Chemical Analysis by Means of Organic Compounds. XVI. Amperometric Titrations. III. Cuprimetric Titrations(1)

By Masayoshi ISHIBASHI and Taitiro FUJINAGA

(Received September 4, 1950)

In the previous paper,(2) we reported that Mg, Zn, Cu and Fe were directly titrated with oxine (8-hydroxyquinoline) by the amperometric method and that this method was applied to the determination of Mg in aluminium alloys and sea-water.

We recently devised a simpler method also by using dropping mercury electrde as indicator electrode. The amperometric titration is carried out by connecting the indicator electrode with the saturated mercuric iodide reference electrode $^{3)}$ through microammeter, and no e. m. f.

---

(1) This work was disserted in the 2nd and 3rd annual meetings of the Chemical Society of Japan held at Tokyo in 1949 and at Kyoto in 1950 respectively.

(2) M. Ishibashi and T. Fujinaga, *Bull. Chem. Soc. Japan*, **23**, 25, 27 (1950).

(3) I. M. Kolthoff and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **18**, 161 (1946).

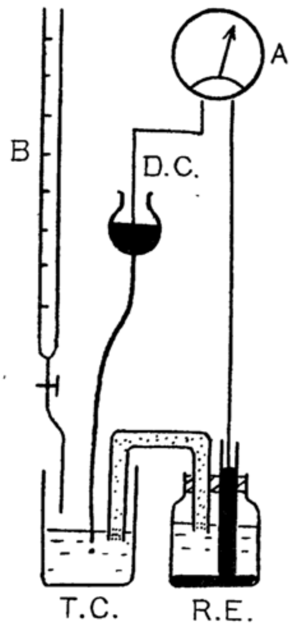

Fig. 1.—Apparatus of titration: A, microammeter; B, burette; T. C., titration cell; D. C., dropping electrode; R. E., reference electrode.

needs to be applied to the cell. So-called "wave compensator"⁽⁴⁾ is used, if necessary, to eliminate the residual current or other disturbing diffusion current, *e. g.*, oxygen current. The reference electrode has an electrode potential of −0.49 volt *vs.* the saturated calomel electrode, so not only single cupric ion but cupriammine ion are reduced at this potential and give the diffusion current proportional to their concentration. Observing this internal electrolytic current due to cupric ion, the end point can be detected amperometrically. So this method of titration should be called the "Amperometric Cuprimetry."

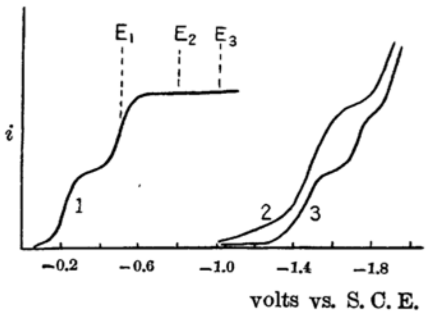

Fig. 2.—Polarograms of cupriammine, α-benzoinoxime and oxine in 1 N-NH_4OH, NH_4Cl: Curve 1, cupriammine; curve 2, benzoinoxime; curve 3, oxine. E_1, potential of mercuric iodide electrode; E_2, potential of mercuric sulfide electrode; E_3, potential of zinc amalgam electrode.

In this paper, the detrmination of copper, zinc and magnesium with oxine and also copper with α-banzoinoxime by the cuprimetric method were described.

Apparatus and Materials

The apparatus and the circuit are shown in Fig. 1. Electrical connection between reference electrode and the titration cell is made by means of a salt bridge filled with a gel of 3% agar and 30% potassium chloride. The electrolyte solution of the reference half cell is prepared by saturating potassium iodide in saturated potassium chloride solution. A layer of mercury serves as anode.

Standard Solutions Used: Cupric Sulfate.—0.1 mol of pure recrystallized cupric sulfate ($CuSO_4 \cdot 5H_2O$) was weighed out and 1 ml. of 0.1 mol sulfuric acid was added to it to prevent the hydrolysis of cupric ion and was diluted to one liter as the standard solution.

8-Hydroxyquinoline.—the same as previously reported.⁽²⁾

α-Benzoinoxime.—synthesised from benzaldehyde, sodium cyanide and hydroxylamine in the usual way and recrystallized from ethanol. 1% of this solution (50% ethanol) was prepared for the intermediate standard solution.

