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Analytical Studies Using the Convection Electrode. XII. Anodic-stripping Voltammetry of Cadmium and Thallous Ions with the Pushed-out Mercury Drop Convection Electrode

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The investigation of the anodic-stripping voltammetry of cadmium or thallous ions in a 0.1 M potassium nitrate solution was carried out by using the pushed-out mercury Drop Convection Electrode (*cf.* J. Suzuki and T. Ozaki, This Bulletin, **37**, 230 (1964)). The metals were deposited on the mercury electrode by rotating the disk at 600—1200 rpm, and the stripping was performed by a linearly-varying potential method. The anodic-stripping peak current was proportional to the square roots of the rotating rate of the disk and of the voltage scanning rate, and to the bulk concentration of cadmium or thallous ions. Using the present stripping procedure, it was possible to determine thallous and cadmium ions at concentrations as low as 1×10^{-7} M with a mean error of about ±2%.

The anodic-stripping voltammetry is especially suitable for the trace analysis of metal ions which can be deposited on the electrode and removed anodically. Lord, O'Neil and Rogers[1] plated several metals on a rotating platinum electrode, removed them anodically, and measured the area under the current-time curve. This area was found to be proportional to the concentration of

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[1] S. S. Lord, R. C. O'Neill and L. B. Rogers, *Anal. Chem.*, **24**, 209 (1952).

the metals. Gardiner and Rogers[2] deposited electrolytically a thin layer of mercury on a platinum electrode and used it as a mercury-coated platinum electrode. They proposed the use of this electrode for the stripping analysis of cadmium and zinc in dilute solutions. This electrode has all the advantages of the mercury electrode, that is, a high hydrogen over-voltage and a good reproducible surface. However, in a strongly acidic or alkaline solution, it shows a lower hydrogen over-voltage than does the ordinary mercury electrode, presumably because a part of the mercury film is broken and the platinum surface is exposed. This unfavorable property is though to be a limitation of the utility of the mercury-coated platinum electrode.

In recent studies,[3-5] a hanging mercury-drop electrode has been used for the stripping voltammetry; it has shown a remarkably high sensitivity. However, this electrode is unsuitable for the practical chemical analysis, because of the difficulties in construction, the complicated manipulation, the insufficient reproducibility, and the change in the drop shape when the solution flows through.

The Pushed-out Mercury Drop Convection Electrode (PMDCE)[6] was proposed by the present author in order to improve these weak points; it gives a good, reproducible mercury drop without any difficulty. Recently, the application of the PMDCE to the cathodic stripping voltammetry of the chloride ion has been investigated by the present author.[7] It was found possible to determine chloride ions at concentrations as low as 3×10^{-5} M with an excellent reproducibility.

In the present paper, the anodic stripping voltammetry of cadmium and thallium(I) with the PMDCE will be discussed.

Experimental

Apparatus. The electrolytic cell, the electrode, and the apparatus rotating the disk were the same as those described in the previous paper.[6] A Toa Electronics Recorder, model EPR-2T, was employed for the measurements of the dissolution current.

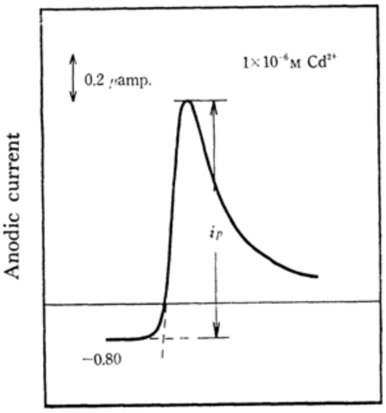
Reagents. Cadmium and thallium(I) solutions were prepared with cadmium nitrate and thallous nitrate of an extra pure grade respectively. The potassium nitrate was purified by recrystallizing extra-pure-grade chemicals 3 times, while the sodium sulfite of an extra pure grade was used without further purification. All the solutions were prepared with redistilled water.

Procedure. The dissolved oxygen was removed by adding 0.3 m*l* of a 1 M sodium sulfite solution prepared freshly to 50 m*l* of a 0.1 M potassium nitrate solution containing cadmium or thallous ions; then about 30 m*l* of the solution was poured into the electrolytic cell. The mercury surface of the electrode was renewed by the procedure described in the previous paper[6]; after 15 min, metals were deposited on the mercury electrode by applying the potential of −0.8V *vs.* SCE, which corresponds to that of the plateau region of the current-voltage curve of cadmium, while rotating the disk at 600—1200 rpm. After this pre-electrolysis process, the deposited metals were stripped by scanning the potential from −0.8 V *vs.* SCE to the positive side, *i. e.*, by a linearly-varying potential stripping method. All the measurements were carried out at 25±0.5°C.

Results

The Reproducibility of the Peak Current. A typical stripping curve obtained by using the PMDCE is shown in Fig. 1; the peak current, i_p, was measured as is illustrated in the figure.

