383. *Polarography of Quinoline Derivatives. Part IV. Amperometric Titration of Copper and Zinc with Quinaldinic Acid.*

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The amperometric titration with quinaldinic acid of copper, zinc, and cadmium in concentrations less than 3×10^{-3}M has been studied. Copper and zinc are precipitated slowly in the cold, but the titration is practicable at 60°. Alternatively, excess of the reagent may be added and back-titrated at room temperature with standard copper or zinc solution. Under certain conditions, copper and zinc in the same solution may be successively titrated, and copper may be determined in the presence of cadmium. Attempts to determine cadmium either directly or by back-titration were unsuccessful.

Many of the selective organic precipitants for metals are polarographically reducible and have been used successfully in amperometric titration (for bibliography, see Kolthoff and Lingane, " Polarography," New York, 1941, pp. 469—472; Stock, *Analyst*, 1947, **72**, 291). Quinaldinic acid, a useful precipitant for copper, etc. (see " Organic Reagents for Metals," Hopkin and Williams, Ltd., London, 1943, p. 122) gives well-defined polarographic reduction waves (Stock, Part I, *J.*, 1944, 427); the present work deals with the use of this reagent in the amperometric titration of copper and zinc in concentrations less than 3×10^{-3}M.

Experimental.

Quinaldinic Acid Solution.—The B.D.H. product was recrystallised twice from benzene, dried at 105°, and used to prepare a 0·025M-stock solution in 50% aldehyde-free alcohol. When necessary, this solution was diluted with the same solvent mixture.

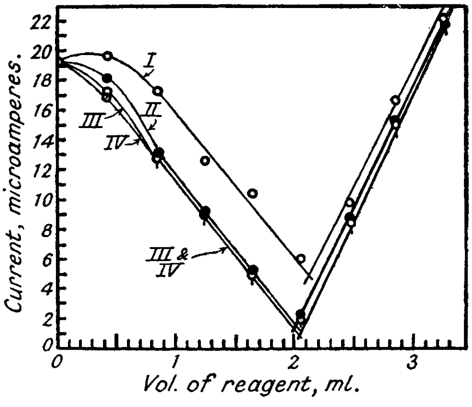
Buffer Solutions.—These were as in Part I, and were examined polarographically for reducible impurities; pH measurements (quinhydrone electrode) were made at room temperature.

Copper, Zinc, and Cadmium Solutions.—0·1M-Stock solutions were prepared from B.D.H. "AnalaR" sulphates and were standardised gravimetrically by precipitation with quinaldinic acid (Rây and Bose, *Z. anal. Chem.*, 1933, **95**, 400). The solutions were diluted as required with the appropriate buffers and sufficient 1% gelatin solution to render them 0·03% with respect to gelatin.

Apparatus.—Three titration cells were used: (*a*) for 20—50-ml. samples, a 100-ml., tall Pyrex beaker fitted with a clamp-on cap (Stock, *Analyst*, 1947, **72**, 291); (*b*) for 5—10-ml. samples, the cell described by Fill and Stock (*Analyst*, 1944, **69**, 178); (*c*) for 0·5—2-ml. samples, an all-glass micro-cell (Stock, *Analyst*, 1946, **71**, 583). A mercury pool anode was used in all experiments. When necessary, the cells were heated in a large beaker of water thermostatically maintained at 60° ± 0·4°.

Applied voltage (E_a) was regulated by a polarising unit (Stock, *ibid.*, p. 585) which incorporated a damping control for the calibrated Cambridge " Spot " galvanometer used to measure the current.

Fig. 1.



10·2 *Ml. of* $2·5 \times 10^{-3}$M-*copper sulphate and* 0·03% *of gelatin in pH* 5·0 *buffer at* 60° *titrated with* 25×10^{-3}M-*quinaldinic acid solution.* $E_a = -1·2$ *volts. Curve I,* 1 *min. after additions; II,* 3 *mins.; III,* 5 *mins.; IV,* 7 *mins.*

The characteristics of the dropping-mercury electrodes were: (*a*) $m = 0·917$ mg. sec.$^{-1}$, $t = 3·39$ secs., $m^{2/3} t^{1/6} = 1·157$; (*b*) $m = 1·511$ mg. sec.$^{-1}$, $t = 3·08$ secs., $m^{2/3} t^{1/6} = 1·588$, determined on open circuit in 0·1N-potassium chloride at 25°. Most of the measurements were made with electrode (*b*).

General.—Solutions were deoxygenated by a stream of nitrogen which was first passed through a bubbler containing a little of the solution under examination at the same temperature as the sample in the cell. Gas was bubbled through the solution after each addition of reagent and was cut off 1 minute before reading the galvanometer. In all cases, the current was corrected for the diluting effect of the added reagent (Kolthoff and Lingane, *op. cit.*, p. 450).

