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DETERMINATION OF LEAD AT THE PARTS PER BILLION LEVEL
BY CATHODIC STRIPPING ANALYSIS

by

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DETERMINATION OF LEAD AT THE PARTS PER BILLION LEVEL BY CATHODIC STRIPPING ANALYSIS

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BRIEF-A sensitive method, based on the cathodic stripping of lead at the conducting glass electrode, can detect lead in the 0 to 100 ppb range with a relative standard deviation of ± 1.8 ppb. The method was developed for the determination of lead in environmental samples.

ABSTRACT-A sensitive and precise analytical method has been developed for the determination of lead in aqueous environmental samples. The method is based on the electrochemical deposition-dissolution of lead as the dioxide at the conducting glass electrode. The relative standard deviation of the method in the 0-100 ppb range is ± 1.8 ppb. The effects of deposition time, deposition potential, scan rate, and other variables were investigated.

INTRODUCTION

Cathodic stripping analysis of metals that form sparingly soluble oxides is a potentially powerful technique for the determination of trace metals in environmental samples. The technique is sensitive to monolayer amounts of deposit and selective because the metal must form a sparingly soluble oxide. Only a modest investment in equipment is required. The method has received little attention since the original suggestion of Brainina.¹

Recently, Miwa, et al.² have reported a cathodic stripping method for lead at the platinum electrode based on the electrolyte exchange technique. The method is applicable to samples containing 0.1 to 2 ppm lead with an error of $\pm 10\%$ at the 1-ppm level.

Most recently, Young and Laitinen³ have reported the cathodic stripping of iron in acetate media. The integrated stripping current at constant deposition time was found to be a non-linear function of concentration, which they attributed to the insulating properties of the ferric hydroxide film at high coverages.

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Studies in this laboratory of the electrochemical behavior of the transuranium elements at the conducting glass electrode (CGE) showed that trace amounts of lead could be quantitatively deposited from dilute sulfuric acid and subsequently determined by cathodic stripping. This approach appeared to offer a 1000-fold increase in sensitivity over that of Miwa, et al.² without requiring an exchange of electrolyte solutions. The anodic deposition-cathodic stripping of lead at the CGE was examined, and a method was developed for the determination of lead in aqueous solution. The technique has been employed to determine lead in rainwater sampled at intervals from various locations in South Carolina.

EXPERIMENTAL

Apparatus

The technique for preparing a conducting glass electrode (CGE) and the design of the electrolysis cell have been described.⁴ A typical CGE has a cylindrical working area of ~ 4 cm² and a resistance of ~ 25 ohms.

The body of the electrolysis cell was cut from the lower part of a 250-ml polyethylene cylinder and fitted with a polyethylene cap drilled to accommodate the electrodes and a sparge tube. The helium sparge tube together with the isolated and reference electrodes were sheathed with heat shrinkable *Teflon*^a tubing to minimize adsorption losses on the exposed borosilicate glass parts. The isolated electrode consisted of a spiral of platinum wire immersed in 0.01M sulfuric acid. A disc of porous *Vycor*^b silicate glass, attached at the end of the isolated electrode tube and held in place by the *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 H₂SO₄) reference electrode (MSE). This electrode has a potential of 0.42 V (including junction potentials) versus the saturated calomel electrode in 0.01M sulfuric acid. The solution in the titration cell was magnetically stirred.

Reagents

Ultrax^c grade nitric and sulfuric acids, 99.9995% lead shot,^d and demineralized distilled

a Trademark, E. I. du Pont de Nemours & Co., Wilmington, Delaware.

b Trademark, Corning Glass, Corning, N. Y.

c Trademark, J. T. Baker Co., Phillipsburg, N. J.

d Ventron Corp., Beverly, Mass.

water were used throughout the study. A stock solution of lead (1 mg/ml) was prepared by dissolving the appropriate weight of lead shot in nitric acid, and diluting to volume with demineralized laboratory distilled water. Standard lead solutions (1-100 ppb) were prepared daily by diluting aliquots of the stock solution (1 mg/ml) with the appropriate volume of 0.01M sulfuric acid. All solutions were prepared and stored in polyethylene containers. The containers were leached with 1M nitric acid and rinsed thoroughly with demineralized distilled water before use. The solutions in the electrolysis cell were sparged with helium that had been bubbled through distilled water.

