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CATHODIC PULSE STRIPPING ANALYSIS OF IODINE AT THE PARTS-PER-BILLION LEVEL

by

R. C. Propst

Savannah River Laboratory
E. I. du Pont de Nemours & Co.
Aiken, South Carolina 29801

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ABSTRACT

The deposition-stripping behavior of iodide films at the hanging mercury drop electrode is investigated. Surface monolayers of Hg_2I and Hg_2I_2 are postulated based on the percentage occupancy of the available sites at the surface of the HMDE. Stripping of less than monolayer amounts as Hg_2I is employed for determination of from 1 to 50 ppb iodine with a standard deviation of 0.3 ppb. The effect of interferences is discussed.

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INTRODUCTION

Sensitive analytical methods are required for environmental studies of the amounts of trace substances released and their ultimate fate. Stripping methods are frequently selected for this application because the capital investment in equipment is low and because the high sensitivity of the method largely eliminates the need for preconcentration of the sample. Existing stripping methods for iodide did not exhibit the 0.5 ppb sensitivity desired for the determination of iodine in surface water.

Perone et al.(1) have described the stripping analysis of iodide at the silver electrode. The deposition-stripping processes were uncomplicated; however, a 30-minute deposition was required to achieve a detection limit of 5 ppb. The nature of our samples precluded incorporation of organic solvent(2) into the electolyte system to improve sensitivity.

Methods for the stripping analysis of iodide at the hanging mercury drop electrode (HMDE) have been plagued by the anomalous deposition-stripping behavior of mercurous-iodide films. Kemula et al.(2) report a detection limit of about 65 ppb for iodide in 0.1M KNO_3. They observed deviations from linear stripping behavior with both more-dilute and more-concentrated solutions of iodide, especially after prolonged electrolysis. Also, the

appearance of two peaks of different heights complicated estimation of the height of the stripping peak.

Perchard et al.(3) report that, for concentrations of less than about 13 ppb I^-, the relationships governing the analytical applications no longer hold. The anomalous deposition-stripping behavior was attributed to the special properties of a monolayer deposit of mercurous iodide.

Boult et al.(4) investigated the formation of halide films on mercury. They report that iodide films do not exhibit interfacial orientation but form loosely organized deposits from dilute solution in which the crystals are mixtures of mercurous iodide, mercuric iodide, and mercuric oxide. Also, the presence of 0.01M HNO_3 apparently prevented formation of mercuric oxide and, to a greater extent, mercuric iodide.

Because of the unknown deposition-stripping behavior of iodide at the HMDE from dilute (<10 ppb) solutions and an anticipated increase in sensitivity with pulse stripping techniques, a limited study of the deposition-stripping behavior of submonolayer deposits of iodide was undertaken. This paper gives the results of that study and describes a pulse stripping method for iodide with a sensitivity of 1.0 ppb.

EXPERIMENTAL

APPARATUS

A Princeton Applied Research (PAR) Model 174 polarographic analyzer and a Metrohm Model BM-503 hanging mercury drop electrode

(HMDE) were used. Current-potential curves were recorded on a Houston Instrument, Series 2000, X-Y recorder at a scan rate of 5 mV/sec. This scan rate represented a compromise between the time required to record a stripping curve and the amount of distortion introduced into the stripping curve by the time constants of the PAR-174(5). Pulse stripping was the most sensitive operational mode of the PAR-174 for the stripping analysis of iodide. However, because of instrumental artifacts, the DC (linear scan) mode was used for most of the development studies. Integrated currents for the controlled-potential accumulation and linear scan voltammetric (LSV) stripping experiments were obtained by connecting a solid-state analog integrator with digital readout to the current (Y-axis) output of the PAR-174. Open circuit potential measurements were obtained via Pins 2 and 9 of J38 on the rear panel of the PAR-174. Values for the surface area of the HMDE were taken from the manufacturers literature(6).

The electrolysis cell (Figure 1) was fabricated from 35-mm borosilicate glass tubing with a depression tooled into the bottom to accommodate a 7/8-in.-dia., *Teflon*-covered (Trademark of Du Pont) magnetic stirrer of finned design (Chemical Rubber Co. Roto Stirrer). The cell cap was machined from *Teflon* plastic. Because the reproducibility of replicate scans on the same solution was a function of the position of the HMDE within the cell, the cap was designed to ensure that the HMDE could be repositioned accurately. A disc of unfired *Vycor* (Trademark of Corning Glass

Co.), attached at the end of the isolated electrode tube and held in place by a *Teflon* sheath, served as the salt bridge between the isolated electrode and the solution in the electrolysis cell. All potentials were measured versus the mercury: mercurous sulfate (1M H_2SO_4) reference electrode (MSE). This electrode had a potential of 0.336V vs the saturated calomel electrode (SCE) in 0.01M HNO_3. The solutions in the electrolysis cell were stirred magnetically.

REAGENTS

Except for the nitric acid, reagent grade chemicals and demineralized-distilled water were used. The nitric acid was Ultrex grade (J. T. Baker). Stock solutions of iodide (1 mg/ml) were prepared from oven-dried (105°C) potassium iodide and from iodine crystals. The potassium iodide was dissolved in water. For dissolution of iodine, the weighed crystals were introduced into a closed borosilicate glass vessel containing 0.01M HNO_3 and a glass-covered, magnetic stirring bar. As the iodine slowly dissolved (hours), the yellow color (due to I_3^-) was cleared at intervals by dropwise addition of 0.168M ascorbic acid. When dissolution was complete, the solution was diluted to volume with 0.01M HNO_3 . The iodide stock solutions were stored in glass. All other solutions were stored in polyethylene that had been leached with HNO_3 and rinsed thoroughly.

Standard solutions of iodide (1, 10, and 100 μg/ml) were freshly prepared as needed by diluting the stock iodide solution

with 0.01M HNO_3. The 0.168M ascorbic acid (3 g/100 ml) decomposed slowly and was freshly prepared. Solutions in the electrolysis cell were sparged with helium that had been bubbled through water.

PROCEDURE

Conventional stripping practices were observed(7). The HMDE was polarized at the accumulation potential during the 30-second rest period. Ascorbic acid was added to stream water samples to prevent loss of volatile iodine when these samples were sparged with helium; however, ascorbic acid was also oxidized at the HMDE at potentials more anodic than -0.25V. Because oxidation of ascorbic acid began in the same potential range as the optimum accumulation potential for iodide (-0.22V)(2,3), an accumulation potential of -0.25V was used for samples that contained ascorbic acid.