Titration of Copper.—In the presence of 0·02—0·03% of gelatin, quinaldinic acid buffered at pH 5 gives a well-defined single wave (Part I). At this pH, precipitation by the reagent of copper, zinc, and cadmium should be virtually complete (Shennan, *Analyst*, 1939, **64**, 14; Flagg and McClure, *J. Amer. Chem. Soc.*, 1943, **65**, 2346). Experiments were accordingly initiated under these conditions.

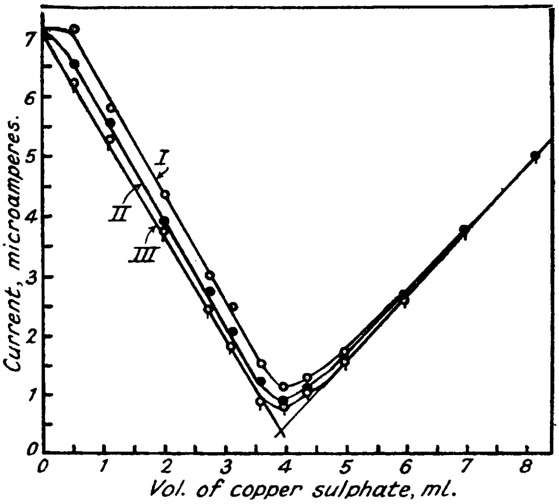
At room temperature, precipitation of copper quinaldinate is slow, and reasonable results are obtainable only if 10 minutes or longer elapse between addition of reagent and the reading of current. Precipitation is more rapid at 60° and the titration then becomes practicable (Fig. 1). Typical results are given in Table I.

TABLE I.

Titration of copper in pH 5·0 *buffer containing* 0·03% *of gelatin with quinaldinic acid solution. Temp.* = 60°; $E_a = -1{\cdot}2$ *volts. Interval between additions,* 5 *mins.*

Vol. of sample, ml.	Concns., M × 10^{-3}. Copper.	Reagent.	Titres, ml. Calc.	Obs.
50	2·5	25	10·00	10·04
44	0·91	20	4·00	3·96
40	2·5	25	8·00	7·98
25	2·0	25	4·00	4·01
10	2·5	25	2·00	1·99, 2·00, 1·98
10	2·0	25	1·60	1·59
10	1·5	25	1·20	1·20, 1·19
10	1·0	25	0·80	0·82
10	0·5	25	0·40	0·42
1·5	2·5	25	0·300	0·292
0·9	1·0	5	0·360	0·355, 0·360, 0·357
0·9	0·5	5	0·180	0·176
0·9	0·25	5	0·090	0·092

FIG. 2.



44 *Ml. of* 1·82 × 10^{-3}M-*quinaldinic acid and* 0·03% *of gelatin in pH* 4·9 *buffer at* 14° *titrated with* 10 × 10^{-3}M-*copper sulphate solution.* $E_a = -1{\cdot}2$ *volts. Curve I,* 1 *min. after additions; II,* 3 *mins.; III,* 5 *mins.*

Traces of precipitate deposited from previous titrations on the burette-tip, cell walls, etc., were noticeably beneficial. Completion of precipitation was most rapid in the smallest cell, which had the lowest ratio of volume to wetted area.

Reversing the procedure, *i.e.*, placing the copper-containing solution in the burette, also facilitates the precipitation. The titration then becomes practicable at room temperature (Fig. 2). Advantageous both in assisting precipitation and in avoiding continual change of solution in the burette is the addition to the buffered copper-containing solution of a known but excess volume of the reagent, followed by back-titration at room temperature with standard copper solution. Typical results are given in Table II.

Titration of Zinc.—Since the solubility product of zinc quinaldinate is higher than that of the copper compound (Flagg and McClure, *loc. cit.*), the titration curves of zinc ($E_a = -1{\cdot}4$ volts) are more rounded near the end-point than are those of copper (cf. Kolthoff and Lingane, *op. cit.*, p. 458). Apart from this and except for more sluggish precipitation, zinc solutions buffered at pH 5 behaved similarly to those of copper and, except at the lowest concentrations, gave results of similar accuracy.

TABLE II.

