elution of phosphoric acid species and the subsequent elution of microgram quantities of iron with 0.15*M* hydrochloric acid was followed qualitatively by using ^{59}Fe. An elution curve obtained from a 20-ml sample containing 1.0 μg of iron per ml, had two peaks, one in the 5.0*M* hydrochloric acid fraction and the other in the 0.15*M* hydrochloric acid eluate. Pulse-height analysis showed photopeaks for ^{60}Co (an impurity in the ^{59}Fe tracer) and ^{59}Fe in the first eluate, but only for ^{59}Fe in the second. The ^{59}Fe γ-ray activity in the fraction that would contain species of $[H_{3-x}PO_4]^{-x}$ was small. After 90 ml of 0.15*M* hydro-

Table 1. Separation factors for phosphate

Sample	Concentration of phosphate		S.F.*
	5.0*M* HCl	0.15*M* HCl	
1	0.0381 g/ml	0.02 μg/ml	1.90×10^6
2	0.0378	0.01	3.78×10^6
3	0.0382	0.07	5.45×10^5

* S.F. = separation factor = $[PO_4^{3-}]$ in 5.0*M* HCl fraction/$[PO_4^{3-}]$ in 0.15*M* HCl fraction.

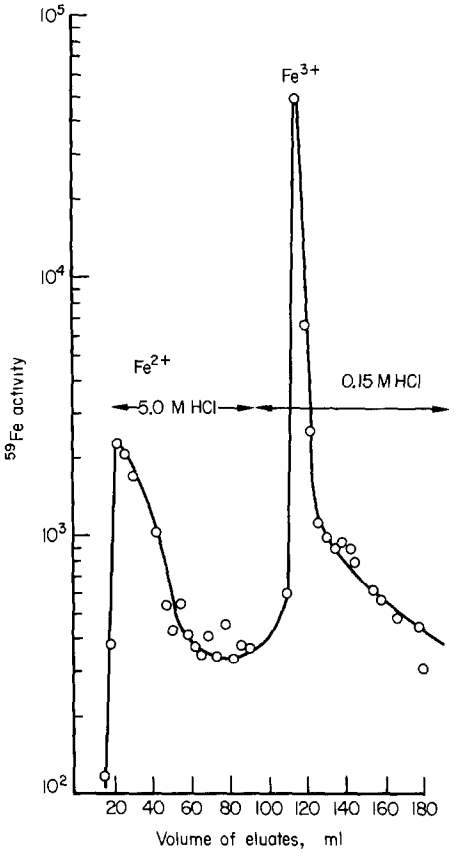

Fig. 2. Elution of submicrogram amounts of iron from a 10-cm column of Amberlite IR 400 with hydrochloric acid.

chloric acid eluate had been collected considerable tailing was observed and the γ-ray activity of the eluate was still ~700 counts above background. A survey of the column with a Geiger-Müller tube showed only a small amount of ^{59}Fe activity remaining on the resin.

By using the elution volumes established from previous experiments (70 ml of 5.0*M* hydrochloric acid and 90 ml of 0.15*M* hydrochloric acid) the efficiency of the ion-exchange method for removing phosphate from the fraction that would contain iron was determined. The separation factors reported for phosphate in Table 1 demonstrate an extremely effective method. The low quantities of phosphate in the 0.15*M* acid eluate will not interfere in the spectrophotometric determination of iron with ferrozine.[6] Also, the Coprex X-ray fluorescence method should be applicable for the iron determination.[7]

The elution of submicrogram amounts of iron was then monitored qualitatively. In this case a 20-ml sample doped only with radiotracer iron (the Fe^{3+} added was estimated from specific activity data to be ≤10 ng) was treated. The elution curve in Fig. 2 shows some ^{59}Fe activity in the 5.0*M* hydrochloric acid fraction, which is attributed to the presence of small amounts of Fe^{2+} or the $[FeH_{3-x}PO_4]^{(3-x)+}$ species. No correlation was observed between the size of this peak and the initial amount of iron in the solution. The tailing of iron(III) during elution could

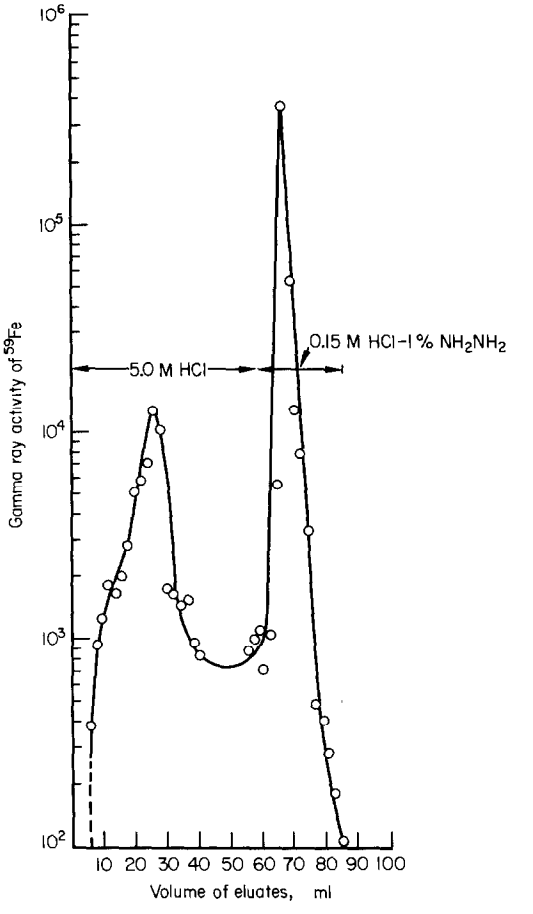

Fig. 3. Elution of submicrogram amounts of iron from a 10-cm column of Amberlite IR 400 with 0.15*M* HCl–1% hydrazine, flow-rate 1 ml/min.

Table 2. Recovery of Fe by elution with 0.15*M* HCl (^{59}Fe tracer only)

Column no.	Activity of 5.0*M* HCl eluate	Activity of 0.15*M* HCl eluate	Retention, %*	Recovery, %†
1	2725	115290	99.3	28.2
2	3256	111920	99.2	27.4
3	2817	107030	99.3	26.2
		409040‡		

* Fraction of initial activity retained by the column.
† Fraction of original activity eluted from the resin in the 0.15*M* HCl fraction.
‡ Total initial activity of sample applied to the column.

Table 3. Quantitative separation of Fe^{3+}

Fe^{3+} added, *ng*	Column Number	Activity of 5.0*M* HCl eluate	Activity of resin	Activity of 0.15*M* HCl–1% NH_2NH_2 eluate	Retention, %*	% Recovery†
125	2	867	—	445440	99.8	~100
	3	3457		445585	99.2	~100
				445455§		
50	1	10506	3953	889270	98.8	98.9
	2	7689	2177	908710	99.1	101
	3	4508	12625	887975	99.5	98.8
				898315§		

* Fraction of initial activity retained by the resin.
† Fraction of original activity eluted in 0.15*M* HCl–1% NH_2NH_2 fraction.
§ Total initial activity of sample applied to the column, mean of 2 or 3 measurements.

Table 4. Quantitative separation of $^{59}Fe^{3+}$

Fe^{3+} added, *ng*	Column Number	Activity of 5.0*M* HCl eluate	Activity of resin	Activity of 0.15*M* HCl–1% NH_2NH_2 eluate	Retention, %*	% Recovery†
25	1	7145	—	428910	98.4	97.3
	2	14671	—	427770	96.6	97.1
	3	13352	—	427910	96.9	97.1
				440697§		
10	1	262	1049	197152	99.9	97.6
	2	250	673	197277	99.9	97.7
	3	4180	409	191821	97.9	95.0
				201868§		

§ Total initial activity of sample applied to the column, mean of 2 or 3 measurements.

result from the presence of carboxyl groups on the resin.[8] A survey of the resin eluted with 0.15*M* hydrochloric acid showed considerable γ-ray activity remaining on the ion-exchange column.

To examine this separation quantitatively, three samples of a synthetically prepared, high-purity hydrolysed stock solution were treated by ion-exchange and the retention and recovery of iron were measured. The results in Table 2 showed (1) negligible loss of iron in the 5.0*M* hydrochloric acid eluate, (2) precise execution of the separation procedure, (3) quantitative retention of the iron and (4) adequately precise, but low recovery values. These observations are consistent with the known behaviour of ultratrace elements during ion-exchange. For example, the ease of purifying water and other solutions attests to the quantitative retention of submicrograms of various elements during ion-exchange. However, procedures for quantitatively and precisely recovering such traces once retained by ion-exchange resins have not yet been developed for general use in trace analysis. Clearly, the present method satisfies the primary conditions [items (1)–(3) listed above] for a quantitative method. However, it would be necessary to determine the recovery values by radioisotope techniques for the entire range from 1 μg to 10 ng of iron. A recovery determination for each sample and for each point on a calibration curve would also be required.

The need to use this involved procedure for determining iron was eliminated by successively recovering submicrogram amounts of iron quantitatively by adding a reducing agent, hydrazine, in 1% concentration to the 0.15*M* hydrochloric acid eluent. This reductant was chosen because it can be easily ultrapurified by a cryogenic sublimation process.[9] The successful use of the new eluent, 0.15*M* hydrochloric acid–1% hydrazine, for quantitatively recovering traces of iron depends on carefully following special procedures during the preparation of the eluent (see EXPERIMENTAL). A sample containing 1.0 μg of iron was processed with this eluent and the graph for the elution of iron is shown in Fig. 3. Several significant improvements in the elution of iron were obtained with this reagent. Forty ml of the hydrazine eluent are sufficient to elute iron from the column. The tailing effect shown in Fig. 2 is eliminated, and the γ-ray activity in the last fractions collected from the column is reduced to the background level.

To determine whether the size of the peak for Fe^{2+} was a function of the conditions of hydrolysis, elution profiles for iron in samples of reagent-grade $POCl_3$, hydrolysed with pure water and also with water containing 0.6% hydrogen peroxide were obtained. These samples were shown by atomic-absorption spectroscopy to contain at least 1 μg of iron per ml. As observed previously, ^{59}Fe peaks were found in the 5.0*M* hydrochloric acid and the 0.15*M* hydrochloric acid–1% hydrazine eluates for both samples. Since the sizes of the respective peaks (peak heights) for each sample were nearly equivalent, any significant

amounts of Fe^{2+} originally present in the $POCl_3$ are oxidized during the hydrolysis. Autoxidation of Fe^{2+} is expected to be rapid since previous comprehensive studies have demonstrated that this process occurs spontaneously in hydrochloric acid of $\geq 4.0M$ concentration.[10]

Estimations (from elution curves) of the fraction of iron lost as $^{59}Fe^{2+}$ were not attempted. In separate experiments designed to optimize all parameters affecting the counting of γ-ray activity in the eluate, the retention and recovery of iron were measured quantitatively. Results for the recovery of 10–125 ng of iron added to hydrolysed $POCl_3$ samples are reported in Table 3. They demonstrate that this method for the ion-exchange separation of submicrogram amounts of iron from a phosphate–chloride medium is satisfactorily quantitative. We have been able to use it consistently and have found it reliable.

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SHORT COMMUNICATIONS

PREPARATION D'UN TAMPON UNIVERSEL DE FORCE IONIQUE 0,3 *M*

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Résumé—On décrit la préparation d'un tampon universel de force ionique 0,3*M*, pour son utilisation dans diverses techniques analytiques. On a calculé la quantité d'electrolyte nécessaire pour ajuster la valeur de cette force ionique et les valeurs théoriques du pH, et on observe une grande similitude entre eux et ceux qui ont été déterminées expérimentalement.

Le tampon de Prideaux,[1] qui a été étudié avec plus de detail par Britton et Robinson,[2] est formé par un mélange d'hydroxyde de sodium et d'acides acétique, phosphorique et borique, et il a été amplement utilisé dans diverses techniques analytiques, spécialement en polarographie.[3]

La petite capacité régulatrice de ce tampon peut être dans certains cas un grand inconvénient, mais malgré cela il présente le grand avantage de couvrir une large marge de pH ce qui est très utile pour mener à bon terme l'étude d'une propriété face à une variation continuelle de l'acidité, chose fréquente dans l'investigation analytique.

Lors d'une étude antérieure[4] nous avons calculé la valeur de sa force ionique à partir des constantes des équilibres ioniques présents. On y a décrit aussi une préparation des diverses solutions tamponnées qui a l'avantage, face à la preparation originale, de maintenir constant le volume final de la solution, mais son utilisation reste encore embarrassante parce qu'il faut varier constamment aussi bien la concentration des acides comme celle de l'hydroxyde de sodium.

Dans la présente étude, par contre on maintient aussi constant le volume final des solutions et en plus on a simplifié sa préparation en variant seulement la quantité de l'hydroxyde de sodium pour modifier le pH, tandis qu'on maintient constante la concentration des acides.

Puis qu'on a démontré que lors des diverses techniques analytiques on doit tenir compte de l'influence de la force ionique,[5–8] nous avons calculé la quantité de chlorure de potassium, ou de n'importe quel électrolyte uni-univalent, que l'on doit ajouter aux solutions tamponnées pour arriver à une force ionique 0,3*M*. Cette valeur est fréquente dans l'analyse polarographique, et c'est la moindre force ionique que l'on peut atteindre avec la préparation que l'on décrit ici. En utilisant des solutions des acides et d'hydroxyde de sodium plus diluées on pourrait diminuer la valeur de la force ionique mais la si petite capacité régulatrice du tampon diminuerait aussi.

Calcul de la quantité d'électrolyte

Pour calculer la quantité nécessaire de chlorure de potassium qui permette ajuster la force ionique de la solution jusqu'à 0,3*M* on a déterminé les coefficients d'activité de chacune des espèces ioniques présentes. Dans une solution de cette force ionique l'équation de Debye–Hückel n'est pas directement applicable;[9] c'est pourquoi nous avons calculé ces coefficients en introduisant l'approximation de Davies.[10]

A partir de ces coefficients d'activité et des constantes d'équilibre de force ionique zéro[11,12] on a calculé les constantes d'equilibre à force ionique 0,3*M* et à 25°, dont les p*K* s'indiquent dans le tableau 1.

Finalement dans le tableau 2 on indique la quantité de chlorure de potassium nécessaire pour maintenir la force ionique de 0,3*M*. On a calculé ces valeurs en les associant au volume d'hydroxyde de sodium ajouté, et on est arrivé à cette relation en tenant compte les huit équilibres de dissociation, la condition d'électroneutralité de la solution, les équations de balance de matière pour les acides acétique, phosphorique et borique et la valeur de la force ionique en fonction des concentrations des différentes espèces ioniques présentes. De la même manière, à partir de ce système d'équations on a calculé les valeurs théoriques du pH de chacune des solutions.

Préparation des solutions tamponnées

Solution acide 0,16*M* dans chacun des acides acétique, phosphorique et borique. Solution d'hydroxyde de sodium 0,80*M*. Solution de chlorure de potassium de 100,00 g/l.

La préparation des différentes solutions tamponnées est menée a bon terme en fioles jaugées de 100 ml, en ajoutant à chacun d'eux 25,00 ml de la solution acide et les volumes de solution d'hydroxyde de sodium et de chlorure de potassium indiqués dans le tableau 2. Le volume de ces solutions occupe environ 50% du total, ce qui laisse une marge suffisante pour ajouter la solution problème en étude. Finalement on amenent toutes les solutions à 100 ml.

Les valeurs de pH indiquées dans le tableau 2 ont été déterminées à 25° avec un potentiomètre Radiometer, pH Meter 26, avec un électrode de calomel R 809 et un autre de verre G 202 B. L'étalonnage a été réalisé à deux valeurs de pH en utilisant les tampons potassium dihydrogénophosphate Merck 4881 (pH = 6,865 à 25°) et borate Merck 6315 (pH = 9,180 à 25°).

Dans la graphique 1 on représente ces valeurs en fonction du volume d'hydroxide de sodium ajouté et en les comparant avec les valeurs calculées théoriquement, repre-

Tableau 1. Constantes de dissociation à $I = 0{,}3M$ (25°C)

	pK_1	pK_2	pK_3
Eau	13,78		
Acétique	4,55		
Phosphorique	1,94	6,72	11,64
Borique	9,02	12,34	13,00

Tableau 2.

pH	NaOH, *ml*	KCl, *ml*	β	pH	NaOH, *ml*	KCl, *ml*	β
1,90	0,00	21,14	0,067	6,79	13,00	12,83	0,021
1,95	0,05	21,02		7,00	13,50	12,25	
2,02	1,00	20,89	0,050	7,17	14,00	11,68	0,014
2,11	1,50	20,75		7,47	14,50	11,13	
2,18	2,00	20,59	0,036	7,75	15,00	10,63	0,011
2,27	2,50	20,42		8,19	15,50	10,23	
2,40	3,00	20,23	0,023	8,46	16,00	9,89	0,018
2,53	3,50	20,03		8,73	16,50	9,57	
2,74	4,00	19,82	0,012	8,90	17,00	9,26	0,023
3,04	4,50	19,60		9,04	17,50	8,95	
3,38	5,00	19,35	0,012	9,25	18,00	8,64	0,021
3,81	5,50	19,07		9,48	18,50	8,32	
4,06	6,00	18,78	0,022	9,63	19,00	8,00	0,013
4,27	6,50	18,48		9,94	19,50	7,65	
4,43	7,00	18,18	0,024	10,24	20,00	7,20	0,012
4,58	7,50	17,87		10,65	20,50	6,58	
4,76	8,00	17,57	0,023	10,89	21,00	5,88	0,022
4,90	8,50	17,25		11,17	21,50	5,16	
5,11	9,00	16,93	0,017	11,26	22,00	4,45	0,030
5,30	9,50	16,58		11,42	22,50	3,74	
5,57	10,00	16,18	0,015	11,53	23,00	3,06	0,044
5,79	10,50	15,69		11,66	23,50	2,39	
6,10	11,00	15,14	0,022	11,71	24,00	1,73	0,067
6,28	11,50	14,58		11,86	24,50	1,10	
6,46	12,00	14,00	0,024	11,91	25,00	0,47	
6,66	12,50	13,41					

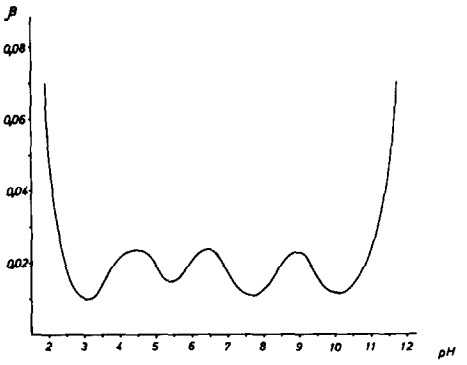

Fig. 2.

Tableau 3. Variations du pH avec la température

20°C	25°C	30°C
2,01	2,02	2,02
4,06	4,06	4,06
6,11	6,10	6,09
8,20	8,19	8,17
9,97	9,94	9,90
12,01	11,91	11,76

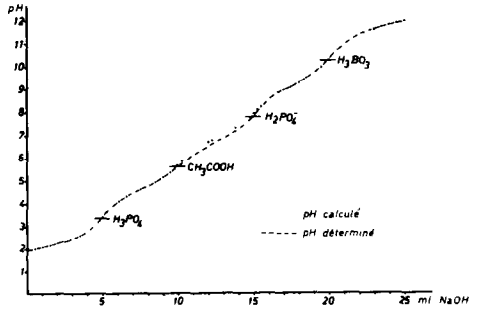

Fig. 1.

sentées aussi dans la même graphique. On observe dans tout l'intérvale, une grande concordance entre ces deux courbes, qui présentent la plus grande déviation entre pH 5,5 et 8. La valeur moyenne des déviations entre les valeurs calculées et les valeurs expérimentales étant de 0,066.

Les valeurs de la capacité régulatrice sont indiquées dans le tableau 2, étant representées dans la figure 2.

On a déterminé aussi la variation du pH en fonction de la température. Les valeurs trouvées s'indiquent dans le tableau 3.

Summary—The paper describes preparation of a universal buffer with ionic strength 0.3*M*. The calculated pH values agree well with those experimentally observed.

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ETUDE DU POUVOIR OXYDANT DE QUELQUES PERIODATES DE TETRAALKYLAMMONIUM EN MILIEU NON AQUEUX

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Résumé—Le pouvoir oxydant de quelques periodates de tétraalkylammonium en milieu non aqueux a été étudié par électrochimie. Des mesures conductimétriques et spectrophotométriques suggèrent l'existence de différentes formes de periodates en fonction de leur concentration et de la nature du solvant. L'étude d'une relation entre leur structure et leur activité a été abordée.

L'acide periodique et ses sels sont peu solubles dans les solvants organiques et de ce fait limitent le champ d'application de la periodimétrie aux substances solubles dans l'eau. Cependant, Qureshi *et al.*[1] et plus récemment Guernet *et al.*[2–5] ont utilisé des periodates d'ammonium quaternaire solubles dans les solvants organiques usuels: ils ont montré la possibilité d'oxyder des molécules organiques insolubles dans l'eau.

Les différentes études en milieu non aqueux effectuées à ce jour concernent essentiellement le domaine d'application et la cinétique d'oxydation d'α-diols en fonction de la nature de l'ammonium quaternaire et du solvant utilisés. Les mécanismes d'oxydation par l'acide periodique ou ses dérivés sont relativement mal connus. Buist *et al.* ont étudié leurs solutions aqueuses et ils ont montré qu'il existait différentes formes d'anions periodates en équilibre en fonction du pH de la solution.[6] La formation en milieu alcalin d'un dimère avec l'oxygène de type $(O_4I–O–IO_4)^{4-}$ a également été proposée.[7]

Comme mécanisme réactionnel, Buist *et al.* ont suggéré la formation d'un complexe cyclique intermédiaire entre le diol et les anions periodates.[8] En milieu non aqueux les phénomènes semblent encore plus complexes, en raison de l'intervention du solvant dont les interactions avec les solutés sont moins bien connues que dans l'eau.

Ce travail* dont nous rapportons ici les premiers résultats, est une tentative d'interprétation des mécanismes d'oxydation des periodates d'ammonium quaternaire en tenant compte de leur pouvoir oxydant dans des solvants de nature différente.

RESULTATS

Les potentiels de demi-vague de réduction de quelques periodates de tétraalkylammonium, synthétisés au laboratoire ont été déterminés: periodates de tétraméthyl, tétraéthyl, tétrabutyl et tétrapentylammonium. Parallèlement une étude de leurs solutions par conductimétrie et spectrométrie ultraviolette dans quatre solvants différents a été réalisée. Enfin, les résultats de l'étude de cinétique de l'oxydation de l'éthane-diol et du mésobutane-diol (pinacol) par le periodate de tétrabutylammonium dans ces solvants sont présentés.

Etude voltampérométrique

Si les periodates d'ammonium quaternaire ne sont pas réductibles à une électrode de platine ou de graphite, ils se réduisent à une électrode de mercure en deux étapes; les courants de diffusion sont dans le rapport 1 à 3. Par analogie avec les résultats obtenus en solution aqueuse,[9,10] il est possible de proposer un schéma réactionnel comparable à celui proposé en milieu aqueux:

$$IO_4^- + 2e^- \rightarrow IO_3^- + O^{2-}$$

$$IO_3^- + 6e^- \rightarrow I^- + 3O^{2-}.$$

En milieu protoné, les réactions deviennent:

$$IO_4^- + 2H^+ + 2e^- \rightarrow IO_3^- + H_2O$$

et

$$IO_3^- + 6H^+ + 6e^- \rightarrow I^- + 3H_2O.$$

Les potentiels apparents de demi-vague de réduction des quatre periodates de tétraalkylammonium dans l'éthanol, l'acide acétique, le dichlorométhane et le carbonate de propylène sont rapportés dans le tableau 1. (Ces potentiels sont calculés par rapport au système ferrocène/ferrocinium dont le potentiel est supposé indépendant du solvant.)

Bien que les systèmes électrochimiques mis en jeu soient des systèmes lents et qu'il ne soit pas possible de relier directement les valeurs trouvées aux potentiels normaux des systèmes, les différences observées d'un solvant à l'autre sont suffisamment importantes pour comparer le pouvoir oxydant des espèces selon la nature du milieu.

Etude conductimétrique et spectrométrique

Les courbes reliant les valeurs des conductibilités équivalentes aux concentrations en periodate de tétrabutylammonium dans trois solvants différents, carbonate de propylène, dichlorométhane et éthanol, de constantes diélectriques respectivement égales à 64,7, 8,9 et 24,3 sont présentées dans la figure 1.

L'étude en spectrométrie ultraviolette des solutions de periodate de tétrabutylammonium permet de classer les solvants précédents en deux groupes.

(1) Dans le carbonate de propylène et le dichlorométhane, on observe par dilution un effet hypsochrome marqué en solution $10^{-3}M$. Le maximum d'absorption se situe à 238 nm alors qu'il se trouve à 210 nm en solution $10^{-5}M$.

(2) Dans l'éthanol et l'acide acétique, la dilution n'a aucune influence sur le maximum d'absorption: il est de 215 nm dans l'éthanol et de 245 nm dans l'acide acétique.

Une étude comparative avec les autres periodates de tétraalkylammonium a montré que la variation de la longueur de la chaîne n'entraîne aucune modification.

Cinétique d'oxydation de l'éthane-diol et du pinacol par le periodate de tétrabutylammonium dans différents solvants

Dans le but de comparer les valeurs des potentiels de demi-vague de réduction du système IO_4^-/IO_3^- calculés par électrochimie, au pouvoir oxydant vis-à-vis des diols, nous avons étudié la cinétique d'oxydation d'un α-diol primaire-

* Ce mémoire est une partie de la Thèse de Doctorat d'Etat en Pharmacie à soutenir par Mademoiselle A. Portalier.

Tableau 1. Potentiel (V) de demi-vague de réduction du système IO_4^-/IO_3^- par rapport au système ferrocène/ferrocinium (electrode à goutte de mercure, $\tau = 1$ sec)

Periodate	Ethanol	Acide acétique	Dichlorométhane	Carbonate de propylène
tétraméthylammonium	−0,500	0,000	insoluble	−0,890
tétraéthylammonium	−0,450	0,000	−0,880	−0,905
tétrabutylammonium	−0,510	0,000	−0,860	−0,900
tétrapentylammonium	−0,445	0,000	−0,865	−0,905

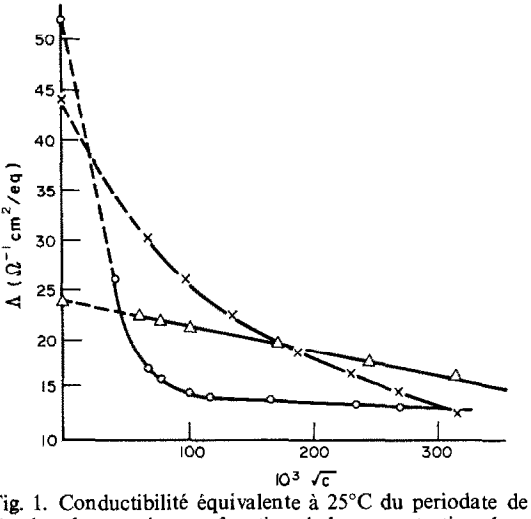

Fig. 1. Conductibilité équivalente à 25°C du periodate de tétrabutylammonium en fonction de la concentration dans ▲ le carbonate de propylène, ○ le dichlorométhane, × l'ethanol.

primaire (éthane-diol) dans les quatre solvants précédents. Nous nous sommes limités au periodate de tétrabutylammonium puisque les valeurs des potentiels de demi-vague ne varient pas significativement en fonction de la longueur des chaînes alkylées. Le rapport des concentrations entre le diol et l'oxydant a été fixé à 40 de manière à pouvoir assimiler l'oxydation à une réaction de pseudo premier ordre.

Les déterminations de la quantité d'oxydant consommé à des temps donnés ont été effectuées selon les concentrations étudiées, soit par la méthode de Malaprade adaptée aux milieux non aqueux[5] soit par ampérométrie à potentiel imposé. Les résultats obtenus sont résumés dans le tableau 2.

Dans l'acide acétique la réaction est pratiquement instantanée; il est impossible d'effectuer des mesures permettant la comparaison valable des temps de demi-réaction en fonction de la dilution.

