On the Determination of Copper by the Polarographic Method.

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For the determination of copper by the polarographic method various kinds of the regulating solutions were recommended, up to the present time, by a large number of investigators.

The earlier investigation of Shikata(1) was of a preliminary nature. Maassen(2) reported the polarograph to be very useful for the determination of copper in steel and Hohn(3) in his monograph described an outline for copper determination in brass and metal alloys. Suchy(4) used the dropping mercury electrode for simultaneous estimation of copper, bismuth, lead and cadmium, and Stout(5) suggested a procedure for polarographic estimation of copper. Reed and Cumming(6) reported the determination of copper in plant materials and Lingane and Kerlinger(7) discussed the polarographic wave of copper in their investigation on the determination of nickel and cobalt.

The regulating solutions recommended by these investigators are shown in Table 1. In these electoryte ferric iron is reduced at a potential more positive than the calomel zero, and hence its diffusion current interferes with the waves of copper and the others when iron is present in large excess.

Table 1.

Regulating solution	Author
Sodium Nitrate (Grundlösung A)	H. Hohn
Ammoniacal Solution of Ammonium Chloride (Grundlösung C)	H. Hohn
Sodium Potassium Tartrate	K. Suchy
Sodium Citrate	J. F. Reed
Potassium Chloride-Pyridine	J. J. Lingane

For this reason copper must be determined after the elimination of ferric iron from the solution. This may be done usually by adding an

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(1) M. Shikata, I. Tachi and N. Hozaki, *Bull. Agr. Chem. Soc. Japan*, **3** (1927), 883.

(2) G. Maassen, *Angew. Chem.*, **50** (1937), 375.

(3) H. Hohn, "Chemische Analysen mit dem polarographen", 84, Berlin (1937).

(4) K. Suchy, *Collection*, **3** (1911), 354.

(5) P. R. Stout, J. Levy and L. C. Williams, *Collection* **10** (1938), 129.

(6) J. F. Reed and R. W. Cummings, *Ind. Eng. Chem., Anal. Ed.*, **13** (1941), 124.

(7) J. J. Lingane and N. Kerlinger, *ibid.*, **13** (1941), 77.

excess of ammonium hydroxide to the boiling solution and filtering, or by reducing with hydroxylamine to ferrous iron that deposits at a more negative potential than ferric iron and copper. On the other hand after copper is seperated from iron by extraction with dithizone, then it can be determined by the use of the regulating solutions described above.

The writer discovered a new regulating solution for the determination of copper in the presence of large amounts of ferric iron, the following solution being used.

Sodium Potassium Tartrate	1 mol
Sodium Hydroxide	1 normal

By means of this electrolyte, ferric iron deposits at a more negative potential than copper, probably owing to the complex formation. Therefore, the copper that accompanies with large amounts of iron can be determined without interference of the latter and the time used for the analytical procedure can be reduced.

As an example the polarographic wave of copper in the presence of large amounts of iron is shown in Fig. 1. In this case the concentrations of copper and iron are 50 γ and 100 mg per 10 cc. respectively, the ratio of iron to copper being 2000 : 1 ; the copper wave is distinctly observed. Moreover, since in this regulating solution the solubility of oxygen is very small, the sensitivity of galvanometer can be raised to 1/2 or more without removing the oxygen by passing of hydrogen or nitrogen gas.

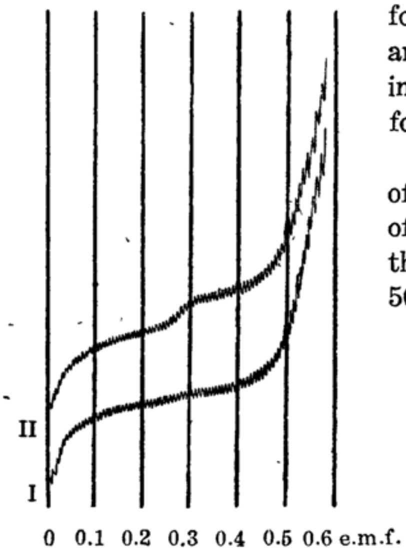

Fig. 1.

Curve I. Wave due to 100 mg of iron in 10 cc of regulating solution.
Curve II. Wave due to 50 γ of cooper and 100 mg of iron in 10 cc. of regulating solution. Sensitivity 1/2.

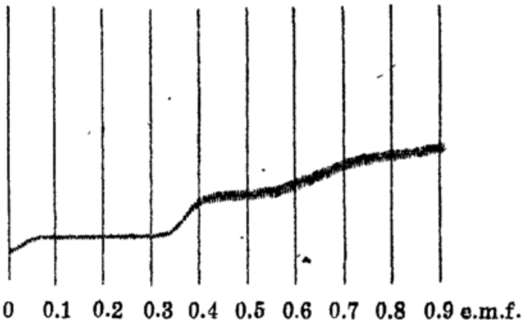

Fig. 2.

Wave due to 1 mg of copper in 8 cc of regulating solution. Sensitivity 1/20.

In this electrolyte copper shows two waves very similar to the double waves obtained in Hohn's Grundlösung C, with half-wave potentials of -0.55 and -0.81 v. vs. the normal calomel electrode (see Fig. 2). The first wave is due to the reduction of the cupric complex to the cuprous complex, and the second to the reduction of the cuprous complex to the metal. The first wave appears in the range of about 0.08 v. along the voltage axis (although the width of the wave varies in accordance with the concentration of metal). The linear spread of the second wave is about 0.15 v with a not steep slope and hence this electrode reaction is so-called irreversible one. Therefore, the second one may not be used and the first wave that has a steep slope and is a reversible one may be used for the quantitative estimation.

To prove that this copper wave can be used for the quantitative analysis, the writer took the polarograms of copper in various concentrations. The results given in Fig. 3 shows that the height of wave is proportional to the concentration of copper in the solution (at about 10^{-8} normal).

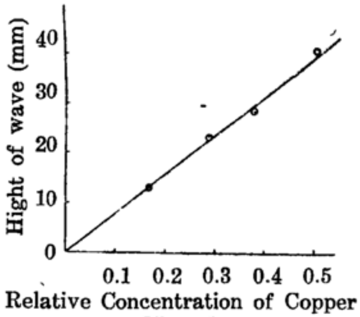

Fig. 3.
Sensitivity 1/20.

Bismuth deposits at -0.7 v. and its reducing wave is not steep. Cadmium gives a steep, reversible wave at -0.8 v., but when copper is present the determination of cadmium and bismuth is impossible in this regulating solution because the cadmium wave is not separated from the second wave of copper and bismuth wave. The reducing wave of ferric iron begins at -1.1 v. and its reaction is irreversible one. As antimony (trivalent) deposits at -1.1 v. too, it is duplicated with iron wave. Zinc deposits electrolytically at -1.4 v., but its diffusion current tends to appear irregularly and shows the slight maximum. Nickel, cobalt and arsenic give the irreversible wave from about -1.2 v. and tinn does not reduced electrolytically before -1.7 v.

It may be concluded that the copper can be determined by the use of its first wave, even in the presence of the many other above-mentioned heavy metals are present. Lead must be removed, because it gives the duplicated wave with copper.

Summary.

A new method for the determination of copper with the dropping mercury electrode was studied and the following regulating solution was used: 1 mol sodium potassium tartrate and 1 normal sodium bydroxide. By this method copper can be determined in the presence of large ammounts of iron.

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