Potential-step Anodic Stripping Voltammetry

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The application of anodic potential-step stripping voltammetry for the determination of metal ion was investigated. From the dependence of stripping current ($i_{a,d}$) on electrode radius, the rotational speed of the stirring rod in electrodeposition and electrodeposition time for Cd(II) in 1 M KCl, the diffusion-controlled process could be theoretically predicted. The calibration curves of Cd(II), Mn(II), Ni(II), Zn(II), and Sb(III) were found to be linear in the range 0.01—0.1 ppm, and those of Tl(I), Cu(II), Pb(II), Sn(II), Bi(III), and In(III) in the range 0.02—0.2 ppm, by analysis at time t=1.25 sec on current-time curves. The ratio $i_{a,d}/i_{a,p}$ increased in the order $n=3<2<1$, where $i_{a,d}$ is the anodic diffusion current obtained by the potential-step method, and $i_{a,p}$ the anodic peak current obtained by the linearly varying potential method. The ratio of irreversible electron transfer reaction differed from that of the reversible one. The coefficient of variation in the measurement of peak heights was ±3% for 0.1 ppm or 0.2 ppm of metal ion.

Anodic stripping voltammetry has been found to be a very sensitive means for the determination of trace metal ions.[1] The metal ion to be determined is first electrodeposited on a stationary electrode and then stripped from this electrode by reoxidation of mercury amalgam. In the latter process, many reoxidation methods such as linearly varying potential method,[2] a.c. polarography,[3] square wave polarography,[4] constant current electrolysis,[5,6] coulostatic method,[7] and pulse polarography[8] have been employed. Mamantov *et al.* used the potential-step method to reoxidize mercury amalgam and applied it for the determination of cadmium ion.[5] Anodic potential-step stripping voltammetry was applied for the determination of the diffusion coefficient of metal atom in a hanging mercury drop electrode by analyzing the anodic current-time curve.[9,10] However, no papers dealing with the determination of metal ion have appeared except for that of Mamantov *et al.* It appeared to be worthwhile to investigate the applicability of anodic potential-step stripping voltammetry to the determination of metal ions and to compare the result with that of anodic stripping voltammetry under lineraly varying potential.

Experimental

Reagents. Standard solution of metal ions were prepared by dissolving metal salts of analytical reagent grade, and were standardized by complexometric titration with EDTA, except for tin(II) which was standardized gravimetrically.[11] Nitrates were used for Tl(I), Pb(II), Ni(II), and Zn(II), and chlorides for others.

Potassium chloride was purified by extracting heavy metals with dithizone–chloroform system, being recrystallized twice and heated at 300 °C in an electric furnace for 3 hr.

All the other reagents were of reagent grade and used without purification. Water was deionized on a mixed-bed ion-exchange resin and then distilled from alkaline permanganate solution.

Apparatus. The instrument for anodic stripping voltammetry with potential-step was set up with an automatic potential controller(Type AP–1, Shimadzu Co., Ltd.) for electrodepositing process and a potentiostat(Type PS–2, Shimadzu Co., Ltd.) for reoxidizing process from mercury amalgams. Switching from electrodepositing potential to reoxidizing potential was done by a mercury-relay(Type MC–1, NEC Co., Ltd.). The load resistance was adjusted with a precision variable resistor(Type 2786, Yokogawa Elec. Work, Ltd.) inserted in series with the load resistor of the potentiostat. *IR* drop across the variable resistor was applied to the recorder input for measuring cell current. A preliminary test showed that the *IR* drop was linearly proportional to the load resistance from 0 to 3000 Ω and from 0 to 10000 Ω. Current-time curves were recorded on a recorder(Type D–5SN, Rikendenshi Co., Ltd.) with 480 mm/min chart speed, a full-scale sensitivity of 10 mV and a nominal full scale response time of 0.4 sec. For anodic stripping voltammetry at linearly varying potential, a conventional polarograph(Type p–8, Yanagimoto Co., Ltd.) with a 1 V/1.1 min sweep rate and 180 mm/min chart speed was used.

