

analytical procedure. In the case of vegetation samples, a precision (as a mean relative standard deviation) of 4.3% is obtained in the range 50–600 ppm F. A corresponding value of 4.1% is obtained for soil samples in the range 30–700 ppm F. These values of 4.3 and 4.1% indicate excellent precision for the method and are a reflection of the fact that the samples undergo a minimum of handling during the analytical procedure. The precision of 4.3% for vegetation samples may be compared with a value of 5.7% reported by Jacobson and Heller (6) for an acid/alkali leach procedure using the SIE method.

Summary. It is evident from the results of this work that the rapid NaOH fusion–SIE procedure described in this work is suitable for the analysis of total fluoride in both soils and vegetation. Since interfering cations can be removed, as insoluble oxides, prior to analysis, the time consuming distillation step recommended in the classical Willard–Winter procedure becomes unnecessary.

Finally, the procedure can easily be extended to include the determination of total atmospheric fluoride if the sample is collected on a 0.45- μ membrane filter impregnated with Na_2CO_3 (12). In this laboratory such filters exposed for a 7-day period at a flow rate of about 15 l./min have been satisfactorily analyzed. Under the conditions just stated, a detection limit for the ambient air of 0.01 $\mu\text{g F/m}^3$ is possible. For a 24-h

sampling period, the detection limit will approach 0.1 $\mu\text{g F/m}^3$.

LITERATURE CITED

- (1) H. H. Willard and O. B. Winter, *Ind. Eng. Chem.*, **5**, 7 (1933).
- (2) J. S. Jacobson, D. C. McCune, L. H. Weinstein, R. H. Mandie, and A. E. Hitchcock, *J. Am. Pollut. Contr. Assoc.*, **16**, 367 (1966).
- (3) R. L. Baker, *Anal. Chem.*, **44**, 1326 (1972).
- (4) P. W. Curtis, A. B. Piecka, and J. A. Thompson, "Evaluation of the Digestion-Selective Ion Electrode Technique for Determining Fluoride in Vegetation," presented at The Annual Meeting of the Pacific Northwest International Section of The Air Pollution Control Association, Vancouver, 1975.
- (5) T. Gyoerkoes, D. A. White, and R. L. Luthy, *J. Metals*, **22**, 29A (1970).
- (6) J. S. Jacobson and L. I. Heller, "Selective Ion Electrode Analysis of Fluoride in Vegetation", in "Proceedings of the Second International Clean Air Congress", H. M. Englund and W. T. Berry, Ed., Academic Press, New York, 1971.
- (7) N. R. McQuaker, unpublished results.
- (8) American Public Health Association, "Standard Methods for the Examination of Water and Wastewater, 13th ed., New York, 1971, p 172.
- (9) E. Bellack, *Am. Water Works Assoc. J.*, **64**, 62 (1972).
- (10) N. R. McQuaker, "A Laboratory Manual for the Chemical Analysis of Ambient Air, Emissions, Soil and Vegetation," Environmental Laboratory, Water Resources Service, Department of Environment, Province of British Columbia, 1976, p 11.
- (11) N. T. Crosby, *J. Appl. Chem.*, **19**, 100 (1969).
- (12) T. Okita, K. Kaneda, T. Yanaka, and R. Sugai, *Atmos. Environ.*, **8**, 927 (1974).

RECEIVED for review July 21, 1976. Accepted October 7, 1976.

Anodic Stripping Peak Currents: Electrolysis Potential Relationships for Reversible Systems

Alberto Zirino* and S. P. Kounaves

Chemistry and Environmental Sciences Group, Naval Undersea Center, San Diego, Calif. 92132

For electrochemically reversible systems, a study has been made of the relationship between peak currents obtained by anodic stripping voltammetry and the applied electrolysis potential. An equation was derived which describes these relationships as sigmoidal or polarographic curves. However, unlike polarography, $E_{1/2}$ is predicted to be a linear function of the electrolysis time t . This relationship was verified for the hanging mercury drop electrode for Cd(II) in 1 M KCl and 0.1 M KNO_3 .

