519. *Polarography of Quinoline Derivatives. Part V. Amperometric Titration of Copper with Quinoline-8-carboxylic Acid.*

By John T. Stock.

Copper in faintly acid solution may be titrated amperometrically with quinoline-8-carboxylic acid solution. Equilibrium is rapidly attained, even in solutions 1×10^{-3}M. or less with respect to copper. Zinc, cadmium, ferrous iron, cobalt, nickel, and lead may be present without interference.

The gravimetric determination of copper by precipitation with quinoline-8-carboxylic acid has been described by Majumdar (*J. Indian Chem. Soc.*, 1941, **18**, 419). Gilbreath and Haendler (*Ind. Eng. Chem. Anal.*, 1942, **14**, 866) showed that in the pH range 3·5—4·0, copper could be quantitatively separated from at least half its weight of either cadmium or zinc, and from unspecified amounts of lead, nickel, mercury, and cobalt ions. The polarographic behaviour of quinoline-8-carboxylic acid having been elucidated (Stock, Part III, this vol., p. 763), the present work deals with the use of this reagent for the amperometric titration of copper in concentrations less than 3×10^{-3}M.

Experimental.

Quinoline-8-carboxylic Acid Solution.—The acid was prepared as described in Part III and used to prepare a 0·025M-stock solution in 50% aldehyde-free ethanol. This solution was diluted as required with the same solvent mixture.

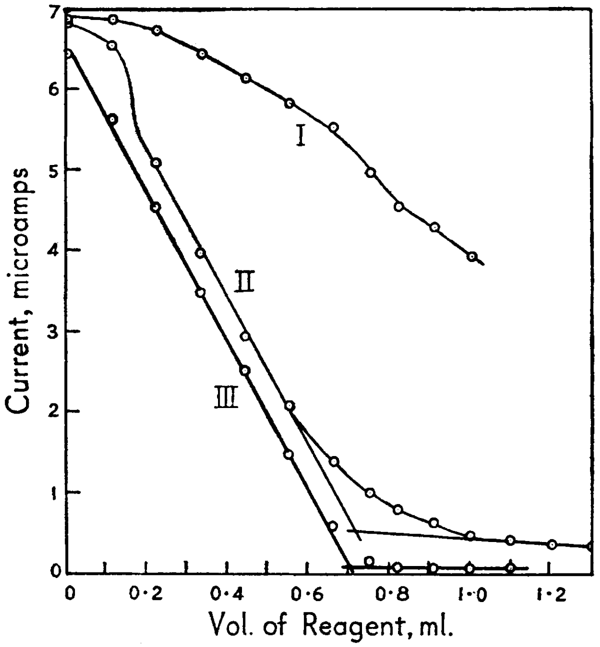
Buffer Solutions.—Hydrochloric acid–sodium acetate buffers, 0·2M. with respect to sodium acetate, were used throughout, and were examined polarographically for reducible impurities. pH Measurements (quinhydrone electrode) were made at room temperature.

Copper Sulphate Solution.—A 0·1M-stock solution was prepared from the B.D.H. "AnalaR" salt, standardised gravimetrically by precipitation with quinaldinic acid (Rây and Bose, *Z. anal. Chem.*, 1933, **95**, 400), and diluted as required with the appropriate buffers. In all cases, the diluted solutions contained 0·03% of gelatin.

Apparatus and General Procedure.—These were as in Part IV (this vol., p. 1793). The characteristics of the dropping-mercury electrode were: $m = 1{\cdot}511$ mg. sec.$^{-1}$, $t = 3{\cdot}08$ sec., $m^{2/3}t^{1/6} = 1{\cdot}588$ (determined on open circuit in 0·1N-potassium chloride at 25°). Mercury-pool anodes were used in all experiments, and current readings were corrected for the diluting effect of the added reagent (Kolthoff and Lingane, "Polarography," New York, 1941, p. 450).