Experiments

(1) Determination of Copper and Zinc with Oxine.—Copper is determined by the residual titration method. Known volume of excess oxine solution is added to the sample solution buffered by ammonium chloride-ammonia or sodium acetate-acetic acid, and the excess reagent is back titrated with standard cupric sulfate solution. The end point is indicated by the diffusion current of cupric ion. added in excess to oxine present in the solution. Copper in the sample is determined by deducing the used volume of cupric sulfate standard solution from its blank value. The titration curves are shown in Fig. 3 and the data are shown in Table 1.

Zinc is titrated by the same method, but zinc oxinate precipitate is filtered off and then the filtrate is titrated in order to avoid the transformation of zinc oxinate to copper oxinate.

(2) Determination of Magnesium with Oxine.—Magnesium can be determined by the same method as zinc, but in this case, better results are obtained by dissolving the magnesium oxinate

---

(4) J. J. Lingane and H. Kerlinger, *Ind. Eng. Chem., Anal. Ed.*, **12**, 750 (1940).

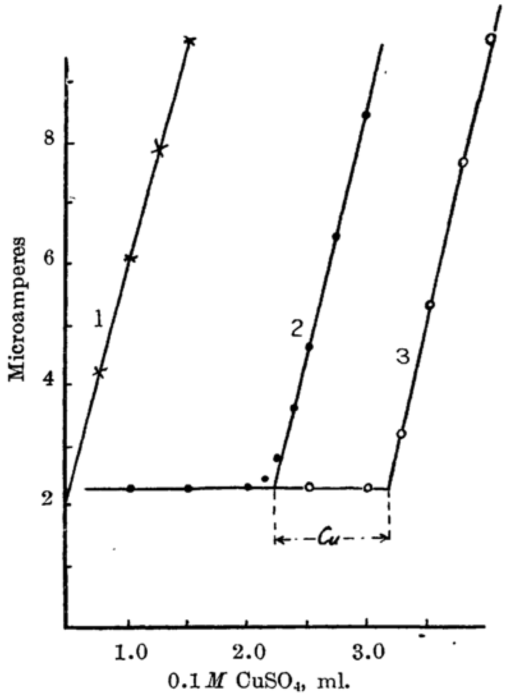

Fig. 3.—Titration of oxine with cupric sulfate: Curve 1, without oxine; curve 2, with Cu and oxine; curve 3, with oxine.

Table 1

Determination of Copper and Zinc (Using Oxine)

	Sample taken, mg.	0.1 *M*-$CuSO_4$, ml.	Metal found, mg.	Error, %
Cu	0	0	0	0
	6.357	1.01	6.420	+1.0
	8.357	1.00	6.357	0
Zn	20.395	3.12	20.399	0
	20.395	3.11	20.333	−0.3

These data are mean values of several titrations.

and titrating the freed oxine with cupric sulfate. To sample magnesium solution buffered by ammonia, excess oxine reagent is added and the precipitate is filtered and washed. Then the precipitate is dissolved with hot dilute hydrochloric acid and the dissolved solution is neutralized with sodium hydroxide (turbidity by the formation of magnesium hydroxide or magnesium oxinate shows this neutralisation) and again acidified with acetic acid and titrated with cupric sulfate standard solution. In this case magnesium in sample is equivalent to cupric sulfate used. This method is simple, accurate, sensible and magnesium can be precipitated even at boiling temperature. This method was applied to the determination of magnesium in sea-water and good result was obtained (Table 2).

Table 2

Determination of Magnesium in Sea-water (Using Oxine)

Sea-water taken, ml.	0.1 *M*-$CuSO_4$, ml.	Mg. found, mg.	Error, %
5.00	2.61	6.347	+0.7
5.00	2.58	6.275	+0.4
5.00	2.60	6.323	+0.3
3.00	1.57	3.818	+0.9
3.00	1.57	3.818	+0.9
3.00	1.55	3.770	+0.3

(3) Determination of Copper with Benzoinoxime.—Benzoinoxime as a reagent for copper is more specific than oxine and even when a small amount of zinc or nickel is present together with copper, it is not interfered by them, but the copper-benzoinoxime salt is fairly soluble in concentrated ammonium hydroxide (see Table 3).