Instrumentation

The electrochemical instrument incorporated operational amplifiers and conventional circuitry. Stripping curves were recorded on a strip chart recorder at a scan rate of 83.3 mV/sec. The analog integrator was read by means of a digital panel meter.

Procedure

Conventional stripping practices were observed.⁵ Upon completion of each analysis, the cell and electrodes were rinsed with 0.1M acetic acid, 1M nitric acid, and finally with copious amounts of demineralized distilled water to remove residual contamination. The cell was filled with 1M nitric acid when not in use.

All sample solutions were 0.01M in sulfuric acid. Approximately 50 ml of sample was required for each analysis. The cell and electrodes were equilibrated with two successive 10-ml portions and drained, and a 20.0-ml aliquot was pipeted into the cell for the analysis. The solution was sparged with helium and stirred for 5 minutes, after which the lead dioxide was deposited at a controlled-potential of 1.35 V for 16 minutes. The helium sparge tube was raised to introduce helium above the solution for the final 30 seconds of the deposition step. Upon completion of the deposition step the stirrer was turned off. After a 30-second rest period, the instrument was switched from the controlled-potential to the stripping mode, and the stripping curve was recorded at 83.3 mV/sec. At the instant the recorder pen crossed the zero current axis, the analog integrator was switched from reset to integrate, and the reduction current was integrated until the recorder pen reached 0.0 V. The individual peak areas were determined by means of a polar planimeter.

RESULTS AND DISCUSSION

Mechanism

The current-potential curves (Figure 1) illustrate the cathodic stripping behavior of lead at the CGE. Two peaks were observed for lead concentrations > 3 ppb; one at 0.7 V and one at 0.4 V. Both peaks were attributed to the reduction of lead from the 4+ to the 2+ oxidation state.

When the initial concentration of Pb^{2+} in solution was < 3 ppb, only the diffuse peak near 0.4 V was observed. The area of this peak was a function of the deposition potential, deposition time, and concentration. With increasing concentration, it approached a maximum (limiting) value which corresponded to a coverage of $\sim 0.1 \mu\text{g Pb/cm}^2$. This coverage represents $\sim 33\%$ occupancy of the estimated 10^{15} sites/cm² on the surface of the CGE.⁶ The charge-to-area ratio for electrodes of different areas was measured at constant concentration and deposition time (Table I) to confirm that the process associated with the peak near 0.4 V involved the deposition of lead ions onto active sites at the surface of the CGE.

The potential of this peak with respect to the peak near 0.7 V, together with its observed dependence on electrode area, indicates that the stripping process probably involves the reduction of a partial monolayer of adsorbed Pb^{4+} atoms.

The peak near 0.7 V appeared when the initial concentration of lead in the solution exceeded ~ 3 ppb and rapidly increased with concentration. Identification of the electrochemical dissolution reaction(s) was complicated by the presence of sulfate ion in the electrolyte. For small amounts of deposit, the rate of diffusion of Pb^{2+} ions from the electrode surface probably exceeded the rate for the formation of lead sulfate such that the dissolution occurred at the potential of the $\text{PbO}_2:\text{Pb}^{2+}$ couple. This was demonstrated by stripping a large ($10 \mu\text{g}$) deposit by stepping the potential anodically in 5-mV steps and integrating the stripping current for 300 seconds at each step. The solution was stirred to minimize the thickness of the diffusion layer and to ensure rapid removal of the Pb^{2+} ions. The results, graphed according to the Nernst equation for a dissolution process (Figure 2), were linear with a slope of -0.0124 V/decade, in good agreement with the theoretical value of -0.0128 V/decade for a two-electron process. The

formal potential was corrected for the activity of the H^+ ion in 0.01M H_2SO_4 ⁷ and for the potential of the MSE (0.66 V vs normal hydrogen electrode). This gave a standard potential for the process of 1.48 V is in agreement with the published value⁸ of 1.455 V for the $PbO_2:Pb^{2+}$ couple in acid solution.