Stream water samples were collected in 500 ml amber glass bottles that contained sufficient HNO_3 to give a 0.01M HNO_3 solution when filled to the neck. These samples were then made 4×10^{-4}M in ascorbic acid and analyzed immediately on receipt.

Approximately 50 ml of sample solution was required for each analysis. The cell and electrodes were rinsed thoroughly with demineralized-distilled water, equilibrated with about 20 ml of sample solution, and drained. A 20.0 ml volume of the sample was then pipetted into cell, and the solution was stirred and sparged with helium for 8 minutes. Next, the helium sparge tube

was raised to admit helium above the solution, and two successive drops (3 divisions) of mercury were extruded. The first drop served to rinse the tip of the capillary of the HMDE and was discarded. Iodide was then accumulated in stirred solution at -0.25V for 4 minutes. After a 30-second rest period, the PAR-174 was switched to scan, and the cathodic stripping curve was recorded at a scan rate of 5 mV/sec.

The cell was filled with 1M HNO_3 when not in use.

RESULTS AND DISCUSSION

ELECTROCHEMICAL BEHAVIOR

The deposition-stripping behavior of iodide films at the HMDE in 0.01M HNO_3 is shown in Figures 2 and 3. Typical stripping curve for macro deposits is shown in Figure 4.

The coulomb-concentration curves (Figure 2) illustrate the deposition behavior of iodide at the HMDE in 0.01M HNO_3. The integrated stripping current was calculated from the area under the stripping peak. The efficiency of the initial stripping process(8) was demonstrated by repeating the stripping step on the drop without prior accumulation. The replicate scan duplicated the results obtained for a background scan on the 0.01M HNO_3 electrolyte solution. No points corresponding to concentrations >333 ppb and a deposition time of 16 minutes are shown on Figure 2 because the HMDE developed a high resistance (became blocked) when excessive deposits were formed. The natural logarithmic plot is used to delineate the deposition behavior over the

concentration range from 3.3 to 1333 ppb.

Each of the curves of Figure 2 represents different deposition times, and all exhibit a limiting slope near midrange which begins near ln (μC) = 0.5 and extends to ln (μC) = 1.2 (i.e., from 1.7 μC to 3.4 μC). This range, when normalized for the area of the HMDE (A = 0.018 cm^2), corresponds with charge-to-surface ratios of 94 $\mu C/cm^2$ to 189 $\mu C/cm^2$. The number of active sites calculated from the molecular volume at the surface of a mercury electrode of 1-cm^2 area is 1.18×10^{15} atoms, equivalent to a charge-to-surface ratio of 189 $\mu C/cm^2$. Therefore, the lower limit indicates a monolayer deposit with a ratio of Hg-to-I of 2:1, and the upper limit indicates a monolayer deposit with a ratio of Hg-to-I of 1:1.

These conclusions are inconsistent with those of Perchard et al.(3) who reported that a surface monolayer of Hg_2I_2 formed at a charge-to-surface ratio of 56 $\mu C/cm^2$. These workers based their conclusions on the charge-to-surface ratio at which the curve for the peak current-vs-deposition-time at constant concentration began to deviate from linear behavior, and on the fact that the corresponding surface coverage in atoms of Hg_2I_2/cm^2 was in excellent agreement with that calculated from the lattice parameters for tetragonal Hg_2I_2, i.e., 58$Å^2$ (calculated) versus 57.2$Å^2$ (theoretical). However, curves of peak height or integrated current versus deposition time at constant concentration were nonlinear in the present study, although the data could be fitted to a cubic equation. This same behavior was apparent

in the published curves of Perchard et al.(3). It is also evident from Perchard's results that their monolayer of Hg_2I_2 was formed at a charge-to-surface ratio which corresponds to a ratio of Hg-to-I at the electrode surface of about 3:1. Because the region of anomalous behavior extended from about 1.7 μC [ln (μC) = 0.5] to 3.4 μC (ln (μC) = 1.2], it was evident that the anomaly was not due solely to the presence of a monolayer of Hg_2I_2 but to a change in the crystalline form of the deposit(2).

The concentration of iodide ion in solution affects the amount of deposit formed (Figure 2). These results indicate that there is a minimum concentration of iodide ion, about 330 ppb, below which greater than monolayer amounts of deposit (as Hg_2I_2) are not formed regardless of the deposition time. However, once this minimum concentration is exceeded, greater-than-monolayer amounts are readily deposited. The reason for this change in behavior with macro deposits is not known.

Several possible explanations for the low deposition efficiency for iodide were examined. In an effort to explain the anomalous behavior in the transition region in terms of a change in deposition current with surface coverage, the effect of concentration on the integrated deposition current at -0.2V was determined for 25 to 2000 ppb I^-. The deposition time was 4 minutes. The integrated deposition current was corrected for the background contribution due to the 0.01M HNO_3 electrolyte solution, and the results were expressed in terms of the following least squares equation:

Integrated current, μC = 0.0416 ppb - 0.56 with $\sigma = \pm 0.57$ μC.

The results indicate that the electrolysis current at -0.2V, and hence the dissolution current for mercury, is a linear function of the concentration of iodide ion. Therefore, the anomalous deposition behavior in the transition region cannot be explained in terms of a decrease in deposition current with surface coverage at constant concentration.

Colovos et al.(8) have reported low efficiencies for the stripping process. In this study, several deposition-stripping cycles were recorded with the same mercury drop and each cycle was followed by a stripping scan (blanks) without prior accumulation. None of the blank scans indicated a residual iodide film on the mercury drop following the stripping step. In view of the possibility of exchange reactions(8), several unsuccessful attempts were made to detect the presence of an oxide film on the HMDE following an extended period of electrolysis at -0.2V. In each instance, the stripping scans with pre-electrolysis essentially duplicated those without pre-electrolysis (background scans). The anomalous results in the transition region strongly suggest the formation of a soluble mercuric species during the conversion of the surface monolayer from Hg_2I to Hg_2I_2; however, no attempt was made to demonstrate the presence of a soluble mercuric species in the solution following the deposition step.