Une étude cinétique précédente[5] a montré que le pinacol, α-diol bitertiaire, en raison de sa configuration stérique s'oxyde relativement lentement: comme les vitesses relatives d'oxydation des différents α-diols simples (éthane-diol, 2,3 butane-diol, 1,2 propane-diol et pinacol) ne sont pas sensiblement modifiées par la nature du solvant,[5] il nous a semblé possible de compléter cette étude en remplaçant, en milieu acétique, l'éthane-diol par le pinacol. Les résultats obtenus figurent dans le tableau 3; ils sont en accord avec ceux du tableau 2.

DISCUSSION

Plusieurs facteurs sont susceptibles d'influencer le pouvoir oxydant des periodates. L'acidité du milieu joue certainement un rôle important, le potentiel normal apparent du système IO_4^-/IO_3^- est directement fonction du pH en solution aqueuse.[10,11] Le pouvoir solvatant et dissociant peut également intervenir par formation éventuelle de paires d'ions dans les solvants peu dissociants. Il semble que le facteur dominant, influençant la valeur des potentiels de demi-vague, soit le pouvoir proto-donneur des solvants étudiés. Plus le solvant est acide, plus les potentiels sont oxydants par rapport au couple ferrocène/ferrocinium pris comme référence. La valeur des potentiels (tableau 1) semble indiquer que le pouvoir oxydant des periodates décroît lorsque l'on passe de l'acide acétique à l'éthanol puis au dichlorométhane et enfin au carbonate de propylène. Il est possible de classer les solvants à partir des résultats de l'étude cinétique et de l'étude électrochimique. Ces deux classements sont différents. En effet, le temps de demi-réaction d'oxydation de l'éthane-diol est plus court dans le dichlorométhane que dans l'éthanol. Buist *et al.*[6] ont montré que la formation du complexe intermédiaire entre un diol et un periodate s'effectue en deux étapes:

—réaction entre l'ion periodate et une des fonctions alcool du diol pour former un composé de type ester,

—fermeture du cycle sur la deuxième fonction alcool.

Il est possible d'émettre l'hypothèse qu'il y ait compétition dans le cas de l'éthanol entre le solvant et le diol lors de la première étape de formation du composé intermédiaire: il en résulterait un ralentissement important de la réaction.

Tableau 3. Temps de demi-réaction (*minutes*) de l'oxydation du pinacol

Concentration en periodate, M	Acide acétique	Ethanol
$2{,}5 \cdot 10^{-2}$	0,25	oxydation très lente
10^{-3}	12	oxydation pratiquement nulle

Tableau 2. Temps de demi-réaction (*minutes*) de l'oxydation de l'éthane-diol

Concentration en periodate, M	Dichlorométhane	Carbonate de propylène	Ethanol	Acide acétique
$2{,}5 \cdot 10^{-2}$	1,8	7,3	4,8	très rapide
10^{-3}	Oxydation très lente	oxydation pratiquement nulle	280	très rapide

D'autre part, si les cinétiques des réactions restent toujours de pseudo premier ordre, les temps de demi-réaction varient en fonction de la dilution, le rapport α-diol/periodate restant constant et égal à 40.

L'examen des tableaux 2 et 3 montre que quel que soit le solvant et quel que soit le diol oxydé, la vitesse de réaction décroît avec la dilution. Les résultats des cinétiques, la conductibilité et la spectrométrie ultraviolette suggèrent que les periodates existent en solution sous des formes différentes selon leur concentration et la nature du solvant.

Les résultats obtenus en conductibilité font apparaître un comportement différent des ions periodates selon la nature du solvant. Les valeurs approchées des conductibilités limites, obtenues en extrapolant les courbes à dilution infinie, augmentent lorsque la constante diélectrique du solvant diminue (figure 1).

Une étude plus fine effectuée sur ordinateur est actuellement en cours, en tenant compte des différentes corrections qui doivent être apportées à la loi d'Onsager, en particulier dans les solvants peu dissociants. Les résultats montrent que les periodates existeraient dans le dichlorométhane et dans l'éthanol sous forme de paire d'ions. La détermination du pourcentage d'ions libres par rapport aux ions associés sera déterminée ultérieurement. Les résultats de l'étude spectrométrique montrent par ailleurs une variation des maximums d'absorption en fonction de la concentration des periodates dans le dichlorométhane et le carbonate de propylène.

Buist et Lewis[7] ont déjà observé dans le cas de l'acide periodique en milieu aqueux un déplacement similaire en spectrométrie qu'ils avaient attribué à une dimérisation en solution relativement concentrée ($10^{-2}M$).

A l'inverse de nos résultats, obtenus en milieu non aqueux, ils avaient émis l'hypothèse qu'en milieu aqueux seule l'espèce présente en solution diluée était susceptible d'oxyder le pinacol.

Ces premiers résultats montrent d'une part un pouvoir oxydant très différent en fonction de la nature du solvant et, d'autre part semblent indiquer une relation entre la structure et la réactivité des periodates en solution, qui varie selon leur concentration et selon la nature du solvant: en particulier les formes existantes en milieu concentré seraient les plus actives.

PARTIE EXPERIMENTALE

L'étude électrochimique a été réalisée à l'aide d'un polarographe Tacussel type PRG5 à une électrode à goutte de mercure. L'électrolyte support est un perchlorate d'ammonium quaternaire dont le cation est identique à celui du periodate étudié, purifié par recristallisation dans l'eau et séché à l'étuve (70°). Il est utilisé à la concentration 0,1*M*. L'électrode de référence est une électrode au calomel à remplissage aqueux (Tacussel type C10), séparée de la solution par une pastille poreuse. Les mesures conductimétriques ont été réalisées à l'aide d'un conductimètre Tacussel type CD 7 N. Les solutions sont thermostatées à 25°. Les spectres ultraviolets ont été enregistrés sur un spectrophotomètre Varian (type 635).

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Summary—The reactivity of some tetraalkylammonium periodates in periodate oxidation has been studied by electrochemistry in non-aqueous media. Conductimetric and spectrometric investigations suggest the existence of different forms of periodate, depending on the concentration and on the properties of the solvents. A study of the relation between structure and reactivity is introduced.

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SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL AND A NON-IONIC SURFACTANT

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Summary—A spectrophotometric method for the determination of trace amounts of manganese with 1-(2-pyridylazo)-2-naphthol (PAN) is described. The method is based on the measurement of absorbance of the manganese–PAN chelate solubilized with a non-ionic surfactant, Triton X-100. No extraction procedure is required in the method proposed. High concentrations of calcium, aluminium and magnesium do not interfere. The presence of up to 10 ppm of lead can be tolerated. Iron, cadmium, zinc, cobalt and nickel can be effectively masked with potassium cyanide. Beer's law is obeyed up to 2 ppm of manganese. The molar absorptivity of the manganese–PAN chelate found was 4.4×10^4 l. mole^{-1}. cm^{-1} at 562 nm. The overall stability constant of $Mn(PAN)_2$ in 0.4% Triton X-100 medium is $10^{16.8}$.

The most widely used method for the spectrophotometric determination of low concentrations of manganese in water, is the permanganate method.[1] This method is tedious because chloride has to be removed first and the oxidation should be done at elevated temperature.

Several more sensitive methods based on the formation of complexes with organic reagents have been proposed. The formaldoxime method is one such.[2–5] Interference from iron can be avoided by selectively decomposing the iron formaldoxime complex and this modification has been applied to continuous monitoring of manganese in water. This method is simple and rapid, but the conditions for selective decomposition of the iron complex are somewhat critical.

The method based on formation of the 4-(2-pyridylazo)resorcinol (PAR) chelate is very sensitive, but the absorbance of the reagent is high and the chelate is rather unstable.

1-(2-Pyridylazo)-2-naphthol (PAN) is also used for the determination of manganese.[6–12] The manganese–PAN chelate is extracted into an organic solvent such as ether or chloroform and the absorbance of the extract is determined.

Cheng and Goydish examined the use of a mixed-solvent system[11] and Cheng and Bray studied the use of gum arabic[12] to eliminate the extraction step. In the mixed-solvent system, a large volume of solvent has to be added to solubilize the manganese–PAN chelate.[11] This is a disadvantage because of the dilution caused. Gum arabic is an effective solubilizing agent, but a synthetic agent would be preferable because natural products may contain impurities.

Recently, one of us found that metal–PAN chelates can be solubilized by a non-ionic surfactant, Triton X-100.[13] Because of the high sensitivity inherent in the use of PAN, it was decided to investigate solubilization with Triton X-100 in the determination of manganese.

EXPERIMENTAL

Reagents

Standard manganese solution. Dissolve manganese sulphate in 0.1 *M* hydrochloric acid and standardize by complexometric titration with Eriochrome Black T as indicator.

PAN solution, 0.1% in methanol.

Triton X-100 solution, 20% v/v.

Triethanolamine solution, 20% v/v.

Potassium cyanide solution, 5% w/v.

Buffer solution, pH 9.2. Prepared by mixing 2*M* ammonia and 2*M* ammonium chloride.

Other metal ion solutions used were prepared from the reagent-grade sulphates, nitrates or chlorides.

Procedure

Transfer a sample containing up to 50 μg of manganese to a 25-ml volumetric flask. Add approximately 10 mg of sodium ascorbate, and then 1 ml each of the triethanolamine, buffer and Triton X-100 solutions and 0.5 ml of potassium cyanide solution. Add 1 ml of PAN solution, make up to volume with distilled water and mix well. After 10 min measure the absorbance at 562 nm against a reagent blank.

RESULTS AND DISCUSSION

Optimum conditions

The maximum absorbance of the manganese–PAN chelate occurs at 562 nm, where PAN does not absorb appreciably.

When PAN, Triton X-100 and cyanide are present in the recommended amounts the formation of the chelate is complete at pH values higher than 8.8. The absorbance of PAN becomes significant when the pH exceeds about 10. A pH of 9.2 was chosen as the optimum for these reasons and because the ammonia–ammonium buffer system has maximum buffer capacity at this pH.

A preliminary test showed that in the absence of reducing agents the red manganese–PAN chelate is decolorized in a few minutes. It is very likely that the dye is catalytically oxidized in the presence of manganese, since atmospheric oxidation of manganese(II) takes place in alkaline media.[14,15] The oxidation can be avoided by addition of a reductant such as hydroxylamine hydrochloride[10] or ascorbic acid.[6]

Table 1. The influence of diverse metal ions.

Metal	Added, μg	Absorbance at 562 nm	Remarks
none	0	0.646	
Cd	70	0.670	
Cu	2500	0.669	
Zn	40	0.668	
Co	2500	0.657	
Ni	2500	0.669	
Fe(II, III)	900	0.659	* More than
Pb	400*	0.668	this amount of
Al	1000*	0.649	metal causes
Ca	1000*	0.646	precipitation.
Mg	8000*	0.656	

Mn taken: 20 μg.

In the present study, sodium ascorbate was used, and yielded consistent and reproducible results.

Donaldson[10] has recommended the use of potassium cyanide as masking agent in the determination of manganese with PAN by the extraction procedure. The influence of potassium cyanide on the colour development and the stability of the chelate were re-examined in the presence of Triton X-100. It was found that the rate of colour development was decreased as the amount of potassium cyanide was increased. The development is complete within 10 min when less than 0.6 ml of the potassium cyanide solution is added, but more than this amount inhibits complete formation of the manganese–PAN chelate. Consequently 0.5 ml of potassium cyanide solution is recommended. The chelate is stable for more than 6 hr. The time required for the full colour development varies with the temperature of the solution. Ten minutes suffice at room temperature (15–30°), but 20 min are required at 10°.

One ml of 20% Triton X-100 solution is enough to solubilize up to 2 ppm of manganese as manganese–PAN chelate. Triethanolamine is added before the buffer solution to prevent the formation of manganese hydroxide. One ml of 20% triethanolamine solution yields consistent and reproducible results.

Sensitivity and precision

Beer's law is obeyed up to 2 ppm of manganese and the molar absorptivity is 4.4×10^4 $l.mole^{-1}.cm^{-1}$. The proposed method is four times as sensitive as the formaldoxime method.

The sensitivity, accuracy and precision of this method are satisfactory for the determination of manganese in natural water samples. In the absence of other ions, the coefficient of variation for the determination of 5–20 ppm of manganese is in the range 1.3–0.4%.

Influence of diverse metal ions

Table 1 shows the effect of various metal ions on the determination. Large amounts of iron(II,III), aluminium, calcium, magnesium, cobalt, copper, nickel and lead do not interfere. Zinc and cadmium slightly affect the determination, but the concentration of these ions in most natural waters is usually low enough for them not to interfere.

Comparison with the atomic-absorption method

In order to test the reliability of the method, manganese in ground-water samples was determined. The results are given in Table 2 together with those obtained by the atomic-absorption method. The agreement is very good.

Table 2. Determination of manganese in ground water

	Mn, *ppm*	
Sample	Proposed method	AA method
A	0.13	0.12
B	0.53	0.55
C	0.31	0.31
D	0.21	0.20
E	0.18	0.18

Composition of the chelate

A continuous variation plot showed that the ratio of PAN to manganese in the complex is 2:1, the same as that reported for the chelate extracted into the organic phase, and in contrast with the Mn(PAN)OH species postulated to exist in the absence of cyanide and Triton X-100.[16] In a non-ionic surfactant system, the chelate is extracted in the micelle phase, so the behaviour of the species may be the same as in solvent extraction systems.

PAN dissociates in two steps. The first is the dissociation of the proton attached to the pyridine nitrogen atom and the second that of the proton of the *o*-hydroxyl group. The p*K* values for these two steps, determined potentiometrically in 50% dioxan medium, have been found to be 2.0 and 12.3.[17] The second pK_a in 0.4% Triton X-100 solution, estimated from the absorbance–pH relationship, is 12.3. The overall stability constant of the chelate was determined by the spectrophotometric method to be $10^{16\,8}$ in 0.4% Triton X-100, at 25°. This is similar to that obtained in 50% aqueous dioxan ($\log \beta_2 = 16.4$).[17]

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DIPHENIC ACID AS A SELECTIVE REAGENT FOR THE AMPEROMETRIC DETERMINATION OF THORIUM(IV)

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Summary—Th(IV) has been titrated amperometrically at an applied e.m.f. of −1.0 V (dropping mercury electrode *vs.* SCE) with diphenic acid (neutralized with sodium hydroxide). Th(IV) in the range 8.0–60.0 mg/100 ml can be determined with an error of ±0.5%. A number of foreign ions including Ce(IV), Zr(IV), La(III), U(IV), U(VI) do not interfere even if present in excess, but traces of Ti(IV) do. The method is rapid and selective and has been used for the determination of Th(IV) in monazite sand.

The analytical chemistry of thorium has been studied extensively during the last few decades. A number of methods have been suggested for its detection[1–4] and determination, but there have been few amperometric methods. The EDTA method[5–9] is subject to certain interferences. Amperometric determination with reagents such as alkali metal tungstates,[10,11] benzenephosphonic acid,[8] thoron,[12] potassium ferrocyanide, oxalic acid and citric acid[13] is also subject to interference. The indirect methods with EDTA[14,15] or rotating tantalum[16,17] and oxide electrodes[18] have been deemed unsatisfactory because of their sensitivity to variation in laboratory conditions, and possible mechanical errors. Wendlandt[19] has reported on the thermolysis of thorium diphenate but its use for the determination of thorium has not been pursued. Diphenic acid provides not only a rapid and accurate method but has the advantage that there are few interferences. Zr(IV), La(III), Ce(IV), Fe(III) *etc.*, which are generally associated with Th(IV) in most of its minerals and ores, do not interfere in the present method.

EXPERIMENTAL

Apparatus

A Toshniwal manual polarograph, type CLO-2, with Pye "Scalamp" galvanometer in the external circuit, was used. The polarographic cell was kept immersed in a water thermostat maintained at 25 ± 1°. A Fischer capillary was used for the dropping mercury electrode, with a drop time of 3.5 sec.

Reagents and solutions

Thorium nitrate, potassium nitrate, diphenic acid and dioxan were all of analytical grade. The solution of diphenic acid was prepared in 40% dioxan, the other solutions were made in distilled water.

Procedure

A measured volume of standard thorium solution was placed in a 100-ml standard flask, then 50 ml of 1.0*M* sodium perchlorate were added and the solution was diluted to the mark with distilled water. An aliquot (10 or 20 ml) of this solution was transferred to a polarographic cell and deaerated by passage of pure nitrogen. An e.m.f. of −1.0 V (*vs.* SCE) was applied, with the d.m.e. as indicator electrode. This potential was found to give sharp end-points and to eliminate most interferences. Measured volumes of reagent solution were added, then stirred in by passage of nitrogen, and the changes in diffusion current were noted. The galvanometer deflection was plotted against volume of titrant added, to locate the end-point (which occurs at a thorium:titrant ratio of 1:2 as expected). In direct titrations (thorium nitrate in the cell), the current first decreases and then shows a slight increase beyond the end-point; in reverse titrations a slight increase in current at the beginning and a sharp increase beyond the end-point is observed. Representative results for both titrations are presented in Table 1.

Table 1. Amperometric determination of thorium(IV) with diphenic acid

Th(IV) present, *mg*	Th(IV) found *mg*	Th(IV) present, *mg**	Th(IV) found, *mg**
50.0	49.8	47.5	47.6
40.5	40.3	35.8	35.9
30.8	30.9	20.0	20.1
20.0	20.1	9.50	9.54

* Reverse titrations.

DISCUSSION

Effect of pH

The most accurate results were obtained at pH 3–5 for thorium and 6–10 for the diphenic acid solution.

Concentration range

From 8 to 60 mg of thorium in 100 ml of solution can be titrated with diphenic acid with an error of ±0.5% (Table 1), Outside this concentration range, the method is less accurate and the end-points are not very sharp. Thorium in monazite was determined by the spectrophotometric Thoron method,[20] and found to be 6.49%. Taking this as the correct value, the present method gives more accurate and precise results than the EDTA method.

Table 2. Determination of thorium in monazite (thorium present* = 6.49%)

Thorium found (A), %	Thorium found (B), %
6.50	6.66
6.48	6.59
6.47	6.62
6.49	6.64

* Thoron as colorimetric reagent.[20]
(A) amperometric method.
(B) EDTA method using Xylenol Orange as indicator.

Determination of thorium in monazite

Monazite powder (100-mesh) was mixed with 5 times its weight of $CaCl_2$ and then heated at 1000° for about 5 hr. The cooled reaction product was extracted with water and hot dilute hydrochloric acid. The hydroxides were precipitated from the acid extract with sodium hydroxide solution, filtered off, washed, dissolved in hydrochloric acid and evaporated to dryness to render the silica insoluble. The residue was again extracted with hot hydrochloric acid and then the solution was treated with oxalic acid. The oxalate precipitate was collected and washed, then extracted with sodium carbonate solution, and the extract heated with perchloric acid to remove the carbonate. The solution was then diluted with distilled water and thorium determined as usual. The results were compared with those for the complexometric determination of thorium(IV), with Xylenol Orange as indicator (Table 2).

Interference studies

Interferences were studied by taking an aliquot of the thorium solution, adding a 5–10-fold amount of the foreign ion and titrating as described above. Li^+, K^+, Rb^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Hg^{2+}, Mn^{2+}, Al^{3+}, Zr^{4+}, La^{3+}, Nd^{3+}, Ce^{3+}, Ce^{4+}, U(IV), U(VI), Cl^-, Br^-, I^-, SO_4^{2-}, S^{2-} do not interfere. The following species do not interfere at the M:Th ratios given: Fe(III) $\leqslant$ 4.5, Cr(III) $\leqslant$ 4.0, Pd(II) $\leqslant$ 4.5, CH_3COO^- $\leqslant$ 4.0, SO_3^{2-} $\leqslant$ 4.0, $S_2O_3^{2-}$ $\leqslant$ 3.0, NO_3^- $\leqslant$ 1.5, SCN^- $\leqslant$ 1.0. The interferences due to the following ions can be removed by the addition of the reagents given in parentheses: Sb(III) (I^-); As(III) (S^{2-}); Cu(II) (ascorbic acid), Co(II) (CN^-); Ni(II) dimethylglyoxime; Pb(II) and Cd(II) (2-mercaptobenzothiazole), F^- and PO_4^{3-} [Zr(IV)]; $P_2O_7^{4-}$ [Mg(II)], MoO_4^{2-} (ascorbic acid). The interferences due to CO_3^{2-} and $C_2O_4^{2-}$ ions can be eliminated by heating the solution with perchloric acid. However, Ti(IV) was found to interfere. Thorium should be separated from titanium by oxalate precipitation before the estimation. The precipitate is ignited and then treated with conc. sulphuric acid to convert it into the sulphate. The thorium is then estimated by the method described.

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SENSITIVITY ENHANCEMENT IN FLAMELESS ATOMIZATION SYSTEMS BY USE OF A RIGID TUNGSTEN COLLAR

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Summary—Sensitivity enhancement was achieved in a flameless atomization system by the insertion of a rigid tungsten "collar" 1 cm long and 0.5 mm thick. With such a collar the electrical and thermal properties of the furnace were essentially those of the original tube, and the existing power pack could be used without modification. A significant improvement in sensitivity was found for the majority of the sixteen elements studied. The system did not appear to suffer from the deformation problems associated with other systems of atomization from metal surfaces.

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of the tungsten, high currents were required to produce suitable temperatures. Without very high output power supplies, only the most volatile elements could be studied. The complete replacement of a graphite "Massmann" type furnace by one made entirely of tungsten has also been suggested[8] but such a system was difficult and expensive to produce and had a very short lifetime because of deformation of the very thin walls. This paper describes a method of signal enhancement involving no alteration to the instrument other than the insertion of a rigid tungsten "collar".

EXPERIMENTAL

Reagents

Solutions of 1 mg/ml concentration were available for all the elements examined and the appropriate working solutions were prepared from these by suitable dilution with distilled water. Argon was used as the inert gas for the graphite furnace.

Instrumentation

The results were obtained by using a Perkin-Elmer 403 atomic-absorption spectrophotometer equipped with a Perkin-Elmer H.G.A. 70 graphite furnace which was connected to the standard power pack. A Hitachi 165 fast-response chart-recorder was used to monitor the signals produced.

Tungsten collars

The tungsten collar was made from pure tungsten tube (99.95% minimum assay) and was 1 cm long, 0.5 mm thick, and 0.87 cm outside diameter. It was slid into position with a brass mandrel until the 2-mm sample-injection hole in the collar was aligned with the existing hole in the graphite furnace. Collars of this type may be obtained from Murex Refractory Metals Ltd., Rainham, Essex or Special Metals Ltd., Rochford, Essex.

Procedure

Comparison of the modified and standard graphite furnaces was achieved by the injection of identical volumes (5–20 μl) of standard solutions (for weight injected see Table 1) and measurement of the resulting signals. Conditions were optimized for each element and the reproducibility and linearity of signal production as a function of injection volume was rigorously established. Distilled water blanks were run for each element examined. The instrument conditions for a given element when the tungsten collar was used were identical to those used for the graphite furnace, with the exception of aluminium, for which a lowering of atomization voltage was necessary for optimum results from the tungsten collar.

The current drawn from the power pack was measured for both systems over the atomization voltage range of 2–10 V, by means of an induced-current ammeter capable of measuring up to 1200 A.

RESULTS AND DISCUSSION

The results obtained for the sixteen elements examined are given in Table 1. In almost all instances the modified furnace gave an enhanced signal, including elements such as manganese which are not considered to form carbides in graphite furnaces. Results for elements in which carbide or oxide formation may present a problem in graphite furnaces are shown in Table 1 together with the atomization route as described by Sturgeon *et al.*[9] The use of a tungsten collar may lead to a better understanding of such processes in flameless atomic spectroscopy.

Figure 1 compares the current drawn by an unmodified and a modified graphite furnace. It shows only a small increase in the current drawn throughout the range and so no modification to the power pack is required.

To achieve satisfactory results it is essential to establish good thermal contact between the metal and graphite surfaces and when this is achieved the electrical and thermal properties observed are essentially those of the graphite. Since the graphite surface is not in contact with the analyte, and the tungsten surface is very durable (there being no sign of the oxide formation often associated with tungsten when used at high temperatures), the modified furnace can be used for much longer than is usually the case. If after many hundreds of injections the graphite tube fails, the tungsten collar can be removed and inserted in a new graphite furnace.

Though the sensitivity enhancement values were obtained with neutral aqueous standards, the proposed system has found application in normal analytical deter-

Table 1. Comparison of sensitivity factors for a graphite furnace fitted with a tungsten collar and for an unmodified furnace

Element	Weight injected, *ng*	Enhancement factor*	Possible atomization mechanism in graphite furnaces
Ag	0.5	1.4	—
Al	2	3.7	Thermal decomp. of oxide[9]
Ba	1	4.3	Stable carbide
Cd	0.05	0.9	Thermal decomp. of oxide[9]
Co	1	†	Reduction of oxide on graphite[9]
Cr	1	†	Reduction of oxide on graphite[9]
Cu	0.2	4.2	Reduction of oxide on graphite[9]
Mn	0.1	3.0	Thermal decomp. of oxide[9]
Ni	1	3.8	Reduction of oxide on graphite[9]
Pb	1	0.9	Reduction of oxide on graphite[9]
Sb	5	0.9	—
Sn	10	12	Reduction of oxide on graphite[9]
Sr	0.1	3.8	Stable carbide
Ti	50	1.4	—
V	10	0.3	Reduction of oxide on graphite[9]
Zr	1000	> 10§	Stable oxide and carbide

* Enhancement factor = Peak height in modified furnace/Peak height in conventional furnace.

† Presence of this element in the tungsten liner used excludes possibility of analysis.

§ The magnitude of the enhancement factor for this element is very dependent on the size of the small peak obtained in the unmodified graphite furnace.

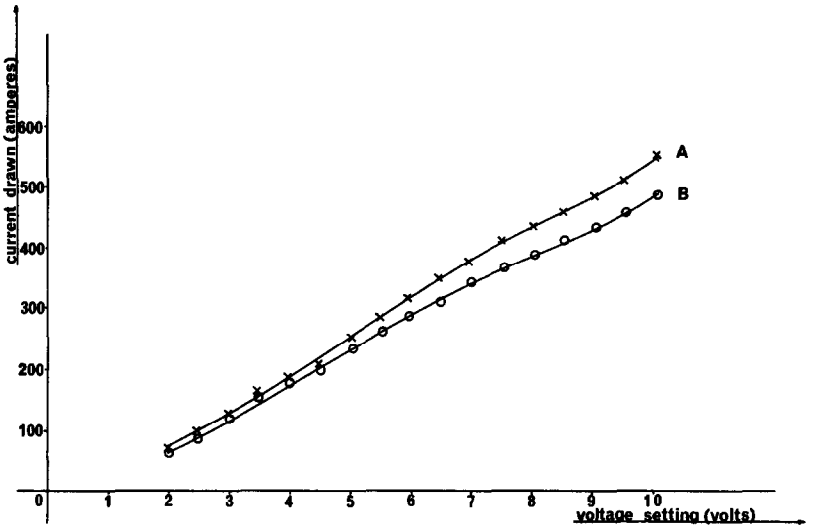

Fig. 1. Comparison of the current drawn by a furnace modified with the tungsten collar (A) and an unmodified graphite furnace (B).

minations, the determination of barium at low levels in 25% hydrofluoric acid being a recent example. Results obtained by using the tungsten collar system and operating the power pack at the "maximum temperature" setting indicate that even better sensitivities might be obtained if temperatures higher than those available with the H.G.A. 70 system could be reached.

Conclusion

Whilst in the past atomization from metal surfaces has not found wide application in flameless atomic spectroscopy, the simple tungsten collar described in this paper appears to offer certain advantages for both sensitivity enhancement and more fundamental studies for a considerable number of elements.

