Application of RADME to the Chelatometric Determination of Metals Employing the Alternating Current Polarographic Method

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Cadmium- and lead-nitrilotriacetate complexes give rise to two polarographic waves in acetate buffer solution (pH 4.5). The first one is a kinetic wave due to the elecrodeposition of metal ions formed by the dissociation of the complex, and the second is the one due to the direct reduction of complex[1,2]. In ammonia-ammonium nitrate buffer solution, the kinetic currents which originate from the dissociation can also be observed. Owing to the presence of the kinetic current, cadmium and lead can not be titrated with nitrilotriacetic acid (NTA) by employing the usual polarographic method.

In the previous paper, the concentration of copper in an acetate buffer solution of pH 6.0 was determined with NTA by the use of the alternating current polarographic method. In the titration, equivalence points were determined by plotting the peak currents of the alternating current polarograms of copper against the volume of NTA solution added.

The present investigation was directed to the application of rapidly dropping mercury electrode (RADME) to the chelatometric determination of copper, cadmium and lead, using the alternating current polarographic method. At RADME, peak currents due to the electrodeposition of these metal ions which were produced by the dissociation of complexes could not be observed. When RADME is used as an indicator electrode, experimental equivalence points agreed with the stoichiometric equivalence points.

Experimental

Apparatus.—A Yanagimoto Model GA-103 galvarecorder equipped with an automatically scanning potentiometer was employed for the measurements of all current-voltage curves and also for the titrations. The current was determined point by point by manual operation.

Dropping mercury electode (DME) and RADME had the chracteristic features indicated in Table I, the measurements being conducted in air-free 0.1 M potassium chloride solutions with open circuit at 25±0.1°C.

TABLE I. CHARACTERISTICS OF THE ELECTRODES MEASURED IN AIR-FREE 0.1 M POTASSIUM CHLORIDE SOLUTION WITH OPEN CIRCUIT AT 25±0.1°C

	Height of mercury head, cm.	t, sec.	m mg./sec.
DME	70.0	4.02	1.23_7
RADME	60.0	0.35_3	15.54

A simple beaker type cell was used for all measurements. A cell was connected to a saturated calomel electrode (S. C. E.) through a potassium nitrate agar bridge (1.5 kΩ). Semimicroburets of 5 ml. and 10 ml. capacity were used for titrations. During the titrations purified nitrogen gas was passed through the solution to remove dissolved oxygen, prior to the measurements of current-voltage curves and titration curves, which also were conducted after every addition of titrant. All polarographic measurements and titrations were carried out at 25±0.1°C. The cell construction which was used fo rthe alternating current polarographic measurements is shown in Fig. 1. A large platinum electrode was inserted into the solution as the third electrode and this was connected to the anode through a condenser of 100 μF in order to keep the impedance of the electrolysis cell as low as possible.

Reagent. — Nitrilotriacetic acid (NTA) of analytical reagent grade (Wakō Pure Chemical Industries, Ltd.) was used without further purification. The stock solution of NTA was standardized with

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[1] J. Koryta and I. Kossler, *Collection Czechoslov. Chem. Communs. Suppl.*, **15**, 241 (1950).

[2] K. Morinaga and T. Nomura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 200 (1958).

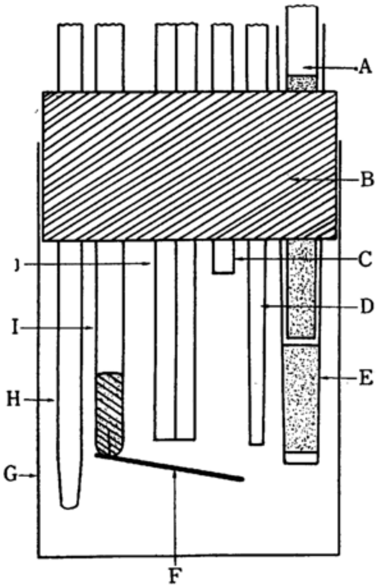

Fig. 1. Cell construction.