Peak current–electrolysis potential relationships (sometimes called pseudopolarographic curves) obtained in anodic stripping voltammetry have been used qualitatively to study trace metals in natural waters at concentrations too low for direct polarographic analysis. Matson (1) and Fitzgerald (2), using the mercury-composite-graphite electrode (MCGE), suggested that the speciation of trace metals in seawater could be studied from peak current–electrolysis potential plots. However, Seitz et al. (3) demonstrated that deteriorating electrodes could also alter the shape of these plots. Recently, Bubić and Branica (4) used stripping polarography with the hanging mercury drop electrode (HMDE) to determine empirically that Cd(II), CdCl(I), and CdCl₂(0) were the predominant species of Cd in seawater.

The following work was undertaken to establish the theoretical basis of stripping polarography in order to assess its applicability to the study of trace metals in natural waters.

THEORY

For a substance O which reduces to a metal R and forms an amalgam with Hg, peak current–applied potential plots resemble polarographic curves because the relationship between the peak current and concentration

$$i_p = kq = knFVC_O^* \quad (1)$$

where i_p = stripping peak current, k = a proportionality constant, q = the total charge passed for deposition of the metal, V = the solution volume, C_O^* = the concentration of substance O in the bulk of the solution and n and F have their usual meaning, is similar to the fundamental relationship of polarography $i \propto C_O^*$, where i is the instantaneous current for the reduction. However, $i \propto C_O^*$ is not readily applicable to the electrolysis currents of anodic stripping because i declines with time as the electrolysis is continued. This occurs because the electrode is of finite volume and tends to "fill up". The decline of i is most pronounced at low overpotentials and negligible in the limiting case. This is indicated in Figure 1, which, for a solution of 8.6×10^{-2} M Cd(II) in 1 M KCl, shows i as a function of plating time and overpotential. The relationship between i and the total charge passed for the deposition of O in a time period t is given by

$$\int_0^t i dt = q \quad (2)$$

In stripping analysis i is generally too small to be measured,

but a useful relationship may be drawn between q and the average current \bar{i} :

$$\bar{i}t = q \quad (3)$$

Now the peak current–electrolysis potential relationship can be derived in terms of an average flux (\bar{F}_O) to the electrode, since

$$\bar{i} = nFA\bar{F}_O \quad (4)$$

where A = the area of the electrode, and n and F have their usual meaning. For a stirred solution a relationship between \bar{F}_O and C_{O^*} can be given by the Nernst diffusion layer:

$$\bar{F}_O = \frac{D_O}{\delta_O} (C_{O^*} - C_{O(O)}) \quad (5)$$

where D_O = the diffusion coefficient of substance O , δ_O = the thickness of the diffusion layer, and $C_{O^*} - C_{O(O)}$ is the average concentration gradient of substance O at the electrode surface.

Because C_{O^*} does not change substantially with time in anodic stripping experiments, expression 5 can be rewritten as

$$\bar{F}_O = \frac{D_O}{\delta_O} (C_{O^*} - \overline{C_{O(O)}}) \quad (6)$$

From the nonlinear time dependence of the electrolysis current, it can be seen that the computed value of $\overline{C_{O(O)}}$ is also dependent on time, thus we can write $\overline{C_{O(O), t}}$. At any time t , $\overline{C_{O(O), t}}$ is related to the average concentration of R at the surface of the electrode ($\overline{C_{R(O), t}}$) by the Nernst equation

$$\theta = \exp \left[\frac{nF}{RT} (E - E^\circ) \right] \quad (7)$$

where E is the potential of the electrode, E° is the standard potential for the amalgam electrode, n , F , R , and T have their usual meaning, and

$$\theta = \frac{\overline{C_{O(O), t}} \gamma_O}{\overline{C_{R(O), t}} \gamma_R} \quad (8)$$

where γ_O and γ_R are the activity coefficients of O and R , respectively.

For the hanging mercury drop electrode (HMDE), Shain and Lewinson (5) give an expression for C_R as a function of t and r , the distance from the center of the drop. For an average flux \bar{F}_O , C_R at the surface of the electrode ($r = r_O$) is given by this expression:

$$\overline{C_{R(O), t}} = \frac{3\bar{F}_O t}{r_O} + \frac{\bar{F}_O r_O}{5D_R} - \frac{2\bar{F}_O r_O}{D_R} \sum_{n=1}^{\infty} \left(\frac{1}{\alpha_n^2} e^{-D_R \alpha_n^2 t / r_O^2} \right) \quad (9)$$