For the determination of adequate experimental



Potential, V *vs.* SCE

Fig. 1. Typical current-voltage curve.

TABLE 1. REPRODUCIBILITY OF THE PEAK CURRENT (μA)

Exp. number	Pre-electrolysis time, min				
	5	8	10	15	30
1	0.485	0.667	0.726	0.840	1.10
2	0.482	0.657	0.731	0.838	1.12
3	0.476	0.660	0.731	0.856	1.06
4	—	—	0.734	0.853	1.05
Average	0.481	0.665	0.731	0.846	1.08
Average deviation, %	0.62	0.75	0.27	0.92	2.55

Applied voltage, −0.80V *vs.* SCE
Rotating rate of the disk, 800 rpm
Voltage scanning rate, 0.2V per minute
Cd^{2+} concentration, 1×10^{-6} M

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[2] K. W. Gradiner and L. B. Rogers, *ibid.*, **25**, 1393 (1953).

[3] R. D. DeMars and I. Shain, *ibid.*, **29**, 1825 (1957).

[4] W. Kemula and Z. Kublik, *Anal. Chim. Acta*, **18**, 104 (1958).

[5] Y. Yamazaki, *Review of Polarography (Japan)*, **13**, 26 (1964).

[6] J. Suzuki and T. Ozaki, This Bulletin, **37**, 230 (1964).

[7] J. Suzuki, *ibid.*, **39**, 1898 (1966).

conditions, about four sets of experimental conditions were made at five different pre-electrolysis times. A summary of the data for cadmium is shown in Table 1. It may be seen that a good reproducibility can always be obtained, with a mean error of about ±1%, except at pre-electrolysis times of 30 min and over. Also, a similar good reproducibility can be obtained for thallium.

The Effect of the Pre-electrolysis Time. The dependence of the pre-electrolysis time on the peak current was investigated by using a 0.1 M potassium nitrate solution containing 1×10^{-6} M cadmium or thallous ions. The results are shown in Fig. 2.

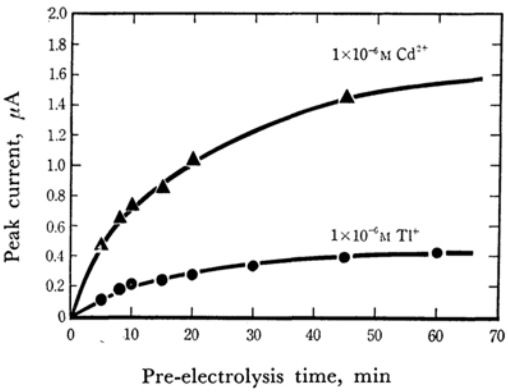

Fig. 2. Relation between the peak current and pre-electrolysis time.

As can be seen from the figure, the peak current shows a saturation curve with an increase in the pre-electrolysis time.

The Influence of the Rotating Rate of the Disk during the Pre-electrolysis Process on the Peak Current. The variations in the peak current with the rotating rate, 600, 800, 1000, or 1200 rpm, were investigated. The data are summarized in Table 2.

TABLE 2. EFFECT OF THE ROTATING RATE ω (rpm) ON THE PEAK CURRENT i_p (μA)

ω	i_p		$i_p/\sqrt{\omega}\times100$	
	Tl^{+}	Cd^{2+}	Tl^{+}	Cd^{2+}
600	0.182	0.580	0.75	0.24
800	0.210	0.731	0.74	0.26
1000	0.239	0.852	0.76	0.27
1200	0.269	1.00	0.78	0.28

Tl^{+}, Cd^{2+} concentration, 1×10^{-6} M
Applied voltage, −0.80V *vs.* SCE
Pre-electrolysis time, 10 min

It can be seen that the peak currents increase gradually with the increase in the rotating rates, as is shown in the table. On the other hand, the peak currents obtained both with and without rotating the disk during the stripping process were found to be almost equal in the range of the concentration from 10^{-6} to 10^{-7} M.

The Effect of the Voltage Scanning Rate on the Peak Current. The peak current was determined at each of four scanning rates, 0.10, 0.20, 0.50 and 1.0 V/min; the results are summarized in Table 3.

TABLE 3. EFFECT OF THE VOLTAGE SCANNING RATE v (V/min) ON THE PEAK CURRENT i_p (μA)

v	i_p*	$i_p/\sqrt{v}$
0.10	0.538	1.65
0.20	0.731	1.63
0.50	1.11	1.58
1.0	1.64	1.64

* Cd^{2+} concentration, 1×10^{-6} M
Rotating rate, 800 rpm
Pre-electrolysis time, 10 min

Gradual increases with the change in the scanning rate are shown in the table.

The Relation between the Peak Current and the Bulk Concentration. Several measurements of the peak current were made at various concentrations of cadmium and thallous ions. The results are shown in Fig. 3.

