The Photometric Determination of Traces of Platinum in Electrolyte using Copper Sulfide as a Collector*

By Yûsuke UJIHIRA and Shizo HIRANO**

(Received February 15, 1963)

In recent years, considerable interest has been aroused concerning the behavior of platinum dissolved from platinum anode during electrolysis. Consequently, a simple, sensitive and accurate method for the determination of microgram quantities of platinum is required.

To determine the platinum content in electrolyte, a preliminary separation step is necessary because of the presence of macro amounts of diverse ions and the need to reduce the solution to a small volume.

Several papers have been published for this purpose.

Wölbling(1) reported the adsorption of platinum with activated charcoal, Beamish(2) separated microgram quantities of platinum from

---

* Presented at the 14th Annual Meeting of the Chemical Society of Japon, Tokyo, April, 1961.

** Present address: Applied Chemistry Department, Faculty of Engineering, Tôyo University, Kawagoe, Saitama.

1) H. Wölbling, *Z. angew. Chem.*, **45**, 1720 (1932).

2) F. E. Beamish and A. G. Marks, *Anal. Chem.*, **30**, 1464 (1958).

macro amounts of iron, nickel and copper by the use of a cation-exchange resin, Salyards[3] concentrated minute quantities of platinum by precipitation with stannous chloride from a hydrochloric acid solution containing 1 mg. of tellurium, Bufatin[4] precipitated platinum sulfide using 10 mg. of copper as a carrier, and Poluektov[5] developed a method for the concentration of platinum with mercury-mercuric chloride.

In this paper, the authors will describe the separation of trace amounts of platinum by the use of carrier precipitation with 1.5 to 3.0 mg. of copper sulfide and subsequent photometric determination by the stannous chloride method.

A photometric stannous chloride method for the determination of platinum in a hydrochloric acid solution has been described by Ayres and Mayer[6,7] and by Maziekien and his coworker,[8] and the nature of the platino-stanno-chloro-complex has been studied by Ayres[9] and Mayer.[10]

In order to reduce interference by diverse ions in the photometric step, the authors studied the color development of the platino-stanno-chloro-complex in an aqueous solution and in ethyl acetate.

The separation of platinum from the interfering elements by this carrier precipitation method is simple, and traces of platinum are determined photometrically by mean of the stannous chloride ethyl acetate extraction method, which has the sensitivity required.

This method has been developed specifically for the determination of platinum in electrolytes for the electrolysis of sodium chlorate, but it can be applied equally well to most aqueous solution samples.

Experimental

Apparatus. — A Hirama photoelectric filter photometer, model II, was used for all measurements of the absorbancy, matched 1 cm. glass cells also being used.

Materials. — A standard platinum solutions was prepared by dissolving 0.998 g. of pure platinum metal in aqua regia and evaporating it to dryness. Then 5 ml. of concentrated hydrochloric acid and 0.1 g. of sodium chloride were added to the residue, and the resulting solution was evaporated again to dryness. The residue was dissolved in 20 ml. of hydrochloric acid (1 : 1) and diluted to 100 ml. with water.

This solution was diluted with hydrochloric acid (1 : 0) to give a solution containing 9.8 μg.-Pt/ml.

A copper solution was prepared by dissolving 1.964 g. of reagent grade copper sulfate in 500 ml. of water. This solution contained 1 mg. of copper per 1 ml.

An ammonium nitrate solutions was prepared by dissolving 80 g. of analytical reagent grade ammonium nitrate in 1000 ml. of water.

Aqua regia was prepared by mixing one portion of concentrated nitric acid and three portions of concentrated hydrochloric acid.

A stannous chloride solution was prepared by dissolving 23 g. of analytical reagent grade stannous chloride dihydrate in 30 ml. of concentrated hydrochloric acid and diluting it to 100 ml. with water.

The ethyl acetate used was of the analytical reagent grade, as were the hydrochloric acid and nitric acid used.

Method. — To determine the recovery of trace quantities of platinum from hydrochloric acid solutions with copper sulfide, an aliquot of the standard platinum solution was placed in a 100 ml. beaker and diluted to 50 ml. with 0.5 to 3.0 N hydrochloric acid. After the addition of 1 to 2 ml. of the copper sulfate solution, a fairly rapid stream of hydrogen sulfide was passed into the solution for 10 min.

This solution was heated to near the boiling point and kept at this temperature for 10 min.; then the gas was passed again for 10 min. The precipitate was filtered off through a paper filter (Toyo Roshi No. 5c (ϕ 5.5 cm.)) and then washed successively with 10 ml. of hydrochloric acid (1 : 10), 10 ml. of the ammonium nitrate solution and a few milliliters of water.