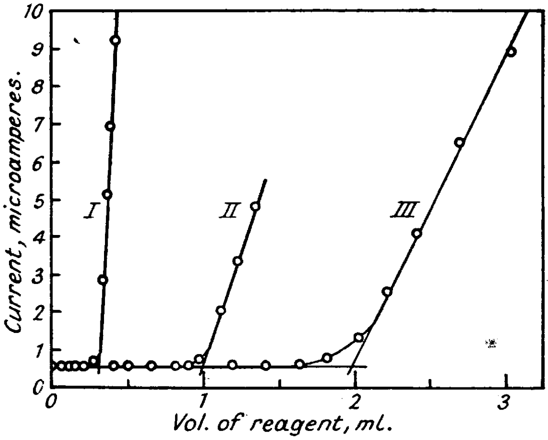
Back-titration of 5 *ml. of* 5 × 10^{-3}M-*quinaldinic acid added to copper-containing solutions buffered at pH* 5·0 *with* 2·5 × 10^{-3}M-*copper sulphate solution. Temp.* = 14—16°; E_a = −1·2 *volts. Interval between additions,* 5 *mins.*

Vol. of sample, ml.	Copper concn., M × 10^{-3}.	Titres, ml. Calc.	Titres, ml. Obs.
5	0	5·00	5·02
5	1	3·00	3·02, 3·02
5	1·5	2·00	1·99, 1·97
5	2·0	1·00	1·00
0·3 *	2·5	0·600	0·581

* 0·9 Ml. of reagent added.

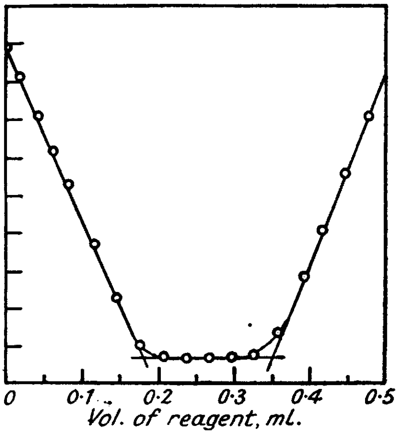
At this pH, with an applied voltage of −1·06, the diffusion current of quinaldinic acid, but not that of zinc, is obtained. The titration curves of zinc with quinaldinic acid are then of the "reversed **L**" form shown in Fig. 3.

FIG. 3.



Zinc sulphate and 0·03% *of gelatin in pH* 5·0 *buffer at* 60° *titrated with* 25 × 10^{-3}M-*quinaldinic acid solution.* E_a = − 1·06 *volts. Curve I,* 1·5 *ml.,* 2·5 × 10^{-3}M *with respect to zinc; II,* 10 *ml.,* 1·25 × 10^{-3}M; *III,* 10 *ml.,* 2·5 × 10^{-3}M.

FIG. 4.



1·8 *Ml. of pH* 5·0 *buffer at* 60° *containing* 0·03% *of gelatin and* 1·25 × 10^{-3}M *of both copper and zinc titrated with* 25 × 10^{-3}M-*quinaldinic acid.* E_a = − 1·06 *volts.*

Stepwise Titration of Copper and Zinc.—The difference in solubility product referred to above causes preferential precipitation of copper when a solution buffered at pH 5 and containing both copper and zinc is titrated with quinaldinic acid. If the applied voltage is −1·06, copper and quinaldinic acid, but not zinc, give diffusion currents, and the titration curve has the form shown in Fig. 4 (cf. Kolthoff and Pan, *J. Amer. Chem. Soc.*, 1939, **61**, 3402). The first break indicates completion of precipitation of copper, the second that of zinc. The results given in Table III indicate no serious co-precipitation, and may permit the development of a method for the micro-titration of brasses and similar alloys.

TABLE III.

Stepwise titration with 25 × 10^{-3}M-*quinaldinic acid of copper and zinc in pH* 5·1 *buffer containing* 0·03% *of gelatin. Temp.* = 60°; E_a = −1·06 *volts. Interval between additions,* 5 *mins.*

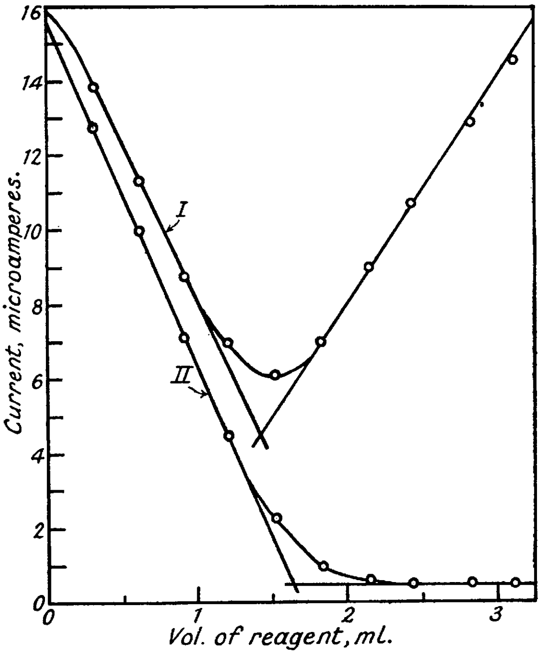
Vol. of sample, ml.	Concns., M × 10^{-3}. Cu.	Concns., M × 10^{-3}. Zn.	Titres, ml. Copper. Calc.	Titres, ml. Copper. Obs.	Titres, ml. Zinc. Calc.	Titres, ml. Zinc. Obs.
44	0·568	0·568	2·00	1·97	2·00	2·03
25	2·0	0·5	4·00	4·02	1·00	1·01
10	1·5	1·0	1·20	1·18, 1·19	0·80	0·85, 0·82
10	1·0	1·5	0·80	0·81, 0·79	1·20	1·15, 1·18
10	0·5	2·0	0·40	0·38	1·60	1·61
1·8	1·25	1·25	0·180	0·182	0·180	0·169
1·0	1·5	1·0	0·120	0·116	0·080	0·081