A	S. C. E.	F	platinum plate
B	rubber	G	beaker type cell
C	gas outlet	H	gas inlet
D	buret	I	platinum electrode
E	sintered glass	J	DME or RADME

standardized nickel solution[3,4]. Standard solutions of copper, lead and cadmium were prepared from chemicals of analytical reagent grade. The concentration of stock solution was determined gravimetrically[5]. The concentrations of copper and of cadmium were determined by amperometric titration[6,7], using the DME as an indicator electrode. Other chemicals used were all analytical reagent grade. The buffer solutions were prepared by the method described in the previous paper[4].

Results and Discussion

Direct Current (D. C.) Polarography.—Current-voltage curves of cadium-nitrilotriacetate complex were obtained with DME at different heights of mercury column in de-aerated ammonia-ammonium nitrate buffer solution of pH 9.2 containing 0.005% gelatine. The ionic strength was adjusted to 0.7 with potassium nitrate.

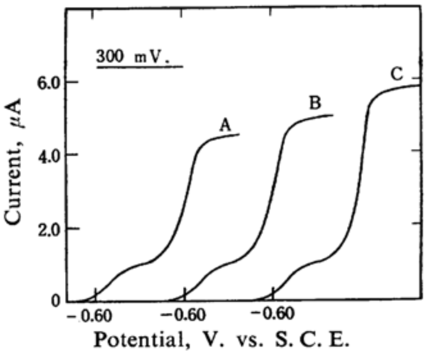

Fig. 2. Current-voltage curves of $1.09_8\times10^{-3}$ M cadmium nitrilotriacetate in an ammonia-ammonium nitrate buffer of pH 9.2 ($\mu=0.7$).

- A Height of mercury column, 50 cm.
- B Height of mercury column, 70 cm.
- C Height of mercury column, 90 cm.

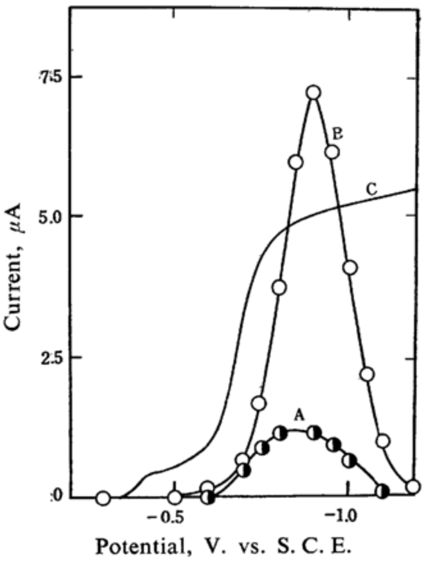

Fig. 3. Current-voltage curves of $1.18_6\times10^{-3}$ M lead-nitrilotriacetate in an ammonia-ammonium nitrate buffer of pH 8.2 ($\mu=0.7$) containig 50 mM tartarate.

- A A. C. polarogram at DME
- B A. C. polarogram at RADME
- C D. C. polarogram at DME

As seen from current-voltage curve A (Fig. 2), the mixture of cadmium and nitrilotriacetic acid at the ratio of exactly 1 to 1, gives a polarogram with a small reduction wave of cadmium (-amine complex) ion. Viewed from the experimental results obtained at different heights of mercury column (curves B and C in Fig. 2), the author's explanation that this small prewave must be kinetic in nature, may be justified. Lead-nitrilotriacetate complex in an ammonia-ammonium nitrate buffer solution of pH 8.2 containing 0.005% gelatin (50 mM sodium tartarate was added to avoid the undesirable hydrolysis of lead) also gave the kinetic current (curve C in Fig. 3). The ionic strength was also adjusted to 0.7 with potassium nitrate.

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3) M. Kodama, A. Shimizu and H. Terakado, ibid. **81**, 1545 (1960).

4) G. Numaziri, M. Kodama and A. Shimizu, ibid., **81**, 454 (1960).

5) F. P. Treadwell and W. T. Hall, "Analytical Chemistry", Vol. 2 (1953), p. 58.

