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**REPORT**

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THE DIRECT DETERMINATION, BY DIFFERENTIAL  
PULSE ANODIC-STRIPPING VOLTAMMETRY AT  
THE THIN MERCURY-FILM ELECTRODE, OF  
CADMIUM, LEAD, AND COPPER

by

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# NATIONAL INSTITUTE FOR METALLURGY

ANALYTICAL CHEMISTRY DIVISION

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THE DIRECT DETERMINATION, BY DIFFERENTIAL PULSE ANODIC-STRIPPING  
VOLTAMMETRY AT THE THIN MERCURY-FILM ELECTRODE,  
OF CADMIUM, LEAD, AND COPPER

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### **SYNOPSIS**

This report describes the development and application of a voltammetric procedure for the direct, simultaneous determination of cadmium, lead, and copper in three SAROC reference materials (carbonatite, magnesite, and quartz). The electrolyte was a mixture of 1 M ammonium chloride, 0,1 M citric acid, and 0,025 M ascorbic acid. No interferences were encountered from Fe(III), As(III), Sb(V), Tl(I), or In(III) at the concentrations present in the samples. Intermetallic interferences were eliminated by the use of thin mercury-film electrodes not less than 80 nm thick. Limits of detection were determined by the degree to which the supporting electrolyte could be purified, and were estimated to be 10 ng/g, 250 ng/g, and 150 ng/g for cadmium, lead, and copper respectively.

### **SAMEVATTING**

Hierdie verslag beskryf die ontwikkeling en toepassing van 'n voltammetriese prosedure vir die regstreekse gelyktydige bepaling van kadmium, lood en koper in drie SAROC-verwysingsmateriale (karbonatiet, magnesiet en kwarts). Die elektroliet was 'n mengsel van 1 M-ammoniumchloried, 0,1 M-sitroensuur en 0,025 M-askorbiensuur. Daar is geen steurings deur Fe(III), As(III), Sb(V), Tl(I) of In(III) by die konsentrasies wat in die monsters aanwesig is, ondervind nie. Tussenmetaalsteurings is uitgeskakel deur die gebruik van dun kwiklaagelektrodes met 'n dikte van minstens 80 nm. Opsporingsgrense is vasgestel deur die mate waarin die ondersteunende elektroliet gesuiwer kan word en is op 10 ng/g, 250 ng/g en 150 ng/g onderskeidelik vir kadmium, lood en koper geskat.

## CONTENTS

1. INTRODUCTION .....		1
2. EXPERIMENTAL METHODS .....		1
2.1. CHOICE OF ELECTROLYTE FOR ANODIC-STRIPPING VOLTAMMETRY .....		1
2.2. VOLTAMMETRY OF CADMIUM, LEAD, AND COPPER IN 1.0M AMMONIUM CHLORIDE, 0.1 M CITRIC ACID, AND 0.025 M ASCORBIC ACID .....		2
2.2.1. Electrode Reactions at Higher Concentrations .....		2
2.2.2. Effect of Deposition Potential on the Peak Currents for the Differential Pulse Stripping of Cadmium, Lead, and Copper in the $10^{-6}$ M Range .....		4
2.3. CHARACTERISTICS OF THE THIN MERCURY-FILM ELECTRODE .....		5
2.4. THE STUDY AND OPTIMIZATION OF EXPERIMENTAL PARAMETERS .....		6
2.4.1. Pre-electrolysis Parameters .....		6
2.4.2. Stripping Parameters .....		9
2.4.3. Other (Chemical) Parameters .....		11
2.5. INTERFERING ELEMENTS AND INTERMETALLIC COMPOUNDS .....		12
3. APPLICATION OF THE METHOD .....		15
4. RESULTS .....		15
5. DISCUSSION .....		15
6. REFERENCES .....		17
Appendix. The determination, by direct differential pulse anodic-stripping voltammetry at a mercury-film electrode, of cadmium, lead, and copper in geochemical reference materials (Laboratory Method no. 48/6) .....		36

## LIST OF TABLES

Table 1.	Single-sweep voltammetry of cadmium, lead, and copper .....	2
Table 2.	Cathodic single-sweep voltammetry of cadmium, lead, and copper .....	3
Table 3.	Conditions and typical results for the conventional polarography of cadmium, lead, and copper .....	4
Table 4.	Relation between the rotation speed of the electrode ( $\omega$ ) and the thickness of the diffusion layer ( $\sigma$ ) .....	7
Table 5.	Data for the calculation of the dependence of theoretical peak currents on the time of pre-electrolysis .....	9
Table 6.	Dependence of peak currents and peak widths at half-peak height on scanning rate ..	10
Table 7.	Effect of pulse amplitude on peak current, peak potential, and peak width at the half-peak heights of cadmium, lead, and copper .....	10
Table 8.	Effect of increase in the memory time-constant on the peak currents and potentials of cadmium, lead, and copper .....	11
Table 9.	Concentration of copper in the amalgam as a function of film thickness .....	12
Table 10.	Dependence of peak currents of cadmium, lead, and copper on concentration .....	13
Table 11.	Effect of copper on the peak currents of cadmium and lead when these elements are present together in solution .....	14
Table 12.	Effect of mercury concentration on the peak current and potential of cadmium in the presence of copper .....	14
Table 13.	The determination of cadmium, lead, and copper in three SAROC and two USGS reference materials .....	15
Table 14.	Blank values for cadmium, lead, and copper obtained for the overall procedure .....	16
Table 15.	Precision of measurement for micropipetting and estimation of peak currents .....	16