In the stripping of large deposits in unstirred solution, the instantaneous concentrations of Pb^{2+} in the diffusion layer probably exceed the solubility product of lead sulfate. Intermediate cases in which the rate of formation of lead sulfate is competitive with the rate of diffusion of Pb^{2+} from the electrode surface are also probable. Peak height (i_p) versus scan rate (ν) experiments were made to study the formation of insoluble lead sulfate. If the product of the stripping process is soluble Pb^{2+} , then the graph of i_p vs $\nu^{1/2}$ should be linear.⁹ Conversely, if the reactant and product were immobilized at the electrode surface (insoluble), then the stripping behavior would be analogous to that for a reversible couple in a thin layer cell,⁶ and a graph of i_p vs ν should be linear. The results, graphed as $\ln i_p$ vs $\ln \nu$ (Figure 3) to handle non-integral powers of ν , show that $i_p/\nu^{0.7}$ is relatively linear. This value of $\nu^{0.7}$ midway between $\nu^{1/2}$ and ν indicates a complex dissolution mechanism exists, possibly involving the formation of insoluble lead sulfate at the electrode surface.

Effect of Deposition Potential

The potential of 1.35 V selected for the deposition of lead dioxide at the CGE was based on studies of the effect of deposition potential on the stripping behavior. Curves showing the quantity of electricity (mC) consumed in the formation of the stripping peaks versus the deposition potential (Figure 4) show the initial limiting slope for the total integrated current curve extends from 1.35 to 1.55 V.

An increase in monolayer coverage causes an increase in total integrated current in the potential range from 1.6 to 1.8 V. The curve for the integrated current for the peak near 0.4 V is evidence for an increase in monolayer coverage with potential. This curve indicates that the occupancy rate of the active sites (at the electrode surface) increases with potential and approaches a limiting value as the coverage approaches 0.5 mC (0.125 mC/cm²). The corresponding decrease in the curve for the peak near 0.7 V indicates that two processes are competing for Pb^{2+} ions at the electrode surface. The selected deposition potential of 1.35 V reduced the effect on the results of the peak near +0.4 V.

Deposition Rate

The deposition rate for Pb^{2+} at the CGE was determined from a graph (Figure 5) of the equation for coulometry in stirred solution which showed a half-time of ~ 1100 seconds deposition.

In this study, the oxidation potential for Pb^{2+} merged with the anodic potential limit for the working range of the CGE in $0.01\text{M H}_2\text{SO}_4$ so that the oxidation current for Pb^{2+} could not be monitored independently of the electrolyte and/or solvent decomposition reaction. The deposition rate constant was determined indirectly by graphing the integrated current (mC) for the stripping curves versus the electrolysis time (t) according to the following equation for the coulometric process in stirred solution:

$$t = - \frac{1}{\beta} \ln \left[\frac{*C-C}{*C} \right]$$

where t = electrolysis time, seconds

β = rate constant, sec^{-1}

*C = integrated current assuming complete deposition, millicoulombs (mC)

The value of $6.5 \times 10^{-4} \text{ sec}^{-1}$ for β was obtained from the results shown in Figure 5. Although a faster rate would appear desirable, the calculated diffusion layer thickness (assuming a value of $10^{-5} \text{ cm}^2/\text{sec}$ for the diffusion coefficient) was $3 \times 10^{-3} \text{ cm}$, a diffusion layer thickness typical of those observed in this laboratory when magnetic stirring is utilized.

Effect of Concentration

The effect of concentration on the development of the individual stripping peaks up to 25 ppb is shown in Figure 1, and a graph of the integrated current versus concentration is shown in Figure 6. The curve areas were determined by means of a polar planimeter. The results show that the development of the (partial) monolayer was $\sim 30\%$ complete before the peak near 0.7 V appeared and that neither process was linear with concentration. The results do indicate, however, that the sums of the integrated areas are linear with concentration and can thus be utilized in the stripping analysis of lead.

Stability of Deposits

The stability of lead dioxide deposits at open circuit was measured to determine if the loss would be significant during the time required for the stripping analysis.

The results (Table II) indicate a rate of loss of 0.0073 ± 0.0034 mC/min, which corresponds to an estimated error of 0.7 ppb for stripping in stirred solution. The error in quiet solution would be considerably less.

Electrode Calibration Curves

Quantitative results were obtained either by the method of standard addition (with a blank correction), or by means of a calibration curve when a large number of samples were to be analyzed.