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REDUCTIMETRIC DETERMINATION OF PEROXYDISULPHATE, HYDROGEN PEROXIDE, SODIUM PERBORATE, NITRATE AND NITRITE IN CONCENTRATED PHOSPHORIC ACID MEDIUM WITH IRON(II)

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Summary—A direct reductimetric method for the determination of peroxydisulphate, hydrogen peroxide, sodium perborate, nitrate and nitrite in fairly concentrated phosphoric acid medium with iron(II) has been developed, with both potentiometric and visual end-point detection. Cacotheline, Methylene Blue, thionine, Azure A, Azure B, Azure C, Toluidine Blue, new Methylene Blue, ferroin, *N*-phenylanthranilic acid, *p*-ethoxychrysoidine and barium diphenylaminesulphonate are used as indicators. The method is useful in the analysis of binary mixtures of peroxydisulphate and peroxide or perborate and in the estimation of the nitrate content of fertilizers.

Peroxydisulphate, hydrogen peroxide and nitrate are generally determined by indirect methods when iron(II) is used as the titrant.[1] A direct method is available for nitrate,[1] but it is time-consuming and complicated. Gopala Rao and Sagi[2] reported that the reductive power of iron(II) is increased considerably in concentrated phosphoric acid medium. The work described in the present paper exploits this for the determination of peroxydisulphate, hydrogen

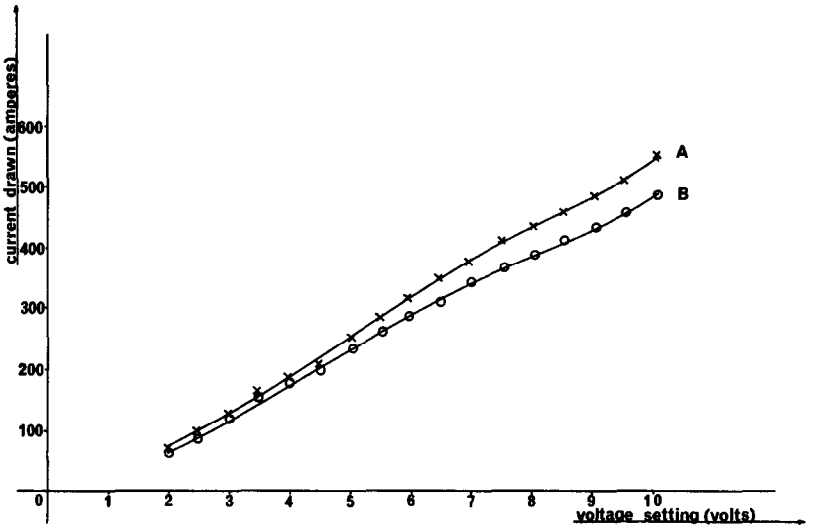

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Table 1. Potentiometric and visual determination of peroxydisulphate, peroxide, perborate, nitrate and nitrite

Sample	End-point detection	Range of acid concentration, *M*	Range of determination, *mg*	Average error, %
Peroxydisulphate	Potentiometric	9–12	4–60	0.2
	Indicators 1–8	9–12	4–60	0.3
Hydrogen peroxide	Potentiometric	6–10	3–18	0.3
	Indicators 1–8	8–10	3–18	0.3
Perborate	Potentiometric	6–10	20–75	0.2
	Indicators 1–8	8–10	20–75	0.3
Nitrate	Potentiometric	9.5–12	7–25	0.4
	Indicators 1–12	10–12	7–25	0.4
Nitrite	Potentiometric	8–12	10–50	0.4
	Indicators 3–9 (except 5)	9–12	10–50	0.5

Indicators: 1, Methylene Blue; 2, thionine; 3, Azure A; 4, Azure B; 5, Azure C; 6, Toluidine Blue; 7, New Methylene Blue; 8, cacotheline; 9, ferroin; 10, *N*-phenylanthranilic acid; 11, barium diphenylamine sulphonate; 12, *p*-ethoxychrysoidine

peroxide, perborate, nitrate and nitrite, the analysis of binary mixtures of peroxydisulphate and peroxide or perborate, and the determination of nitrate in fertilizers.

EXPERIMENTAL

Apparatus

The assembly used for potential measurements is the same as that described earlier.[3]

Reagents

Solutions (0.1*N*) of peroxydisulphate, peroxide, perborate, nitrate and nitrite were prepared and standardized. Syrupy phosphoric acid was used. Iron(II) ammonium sulphate solution (0.1*N*) was prepared in 1*N* sulphuric acid. Aqueous 0.1% Methylene Blue, thionine, Azure A, Azure B, Azure C, *p*-ethoxychrysoidine, Toluidine Blue, New Methylene Blue and *N*-phenylanthranilic acid solutions, 0.2% cacotheline and barium diphenylaminesulphonate solutions, and 0.025*M* ferroin were prepared. A 1% solution of manganese(II) sulphate was used.

Procedures

Titrimetric determination of peroxydisulphate and nitrate. The volume of phosphoric acid required to give a 10–11*M* concentration at the end-point (plus 0.2 ml of 1% manganous sulphate solution in the case of nitrate), a known volume of the test solution, and 0.2 ml of indicator solution (0.5 ml in the case of cacotheline) are taken in the titration vessel. Carbon dioxide is passed through the mixture for 10 min and then the contents are titrated with iron(II) solution to the sharp colour change of the indicator. Alternatively the indicator is omitted and potentiometric titration done. The acid concentration ranges and indicators used and the values obtained are given in Table 1. In the potentiometric titrations, the potentials immediately attain steady values throughout the titration.

Determination of peroxide, perborate and nitrite. The volume of syrupy phosphoric acid required to give a 10*M* concentration near the end-point is taken in the titration vessel. Carbon dioxide is passed through it for 10 min, then a known volume of iron(II) solution is added together with 0.2 ml of indicator solution (0.5 ml for cacotheline), and titrated with the oxidant to the sharp colour change of the indicator. Alternatively the indicator is omitted and potentiometric titration used. Results are given in Table 1.

Analysis of binary mixtures of peroxydisulphate and peroxide or perborate. The total amount of peroxydisulphate and peroxide or perborate is determined by titrating iron(II) solution with the mixture of oxidants as described above. The amount of peroxydisulphate is determined by direct titration after destruction of peroxide or perborate according to the procedure given by van der Meulen.[4] From the two values the amount of peroxide or perborate can be assessed. Typical results are presented in Table 2.

RESULTS AND DISCUSSION

Chloride, sulphate, acetate, borate, tartrate, citrate, glucose, sucrose, fructose, Al(III), Mn(II), Zn(II), Hg(II) and As(III) do not interfere at any concentration. Cu(II), sulphide and sulphite interfere at all concentrations.

The method has been tested for the determination of nitrate in fertilizers such as calcium ammonium nitrate and NPK, and also in nitric acid. The values obtained agree with those obtained by conventional methods with an average relative error of 0.4%. Peroxide and perborate are determined by reverse titration because in the direct titration low values are obtained, probably because of complex formation by peroxide or perborate with iron(III) in the presence of phosphate, similar to that observed by earlier workers[5] in the case of EDTA.

In the nitrite determination, the tip of the burette containing the solution should dip just below the surface of the titrand, otherwise low values are obtained.

In the potentiometric titration of nitrate it has been observed that in the absence of manganese(II) an interval of 1–2 min is required for the potentials to stabilize at the start of the titration, whereas in its presence the potentials are immediately stabilized throughout. The catalytic ac-

Table 2. Determination of peroxydisulphate and hydrogen peroxide or sodium perborate

Taken, *mg*			Found, *mg*		
Peroxydisulphate	Peroxide	Perborate	Peroxydisulphate	Peroxide	Perborate
71.3	32.4		71.5	32.4	
118.9	23.1		118.6	23.2	
166.5	13.9		166.5	13.9	
59.5		152.9	59.7		152.5
107.0		112.1	107.2		112.3
154.6		71.4	154.8		71.4

tivity of Mn(II) can be explained if nitrate oxidizes the Mn(II) to Mn(III) which then reacts rapidly with iron(II) and is reduced back to Mn(II).

During the work the transition potentials of cacotheline, Azure A, Azure B, Azure C, Toluidine Blue and New Methylene Blue in 10–12*M* phosphoric acid medium, were determined, the values being 538 ± 4, 532 ± 3, 538 ± 3, 550 ± 6, 525 ± 5 and 525 ± 5 mV respectively.

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PHOTOMETRIC DETERMINATION OF MICRO AMOUNTS OF THIOSULPHATE BY MEANS OF ITS CYANOLYSIS WITH LANTHANUM(III) AS CATALYST

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Summary—Lanthanum(III) has been found to catalyse the reaction of thiosulphate with cyanide. The effects of pH, reaction time and temperature, amount of cyanide and lanthanum, and order of addition of reagents have been investigated. Temperature has little effect in the range 10–30°, but at both 35° and 40° the rate is noticeably faster. Reaction is complete at room temperature in 1.5 hr at pH 9.3–9.6, and in 3 hr at pH 9.1–9.6. The method can be applied to the determination of 1.0×10^{-5}–$6.0 \times 10^{-4}M$ thiosulphate, with a relative standard deviation of 0.3% for $4 \times 10^{-4}M$ thiosulphate.

There has been a growing interest in sulphur chemistry and accurate determination of sulphur compounds in mixtures. Sörbo has found that copper(II) catalyses the conversion of thiosulphate into thiocyanate, and reported a method for determination of thiosulphate by photometric measurement of the thiocyanate formed.[1] The sensitivity can be increased about sixtyfold by extracting the Methylene Blue ion-association complex of the thiocyanate.[2] The copper(II)-catalysed cyanolysis of thiosulphate has played a critical role in development of methods for the analysis of mixtures of polythionates.[3–6] Kelly *et al.*[4] and Mizoguchi *et al.*[5] have proposed photometric methods for thiosulphate, trithionate and tetrathionate in their mixtures, by means of cyanolysis with and without cupric ions, followed by photometric measurement of the thiocyanate with ferric ions. However, trithionate was not stoichiometrically converted into thiocyanate, because some of it is hydrolysed to thiosulphate. A catalyst for complete cyanolysis of both thiosulphate and trithionate is therefore needed.

We have already reported that lanthanum(III) quantitatively catalyses the cyanolysis of trithionate.[7] We now show it also catalyses the conversion of thiosulphate into thiocyanate under the same conditions as those for trithionate.

EXPERIMENTAL

Reagents

Standard thiosulphate solution. Dissolve sodium thiosulphate in freshly boiled and cooled redistilled water containing a small amount of sodium carbonate, and standardize by iodimetry a week after preparation. Prepare working solutions by suitable dilution.

Standard thiocyanate solution. Standardize a thiocyanate solution by Volhard's method. Prepare working solutions by suitable dilution.

Lanthanum solution. Dissolve 48.9 g of freshly ignited lanthanum oxide, in small portions, in 70 ml of conc. nitric acid with cooling, and dilute to 200 ml.

Procedure

Add 1 ml of lanthanum solution, 2 ml of 1*M* acetic acid, 10 ml of sample solution containing thiosulphate, and then 3.5 ml of 4*M* sodium cyanide solution to a 25-ml standard flask (painted black except for small vertical areas on opposite sides near the graduation mark). The pH is thereby brought to 9.5. Allow to stand at room temperature for 1.5 hr, then add 3 ml of 60% perchloric acid and 3 ml of 1.5*M* ferric nitrate in 4*M* perchloric acid, and dilute to the mark with redistilled water. Mix well, and measure the absorbance against distilled water at 460 nm. Subtract the reagent blank from all the absorbances measured.

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The calibration curves are linear for both thiocyanate and thiosulphate up to $6.0 \times 10^{-4}M$ and coincide exactly, confirming that the reaction $S_2O_3^{2-} + CN^- \rightarrow SO_3^{2-} + SCN^-$ proceeds quantitatively.

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It was observed[7] that the cyanolysis of trithionate in the presence of lanthanum does not go stoichiometrically at temperatures above 20°, so the effect of temperatures ranging from 10° to 30° was investigated at the optimal pH of 9.5. The results in Table 2 show that the cyanolysis

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Table 1. Effect of order of addition of reagents*

Sample	Absorbance Procedure A 4.0 × $10^{-4}M$	Procedure A 6.0 × $10^{-4}M$	Procedure B 4.0 × $10^{-4}M$	Procedure B 6.0 × $10^{-4}M$	Procedure C 4.0 × $10^{-4}M$	Procedure C 6.0 × $10^{-4}M$	$10^{-4}M$ ^{h}N9
SCN^-	0.724	1.081	0.724	1.081	0.722	1.080	
$S_2O_3^{2-}$	0.722	1.079	0.722	1.081	0.705	0.916	
	0.722	1.080	0.727	1.081	0.698	0.905	

* The amount of reagents added is the same as in the procedure.
Procedure A: lanthanum, acetic acid, thiosulphate, and then cyanide were added.
Procedure B: thiosulphate, cyanide, acetic acid, and then lanthanum were added.
Procedure C: lanthanum, cyanide, acetic acid, and then thiosulphate were added.

Table 2. Effect of temperature on the cyanolysis of $4 \times 10^{-4}M$ thiosulphate at pH 9.5

Time, *min*	Absorbance 10°	15°	20°	25°	30°
	0.732*	0.724*	0.727*	0.724*	0.727*
5	0.637	0.640	0.666	0.686	0.696
15	0.689	0.692	0.710	0.712	0.710
30	0.714	0.714	0.715	0.716	0.719
45	0.716	0.719	0.721	0.721	0.724
60	0.730	0.720	0.722	0.726	0.723
75	0.727	0.720	0.725	0.722	0.723
90	0.731	0.723	0.723	0.722	0.723
105	0.730	0.725	0.724	0.720	0.723
120	0.727	0.723	0.722	0.723	0.724

* Expected maximum value.

was almost complete in 45 min; it was complete in 15 min at 35° and 5 min at 40°. However, the reproducibility was poorer at the higher temperatures and the absorbance decreased on standing, so room temperature was selected for further work.

Figure 1 shows the rate of cyanolysis of thiosulphate at room temperature (25°) for various pH values. The maximal absorbance was reached in 3 hr at pH 9.1, 1.5 hr at pH 9.3, and 45 min at pH 9.5. Figure 2 shows that thiosulphate is quantitatively converted into thiocyanate in 1.5 hr over the pH range 9.3–9.6. It is well known that thiosulphate is stable at high pH levels. Accordingly, the incomplete cyanolysis at pH > 9.6 seems to be caused by a decrease in the catalytic action of lanthanum. At lower pH the rate of cyanolysis is lower (Fig. 1), presumably because of protonation of the cyanide ion. The optimal pH range can be extended to lower pH values by making the cyanolysis time longer, *e.g.*, 3 hr at pH 9.1–9.6.

Table 3. Effect of diverse ions: thiosulphate taken: 437 μg*

Ion	Added as	Amount*, *mg*	Error %
Na^+	$Na_2SO_4.10H_2O$	10	+0.9
K^+	K_2SO_4	10	−0.2
NH_4^+	$(NH_4)_2SO_4$	10	−0.2
Mg^{2+}	$MgSO_4.7H_2O$	10	−0.2
Ca^{2+}	$Ca(NO_3)_2$	10	−0.7
Zn^{2+}	$ZnSO_4.7H_2O$	10	−0.9
Al^{3+}	$Al_2(SO_4)_3.17H_2O$	10	0
Fe^{2+}	$Fe(NH_4)_2(SO_4)_2.6H_2O$	1	+0.5
Pb^{2+}	$Pb(CH_3COO)_2.3H_2O$	1	+1.6
F^-	NaF	10	−1.4
Cl^-	KCl	10	−1.1
Br^-	KBr	1	−1.8
I^-	KI	10	−0.5
NO_3^-	KNO_3	10	−0.2
SO_4^{2-}	Na_2SO_4	10	+0.5
SO_3^{2-}	Na_2SO_3	5	+0.9
CO_3^{2-}	Na_2CO_3	1	+0.7
S^{2-}	$Na_2S.9H_2O$	0.1	−1.1
PO_4^{3-}	Na_3PO_4	0.5	−1.1
$HAsO_4^{2-}$	$Na_2HAsO_4.7H_2O$	0.5	−1.4
Silicate ion	(as SiO_2)	10	−0.9
Borate ion	H_3BO_3	10	+0.5

* In 10 ml of sample solution.

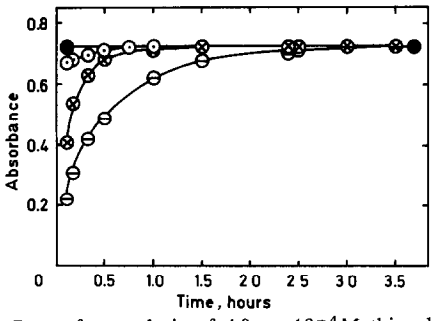

Fig. 1. Rate of cyanolysis of 4.0 × $10^{-4}M$ thiosulphate at various pH values. ●, expected value; ⊖, pH 9.1; ⊗, pH 9.3; ⊙, pH 9.5. All other conditions are as in the procedure.

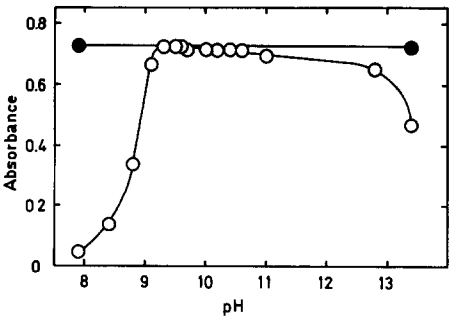

Fig. 2. Effect of pH on the cyanolysis of 4.0 × $10^{-4}M$ thiosulphate. ●, expected value; ○, experimental values. All other conditions are as in the procedure.

The effect of amount of cyanide was examined by using 3.5 ml of 0.05, 0.1, 0.5, 2, and 4*M* cyanide, the other conditions being optimal. The cyanolysis was incomplete with the 0.05–2*M* cyanide, though the calibration graphs were linear. When 4*M* cyanide was used, the calibration graph for thiosulphate coincided exactly with that for thiocyanate. It was also confirmed that the cyanolysis was quantitative with 3–4 ml of 4*M* cyanide and that excess of cyanide had no adverse effect.

A similar investigation of the amount of lanthanum(III) needed as catalyst showed that 1 ml of 0.5, 0.6, or 0.7*M* lanthanum was insufficient but 0.8–1.3 ml of 1.5*M* lanthanum gave a calibration curve in exact accord with that of thiocyanate. Excess of lanthanum has no adverse effect.

Effect of diverse ions

Aliquots (10 ml) of solution containing various amounts of diverse ions, in the presence and absence of thiosulphate, were treated exactly as in the procedure. The maximum permissible amounts of other ions in the determination of 437 μg of thiosulphate with an error of 2% are shown in Table 3. Phosphate and arsenate interfered by forming insoluble lanthanum salts. Sulphide interfered by being oxidized aerially to sulphur, which reacted with cyanide to form thiocyanate.

Precision

Eleven solutions (thiosulphate 44.9 μg/ml) were analysed and gave a relative standard deviation of 0.3%.

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USE OF THE CELLULOSE EXCHANGERS CELLEX D AND CELLEX T TO SEPARATE PLATINUM AND RHODIUM

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(*Received* 8 *March* 1977. *Revised* 19 *July* 1977. *Accepted* 23 *August* 1977)

Summary—Conditions for the separation of Pt and Rh by ion-exchange on two cellulose anion-exchangers have been established.

Our aim was to verify the feasibility of using the cellulose anion-exchangers Cellex D and Cellex T to separate platinum and rhodium. The affinity of these exchangers for chloride and other complexes of platinum metals is lower[1] than that of other anion-exchangers, and this should facilitate the separation and quantitative isolation of the components separated from the exchanger phase.

According to the literature, with the usual ion-exchangers there is difficulty in eluting the last traces of some platinum metals.[1–8] This is usually attributed to irreversible sorption. In the case of chloride complexes of Rh there is irreversible sorption on anion-exchangers, probably caused by retention of the polymerized sodium salts in small quantities.[9]

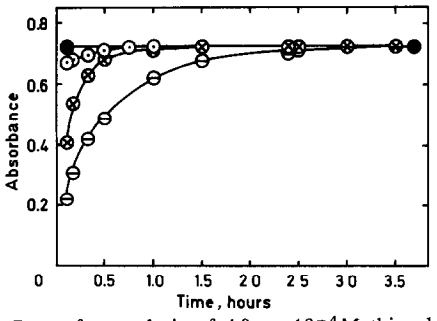
In this work the platinum and rhodium chloride complexes were separated by use of two systems: (1) exchanger with metal-ion solution in aqueous sodium (or potassium) chloride/hydrochloric acid medium at constant pH value, and (2) exchanger with metal-ion solution in hydrochloric acid medium. The effect of acetic acid on retention of chloride complexes[10] was also checked.

EXPERIMENTAL

Reagents

Exchangers. The DEAE-cellulose and TEAE-cellulose exchangers Cellex D and Cellex T (Bio-Rad Laboratories) were used.

Solutions of Pt and Rh. A 2.45 × $10^{-4}M$ solution of platinum was prepared from H_2PtCl_6 solution of known



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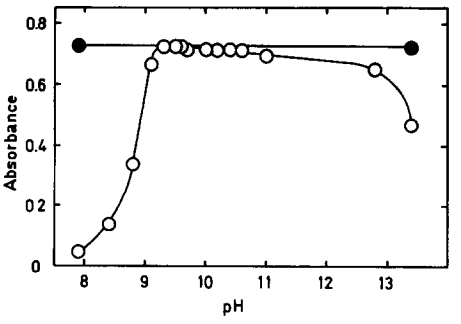

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Table 1. Distribution coefficients of Pt and Rh (15 μg ml) at various HCl concentrations

[HCl], *M*	Cellex D		Cellex T	
	Pt	Rh	Pt	Rh
0.01		31.6		28.9
0.1	941	15.2	926	16.1
0.3	117	8.2	94	4.4
0.5	53	6.0	58	3.3
1.0	32	4.2	28	1.7
1.5	27	1.8	23	0.5
2.0	21	1.3	20	0.3

platinum content. Solutions of other concentrations were obtained by further dilution. Rhodium solutions were prepared from a solution of known Rh content.

Distribution coefficient

The distribution coefficient is defined as:

$$K_d = \frac{\text{mmole/g of dry exchanger}}{\text{mmole/ml of solution}}.$$

The distribution coefficient was determined by the static method with 400 mg of exchanger and 40 ml of solution containing 7.7 μmole of Pt and 9.8 μmole of Rh. The distribution coefficients were determined as a function of hydrochloric acid concentration (0.01–2.0*M*) and sodium chloride concentration (0.1–0.8*M*) at constant pH. The results are given in Tables 1 and 2.

In the static-method investigations Rh and Pt were determined colorimetrically by the stannous chloride method.[11,12] In the dynamic method investigations flameless atomic-absorption spectroscopy was used (Perkin-Elmer Model 300 atomic-absorption spectrophotometer and Perkin-Elmer platinum and rhodium lamps).

Static investigations

Retention of Pt and Rh decreases with increase in hydrochloric acid concentration and the distribution coefficients are markedly higher for Pt.

The differentiation in affinity is even greater in the chloride solution at pH 2 for Cellex D, and when this exchanger is used a better separation ought to be obtained in chloride salt media than in hydrochloric acid solutions.

Interesting results were obtained for the effect of acetic acid on retention of Pt and Rh. In solutions with an initial hydrochloric acid concentration of 0.01*M* (pH 2.0) the distribution coefficient for Pt decreases on addition of acetic acid and increases with increasing acetic acid concentration but never to the same level as in its absence, whereas the coefficient for Pt is always increased, becoming larger with higher acetic acid concentration.

Table 2. Distribution coefficients of Pt (15 μg ml) and Rh (10 μg ml) on Cellex D at pH 2.1 and various NaCl concentrations

$[Cl^-]$, *M*	Pt	Rh
0.1	1620	6.7
0.3	233	2.4
0.5	120	1.9
0.8	81	1.0

Table 3. Distribution coefficients of Pt and Rh at various acetic acid concentrations

$[CH_3COOH]$, % *v/v*	Cellex D		Cellex T	
	Pt (15 μg ml)	Rh (15 μg ml)	Pt (15 μg ml)	Rh (15 μg ml)
40	77	124	63	120
70	185	141	210	137
90	713	302	560	286

The difference in affinity is thus decreased (Table 3). The optimum sodium chloride concentration has been determined statistically and should make it possible to separate Pt from Rh. The feasibility of separation has been checked under dynamic conditions.

Separation of Pt and Rh by column process

Pt and Rh solutions (10 ml) were introduced into an exchanger column (9.8 mm diameter) in presence of 0.1*M* sodium chloride and 0.01*M* hydrochloric acid. The bed length was 8.5 cm (1.4 g of exchanger). The flow-rate was regulated at 0.6 ml/min by means of a pump. Rh was eluted with 80 ml of 0.1*M* sodium chloride in 0.01*M* hydrochloric acid. Pt was eluted with 100 ml of 1*M* hydrochloric acid. Rh and Pt were determined both spectrophotometrically and by atomic absorption. The mean error for four determinations was 1% for 4.7 mg of Pt and 3% for 2.5 mg of Rh. Non-equivalent quantities of Pt and Rh were similarly separated, Rh being eluted with 40 ml of 0.1*M* sodium chloride in 0.01*M* hydrochloric acid and then 20 ml of 0.3*M* sodium chloride in 0.01*M* hydrochloric acid. Pt was eluted with 100 ml of 1*M* hydrochloric acid. The elution conditions were changed to give better resolution. The reduced volume of eluent used for Rh meant that a higher concentration had to be used to ensure complete elution, but that entailed a risk of loss of Pt. For this reason the volume of the more concentrated eluent had to be restricted. The mean error for three determinations was 7% for 0.3 mg of Pt and 1% for 2.5 mg of Rh, irrespective of whether 1.4 or 1.5 g of exchanger was used.

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PRELIMINARY COMMUNICATION

NEW CONVENIENT COLORIMETRIC DETERMINATION OF POTASSIUM IN BLOOD SERUM *

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Potassium and sodium have mostly been determined by flame emission spectrophotometry, and no practical method has been reported for the absorption photometry of alkali metal ions in solution.[1]

We have been studying this problem, especially the determination of potassium and sodium.

One approach to this goal is to develop a new chromogenic reagent which complexes selectively with potassium or sodium to give a colour change. An example has recently been reported by one of us.[2] Another approach is utilization of complex formation with a crown-ether and solvent extraction of the ion-pair formed by this complex and a highly coloured anion.

This communication reports a highly sensitive and selective extractive spectrophotometric determination of potassium in the presence of a large excess of sodium. The principle of this method is based on the selective complex formation of 18-crown-6 with potassium, followed by the solvent extraction of the ion-pair formed with Bromocresol Green. This method has been successfully applied to the determination of potassium in serum.

EXPERIMENTAL

Reagents

The reagent solutions are 0.3% 18-crown-6 in benzene, 0.1% Bromocresol Green in aqueous ethanol (20% ethanol), standard potassium chloride and 0.2M acetic acid - lithium acetate buffer of pH 3.9. All other reagents are of analytical grade.

Solvent extraction and continuous variation study for three-component system

Aliquots of standard potassium solution and Bromocresol Green solution and 1 ml of buffer solution were transferred into a 50-ml centrifuge tube equipped with a stopper, and diluted to 10 ml with water. Then 10 ml of crown ether solution in benzene were added. Varying amounts of potassium, Bromocresol Green and crown ether were taken to give a total concentration of 1×10^{-3}M for the three components. The resulting mixture was shaken at room temperature ($26 \pm 1°$) for 20 min and allowed to stand for 20 min to complete the phase separation. The concentration of Bromocresol Green complex in the organic phase was

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determined spectrophotometrically at 410 nm with a 10-mm cell against benzene. The result is shown in Fig. 1.

The extraction constant was evaluated by the procedure previously reported,[4] with slight modifications.

Recommended procedure for serum potassium determination

Place 0.1 ml of serum sample in a 10-ml centrifuge tube and add 4.9 ml of 1.5% aqueous trichloroacetic acid. Mix well, then centrifuge the mixture for 5 min. Transfer 2 ml of the supernatant liquid into another 10-ml centrifuge tube, add 0.2 ml of 11% aqueous lithium acetate solution, 0.4 ml of 0.2M lithium acetate buffer solution, 1.4 ml of Bromocresol Green solution and 4.0 ml of crown ether solution in benzene, shake for 5 min with a mechanical shaker, and centrifuge for 1 min. Measure the absorbance of the organic phase at 410 nm against a reagent blank.