where D_R is the diffusion constant of R in the amalgam and α_n for $n = 1, 2, 3, \dots$ are the positive roots of $\tan \alpha = \alpha$. Shain and Lewinson (5) suggested that at $t > 25$ s the right-hand term in Equation 9 may be neglected so that the expression condenses to a term linear in time plus a term which corrects for diffusion within the drop. Thus using Equations 3, 4, 6, and 9, $\overline{C_{O(O), t}}$ and $\overline{C_{R(O), t}}$ can be expressed in terms of q . Substituting these results into Equation 8 yields

$$\theta = \frac{\left(\frac{nFA \left(\frac{D_O}{\delta_O} \right) C_{O^*} t - q}{nFA \left(\frac{D_O}{\delta_O} \right) t} \right) \gamma_O}{\left(\frac{15D_R q t + q r_O^2}{nFA t 5D_R r_O} \right) \gamma_R} \quad (10)$$

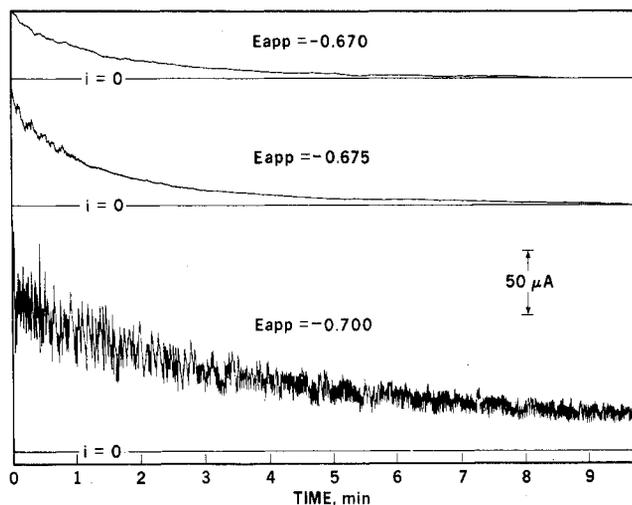


Figure 1. Decay of the electrolysis current with time at several applied potentials. Conditions: 8.6×10^{-2} M Cd(II) in 1 M KCl. Current in lower plot is undamped

where $nFA(D_O/\delta_O)C_{O^*}t$ is the charge accumulated under limiting conditions, q_L , and

$$\theta = \left(\frac{q_L - q}{q} \right) \left(\frac{(r_O \delta_O \gamma_O) / (3\gamma_R D_O)}{t + (r_O^2 / 15D_R)} \right) \quad (11)$$

By substituting Equation 1 into Equation 11, and then inserting the result into Equation 7, we obtain the peak current–electrolysis potential relationship:

$$E = E^\circ + \frac{RT}{nF} \ln \left(\frac{i_{pL} - i_p}{i_p} \right) + \frac{RT}{nF} \ln \left(\frac{r_O \delta_O \gamma_O}{3D_O \gamma_R} \right) - \frac{RT}{nF} \ln \left(t + \frac{r_O^2}{15D_R} \right) \quad (12)$$

where i_{pL} is the peak current obtained under limiting conditions.

When $i_p = i_{pL}/2$, an expression for the “half wave” potential ($E_{1/2}$) is obtained:

$$E_{1/2} = E^\circ + \frac{RT}{nF} \ln \left(\frac{\gamma_O \delta_O r_O}{3D_O \gamma_R} \right) - \frac{RT}{nF} \ln \left(t + \frac{r_O^2}{15D_R} \right) \quad (13)$$

$E_{1/2}$ varies with the electrode area, with the stirring rate, and with the time of electrolysis. In this respect, the HMDE is completely analogous to the rotating mercury electrode of Lee (6) as described by Delahay (7).

EXPERIMENTAL

Instrumentation. All current–voltage measurements were made with a Princeton Applied Research (PAR) Model 174 Polarographic Analyzer and recorded with a Sargent-Welch SRG strip-chart recorder. The radius of the HMDE was measured with an optical micrometer.

Electrodes and Cell. The electrolysis cell consisted of a PAR No. 9323 HMDE fitted into a PAR No. 9300 polarographic cell top. A vessel corresponding to the PAR No. 3343 polarographic cell bottom was machined from acrylic plastic and threaded to fit into a specially designed, acrylic plastic water jacket. In the cell, temperature was maintained at 25.9 ± 0.2 °C with a circulating water bath. The solution was stirred with a 1.1-cm Teflon-covered stirring bar coupled to a Sargent-Welch 600-rpm synchronous-speed magnetic stirrer. A Beckman fiber-junction saturated-calomel electrode (SCE) was used as reference while a Pt foil wound around the SCE served as a counter electrode. Room temperature was 26 ± 1 °C.