The precipitate and the filter paper were ignited in a casserole, and the residue was dissolved in 0.4 ml. of aqua regia. This solution was transferred to a 50 ml. Terex beaker, and the same treatment was repeated with another 0.5 ml. of aqua regia. The casserole and rod were then washed several times with a few milliliters of hydrochloric acid (1 : 1), and the washings were drawn into the same beaker.

The solution was evaporated to dryness on a water bath without prolonged heating, the residue was dissolved in 2.0 ml. of hydrochloric acid (1 : 7), and 0.5 ml. of the stannous chloride solution was added. The colored solution was transferred to a glass-stoppered test tube and was shaken for 1 min. with 2.5 ml. of ethyl acetate.

The color intensity of the organic phase was measured at 420 mμ with a photometer.

The investigation of the photometric stannous chloride method and the tests of the effect of diverse ions were made as follows unless otherwise stated.

The desired volume of the standard platinum solution, and, if necessary, of a diverse ion solution was placed in a 50 ml. Terex beaker and

---

[3] L. B. Salyards, Data obtained from Sandell's "Colorimetric Determination of Traces of Metals," Interscience Publ., N. Y. (1959), p. 721.

[4] O. I. Bufatin et al., *Zhur Anal. Khim.*, **13**, 116 (1958).

[5] N. S. Poluektov and F. G. Spivak, *Zavodskaya Lab.*, **11**, 398 (1945); *Chem. Abstr.*, **40**, 1418 (1946).

[6] G. H. Ayes and A. S. Mayer, Jr., *Anal. Chem.*, **23**, 299 (1951).

[7] G. H. Ayres and A. S. Mayer, Jr., *J. Am. Chem. Soc.*, **77**, 2671 (1955).

[8] I. Maziekien et al., *Anal. Chem.*, **32**, 645 (1960).

[9] G. H. Ayres, ibid., **25**, 1622 (1953).

[10] A. S. Mayer, Jr., and G. H. Ayres, *J. Am. Chem. Soc.*, **79**, 49 (1957).

evaporated to dryness on a water bath. The residue was dissolved in 4 ml. hydrochloric acid (1 : 7), and 1.0 ml. of the stannous chloride solution was added. One half of the volume of this solution was extracted with an equal volume of ethyl acetate. The intensities of the resulting color in the aqueous solution and in ethyl acetate were measured at 420 mμ.

Results and Discussion

The recovery of platinum from a solution with copper sulfide is shown in Table I. Table I indicates that 1 mg. of copper is sufficient for gathering microgram quantities of platinum from a 3 N hydrochloric acid solution. This amount of copper does not interfere at all with the photometric step.

Though the carrier precipitation with copper sulfide is somewhat lacking in selectivity, a trace amount of platinum is completely collected and separated from macro amounts of salt or other diverse ions (especially chromium).

Filtration of the precipitate by a sintered glass filter is unsuitable because of the difficulty of dissolving copper sulfide completely in nitric or hydrochloric acid.

The decomposition of the precipitate and of the filter paper was attained by burning them in a casserole. Their ashes are easily dissolved in 0.4 ml. of aqua regia.

TABLE I. RECOVERY OF PLATINUM BY CARRIER PRECIPITATION WITH COPPER SULFIDE

Cu added mg.	Acidity of solution HCl, N	Pt added μg.	Pt found μg.
1	1	0	0
1	3	0	0.1
2	3	0	0
1	0.3	4.9	4.8
1	3.0	4.9	5.0
1	3.0	9.8	9.8
2	1.0	9.8	9.9
1	3.0	19.6	20.0
1	0.3	19.6	19.5
2	1.0	19.6	19.8
1	3.0	29.4	30.5

TABLE II. COLOR DEVELOPMENT OF PLATINO-STANNO-CHLORO-COMPLEX WITH VARIOUS AMOUNTS OF PLATINUM

Platinum μg./2.5 ml.	Absorbance	
	In water	In ethyl acetate
0	0.000	0.000
4.9	0.072	0.072
9.8	0.145	0.144
19.6	0.289	0.286
39.2	0.575	0.570

TABLE III. EFFECT OF STANDING TIME ON COLOR DEVELOPMENT (Platinum 14.7 μg./2.5 ml.)

Time min.	Absorbance	
	In water	In ethyl acetate
1	0.217	0.218
2	0.217	0.218
5	0.216	0.217
10	0.216	0.216
20	0.216	0.216
30	0.216	0.210
40	0.216	0.030

The results of a study of the color development of the platino-stanno-chloro-complex in the aqueous phase and in the ethyl acetate phase, and the effect of the presence of diverse ions (especially chromium) in the photometric step are shown in Tables II, III and IV.