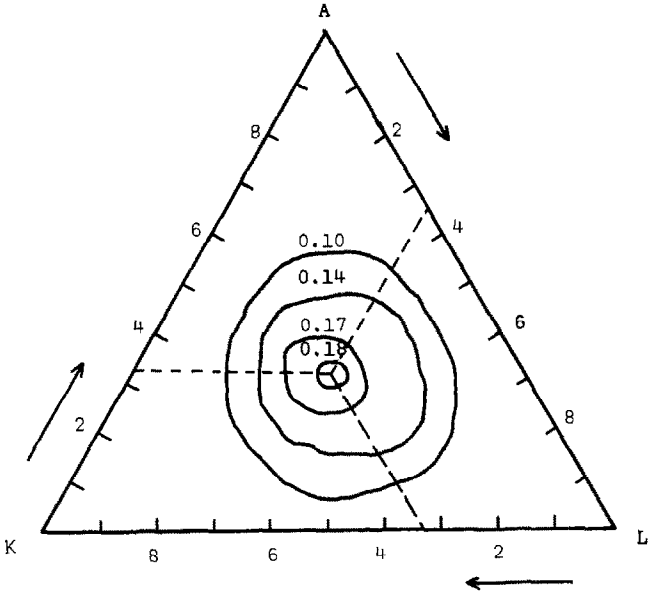

Fig. 1. Continuous variation method applied to three-component system

RESULTS AND DISCUSSION

Stoichiometry and equilibria

The equilibria existing in this system may be illustrated by Fig. 2. The overall extraction equilibrium between an aqueous solution containing potassium (M) and Bromocresol Green anion (A), and a benzene solution containing the crown ether (L), can be written as:

$$M^+_a + L_o + A^-_o = MLA_o$$

$$K_{ex} = \frac{[MLA]_o}{[M^+]_a\,[L]_o\,[A^-]_a} = 10^{4.7} \qquad (1)$$

where MLA denotes the ion-pair complex extracted into the organic phase.

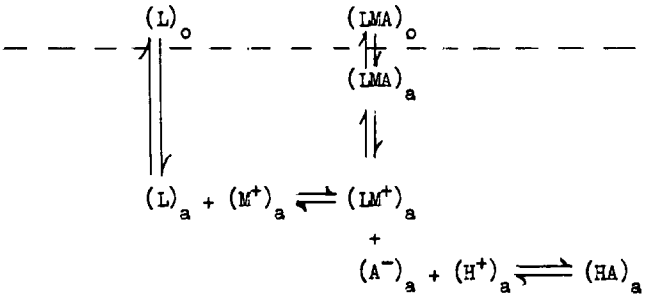

Fig. 2. Equilibria in the system

The continuous variation study on the three-component system of M-L-A indicates that the ion-pair complex, MLA, is the only species to be extracted into the organic phase. The extraction constant was found to be $10^{4.7}$, which shows that about 25% of the potassium is extracted into the organic phase when equal volumes of 10^{-4}M benzene solution of crown ether and of the aqueous solution containing potassium (10^{-4}M) and Bromocresol Green (10^{-3}M) are equilibrated at room temperature.

The extraction equilibrium shown in equation (1) is not dependent on the pH of the aqueous phase; however, the pH range where Bromocresol Green exists as the yellow singly charged anion is below 4, so the extraction has to be done at pH < 4. At pH >5 the green doubly charged anion is present, which can hardly be extracted as an ion-pair.

The calibration curve prepared with a standard potassium solution is linear up to 5 ppm of potassium. Sodium up to 500 ppm does not interfere with the potassium determination over this concentration range.

As an important application of this method, potassium in serum was determined by the procedure given above. The result was found to be quite satisfactory in comparison with that obtained by flame emission photometry, as shown in Table 1. The method is so sensitive that the sample serum can be reduced to 20 µl at this potassium concentration level.

Table 1. Analytical result for serum potassium determination

Sample	Potassium, ppm	
	This method	Flame photometry
1	175	183
2	165	174
3	192	201
4	203	201

There is a wide range of freedom in choosing crown ethers or cryptands as a ligand, dyes as a pairing anion and solvents for extraction. Our investigations are being continued to develop highly selective and sensitive absorption photometric methods for determination of traces of alkali metal ions.

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TALANTA REVIEW*

APPLICATIONS OF AUGER-ELECTRON SPECTROMETRY

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The radiationless reorganization of atomic electronic shells was first experimentally established by Auger[1–3] in 1923. There was a considerable induction period before the theoretical and experimental research of atomic physicists in the late 1950s and early 1960s led to a greater understanding of the Auger effect. (This work is well documented in references 4 and 5.) The development of electron-stimulated Auger-electron spectrometry (AES) as a powerful tool for the analysis of surfaces began with the work of Harris and of Weber and Peria in 1967. Harris[6] demonstrated the potential of differentiation of the Auger-electron energy-distribution and used the technique in studies of surface segregation[7] and carbon evaporation from a cathode.[8] The important contribution of Weber and Peria[9] was to show that the profusion of low-energy electron diffraction (LEED) instruments available at that time could be modified for use in Auger spectrometry in the differential mode. (The considerable quantity of LEED work carried out in the 1960s is catalogued in the bibliography by Haas *et al.*[10]) Concurrent with these developments increasing efforts were being made to produce electron spectrometers of higher resolution and sensitivity.[11,12] In 1969, Palmberg, Bohn and Tracy[13] demonstrated that the cylindrical-mirror analyser could be used to achieve high sensitivity in AES with resultant increase in the speed of an analysis.

A more recent development has been the use of scanning techniques which make it possible to produce a two-dimensional map or image of the surface distribution of a chosen element. The method can be used in conjunction with "physical" imaging by scanning electron-microscopy. Indeed the AES map can be obtained from Auger electrons produced in the scanning electron-microscope.[14–16] Finally, it is worth pointing out that the advances outlined above have all been carried out during a period of significant improvement in ultrahigh-vacuum technology.

The growth in the number of applications of AES described in the literature has been very marked since approximately 1970. Undoubtedly this has been due to a combination of increasing interest in the surface properties of materials and the unique blend of properties of AES. Not only can an elemental analysis be performed but the technique can also yield information concerning the chemical environment of surface atoms. Furthermore high sensitivity and spatial resolution, and fast responses can be obtained. Recently it has been suggested that because of some of these properties, there is considerable analytical potential for AES in the gas-phase.[17]

This review concentrates on a selection of applications of AES in qualitative surface analysis. Additionally, a discussion of quantification of surface Auger signals and an evaluation of the potential of gas-phase AES are included. A list of some review articles on AES is given at the end of the paper.

SURFACE STUDIES

The great number and variety of published papers on electron-excited AES of surfaces creates difficulties in the task of categorizing material according to the nature of application, material examined or particular Auger technique employed. In the present review, all these topics are discussed with specific examples; however, it should be emphasized that certain studies could clearly be included in more than one area. There is no attempt to encompass the whole field.

Surface chemistry and Auger chemical shift

The adsorption and reactions of gases at a clean metal surface are the main subject of this section. These studies are clearly relevant to problems in corrosion, catalysis, *etc.* (Specific examples of the latter are considered in the next section.) Much of the work in this area has been concerned with the reaction of oxygen with a clean metal surface prepared by thermal treatment and/or argon ion-bombardment.

An early report of an Auger study of metal oxidation was that of Haas and Grant[18] who followed the 164-eV $N_5N_6N_6$ tantalum transition on reaction of a tantalum (110) surface with oxygen. A shift of -6 eV was found when the sample was fully oxidized.

*For reprints of this Review, see Publisher's announcement near the end of this issue, TALR 59.

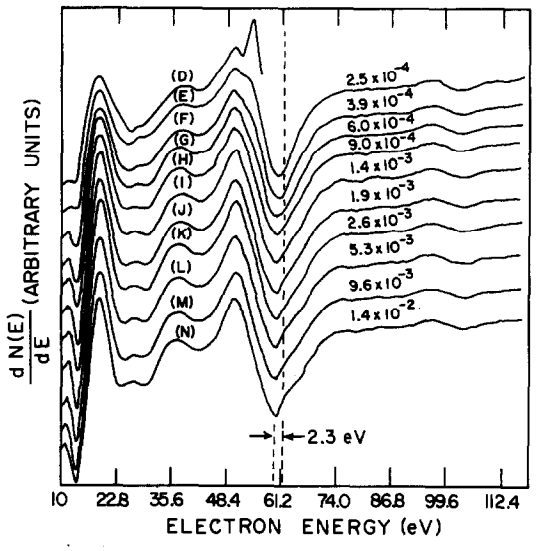

Fig. 1. A. M. Horgan and I. Dalins.[19] Auger-electron spectra showing changes in the $M_{2,3}VV$ peak (61 eV) of nickel on dosing with oxygen. Exposure times are in torr-sec. The dotted line indicates the position of the 61 eV peak of the "clean" Ni(111) surface (by permission of the copyright holders, North-Holland Ltd.).

This type of change of an Auger energy has generally become known as the Auger chemical shift by analogy with the changes in energies of photoemitted electrons in ESCA. The shift is associated with the changes in binding energy of the electrons involved in the Auger transition. An increase in the electropositive character of a metal atom due to oxide formation can be regarded naively as causing a "tightening" of the core levels and hence a shift to higher energies.

Auger transitions can be divided into two categories, (*a*) XYZ and (*b*) XYV or XVV, the members of the latter two often being referred to as valence spectra. Any energy shift in particular XYV or XVV transitions on reaction corresponds to changes in both core level energy and distribution of valence-band electrons. Shifts observed for the type XYZ are considered to be "true" chemical shifts associated only with changes in inner levels caused by valence-band charge-transfer. It should be pointed out that this distinction has not always been made.

In several cases shifts in metal Auger-transition energy (E_{XYZ}) on oxidation have been interpreted by using the empirical equation:

$$E_{XYZ}(z) = E_X(z) - E_Y(z) - E_Z(z + \Delta) \qquad (1)$$

where E_X, E_Y and E_Z are the energies of the levels involved in the Auger transition of the element with the atomic number shown in brackets. The $(z + \Delta)$ term (where Δ is often 1, so the element is the next to z in the Periodic Table) is to allow for the coulombic re-distribution of electrons as a result of ionization. The equation has been quoted in a variety of forms in the literature. Binding energies can be obtained from ESCA for the metal and metal oxide, and approximate Auger energies computed, allowing prediction of Auger chemical shifts.

A good example of the study of a metal–oxygen system is that by Horgan and Dalins[19] who investigated the adsorption of oxygen on the clean (111) surface of a single crystal of nickel. Auger data for a coverage $\theta < 1$ were produced by lightly doping the sample with a molecular beam of oxygen. The results under these conditions were consistent with two chemisorbed states for oxygen adsorbed on the nickel surface. No energy shifts for nickel peaks or the oxygen peak at 516 eV were observed. The coverage condition $\theta > 1$ was produced by maintaining a steady-state gas pressure in the reaction chamber. Studies were confined to the four most intense and easily resolvable nickel peaks at 61 eV ($M_{2,3}VV$), 716 eV ($L_3M_{2,3}M_{2,3}$), 782 eV ($L_3M_{2,3}V$) and 849 eV (L_3VV). Figure 1 shows Auger-electron spectra in the energy range 10–120 eV, which illustrate the changes in the $M_{2,3}VV$ transition on increased doping with oxygen. The 61-eV peak is seen to broaden and undergo a shift to lower energies with increasing oxygen exposure. A final shift of 2.3 eV is reported. Similarly shifts of 1.8 and 2.1 eV are observed for the $L_3M_{2,3}V$ and $L_3M_{2,3}M_{2,3}$ transitions, respectively. The energy changes are rationalized in terms of empirical calculations involving a modified form of equation (1).

Another example of an oxidative study is that of Allen and Wild[20] who examined clean uranium and oxidized uranium surfaces. Figure 2 shows the

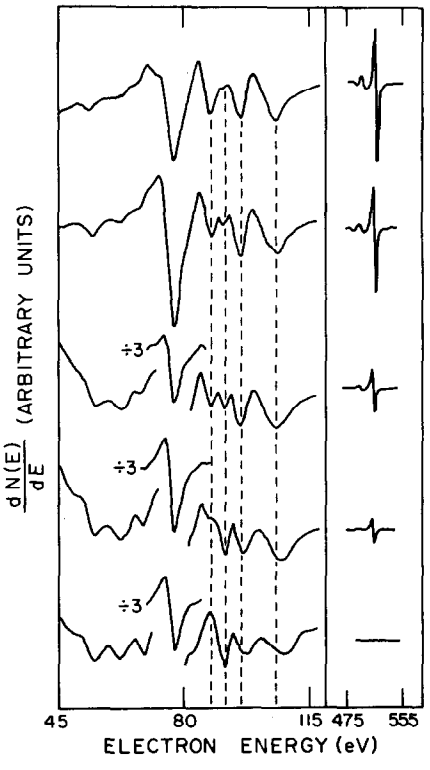

Fig. 2. G. C. Allen and R. K. Wild.[20] Auger spectra from uranium metal foil as a function of oxygen 515-eV peak-height (by permission of the copyright holders, the Chemical Society).

changes occurring in the peaks of the oxide-free surface at 75.5, 53.0, 60.3, 89.9, 95 and 106 eV and the oxygen 515-eV peak, with increased exposure to oxygen. Again several of the peaks change their shape and shift to lower energy. As with the previous study an empirical equation was used to compute Auger energies from ESCA data for the free metal and oxide.

There have been many other studies of metal–oxygen systems of which the following are a few examples—lithium,[21] beryllium,[22–24] sodium,[25] magnesium,[26,27] aluminium,[28] silicon,[29,30] vanadium,[31] chromium,[32] manganese,[28] iron,[26,33–36] yttrium,[37] molybdenum,[38] tungsten,[39,40] platinum,[41,42] samarium, gadolinium and terbium,[43] platinum/tin[44] and silicon/iron alloys.[45]

Experiments have not been confined to the metal–oxygen system, since there have been a number of studies of interactions of other gases, notably CO, with surfaces. The investigation of the adsorption of carbon monoxide and ethylene on a tungsten (100) surface is a typical example.[46] The Auger spectrum in the case of ethylene adsorption at 80 K is attributed to undissociated chemisorbed ethylene. However, the carbon peak shape for adsorption at 300 K is characteristic of surface carbide. The situation with regard to CO may be complicated by the effect of the primary electron beams (in these experiments 2.5 keV) in that the carbide peak shape, indicative of dissociated CO, is observed at both 80 and 300 K. Thus the subjection of the adsorbate to a flux of electrons of 2.5 keV energy *may* cause conversion of virgin CO into another form. The authors of that work quite rightly point out that derivative Auger spectrometry is only useful in indicating the gross changes in the nature of surface-adsorbed species, because of the peak-broadening effects generally observed in "solid-phase" spectra. ESCA spectra have perhaps proved more useful; for example, the dissociation of CO on a molybdenum surface at room temperature has been well characterized.[47]

More recently, high-resolution Auger spectra of surface-adsorbed molecules have been obtained in the non-differentiated mode, in contrast to previous work.[48,49] The spectra of ammonia adsorbed on molybdenum at 450° are indicative of nitride formation whereas at room temperature chemisorption is prominent.[48] The comparison of these spectra with the spectrum of gas-phase NH_3 (obtained in the work of Thompson *et al.*[17]) is interesting (Fig. 3). It is likely that such comparisons will figure more prominently in the literature as the number of available gas-phase spectra increases. Clearly the monitoring of the behaviour of surface-adsorbed species is of considerable importance in catalysis. Similar results to those from the work above have been reported for the interaction of nitrogen with iron and molybdenum.[49]

Other examples of studies of molecules adsorbed on surfaces are silicon/phosphine,[50] aluminium/hydrogen chloride,[51] and silver/sulphur dioxide and carbon dioxide.[52]

Most of the research on gas adsorption has been of this type, where only the interaction of the particular molecule with the surface is considered. However, it is possible to examine a surface reaction between an adsorbed species and molecules in the gas-phase. An example is the work of Bonzel[53] who investigated the kinetics of a surface reaction between adsorbed sulphur and gas-phase oxygen on a copper (110) crystal surface in the temperature range 610–830°. The clean Cu surface was exposed to H_2S and then heated to between 610° and 830° to allow for initial diffusion of some of the adsorbed sulphur into the bulk of the sample. When this process became sufficiently slow the reaction with oxygen was carried out at a constant partial pressure as monitored by a quadrupole mass analyser. The surface sulphur concentration was recorded by AES as a function of time. The only product was SO_2. An analysis of the kinetics of the reaction led to the conclusion that the fast surface reaction between adsorbed sulphur and oxygen probably occurs according to the Langmuir–Hinshelwood mechanism and could be surface-diffusion controlled.

In the last two or three years there has been increased attention paid to the effects of the primary electron beam on gas adsorption. For example, Kirby *et al.*[54,55] have examined electron-beam induced effects on the CO_2 and O_2/silicon systems. It was shown that the impact of the primary beam can create both electronic and thermal effects. Electronically, the

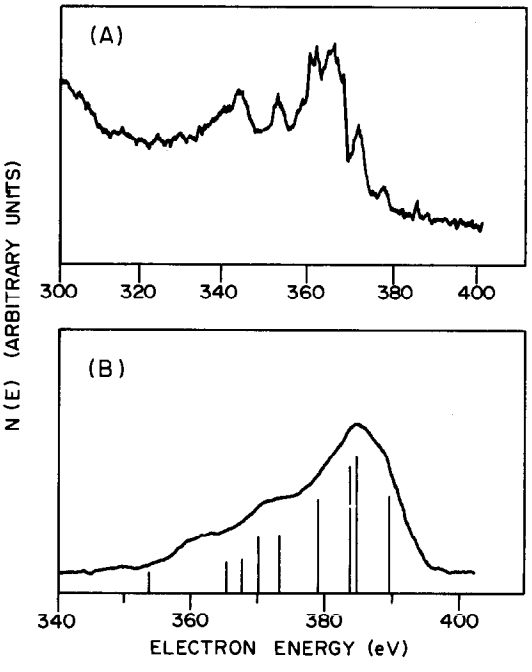

Fig. 3. M. Thompson, P. A. Hewitt and D. S. Woolliscroft.[17] Auger spectrum of NH_3 in the gas-phase (A). (Reprinted with permission: copyright by the American Chemical Society). T. Kawai, K. Kunimori, T. Kondow, T. Onishi and K. Tamaru.[48] Similar spectrum of NH_3 adsorbed on molybdenum at room temperature (B). (By permission of the copyright holders, the American Institute of Physics.)

beam can dissociate surface molecules, desorb molecules and atoms, break bonds in the bulk, and cause surface and bulk excitations. Also, "true secondary" electrons of energy 0–50 eV can reach the surface and cause dissociation of the surface-adsorbed molecules. Local heating by the beam should not be neglected since it may cause, for example, increased diffusion of atomic species such as O into the bulk.

Barrie and Brundle[56] point out that although high beam-currents may be necessary for fast Auger analysis they can have disadvantageous results. These workers compared ESCA and Auger spectrometry of CO adsorbed on polycrystalline molybdenum. Signal intensities in the Auger spectrometry were significantly altered by surface effects induced by the electron beam. Baker and Sexton[57] have shown that electron-beam surface-heating and impact-desorption effects are important in the physisorption of xenon on nickel and platinum. Furthermore, with regard to surface cleaning by inert-gas ion-bombardment before adsorption experiments, the surface structural condition and impurities introduced by ion-implantation have generally not been considered (this topic is discussed in more detail in the section dealing with surface cleaning). Clearly, in the future great care must be taken in the interpretation of Auger data from surface adsorption experiments.

For further detail of electron spectroscopic studies of adsorption of gases and oxidation the reader should consult the review by Brundle.[58]

Catalysis

The potential of AES for the study of heterogeneous catalysis has been cited by several authors, the review by Yates[59] being a good example. In practice many experiments have been concerned with the correlation of the surface elemental composition of a catalyst (obtained by AES) with its performance in chemical processes. For example, Somorjai *et al.*[60] investigated the cleanliness of platinum surfaces with respect to carbon before their use as catalysts for the dehydrocyclization of *n*-heptane to toluene. Takasu and Shimizu[61] used AES to examine the changes in surface composition of copper–nickel plates with pretreatment and related these to catalytic activity. The samples were pretreated by either oxidation and reduction or heat treatment at around 300°. In both cases the surfaces of nickel-rich alloys were enriched with copper, while those of the copper-rich alloys were enriched with nickel. The authors discussed the results in terms of the catalytic activity of copper–nickel alloys for the hydrogenation of ethylene.

Other workers have studied the "working state" of a molybdenum surface on which a reaction occurred between segregated sulphur and ambient oxygen.[62] At temperatures in the range 700–800° it was found that the reaction takes place through direct interaction of oxygen molecules and surface sulphur whereas at higher temperatures of around 1200° it proceeds between sulphur and chemisorbed oxygen. Bhasin[63] examined the AE spectra of two commercial samples of a copper catalyst used for the reaction between methyl chloride and silicon. The surface level of lead in one sample was approximately three times the level in the other catalyst. Apparently such a high level of lead in the "poor" catalyst can be related to the killing of the activity of that particular sample.

It was in 1974 that Yates[59] pointed out that the advance of "clean surface" workers to studies of heterogeneous catalysis was imminent. An examination of the literature today clearly reveals that this progress has taken place, particularly with regard to the techniques that constitute the general area of electron spectroscopy.

Surface cleaning

The advent of studies of surfaces has resulted in the requirement for the rigorous cleaning of the surfaces of single crystals and other materials. The major methods are chemical treatment, sputtering by argon ion-bombardment and cleaving in vacuum. Annealing is frequently used in the first two cases to restore an "ordered" surface. AES is now used routinely to detect surface impurities before and after cleaning. A few examples of AES study of cleaning techniques are considered in this section together with recent work on the structure of ion-bombarded surfaces. Applications of ion-bombardment in repetitive removal of surface layers are discussed at greater length in a later section.

Moon and James[64] examined the effect of HCl vapour-etching (at 800°) of n^+ GaAs (100) substrates doped with silicon, tin or tellurium. Before the etching all Auger spectra were characterized by C, N, O, Ga and As peaks. After treatment the Si and Te-doped samples exhibited unchanged spectra but an accumulation of Sn was observed on the surface of the Sn-doped substrate. The behaviour of the Si and Sn samples, which is contrary to what is expected in terms of the vapour pressure of the elements, was correlated with the equilibrium pressure of Si chlorides being much greater than that of the Sn chlorides (*e.g.*, $P_{SiCL_4}/P_{SnCl_4} \approx 10^7$).

AES data have been recorded for various chemical etchings of n-type germanium wafers.[65] Representative spectra are shown in Fig. 4. The complete list of elements detected was Ge, O, N, C, Ca, F and P although the last three were found only in certain cases. Fluorine contamination was seen only when HF was used. Other workers have examined cleaning by peroxide solutions[66] and abrasion with emery papers.[67,68]

The use of argon ion-bombardment for the cleaning of surfaces before other experiments is widespread. In fact the ion-gun is now a standard fixture on commercial instruments. AES has been used to assess the effectiveness of this technique and also the high-temperature oxygen reaction with reference to nickel (111), nickel (100) and nickel sheet.[69] It was found that heavy carbon deposits on the nickel (100) surface

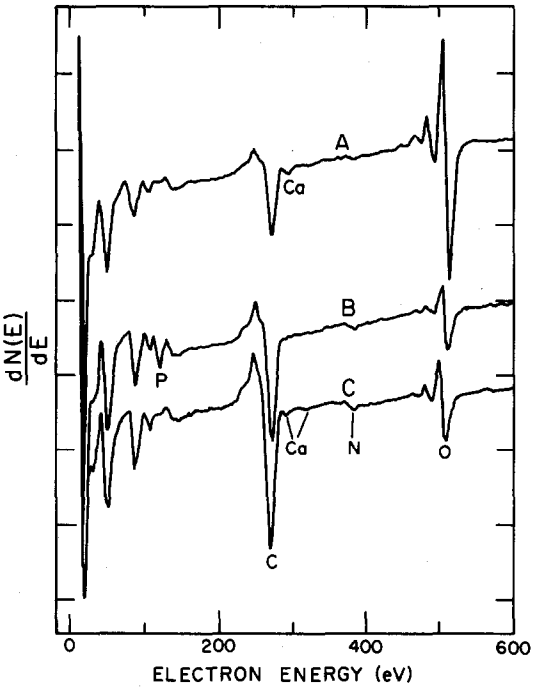

Fig. 4. D. A. Kiewit, I. J. D'Haenens and J. A. Roth.[65] Auger spectra of chemically etched germanium samples. *A*—$HCl:H_2O_2:H_2O$ (1:1:60) + 1%Na_2EDTA, *B*—methanol, acetone, and *C*—$HCl:H_2O_2:H_2O$ (1:1:5). (By permission of the copyright holders, the Electrochemical Society Inc.)

could only be removed after reaction with oxygen at high temperature (~900°) and low pressure (~10^{-6} mmHg). In the case of S on the same surface the contaminant could be removed by argon ion-sputtering at 20° (gun-energy 250 eV and current density 3×10^{-6} A/cm^2) as well as by the oxygen reaction.

Recently Walls, Southworth and Martin[70] carried out a careful study of the effect of ion-bombardment on tungsten surfaces, by AES, LEED and field-ion microscopy (FIM). The last two techniques yield information on the crystalline nature of the surface whereas AES provides an analysis of the inert gas trapped in the surface. FIM images are generally derived from the first atomic layer whereas the AES signal originates (in the case of tungsten electrons) from at least the first six layers, and LEED examines the first two layers. Comparison of FI micrographs of the clean surface with those of the surface after xenon, argon or neon bombardment (800 eV, 1×10^{-6} A/cm^2) showed the surface disorder produced by sputtering. The damage was correlated with the relative sputtering yields of the inert gas ions, *i.e.*, xenon > argon > neon.

Auger analysis of the surface after bombardment with xenon ions (800 eV, 10×10^{-6} A.min.cm^{-2}) revealed that the amount of gas atoms trapped was below the detection limit of the instrument. Furthermore the LEED pattern remained undisturbed. In the case of argon ion-bombardment at 800 eV and 50×10^{-6} A.min.cm^{-2}, argon was detected by means of its peak at 217 eV ($KL_{2,3}L_{2,3}$). With neon, increasing implantation was observed by both Auger and LEED analysis over the bombardment range 10–80 $\times 10^{-6}$ A.min.cm^{-2}. These results are in line with data on trapping probability.

The experiments outlined above emphasise the problems in using ion-bombardment as a cleaning technique before surface studies on, for example, adsorption or catalysis. Subsequently the best species for sputter-cleaning of tungsten surfaces was investigated.[71] From consideration of sputtering yield, trapping probability and surface damage, xenon is the best ion species. However, the authors point out that for cleaning of contaminated rather than pure metal surfaces, other factors may have to be taken into consideration.

Segregation

Perhaps the most important industrial application of AES is in the analysis of segregation of species on a surface or at grain boundaries of metals. Correlation of the results of such studies with the mechanical and chemical properties of materials is now carried out on a routine basis.

Dooley[72] studied surface segregation in zirconium alloys and related the results to previously established properties such as strain-rate sensitivity. Polycrystalline samples were argon ion-sputtered and/or heated to various temperatures before AES analysis. Spectra of a sputtered alloy which contained Sn, Fe, Cr and Ni as minor components are shown in Fig. 5. In the room-temperature spectrum, only zirconium, tin (barely distinguishable), and carbon and oxygen (contaminants) peaks are evident. At 500° the Sn, Fe and C surface-contents increased. Heating to 700° resulted in a decrease of the carbon peak but Fe, Ni and Sn were then present. Between 700 and 900° increasing amounts of sulphur and a general decrease in O and C content were observed. Chromium was only observed at around 900° even though its concentration in the bulk was twice that of nickel. The author related the formation of surface metal carbide to decreased ductility.