Solutions. Solutions were made from reagent-grade salts. Purified N_2 was used for sparging without further treatment.

Procedure. An electrode of suitable size was produced by turning the micrometer portion of the HMDE until a Hg bead just formed

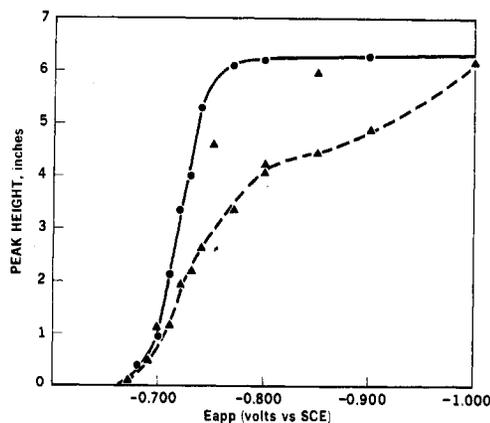


Figure 2. Stripping peak current as a function of applied potential. Conditions: 4.00×10^{-4} M Cd(II) in 1 M KCl, $t = 1200$ s; (●) drop renewed, (▲) single drop.

outside the capillary. The micrometer was then turned four additional divisions. The mean vertical length of 11 drops formed in this manner (measured with an optical micrometer) was 0.0928 ± 0.0014 cm. Test solutions were sparged with N_2 for approximately 15 min; then the flow was diverted over the surface while maintaining stirring. To avoid systematic errors, an electrolysis potential (E_{app}) was selected randomly from a list of those bracketing E° and applied for a designated period of time t . Afterwards, the stirring was stopped, the solution was allowed to come to rest for 30 s, while maintaining E_{app} , and the reduced metal was stripped out of the drop by reducing the applied voltage at a rate of 20 mV/s.

Two solutions were studied. For the first, 4.00×10^{-5} M Cd(II) in 1 M KCl, three separate experiments were conducted by applying a set of discrete electrolysis potentials for $t = 120, 300,$ and 1200 s. The solution temperature was maintained at $T = 25.9 \pm 0.2$ °C and a single Hg drop was used for all of the plating–stripping cycles needed to completely describe the peak current–electrolysis potential relationship. Use of a single drop, however, produced anomalous results for the 1200-s experiment. The latter was then repeated using a newly formed drop for each plating–stripping cycle.

The second solution studied was 4.00×10^{-5} M Cd(II) in 0.1 M KNO_3 . Individual experiments were carried out in the same manner as for the KCl solution, except that $t = 15, 30, 60, 90, 120, 200, 300, 550, 900,$ and 1200 s. The work was performed over a period of approximately one week and because the cell was not thermostated, the temperature of the solution was measured to be within 24 ± 1 °C.

RESULTS AND DISCUSSION

Peak Current–Electrolysis Potential Plots. For both the KCl and KNO_3 solutions, when the Cd stripping peak currents were plotted as a function of the applied potential, polarographic (sigmoidal) curves were obtained for every electrolysis time t . Plots of E_{app} vs. $\log((i_{pl} - i_p)/(i_p))$ were linear with slopes of $30 \text{ mV} \pm 1 \text{ mV}$ (Figure 3). An aberrant curve was obtained for the 1200-s experiment with the KCl solution using a single mercury drop (Figure 2). When the experiment was repeated using a new drop every plating–stripping cycle, the familiar sigmoid curve was again reproduced. This suggested that the surface of the Hg drop had deteriorated during the long experiment. Deterioration was also evident from a broadening of the stripping peaks, and it was additionally observed that Cd could not be stripped fully from the amalgam during the voltage scan.