A separate calibration curve is required for each CGE because of small but significant differences in area between individual electrodes. These curves were prepared by determining electrode response for successive 1:2 dilutions of the most concentrated standard until the lead content of the final dilution was ~ 1 ppb. Duplicate determinations on each dilution beginning with a blank on the reagents were analyzed by the method of least squares. The results for a typical calibration in the 0-100 ppb range were:

$$\text{lead (ppb)} = 98.14 \text{ mC} - 4.88$$

where mC is the integrator reading (millicoulombs), and the standard deviations (σ) for 18 points were:

$$\begin{aligned} \sigma(\text{single determination}) &= \pm 1.8 \text{ ppb} \\ \sigma(\text{slope}) &= \pm 1.3 \text{ ppb/mC} \\ \sigma(\text{intercept}) &= \pm 0.56 \text{ ppb} \end{aligned}$$

The intercept represents the contribution of background processes and the lead content of the demineralized laboratory-distilled water. When the solutions were prepared with reagent-grade sulfuric acid, the intercept increased to ~ 9 ppb.

The sensitivity of the method was estimated by means of the Student's t test.¹⁰ If a large number of blank determinations, n , have been run such that the standard deviation, σ , of the blank is known, then the equation for the difference between an unknown and a blank can be written,

$$t = \frac{\Delta S}{\sigma \sqrt{2}}$$

where t = value obtained from t Table with $N = 1$ degree of freedom,

ΔS = difference between sample and blank determinations, and

σ = standard deviation of the blank.

The average blank in this study was equivalent to 1.0 ± 0.1 ppb lead. Thus, with $t = 6.314$ (0.1 confidence level), a difference of 0.9 ppb can be detected with 90% certainty.

Interferences

Metal ions that form insoluble oxides at the CGE in acid solution represent potential interferences. Likely candidates included nickel, iron, chromium, and manganese. Of these, only manganese could be oxidized to the insoluble manganese dioxide in dilute acid solution. By increasing the deposition potential to ~ 1.8 V, the Mn^{2+} was oxidized to soluble MnO_4^- , and samples containing $< 10^{-5}$ M Mn^{2+} could be analyzed without interference from manganese.

CREDIT

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TABLE 1. Coulometric Charge-To-Area Ratios for Peak Near +0.4V ^a

<i>Electrode Area, cm²</i>	<i>Charge, mC</i>	<i>Ratio:mC/cm²</i>
1.1	0.017	0.016
1.5	0.021	0.014
2.2	0.030	0.014
3.0	0.032	0.011
		Avg. 0.014 ±0.002

a. 6×10^{-8} g Pb in 20 ml of 0.01M H₂SO₄; electrolyzed 16 min at 1.35 V.

TABLE II Loss of Lead Oxide at Open Circuit (Stirred Solution) ^a

<i>Time on Open Circuit,</i> <i>min</i>	<i>Integrated Stripping Current, ^b</i> <i>mC</i>
1	0.73
2	0.77
4	0.71
8	0.63
16	0.65

a. 500 ppb Pb²⁺ in 20.0 ml 0.01M H₂SO₄; deposited for 2 min at 1.35 V.

b. By least squares, $mC = -0.73 \times 10^{-2} t + 0.74$.