Table 3

Determination of Copper in Brass (Using Benzoinoxime)

Brass taken, ml.	Conc. of NH_4OH, *M*/l.	Std. benzoinoxime added, ml.	0.1 *M*-$CuSO_4$ used, ml.	Cu in brass, %
0	1.0	10.0	—	
0	0.1	10.0	1.32	
0	0.05	10.0	1.48	
0	0.03	10.0	1.52	
0	0.01	10.0	1.53	
0	0.01	10.0	1.54	
0	0.01	10.0	1.53	
5.0	0.01	10.0	0.89	81.21
5.0	0.01	10.0	0.93	77.36
5.0	0.01	10.0	0.90	79.94

In this titration, 501 mg. of brass was dissolved in 500 ml. of dilute nitric acid and the aliquot sample was titrated. By the gravimetric analysis, copper in this sample was determined to be 78.57%.

So, from the result of experiments, it is seen that this titration must be performed below the concentration of 0.03 mol ammonium hydroxide. Benzoinoxime is reduced at $E_{1/2} = -1.53$ volts *vs.* S.C.E. in 1 *N*-ammonium chloride and ammonia (see Fig. 2), so in using the mercuric iodide electrode as anode, it is not reduced at the dropping electrode without an outside e. m. f. The titration curves of benzoinoxime is therefore analogous to that of oxine.

For the application of this titration, copper in brass was decided. The procedure is as follows: A definite weight of brass is dissolved in concentrated nitric acid and evaporated to dryness. A little dilute nitric acid is added to dissolve it and then it is filtered and washed. The filtrate is neutralized with ammonia water to a condition just before the greenish white precipitate of basic copper salt is formed and ammonium chloride-

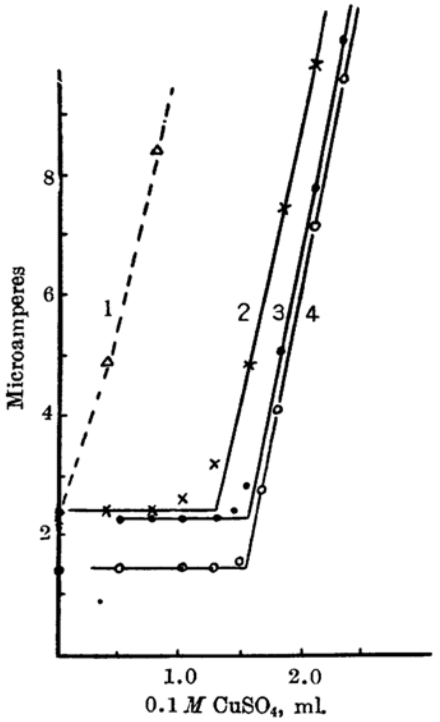

Fig. 4.—Titration of benzoinoxime with cupric sulfate: Curve 1, in 1 N-NH_4OH; curve 2, in 0.1 N-NH_4OH; curve 3, in 0.01 N-NH_4OH; curve 4, same as curve 3, but in H_2 atomosphere.

ammonium hydroxide buffered solution is then added to the solution to about 0.01 mol in ammonium hydroxide. Definite volume of standard benzoinoxime is added in excess and the excess is back titrated with cupric sulfate standard solution as in the case of titration with oxine.

(4) Determination of Other Substances.—As will be seen from the above experiments, many organic substances which react fast and stoichiometric enough with cupric ion such as salicylaldoxime, quinaldic acid, etc. may be determined by the cuprimetric method and the possiblities are now under research.

Discussion

These short-circuited cuprimetric titrations mentioned above are performed by using the mercuric iodide electrode ($E = -0.49$ volt *vs.* S. C. E.). However, we found that mercuric sulfide electrode ($E = -0.81$ volt *vs.* S. C. E.) and zinc amalgam electrode ($E = -1.02$ volts *vs.* S. C. E.) is more conveniently applicable in these titrations and by using them, less noble elements like lead ion can be reduced, so sulfate or chromate etc. can be titrated by this simple amperometric method. These analyses will be discussed in other cases.

Summary

(1) Cuprimetric amperometry using cupric sulfate as a standard solution was introduced in the determination of copper, zinc and magnesium.

(2) Oxine, benzoinoxime or other organic reagents were used as intermediate reagent in this titration, so on the other hand, some organic substances would be determined by this method.

(3) The procedure is simple and sensible to 10^{-4} mol Cu per liter, if suitable measures are taken.

Laboratory of Analytical Chemistry,
Faculty of Science,
Kyoto University, Kyoto