## LIST OF ILLUSTRATIONS

Figure 1.	Anodic-stripping voltammogram for cadmium, lead, and copper in 1,0 M ammonium chloride, 0,1 M citric acid, and 0,025 M ascorbic acid .....	18
Figure 2.	Plots of $\log I/(I_a - I)$ versus $E$ for cadmium, lead, and copper in 1 M ammonium chloride, 0,1 M citric acid, and 0,025 M ascorbic acid .....	19
Figure 3.	Effect of pre-electrolysis potential on the peak current of cadmium and the plot of log slope versus $E$ .....	20
Figure 4.	Effect of pre-electrolysis potential on the peak current of lead and the plot of log slope versus $E$ .....	21
Figure 5.	Effect of pre-electrolysis potential on the peak current of copper and the plot of log slope versus $E$ .....	22
Figure 6.	Anodic-stripping voltammetry of mercury at a rotating glassy-carbon electrode .....	23
Figure 7.	Dependence of peak current and film thickness on concentration of mercury in solution (linear-ramp stripping) .....	24
Figure 8.	Dependence of the thickness of the thin mercury-film electrode on the concentration of the mercury in solution (differential pulse mode) .....	24
Figure 9.	Dependence of film thickness on time of pre-electrolysis .....	25
Figure 10.	Dependence of peak current on rotation speed of thin mercury-film electrode .....	26
Figure 11.	Dependence of peak potential on thickness of diffusion layer .....	27
Figure 12.	Dependence of peak currents for lead on time of pre-electrolysis .....	28
Figure 13.	Dependence of peak currents for cadmium on time of pre-electrolysis .....	29
Figure 14.	Dependence of peak currents for copper on time of pre-electrolysis .....	29
Figure 15.	Dependence of peak potentials for cadmium, lead, and copper on the thickness of the thin mercury-film electrode .....	30
Figure 16.	Dependence of peak potentials for cadmium, lead, and copper on time of pre-electrolysis .....	31
Figure 17.	Dependence of peak potentials for cadmium, lead, and copper on scanning rate .....	32
Figure 18.	Dependence of peak currents for cadmium, lead, and copper on the concentration of mercury in solution .....	33
Figure 19.	Dependence of peak potentials for cadmium, lead, and copper on the thickness of the thin mercury-film electrode .....	34
Figure 20.	Relation between precision of results and concentration of metals in samples .....	35

## 1. INTRODUCTION

Anodic-stripping voltammetry (ASV) is a natural choice for the determination of trace elements in high-purity ores and minerals. The inherent sensitivity of the technique is best realized in the ultimate variation that employs differential pulse ASV (DPASV) from a rotating thin mercury-film electrode (TMFE). The TMFE is most conveniently formed for routine use by deposition *in situ* simultaneously with the analyte elements<sup>1</sup>. With DPASV, the combined procedure is currently an accepted approach to the determination of toxic metals in biomatrices and samples in aqueous environments<sup>2-4</sup>. In such applications, up to four elements are determined directly and simultaneously in concentrations lower than micrograms per litre without prior external concentration.

Besides their intrinsic value for the certification of reference materials, the concentrations of toxic metals in rocks and sediments are needed as blank materials for studies of environmental pollution. For the estimation of trace elements in geochemical samples by flame atomic-absorption spectrophotometry (AAS), large masses of the sample and complex schemes for pre-concentration and separation are required. Even the use of AAS with electrothermal atomization requires the prior separation of trace elements so that matrix effects can be avoided.

So far, differential pulse polarography has found little application in the geochemical and metallurgical fields. Pilkington *et al.*<sup>5</sup> determined a number of trace elements in zinc sulphate electrolyte by DPASV from the hanging mercury-drop electrode (HMDE). Values for lead, copper, and zinc in the NIMROC reference materials were also obtained by DPASV from the HMDE<sup>6,7</sup>, while De Capitani and Maccagni<sup>8</sup> analysed some plutonic rocks for lead and copper by staircase stripping from the TMFE deposited in a tubular graphite electrode. However, the specific combination of DPASV from a TMFE deposited on a rotating glassy-carbon electrode (RGCE) does not seem to have been used in the determination of trace elements in minerals and ores. This report describes such an application, in which cadmium, lead, and copper were determined in three reference materials from the SAROC range that were prepared at the National Institute for Metallurgy (NIM).

## 2. EXPERIMENTAL METHODS

The PARC 174A Polarographic Analyzer and 315 Automatic Controller were used for automated DPASV. The rotating glassy-carbon electrode was a Metrohm 628 with a synchronous multispeed controller and EA 289/1 glassy-carbon tip. The Ag/AgCl/saturated KCl reference electrode was a Metrohm EA 441/5 with a porous Vycor frit. A platinum rod (Metrohm EA 282/1) served as the auxiliary electrode. Voltammograms were drawn with a Model RE 0074 X-Y recorder, and oxygen was removed from the sample solution with high-purity nitrogen purified further by bubbling through vanadous sulphate solution.

For optimization of the instrument parameters, the following general conditions were observed. A mixture of cadmium, lead, and copper in purified electrolyte (1 M ammonium chloride, 0,1 M citric acid, and 0,025 M ascorbic acid) was spiked with mercuric nitrate solution to give a final concentration of between  $(1,25 \text{ to } 1,75) \times 10^{-4}$  M. The pre-electrolysis time was 300 seconds at  $-0,85$  V, and the electrode rotated at 750 r/min, a thin mercury film being formed *in situ* simultaneously with the deposition of the analyte metals. After a quiescent period of 15 seconds, DPASV proceeded at a scanning rate of 5 mV/s with pulses having an amplitude of 25 mV.

Full details of the final experimental method are given in the Appendix.

### 2.1. Choice of Electrolyte for Anodic-stripping Voltammetry

A number of supporting electrolytes of complex-forming agents that are listed in the tables of Vydra *et al.*<sup>9</sup> were screened for optimum resolution of the peak currents of cadmium, lead, and copper. Acidic media containing the ammonium ion with acetate, tartrate, or citrate, as well as a simple mixture of potassium nitrate with ethylenediaminetetra-acetic acid (EDTA), were found to be electrochemically suitable. The combination of citric acid with ascorbic acid in a buffered ammoniacal electrolyte gave a mixture that would tolerate a large excess of iron(III) through its initial reduction to the iron(II) state, and then form a complex with citric acid. This supporting electrolyte yielded peak currents for copper, lead, and cadmium that showed good resolution (Figure 1), but no stripping peak from iron in the usable range of voltages.

The composition of the supporting electrolyte finally chosen was 1 M ammonium chloride with 0,1 M citric acid and 0,025 M ascorbic acid at a pH value of about 2,5. It was purified by liquid-liquid extraction of the heavy metals into chloroform after chelation with ammonium pyrrolidine dithiocarbamate, as described in the Appendix.