A balanced head stationary hanging mercury drop electrode (HMDE)[12] and a saturated calomel electrode with KNO_3 agar-bridge were arranged with a beaker type electrolysis cell (*ca.* 100 ml). The characteristics of HMDE used were: t=4.25 min, m=3.6 mg/min. The electrode surface area was 0.028 cm^2, unless otherwise stated. The characteristics of another HMDE used for examining the relation between anodic diffusion current and the electrode radius were: t=22.25 min, m=1.1 mg/min.

All the experiments were carried out at room temperature.

Procedure. The method followed standard anodic stripping procedure.[13] A 50 ml solution containing the desired amount of metal and supporting electrolyte was transferred into the electrolysis cell. High purity nitrogen gas was passed through the solution for at least 15 min to remove oxygen. The solution was stirred with 360 rpm (driven by a synchronous rotating motor, unless otherwise

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[13] I. Shain, "Treatise on Analytical Chemistry," ed. by Koltoff and Elving, Part 1, Sec. D–2, Chap. 50, Interscience, New York (1963).

TABLE 1. COMPARISON BETWEEN ANODIC STRIPPING VOLTAMMETRY BY THE POTENTIAL-STEP METHOD AND LINEARLY VARYING POTENTIAL METHOD

Metal ion	Concen (ppm)	Supporting electrolyte	Deposition potential V *vs.* SCE	Reoxidation potential V *vs.* SCE	$i_{a,d}$ (μA)	$i_{a,p}$ (μA)	$i_{a,d}/i_{a,p}$	$E_{a,p}-E_{a,p}$
Tl(I)	0.2	1 M KCl	−0.70	−0.40	−0.80	−0.67	1.20	59
Cu(II)	0.2	1 M KCl	−0.45	−0.05	−1.04	−0.88	1.20	59
Cd(II)	0.1	1 M KCl	−0.95	−0.55	−0.95	−0.99	0.96	29
Pb(II)	0.2	1 M KCl	−0.60	−0.35	−0.97	−1.03	0.96	29
Sn(II)	0.2	1 M HCl	−0.80	−0.30	−0.74	−0.77	0.95	29
Zn(II)	0.2	1 M KCl	−1.20	−0.95	−2.78	−2.78	1.00	33
Zn(II)	0.2	0.5 M NH_3 +1 M NH_4Cl	−1.40	−0.60	−3.80	−1.90	2.00	106
Mn(II)	0.1	1 M KCl	−1.65	−1.10	−1.58	−0.46	3.46	166
Ni(II)	0.1	1 M KSCN	−0.80	−0.30	−0.65	−0.38	1.70	76
In(III)	0.2	1 M KCl +0.1 M HCl	−0.60	−0.35	−0.68	−0.96	0.71	19
Bi(III)	0.2	1 M H_2SO_4	−0.15	+0.10	−1.28	−1.76	0.72	19
Sb(III)	0.1	1 M H_2SO_4 +0.01 M KSCN	−0.25	−0.02	−0.88	−1.08	0.81	20

stated). During the course of the experiment, the solution was kept under nitrogen atmosphere. The deposition and reoxidation potentials of each metal ion are given in Table 1.

After deposition for 5 min, stirring was stopped for 30 sec, the chart was driven to record the current-time curve and the potential was switched from electrodeposition potential to reoxidation potential by a mercury-relay.

Results and Discussion

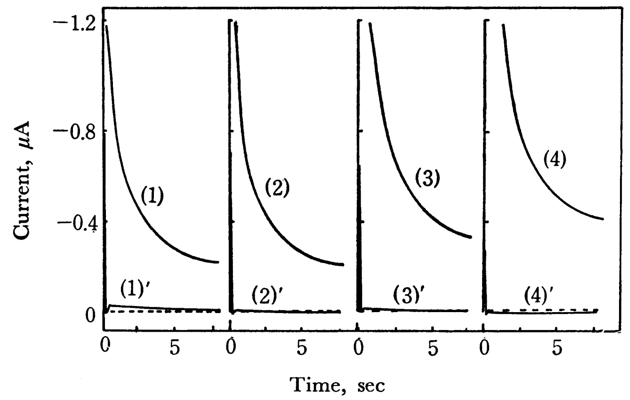

Fig. 1. Typical anodic stripping curves of Cu(II), Pb(II), Cd(II), Cu(II), and KCl.
(1) Cu(II), 0.1 ppm; (1)′ 1 M KCl
(2) Pb(II), 0.1 ppm; (2)′ 1 M KCl
(3) Cd(II), 0.1 ppm; (3)′ 1 M KCl
(4) Zn(II), 0.1 ppm; (4)′ 1 M KCl
Electrodeposition time for all metal ions, 5 min and for KCl, zero time.