The mechanism of the segregation of sulphur from the bulk of a sample of clean polycrystalline molybdenum was examined by the monitoring of sulphur $L_{2,3}M_{2,3}M_{2,3}$ peaks at 152 eV.[73] Dynamic experiments in the temperature range 750–1350° were carried out rapidly over 90 sec and over longer periods of up to 20 min. During the initial stage of segregation the sulphur content at the surface was found to increase linearly with time, implying that there was a constant rate of diffusion of the element from the bulk. The results were said to be consistent with the diffusion of sulphur along grain boundaries. The non-differentiated spectrum (corrected for background) of segregated sulphur measured at high resolution is shown in Fig. 6. The peaks at 152.2 and 155 eV (shoulder) were ascribed to the $L_{2,3}V_2V_2$ and

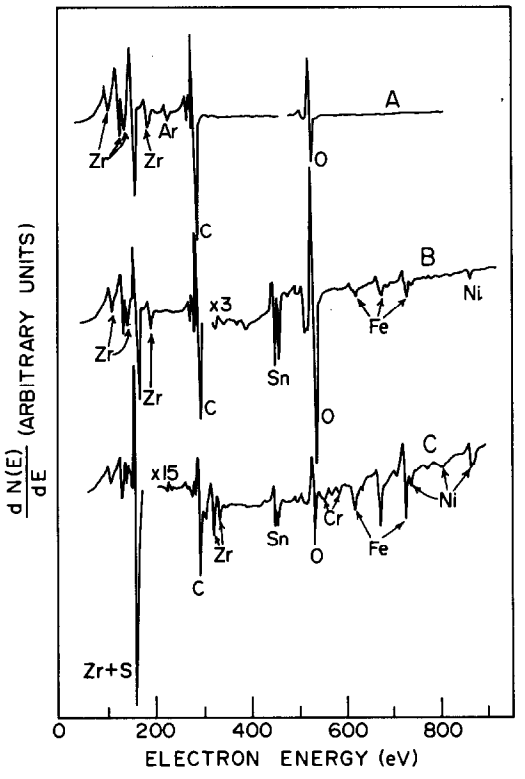

Fig. 5. G. J. Dooley III.[72] Auger spectra of zirconium alloy after argon ion-bombardment. *A*—room temperature, *B*—700°C, *C*—900°C. (By permission of the copyright holders, the American Institute of Physics)

$L_{2,3}V_1V_2$ transitions of molybdenum disulphide, respectively. Hence, the authors were able to glean some information concerning the chemical environment of the segregated element in these experiments.

Further examples of work on segregation are the studies of S, C and P on thorium[74] and S on titanium.[75]

Several workers have attempted to place the surface concentration of segregated species on a quantitative footing. The iron peak at 43 eV and the 119-eV signal of phosphorus were monitored for experiments performed on an Fe–0.063 at% P alloy at various temperatures and times.[76] The equation

$$c_P/c_{Fe} = n_P/n_{Fe} = K(A'_P + b_P)/(A'_{Fe} + b_{Fe}) \quad (2)$$

where c_P and c_{Fe} are surface concentrations, n_P and n_{Fe} are the number of atoms per unit area, A'_P and A'_{Fe} are peak amplitudes, b_P and b_{Fe} are background factors and K is a proportionality constant, was calibrated by measurement of the peak amplitude ratio, A_P/A_{Fe} (in this case corrected for background slope, *i.e.*, (A'_P/A'_{Fe}) and use of the Crank[77] equation for calculation of phosphorus surface concentration under specific conditions. A value of 5.47 was found for the proportionality constant K, which compared favourably with the value of 4.59 computed theoretically on the basis of effective ionization cross-section with inclusion of Coster–Krönig transition contributions.

Another example of empirical quantitative measurement of segregation is the work of Ueda and Shimizu[78] on elements on the surface of an iron–silicon alloy.

In metallurgy, the analysis of segregation at grain boundaries is vital to the understanding of intergranular weakness. This property can result in temper brittleness which is an important problem in the steel industry. AES has proved particularly fruitful in this area. For the study of segregation the specimen is usually fractured under high vacuum to expose a fresh surface for analysis, although this procedure does place obvious constraints on the boundaries to be examined. A good example is the work of Seah and Hondros[79] who examined segregation levels in binary and ternary iron alloys with tin and sulphur over a wide range of temperatures and times. The specimens were heated under vacuum in solid ampoules to develop a similar grain size. After being held at temperatures between 500° and 850° for varying times the samples were water-quenched and then subjected to AES analysis of a cloven area. A comparison of an Auger spectrum typical of a fracture surface with that of pure iron is reproduced in Fig. 7. Tin and sulphur peaks are clearly seen in the spectrum of the alloy.

Depth-concentration profiling

The continuous removal of surface material by inert-gas ion-bombardment (ion-milling) with simultaneous AES monitoring of element concentrations on the "fresh" surface is used to obtain a composition

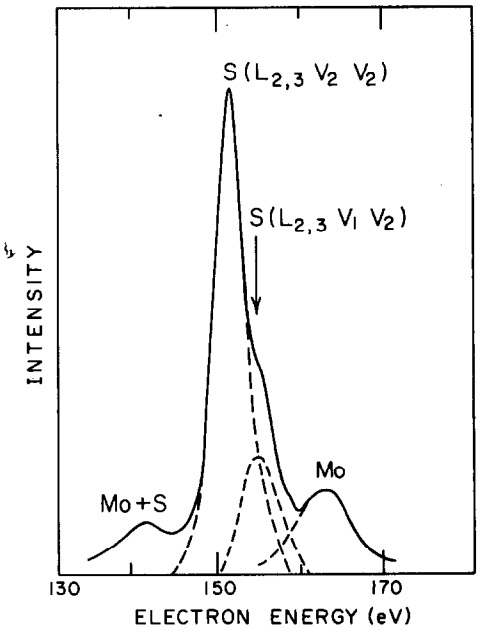

Fig 6. K. Kunimori, T. Kawai, T. Kondow, T. Onishi and K. Tamaru.[73] High-resolution Auger spectrum [$N(E)$ *vs.* E) of sulphur adsorbed on molybdenum. The broken curves are the individual Auger peaks, derived on the assumption of a Gaussian shape. (By permission of the copyright holders, North-Holland Ltd.)

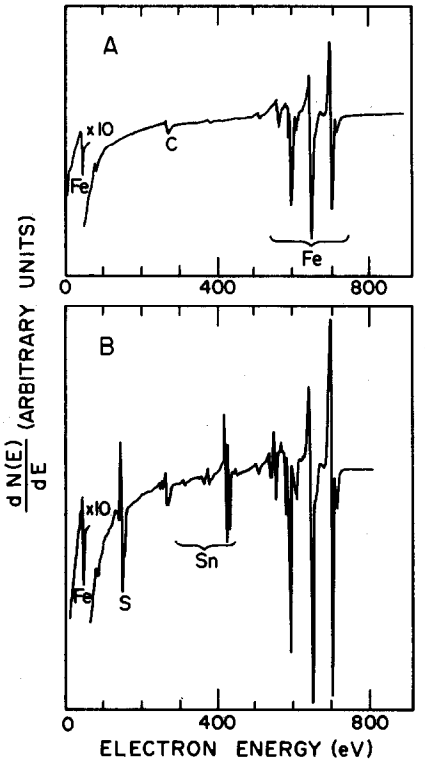

Fig. 7. M. P. Seah and E. D. Hondros.[79] Auger spectra from fracture surfaces. *A*—pure iron and *B*—grain-boundary fracture surface in an iron–1% tin–sulphur ternary alloy quenched from 600°C. (By permission of the copyright holders, the Royal Society.)

profile normal to the solid–vacuum interface. The technique has been applied in several fields, notably to steels, alloys and electrical devices; in this section, some examples of depth-concentration profiling (DCP) are considered together with a brief discussion of the problems associated with interpretation of the profile.

Several of the earlier experiments were performed in a stepwise fashion, often involving transfer of the specimen to the spectrometer, in contrast to the *in situ* method in general use today. For example, Stoddart and Hondros[80] obtained profiles of thin oxide films on stainless steel and an aluminium bronze by a stepwise technique. Samples were ion-etched for various times and then transferred to a spectrometer for Auger analysis. The DCP for the stainless-steel sample is shown in Fig. 8. Enrichment of the oxide layer with Cr, Mn and V is evident whereas with Ni there is depletion. The authors point out that such profiles can be used to analyse protective oxide films that are important in the area of corrosion.

Similar studies by DCP have been carried out on copper/nickel[81,82] and platinum/tin[83] alloys.

Both ramp-etching and *in situ* ion-milling were used by Chang *et al.*[84] in a depth-profiling study of phosphorus-doped SiO_2. The latter is produced by reaction of silane and phosphine with oxygen for electrical application in integrated circuits. The phosphorus and silicon peaks at 120 and 107 eV, respectively, were measured in 12 sec to avoid problems with phosphorus effusion caused by the primary electron beam in the analysis. Figure 9 shows a depth-concentration profile produced by ion-milling of a layer of P-doped SiO_2 (0.5 at% P) on a silicon substrate. The occurrence of a phosphorus-rich layer with an adjacent P-depleted region is evident. From other experiments the authors reached the conclusion that the P-rich layer could not be attributed to phosphorus drift caused by the electron and/or ion beams. Rather, the region could be explained in terms of the rapid reaction of PH_3 at the silicon surface. When the deposition begins the oxide film is thin enough to allow

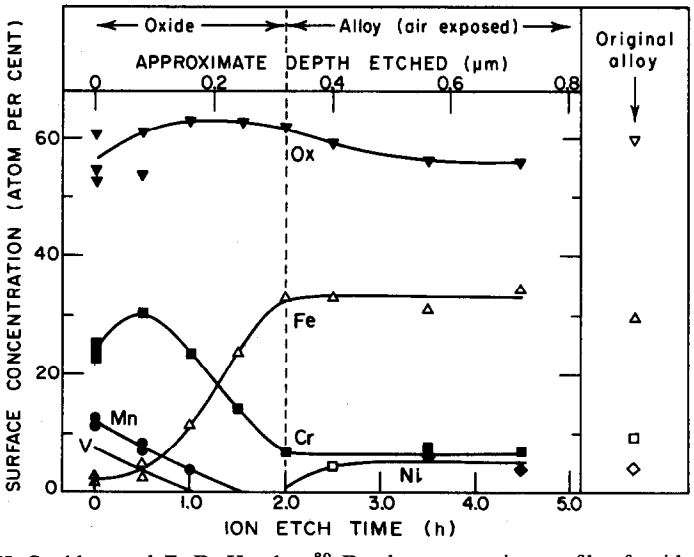

Fig. 8. C. T. H. Stoddart and E. D. Hondros.[80] Depth-concentration profile of oxide layer formed on a stainless-steel sample after 2 hr in air at 900°C. (By permission of the copyright holders, Macmillan Ltd.)

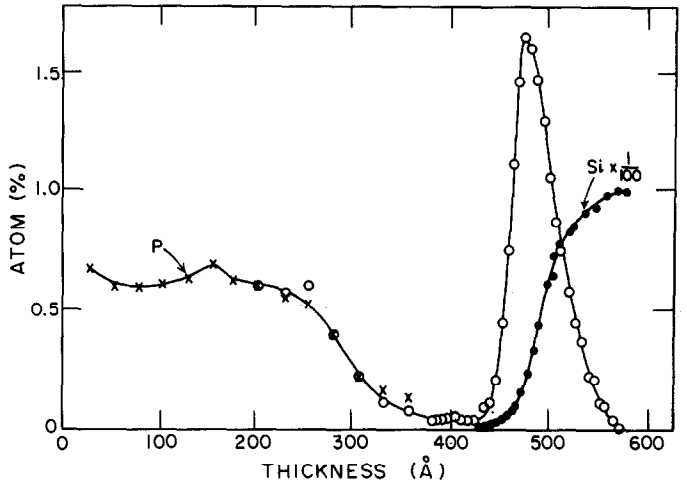

Fig. 9. C. C. Chang, A. C. Adams, G. Quintana and T. T. Sheng.[84] Depth-concentration profile of phosphorus in a P-doped SiO_2 sample (silicon substrate). (By permission of the copyright holders, the American Institute of Physics.)

diffusion of PH_3 to the silicon surface, resulting in a P-rich region. Eventually a steady-state condition is reached, as evidenced by the 0–250-Å region of Fig. 9.

An interesting study was that due to Morabito[85] on the analysis of tantalum films by AES and secondary-ion mass-spectrometry (SIMS). The oxygen, nitrogen and carbon contents of sputtered Ta films have an important bearing on their electrical properties. The homogeneous distribution of these elements in standards prepared by reactive sputtering was established by SIMS and in-depth AES profiling. The results of this investigation demonstrated that, in general, secondary-ion emission is a more sensitive technique than ion-sputtering Auger-spectrometry.

Certain problems associated with ion-sputtering were alluded to in the section dealing with surface cleaning. Because of the nature of the milling technique there are also difficulties in achieving high depth-resolution and an accurate depth-profile. Normally, the depth of sample sputtered is "calibrated" by using the sputtering coefficient of the material under study. However, in a multicomponent system preferential sputtering of one constituent can seriously affect the accuracy of the profile. Other factors to be considered are induced ion-mobility, non-uniform ion-density and destruction of the surface structure (or "roughness"). Recently it was shown that the etching rate can be somewhat higher on that region of the specimen which is exposed to the primary-electron beam than on the area subjected to ion-bombardment only.[86] This effect was attributed to electron-stimulated desorption of surface oxygen with consequent enhanced sputtering in the electron-irradiated area. Thus, the depth-resolution of the DCP technique can be adversely influenced by this artefact.

In earlier applications of DCP many of these factors were largely ignored; however, research activity is currently being devoted to several aspects of the subject. Undoubtedly, the accuracy of the depth profile will increase with information obtained from these experiments.

For further detail on DCP the reader should consult the review by Holloway.[87]

Electrodes and electroplating

Surface composition has an important influence on the nature of electro-deposits. AES has been used with some success in this area; for example, Marcus *et al.*[88] have studied the chemical composition at electro-deposited nickel–nickel interfaces. Nickel laminates were prepared by several cycles of electrodeposition, with intervening polishing and cathodic activation treatment, to give a final thickness of 1 inch. Some samples exhibited minimal resistance to crack formation along a bond. Figure 10*a* shows the AE spectrum from a fracture surface, dominated by characteristic silver peaks. In the spectrum of the surface obtained after argon-ion bombardment (Fig. 10*b*), the peaks due to silver are absent. Thus, the source of the silver deposited at the bond surface was attributed to an activation solution used in a preceding processing step.

A further example of a study of the integrity of electro-deposits is that of Diri and Musket[89] who examined aluminium and uranium samples.

The nature of thin films on the surfaces of platinum anodes in electrolytic cells has been investigated by Johnson and Heldt.[90] Platinum electrodes previously cleaned by inert-gas ion-sputtering were anodized in either sulphuric acid or sodium chloride solution. Only Pt and O peaks were present in the AE spectrum of the surface of Pt anodized in the acid. The results were discussed in terms of the formation of a stable PtO layer. In the case of Pt anodized in sodium chloride solution, Cl was observed as well

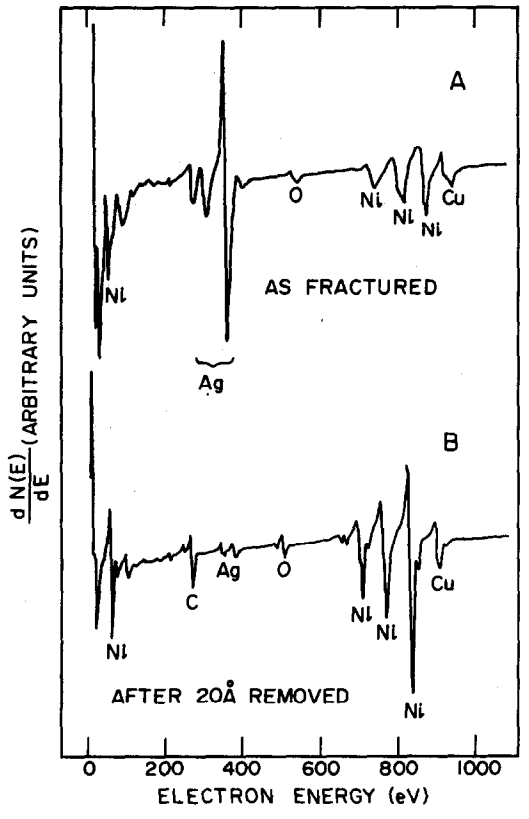

Fig. 10. H. L. Marcus, J. R. Waldrop, F. T. Schuler and E. F. C. Cain.[88] Auger electron spectra of Ni–Ni bond surface. *A*—as fractured and *B*—after 20 Å removed from surface. (By permission of the copyright holders, the Electrochemical Society Inc.)

as Pt and O. These elements were not as strongly bound as the O in the acid-anodized experiment, since they could be partially removed by electron bombardment.

Semiconductors

Several semiconducting materials have been examined by AES for the possibility of surface contamination. For example, Grant and Hass[91] confirmed the work of Taylor[92] regarding the possibility of the Si (111) 7 surface structure being due to an iron impurity. These workers showed that the 45-eV "iron" peak in the Si spectrum is probably due to silicon itself. Further work has shown a similar absence of impurities on Ge (111), GaAs (111), InSb (111)[93] and InAs[94] surfaces.

Alloyed multilayer films have been employed as ohmic contacts to n-GaAs. AES together with DCP was used by Robinson and Jarvis[95] in a study of Ni/Au–Ge contacts on GaAs. Gold and germanium were vacuum-deposited to form a film of eutectic composition on GaAs (100) and GaAs (111) substrates. Nickel was deposited over the Au–Ge and then alloyed at 460° for about 40 sec in a nitrogen atmosphere. Figure 11 shows Auger/depth-composition profiles for the GaAs (111) surface; the curves on the left were obtained before alloying and those on the right after alloying. The results demonstrate that, before alloying, the Ni, Ge and Au covered the substrate in a layered form. After alloying, Ga and As in addition to Ni, Ge and Au are observed near the surface. The authors attribute the relatively high accumulation of Ga near the surface to effusion of the element.

AES and scanning electron microscopy (SEM)

In SEM, changes in collected secondary-electron current with the position of the electron-beam yield information on surface topography. Since the first commercial instrument became available in 1965 the technique has become a powerful research tool. In earlier applications SEM was mainly used to solve problems involving surface topography, but more recently there has been an increasing interest in the correspondence of the surface micrograph with a specific elemental analysis of localized volumes. X-ray spectroscopy combined with SEM is a well-known example of this. In 1970, MacDonald and Waldrop[14,16] demonstrated that the SEM could be interfaced with an Auger spectrometer. Elements in a particular area of a specimen were detected in a point-by-point fashion by high spatial-resolution AES and presented as an Auger-electron image. The image could then be compared with the conventional micrograph. Figure 12 shows the example presented by MacDonald and Waldrop[16] of Auger images (Fe 605 eV and Cu 875 eV) obtained from an iron–copper composite structure. In each image, a point is white if its associated Auger signal-height is at least 25% of the height obtained, just before beginning the image

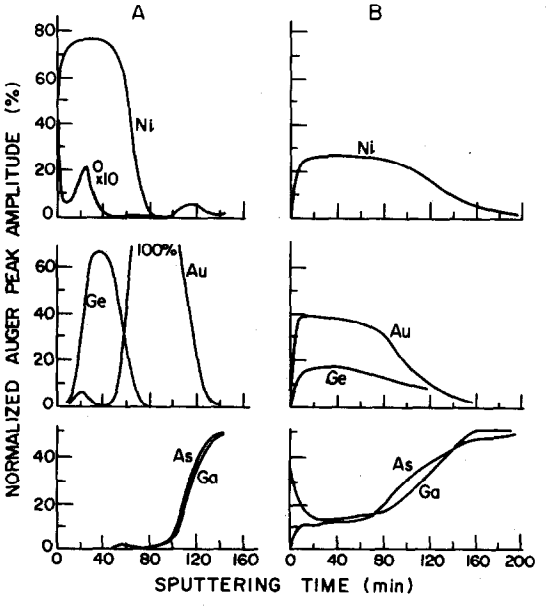

Fig. 11. G. Y. Robinson and N. L. Jarvis.[95] Depth-concentration profile for the ohmic contact structure Ni/Au–Ge on (111) GaAs. *A*—before alloying and *B*—after alloying at 460°C for 40 sec. (By permission of the copyright holders, the American Institute of Physics.)

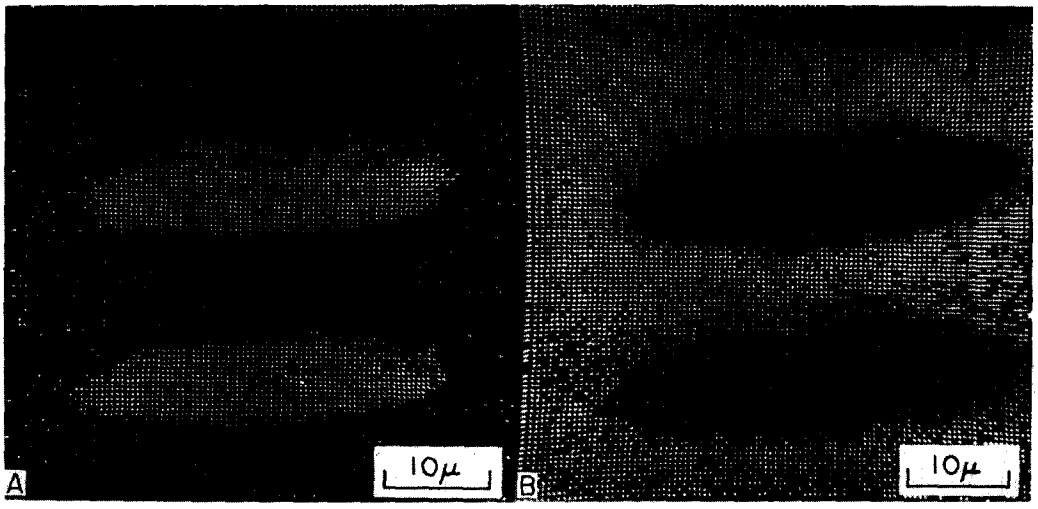

Fig. 12. N. C. MacDonald and J. R. Waldrop.[16] Auger-electron images of an iron–copper composite structure. *A*—iron image and *B*—copper image. (Reprinted by permission of the copyright holders, the American Institute of Physics.)

procedure, from an area known to consist of the corresponding element. The authors pointed out that the spatial resolution is determined by the primary-beam diameter; hence, with the appropriate electron-gun and beam current, submicrometre resolution can be obtained. Furthermore, it shoud be possible to quantify the image by relating the image intensity to Auger peak-height and also to achieve three-dimensional surface analysis by using ion-sputtering.

A number of interesting applications of AES–SEM have been reported in the literature. For example, Marcus *et al.*[88] (see the preceding section) were able to produce an Auger image of the silver present at the surface of the fractured nickel–nickel electrodeposit and compare it with a conventional micrograph (Fig. 13). Another example is the study of Takahashi, Okada and Hotta[96] on the ploughing aspects of frictional force. A sample of MoS_2 was scribed with a diamond tip to determine the relationship between surface damage and change of distribution of elements in the track formed. Auger images of Mo (230 eV) and S (159 eV) showed that the sulphur concentration was higher at the bottom of the track than outside it. This result was associated with the easy cleavage of the crystal because of S–S glide.

The advent of commercial AES–SEM instrumentation should result in the exciting potential for applications in metallurgy, study of electrical devices, for-

Fig. 13. H. L. Marcus, J. R. Waldrop, F. T. Schuler and E. F. C. Cain.[88] Auger-electron image of Ag over bond surface (*A*) and SEM micrograph of same surface (*B*). (Reprinted by permission of the copyright holder, The Electrochemical Society, Inc.)

ensic science and other areas, being fully realized. For an interesting comparison of the possibilities of X-ray, Auger or secondary-ion mass-spectroscopy combined with SEM the reader might consult the paper by Pease.[97] Advantages and disadvantages of the Auger combination as reviewed by this author are reproduced in Table 1.

Table 1. Aspects of AES–SEM[97] (by permission of the copyright holders, Maclean-Hunter Ltd.)

Advantages	Disadvantages
High depth-resolution (5–10 Å)	Spatial resolution 2 μm (?)*
Low detection-limit (10–800 ppm)	High vacuum required
Non-destructive (?)*	Semi-quantitative
Detects elements with $z \geq 3$	Surface-condition dependent
Depth profiling can be used	Difficult to interface AES with SEM
	Slow data acquisition
	Complex instrumentation

* Queries added by the present author.

QUANTIFICATION OF SURFACE AES

The determination of elements present on a surface has been a formidable problem for the Auger spectrometrist for some time. The relationship of the Auger signal to surface concentration is a complex one for several reasons. Inhomogeneity of surface concentration and problems associated with surface morphology are examples. Generally two approaches have been used. The first involves direct or indirect calibration of the surface concentration of a particular element by another technique, and the second is based on experiments concerned with an understanding on a theoretical basis of the factors that contribute to the Auger signal. The latter will be considered first.

Theory

The parameters that contribute to the Auger signal can be written in a simplified expression based on the earlier work of Bishop and Rivière.[98] The Auger current I_A resulting from a transition XYZ in a particular element of concentration N atoms/unit volume is given by

$$I_A = I_P \cdot G \cdot r(E_P) \cdot \tau(E_{XYZ}) \cdot \Phi(E_P, E_X) \cdot \gamma_{XYZ} \cdot N \quad (3)$$

where

I_P = primary current in exciting beam
G = geometrical factor dependent on the instrumental collection efficiency and on the angular distribution of Auger electrons
E_P = energy of exciting beam
$r(E_P)$ = back-scattering factor at E_P
$\tau(E_{XYZ})$ = mean escape depth of electrons with energy E_{XYZ} in the Auger transition XYZ
$\Phi(E_P, E_X)$ = cross-section for ionization of level X of binding energy E_X by an electron of energy E_P
γ_{XYZ} = probability of relaxation by the Auger transition XYZ following ionization of X.

With regard to a particular Auger transition, I_P, E_P and G are generally known; thus the important remaining parameters are r, τ, Φ and γ.

The back-scattering factor r is concerned with the additional contribution to the Auger signal that occurs as a result of ionization by electrons inelastically scattered at the surface. It depends on the energy of the exciting beam E_P and the substrate involved (and therefore E_X). Several workers[98–101] have demonstrated this dependence for a primary beam at normal incidence. Neave, Foxon and Joyce[102] examined Auger yield as a function of primary-beam energy at both normal and glancing incidence, using a silicon (111) surface ($L_{2,3}VV$ Si transition) and a carbon-contaminated silicon surface ($KL_{2,3}L_{2,3}$ C transition). At normal incidence the number of electrons capable of causing ionization, *i.e.*, with energy $> E_X$, reached a maximum at $E_P \sim 6E_X$, whereas at glancing incidence the number continued to increase up to at least $E_P = 22E_X$. Thus, the major determining factor in this case was taken to be the energy distribution of the back-scattered electrons. The contribution of the primary beam was said to be small.

Goto *et al.*[103,104] have used the so-called δ–η method to estimate the contribution of back-scattered electrons to Auger and secondary-electron yields; the system employed was a beryllium deposit on a copper substrate, with normal incidence of the electron beam. The total secondary-electron yield σ and back-scattering coefficient η were obtained experimentally. The true secondary-electron yield δ is found by subtracting η from the total yield. Experiments on Auger electron yield δ_A were carried out at values of E_P from 200 eV to 2.0 keV. Table 2 summarizes the results obtained. In these data, S_A reflects the efficiency of back-scattered electrons in producing Auger electrons and δ_{A_0} the yield due to primary electrons only, both expressed in arbitrary units. Additionally, β_A is the ratio of S_A to δ_{A_0}. The values of r_A are as given by equation (3). The results clearly confirm that back-scattered electrons contribute significantly to the Auger yield, as pointed out by Neave, Foxon and Joyce.

The amount of data available on measurements of electron-scattering lengths or escape-depths τ has

Table 2. Auger-electron characteristics of beryllium[104] (by permission of the copyright holders, North-Holland Ltd.)