This degradation of the surface did not change the appearance of the drop and could not be observed through the micrometer microscope. It is suggested that deterioration of the Hg surface may be an important source of variation in stripping analyses where prolonged electrolysis times are required. For the 1200-s experiment, signs of deterioration of the electrode could be detected from changes in the shape of the peak current after the first plating–stripping cycle, or about 30 min of use. Thus, it became advisable to replace the Hg drop every cycle. The error introduced from the variation

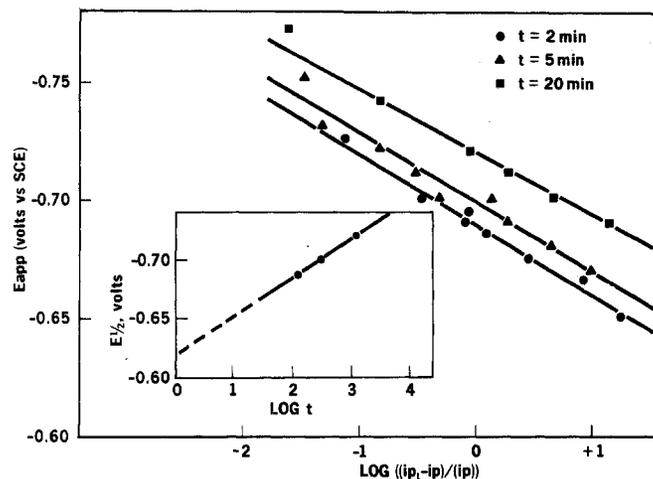


Figure 3. Cd(II) in 1 M KCl; applied potential vs. $\log((i_{pl} - i_p)/(i_p))$ for several electrolysis times. Insert: Half-wave potential vs. $\log t$

in the surface area is approximately 3% and is negligible for this and most trace determinations.

Variations of $E_{1/2}$ with Electrolysis Time. Plots of $E_{1/2}$ vs. $\log t$ were linear for both the KCl and the KNO_3 solution. For Cd(II) in 1 M KCl, $\Delta E_{1/2}/\Delta \log t = 30 \text{ mV}$ (Figure 3 inset). For Cd(II) in 0.1 M KNO_3 , $\Delta E_{1/2}/\Delta \log t$ was calculated by regression to be 27 mV. The difference between the two solutions is within experimental error and not significant.

The linearity of the $E_{1/2}$ vs. $\log t$ function indicates that for anodic stripping experiments, the $r_0^2/15D_R$ term occurring in expressions 12 and 13 may be neglected.

This extra term occurs in Equations 12 and 13 because their derivation assumed a motionless Hg drop. In most anodic stripping experiments the drop is agitated by the stirrer (this can be observed from the fluctuations in the undamped electrolysis current illustrated in Figure 1) and the diffusion constant D_R actually approaches D_R/δ_R where δ_R is the thickness of the diffusion layer within the drop. By substituting reasonable values of r_0 , δ_R , and D_R it can be verified that $r_0^2\delta_R/15D_R$ is insignificant at any practical value of t . Thus a simplified equation can be written which relates $E_{1/2}$ and t :

$$E_{1/2} = E^\circ + \frac{RT}{nF} \ln \frac{\gamma_O \delta_O r_0}{3D_O \gamma_R} - \frac{RT}{nF} \ln t \quad (14)$$

Interestingly, Equation 14 could have been obtained by making the a priori assumption that the gradient within the drop is small and that

$$C_{R(O), t} = \frac{3it}{4\pi nFr_0^3} \quad (15)$$

This is the observation made by Shain and Lewinson (5) for an immobile Hg drop and it becomes an even better approximation when the drop is agitated as commonly occurs in anodic stripping experiments.

Calculation of the Activity Coefficient γ_O . At $t = 1$ s, Equation 14 can be solved for the activity coefficient of O:

$$\ln \gamma_O = \frac{(E_{1/2}(t=1) - E^\circ)nF}{RT} - \ln \frac{r_0 \delta_O}{3\gamma_R D_O} \quad (16)$$

If it is assumed that in the dilute amalgam γ_R is unity, then γ_O can be expressed in easily measurable quantities.

An activity coefficient for Cd(II) in 1 M KCl may be obtained from Equation 16. δ_O/D_O may be calculated from the limiting current to be $2.64 \times 10^2 \text{ s/cm}$. $E_{1/2}(t=1) = -0.620 \text{ V}$ from extrapolation of the data in Figure 3. E° for Cd(II)|Cd – Cd_x(Hg) 11% can be calculated from the data of Harned and Fitzgerald (8) to be -0.345 V at 26 °C. The potential of the

SCE used in this work was measured against an Ag/AgCl electrode to be -0.268 V. Thus, if γ_R is assumed to equal unity, $\gamma_O = 0.14$. This value may be compared with γ^\pm for 1 M CdCl₂ which is 0.07 (9). The error in γ_O chiefly lies in the value of E° as applied to the dilute amalgam formed in this experiment. Nevertheless, the technique offers the opportunity to study the relative activities of trace metals in highly concentrated salt solutions such as seawater.