Typical anodic current-time curves for Zn(II), Cd(II), Pb(II), Cu(II), and supporting electrolyte are shown in Fig. 1. Their residual currents which result from charging of the electrical double layer suddenly rise to a maximum and then decay to zero. Anodic current at constant potential electrolysis under the diffusion-controlled condition($i_{a,d}$) is given by[10)]

$$i_{a,d} = nFAD_RC_R^* [-1/\sqrt{\pi D_Rt} + 1/r_0 - (2/\sqrt{\pi D_Rt}) \sum_{n=1}^{\infty} \exp - (n^2r_0^2/D_Rt)] \qquad (1)$$

where C_R^* is the initial uniform concentration of deposited metal in the spherical mercury drop electrode, D_R the diffusion coefficient, t the time elapsed from beginning of stripping electrolysis, n the number of electron involved in the electron transfer reaction, r_0 the electrode radius, and A the area of electrode surface. The following semi-empirical equation for the electrodeposition process indicates that the limiting cathodic current i_c for an HMDE is a function of the radius of mercury drop r_0, the diffusion coefficient D_0(cm²/sec), the bulk concentration of the metal ion O to be determined C_o^*(mM), the rpm of the stirring rod U and constant k[1)]:

$$i_c = (4\pi r_0nFD_oC_o^* + knr_0^2D_o^{2/3}C_o^*U^{1/2}) \ \mu\text{A} \qquad (2)$$

where the first term in the right hand side is the value of i_c at $U=0$. This can be neglected if the rotational speed is high.[14)] The concentration of the reductant C_R^* is expressed as follows by means of cathodic current i_c and electrodeposition time τ.[15)]

$$C_R^* = \frac{3i_c\tau}{4\pi nFr_0^3} \qquad (3)$$

Since the third term in the right hand side of equation (1) is small when t is less than about 30 sec,[10)] anodic diffusion current ($i_{a,d}$) is expressed as follows from equations (1), (2) and (3).

$$i_{a,d} = 4\pi knFD_R\tau D_o^{2/3}C_o^*U^{1/2}\left(\frac{-1}{\sqrt{\pi D_Rt}}r_0 + 1\right) \qquad (4)$$

The dependence of $i_{a,d}$ upon r_0, $U^{1/2}$ and τ was examined for Cd(II) in 1 M KCl, Mamantov *et al.* having reported that its electrode reaction was dif-

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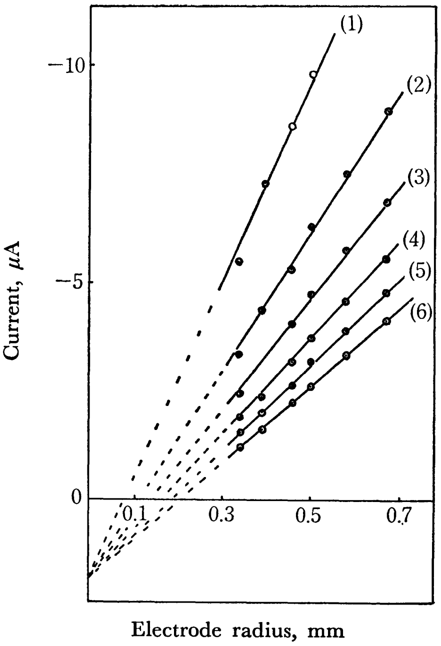

Fig. 2. Relation between anodic diffusion current and the radius of stationary mercury drop electrode.
(1) $t=1.25$ sec, (2) 2.50 sec, (3) 3.75 sec, (4) 5.0 sec, (5) 6.25 sec, (6) 7.50 sec.
Cd(II), 1 ppm in 1 M KCl; electrodeposition potential, −0.95 V *vs.* SCE; reoxidation potential −0.55 V *vs.* SCE; electrodeposition time, 5 min.