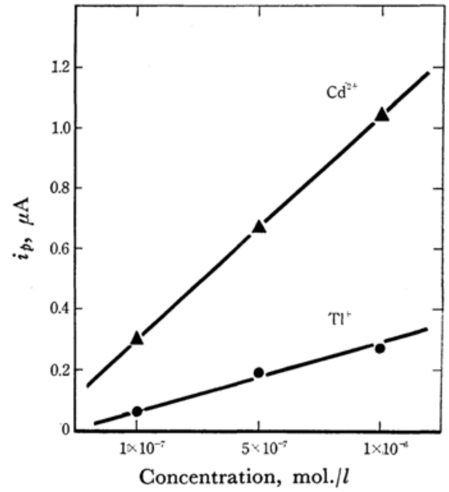

Fig. 3. Calibration curves of cadmium and thallium (I) (pre-electrolysis time: 20 min).

It can be seen from the figure that a satisfactory proportionality between the peak current and the bulk concentration was established.

Discussion

Pre-electrolysis Time and Peak Current. One of the important factors affecting the anodic peak current is the amount of metal deposited, which varies with the duration of the pre-electrolysis. When a solid electrode such as platinum is used for the deposition of metal ions, the metal ions must be recovered by anodic dissolution with an efficiency of 100%. In this case, it is expected that the peak current will increase linearly with the increase in the pre-electrolysis time.

On the other hand, when a mercury electrode such as the PMDCE is used, the peak current increases not linearly but curvedly, as is shown in Fig. 2, in spite of the fact that the amount of metal deposited increases linearly with the increase in the deposition time. This indicates that some portions of the deposited metal always diffuse away from the surface into the bulk of the mercury and are not available for the stripping process. Namely, on an increase in the pre-electrolysis time, the unavailable amount of the metal diffused away into the mercury increases gradually until it at last becomes almost equal to the metal deposited further from the solution. Therefore, the available accummulation of metal effective for the stripping does not increase, and no further increase in the peak current can be observed. Recently, the magnitude of the loss of the deposited metal has been studied coulometrically by Nikelly and Cooke⁸⁾; when the amount of electricity corresponding to the deposited metal was below several microcoulombs, it was found that about 50% of the deposited metal was lost by diffusion and unavailable for the stripping. When the amount of electricity was beyond this value, the percentage of metal lost by diffusion was found to decrease sharply. In the present work no coulometric investigation was carried out.

The Rotating Rate at the Pre-electrolysis and Peak Current. The amounts of the deposited metal are governed by the rate of the transport of metal ions to the electrode surface, that is, the rate of convectional transport caused by stirring the solution. The variation in the peak current with the increase in the rotating rate was also studied; the peak current was found to be proportional to the square root of the rotating rate, as is indicated by the data in the right-hand column of Table 2. This result was the same as that obtained in cathodic stripping voltammetry.⁷⁾

The Scanning Rate at the Stripping Process and Peak Current. An equation for the cathodic peak current in oscillographic polarography was independently derived by Randles⁹⁾ and by Sevcik¹⁰⁾:

$$i_{max}=kAn^{3/2}v^{1/2}D^{1/2}C \tag{1}$$

where k is the constant; A, the electrode area; n, the number of electrons involved in the electrode reaction; v, the rate of voltage scanning; D, the diffusion coefficient, and C, the bulk concentration.

The application of the Randles and Sevcik relationship to the anodic peak current obtained by the stripping method was investigated by Nikelly and Cooke.⁸⁾ They found that the relation between the anodic stripping peak current and the scanning rate was the same as that of Eq. (1); *i. e.*, the anodic stripping peak current was proportional to one-half the power of the scanning rate.

In the present work, the peak current changes linearly with one-half the power of the scanning rate, as can be seen from the data in the right-hand column of Table 3. A similar result was obtained for thallous ions. This is in good agreement with Nikelly's results.

Summary

The anodic-stripping voltammetry of cadimum and thallous ions in a potassium nitrate solution has been studied by using the PMDCE. The anodic stripping peak current has been found to be proportional to the bulk concentration of thallous or cadmium ions, and to the square roots of the rotating rate and the voltage scanning rate. These results are the same as those obtained in Nikelly's investigation, except for the factor of the rotating rate.

Using the present stripping procedure with the PMDCE, it has been possible to determine thallous and cadmium ions at concentrations as low as 1×10^{-7} M with a better reproducibility than with the other stripping method.⁸⁾

The author wishes to express his hearty thanks to Professor Tokuro Ozaki, Shizuoka University, for his valuable suggestions, and to Miss Haruko Matuura and Mr. Kiyoshi Hanai for their earnest assistance.

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8) J. G. Nikelly and W. D. Cooke, *Anal. Chem.*, **29**, 933 (1957).

9) J. E. B. Randles, *Trans. Faraday Soc.*, **44**, 327, 334 (1948).

10) A. Sevcik, *Collection Czechoslov. Chem. Commun.*, **13**, 349 (1948).