2.2. Voltammetry of Cadmium, Lead, and Copper in 1,0M Ammonium Chloride, 0,1 M Citric Acid, and 0,025 M Ascorbic Acid

The system was examined first by conventional polarography with concentrations of the metals in the range  $10^{-4}$  M to  $10^{-5}$  M.

2.2.1. Electrode Reactions at Higher Concentrations

Single-sweep voltammograms were recorded in the cathodic and anodic directions between  $-0,01$  and  $-0,95$  V from an unstirred solution under the conditions given in Table 1. For a reversible system, the single-sweep peak potential should be independent of the ramp rate, which was the case in this instance for all three metals.

TABLE 1

*Single-sweep voltammetry of cadmium, lead, and copper*

Conditions: PARC 174A Analyzer with 303 standing mercury-drop electrode  
 Area of HMDE (large) 2,49 mm<sup>2</sup>  
 Single sweep, d.c. mode  
 Cd concn  $12,7 \times 10^{-4}$  M  
 Pb concn  $6,9 \times 10^{-4}$  M  
 Cu concn  $22,5 \times 10^{-4}$  M

Metal	Sweep rate mV/s	Peak potential ( $E_p$ ), V	
		Cathodic sweep	Anodic sweep
Cd	20	-0,718	-0,678
	50	-0,720	-0,674
	100	-0,718	-0,674
Pb	20	-0,516	-0,479
	50	-0,515	-0,450
	100	-0,513	-0,477
Cu	20	-0,260	-0,198
	50	-0,260	-0,200
	100	-0,264	-0,195

The form of the peak obtained from cathodic single sweeps at 100 mV/s was examined in more detail for comparison with the theoretical relation derived by Nicholson and Shain<sup>10</sup> for the reversible electrode reaction at a stationary-plane electrode. For the reversible system,

$$E_p = E_1 - \frac{0,0285}{n}$$

where

$E_p$  is the single-sweep potential,

$E_1$  is the half-wave potential (which occurs at a point 85,17 per cent of the way up the wave of the voltammogram for the stationary electrode), and

$n$  is the number of electrons involved in the reaction,

and

$$E_p = E_{p/2} - \frac{0,0565}{n}$$

DETERMINATION OF CADMIUM, LEAD, AND COPPER

where

$E_{p/2}$  is the potential at half-peak height for the single-sweep voltammogram.

Experimental values for  $(E_p - E_1)$  and  $(E_p - E_{p/2})$  are given in Table 2, and are in excellent agreement with the theory for the chosen number of electrons involved in the reduction.

TABLE 2

*Cathodic single-sweep voltammetry of cadmium, lead, and copper*

Conditions: Cathodic sweep at 100 mV/s between -0,01 and -0,95 V

PARC 174A Analyzer with 303 SMDE

Area of HMDE (large) 2,49 mm<sup>2</sup>

Single sweep, d.c. mode

Cu concn  $22,5 \times 10^{-4}$  M

Pb concn  $6,9 \times 10^{-4}$  M

Cd concn  $12,7 \times 10^{-4}$  M

Metal	V versus Ag/AgCl/sat.KCl electrode		
	Copper	Lead	Cadmium
$E_p$	- 0,264	- 0,513	- 0,718
$E_1$	- 0,235	- 0,499	- 0,705
$(E_p - E_1)$ , mV	-29	-14	-13
$-28,5/n$ , mV	-28,5	-14,2	-14,2
$E_{p/2}$	- 0,207	- 0,486	- 0,688
$(E_p - E_{p/2})$ , mV	-57	-27	-30
$-(56,5/n)$ , mV	-56,5	-28,2	-28,2

$n = 1, 2,$  and  $2$  for copper, lead, and cadmium respectively

For cadmium, lead, and copper in the  $(1 \text{ to } 3) \times 10^{-4}$  M concentration range in 1 M ammonium chloride and 0,025 M ascorbic acid, there was no change in the half-wave potentials ( $E_1$ ) nor the diffusion currents ( $I_d$ ) of conventional-current potential polarograms when the citric acid concentration was increased step by step from 0 M to 0,1 M. In the chosen supporting electrolyte containing 0,1 M citric acid, it must therefore be assumed that cadmium, lead, and copper exist as the same simple aquo ions or chloride complexes as they did in the original 1 M chloride solution.

Conventional polarograms for current versus potential were recorded at the standing mercury-drop electrode (SMDE) for cadmium, lead, and copper under the conditions given in Table 3. The capillary characteristic,  $m$ , was determined by timing of the duration of each polarographic scan and weighing of the total amount of mercury that had fallen during this period. Cadmium and lead gave well-defined single waves with  $E_1$  values of -0,637 and -0,433 V versus the Ag/AgCl/saturated KCl electrodes. Copper yielded a double wave, of which only the half that corresponded to the reduction of cuprous copper to copper metal ( $E_1 = -0,210$  V) was analytically useful.

The number of electrons involved in the reduction of each metal was calculated from the Heyrovsky-Ilkovic equation, a reversible system being assumed in each instance, as follows:

$$d \left[ \log \frac{I}{I_d - I} \right] = - \frac{2,203RT}{n} \dots \dots \dots (1)$$

where

$I$  is the current at potential  $E$ ,

$I_d$  is the diffusion current,

$n$  is the number of electrons involved in the reduction, and

$R$  and  $T$  have their usual notations, i.e., gas constant and absolute temperature, respectively.



TABLE 3

Conditions and typical results for the conventional polarography of cadmium, lead, and copper

Conditions: PARC 174A Analyzer with 303 SMDE  
 Electrolyte Mixture of 1 M NH<sub>4</sub>Cl, 0.1 M citric acid, and 0.025 M ascorbic acid (pH value = 2,8)  
 Capillary characteristics  $t = 1,00\text{ s}$ ,  $m^* = 2,05\text{ mg/s}$   
 Scanning speed 5 mV/s  
 Low-pass filter setting 3 s  
 Temperature 24,8 °C

Element	Scan	Concentration (C) M × 10 <sup>-5</sup>	$I_d$ A × 10 <sup>-6</sup>	$I_d/C$
Cd	1	8,90	7,35	0,65
	2	13,3	10,9	0,82
	3	17,8	15,1	0,84
	4	22,2	18,2	0,82
Pb	1	4,83	5,19	1,26
	2	9,66	11,0	1,14
	3	14,5	16,6	1,14
	4	19,3	19,9	1,03
	5	24,1	25,5	1,06
Cu	1	7,86	4,51	0,57
	2	15,7	9,01	0,57
	3	23,6	13,7	0,58
	4	31,4	18,9	0,60
	5	39,3	24,4	0,62

\*m = rate of flow of mercury, mg/s  
 $I_d$  = diffusion current, A × 10<sup>-6</sup>

A plot of  $E$  versus  $\log I/(I_d - I)$  at 25 °C should be a straight line with an intercept  $E_1$  and a slope of  $-0,0591/n$ . Plots for cadmium, lead, and copper are given in Figure 2. The reciprocal slopes for cadmium, lead, and copper were  $-0,0286$ ,  $-0,0295$ , and  $-0,0621$ , giving values for  $n$  of 2,07, 2,00, and 0,95 respectively.