E_p *keV*	0.8	1.0	1.5	2.0
S_A	4.0	6.5	6.5	5.5
δ_{A_0}	3.3	2.75	2.15	1.75
β_A	1.2	2.4	3.0	3.1
r_A	1.1	1.2	1.2	1.25

continued to expand over recent years. Values determined by a variety of methods have been assembled by Lindau and Spicer[105] and plotted as a function of the electron energy above the Fermi level for metals and above the valence-band maximum for non-metals (Fig. 14). The logarithmic energy scale ranges from 0 to 3000 eV. The general behaviour is first a sharp decrease with increasing energy followed by a flat minimum in the 50–500 eV range. At higher energies the curve rises again to increased escape-depth. In addition to the large energy-dependence, extremely short τ-values are observed for Cs, Ba, Sr and Yb, and tervalent metals such as Gd and Ce have much greater scattering lengths than bivalent metals such as Ba and Sr. Undoubtedly many more measurements of this parameter will be added in the future. For examples of the techniques involved in escape-depth determination the reader should consult the papers listed in reference 105.

Relatively few measurements of the cross-section Φ (important for AES) have been documented. A significant proportion of those that have been measured have been determined in the gas-phase; for example, Glupe and Melhorn[106] have given K-level cross-sections for the elements in CH_4, N_2, O_2 and Ne. However, a number of semi-empirical expressions have been developed that generally have the form:

$$\Phi(E_p,E_X) = [b/(E_X)^2]f(E_p/E_X) \quad (4)$$

where b is a constant which can take different values, for example, for a K or L level, and f is a function of the ratio of the primary-beam energy to the inner-shell ionization energy. Smith and Gallon used a simple model to estimate Φ by AES for carbon, silicon, selenium, silver, gadolinium and gold. In the equation:

$$I_A = C(I_P\Phi + \alpha\beta) \quad (5)$$

C is a constant and the term $\alpha\beta$ represents the back-scattering contribution. The relative Auger current was measured experimentally for a number of E_p values and the energy-distribution of back-scattered current was also determined. Values of Φ were then computed by an iterative procedure. Generally the cross-sections increase sharply from those for $E_p = E_X$ to a maximum at $E_p \approx 3E_X - 6E_X$, then decrease slowly.

Finally, γ can generally be neglected since it is close to unity, owing to the fact that in conventional AES only shallow inner levels are ionized. Under these conditions the X-ray fluorescence yield is very low compared to Auger-electron production.

Calibration

As with many other analytical techniques, a quantitative analysis can be achieved through calibration procedures, *i.e.*, by correlation of the magnitude of the Auger signal with a measure of surface concentration from another technique. Several independent methods have been used, of which some are direct in that the surface concentration can be obtained from the technique used, whereas others require calibration themselves. Generally, with all these methods, it has been found that there is a linear relationship of surface concentration to Auger-electron count up to monolayer coverage. However, where more layers on a surface are involved the relationship can be somewhat more complex because, for example, of the

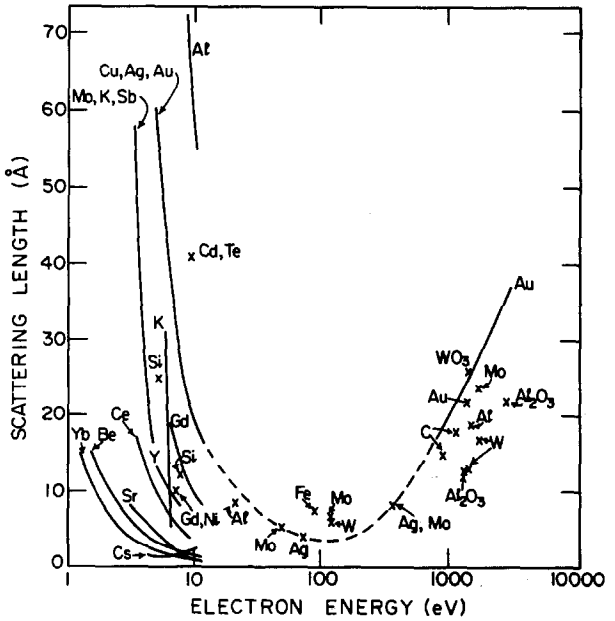

Fig. 14. I. Lindau and W. E. Spicer.[105] Escape depth in Å as a function of the electron energy above the Fermi level for a number of materials. Data sources are listed in reference 105. (By permission of the copyright holders, Elsevier Ltd.)

formation of islands. A few examples of calibration methods are now described.

Perdereau[107] measured the amount of sulphur adsorbed on nickel (111) and (100) surfaces by using hydrogen sulphide labelled with ^{35}S. The amplitudes of the nickel $M_3M_{4,5}M_{4,5}$ peak at 62 eV and sulphur $L_{2,3}MM$ peak at 150 eV were measured as a function of the quantity of sulphur adsorbed on the surface. The radioactivity method for finding the latter was carried out with a precision of $\pm 2 \times 10^{-9}$ g/cm^2. A linear calibration plot was obtained up to saturation of the nickel surface with sulphur. An ion-counting method was used by Thomas and Haas.[108] Sodium, potassium, rubidium and caesium ions from zeolite sources were deposited on a molybdenum (110) surface. The coverage of the surface in each case was calculated from the ion flux to the example. Both alkali-metal ion peaks (Cs 47 eV, Rb 75 eV, K 251 eV) and molybdenum peaks were monitored as a function of coverage. Again linear graphs were obtained under the conditions used.

Several workers[109–111] have employed a quartz crystal oscillator to measure coverage as a function of AE signal. An example of such a quantitative study is that on the adsorption of phosphorus on a silicon (111) surface.[110] In this experiment, a beam of phosphorus particles, largely consisting of P_2 molecules, was impinged at the same rate on both the sample and a quartz crystal oscillator (microbalance) in a series of evaporations. The particles reflected from the silicon and oscillator were monitored by a mass spectrometer to allow determination of the rate of phosphorus adsorption. The ratios of silicon (91 eV) and phosphorus (121 eV) Auger signals were plotted against phosphorus coverage in atoms/cm^2. The main disadvantage with this type of method is that the calibration does not apply to the same surface as that examined by AES. Meyer and Vrakking[99,112] have calibrated Auger peaks by ellipsometry. In ellipsometry the change in the state of polarization of polarized light upon reflection from a surface is measured. The data from the technique can be interpreted quantitatively in terms of surface coverage. The authors have studied the adsorption of O_2 on silicon (111)[99] and PH_3, CH_3SH, CH_3Cl, CH_3OH, NH_2 and other molecules on silicon and germanium surfaces[112] in this manner.

ANALYTICAL POTENTIAL OF GAS-PHASE AES

Despite the growing number of applications of electron-excitation AES in surface studies, relatively little attention has been paid to the analytical potential of the Auger effect in the gas-phase. With the latter it is not necessary to operate the spectrometer in the differential mode as is generally the case with solids. Furthermore, solid-state broadening problems are avoided.[113] Much of the earlier work in the gas-phase was confined to the rare gases.[114–116] In later work, the spectra of several small molecules were recorded, for example N_2, O_2, NO, CO, CO_2 and H_2O,[117] C_3O_2[118] and brominated methanes.[119] Other papers have referred to germanium[120] and organochlorine compounds,[121] and to theoretical analyses of Auger spectra of HF[122] and CH_4.[123]

The possibilities for gas-phase Auger spectrometry in analytical chemistry have recently been discussed by Thompson, Hewitt and Wooliscroft.[17] The factors that contribute to the analytical potential are given below together with one or two comparisons with X-ray excitation.

1. *Qualitative analysis.* The theory of the Auger effect suggests that the technique can provide at least a qualitative elemental analysis for all elements with the exception of hydrogen and helium. Also, in the gas-phase, the valence spectrum observed within the Auger elemental region can yield information about molecular structure. Furthermore, the valence spectrum can be used in a "fingerprint" fashion for the purpose of qualitative identification. With X-ray excitation much of the valence spectrum can be obscured, owing to the energy-width of the exciting source.

2. *Sensitivity and quantitative analysis.* The combination of the availability of electron beams of high flux, and the relatively high inner-shell cross-sections for ionization by electrons leads to the very sensitive nature of the technique. Moreover, the sensitivity is "increased" by multiple excitation from the primary beam, and from back-scattered electrons.

The X-ray flux is considerably smaller and also the cross-sections for ionization of levels of binding energy < 500 eV are lower than with electrons.

3. *Auger theory.* Gas-phase AES offers the opportunity to further understand Auger chemical shifts, ionization cross-sections and Auger quantification.

4. *Surface studies.* Correlation of results for the gas-phase with the spectra of gases adsorbed at surfaces should prove useful in the interpretation of the bonding character of surface-adsorbed species.

Some drawbacks of the technique are as follows.

1. A secondary-electron background is observed, which can be a disadvantage, although this is not as serious as in analysis of solids.

2. Owing to a number of factors such as primary-beam multiple excitation, quantification is difficult.

3. Spectra can be difficult to interpret because of the relatively complex nature of the Auger process and the presence of satellite peaks due to other transitions.

4. The reactivity of the electron must be considered.

5. Instrumentation is both complex and expensive.

Compared to the conventional spectrometer designed for surface work, the gas-phase instrument must include adequate differential pumping for the electron-source, and an electron-energy analysis system capable of greater resolution. A schematic diagram of the spectrometer used by the author is shown in Fig. 15. The electron beam passes through a differential pumping system made between a bridge-piece

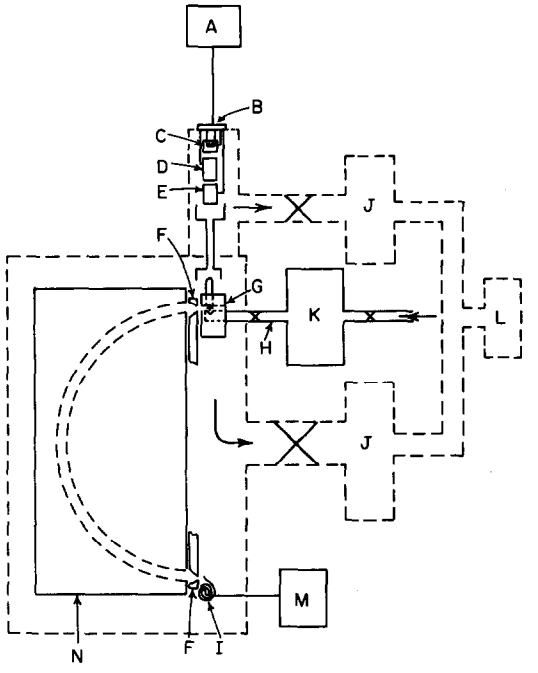

Fig. 15. M. Thompson, P. A. Hewitt and D. S. Woolliscroft.[17] Schematic of gas-phase Auger spectrometer. *A*—electron-gun power-source, *B*—electron-gun base, *C*—gun filament, *D*—focusing anodes, *E*—quadrupoles, *F*—slits, *G*—target chamber, *H*—gas-introduction probe, *I*—electron multiplier, *J*—pumping, *K*—rough pumping, *L*—backing pump, *M*—recorder , *N*—hemispherical analyser. (Reprinted by permission: copyright the American Chemical Society.)

and the electron-gun. The bridge is situated at the entrance side of the analyser and contains a gas-inlet block and vertical inlet tube. Electrons from the tube pass through a variable entrance slit into a 150° hemispherical analyser.

Although this system was used to produce spectra of several molecules, several modifications have been recommended which should increase the sensitivity and ease of application of the instrument.[124]

The sensitivity of the Auger instrument, for a particular transition, can be expressed through the equation

$$I_A = I_p \cdot G \cdot r \cdot \Phi \cdot \gamma \cdot S \cdot P \qquad (6)$$

where P is the gas pressure, S is the probability of Auger-electron escape without prior collision, and the other parameters are as given for equation (3).

As mentioned previously, the potential of AES for sensitive gas analysis lies in the parameter I_p, since high electron fluxes can be obtained with commercial electron-guns. For example, under appropriate conditions, argon present in air is easily detected at 1000 cps. From a quantitative point of view, as with many analytical techniques, it is clearly desirable to calibrate the instrument in terms of Auger count-rate and concentration rather than by use of the several factors in the equation, The importance of one of these parameters, S, is shown in Fig. 16 where the effect of scattering of Auger electrons increases with rising pressure (measured in the differential pumping line).

With respect to the qualitative aspects of the technique, the spectra of molecules in their particular elemental Auger regions are highly characteristic; Fig. 17 shows those obtained from acetylene and ethylene. Interpretation of the spectra can be achieved tentatively through empirical calculations of Auger energies from data from X-ray and ultraviolet photoelectron spectroscopy and equations such as those described previously. For example, the assignment of carbon 1*s*2*m*2*n* transitions of acetylene is given in Table 3.

Where mixtures of gas molecules are involved it is envisaged that prior separation by gas-chromatography will be required. The interfacing of the spectrometer with GLC instruments should present no serious problems in view of the present molecular-separator technology available in analysis by GLC-mass spectrometry.

With regard to the understanding of the Auger chemical shift Siegbahn and co-workers[125] have recently carried out gas-phase AES experiments on several organosulphur and organosilicon compounds. The results were correlated with shifts observed in X-ray photoelectron spectroscopy. It is clear that this area will be a fruitful one for electron spectroscopists in the future.

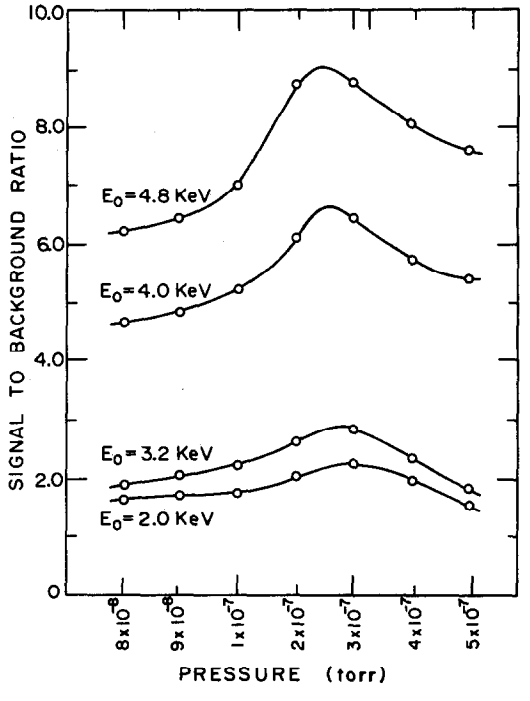

Fig. 16. M. Thompson, P. A. Hewitt and D. S. Woolliscroft.[17] Auger signal-to-background ratio for the argon $2p_{3/2}3p3p$ ($^1D_2$) transition as a function of differential pumping-pressure and incident-beam energy. (Reprinted by permission; copyright by the American Chemical Society.)

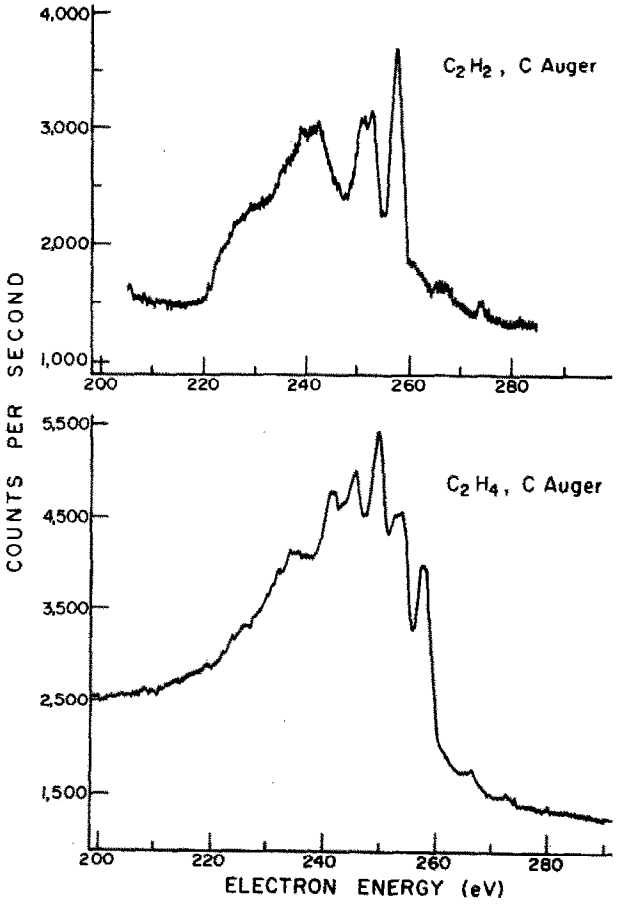

Fig. 17. M. Thompson, P. A. Hewitt and D. S. Wooliscroft.[17] Auger spectra of acetylene and ethylene in carbon 1*s*2*m*2*n* region. (Reprinted by permission; copyright by the American Chemical Society.)

Table 3. Assignment of carbon 1*s*2*m*2*n* Auger transitions of acetylene (adapted from *Anal. Chem.*, 1976, **48**, 1336 by permission. Copyright by the American Chemical Society)

Experimental, *eV*	Empirically calculated, *eV*	Assignment
256.9	256.9	$1s2p\pi^b2p\pi^b$
252.3	252.0	$1s2p\pi^b2p\sigma^b$
250.6	249.9	$1s2p\pi^b2s^*$
247.3	247.1	$1s2p\sigma^b2p\sigma^b$
243.5	242.7	$1s2s\sigma^*2s\sigma^*$
241.9	239.9	$1s2p\sigma^b2s\sigma^*$
238.4	237.8	$1s2s\sigma^b2s\sigma^b$
232.4	232.8	$1s2s\sigma^b2s\sigma^b$

Finally, Vrakking and Meyer[126] have used gas-phase Auger spectrometry with some success to obtain ionization cross-sections for elements in several organic compounds.

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SOME REVIEWS ON THE AUGER EFFECT AND AES

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NOTICE

INTERNATIONAL CONFERENCE ON COMPUTERS AND OPTIMIZATION IN ANALYTICAL CHEMISTRY, AMSTERDAM, 5–7 APRIL 1978

The topics will be as follows.
Application of computers, including microprocessors, data retrieval, data acquisition and data processing. Formal techniques for optimization and evaluation of analytical procedures and results. Systems theory, information theory, operations research and chemometrics.

Final date for receipt of abstracts is 15 December 1977.

For further information and registration write to:

Secretary,
Computers and Optimization in Analytical Chemistry,
Laboratory for Analytical Chemistry,
Nieuwe Achtergracht 166,
Amsterdam,
The Netherlands

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PAPERS RECEIVED

Analysis of Kunifer alloys with EDTA: A. B. SAMUI, M. B. DESHMUKH and J. C. CHAUDHURI. (13 *June* 1977)

Phenanthrenequinone monoxime as a selective reagent for the spectrophotometric determination of iridium(III) and platinum (IV) by solvent extraction: FASIHUDDIN KAMIL, S. K. SINDHWANI and R. P. SINGH. (14 *June* 1977)

Untersuchungen zur atomspektroskopischen Spurenanalyse in $A^{III}B^{V}$-Halbleitermikroproben–II: Untersuchungen zur Bestimmung von Ga-Spuren in In und InAs und von In-Spuren in Ga, GaAs und GaP durch AAS mit elektrothermischer Atomisierung: K. DITTRICH. (31 *May* 1977)

Determination of ferrous oxide in chondritic meteorite: N. R. SEN GUPTA and A. N. CHOWDHURY. (14 *June* 1977)

Hydroxide complexes of cerium(III): J. KRAGTEN and L. G. DECNOP-WEEVER. (20 *June* 1977)

Use of precision colorimetry for elemental microanalysis: E. DEBAL and R. LEVY. (20 *June* 1977)

Liquid–liquid extraction of rhenium thiocyanate with hexamethyl phosphoroamide and direct spectrophotometric determination in the organic phase: MONIDIPA MITRA and B. K. MITRA. (27 *June* 1977)

Sensitivity calibration for the spark-source mass-spectrometric analysis of aluminium and its alloys: E. VAN HOYE, F. ADAMS and R. GIJBELS. (27 *June* 1977)

A sensitive test for microgram detection of *p*-dimethzylaminocinnamaldehyde with ion-exchange resin beads: SAIDUL ZAFAR QURESHI and NIZAM AHMAD. (29 *June* 1977)

Ion-pair extraction of Na^+, K^+ and Ca^{2+} with some organic counter-ions and dicyclohexyl-18-crown-6 as adduct-forming reagent: MOHAMMAD JAWAID and FOLKE INGMAN. (29 *June* 1977)

The determination of polythionates and thiosulphate in mining effluents and mill circuit solutions: R. MAKHIJA and A. HITCHEN. (3 *May* 1977)

Adsorption of molecular iodine on silver-impregnated Amberlite IR-120 resin: S. B. HINGORANI and K. S. VENKATESWARLU. (29 *June* 1977)

Concentration and determination of trace organic pollutants in water: RICHARD C. CHANG and JAMES S. FRITZ. (4 *July* 1977)

Equivalence and inflection points: G. L. SILVER. (5 *July* 1977)

A simple method for determination of selenium in biological materials by flameless atomic-absorption spectrometry with a carbon-tube atomizer: MUTSUO ISHIZAKI. (5 *July* 1977)

Use of hydrazine hydrochloride as a reductimetric titrant in iodometry: Determination of potassium metaperiodate: K. N. UPADHYAYA. (6 *July* 1977)

Composition of phosphoric acids solution obtained after heating of orthophosphoric acid in the presence of nitric acid, sulphuric acid and iron(III): N. JORDANOV, B. NIKOLOVA and I. HAVESOV. (6 *July* 1977)

Comportement electrochimique des antiimflammatoires dérivés de la pyrazolone: Application au dosage dans les medicaments: C. PELINARD, E. NIVAUD and P. BOUCLY. (6 *July* 1977)

Least-squares optimization of an overdetermined coefficient matrix: D. W. ROGERS. (17 *May* 1977)

Electrochemical studies of *p*-nitroanaline–formaldehyde polymer: V. B. AGRAWAL, MOHAN KATYAL and S. MUKHOPADHYAY. (14 *July* 1977)

Extractive spectrophotometric determination of anionic surfactants in waters with Remacrylblau B and Remacrylrot 2BL: ST. JANEVA and R. BORISSOVA-PANGAROVA. (14 *July* 1977)

Pharmaceutical analysis of some tranquilizers and anti-depressants with iodine monochloride: Y. A. BELTAGY, A. S. ISSA and M. S. MAHROUS. (14 *July* 1977)

A spectrophotometric and polarographic investigation of three new cyclohexene-substituted benzodiazepines: J. VOLKE, M. M. ELLAITHY and O. MANOUŠEK. (14 *July* 1977)

Determination of fluoride with thorium nitrate by catalytic titration: FERENC F. GAÁL, BILJANA F. ABRAMOVIĆ and VELIMIR D. CANIĆ. (18 *July* 1977)

On the condensation of salicylaldehyde with hydrazine: EMMANUEL CHUKWUEMEKA OKAFOR. (18 *July* 1977)

Catalytic effect of copper on the hexacyanoferrate(III)-cyanide redox reaction—II: Kinetic study of the catalysed reaction: J. A. CASADO-RIOBO and G. LÓPEZ-CUETO. (18 *July* 1977)

Catalytic effect of copper on the hexacyanoferrate(III)–cyanide redox reaction—III: Catalytic determination of copper: G. LÓPEZ-CUETO and J. A. CASADO-RIOBO. (18 *July* 1977)

Microdetermination of metals in inorganic and organometallic compounds with morpholinium morpholine-*N*-dithiocarboxylate—I: Chromium, manganese, iron(II), iron(III), cobalt, nickel, copper, zinc, silver, cadmium, mercury, lead, bismuth and uranium: A. B. SAKLA, A. A. HELMY, W. BEYER and F. E. HARHASH. (22 *July* 1977)

Potentiometric determination of metals in inorganic and organometallic compounds with morpholinium morpholine-*N*-dithiocarboxylate—II: Chromium, iron(III), iron(II), cobalt, nickel, copper, zinc, silver, cadmium, mercuric, lead and uranium: A. B. SAKLA, A. A. A. HELMY and F. E. HARHASH. (22 *July* 1977)

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Critical review of the high-temperature analytical uses of vanadium(V) oxide: B. NEBESAR. (22 *July* 1977)

Chemico-spectrographic determination of trace elements in mild steels, using 2-hexylpyridine for the extraction of iron: MADASSAR A. QURESHI, M. FARID, A. AZIZ and M. EJAZ. (22 *July* 1977)

Analytical error, observational, manipulative and evaluative: W. E. HARRIS. (15 *July* 1977)

The selective detection of carboxylic acids, ureas and phenols and the semiquantitative determination of citric acid by capillary solid-state spot-tests: MD. NAYEEM AKHTAR, H. S. RATHORE and MOHSIN QURESHI. (25 *July* 1977)

Fluorimetric determination of sulphide: D. A. TINSLEY and J. D. PHILLIPS. (27 *July* 1977)

Quantitative treatment of substituent effects in the polarographic investigations of some potential anti-neoplastic 2-amino-4-aryl-5-phenylazothiazoles: WAHID U. MALIK, R. N. GOYAL and RAJEEV JAIN. (27 *July* 1977)

The behaviour of solid electrodes in normal and differential pulse voltammetric methods: J. W. DIEKER, W. E. VAN DER LINDEN and H. POPPE. (16 *August* 1977)

Spectrophotometric determination of bismuth in concentrates and non-ferrous alloys by the iodide method after separations by diethyldithiocarbamate and xanthate extractions: ELSIE M. DONALDSON. (16 *August* 1977)

The spectrographic determination of gold and platinum metals in geological and other materials with fire assay preconcentration: A. M. HARRIS, J. B. LENGTON and F. FARRELL. (16 *August* 1977)

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A simple method of dissolution of tantalum pentoxide and the separation of Ti^{4+} and Th^{4+} from Cu^{2+}, Ni^{2+}, Co^{2+}, VO^{2+}, UO_2^{2+} and Fe^{3+} on tantalum tungstate columns: MOHSIN QURESHI, H. S. RATHORE and JAGAT S. THAKUR. (18 *August* 1977)

On the confidence interval of the equivalence point in linear titration: CANDIN LITEANU, ION RÍCĂ and VICTOR LITEANU. (18 *August* 1977)

Equilibrium studies on phosphonated toluene–phenol–formaldehyde: E. A. HASSAN, M. F. EL-HADI and A. M. WASFY. (18 *August* 1977)

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IUPAC PROVISIONAL NOMENCLATURE REPORT ON X-RAY EMISSION SPECTROSCOPY

This report, on nomenclature, symbols, units and their usage in X-ray emission spectroscopy is open to criticism and review until August 1977. Copies may be obtained from IUPAC Secretariat, Bank Court Chambers, 2–3 Pound Way, Cowley Centre, Oxford, England. Ask for PNA 54.

8th ANNUAL SYMPOSIUM ON THE ANALYTICAL CHEMISTRY OF POLLUTANTS

Geneva, 5–7 April 1978

There will be invited plenary lectures, invited and submitted research lectures and panel discussions on topics of environmental analysis and aspects of the relations between government, industry and universities in this field. Those interested in giving a research lecture (20 minutes including discussion) should send a 200-word abstract to the Congress Secretariat by end of July 1977. Papers submitted will be subjected to refereeing. The proceedings will be in English, with no simultaneous translation. The address of the Secretariat is P.O. Box 182, CH-4013 Basle, Switzerland.

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Symposia have been organized on 20 different topics, but papers from *all* fields of analytical chemistry may be submitted. Three copies of a 300-word abstract should be sent to Robert W. Baudoux, United States Steel Corporation, Research Laboratory, MS 57, Monroeville, Pa. 15146, U.S.A. to *arrive* by 29 August 1977. The abstract should show the title of the paper, the names and complete addresses of all the authors, and the name of the organization where the work was done. The name of the author giving the paper should be underlined, and the abstract should be signed and dated to certify that the paper has not been previously published or presented.

ERRATA

In the paper by E. E. Chao and K. L. Cheng, *Talanta*, 1977, **24**, 247, there are two corrections to be made.

The last sentence of the summary should read "The pK_{sp}-values..... are shown to decrease linearly.....".

In the last paragraph on p. 250 the first sentence should read "It is..... $PbCro_4$(13.8), $PbMoO_4$ (12.9), and $PbWO_4$ (10.2).....".