6) N. Tanaka, I. T. Oiwa and M. Kodama, *Anal. Chem.*, **28**, 1555 (1956).

7) N. Tanaka, M. Kodama, M. Sasaki and M. Sugino, *Japan Analyst* (*Bunseki Kagaku*), **6**, 86 (1957).

Alternating Current (A. C.) Polalography.— Alternating current polarograms of cadmium, lead and copper were recorded, using DME or RADME, under the same conditions as those used for direct current polarographic measurements. It was found for lead-nitrilotriacetate complex that the reduction wave of lead ion due to the dissociation of complex entirely disappeared at DME or RADME as shown in Fig. 3 (curves A and B). This phenomenon was also obtained in the reduction of cadmium-nitrilotriacetate complex, when RADME was employed as an indicator electrode (Fig. 4).

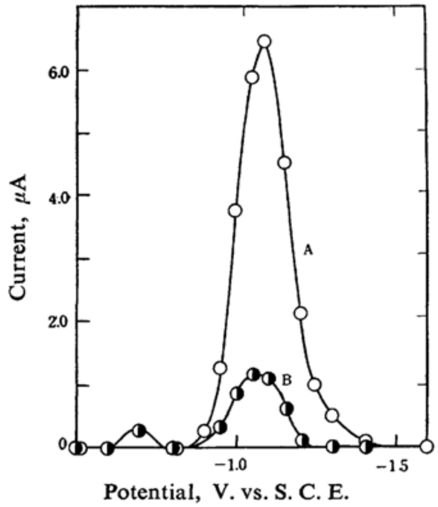

Fig. 4. Alternating current polarograms of $1.09_8\times10^{-3}$ M cadmium-nitrilotriacetate in an ammonia-ammonium nitrate buffer of pH 9.2 (μ=0.7).

A at RADME B at DME

These results may indicate that the rate of the dissociation reaction of metal-nitrilotriacetate complex on the electrode surface is not sufficiently rapid to supply the requisite amount of metal ion to give the kinetic current during the short interval (0.02 sec.) of each alternating current voltage sweep at DME or RADME.

The value of the peak current of metal-nitrilotriacetate conmplex observed at RADME is higher than that observed at DME. In the potential range at which experiments were conducted, the surface-active substance, gelatine, is adsorped on the electrode surface to cover it. The extent of coverage of the rapidly dropping mercury electrode surface differs from that of the ordinary dropping mercury electrode surface, because the drop time of RADME is quite different from that of DME. This difference is related to the extent of inhibition of the electro-oxidation-reduction reaction of complex ion, which may be the reason why the peak current at RADME is higher than that at DME. The adsorption of gelatine on the mercury drop occurs over the entire range of potentials (about +0.4 to −2.0 V. vs. S.C.E.), and the tensammetric peaks due to the adsorption and the desorption of gelatine can not be observed under ordinary experimental conditions. In the case of camphor, however, two tensammetric peaks can be observed at about −0.25 and −1.15 V. vs. S.C.E. The peak in the positive potential region results from the adsorption of camphor, and the peak

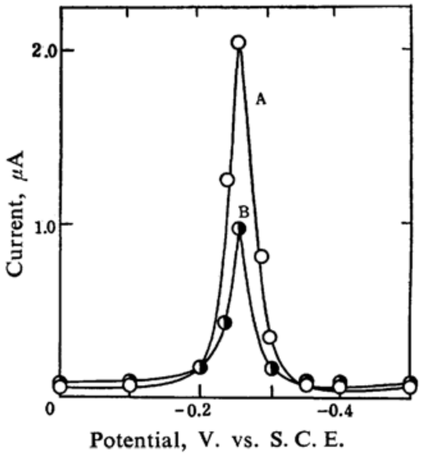

Fig. 5. Alternating current polarograms of 0.5 M KNO_3 solution containing 1.5×10^{-3} M camphor.