TABLE IV. DETERMINATION OF PLATINUM IN PRESENCE OF OTHER METALS

Diverse ion added	Absorbance	
	In water	In ethyl acetate
Cu 1 mg.	0.142	0.141
Cu 2 mg.	0.143	0.142
Cr 50 μg.	0.145	0.141
Cr 100 μg.	0.151	0.140
Cr 200 μg.	0.164	0.141
Cr 300 μg.	0.174	0.142
Cr 500 μg.	0.190	0.142
Cr 1 mg.	0.219	0.141
Fe 3 mg.	0.150	0.143
Hg 50 μg.	0.120	0.140
Te 1 μg.	0.150	0.149
Au 2 μg.	0.144	0.143
As 10 mg.	0.145	0.143

Table II indicates that the colored substance is almost quantitatively extracted into ethyl acetate, in which it has essentially the same characteristics as in the aqueous solution.

Table III indicates that this colored complex gives a reproducible color that is stable for half an hour.

Table IV indicates that any interference, in the measurement of the color intensity of the platino-stanno-chloro-complex, caused by the presence of chromium is remarkably reduced by ethyl acetate extraction.

The Determination of Platinum in Electrolytes

The methods described in the preceding chapter were applied to the determination of platinum in electrolytes containing large

TABLE V. PLATINUM CONTENT OF ELECTROLYTE FOR THE ELECTROLYSIS OF SODITM CHLORATE

	Constituents of sample solution w/v %			Pt added μg.	Pt found μg.	Content of Pt p.p.m.	Other methods	
							(1)	(2)
A	NaCl	13		0	0.2	<0.004	0	0
	$NaClO_3$	46.5		9.8	10.0			
				9.8	9.9			
	$Na_2Cr_2O_7$	0.2		19.6	20.2			
B	NaCl	12.2	—*a*	0	5.6	0.22	0.19	0.23
	$NaClO_3$	53						
	$Na_2Cr_2O_7$	0.2	—*b*	0	13.2	0.53	0.50	0.50
C	NaCl	7.8	—*a*	0	4.1	0.16	0.17	0.18
	$NaClO_3$	37.5						
	$Na_2Cr_2O_7$	0.2	—*b*	0	56.0	2.24	2.16	1.80

(1) Data obtained by amalgamation method.
(2) Obtained by ion exchange method.

—*a* Clear solution.
—*b* Solution containing mud.

amounts of sodium chloride, sodium chlorate and sodium bichromate.

Twenty-five milliliters of a sample solution was taken in a 200 ml. beaker, then concentrated and hydrochloric acid was carefully added. The quantities and the speed of the addition of the acid were experimentally selected to avoid the spraying of the sample solution by the rapid evolution of chlorine gas.

After evolution had ceased, the solution was warmed to ensure the complete decomposition of the oxidizing substances. Then platinum was isolated by carrier precipitation with copper sulfide and was determined photometrically by the stannous chloride method described previously.

The results of eight determinations of micro amounts of platinum in electrolytes sodium chlorate electrolysis are shown in Table V. The results are in good agreement with those obtained by other methods of analysis. The blank value obtained by running the full procedure corresponded to less than 0.1 μg. of platinum.

Summary

A method of separation has been developed for the photometric determination of trace amounts of platinum in electrolytes for the electrolysis of chlorate by the use of carrier precipitation with copper sulfide.

After a sample solution had been treated with concentrated hydrochloric acid, the preliminary separation of platinum was made by carrier precipitation with copper sulfide, and, following the ignition of the precipitate, the ashes was introduced into a hydrochloric acid solution. The orange-colored substance which was produced by the addition of the stannous chloride solution was extracted into ethyl acetate, and the color intensity of the ethyl acetate phase was measured at 420 mμ.

The recovery of platinum was quantitative, and the removal of macro amounts of salt and divers ions was satisfactory.

Experiments using synthetic sample solutions indicate that trace quantities of platinum in electrolytes for the electrolysis of sodium chlorate could be determined by this method with an accuracy of from 5 to 10% in the range between 0.02 and 0.00 p.p.m.

The authors wish to express their grateful thanks to Dr. Atsushi Mizuike of the University of Tokyo for his continuous interest and encouragement throughout this investigation.

Institute of Techno-Analytical Chemistry
Faculty of Engineering
The University of Tokyo
Hongo, Tokyo