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LOUIS GORDON MEMORIAL AWARD

The Editorial Board and Publisher of *Talanta* take great pleasure in announcing that the Louis Gordon Memorial Award for the best-written paper published in *Talanta* in 1976 is made to Emeritus Professor Folke Nydahl, University of Uppsala, Sweden, for his paper "On the optimum conditions for the reduction of nitrate to nitrite by cadmium", *Talanta*, 1976, **23**, 349.

TAL. 24/5—A

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TALANTA MEDAL

PROFESSOR RONALD BELCHER

The Editorial Board of *Talanta* has pleasure in announcing that, with the approval of the Advisory Board, the Eighth Award of the Talanta Medal has been made to

PROFESSOR RONALD BELCHER

of the Chemistry Department, University of Birmingham, England.

For many years Professor Belcher has been recognized as one of the outstanding world figures in analytical chemistry, with a profound influence on the development of research and its publication. His school of analytical chemistry at Birmingham is well known, and his former research students have played an important role in British analytical chemistry. His clarity of presentation of lectures at conferences has been widely acclaimed, and he is generally held in high esteem. In this the year of his retirement from his Chair at Birmingham, it is felt particularly fitting that he should be awarded the Talanta Medal.

TAL. 24/4—A

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NOTICES

FOURTH AUSTRALIAN SYMPOSIUM ON ANALYTICAL CHEMISTRY BRISBANE 77

This symposium will be held in Brisbane from 29 August to 2 September 1977 (in the jubilee year of the Royal Australian Chemical Institute), at the University of Queensland, St. Lucia. The main themes will be analysis in the minerals and energy industries, forensic analysis, and chromatographic analysis of biologically important substitutes. Details and registration forms can be obtained from Mr. J. C. Drinnan, Secretary, Analytical Chemistry Division, R.A.C.L., C.S.I.R.O., Cunningham Laboratory, Mill Road, St. Lucia, Queensland 4067, Australia.

CONGRES DE CHIMIE ANALYTIQUE 33ème CONGRES DU G.A.M.S.

The Group for Advancement of Spectroscopic and Physicochemical Methods of Analysis (G.A.M.S.) in association with the Analytical Chemistry Division of the French Chemical Society and the Industrial Chemistry Group of the Society of Industrial Chemistry is organizing this congress to be held in the Parc des Expositions de la Porte de Versailles (Paris) from 29 November to 2 December 1977. The congress will be national in character, with some international participation. The language for the congress will be French, but papers in English will be accepted. The themes will be chromatography, atomic and molecular spectrometry, automation, analytical problems in pollution and toxicology, surface analysis, analysis of pure materials, electrochemical analysis, analytical biochemistry, and the teaching of analysis. Information may be obtained from Secrétariat du G.A.M.S. (Congrès), 88 Boulevard Malesherbes, 75008 Paris, France.

EUROANALYSIS III

This conference will be held in Dublin, Ireland, from 20 to 25 August 1978, and will deal with all branches of analytical chemistry. Abstracts of papers offered should arrive by 28 February 1978. The conference language will be English. Further details may be obtained from Conference Officer, Euroanalysis III, Institute for Industrial Research and Standards, Ballymun Road, Dublin 9, Ireland.

SIXTH INTERNATIONAL CONFERENCE ON MODERN TRENDS IN ACTIVATION ANALYSIS 1980

Successful conferences on Modern Trends in Activation Analysis have been held in College Station, Texas (1961 and 1965), Washington (1968), Paris (1972) and Munich (1976). The 1980 meeting will deal with original recent work on techniques and applications of activation analysis in many areas of science, technology and medicine. The Conference will last for three to five days and will attract between two hundred and five hundred participants. A commercial exhibition will be held concurrently with the Conference. The proceedings of the Conference will, as on previous occasions, be published in book form. The choice of a site for the Conference will, it is hoped, be made early in 1978. Organisations or individuals wishing to be included in the consultations leading to the selection of a site are invited to apply for further information to Professor J. M. A. Lenihan, Department of Clinical Physics and Bio-Engineering, 11 West Graham Street, Glasgow, G4 9LF, Scotland.

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This conference will be held in Dublin, Ireland, from 20 to 25 August 1978, and will deal with all branches of analytical chemistry. Abstracts of papers offered should arrive by 28 February 1978. The conference language will be English. Further details may be obtained from Conference Officer, Euroanalysis III, Institute for Industrial Research and Standards, Ballymun Road, Dublin 9, Ireland.

SIXTH INTERNATIONAL CONFERENCE ON MODERN TRENDS IN ACTIVATION ANALYSIS 1980

Successful conferences on Modern Trends in Activation Analysis have been held in College Station, Texas (1961 and 1965), Washington (1968), Paris (1972) and Munich (1976). The 1980 meeting will deal with original recent work on techniques and applications of activation analysis in many areas of science, technology and medicine. The Conference will last for three to five days and will attract between two hundred and five hundred participants. A commercial exhibition will be held concurrently with the Conference. The proceedings of the Conference will, as on previous occasions, be published in book form. The choice of a site for the Conference will, it is hoped, be made early in 1978. Organisations or individuals wishing to be included in the consultations leading to the selection of a site are invited to apply for further information to Professor J. M. A. Lenihan, Department of Clinical Physics and Bio-Engineering, 11 West Graham Street, Glasgow, G4 9LF, Scotland.

Talanta, Vol 24, p. i Pergamon Press, 1977 Printed in Great Britain

NOTICES

FOURTH AUSTRALIAN SYMPOSIUM ON ANALYTICAL CHEMISTRY BRISBANE 77

This symposium will be held in Brisbane from 29 August to 2 September 1977 (in the jubilee year of the Royal Australian Chemical Institute), at the University of Queensland, St. Lucia. The main themes will be analysis in the minerals and energy industries, forensic analysis, and chromatographic analysis of biologically important substitutes. Details and registration forms can be obtained from Mr. J. C. Drinnan, Secretary, Analytical Chemistry Division, R.A.C.L., C.S.I.R.O., Cunningham Laboratory, Mill Road, St. Lucia, Queensland 4067, Australia.

CONGRES DE CHIMIE ANALYTIQUE 33ème CONGRES DU G.A.M.S.

The Group for Advancement of Spectroscopic and Physicochemical Methods of Analysis (G.A.M.S.) in association with the Analytical Chemistry Division of the French Chemical Society and the Industrial Chemistry Group of the Society of Industrial Chemistry is organizing this congress to be held in the Parc des Expositions de la Porte de Versailles (Paris) from 29 November to 2 December 1977. The congress will be national in character, with some international participation. The language for the congress will be French, but papers in English will be accepted. The themes will be chromatography, atomic and molecular spectrometry, automation, analytical problems in pollution and toxicology, surface analysis, analysis of pure materials, electrochemical analysis, analytical biochemistry, and the teaching of analysis. Information may be obtained from Secrétariat du G.A.M.S. (Congrès), 88 Boulevard Malesherbes, 75008 Paris, France.

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TALANTA ADVISORY BOARD

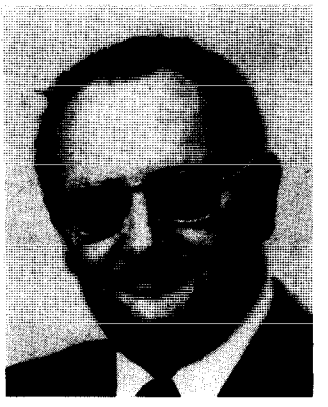
The Editorial Board and Publishers of *Talanta* take pleasure in welcoming the following new members to the Advisory Board of the journal.

J. BARTOS
P. N. KELIHER
A. P. KRESHKOV
R. PERRY

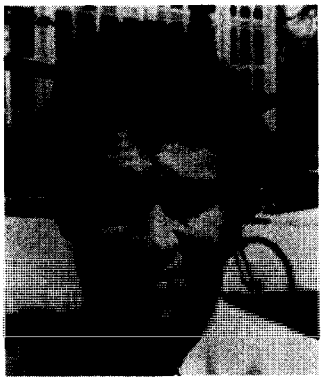
They also wish to record their sincere thanks for the help given by

D. JAGNER
W. F. PICKERING
I. VOINOVITCH

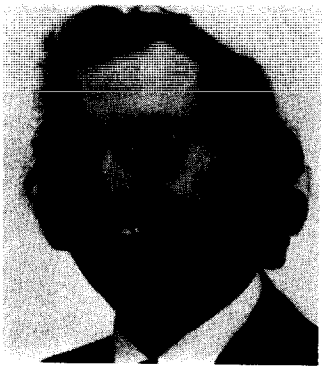
who retire from the Advisory Board.



JAROSLAV BARTOS was born in Paris in 1921. He graduated as Ingénieur-Chimiste de l'Ecole Nationale Supérieure de Chimie de Paris in 1946. He is Head of the Analytical Research Laboratory at Roussel-Uclaf, where he has been employed since 1947. He has authored or co-authored 81 research papers primarily concerned with the colorimetric and fluorimetric determination of organic compounds through functional group reactions, has written three monographs (on diazo-coupling in organic analysis, circular dichroism, and DTA), and is co-author of three books: "Pratique de l'Analyse Organique Colorimétrique", "Colorimetric and Fluorimetric Analysis of Organic Compounds and Drugs", and "Colorimetric and Fluorimetric Analysis of Steroids". He is currently a titular member of the IUPAC Commission V-1 (Analytical Reactions and Reagents). He is a member of the Advisory Board of "Analusis" and also belongs to the Chemical Society of France and the Bureau of the Analytical Group of the French Industrial Chemistry Society.



DR. PETER N. KELIHER is Associate Professor of Analytical Chemistry at Villanova University, Villanova, Pennsylvania, U.S.A. He received his A.B. in Chemistry from St. Michael's College, Vermont in 1962. After three years of high school teaching in the suburban Boston area, he began graduate studies in the department of Professor T. S. West at Imperial College, University of London. Dr. Keliher recieved his M.Sc. from the University of London in 1967 and also the Diploma of Membership of Imperial College (D.I.C.). His Ph.D. thesis (1969) was an investigation into the analytical utility of electrogenerated chemiluminescence, under the supervision of Drs. Bernard Fleet and Gordon F. Kirkbright. He joined the staff at Villanova as Assistant Professor in 1969 and was promoted to Associate Professor in 1973. At Villanova he has done research in analytical atomic spectrometry with emphasis on the use of echelle spectrometer systems for atomic analysis. He has also worked in the area of trace organic analysis in environmental systems and has published approximately 20 papers. Dr Keliher is a member of several scientific societies and is Chairman of the Analytical Group, Philadelphia section, American Chemical Society.



From 1956 until 1961 DR. ROGER PERRY divided his time between research in the paint industry and the Post Office Engineering Department where he gained experience in the field of water analysis and waste treatment. In October 1961 he was awarded an industrial bursary by the Civil Service Commission and obtained first-class honours in Chemistry at Birmingham University in 1964. He spent two years in school teaching then returned to Birmingham University and obtained a Ph.D in 1968, following this by work in the field of air pollution and combustion. In 1970 he moved to Imperial College, London, as lecturer in Public Health Engineering with the responsibility of setting up a multidiscipline research group concerned with air and water pollution problems. He has since lectured and done advisory and consultancy work in many parts of the world, and was given the McNaughton Award for 1976 by the Public Works Congress to enable him to spend three months in an advisory capacity in the developing countries.

TAL. 24/1—A

Talanta, Vol 24, pp i–ii. Pergamon Press, 1977. Printed in Great Britain

PAPERS RECEIVED

Recent developments in chemical analysis using chemiluminescent and bioluminescent techniques: D. B. PAUL (19 *August* 1977)
Separation and estimation of thorium and cerium from a mixture: S. K. BRAHMA and A. K. CHAKRABURTTY. (19 *August* 1977)
Inflection point error in titrimetry: B. W. BUDESINSKY. (12 *August* 1977)
Rapid referee method, free from mercury pollution, for total iron determination in iron ores, sinter and related materials: OM. P. BHARGAVA. (12 *August* 1977)
Spectrophotometric method for assessing oxidation of chalcopyrite-bearing ores and concentrates: G. H. FAYE. (17 *August* 1977)
Applications of the Zeeman effect to analytical atomic spectroscopy—V: Use of commercial hollow-cathode lamp sources: G. F. MURPHY and R. STEPHENS. (25 *August* 1977)
Applications of the Zeeman effect to analytical atomic spectroscopy—VI: A comparison of some experimental and theoretical detection limits: R. STEPHENS. (25 *August* 1977)
A study on the volumetric potassium silicofluoride method for determination of silica in aluminosilicate materials: B. C. SINHA, M. R. SAHA and S. K. ROY. (26 *August* 1977)
Spectrophotometric determination of scandium and zirconium with rufigallic acid: MICHAEL D. MULLIN and RICHARD B. HAHN. (22 *August* 1977)
A specific spot-test for palladium with diphenyldisulphide-2,2′-dicarboxylic acid: S. C. SOUNDAR RAJAN, B. V. NARAYANA and N. APPALA RAJU. (30 *August* 1977)
The drying of sulphide-bearing materials in a microwave oven: A CAVEAT: H. F. STEGER, E. MARK and LEO E. DESJARDINS. (31 *August* 1977).
Compositional analysis of single crystals of flux-grown magnetic garnets by atomic-absorption spectrophotometry: KOHEI AMETANI. (31 *August* 1977)
Sources of copper and cadmium contamination in microbiological samples: RALPH G. SMITH, JR. (31 *August* 1977)
Applications of the Zeeman effect to analytical atomic spectroscopy—VII: Line interferences: R. STEPHENS and G. F. MURPHY. (31 *August* 1977)
Kinetic ultramicrodetermination of chromium(III) and osmium(VIII), based on their accelerating effect on the periodate–arsenite reaction: D. P. NIKOLELIS and T. P. HADJIIOANNOU. (2 *September* 1977)
***N*-Hydroxy-*N*,*N*′-diphenylcinnamamidine (HDPCA) as a new reagent for extractive separation and photometric determination of vanadium(V)**: KANAK KANTI DEB and RAJENDRA K MISHRA. (7 *September* 1977)
Liquid–liquid extraction of zinc from aqueous thiocyanate solutions with 5-(4-pyridyl)nonane in benzene: M. IQBAL, MUDASSAR A. QURESHI and M. EJAZ. (7 *September* 1977)
Analysis of metals by solid–liquid separation after liquid–liquid extraction. Spectrophotometric determination of bismuth and palladium by molten naphthalene extraction of their complexes: MASATADA SATAKE and YASUHIRO TAKAGI. (7 *September* 1977)
Limitations of the use of the ion-exchange method to measure stabilities of organo-metallic complexes, with special reference to heavy metal pollution in the environment: GERARDO GALINDO and HUGO ZUNINO. (8 *September* 1977)
Spectrophotometric determination of some phenothiazine derivatives and opipramol by chloramine-T: A. S. ISSA, Y. A. BELTAGY and M. S. MAHROUS. (14 *September* 1977)
Use of *p*-dimethylaminobenzaldehyde as a colorimetric reagent: H. S. RATHORE, ALI MOHAMMAD and ATMA PRAKASH. (16 *September* 1977)
Spectrophotometric determination of nickel with biacetyl bis-(4-phenyl-3-thiosemicarbazone): A. G. ASUERO and J. M. CANO. (16 *September* 1977)
A study of the solubility of nickel dimethylglyoximate in three alcohol/water solvent systems: K. R. WILLIAMS and ZAIDA C. MARTINEZ. (20 *September* 1977)
Use of chromium ferrocyanide membrane electrode in the potentiometric titration of hexacyanoferrate(II) ion against metal ions: AJAY K. JAIN, SURESH K. SRIVASTAVA, SUSHMA AGRAWAL and RAJ P. SINGH. (21 *September* 1977)
Analytical application of condensed phosphoric acid—I: Determination of ferrous and total iron in iron ores with strong phosphoric acid decomposition method: TADAAKI MIZOGUCHI and HAJIME ISHII. (27 *September* 1977)
An improved biamperometric method for remote analysis of uranium: A. PALAMALAI, T. S. THANKACHAN and G. R. BALASUBRAMANIAN. (27 *September* 1977)
Determination of plasma theophylline by oxidation at the stationary carbon-paste electrode: JAMES W. MUNSON and HASSAN ABDINE. (16 *September* 1977)
Desorption of the oxygen and nitrogen on iron surfaces: Application of X-ray photoelectron spectroscopy to the surface analyses: FUMIHIRO HONDA and KICHINOSUKE HIROKAWA (28 *September* 1977)
Iodometric microdetermination of certain organic acids: S. N. NEMA and R. M. VERMA. (28 *September* 1977)
Separation of carrier-free ^{97}Nb from ^{97}Zr on an alumina column as ion-exchanger: D. K. BHATTACHARYYA and S. BASU. (28 *September* 1977)
The kinetics of thiosulphate decomposition by formaldehyde in acetic acid–acetate buffers in the Wollak titration: WILLIAM KILROY. (26 *September* 1977)
Metal–pyridine–picrate. A ternary system. Copper determination: A. MORALES, M. I. TORAL, A. JADUE and E. TAPIA. (4 *October* 1977)
Spectrophotometric determination of bismuth(III) with 1,3-cyclohexanedione bisthiosemicarbazone monohydrochloride: M. ROMÁN CEBA, J. A. MUÑOZ LEYVA and J. J. BERZAS NEVADO. (4 *October* 1977)

The stability constant of Pd–EDTA: J. KRAGTEN. (7 *October* 1977)
Bestimmung von Stickstoff in Refraktärmetallen—II: Titan: E. GRALLATH and D. HIRSCHFELD. (10 *October* 1977)
2-Thiohydantoin as spectrophotometric analytical reagent. Derivatives obtained by condensation at C-5 with pyridine aldehydes and ketones: M. T. MONTAÑA GONZALEZ, J. L. GÓMEZ ARIZA, F. PINO and R. GARCIA VILLANOVA. (10 *October* 1977)
Potentiometric studies on complex formation between methylmercury(II) and EDTA: MOHAMMAD JAWAID. (13 *October* 1977)
Non-ionic surfactant as a new solvent for liquid–liquid extraction of zinc(II) with 1-(2-pyridylazo)-2-naphthol: HIROTO WATANABE and HIROAKI TANAKA. (17 *October* 1977)
La linéarisation des courbes de titrage potentiométrique—III: Le titrage d'un acide bivalent avec de la base forte: J. ZSAKÓ and F. MAKKAY. (30 *September* 1977)
Polarographic study of the complexes formed by 2-furoate ions with Zn(II) and Eu(III): S. K. BHASIN, OM. PARKASH and J. N. GAUR. (19 *October* 1977)
Study of the molecular interactions of some 1,2,4-substituted anthraquinone derivatives: C. N. ZAHARIA, C. TĂRĂBĂŞANU-MIHĂILĂ, O. L. HÖRER and MARGARETA GIURGEA. (21 *October* 1977)
Spectrophotometric determination of bismuth with diethylenetriaminepenta-acetic acid: P. NENOVA, D. KANTCHEVA and B. KARADAKOV. (21 *October* 1977)
Spectrophotometric determination of vanadium in biological materials with *N*-benzylbenzohydroxamic acid: R. R. NANEWAR and USHA TANDON. (25 *October* 1977)
Polarography of some 3-arylazo-3-bromopentane-2,4-diones: R. N. GOYAL and SUDHA TYAGI. (25 *October* 1977)
Nitrogen determination in coal and coke with an ammonia electrode: K. J. DOOLAN and C. B. BELCHER (25 *October* 1977)
Studies on the extraction of platinum metals with tri-iso-octylamine/CCl_4 from HCl solution: Extractive separation and spectrophotometric determination of palladium: M. Y. MIRZA and IK F. NWABUE. (17 *September* 1977)
Studies on the extraction of platinum metals with tri-iso-octylamine from hydrobromic acid solution: Simultaneous extractive photometric determination of palladium and platinum, gold and platinum: M. Y. MIRZA. (17 *September* 1977)
Simultaneous extractive spectrophotometric determination of gold and palladium with hydrochloride salt of tri-iso-octylamine: M. Y. MIRZA. (17 *September* 1977)
New convenient colorimetric determination of potassium in blood serum: HIDEO SUMIYOSHI, KEISHI NAKAHARA and KEIHEI UENO. (25 *October* 1977)
Solvent extraction separation of hafnium with 4-methyl-3-pentene-2-one: S. KALYANARAMAN and S. M. KHOPKAR. (31 *October* 1977)
4-Amino-3-methyl-5-mercapto-4,1,2-triazole as a gravimetric reagent for silver determination in silver compounds, alloys and complexes: R. V. GADAG and M. R. GAJENDRAGAD. (1 *November* 1977)
Spectrophotometric determination of self-adducts of nickel chelates of 8-quinolinol and 5-nitro-8-quinolinol: KASHINATH S. BHATKI and ARVIND T. RANE. (1 *November* 1977)
Extractive spectrophotometric determination of platinum, rhodium and iridium: KRYSTYNA BRAJTER and URSZULA KOZICKA. (3 *November* 1977)
Extraction of Cu(II) with lauric acid: S. JIMÉNEZ-GÓMEZ, J. PÉREZ-SARMENTERO and A. MOLINA. (9 *November* 1977)
Colorimetric method for the determination of nitrazepam: N. M. SANGHAVI and N. G. JIVANI. (9 *November* 1977)
1-(6′-Ethoxy-2′-benzothiazolylazo)-2-naphthol as a new photometric reagent for copper(II) ions: HAVARD R. HOVIND. (9 *November* 1977)
Electrochemical properties of metal complexes with dithio-acid derivatives and their applications in extraction polarography: V. F. TOROPOVA, G. K. BUDNIKOV and N. A. ULAKHOVICH. (9 *November* 1977)
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Spectrophotometric studies of streptomycin–copper complex, with sodium potassium tartrate as an auxilliary ligand: J. K. AGRAWAL, S. G. HARMALKAR and R. VIJAYAVARGIYA. (11 *November* 1977)
Non-aqueous titration of certain antibiotics in tetramethylurea: M. RIZK and M. I. WALASH. (14 *November* 1977)

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PAPERS RECEIVED

The determination of halide ions by cathodic stripping analysis: KRISHNA MANANDHAR and DEREK PLETCHER. (20 *September* 1976)

Anion-exchange behaviour of metals on DEAE-cellulose in hydrochloric acid–acetic acid media: NOBUTAKA YOSHIKUNI and ROKURO KURODA. (1 *September* 1976)

Recent applications of digital computers in analytical chemistry: D. D. PERRIN. (28 *September* 1976)

Spectrophotometric studies on copper and iron dinitrosoresorcinol sulphonate complexes: MAMDOUH S. MASOUD, T. M. SALEM and M. M. ELESSAWY. (28 *September* 1976)

Molybdenum(VI) complex with oxycarboxylic acids—I: The mechanism of the electroreduction of Mo(VI)–citrate complex in neutral buffer solution: KOTARO OGURA and YUTAKA ENAKA. (28 *September* 1976)

Polarographic study on blue perchromate: S. P. SINGH, D. S. JADON, RAJ PAL and R. C. RAY. (28 *September* 1976)

Indirect complexometric determination of scandium(III), gallium(III), indium(III), iron(III), chromium(III) and aluminium(III) with pyridinol-azo-dyes: J. P. GUPTA, B. S. GARG and R. P. SINGH. (28 *September* 1976)

Analytical application of organic reagents in hydrophobic gel media—IV: Selective preconcentration of cobalt(II) with 1-nitroso-2-naphthol gel: MASASHIGE KUBO, TAIROKU YANO, HIROSHI KOBAYASHI and KEIHEI UENO. (28 *September* 1976)

Colorimetric determination of some pharmaceutical primary aromatic amines: S. BELAL, A. EL SAYED and EL NENSEY. (28 *September* 1976)

Colorimetric determination of penicillins, probenecid, picric, salicylic and acetylsalicylic acid with magenta: YOUSSEF A-BELTAGY. (28 *September* 1976)

Selectivity of composite cation-exchangers: PADMA VASUDEVAN and N. L. N. SARMA. (30 *September* 1976)

Etude de la basicité dans le phénol aqueux: Application au titrage de bases organiques: PAR FERNAND PELLERIN and DANIÈLE BAYLOCQ-QUINAULT. (29 *September* 1976)

Improved scheme for the analysis of high-purity talc: GEORGE NORWITZ and HERMAN GORDON. (1 *October* 1976)

An application of the Zeeman effect to analytical atomic spectroscopy—IV: Capacitively coupled radio frequency spectral sources: R. STEPHENS. (4 *October* 1976)

Colorimetric determination of peroxodiphosphate with hexacyanoferrate(II) in acid medium: LALIT MOHAN BHARDWAJ, D. N. SHARMA and Y. K. GUPTA. (4 *October* 1976)

Non-volumetric titrations: T. DAMOKOS and J. HAVAS. (4 *October* 1976)

Direct atomic-absorption spectrometric analysis of geological materials: A review: F. J. LANGMYHR. (4 *October* 1976)

Evaluation of a pulsed EIMAC source for atomic-fluorescence spectrometry: D. J. JOHNSON, W. K. FOWLER and J. D. WINEFORDNER. (5 *October* 1976)

The determination of gold in tissue by carbon-furnace atomic-absorption spectrometry: H. KAMEL, D. H. BROWN, J. M. OTTAWAY and W. E. SMITH. (5 *October* 1976)

Trace determination of platinum—I: A catalytic method using pulse polarography: P. W. ALEXANDER, R. HOH and L. E. SMYTHE. (6 *October* 1976)

Trace determination of platinum—II: Analysis in ores by pulse polarography after fire-assay collection: P. W. ALEXANDER, R. HOH and L. E. SMYTHE. (6 *October* 1976)

Amperometric complex-formation titrations at a dropping mercury electrode employing normal pulse polarography: J. W. DIEKER, W. E. VAN DER LINDEN and G. DEN BOEF. (8 *October* 1976)

Quantitative reflectometry—IV: Determination of copper in nickel-plating solutions: DAVID KEALEY and JAMES JOHNSTON. (8 *October* 1976)

Haems as potential reagents for carbon monoxide: S. H. MEHDI and A. CORSINI. (1 *October* 1976)

Perchloric acid dissolution of graphite and pyrolytic carbon: GEORGE BUZZELLI and ARTHUR W. MOSEN. (27 *September* 1976)

Oxidation of sulphide minerals—II: Determination of metal in the oxidation products of galena, sphalerite and chalcocite: H. F. STEGER. (11 *October* 1976)

Anion-exchange properties of insoluble solids: M. QURESHI, K. G. VARSHNEY and SAMEEM NAHEED. (12 *October* 1976)

Atom formation and interferences in furnace atomization—I: Effect of anions on atomization temperatures: E. J. CZOBIK and J. P. MATOUSEK. (13 *October* 1976)

Structure and bonding in the metal complexes of ethylenediaminetetra-acetic acid: R. H. NUTTALL and D. M. STALKER. (14 *October* 1976)

Analytical reactions of hydroxyflavones: MOHAN KATYAL and SHRI PRAKASH. (15 *October* 1976)

Influence of aromatic compounds in sugar chromatography on anion-exchange resins: MICHEL PALU and OLOF SAMUELSON. (15 *October* 1976)

Investigation of the problem of storage of dilute solutions, by automated differential-pulse anodic-stripping voltammetry: A. M. BOND and B. W. KELLY. (18 *October* 1976)

The determination of thallium in urine by atomic-absorption spectroscopy and emission spectrography: C. D. WALL. (18 *October* 1976)

The oxidation of benzohydroxamic acid by potassium permanganate in sulphuric acid: M. K. AHMED and C. SUBBA RAO. (18 *October* 1976)

An investigation into the selective dissolution of sulphide phases from geochemical exploration samples: D. PEACHEY and B. P. ALLEN. (19 *October* 1976)

Atomic emission in furnace atomization—I: An experimental study of lithium emission: J. P. MATOUSEK and L. E. SMYTHE. (20 *October* 1976)

Microscopic acid dissociation constants of 3,4-dihydroxyphenylpropionic acid and its related compounds: T. ISHIMITSU, S. HIROSE and H. SAKURAI. (21 *October* 1976)

Mixed-ligand complex of niobium(V) with pyrogallol and *trans*-1,2-diaminocyclohexanetetra-acetic acid: A spectrophotometric determination of niobium: M. SUBBA RAO and K. SRINIVASULU. (21 *October* 1976)