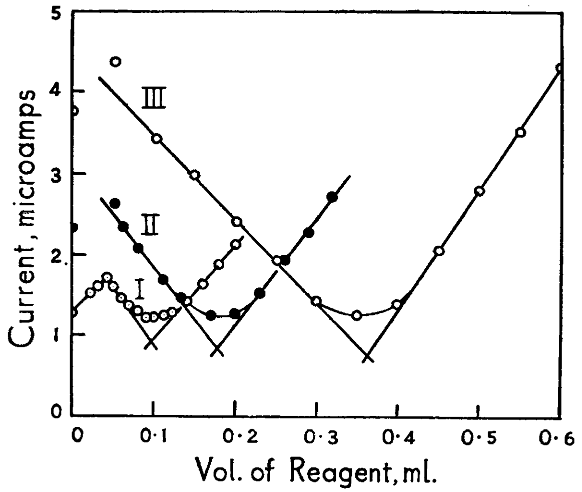
Titration of Copper.—Since quinoline-8-carboxylic acid is not reduced at an applied voltage (E_a) of $-0{\cdot}4$ (cf. Part III), titration of copper under these conditions should cause the current to fall to a small value near the end-point and then to remain sensibly constant as more reagent is added. Attempted titration with 5×10^{-3}M-quinoline-8-carboxylic acid solution of 1·0-ml. portions of $1{\cdot}75 \times 10^{-3}$M-copper solution buffered at pH 3·0 failed completely, the current still decreasing after the theoretical titre (0·7 ml.) had been exceeded by 50% (Fig. 1, curve I). Repetition at pH 4·0 gave a titration curve of the expected shape (Fig. 1, curve II), but pronounced rounding in the region of the end-point, indicative of the appreciable solubility of the precipitate, occurred. Increasing the pH to 5·0 gave well-defined titration curves (cf. Fig. 1, curve III), from which accurate results are obtainable (see Table II). Equilibrium is established rapidly at room temperature, and the titration may be performed directly or by running the copper-containing solution into that of the reagent.

FIG. 1.



Curve I, pH 3·0; *II, pH* 4·0; *III, pH* 5·0.

FIG. 2.



Titration with 5×10^{-3}M-*quinoline-8-carboxylic acid solution of* 0·9-*ml. portions of pH* 5·0 *buffer containing* 0·03% *of gelatin and the following concentrations of copper: curve I,* $0{\cdot}25 \times 10^{-3}$M.; *II,* $0{\cdot}5 \times 10^{-3}$M.; *III,* 1×10^{-3}M.

Although the main waves of quinoline-8-carboxylic acid are poorly defined in a medium of pH 5·0, titration at an applied voltage of —1·35 enables V-shaped curves (Fig. 2) to be obtained. Typical results are given in Table I.

TABLE I.

Titration of copper in pH 5·0 buffer containing 0·03% of gelatin with quinoline-8-carboxylic acid solution. Temp. = 14—18°; $E_a = -1\cdot35$ volt. Interval between additions, 4 mins.

Vol. of sample, ml.	Concns., $\times 10^{-3}$M.		Titres, ml.	
	Copper.	Reagent.	Theor.	Obs.
10	2·5	25	2·00	2·00, 2·00, 1·99
10	1·25	25	1·00	0·98
10	0·625	5	2·50	2·49, 2·48
0·9	1·0	5	0·360	0·358, 0·362
0·9	0·5	5	0·180	0·182, 0·181
0·9	0·25	5	0·090	0·099

Titration of Copper in the Presence of Other Metallic Ions.—In an attempt to titrate zinc under the above conditions, no precipitate was formed, and, using an applied voltage of —1·35, the current was found to increase linearly with the volume of reagent added. Similar results were obtained with cadmium. Titrations of copper in the presence of zinc and of cadmium at an applied voltage of —0·4 (under which conditions copper is the only wave-forming substance) showed no signs of co-precipitation. Cobalt, manganese, lead, ferrous iron, and nickel likewise did not appear to interfere. Except for lead, which was used as the acetate, the foreign ions were introduced as sulphates. Results obtained are given in Table II.

TABLE II.

Titration of 1-ml. portions of pH 5·0 buffer $1\cdot75 \times 10^{-3}$M. with respect to copper and containing 0·03% of gelatin and foreign ions. Reagent: strength = 5×10^{-3}M.; theoretical titre = 0·700 ml.; temp. = 14—16°; $E_a = -0\cdot4$ volt; interval between additions, 4 mins.

Foreign ion.	Concn., $\times 10^{-3}$M.	Titres, ml.	Foreign ion.	Concn., $\times 10^{-3}$M.	Titres, ml.	Foreign ion.	Concn., $\times 10^{-3}$M.	Titres, ml.
Nil	Nil	0·700, 0·697, 0·701	Zn	5·0	0·696	Pb	5·0	0·699
			,,	15·0	0·701	,,	15·0	0·697
Cd	0·6	0·699	Co	5·0	0·699	Fe^{II}	5·0	0·696
,,	3·0	0·696	,,	30·0	0·697	,,	15·0	0·694
,,	30·0	0·697	Mn	5·0	0·701	Ni	3·0	0·696
Zn	1·0	0·698	,,	30·0	0·700	,,	15·0	0·701

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