2.2.2. Effect of Deposition Potential on the Peak Currents for the Differential Pulse Stripping of Cadmium, Lead, and Copper in the 10<sup>-6</sup> M Range

For the remaining development work, including that described in this section, the experimental conditions appropriate to DPASV from the TMFE, as given in Section 2, were used. The effect of anodic change in pre-electrolysis potential on the peak currents of cadmium, lead, and copper is shown in Figures 3 to 5. The curves have the sigmoidal shape typical of conventional current-potential polarograms, indicating that, for each metal, a limiting pre-electrolysis potential was eventually reached at which the peak current was no longer a maximum. These limiting values were sufficiently widely separated for an electrochemical separation of the three metals to be achieved, if required, by an appropriate choice of pre-electrolysis potential.

A theoretical relation between the peak current and pre-electrolysis potential was derived only very recently<sup>11-13</sup>. For reversible, simple-ion systems, Zirino and Kounaves<sup>11,13</sup> showed that the curve for deposition potential versus peak current could be described theoretically by a relation of the following form:

$$E_d = E^0 + \beta \ln \left( \frac{I_{p \text{ max}} - I_p}{I_p} \right) + \beta \ln k - \beta \ln t, \dots \dots \dots (2)$$

where

- $E_d$  is the deposition or pre-electrolysis potential,
- $E^\circ$  is the standard potential of the amalgam electrode,
- $I_p$  is the peak current at any given value of  $E_d$ ,
- $I_{p \max}$  is the limiting peak current,
- $k$  is a constant that includes parameters such as the thickness of the diffusion layer, the diffusion coefficient of the simple metal ion, the area of the electrode, and the activity coefficients for the electrode amalgam and simple metal ion,
- $t$  is the time of pre-electrolysis, and
- $\beta$  is  $RT/nF$ , where these have their usual notations.

This relation is therefore similar to the classical Heyrovsky-Ilkovic equation for the reversible current-potential polarogram, but there is, in addition, a linear dependency on  $\log t$ . Equation (2) can be used to extend existing d.c. polarographic methodology to trace metals at concentrations below  $10^{-6}$  M.  $E^\circ$  is dependent upon the area of the electrode and rate of rotation. With these parameters held constant, a plot of

$$\log \left( \frac{I_{p \max} - I_p}{I_p} \right) - \log t$$

should give a straight line of slope  $n/2,303 RT$ . Such plots are given in Figures 3 to 5 where the slopes are 36.1, 33.9, and 34.0, giving values for  $n$  of 2.13, 2.00, and 2.01 for cadmium, lead, and copper respectively. These results indicate reversible, two-electron reactions for cadmium and lead, which was the condition for conventional polarography at a concentration of  $10^{-5}$  M. However, at these low concentrations and for the kinetic conditions chosen for DPASV, the cuprous state for copper appears to be unstable, and the electrode reaction is a single-stage, two-electron oxidation to the cupric ion.

### 2.3. Characteristics of the Thin Mercury-film Electrode

The method of deposition *in situ* and simultaneously with the analyte elements, as first proposed by Florence<sup>1</sup>, was used. An aliquot volume of a  $5 \times 10^{-2}$  M solution of mercuric nitrate (prepared from triply distilled mercury and high-purity nitric acid) was added to the supporting electrolyte before pre-electrolysis. The glassy-carbon electrode was stripped electrochemically at the commencement of each cycle by being conditioned at 0 V and 750 r/min for 180 seconds. After each investigation or analytical determination (normally 6 to 10 cycles), the surface of the glassy carbon was renewed by being polished briefly with a slurry of  $\alpha$ -alumina on a plastic cloth.

Two ranges of mercury concentrations were examined. For concentrations below  $6 \times 10^{-5}$  M, the electrochemical characteristics of the film were determined from the corresponding peak currents for d.c. linear-ramp stripping and estimates of the film thickness. The calculations of the latter are described later. In this concentration range, mercury yielded a single, sharp stripping peak with a peak potential,  $E_p$ , of +0.12 V (Figure 6). At the higher concentrations applicable to later DPASV work, the thickness of the TMFE was calculated from the appropriate deposition current and time of pre-electrolysis. The experimental conditions described at the beginning of this section were used. Deposition of the metal during the pre-electrolysis period (300 seconds) proceeded smoothly, as was evidenced by tracings of the deposition current, from which the average current during pre-electrolysis was estimated. Although it is doubtful that mercury is deposited as a continuous film from low concentrations in solution, the average thickness ( $l$ ) of the film was calculated from the following equation<sup>14</sup>:

$$l = \frac{10^{-6} I_i \cdot Wt}{\pi n F d r^2} \dots \dots \dots (3)$$

where

- $l$  is the average film thickness, (cm),
- $I_i$  is the limiting deposition current for the mercuric ion ( $\mu$ A),
- $W$  is the atomic mass of mercury (200.6),
- $t$  is the time of pre-electrolysis (300 seconds),
- $n$  is the number of electrons involved in the reduction (2),
- $d$  is the density of the mercury ( $13.6 \text{ g/cm}^3$ ), and
- $r$  is the radius of the surface of the plane electrode (0.24 cm).