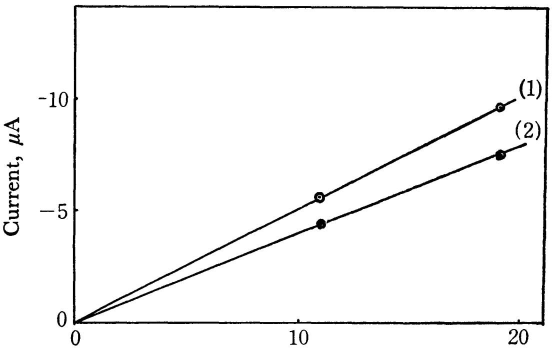

Fig. 3. Relation between anodic diffusion current and square root of speed of stirring rod.
Cd(II), 1 ppm in 1 M KCl; Electrode surface area, (1) 0.028 cm^2; (2) 0.018 cm^2; $t=1.25$ sec; Other conditions as in Fig. 2.

fusion-controlled. The relation between $i_{a,d}$ and r_0 is shown in Fig. 2. The various radii of the stationary mercury drop electrode were obtained by changing mercury run-off time. The $i_{a,d}$ for all the fixed times of the current-time curve after the start of reoxidation was linearly proportional to r_0. When extrapolated to zero radius, each line intersected at the same point. Since the spherical diffusion process is divergent, spherical correction acts to reduce the current below the value expected for a plane electrode. As a result, the $i_{a,d}$ *vs.* r_0 and also $i_{a,d}$ *vs.* $1/\sqrt{t}$ plots(Figs. 5 and 6) were extrapolated to a positive value. The relation between $i_{a,d}$ and $U^{1/2}$ is shown in Fig. 3. The $i_{a,d}$ was measured at two rotational speeds (rpm 360 and

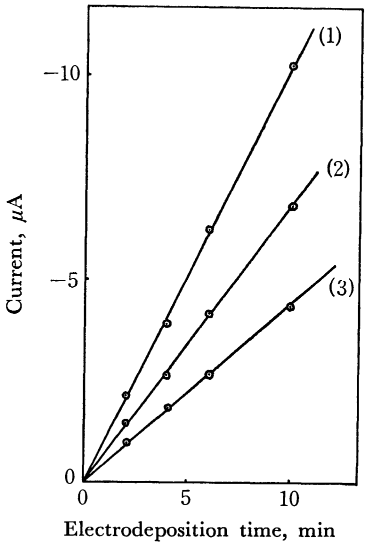

Fig. 4. Relation between anodic diffusion current and electrodeposition time.
(1) $t=1.25$ sec, (2) 2.50 sec, (3) 3.75 sec.
Cd(II), 1 ppm in 1 M KCl; Other conditions as in Fig. 2.

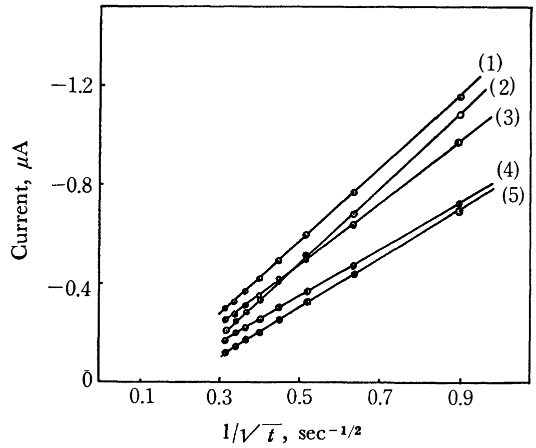

Fig. 5. Relation between i_a and $1/\sqrt{t}$.
Concentration of each metal ion, 0.1 ppm; electrodeposition time, 5 min; electrodeposition potential and reoxidation potential are given in Table 1.
(1) Zn(II) in 1 M KCl, (2) Mn(II), (3) Sb(III), (4) Cd II), (5) Ni(II).

120), and was found to be linearly proportional to $U^{1/2}$ for two different electrode surfaces. The $i_{a,d}$ *vs.* $U^{1/2}$ plots for both surfaces pass through the origin. The relation between $i_{a,d}$ and τ is shown in Fig. 4, The $i_{a,d}$ at the fixed time of the current-time curves is linearly proportional to τ from 1 to 10 min. All these lines pass through the origin.