The change in nature of the surface monolayer in the transition region was also reflected in the shape of the stripping curves (Figure 3) recorded by linear scan voltammetry. The curve areas

of the Figure 3 are given in μC and ln (μC) so that these results can be compared with those in Figure 2. When the surface coverage corresponded to less than a monolayer as Hg_2I (<1.7 μC of deposit), only a single diffuse peak, which shifted in the anodic direction with increasing coverage, was observed. As the coverage entered the transition region (1.7 < μC < 3.4), corresponding to the conversion of the surface monolayer from a film of Hg_2I to Hg_2I_2, a shoulder near +0.4V appeared on the anodic side of the diffuse peak. This shoulder developed into a separate peak as the amount of deposit approached 3.4 μC (189 μC/cm^2). When the coverage exceeded monolayer amounts (as Hg_2I_2), the peak at -0.4V assumed the characteristic shape of a stripping peak in which the activity of the deposit was unity (Figure 4).

From the above results, the stripping process corresponding to the dissolution of a partial monolayer of Hg_2I might be used to determine trace amounts of iodide, provided a more-sensitive technique than LSV is employed to record the stripping current.

Turner et al.(9) have weighed the relative merits of normal and differential pulse polarography and concluded that the differential pulse technique should not be used where insoluble films are formed at the HMDE. The same basic arguments also apply to the stripping of iodide films. The normal pulse operational mode of the PAR-174, which was 2.5 to 5 times more sensitive than the DC mode, was used in the remainder of this study.

The sensitivity of the pulse stripping method for the determination of trace amounts of iodine is shown in Figure 5. These curves are typical of those obtained in this study for analysis of trace amounts of iodide and demonstrate that concentrations as small as 0.67 ppb produce a perceptible peak.

The iodide films were formed in a stirred solution at a controlled potential of -0.2V for 4 minutes but only that portion of the stripping curve from -0.5 to -0.95V is included in Figure 5. The broad peak near -0.75V is attributed to the stripping (reduction) of a partial monolayer of mercurous iodide as Hg_2I at the HMDE. As the concentration of iodide is increased, the peak potential shifts in the anodic direction and is essentially constant for concentrations $\geq$50 ppb (Figure 6). The sharp peak near -0.66V (Figure 5), is attributed to an unknown impurity tentatively identified as the thiosulfate ion, which was present at a constant level in all samples run on a given day; however, the amount present changed each day. This substance was particularly bothersome during periods of high humidity. Efforts to isolate the source to a specific reagent were unsuccessful. The source was finally attributed to an airborne mercaptan-type pollutant. Fortunately, this substance did not seriously interfere in the measurement of the height of the iodide wave. The occurrence does, however, indicate the extreme sensitivity of the cathodic pulse stripping method for trace amounts of airborne mercaptan-type substances.

EFFECT OF VARIABLES

The effect of variables was determined at a deposition potential of -0.25V. The deposition time was 4 minutes unless otherwise noted. The method of least squares was used to obtain empirical equations that fit the experimental data; the standard deviation, σ, is included with each equation.

The effect of concentration in ppb on peak height (i_p) is shown in Figure 7. The equation of the curve

$$\text{ppb} = 0.09822 + 74.1206\ i_p(\mu A) - 68.3446\ i_p^2(\mu A^2) + 33.1895\ i_p^3(\mu A^3)$$

where N = 11 and σ = 0.25 ppb

was valid for the range from 0 to 50 ppb. The result for i_p at the 100 ppb level was not included in the calculations because this point was low (the coverage limitation of 94 $\mu C/cm^2$ was probably exceeded). The observed standard deviation and bias (ppb with $i_p = 0$) were acceptable and indicated that the method could be applied at the 1 ppb level.

The effect of deposition time on peak height at 2.5 ppb was determined for deposition times of 0.5, 1, 2, 4, 8, and 16 minutes. Except for a linear segment from 0 to 4 minutes, the curve for i_p versus time was nonlinear and was described by the equation

$$\mu A = 0.001241 + 0.006746t - 0.00009332t^2 - 0.00000178t^3$$

where t = time in minutes and, σ = 0.00047 μA.

Time dependence was the same as that in the curves of Figure 2.

The above result, together with those of Figures 2 and 7, indicate the complex dependence of peak height on concentration and deposition time. Thus, for a given concentration range, an optimum deposition time could be selected so that the entire peak height versus concentration curve would conform to a third-degree polynomial. For the 0-50 ppb range, the optimum deposition time was 4 minutes, but deposition times >4 minutes might be used to extend the detection limits to <0.5 ppb. Extended deposition times were avoided, however, because of the presence of the impurity noted earlier.

The effect of electrode area on the peak height was determined at the 2.5-ppb level. The results are expressed in terms of the following equations

$i_p(\mu A) = 0.01812A - 0.00479$, and $\sigma(i_p) = 0.00135\ \mu A$

where A = Drop Area, mm^2

and $i_p(\mu A) = 0.006874D - 0.00863$

where D = micrometer divisions = 8.236×10^{-5} cm^3/division, and $\sigma(i_p) = 0.00094\ \mu A$

The apparent linear dependence of i_p on both area and micrometer reading in divisions (volume) is due to the nearly linear dependence of drop area on volume over the range studied and the relative precision (∿10%) of the stripping method. The volume of the drop was determined by weighing the amount of mercury expelled when the micrometer was advanced 200 divisions. A drop area of 0.018 ±0.0005 cm^2 (3 micrometer divisions) was optimum for this study because this was the maximum size that could be used without dislodging the drop into the stirred solution.

The optimum scan rate for the pulse stripping of iodide films was 5 mV/sec. At scan rates <5 mV/sec, peak height decreased rapidly with scan rate; at scan rates >5 mV/sec, distortion of the waveform increased with little increase in sensitivity (Figure 8).

The effect of scan rate on the peak height, as determined by pulse stripping analysis, was determined at the 2.5-ppb level. Normally, the peak height would be expected to vary either directly with the scan rate or as the square root of the scan rate(3). This behavior was not observed. Because instrumental artifacts(5) could contribute to the observed anomalous behavior, the effect of scan rate was determined by linear stripping voltammetry. The results were expressed in terms of the following equation

$$i_p(\mu A) = 0.00647\ [V,\ mV/sec]^{0.9316}$$

where RMS error (in μA) = 4.3%

which was valid for the range from 1 to 500 mV/sec. Again, this result indicated the complex nature of the stripping process.