Substitution of the appropriate values reduces equation (3) to:

$$l = (1.27 \times 10^{-7}) i_p \dots \dots \dots (4)$$

The dependence of peak current and film thickness on the concentration of mercuric ion in solution is given in Figure 7 for the  $10^{-5}$ M concentration range. The calculated film thickness was directly proportional to the mercury concentration, but stripping currents indicated the presence of two phases in the TMFE. For mercury concentrations one decade higher, three distinct phases could be distinguished for film thicknesses calculated from the average deposition current (Figure 8). In subsequent analytical work, a film thickness of about  $(4 \text{ to } 5) \times 10^{-6}$  cm, corresponding to a mercury concentration of  $5 \times 10^{-5}$  M, was used for the SAROC samples and the blank solutions so that adequate detection limits could be attained; a thicker film, corresponding to a mercury concentration of  $1.67 \times 10^{-4}$  M, was used for the analysis of the controls (United States Geological Survey reference materials) so that intermetallic interferences could be avoided.

The correlation between the thickness of the mercury film and the time of pre-electrolysis is shown in Figure 9. Calculations of film thicknesses were again based on equation (3), on the assumption that the film was continuous and evenly distributed over the whole surface of the electrode. Discontinuities in the slopes therefore reflected uneven build-up on areas with different surface activities. However, for pre-electrolysis times of more than about 150 seconds, deposition proceeded smoothly, probably over the complete surface of the electrode, at a rate that was a direct function of time.

**2.4. The Study and Optimization of Experimental Parameters**

The experimental conditions examined in this section of the work comprised the instrumental parameters (pre-electrolysis and stripping) and a number of tests related to the kinetics of the electrode reactions.

**2.4.1. Pre-electrolysis Parameters**

The effect of the speed of rotation of the electrode on the peak currents of cadmium, lead, and copper is shown in Figure 10. Over the range tested (755 to 2200 r/min), the peak currents were proportional to the square root of the rotation speed. This result agrees with the theoretical equations of Levich<sup>15</sup>, which govern the flux and current density at the surface of a rotating-disc electrode.

The relation between the peak potential,  $E_p$ , and the rotation speed of the glassy-carbon electrode is given indirectly by the following equation<sup>16</sup>:

$$E_p = E_1 + \left( \frac{2.3 RT}{nF} \right) \log \left( \frac{\sigma n F l v}{DRT} \right) \dots \dots \dots (5)$$

where

- $E_1$  is the polarographic half-wave potential (V),
- $D$  is the diffusion coefficient of analyte ion ( $\text{cm}^2/\text{s}$ ),
- $\sigma$  is the thickness of the diffusion layer (cm),
- $v$  is the scanning rate (V/s), and
- $l$  is the thickness of the mercury film (cm).

The thickness of the diffusion layer is related to the speed of rotation of the glassy-carbon electrode by means of a Levich equation<sup>17</sup>, as follows:

$$\sigma = 1.61 \times D^{1/3} \nu^{1/6} \omega^{-1/2} \dots \dots \dots (6)$$

where

- $\omega$  is the speed of rotation (rad/s),
- $\nu$  is the kinematic viscosity (St, i.e.,  $1.0 \times 10^{-4} \text{ m}^2/\text{s}$ ), and
- $D$  is the diffusion coefficient of the metal ion ( $\text{cm}^2/\text{s}$ ).

Values of  $\sigma$  relevant to the electrode speeds used in this work and calculated from equation (6) are given in Table 4. The experimental values of  $E_p$  for cadmium, lead, and copper (up to 1500 r/min) were a

TABLE 4

Relation between the rotation speed of the electrode ( $\omega$ ) and the thickness of the diffusion layer ( $\sigma$ )

$\omega$ , r/min	$\sigma$ , cm $\times 10^{-3}$	$\log \sigma$
755	5.09	-2.29
1320	3.86	-2.41
1500	3.62	-2.44
1750	3.35	-2.47
2000	3.13	-2.50
2200	2.98	-2.52

\* Calculated from equation (6) for average values of  $D = 7.5 \times 10^{-6}$  cm<sup>2</sup>/s, and  $\nu = 1 \times 10^{-2}$  cm<sup>2</sup>/s

direct function of  $\log \sigma$  (Figure 11), which is in agreement with the theoretical predictions that can be made by use of equation (5). However, above 1500 r/min, a change in electrode kinetics affected the peak potential of copper, but not its peak current (Figure 10). For analytical applications, adequate sensitivity was obtained with a rotation speed of 750 r/min, which was chosen only so that the manual switching of electrode speeds between conditioning and pre-electrolysis steps could be avoided.

The dependence of the peak currents of lead, cadmium, and copper on the time of pre-electrolysis is shown in Figures 12 to 14 respectively. For all three metals, the peak current was directly proportional to the time of pre-electrolysis up to 300 seconds. For anodic pulse stripping from the TMFE, Osteryoung and Christie<sup>18</sup> derived the following simple relation:

$$I_p = -0.138 q_M / t_p \dots\dots\dots (7)$$

where

$I_p$  is the anodic peak current (A),  
 $q_M$  is the total charge passed during deposition (C), and  
 $t_p$  is the pulse width (s), which is fixed at 0.060 s for the PARC 174A Polarizer.

The total charge,  $q_M$ , is given by the following equation<sup>18</sup>:

$$q_M = nFAiC_{M,0,t} \dots\dots\dots (8)$$

where

$n$  is the number of electrons involved in the electrode process (viz 2 for cadmium, lead, or copper),  
 $A$  is the area of the RGCE (0.181 cm<sup>2</sup>),  
 $i$  is the average thickness of the mercury film on the RGCE, i.e., from equation (3),

$$i, \text{cm} = 4.23 \times 10^{-10} I_p t, \text{ and} \dots\dots\dots (9)$$

$C_{M,0,t}$  is the concentration of the analyte metal, M, in the amalgam at the end of pre-electrolysis (mol/cm<sup>3</sup>).

Average deposition currents (corrected for the blank current), as measured during each pre-electrolysis period, are given in  $\epsilon$  of Table 5. In view of the low concentrations of the analyte elements in solution, the deposition currents could be attributed entirely to reduction of the mercuric ion. Although the concentration of mercuric ion was constant ( $1.25 \times 10^{-4}$  M), the recorded deposition currents showed a small but steady increase as the test sequence progressed, probably reflecting the changing activity of the surface of the electrode after electrochemical conditioning between the pre-electrolysis and stripping

cycles. An average value of  $47,5 \mu\text{A}$  was assumed for the limiting deposition current, when equation (9) reduced further to

$$l = 2,01 \times 10^{-8} t, \dots\dots\dots (10)$$

where

$t$  is the time of pre-electrolysis, s.