If the electrode reaction is diffusion-controlled, the $i_{a,d}$ *vs.* $1/\sqrt{t}$ plot should be linear. $i_{a,d}$ was plotted against $1/\sqrt{t}$ over the time interval 1.25—10 sec after the start of reoxidation for all the metals used. All the resulting curves are linear and their electrode reactions found to be diffusion-controlled. The results are shown in Figs. 5 and 6. Although Ni(II) can easily form intermetallic compounds, the current-time curve of Ni(II) decayed with $t^{-1/2}$ at 0.1 ppm

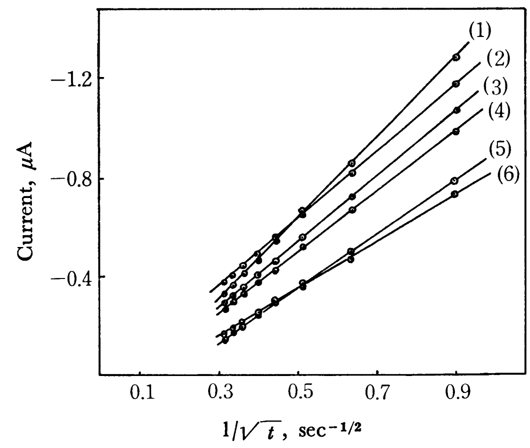

Fig. 6. Relation between i_a and $1/\sqrt{t}$.
Concentration of each metal ion, 0.2 ppm; electrodeposition time, 5 min; electrodeposition potential and reoxidation potential are given in Table 1.
(1) Bi(III), (2) Cu(II), (3) Pb(II), (4) In(III), (5) Sn(II), (6) Tl(I).

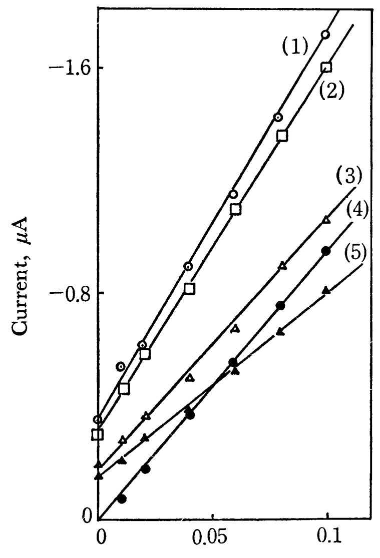

Fig. 7. Calibration curves of metal ions.
(1) Zn(II) in 1 M KCl, (2) Mn(II), (3) Sb(III), (4) Cd(II), (5) Ni(II).
Electrodeposition potential, reoxidation potential and supporting electrolytes are given in Table 1.

concentration, showing that the electrode reaction is diffusion-controlled. Calibration curves are shown in Figs. 7, 8 and 9. 5 min was chosen as electrodeposition time for all the metal ions. The reoxidation potential was chosen to have a positive value to make anodic diffusion current independent of potential. The $i_{a,d}$ was measured at $t = 1.25$ sec on the current-time curve. The value at zero concentration for each metal ion was due to impurities in the supporting electrolyte. Straight lines were obtained from 0.01 to 0.1 ppm for Cd(II), Mn(II), Ni(II), Zn(II), and Sb(III), and from 0.02 to 0.2 ppm for Tl(I), Cu(II), Pb(II), Sn(II), In(III), and Bi(III). It is of interest that even 0.01 ppm Mn(II) was determined by this method. 0.1 ppm Mn(VII) at most was determined by colorimetric determination[16] and 0.05 ppm Mn(III) by square wave polarography.[17]

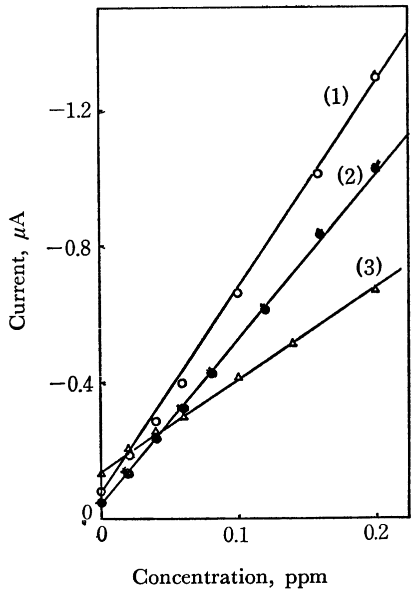

Fig. 8. Calibration curves of metal ions.
(1) Bi(III), (2) In(III), (3) Tl(I).
Electrodeposition potential, reoxidation potential and supporting electrolytes are given in Table 1.