The effect of stirrer speed on peak height at the 2.5-ppb level was given by the following empirical equation(10).

$$\ln\ [i_p,\ \mu A] = 2.069\ \ln\ [r] - 11.62$$

which was valid for rheostat settings from r = 40 to 70 with a RMS error of ±0.00064 μA. A rheostat setting of 60 was arbitrarily selected as representing the optimum compromise between sensitivity (i_p) and minimum risk of drop dislodgment.

The observed peak height for the pulse stripping of iodide

films was a critical function of the position of the mercury drop with respect to the stirrer and the cell wall indicating the existence of steep velocity gradients within the cell. Small changes in position of the HMDE with respect to the cell wall produced changes in the peak height of as much as 25%. In an effort to minimize this difficulty, the cell was redesigned (Figure 1) and the operations were standardized to ensure reproducible reassembly following a sample change. Nevertheless, stirring and electrode placement remained the critical variables.

Ascorbic acid was added to the electrolyte to ensure retention of volatile iodine during the sparge step. The effect of ascorbic acid concentration on peak height at the 2.5 ppb level is given in Table 1.

The results for the average peak height were within the observed experimental error for replicate scans; therefore, ascorbic acid has a negligible effect on peak height when 50 µl of a 0.168M solution is added to 20.0 ml of 0.01M HNO_3. There was, however, an anodic shift in peak potential (E_p) with increasing concentrations of ascorbic acid, perhaps indicating that ascorbic acid was absorbed at the HMDE.

INTERFERENCES

The effect of diverse substances on the pulse stripping analysis of iodide was determined at the 2.5-ppb I^- level. The results (Table 2) show that the method is subject to numerous

types of interferences; however, most substances native to surface water (except for surfactants) are normally present in amounts that represent no serious interferences.

The substances listed in Table 2 were selected to demonstrate various types of interference. The material designated *FR* Solids consisted of decayed organic matter from the bottom of a spring and was included to show the effect of organic species derived from this source. The material was subjected to a crude fractionation procedure in which the acid, ammonium hydroxide, and sodium hydroxide soluble fractions were isolated. These fractions were evaluated separately. Commercial cleaning agents were included in an attempt to duplicate the behavior of an unidentified surfactant which was present in some stream water samples.

Most of the interferences (Table 2) can be explained in terms of well-recognized processes, although other processes, such as catalytic and exchange reactions, cannot be ignored. The mercury(II) interference was attributed to the formation of a mercuric iodide complex in the solution phase. Cadmium, copper, and lead interfered by reducing at the HMDE in the same potential range as the Hg_2I stripping process. Indeed, the presence of 500 ppb lead completely masked the Hg_2I stripping peak. The bromide, sulfide, thiosulfate, and thiocyanate anions were deposited as insoluble films at the HMDE. Both the sulfide and thiosulfate films strip in the same potential range as Hg_2I and completely mask the iodine stripping peak. The observed interference in the case of the cleaning agents was attributed to the

adsorption of the surface active component at the surface of the HMDE.

The method was evaluated for the analysis of samples of surface water in the vicinity of the Savannah River Plant site. Of the interferences listed in Table 2, only the presence of the previously mentioned impurity ($S_2O_3^{=}$) and the occasional occurrence of an unidentified surfactant were observed in the stream water samples. The surfactant produced an anodic shift in the potential of the stripping peak but did not seriously interfere in the determination of iodide. A typical scan of iodide in the presence of the surfactant is shown in Figure 9. The effect was duplicated in the laboratory by adding about 2 ppm of a detergent to the test solution.

Occasional samples of well water were also analyzed. These contained variable amounts of heavy metals which were derived from the well casings and sand points. In some cases, a large-scale pre-electrolysis at -1.6V was required to remove the heavy metals before the iodide determination.

PRECISION AND SENSITIVITY

The reproducibility of the method was estimated by replicate scans of the same same solution and by analyzing dilutions of the standard iodide solutions, two of which were prepared from iodine crystals. These dilutions ranged from 0 to 5 ppb, and the study covered a period of 25 calendar days. The results were as follows:

Conc, ppb	n	Rel. Std. Dev.
2.5	6	7.0%
25.0	6	2.6%
0-5	38	0.32 ppb

Thus, the precision (2σ) of the method was about 13% at the 5-ppb level.

The sensitivity of the method was estimated by means of the Student's Test(11). The standard deviation of the intercept of the least squares calibration curve of ±0.11 ppb was assumed to be equivalent to the standard deviation of the blank. With $t = 6.314$ (0.1 confidence level), a difference of 1.0 ppb could be detected with 90% certainty.

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TABLE 1

Effect of Ascorbic Acid on Peak Height[a]

Volume of 0.168M Ascorbic Acid, μℓ	i_p, μA	E_p, *volts*
0	0.032	-0.745
50	0.036	-0.720
100	0.034	-0.710
150	0.031	-0.705
200	0.027	-0.700
250	0.029	-0.690
	0.032 ± 0.003	

a. 2.5 ppb I^-, 20.0 ml of 0.01M HNO_3, electrolysis potential = -0.25V, deposition time = 4 minutes, stirrer setting = 60.

TABLE 2

Results of Interference Studies[a]

	Bias, %	*Comments*
Cations		
Bismuth	0	High background
Cadmium	-18	Reduces near -0.9V
Calcium	0	No interference
Copper	-8	High background
Iron	0	No interference
Lead	Masked I^- peak	Reduces near -0.7V
Magnesium	0	No interference
Manganese	0	No interference
Mercury (II)	-40	Decrease in i_p
Zinc	0	No interference
Anions		
Bromide	-30	Strips near -0.4V
Chloride	-12	Decrease in i_p
Nitrite	-10	Decrease in i_p
Sulfide	Masked I^- peak	Strips in vicinity of iodide wave
Sulfite	0	No interference
Phosphate	0	No interference
Thiocyanate	Masked I^- peak	Prewave beginning near -0.3V merges with iodide peak
Thiosulfate	Masked I^- peak	Strips in vicinity of iodide wave
Other		
Alconox[b]	0	30 mV anodic shift in E_p
Aerosol	0	No interference
Disodium ethylene diamine tetraacetic acid	0	No interference
FR Solids		
H^+ soluble	0	No interference
NH_4OH soluble	0	No interference
NaOH soluble	0	No interference
Humic acid		
Nitrilotriacetic acid	0	No interference
Phenol disulfonic acid	+50	Broadens peak 60 mV anodic shift in E_p
"Soilax A"[c]	0	No interference
"Sunbrite"[d]	0	No interference
"Tide"[e]	+20	100 mV anodic shift in E_p
Sodium tripolyphosphate	0	No interference

a. 2.5 ppb I^-; 500 ppb test substance in 20.0 ml 0.01M nitric acid - 4 x 10^{-4}M ascorbic acid

Initial potential = -0.25V; deposition time = 4 minutes; rest period = 30 seconds; scan rate = 5 mV/sec.

b. Registered Trademark of Product of Standard Scientific Supply Company.

c. Registered Trademark of Economics Laboratory, Inc.

d. Registered Trademark of Swift & Co.

e. Registered Trademark of Proctor & Gamble.