Thin-Film Electrodes and Flowing Systems. If C_R is homogeneously distributed in a thin-film electrode such as the MCGE of average thickness l , then

$$C_R = \frac{\bar{F}_O t}{l} \quad (17)$$

and the expression for $E_{1/2}$ becomes

$$E_{1/2} = E^\circ + \frac{RT}{nF} \ln \frac{\gamma_O \delta_O l}{D_O \gamma_R} - \frac{RT}{nF} \ln t \quad (18)$$

For $l = 5 \times 10^{-4}$ cm (1), we find that $E_{1/2}$ for a thin film lies approximately 90 mV cathodic of $E_{1/2}$ for the Hg drop.

Recently Lieberman and Zirino (10) used a tubular mercury-graphite electrode (TMGE) to measure Zn in seawater. They observed that the Zn peak current declined with time of electrolysis and that a semilog relationship existed between the Zn peak current and the flow rate of the seawater through the electrode, rather than an expected log-log function. Because they had used high flow-rates in their experiment, they suggested that their observation was the result of "friction". An alternate or additional explanation may also be offered: the flow through the electrode may be related to the mass transport by the expression

$$\frac{D_O}{\delta_O} = N \frac{V}{A} \quad (19)$$

where V = the flow rate (cm³/s), A = the surface area of the electrode (cm²), and N = a dimensionless proportionality constant.

Substitution of the right side of Equation 19 into the expression for \bar{F}_O and solving for E yields

$$E = E^\circ + \frac{RT}{nF} \ln \left(\frac{i_{PL} - i_P}{i_P} \right) + \frac{RT}{nF} \ln \frac{\gamma_O A l}{N V \gamma_R} - \frac{RT}{nF} \ln t \quad (20)$$

Thus, E will approach E_{app} proportionately to the magnitude of the terms on the right-hand side of Equation 20. Because E_{app} for reduction of Zn on the Hg film is generally held at -1.4 V vs. Ag/AgCl or less to avoid reduction of H⁺, it is possible to "fill up" the electrode with respect to this metal. Proof of Equation 20 awaits demonstration that the Hg film is invariant with flow rate and time of electrolysis (11).

CONCLUSION

Peak current-electrolysis potential relationships obtained by anodic stripping present the possibility of applying classical polarographic techniques to the study of trace metals in natural media at very low concentrations. The HMDE is particularly suited to this work because its surface is easily renewable and because the equation relating the peak current to the applied potential is expressed in experimentally measurable quantities. However, rigorous application of pseudopolarographic curves to the study of complexation of trace metals in natural media has not yet been attempted, and it is anticipated that it may be difficult to separate effects occurring on the electrode from those produced by complexation.

LITERATURE CITED

- (1) W. R. Matson, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1968.
- (2) W. F. Fitzgerald, Ph.D. Thesis, Massachusetts Institute of Technology and Woods Hole Oceanographic Institution, Cambridge, Mass., 1969.
- (3) W. R. Seltz, R. Jones, L. Klatt, and W. D. Mason, *Anal. Chem.*, **45**, 840 (1973).
- (4) S. Bubić and M. Branica, *Thalassia Jugosl.*, **9** (1/2), 47 (1973).
- (5) I. Shain and J. Lewinson, *Anal. Chem.*, **33**, 187 (1961).
- (6) T. S. Lee, *J. Am. Chem. Soc.*, **74**, 5001 (1952).
- (7) P. Delahay, "New Instrumental Methods in Electrochemistry", Interscience, New York, 1954.
- (8) H. S. Harned and M. E. Fitzgerald, *J. Am. Chem. Soc.*, **58**, 2624 (1936).
- (9) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", Reinhold, New York, 1958, p 742.
- (10) S. H. Lieberman and A. Zirino, *Anal. Chem.*, **46**, 20 (1974).
- (11) D. N. Hume and J. N. Carter, *Chem. Anal. (Warsaw)*, **17**, 747 (1972).

RECEIVED for review April 11, 1975. Accepted September 17, 1976. This work was supported by the Office of Naval Research under contract number NR 083-301.