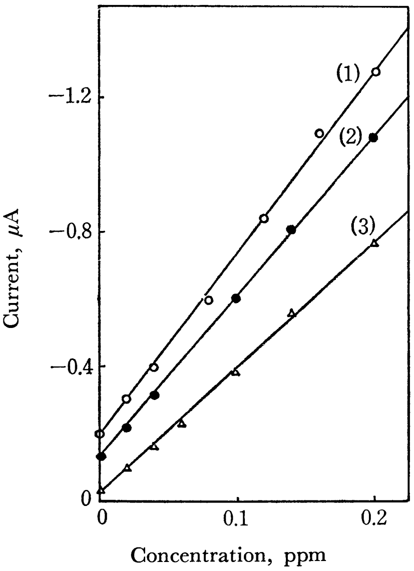

Fig. 9. Calibration curves of metal ions.
(1) Cu(I), (2) Pb(II), (3) Sn(II).
Electrodeposition potential, reoxidation potential and supporting electrolytes are given in Table 1.

As anodic diffusion current decreases with $1/\sqrt{t}$, it will be possible to determine a wide range of concentration of the metal ion from a current-time curve. According to Mamantov's suggestion,[5] concentration below 10^{-7} M of metal ion could be determined, if the current at a shorter time than $t = 1.25$ sec has been measured.

Anodic diffusion current($i_{a,d}$) obtained by the potential-step reoxidation method were compared with

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[16] JIS K 0102 (1971).

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anodic current($i_{a,p}$) obtained by the linearly varying potential method. The results, including the potential difference between anodic peak potential ($E_{a,p}$) and anodic half-peak potential($E_{a,p/2}$) are given in Table 1. In the case of Cu(II), the electrodeposition potential and reoxidation potential correspond to $Cu(0) \rightarrow Cu(I)$ or one electron reoxidation.[18]

The ratio $i_{a,d}/i_{a,p}$ of reversible electron transfer reaction in which $E_{a,p}-E_{a,p/2}$ is $58/n$, increases in the order $n=3<2<1$.

Although the ratios can be varied by changing the sweep rate, the order $n=3<2<1$ will not change. This is because $i_{a,d}$ is in direct proportion to n, and $i_{a,p}$ is in direct proportion to $n^{3/2}$ under the diffusion-controlled condition.[19]

The ratio $i_{a,d}/i_{a,p}$ of Ni(II), Mn(II), and Zn(II) is larger than that of reversible two electron transfer reaction, and the ratio of Zn(II) in 1 M KCl differs from that in 0.5 M NH_3+1 M NH_4Cl. This is because $i_{a,p}$ is affected by α which may have a different value depending on the kind of supporting electrolytes.[20,21] The $i_{a,d}$ value of irreversible electron transfer reaction is considered to be close to the value of the reversible electron transfer reaction, since the reoxidation potential was chosen so as to be far more anodic than the anodic half-wave potential in this experiment.[22] This is why the ratio $i_{a,d}/i_{a,p}$ of Sb(III) differs from the other reversible three electron transfer reactions. Jacobsen and Rojahn reported that Sb(III) was not a strictly reversible process in 1 M H_2SO_4+0.01 M KSCN.[23]

The value $i_{a,d}/i_{a,p}$ indicates that anodic stripping voltammetry with potential-step method is more sensitive than linearly varying potential method for metal ions of which electron transfer reaction is irreversible. However, it has the disavantage of being more difficult to render analysis of certain ion mixtures with proximate anodic peak potentials or adverse relative concentration.

Acknowledgement

The author wishes to express his gratitude to Dr. H. Kakiyama for his encouragement throughout this work.

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19) P. Delahay, "New Instrumental method in Electrochemistry," Interscience, New York (1964), p. 118.

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21) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

22) Ref. 19, p. 79.

23) E. Jacobsen and T. Rojahn, *Anal. Chim. Acta*, **54**, 261 (1971).