FIGURE CAPTIONS

Figure 1. Electrolysis Cell Assembly

Figure 2. Logarithmic Plot of Integrated Stripping Current as a Function of Iodide Concentration

Figure 3. Typical Stripping Curves

Figure 4. Stripping Curves for Macro Deposits

Figure 5. Stripping Curves for Trace Iodide

Figure 6. Anodic Shift in Potential of Stripping Peak with Concentration

Figure 7. Effect of Concentration on Peak Height

Figure 8. Peak Height as a Function of Scan Rate

Figure 9. Effect of Unidentified Surfactant

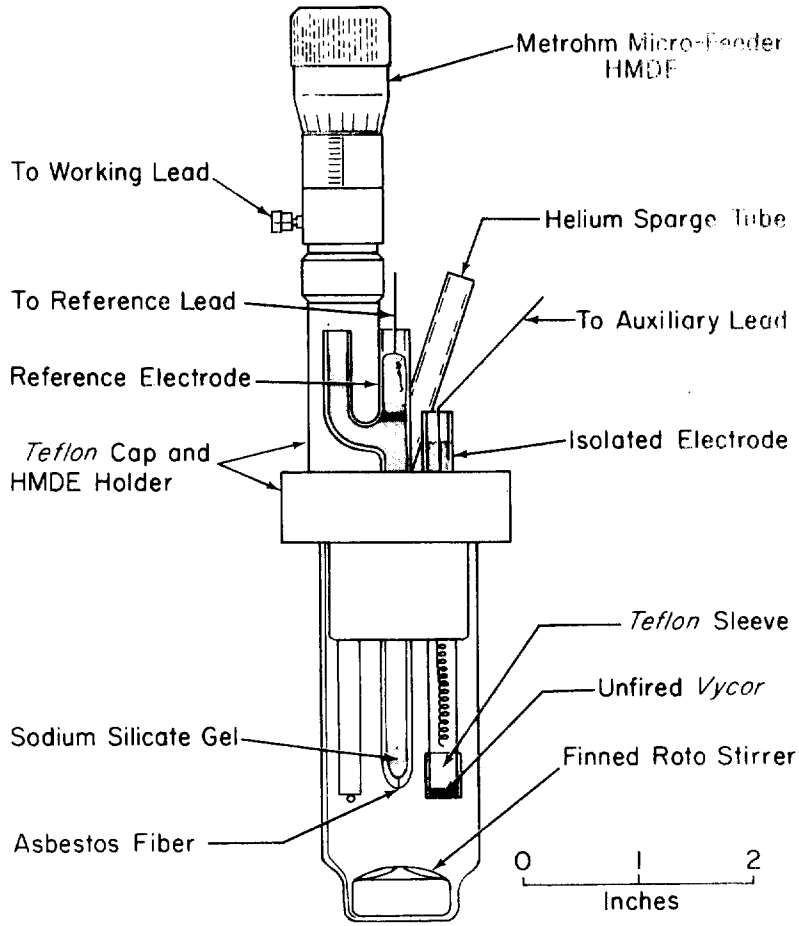

FIGURE 1. Electrolysis Cell Assembly

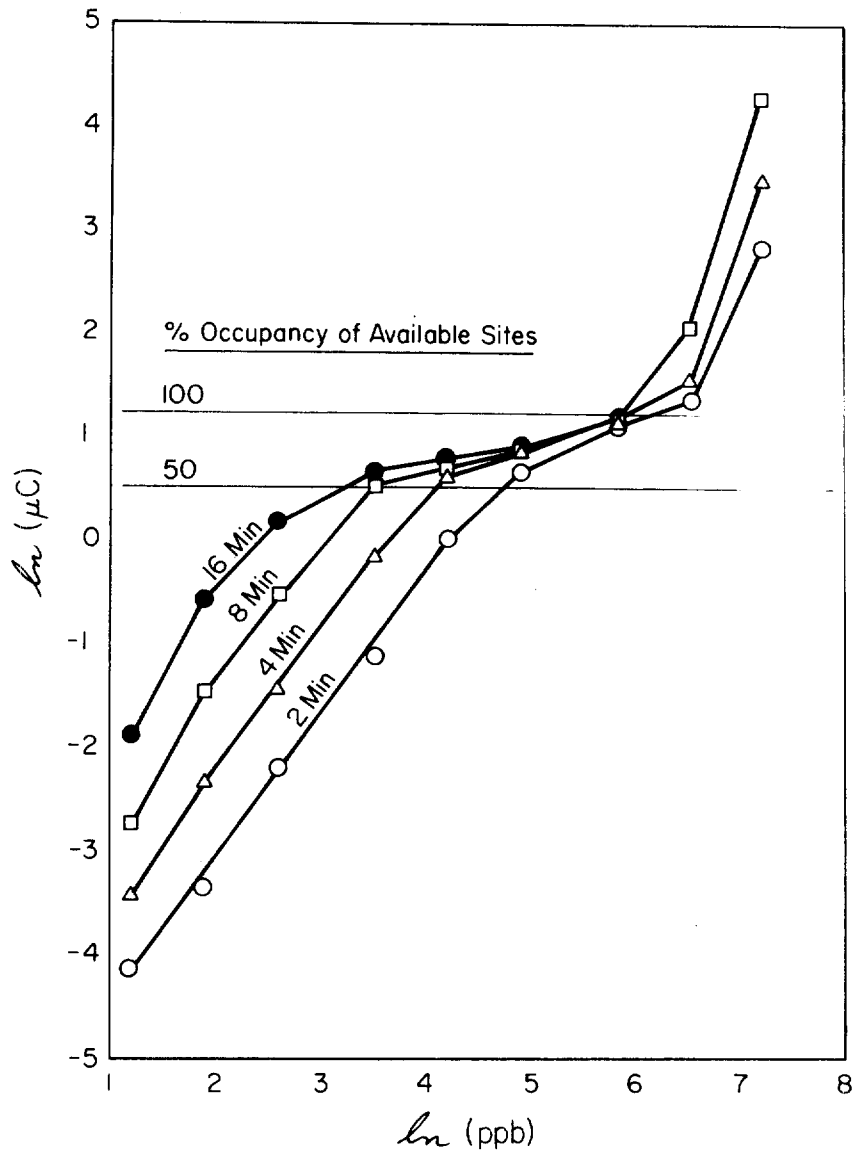

FIGURE 2. Logarithmic Plot of Integrated Stripping Current as a Function of Iodide Concentration