A at RADME B at DME

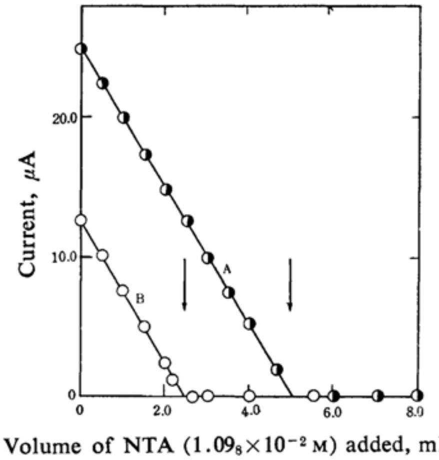

Fig. 6. Titration curves of cadmium with NTA in an ammonia-ammonium nitrate buffer of pH 9.2 (μ=0.7).

A 50 ml. of $1.09_5\times10^{-3}$ M cadmium
B 50 ml. of $5.47_5\times10^{-4}$ M cadmium

Stoichiometric equivalence points are indicated by arrows.

in the negative potential region from the desorption of camphor. The peak currents of positive tensammetric wave of camphor obtained at DME and RADME in the nitrate media are shown in Fig. 5. The value of the peak current observed at RADME differs from that observed at DME. This fact also implies that the extent of coverage of the rapidly dropping mercury electrode surface by the surface-active substance is quite different from that of the dropping mercury electrode surface.

A. C. Poralographic Titrations. — From the above results and the well-known facts[8] that in the reversible case, the A. C. polarographic method is advantageous in the resolution of two component systems and in the determination of low concentration; it seems desirable to employ the A. C. polarographic method to determine the concentration of cadmium or lead with NTA at RADME in an ammnia-ammonium nitrate buffer solution.

Polarographic titration employing the A. C. polarographic method (A. C. polarographic titration) was carried out, under the same conditions as that used for the polarographic measurements, in the concentration range from 1×10^{-3} M to 1×10^{-5} M. Titration curves were obtained by plotting the peak currents due to the electro-reduction of metal ions against the volume of NTA solution added. Typical examples of the titration curves are given in Figs. 6 and 7. These curves were corrected for dilution effect by the addition of titrant. The potential at which the peak currents are given were held constant during the titration. The results of the titration obtained are listed in Tables II and III. Experimental equivalence points agreed with calculated equivalence points satisfactorily. The results of the titration obtained for copper are also listed in Table IV.

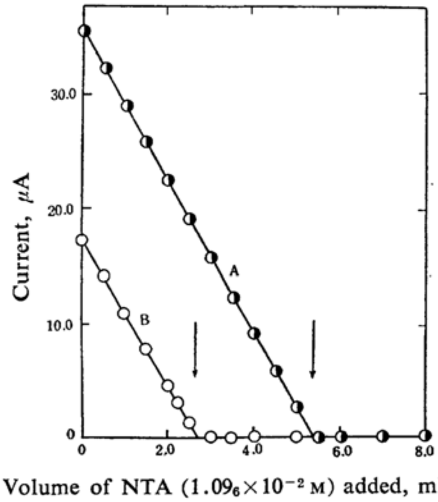

Fig. 7. Titration curves of lead with NTA in an ammonia-ammonium nitrate buffer of pH 9.2 (μ=0.7).

A 50 ml. of $1.18_8\times10^{-3}$ M lead.
B 50 ml. of $5.93_0\times10^{-4}$ M lead.
Stoichiometric equivalence points are indicated by arrows.

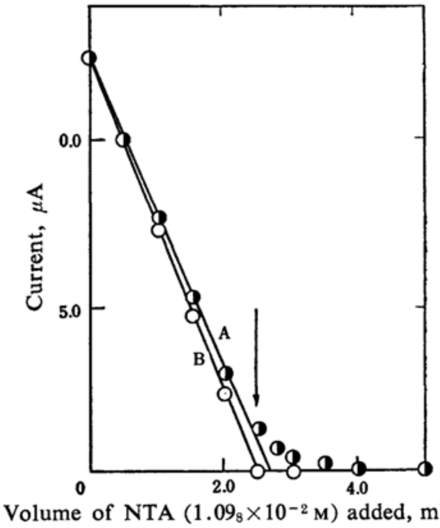

Fig. 8. Titration curves of cadmium with NTA in an ammonia-ammonium nitrate buffer of pH 9.2 (μ=0.77); 50 ml. of $5.47_5\times10^{-4}$ M cadmium.