Non-aqueous redox determination of ascorbic acid with copper(II): BALBIR CHAND VERMA and SWATANTAR KUMAR. (22 *October* 1976)

Oxygen determination in fluoro-organic compounds by use of a glassy carbon pyrolysis tube: KAZUO IMAEDA, TAKEO KURIKI and KEIKO OHSAWA. (25 *October* 1976)

Ternary chelates of Zn(II) with some biologically active ligands: D. N. SHELKE and D. V. JAHAGIRDAR. (25 *October* 1976)

Phenanthrenequinone monoxime as an extractive indicator for chelatometric determinations: FASIHUDDIN KAMIL, S. K. SINDHWANI and R. P. SINGH. (25 *October* 1976)

Determination of aluminium in aerosols by flameless atomic-absorption spectrometry: A. PILATE, P. GELADI and F. ADAMS. (25 *October* 1976)

Direct photometric titration of thallium(I) with vanadate: S. R. SAGI and G. S. PRAKASH RAJU. (26 *October* 1976)

A new gravimetric method for the determination of thallium(III): S. R. SAGI, K. V. RAMANA and M. S. PRASADA RAO. (26 *October* 1976)

Acid dissociation of 2-mercaptohistamine and its related compounds: H. SAKURAI and S. TAKESHIMA. (26 *October* 1976)

A highly sensitive spectrophotometric determination of gallium with Pontachrome Azure Blue B and cetyltrimethylammonium chloride: K. UESUGI and T. SHIGEMATSU. (29 *October* 1976)

Analysis of binary alcohol–alcohol and alcohol–water mixtures by the quenching of uranyl luminescence: HUGH D. BURROWS and M. I. VENTURA BATISTA. (1 *November* 1976)

Conductometric titration with indicating resistance—IV: The use of indicating resistances, MPMA membrane + organic acids ± Na-Alassion CS, in the titration of HCl in a highly conducting medium (5*M* NaCl): LUCRETIA GHERGARIU and CANDIN LITEANU. (1 *November* 1976)

Conductometric titration with indicating resistance—V: The use of indicating resistances, MPMA membrane or collodion + inorganic acids ± Na-Alassion CS, in HCl titration in a highly conducting medium (5*N* NaCl): LUCRETIA GHERGARIU and CANDIN LITEANU. (1 *November* 1976)

The determination of thallium in rock and soil samples: R. G. BÖHMER and PETER PILLE. (2 *November* 1976)

Substoichiometric determination of zinc by the isotope-dilution method, using a resin loaded with chelating agent: HIDEO AKAIWA, HIROSHI KAWAMOTO and KAZUKO OGURA. (2 *November* 1976)

A new catalytic reaction of rhenium and its analytical application: N. JORDANOV, M. PAVLOVA and S. STEFANOV. (4 *November* 1976)

Radiotracer studies on ion-selective membranes based on poly(vinyl chloride) matrices: G. J. MOODY, J. D. R. THOMAS and ANNE WILLCOX. (5 *November* 1976)

Studies of vanadium(V) as an oxidant for thiol compounds: R. S. RAMAKRISHNA and M. WILLIAMS. (8 *November* 1976)

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ERRATUM

On p. 695 of Volume 23 (October issue, 1976), equation (5) should read as follows:

$$D = \log [1 + \Sigma f^{a}_{Sm}(I^{a}_{m}/I_0) + \Sigma f^{s}_{Sm}(I^{s}_{S}/I_0) + J^{q}_{\lambda_0}\Delta\lambda_M/I_0] -$$

$$\log [10^{-a_0 w_A} + \Sigma f^{a}_{Sm}(I^{a}_{m}/I_0)10^{-a_m w_A} + \Sigma f^{s}_{Sm}(I^{s}_{m}/I_0) + (J^{q}_{\lambda_0} + J^{r}_{\lambda_0})\Delta\lambda_M/I_0]$$

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The application of diethazine hydrochloride for extractive colorimetric and chromatometric determination of uranium: HELENA PUZANOWSKA-TARASIEWICZ, MIKOŁAJ TARASIEWICZ and ALINA GRUDNIEWSKA. (22 *November* 1976)

Non-aqueous cerimetric determination of ascorbic acid—use of chemical indicators: BALBIR CHAND VERMA and SWATANTAR KUMAR. (23 *November* 1976)

Complexation reactions of biologically active compounds—I: Spectrophotometric study on the reaction of Mn(II) with 4-methyldaphnetin: DEVENDER SINGH and H. B. SINGH. (30 *November* 1976)

Iodometric determination of mercaptans with potassium dichromate by potentiometric and visual methods: N. KRISHNA MURTY and K. RAMA RAO. (1 *December* 1976)

Construction of a new Hg^{2+}-selective liquid state electrode: G. E. BAIULESCU, V. V. COȘOFREȚ and P. G. ZUGRĂVESCU. (1 *December* 1976)

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Spectrophotometric determination of selenium in concentrates and high-purity copper metal with 3,3′-diaminobenzidine after separation by xanthate extraction: ELSIE M. DONALDSON. (13 *December* 1976)

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Applications de la colorimètrie de précision a la microanalyse élémentaire: Dosages de l'aluminium, du cobalt, de l'étain et du fer. Quelques remargues relatives au dosage du titane, du platine, du palladium, du molybdène et du phosphore: E. DEBAL, R. CHASSIN, S. PEYNOT and O. POLIAKOFF. (10 *January* 1977)

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Acetaldehyde as an end-point indicator in the catalytic thermometric titration of weak acids: E. J. GREENHOW and L. E. SPENCER. (24 *January* 1977)

Benzylthiuronium chloride, an acidimetric standard in non-aqueous titrimetry: NEELAM KHANNA and K. S. BOPARAI. (27 *January* 1977)

The analysis of human breath and urine for organic components by chromatographic and mass spectrometric techniques: A review: S. K. PIERCE, H. L. GEARHART and D. PAYNE-BOSE. (20 *January* 1977)

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Spectrophotometric determination of picric acid with zinc and ammonium chloride: J. P. RAWAT, J. P. SINGH and PRITI BHATTACHARJEE. (1 *February* 1977)

Extraction and spectrophotometric determination of thallium(III) with thiothenoyltrifluoroacetone: P. S. PATIL and V. M. SHINDE. (1 *February* 1977)

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OBITUARY

PROFESSOR G. FREDERICK SMITH

Professor Smith died on 23 September 1976 at the age of 85. A biographical sketch appeared in the G. F. Smith Honour Issue of *Talanta* in July 1966, and his contributions to analytical chemistry will be remembered as long as perchloric acid and ferroin are used as reagents. He was a founder member of the Advisory Board of *Talanta*. Professor Smith will be remembered by all who have met him, for his comments on life in general. He is survived by his wife and three children, and his brother, and leaves seven grandchildren and three great-grandchildren.

Talanta, Vol. 24, p. iii. Pergamon Press, 1977. Printed in Great Britain.

PUBLICATIONS RECEIVED

Spectrochemical Analysis of Pure Substances: KH. I. ZIL'BERSHTEIN (ed.), Adam Hilger Ltd., Bristol, 1977. Pp. xv + 435. £27.00.

This book has been translated by J. H. Dixon from the original Russian work published in 1971. The translation has been edited, revised and updated to include material which has become available since that date. It is essentially an advanced treatise concerned with the application of optical emission spectrophotometry to the analysis of high purity substances. There is, therefore, no general introduction to the technique or instrumentation as the reader is assumed to be familiar with the basic principles. Part I is devoted to the relationship between the conditions for excitation of the spectral lines and the limits of detection for trace elements in the sample. Alternative means of excitation and of recording are discussed, together with the interpretation and processing of the data. Part II, which consists of seven chapters, deals with methods for the prior concentration of impurities before carrying out spectral analysis. The techniques described include those of sublimation, crystallisation and zone refining, distillation, ion exchange and precipitation, electro-deposition and chromatography. Part III outlines some practical problems associated with the spectrographic analysis of pure substances, such as the preparation of suitable standards, the provision of non-contaminating environments and the preparation of high purity reagents. This book will be of the greatest value to all practising analytical chemists concerned with the determination of trace elements and the monitoring of the production of high purity materials, a task which is becoming increasingly important at the present time.

Kinetics of Chemical and Enzyme-Catalyzed Reactions: DENNIS PISZKIEWICZ, Oxford University Press, 1977. Pp. ix + 235. £5.75.

It is not an easy matter to identify the class of readers which the author had in mind when writing this book. While the later chapters are specific and detailed, and presuppose that the reader is at least a final year biochemistry student, the earlier chapters contain material available in elementary primers of physical chemistry which will be familiar to the pre-University student. This material comprises an introduction to the concepts of kinetics, thermodynamics and catalysis. It is followed by an account of enzyme-catalysed reactions with a description of the general mechanism and kinetics of typical reactions including selected examples. The final two chapters are those of the greatest use to the graduate student and are concerned with theories of the mechanism of enzyme reactions and the part which they play in the regulation of metabolic processes. While it is true that methods of analysis have been based upon the kinetics of enzyme-catalysed reactions, there is little in this book which will be of general interest to the analytical chemist. On the other hand, the problems presented at the end of each chapter, are of real value to all students of biochemistry and allied disciplines.

ERRATUM

In the paper by K. Srimamam (*Talanta*, 1977, **24**, 31), on p. 35 reactions (*i*) and (*iv*) are irreversible and should be characterized by single arrows, not double:

$$2DA \xrightarrow{-2H^+} DBV + 4e \qquad (i)$$

$$p\text{DBV} \xrightarrow{\text{disproportionation}} q\text{DB} + \text{unidentified irreversible oxidation products} \qquad (iv)$$

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A general method for the spectrophotometric determination of aromatic aldehydes: MOHSIN QURESHI and IFTEKHAR AHMED KHAN. (19 *November* 1976)

Spectrophotometric microdetermination of scandium, yttrium and some lanthanides with Pyrocatechol Violet and micelle-forming cationic surfactant: CHANDRASHEKHAR VEKHANDE and K. N. MUNSHI. (19 *November* 1976)

ERRATUM

On p. 695 of Volume 23 (October issue, 1976), equation (5) should read as follows:

$$D = \log [1 + \Sigma f^{a}_{Sm}(I^{a}_{m}/I_0) + \Sigma f^{s}_{Sm}(I^{s}_{S}/I_0) + J^{q}_{\lambda_0}\Delta\lambda_M/I_0] -$$

$$\log [10^{-a_0 w_A} + \Sigma f^{a}_{Sm}(I^{a}_{m}/I_0)10^{-a_m w_A} + \Sigma f^{s}_{Sm}(I^{s}_{m}/I_0) + (J^{q}_{\lambda_0} + J^{r}_{\lambda_0})\Delta\lambda_M/I_0]$$

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Talanta, Vol 24, p iv Pergamon Press, 1977 Printed in Great Britain

CORRIGENDUM

In the paper "An interlaboratory comparison of potassium determination in rocks and minerals" by T. D. Rice, *Talanta*, 1976, **23**, 359, the second sentence of the first paragraph in the right-hand column of p. 365 should read:

As mentioned for sample NSWMD-2 in Table 6, Laboratories E, F and G obtained...

Talanta, Vol. 24, pp iii–v Pergamon Press, 1977 Printed in Great Britain

PUBLICATIONS RECEIVED

Handbook of Enzymatic Methods of Analysis: GEORGE G. GUILBAULT. Dekker, New York, 1976. Pp. xi + 738. SFrs. 126.

This book follows the author's first book on the topic only six years later, which reflects the rapid growth of interest and development in this field. The techniques for immobilizing enzymes and for using them to make ion-selective electrodes have led to greatly extended use of enzyme methods in analysis and have completely shifted the emphasis in application. The possibilities for specific analysis by use of coupled enzymes seem very wide indeed, and of great importance for biochemical, clinical and food analysis. This handbook, written by one of the leading practitioners in the field, gives an excellent survey of the whole field.

Reaction Mechanisms in Organic Chemistry: FLORIN BADEA. Abacus Press, Tunbridge Well, England, 1977. Pp. 701. £18.85.

This English translation of the third edition of the Romanian text has been updated and revised, and though not of immediate interest to analysts in general, should be useful to those developing reactions for organic analysis and seeking explanations for them, and also to polarographers working on electrode reaction mechanisms.

Säurehydrolyse glykosidischer Bindungen: JÓZSEF SZEJTLI. Akadémiai Kiadó, Budapest, 1976. Pp. 399. £14.40.

For those working in the field of glycoside and carbohydrate chemistry, this monograph on the acid hydrolysis of glycosides will prove a very useful compendium of information and a guide to the literature and chemistry of the topic. The technical aspects are also covered, making the book useful to industrial chemists in this field.

Chromatography of steroids. E. HEFTMANN. Elsevier, Amsterdam, 1976. Pp. xiii + 203. Dfl.90, $34.75.

The many advances in steroid technology made since the publication of Naher's classic "Steroid Chromatography" in 1974 are well documented in Erich Heftmann's latest book on steroid analysis. This small but expensive volume, which is essentially a laboratory handbook, covers almost 1200 references, and consists of two main parts. The first five chapters deal with the chromatographic techniques—column chromatography (including high-speed liquid chromatography), paper and thin-layer chromatography (with details of methods of detection and derivatization), and gas chromatography (including the use of capillary columns), and concludes with a useful discussion of the relationships which have been established between steroid structure and mobility in these various systems. The remaining eleven short chapters cover individual classes of steroids; a separate chapter on steroid conjugates would have been valuable in this section. There are extensive tables of retention data, serviced by a thorough subject index. The references themselves, complete with titles, occupy fully one-third of the book. Much paper could have been saved, and the cost of the book correspondingly reduced, by including them, without titles, on the blank pages to be found at the end of almost every chapter.

Tables of Wavenumbers for the Calibration of Infrared Spectrometers (2nd Ed.): A. R. H. COLE (ed.), Pergamon, Oxford, 1977. Pp. ix + 219. £12.50.

This is an internationally approved list of the frequencies of absorption bands in the infrared region for a series of known compounds. There are two separate sections, the first listing those compounds suitable for calibrating high resolution instruments and the second those compounds and mixtures suitable for the calibration of medium and low resolution instruments. In addition to the tables of wavenumbers there are illustrations of the infrared absorption spectra of the compounds in the appropriate frequency range. A feature of this second edition is that the coverage has been extended to include the far infrared region down to 1 cm^{-1}. Full details are given for the determination of each of the absorption spectra, including references to the original literature. There are Appendices which contain a computer programme for a least-squares fitting of the calibration curve, tables and formulae for the refractive index, of air, and a list of calibration compounds.

Electrochemical Studies of Biological Systems: D. T. SAWYER (ed.), American Chemical Society, Washington D.C., 1977. Pp. viii + 216. $15.50.

This is a collection of twelve papers delivered at a symposium sponsored by the Division of Analytical Chemistry at the 172nd meeting of the American Chemical Society, San Francisco, California, August 1976. There is however, little which will be of direct interest to the practising analytical chemist and the theme of the book is the parallel between electron-transfer processes in biological systems and electrochemistry. A notable exception is a paper describing the polarographic determination of ethylenediaminetetra-acetic acid and nitrilotriacetic acid. Among the newer techniques which are described are the use of rotating-disc enzyme electrodes, the simultaneous examination of absorption spectra and electrochemical behaviour using transparent electrodes and measurements of differential capacitance. The remainder of the text is concerned with the redox properies of the metal derivatives of macrocyclic pigments and the electrochemical behaviour of simple model compounds analogous to large biologically-active molecules.

Colloquium Spectroscopicum Internationale—XVIII: J. P. ROBIN (ed.), Pergamon, Oxford, 1976. Pp. 87. £4.45.

This is a collection of the seven plenary lectures delivered at the XVIII Colloquium Spectroscopicum Internationale at Grenoble in September, 1975. The Conference was sponsored by IUPAC (Physical Chemistry Division) in conjunction with GAMS (France) and was devoted to physical methods of analysis. Three of the seven contributions are in French

but are provided with short summaries in English. The topics dealt with include X-ray fluorescence, Mössbauer spectroscopy, fluorimetry, emission spectra, electron spectroscopy and magnetic resonance. The applications of these techniques are reviewed and in some cases predictions are made about their probable future development.

Advances in Chromatography, Vols 14 and 15: J. C. GIDDINGS, G. GRUSHKA, J. CAZES and P. R. BROWN (eds.). Dekker, New York, 1976 and 1977. Vol. 14, pp. xiii + 459; SFrs. 114-. Vol. 15, pp. xv + 331, SFrs. 98-.

These volumes follow the pattern of the series. They contain diverse articles on all aspects of chromatography. The authors write well and are reasonably critical, but again they have been ill served by the publishing time lag. The balance of articles in Vol. 14 is towards the use of chromatography for making physicochemical measurements of activity coefficients, equilibrium and rate constants, *etc.* The most lengthy (111 pages) contribution is by David C. Locke, who surveys the field comprehensively and critically. There are also accounts of the application of HPLC to nutrients (Andrew J. Clifford) and GLC to drug analysis (W. J. A. Vanden Heuvel and A. G. Zacchei) but Vol. 15 is of more analytical interest. The majority of the contributors are concerned with the application of chromatography to biological problems. There is also an interesting account of signal and resolution enhancement by various computational procedures (R. Annino).

Annual Reports on Atomic Spectroscopy, Vol. 5: C. W. FULLER (ed.). The Chemical Society, London, 1976. Pp. viii + 267. £15.00, $30.00.

This fifth volume of ARAS covers the literature for 1975, a matter of 1573 references. The whole is arranged for the greatest convenience of the user. There are chapters on relevant aspects of fundamentals, instrumentation and applications and the text is admirably complemented by numerous tables, which provide thumbnail sketches of procedures and commercially available instrumentation. The group of enthusiasts who have now assembled five of these reviews with little in the way of recompense, and in the face of numerous obstacles can justly be proud of their success in providing an essential *vade mecum* for the analytical atomic spectroscopist.

Using Computers: B. MEEK and S. FAIRTHORNE. Ellis Horwood, Chichester, 1977. Pp. 208. £7.50 (hard covers), £2.50 (paper).

This book, as its title suggests, is written for computer *users* and not for computer *experts* (actual or potential). The typical computer user, for example, the analytical chemist when he makes use of a computer, learns how to write programs in high-level languages and how to make these programs run on a particular computer. However, with most large present-day computer systems, he is likely to know very little about other aspects of the computer, and he may never even see the machine he is using. The authors of this book attempt, in a very readable way, to give a great deal of background information which will be of interest to such a computer user. They begin by giving a brief history of the development of computers from the Babylonians, by way of Charles Babbage's "Difference Engine" (1812), to the present day. In the section on "The Computer as a Machine", they describe the structure and function of the many varied parts of a modern computing system, from central processors to line printers and incremental plotters. The diagrams and photographs included are most useful. This chapter should greatly assist the computer user to understand what actually happens when he submits his programs, and therefore, perhaps, to improve their efficiency. Other subjects discussed include assemblers and high-level languages, and applications of computers for number-crunching (scientific computing), data-handling (commercial computing), process-control ("real-time computing"), entertainment (computer games, music-production, *etc.*). The conclusion considers "The Computer as a Social Force". Most computer users will find this an interesting, informative and enjoyable book, especially at such a modest price.

Fluorescence and Phosphorescence Spectroscopy: S. SCHULMAN. Pergamon, Oxford, 1977.

This book makes a most useful contribution to the literature as it brings together an understanding of theoretical principles and experimental applications. The book should be a good reference work and might well serve as a text-book for a short course in luminescence spectroscopy. One of the strongest points in the book is a discussion of the fate of the excited state, since the various photophysical processes that can take place have a profound influence on fluorescence and phosphorescence spectra and quantum yields. The book contains an especially thorough discussion of the effect of pH on the excited state. The practising analyst will find the applications section useful, as it contains lists of suitable solvents and methods.

Introduction to High Performance Liquid Chromatography: R. J. HAMILTON and P. A. SEWELL. Chapman & Hall, London, 1977. Pp. xii + 184. £8.00

This book shows signs of haste in production, and though useful as a general introduction to the field, is likely to irritate the reader and so lose some of its value to him. Thus on page 2 we are told there is only one competing phase in gas chromatography, and though we can see what the authors *mean*, it would be kinder to us if they phrased it better. On page 142 it is not clear whether some of the ultraviolet spectra published in the 1930s were of the authors, the journals, or something else unspecified. The last sentence on page 143 almost defies analysis. On page 159 the third reference has the year wrong, and the second cannot possibly be correct (Science has crept in somewhere). The bibliography referred to on page 142 proved elusive. These are all minor criticisms, of course, but how is the uninformed reader to know which mistakes are serious and which are not, or indeed whether mistakes have been made or not? A useful book if read with care and attention.

Annual Reports on Analytical Atomic Spectroscopy 1976, Vol. 6: C. W. FULLER (ed.). Chemical Society, London, 1977. Pp. viii + 282. £18.00, $36.00.

Listing 1682 references and giving a brief indication of their contents, this volume continues the good work of its predecessors, supplying the reader with a handy guide to the major developments in the field during the past year, with the subject divided into various categories such as fundamentals, instrumentation and applications. Owners of the earlier volumes will want this one as well, but overseas buyers should note the dollar premium and take whatever action appeals to them.

Chemical Equilibria in Carbon–Hydrogen–Oxygen Systems: ROBERT E. BARON, JAMES H. PORTER and OGDEN H. HAMMOND, JR. MIT Press, London, 1976. Pp. xii + 110. £7.50.

A compilation of computer print-outs (tables and graphs) for the systems indicated by the title (nitrogen is included as well). SI addicts will need a set of conversion factors from temperatures in degrees Fahrenheit and enthalpy changes in BTU/scf. Strictly for chemical engineers.

The Metallic Elements: R. V. PARISH. Longmans, London, 1977. Pp. xii + 274. £7.95.

As a succinct guide to the sources, properties, uses and general chemistry of the metals and their compounds, this book should be available in every analytical laboratory dealing with inorganic work. The only thing it lacks is analytical chemistry, but then it is not intended to have any, and in any case its value to the analyst is in providing the information and analytical texts so seldom have, although it is often wanted by the analyst. The text could be read profitably by chemists of all kinds, especially by those who do not normally see any chemistry beyond the bounds of their own little back-yard of specialization within a subsection of a single branch of chemistry.

Aquametry, Part 1, 2nd Ed.: JOHN MITCHELL, JR. and DONALD MILTON SMITH. Wiley-Interscience, New York, 1977. Pp. xi + 632. £22.45, $38.00.

The new edition of the authors' encyclopaedic work on the determination of water, published nearly thirty years after the first appearance of the book, has been divided into three parts, of which this is the first, dealing with all methods except those based on electrical measurement (Part II) and the Karl Fischer reagent (Part III). The need to do this reflects the enormous development of analytical chemistry during that time, and the importance of water as a ubiquitous component of materials. Mitchell and Smith have made this part of analysis particularly their own, and the second edition needs no recommendation beyond the authors' names. For information on water and its determination, this book is an essential.

Talanta, Vol. 24, pp. iv–v. Pergamon Press, 1977. Printed in Great Britain.

PUBLICATIONS RECEIVED

Nuclear and Atomic Activation Analysis: W. S. LYON, T. BRAUN and E. BUJDOSÓ, editors, Akadémiai Kiadó, Budapest, 1976. Pp. 242. £16.10.

This volume consists of the proceedings of the conference named in the title, and of the 19th annual meeting on analytical chemistry in nuclear technology, held in Gatlinburg, Tennessee in 1975, and is reprinted from the Journal of Radioanalytical Chemistry. In these times of increasing emphasis on the environment, the papers on activation methods in biology and in environmental science will probably be most interesting for the general reader, but the specialist will find useful material on charged-particle and photon activation analysis, neutron activation analysis, X-ray fluorescence, and other excitation methods.

Nuclear Methods in Physical Chemistry: T. BRAUN and E. BUJDOSÓ, editors, Akadémiai Kiadó, Budapest, 1976. Pp. 601. £28.50.

This volume contains the proceedings of the 8th Radiochemical Conference, held at Mariánské Lázně, Czechoslovakia, in 1975, reprinted from the Journal of Radioanalytical Chemistry. Most of the papers seem rather unexciting to the analytical chemist. The publishers offer to replace defective copies irrespective of time elapsed since purchase. The review copy already had a split at page 16, but a little glue would cost less than the postage for requesting a replacement, especially if the original copy had to be returned (it is printed on a heavily loaded paper).

Selected Annual Reviews of the Analytical Sciences Volume 4: L. S. BARK, editor, The Chemical Society, London, 1976. Pp. v + 73. £9.50; $19.00.

What can one say about this book except that it contains two review articles, one on advances in voltammetric techniques and the other on high-frequency electrodeless plasma spectrometry, both being written by well-known experts in the field, that the book was held up for something like two years, for unspecified reasons, that it was updated only to 1975, and that it is impossible to think of a justification for what can only be called an outrageous price. Perhaps in future the news organs of the publishers will contain fewer castigations of the prices charged by publishers of "commercial" journals.

Lecture Experiments in Analytical Chemistry: I. P. ALIMARIN, V. I. FADEEVA and E. N. DOROKHOVA, Mir, Moscow, 1976. Pp. 306. R1.Kp93.

This little book contains nearly 200 lecture demonstrations covering most aspects of solution chemistry, and should be bought by every lecturer on the topic. At the price it can only be described as the bargain of the year. It lacks an index, but most readers will want to look at the whole lot anyway, and will soon it find opening automatically at their favourite demonstrations.

Instrumental Liquid Chromatography: N. A. PARRIS, Elsevier, New York, 1976. Pp. x + 329. $38.50.

This is Volume 5 of the "Journal of Chromatography Library", a series of texts dealing with various aspects of chromatography and its application in science. It is a practical handbook, directed towards those using, or contemplating the use of, high-performance liquid chromatography in the course of their investigations. It has a small theoretical section and an outline of instrumental design and operation, but the bulk of the text is devoted to the description of experimental methods in which the technique has been successfully applied to the solution of problems. The value of the technique to analytical chemists is emphasized in sections dealing with quantitative determinations, qualitative identifications and the measurement of trace amounts. There is an excellent bibliography and subject index and practising analysts will find particularly useful appendices containing lists of instrument manufacturers and suppliers of well characterized polymer samples for molecular weight standards.

Chemical Derivatization in Liquid Chromatography: J. F. LAWRENCE and R. W. FREI, Elsevier, New York, 1976. Pp. vii + 213. $34.75.

This book constitutes Volume 7 of a series under the general title "Journal of Chromatography Library". It is intended to be a laboratory handbook for the use of analysts working in the field of separation. Despite the title, only half of the text is devoted to descriptions of specific derivatizations, the remainder dealing largely with the theoretical background of the subject and the instrumentation available. The early sections cover the theory of optical absorption and emission and also of radioactivity. The instrumentation section is unexpectedly full, with numerous photographs of commercial instruments and diagrams illustrating the mode of operation. The applications of derivatization methods in both thin-layer and high-pressure liquid chromatography are reviewed in the final chapter under the separate headings of UV–visible, fluorescence and radiochemical methods. In addition to the contents list at the beginning of the book, each chapter has a more detailed list preceding the text and a collection of references following it. There is a comprehensive subject index at the end of the book.

Quadrupole Mass Spectrometry and its Applications: P. H. DAWSON, editor, Elsevier, Amsterdam, 1976. Pp. xxi + 349. No price given.

This book consists of a series of some thirteen articles dealing with various aspects of the newer forms of mass spectrometry based upon oscillatory electric fields. The early sections of the book are written by the editor, an internationally acknowledged authority on the theory and design of mass filters. They are devoted to the basic theory

of mass selection in quadrupole fields and to the operating characteristics of these devices. Subsequent chapters describe alternative geometrical arrangements of oscillating fields using single-rod electrodes or three-electrode, three-dimensional systems. There is also an account of a lesser known type of mass spectrometer based on the time-of-flight principle. The final chapters review the fields of application of mass filters, including their use as gas-chromatographic detectors, their employment in studies of the upper atmosphere and their increasing involvement in disciplines as diverse as physics and medicine. It is these final chapters which will be of interest to the analyst; much of the early part of the book will only be read by those concerned with instrumental design and construction.

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