For deposition *in situ*, the thickness of the mercury film increases with deposition time concomitantly with the mass of the analyte element. The concentration of the analyte,  $M$ , in the mercury film therefore remains approximately constant, and is given by the following equation<sup>14</sup>:

$$C_{M,HK} = \frac{C_M}{C_{HK}} \cdot \left( \frac{D_M}{D_{HK}} \right)^{2/3} \cdot \left( \frac{d}{W} \right), \dots\dots\dots (11)$$

where  $C_{M,HK}$  is the concentration of the analyte metal,  $M$ , in the amalgam ( $\text{mol}/\text{cm}^3$ ),  
 $C_M$  is the concentration of the analyte metal,  $M$ , in the electrolyte ( $\text{mol}/\text{cm}^3$ ),  
 $C_{HK}$  is the concentration of mercuric ion in solution ( $1,25 \times 10^{-4} \text{ mol/l}$ ),  
 $D_{HK}$  is the diffusion coefficient of  $\text{Hg}^{2+}$  in the electrolyte ( $8,3 \times 10^{-6} \text{ cm}^2/\text{s}$ ),  
 $D_M$  is the diffusion coefficient of the metal ion in the electrolyte ( $\text{cm}^2/\text{s}$ ) as can be seen in  $b$  of Table 5,  
 $d$  is the density of the mercury ( $13,6 \text{ g}/\text{cm}^3$ ), and  
 $W$  is the atomic mass of the mercury (200,6).

Substitution of these values into equation (11) gives

$$C_{M,HK} = 1,32 \times 10^6 C_M D_M^{2/3} \dots\dots\dots (12)$$

Amalgam concentrations for cadmium, lead, and copper, calculated by substitution of the appropriate values in Table 5 for the terms in equation (12), are given in  $d$  of Table 5. With  $C_{M,HK}$  known and  $l$  given by equation (10), the  $q_M$  values for cadmium, lead, and copper can be calculated from equation (8) for the various pre-electrolysis times, and the  $l_p$  values from equation (7). The calculated values of  $l_p$  are also given in Figures 12 to 14. If the number of assumptions is considered, the calculations agree very well with the experimental data. The concurrence for copper shown in Figure 14 confirms the conclusion mentioned in Section 2.2.2 that, for DPASV in the  $10^{-7} \text{ M}$  range, the electrode reaction was a reversible, two-electron transfer.

The peak potentials for cadmium, lead, and copper moved anodically as the time of pre-electrolysis was increased. The controlling parameter was the thickness of the mercury-film electrode ( $l$ ). In Figure 15, peak potentials were plotted as a function of  $\log l$  (cm), calculated from equation (9) for an average limiting deposition current of  $47,5 \mu\text{A}$ . The linear dependence on  $\log l$  for cadmium and lead was in agreement with that shown in equation (5). The break in the relation for copper suggested a sudden transition to a second phase, and was noted earlier during the work on electrode rotation (Figure 11). It is probably related to the low solubility of copper in mercury<sup>20</sup> ( $\text{Cu} = 3 \times 10^{-3}$  per cent by mass,  $\text{Pb} = 1,1$  per cent by mass, and  $\text{Cd} = 5,3$  per cent by mass). The calculated concentration of copper in the amalgam ( $d$  of Table 5) represented about  $3,6 \times 10^{-2}$  per cent by mass, and a pure metallic phase should be present. If, in practice, the deposition of mercury proceeded somewhat faster than that of copper, the break after 120 seconds of pre-electrolysis could represent a transition to a homogeneous amalgam. Theoretical values of  $E_p$  can be calculated from equation (5) by use of the data given in Tables 4 and 5. Practical values for half-wave potentials in 1,0 M ammonium chloride, 0,1 M citric acid, and 0,025 M ascorbic acid were determined in Section 2.2.1. Calculated and experimental values for  $E_p$  are compared in Figure 16. The agreement for cadmium and copper is good in view of the assumptions made in the calculations. For lead, there is a divergence for pre-electrolysis times of more than 1 minute.

The effect of change in deposition potential was reported in Section 2.2.2. From the curves for peak current versus deposition potential given in Figures 3 to 5, it was decided that cadmium, lead, and copper should be determined sequentially in that order after pre-electrolysis at  $-0,85$ ,  $-0,65$ , and  $-0,45 \text{ V}$  respectively. This separation effectively eliminated interelement effects between the three metals.

TABLE 5

Data for the calculation of the dependence of theoretical peak currents on the time of pre-electrolysis

<b>a. Experimental conditions:</b>					
Pre-electrolysis	-0,85 V at 750 r/min				
DPASV	Scanning rate 5 mV/s Pulse amplitude 25 mV				
Conditioning	180 s at 0 V and 750 r/min				
<b>b. Voltammetric parameters and constants:</b>					
Pulse width, $t_d$	60 ms				
Radius of RGCE	0,24 cm				
Diffusion coefficients, $D_M^{19}$	<table border="0"> <tr> <td>Cd, Cu</td> <td><math>7,2 \times 10^{-6} \text{ cm}^2/\text{s}</math></td> </tr> <tr> <td>Pb</td> <td><math>9,8 \times 10^{-6} \text{ cm}^2/\text{s}</math></td> </tr> </table>	Cd, Cu	$7,2 \times 10^{-6} \text{ cm}^2/\text{s}$	Pb	$9,8 \times 10^{-6} \text{ cm}^2/\text{s}$
Cd, Cu	$7,2 \times 10^{-6} \text{ cm}^2/\text{s}$				
Pb	$9,8 \times 10^{-6} \text{ cm}^2/\text{s}$				
<b>c. Concentrations:</b>					
Cd	$2,68 \times 10^{-8} \text{ M}$				
Pb	$3,80 \times 10^{-8} \text{ M}$				
Cu	$1,57 \times 10^{-7} \text{ M}$				
Hg	$1,25 \times 10^{-4} \text{ M}$				
<b>d. <math>C_M</math> (calculated):</b>					
Cd	$1,32 \times 10^{-5} \text{ mol/cm}^3$				
Pb	$2,30 \times 10^{-5} \text{ mol/cm}^3$				
Cu	$7,73 \times 10^{-5} \text{ mol/cm}^3$				
<b>e. Experimental limiting deposition currents:</b>					
Time of pre-electrolysis, s	Limiting deposition current, $\mu\text{A}$				
30	40				
60	40				
90	42				
120	45				
150	47,5				
180	47,5				
216	50				
240	52				
270	55				
300	55				
Mean	47,5				