Titration of Cadmium.—Shennan (*loc. cit.*) has shown that, under gravimetric conditions, cadmium is completely precipitated by quinaldinic acid in the pH range 3·9—7·2. Attempted titration with quinaldinic acid of pH 5 buffers containing up to $2{\cdot}5 \times 10^{-3}$M of cadmium showed that the precipitate was very slow in appearing at 60°. With an applied voltage of −0·9 (cadmium, but not the reagent, reduced), equilibrium is not established even with 10 minutes between additions of reagent, and after the theoretical titre had been exceeded by 100%. With an applied voltage of −1·2, the current *increased* irregularly from the first addition of reagent.

Since increased pH should reduce the solubility of the precipitate (Flagg and McClure, *loc. cit.*), experiments were repeated in a borate buffer of pH 7·1. Both addition of the reagent to the cadmium-containing solution and the reverse gave unsatisfactory results.

Titration of Copper in the Presence of Cadmium.—Although the completeness of the separation has been questioned (Shennan, *loc. cit.*; Lindsey and Shennan, *Analyst*, 1940, **65**, 636), the accurate gravimetric determination of copper as quinaldinate in the presence of cadmium has been reported (Rây and Bose, *loc. cit.*; Majumdar, *Analyst*, 1939, **64**, 874; Pritchard and Chirnside, *ibid.*, 1943, **68**, 244; see also Flagg and McClure, *loc. cit.*). According to Majumdar (*loc. cit.*), separation is possible in the pH range 1·22—2·15. The behaviour of dilute copper solutions buffered at pH 2·1 was therefore investigated. Typical titration curves are shown in Fig. 5. The pronounced rounding of the curves near the end-point shows that the more acid conditions increase the solubility of the precipitate (cf. Lindsey and Shennan, *loc. cit.*). Low results are obtained by operating at −0·8 volt (curve I), but the "L" curves obtained with an applied voltage of −0·4 (curve II) give nearly theoretical titres (Table IV), not affected by the presence of cadmium.

Fig. 5.



10 Ml. of 2×10^{-3}M-*copper sulphate and* 0·03% *of gelatin in pH* 2·1 *buffer at* 60° *titrated with* 25×10^{-3}M-*quinaldinic acid solution. Curve I,* E_a = − 0·8 *volt; II,* E_a = − 0·4 *volt.*

TABLE IV.

Titration of 10-*ml. portions of pH* 2·1 *buffers containing copper, cadmium, and* 0·03% *of gelatin with* 25×10^{-3}M-*quinaldinic acid solution. Temp.* = 60°; E_a = −0·4 *volt. Interval between additions,* 5 *mins.*

Concns., M × 10⁻³.		Titres, ml.		Concns., M × 10⁻³.		Titres, ml.	
Cu.	Cd.	Calc.	Obs.	Cu.	Cd.	Calc.	Obs.
2	0	1·60	1·57, 1·59	2	1	1·60	1·57, 1·59
1·5	0	1·20	1·17	2	2	1·60	1·61
1	0	0·80	0·83	2	3	1·60	1·63
2	0·5	1·60	1·57	2	5	1·60	1·59

Manganese, nickel, and cobalt, in concentrations similar to that of cadmium, likewise do not interfere with the titration of copper under these conditions.

Titration of Copper and Zinc in the Presence of Ferrous Iron.—Addition of quinaldinic acid to a pH 5 buffer at 60° containing ferrous iron and 0·03% of gelatin gives an intense red colour (Rây and Bose, *loc. cit.*). With an applied voltage of −1·2, the current increases linearly with the volume of reagent added. Titration of copper under these conditions, in the presence of up to 1×10^{-3}M of ferrous iron, gives good results. On the other hand, addition of excess of reagent and its back-titration with standard copper solution is unsatisfactory; the colour of the precipitate indicates pronounced co-precipitation of iron.

In the case of zinc, poor results due to pronounced co-precipitation of iron are obtained in both modes of titration.

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