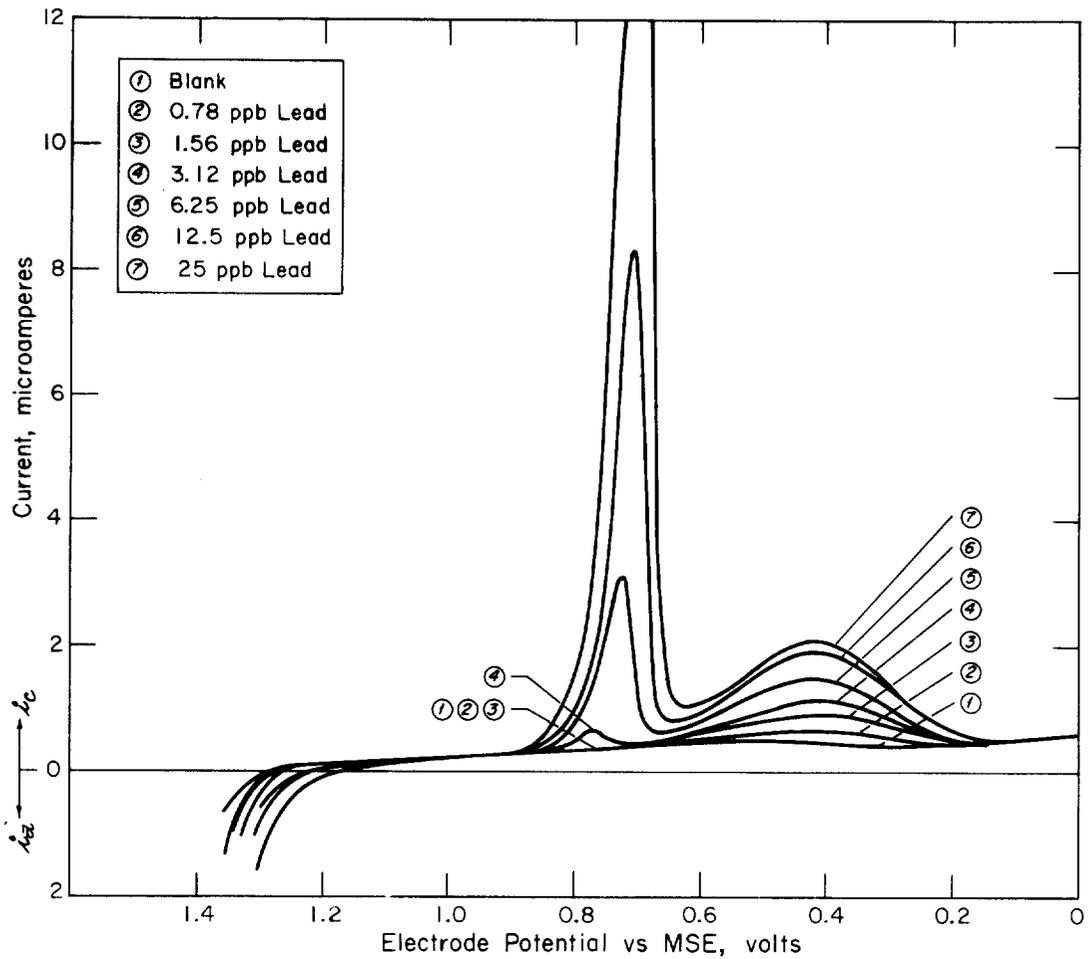


FIGURE 1. CONCENTRATION EFFECT. Lead in 0.01M H₂SO₄ after deposition at 1.35 V for 16 minutes.

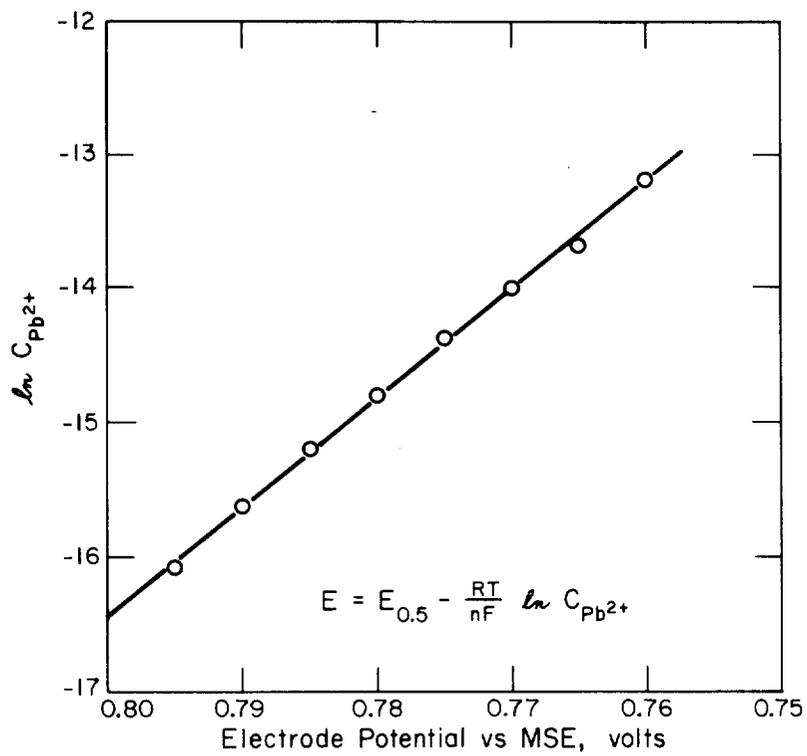


FIGURE 2. NERNST RELATIONSHIP. Stepwise stripping of lead dioxide in stirred solution.