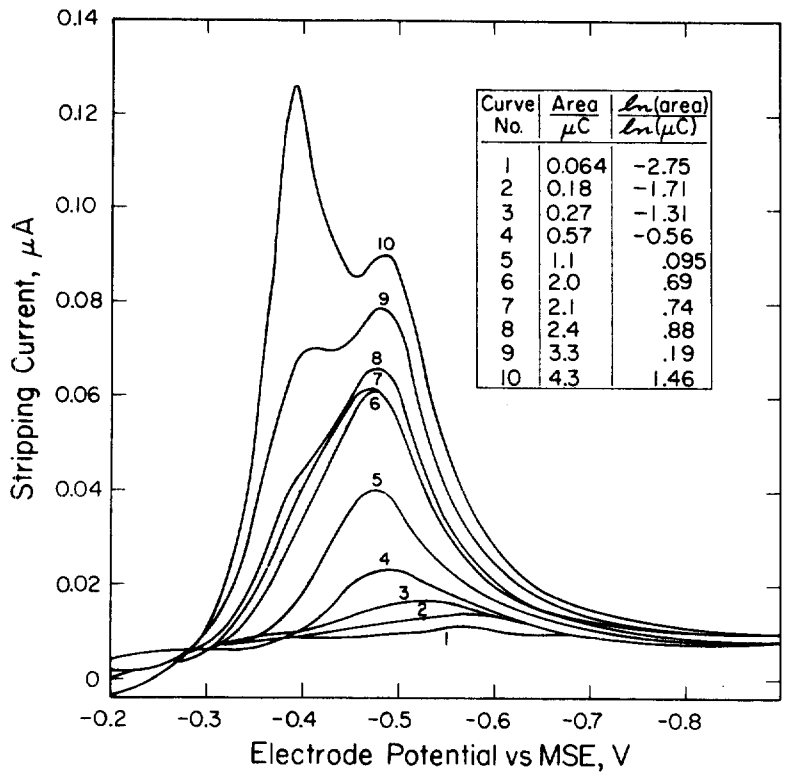

FIGURE 3. Typical Stripping Curves (LSV)