#### 2.4.2. Stripping Parameters

The dependence of the peak currents and peak widths at half-peak height ( $b_p$ ) on the scanning rate are given in Table 6. The peak currents increased with the scanning rate up to 5 or 10 mV/s. The relation was not rectilinear, but similar to the curve given by Copeland *et al.*<sup>21</sup>. However, Figure 17 shows that the peak potentials moved anodically as a function of the log scanning rate, as could be predicted from equation (5). Only slow scanning rates were available before the stripping peak was distorted, and the number of pulses per peak were severely reduced (Table 6). A scanning rate of 5 mV/s was chosen for the later analytical work.

The effect of pulse amplitude on the peak current, peak potential, and peak width at the half-peak heights of cadmium, lead, and copper are given in Table 7. The peak currents of cadmium and lead were a linear function of the pulse amplitude up to 25 mV, and that for copper up to 50 mV. For pulses larger than

DETERMINATION OF CADMIUM, LEAD, AND COPPER

TABLE 6

*Dependence of peak currents and peak widths at half-peak height on scanning rate*

Conditions:

Cd concn  $4,46 \times 10^{-8} \text{ M}$   
 Pb concn  $3,24 \times 10^{-8} \text{ M}$   
 Cu concn  $6,29 \times 10^{-7} \text{ M}$   
 Hg concn  $1,25 \times 10^{-4} \text{ M}$   
 Pre-electrolysis 100s at  $-0,85 \text{ V}$  and 750 r/min  
 DPASV Pulse amplitude 25 mV  
 Conditioning 90s at 0 V and 750 r/min

Scanning rate mV/s	Peak current, $A \times 10^{-6}$			$b_{1/2}$ , mV			Number of pulses per peak		
	Cd	Pb	Cu	Cd	Pb	Cu	Cd	Pb	Cu
0,5	3,14	7,84	6,08	40	40	45	N.D.	N.D.	N.D.
1,0	3,72	9,41	8,82	38	38	46	N.D.	N.D.	N.D.
2,0	4,12	10,6	15,5	41	38	43	N.D.	N.D.	N.D.
5,0	5,09	11,2	24,9	45	45	61	44	52	77
10	5,49	9,60	24,7	51	56	83	31	29	47
20	3,33	6,86	22,9	61	66	121	14	15	23

$b_{1/2}$  = peak width at half-peak height  
 N.D. = Not determined

TABLE 7

*Effect of pulse amplitude on peak current, peak potential, and peak width at the half-peak heights of cadmium, lead, and copper*

Conditions:

Cd concn  $4,46 \times 10^{-8} \text{ M}$   
 Pb concn  $3,24 \times 10^{-8} \text{ M}$   
 Cu concn  $6,29 \times 10^{-7} \text{ M}$   
 Hg concn  $1,25 \times 10^{-4} \text{ M}$   
 Pre-electrolysis 100s at  $-0,85 \text{ V}$  and 750 r/min  
 DPASV Scanning rate 5 mV/s  
 Conditioning 90s at  $+0,3 \text{ V}$  and 750 r/min

Pulse amplitude mV	Peak current, $A \times 10^{-6}$			Peak potential, V			$b_{1/2}$ , mV		
	Cd	Pb	Cu	Cd	Pb	Cu	Cd	Pb	Cu
+ 5	0,88	1,76	1,76	-0,695	-0,498	-0,309	43	41	68
+ 10	1,96	3,92	4,70	-0,695	-0,500	-0,309	43	41	59
+ 25	5,1	10,4	15,1	-0,702	-0,507	-0,316	41	37	51
+ 50	8,1	16,7	32,1	-0,725	-0,525	-0,327	42	42	52
+ 100	6,5	17,8	50,0	-0,768	-0,568	-0,362	41	43	59

$b_{1/2}$  = peak width at half-peak height

DETERMINATION OF CADMIUM, LEAD, AND COPPER

5 mV, the peak current was suppressed, an effect that agreed with the theory and practice of differential pulse polarography at the dropping-mercury electrode<sup>22</sup>. Similarly, peak potentials moved cathodically with increasing positive pulses according to a linear relation that was in agreement with the theory of differential pulse stripping. However, the rates of increase for the TMFE were somewhat higher than that expected from the relation given by Batley and Florence<sup>23</sup> for the HMDE:

$$E_p = E_1 - 1,1 (RT/nF) - \Delta E/2, \dots\dots\dots (12)$$

where

$E_1$  is the half-wave potential (V), and  
 $\Delta E$  is the amplitude of the differential pulse (V).

This anomaly was also confirmed experimentally by those investigators<sup>23</sup>. Peak widths were narrowest in the middle of the range of pulse amplitudes tested, and a pulse amplitude of 25 mV was chosen for all the later analytical work.

Stripping from a stationary TMFE was compared with that from the same film on a glassy-carbon electrode rotated at 750 and 1500 r/min. Rotation of the electrode during stripping resulted in inferior voltammograms, since the peak current decreased, pulse recordings were exaggerated, and the background noise increased.

The effect of an increase in the memory time-constant (pulse repetition time) is shown in Table 8. This trend is confirmed by other workers<sup>2</sup>, including those who modified their equipment to make much shorter pulse repetition times possible than the period of 500 ms available with the PARC 174A Polarizer.