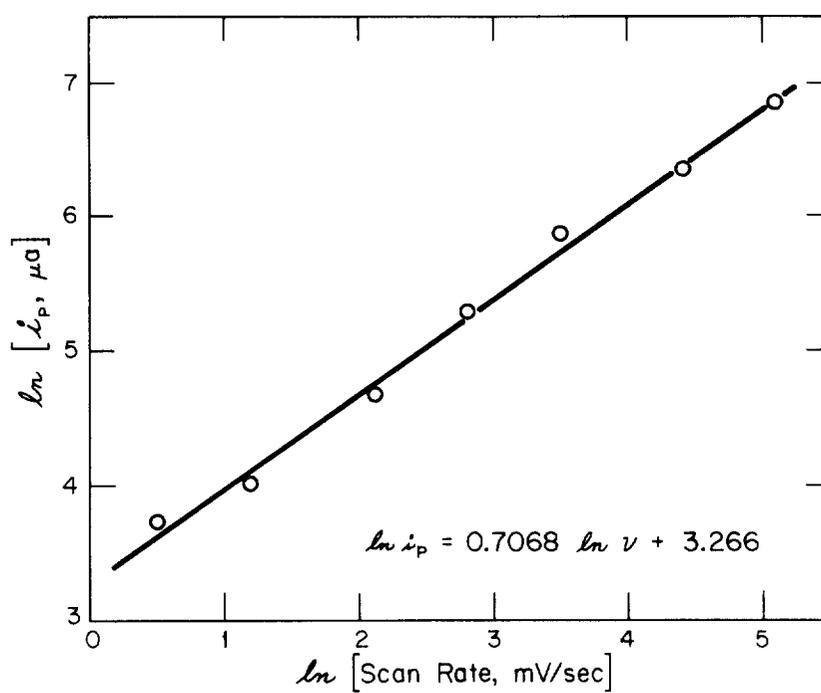


FIGURE 3. EFFECT OF SCAN RATE ON PEAK HEIGHT.

Solution contained 500 ppb Pb^{2+} in 0.01M H_2SO_4 .

PbO_2 deposited at 1.35V for 2 minutes.

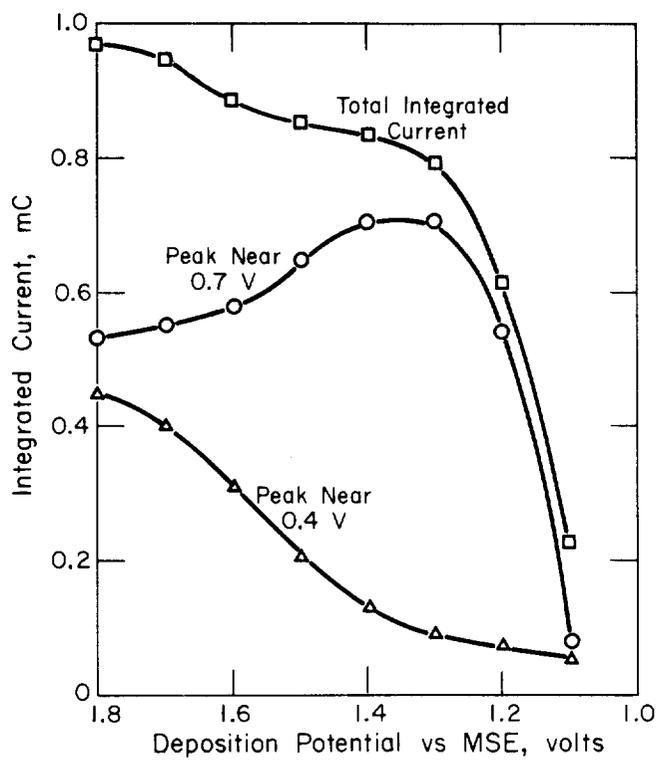


FIGURE 4. EFFECT OF DEPOSITION POTENTIAL ON INTEGRATED STRIPPING CURRENT.

Solution contained 500 ppb Pb^{2+} in 0.01M H_2SO_4 .

PbO_2 deposited at 1.35V for 2 minutes.