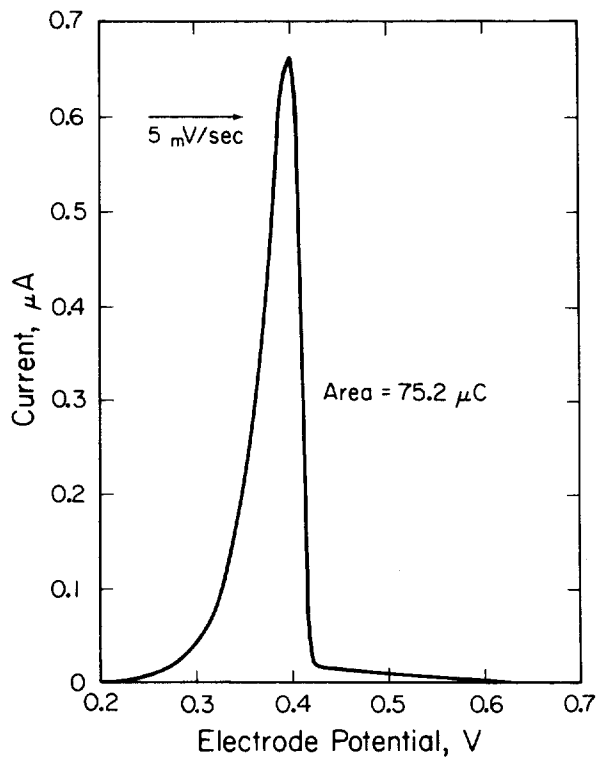

FIGURE 4. Stripping Curves for Macro Deposits

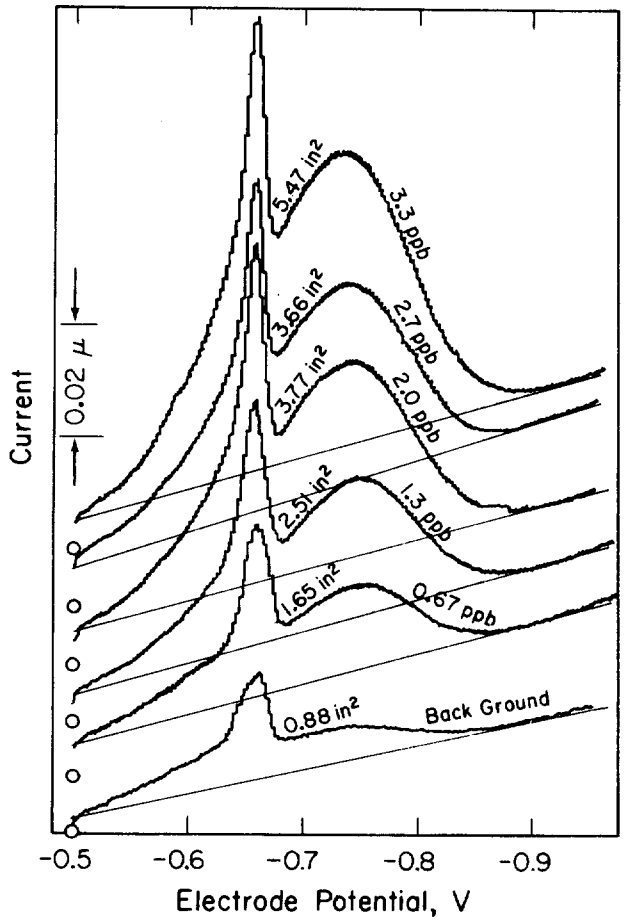

FIGURE 5. Stripping Curves for Trace Iodide

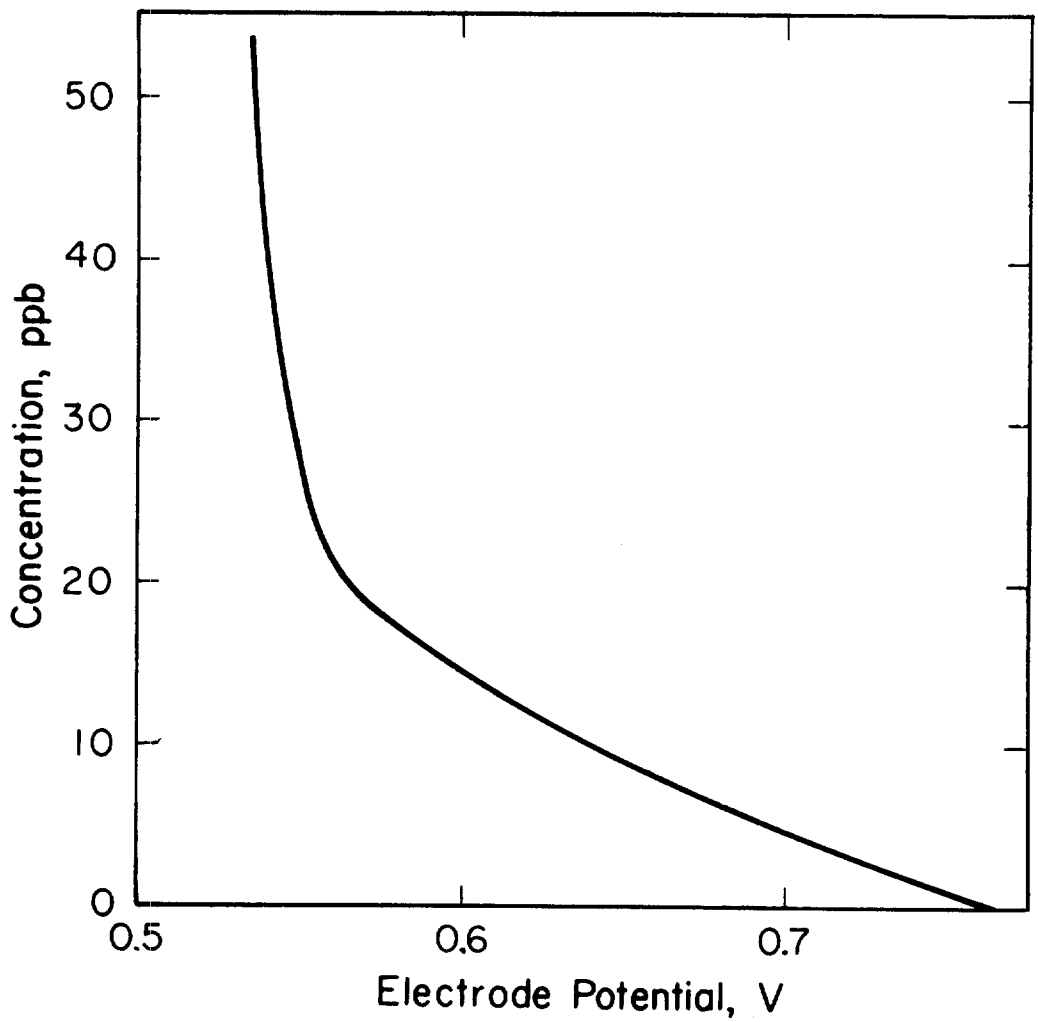

FIGURE 6. Anodic Shift in Potential of Stripping Peak with Concentration

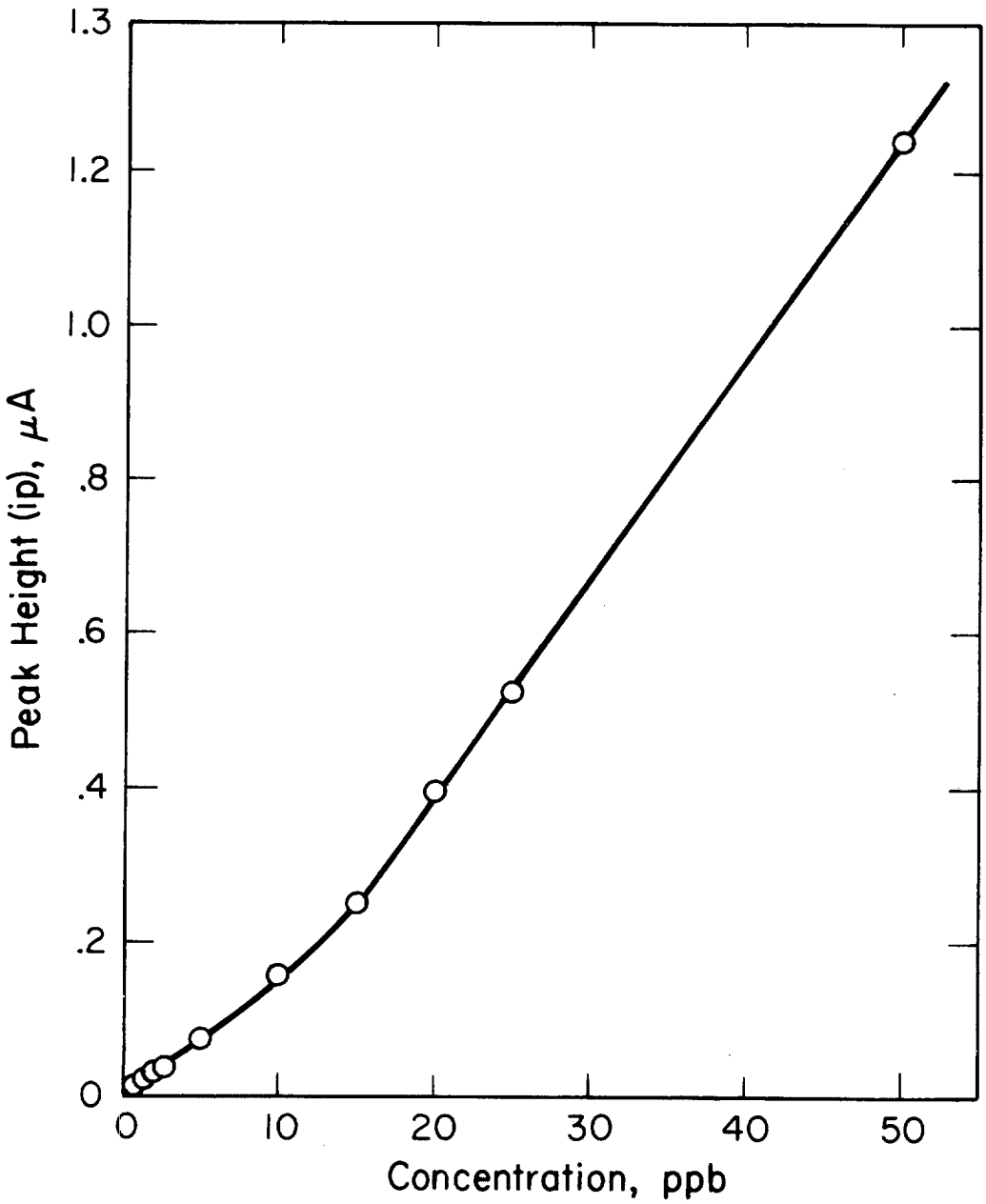

FIGURE 7. Effect of Concentration on Peak Height

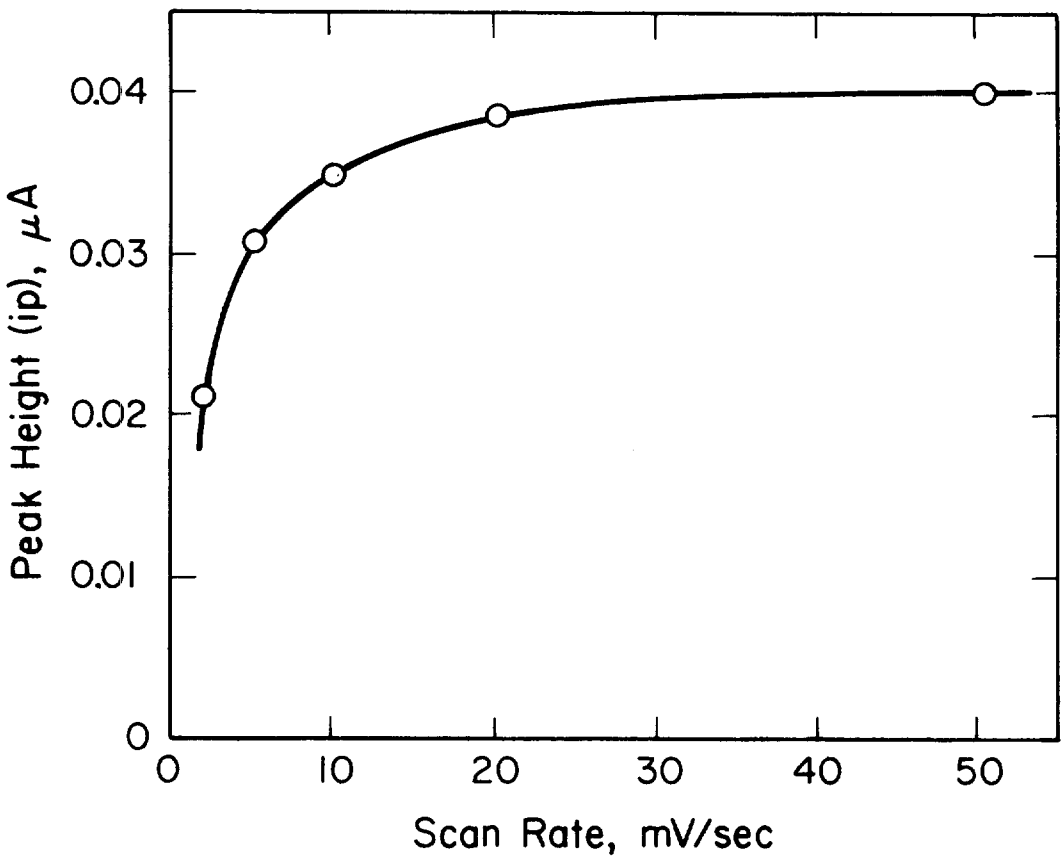