A 0.4 M ammonia B 0.1 M ammonia

TABLE II. A. C. POLAROGRAPHIC TITRATION OF CADMIUM WITH NTA USING RADME (INITIAL VOLUME 50 ml.)

Concentration of cadmium, M	Concentration of NTA used for titration, M	NTA required, ml. Stoichiometric	NTA required, ml. Experimental	Error, %
$1.09_5\times10^{-3}$	$1.09_8\times10^{-2}$	4.98_7	5.00	+0.1
$5.47_5\times10^{-4}$	$1.09_8\times10^{-2}$	2.49_4	2.48	−0.6
$2.73_8\times10^{-4}$	$1.09_8\times10^{-2}$	1.24_7	1.24	−0.6
$1.09_5\times10^{-4}$	$1.09_8\times10^{-3}$	4.98_7	4.96	−0.6
$5.47_5\times10^{-5}$	$1.09_8\times10^{-3}$	2.49_4	2.50	+0.3
$3.28_5\times10^{-5}$	$1.09_8\times10^{-3}$	1.24_7	1.45	−3.0

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[8] P. Delahay, "New Instrumental Method in Electrochemistry" (1954), p. 176.

TABLE III. A. C. POLAROGRAPHIC TITRATION OF LEAD WITH NTA USING RADME (INITIAL VOLUME 50 ml.)

Concentration of lead, M	Concentration of NTA used for titration, M	NTA required, ml.		Error, %
		Stoichiometric	Experimental	
$1.18_6\times10^{-3}$	$1.09_8\times10^{-2}$	5.40_0	5.40	0
$5.93_0\times10^{-4}$	$1.09_8\times10^{-2}$	2.70_0	2.69	−0.6
$2.37_4\times10^{-4}$	$1.09_8\times10^{-2}$	1.08_0	1.07	−1.0
$1.18_6\times10^{-4}$	$1.09_8\times10^{-3}$	5.40_0	5.42	+0.4
$5.93_0\times10^{-5}$	$1.09_8\times10^{-3}$	2.70_0	2.72	+0.8
$2.37_4\times10^{-5}$	$1.09_8\times10^{-3}$	1.08_0	1.05	−3.0

TABLE IV. A. C. POLAROGRAPHIC TITRATION OF COPPER WITH NTA USING RADME (INITIAL VOLUME 50 ml.)

Concentration of copper, M	Concentration of NTA used for titration, M	NTA required, ml.		Error, %
		Stoichiometric	Experimental	
$1.13_0\times10^{-3}$	$1.09_8\times10^{-2}$	5.15_0	5.15	0
$5.65_0\times10^{-4}$	$1.09_8\times10^{-2}$	2.57_5	2.58	+0.2
$2.26_5\times10^{-4}$	$1.09_8\times10^{-2}$	1.03_0	1.02	−1.0
$1.13_0\times10^{-4}$	$1.09_8\times10^{-3}$	5.15_0	5.16	+0.2
$5.65_0\times10^{-5}$	$1.09_8\times10^{-3}$	2.57_5	2.57	−0.2

When a great excess of ammonia is presented in the solution, experimental equivalence points were somewhat greater than the stoichiometrical ones. This fact reveals that the presence of excess ammonia favors the dissociation reaction of the metal-nitrilotriacetate complex (Fig. 8).

Summary

RADME was applied to the chelatometric determination of copper, cadmium and lead with NTA by employing the A. C. polarographic method. At RADME practically no kinetic effects due to the dissociation of metal-nitrilotriacetate complex were observed and the concentration of metal ions could be determined accurately in the concentration range from 1×10^{-3} M to 1×10^{-5} M.

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