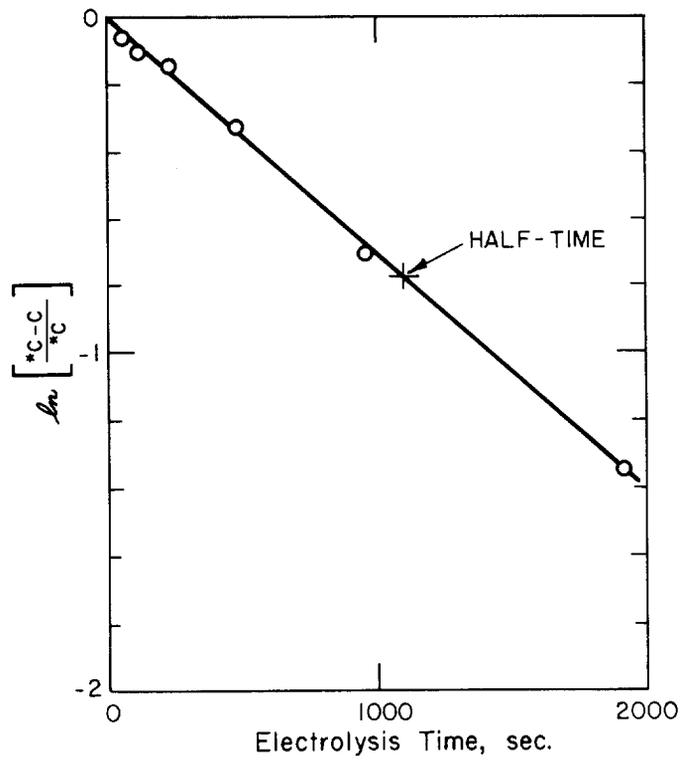


FIGURE 5. COULOMETRIC RELATIONSHIP.

Solution contained 500 ppb Pb^{2+} in 0.01M H_2SO_4 .

PbO_2 deposited at 1.35V.

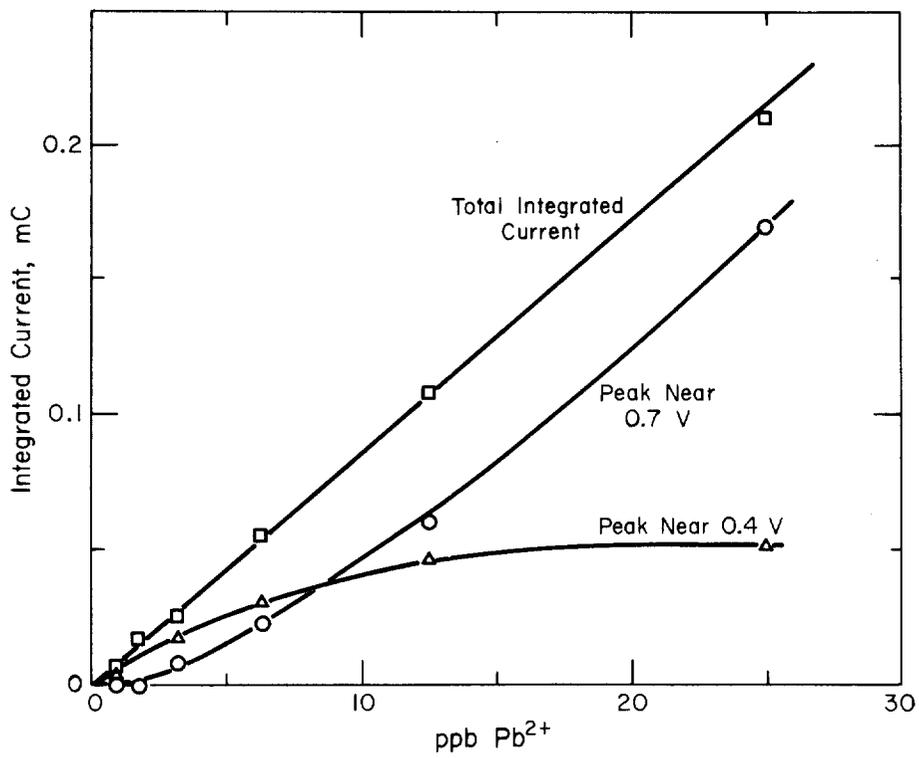


FIGURE 6. EFFECT OF Pb²⁺ CONCENTRATION. Deposition of lead dioxide from 0.01M H₂SO₄ solution after 16 minutes at 1.35 V.