FIGURE 8. Peak Height as a Function of Scan Rate

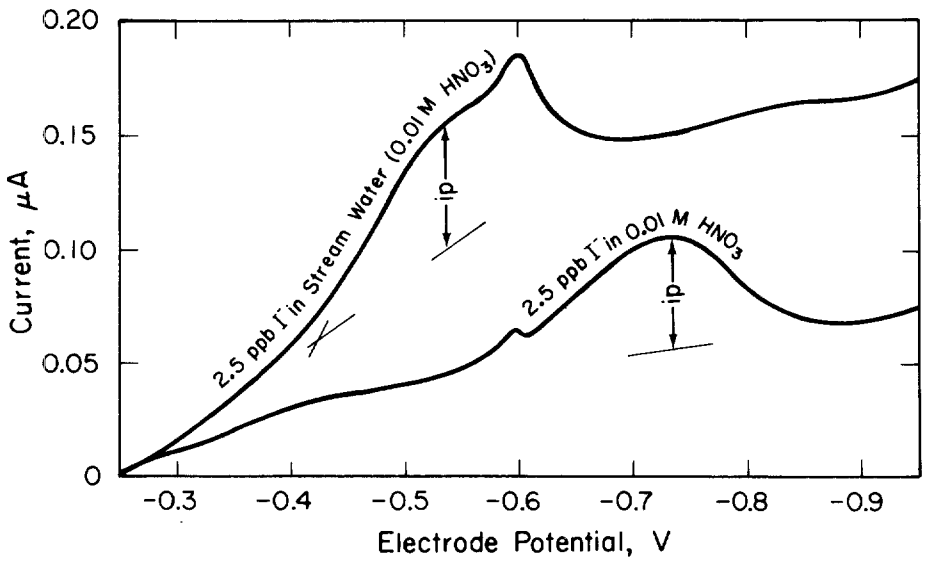

FIGURE 9. Effect of Unidentified Surfactant

BRIEF

The controlled-potential deposition and voltammetric dissolution behavior of iodide at the hanging mercury drop electrode is described. Pulse stripping analysis is used to determine iodide in surface water in the 0-50 ppb range. At 2.5 ppb, the standard deviation is 12%.