TABLE 8

*Effect of increase in the memory time-constant on the peak currents and potentials of cadmium, lead, and copper*

Condition:;

Pre-electrolysis 300 s  
 DPASV Scanning rate 5 mV/s  
 Pulse amplitude 25 mV  
 Other parameters as given in Table 7

Memory-time constant s	Peak currents, A × 10 <sup>-6</sup>			Peak potential, V		
	Cd	Pb	Cu	Cd	Pb	Cu
0,5	4,0	20,1	10,5	-0,705	-0,485	-0,288
1,0	2,6	15,9	12,7	-0,688	-0,477	-0,279
2,0	1,6	9,9	8,0	-0,675	-0,468	-0,271

2.4.3. Other (Chemical) Parameters

When the instrumental parameters previously mentioned had been optimized, the effect was determined of the concentration of mercury in the supporting electrolyte, and hence of the thickness of the TMFE deposited *in situ*, on the peak currents and peak potentials of cadmium, lead, and copper. After each addition of mercury to the standard solution of the metals, the average limiting deposition current (corrected for the blank current) was measured during the pre-electrolysis period, and the thickness of the TMFE was calculated by use of equation (3). The results are given in Figure 8. Corresponding peak currents of cadmium, lead, and copper are shown in Figure 18. At very low concentrations of mercury, the peak currents were dependent upon the thickness of the TMFE. Comparison with Figure 8 shows that the anomalous trend for copper is probably due to the progressive formation of a metallic phase as a result of the low solubility of the metal in the amalgam electrode. For mercury concentrations above about 1 × 10<sup>-4</sup> M, corresponding with film thicknesses of more than 5 × 10<sup>-6</sup> cm, the peak currents of the three metals



became constant and independent of the thickness of the TMFE. This result agreed with a similar practical deduction made by Copeland *et al.*<sup>21</sup> for lead over a wide range of mercury concentrations and for pre-electrolysis times of 600 to 1800 seconds.

Under the same experimental conditions, when the concentrations of the analyte metals were held constant, the peak potentials of lead and cadmium were found to shift anodically at a rate that was a function of the log of the thickness of the mercury film (Figure 19). This result was expected from equation (5). The completely anomalous behaviour of copper must again be attributed to its low solubility in mercury. The concentrations of copper in the mercury film, as calculated from equation (10) for the conditions given in Figures 18 and 19, are given in Table 9. For the thinner films, the solubility of copper in mercury was approached or exceeded, and a metallic copper phase was present. Under such conditions, the potential of the amalgam is independent of the concentration of copper in the amalgam, and becomes the potential of the pure metal.

TABLE 9

*Concentration of copper in the amalgam as a function of film thickness*

Conditions: Given in Figures 17 to 19

$C_{\text{Hk}}$ in bulk solution M	log film thickness cm	Concn of copper in TMFE Mass, %
$2,5 \times 10^{-7}$	-6,22	$4,45 \times 10^{-3}$
$1,25 \times 10^{-6}$	-5,72	$8,9 \times 10^{-4}$
$2,25 \times 10^{-6}$	-5,89	$5,0 \times 10^{-4}$
$6,25 \times 10^{-6}$	-5,66	$1,8 \times 10^{-4}$
$1,025 \times 10^{-5}$	-5,64	$1,1 \times 10^{-4}$
$3,5 \times 10^{-5}$	-5,42	$3,2 \times 10^{-5}$
$8,5 \times 10^{-5}$	-5,29	$1,3 \times 10^{-5}$
$1,35 \times 10^{-4}$	-5,26	$8,3 \times 10^{-6}$
$1,85 \times 10^{-4}$	-5,18	$6,0 \times 10^{-6}$
$2,5 \times 10^{-4}$	-5,07	$4,8 \times 10^{-6}$
$2,85 \times 10^{-4}$	-4,97	$3,9 \times 10^{-6}$
$3,35 \times 10^{-4}$	-4,85	$3,3 \times 10^{-6}$
$3,85 \times 10^{-4}$	-4,90	$2,9 \times 10^{-6}$

The dependence of peak currents on the concentrations of cadmium, lead, and copper are given in Table 10, in which the experimental conditions are those finally chosen for the quantitative analytical work. The concentration ranges for cadmium, lead, and copper were equivalent to 1 to 3 ng/ml, 20 to 60 ng/ml, and 2 to 15 ng/ml respectively. The degree of concurrence of the calibration points is given by the correlation coefficient of the least-squares regression lines, which were obtained by the use of a desk-top computer programmed to include the origin of the plot. The precision of the data indicated that the metals could be determined from a calibration line prepared from pure solutions or by the method of three-point standard additions.

#### 2.5. Interfering Elements and Intermetallic Compounds

For a film thickness equivalent to pre-electrolysis for 300 seconds at  $-1,2$  V in the presence of mercury at a concentration of  $2,67 \times 10^{-5}$  M, arsenic(III) had no effect on the peak currents of cadmium or lead when present in concentrations up to 33 times that of cadmium or 10 times that of lead. Under the same experimental conditions, antimony(V) had no effect on the peak currents of cadmium or lead when present in concentrations 10 times that of cadmium or lead. At the maximum concentrations given above, no separate stripping peaks for arsenic or antimony appeared, and there were no changes in the peak potentials of cadmium or lead. It was therefore inferred that arsenic and antimony would not interfere when stripped from films equivalent to  $2,67 \times 10^{-5}$  M or higher concentrations of mercury in solution.

The peak potential for the stripping of thallium(I) was  $-0,56$  V versus Ag/AgCl/saturated KCl electrode in the appropriate supporting electrolyte. It therefore fell between the peak potentials of

TABLE 10

*Dependence of peak currents of cadmium, lead, and copper on concentration*

## Conditions:

High concn	$1,67 \times 10^{-4} \text{ M}$
Pre-electrolysis	For Cd, 300s at $-0,85 \text{ V}$ and 750 r/min For Pb, 100s at $-0,65 \text{ V}$ and 750 r/min For Cu, 100s at $-0,45 \text{ V}$ and 750 r/min
DPASV	Scanning rate 5 mV/s Pulse amplitude 25 mV
Conditioning	90s at 0V and 750 r/min

Metal	Concentration M	Peak current $\text{A} \times 10^{-6}$	Ratio of peak current/concn	Correlation coefficient
<i>Cadmium</i> Calibration 1	$4,83 \times 10^{-9}$	2,51	0,52	0,9989
	$9,66 \times 10^{-9}$	4,79	0,50	
	$14,5 \times 10^{-9}$	6,82	0,47	
Calibration 2	$4,83 \times 10^{-9}$	2,43	0,50	0,9993
	$9,66 \times 10^{-9}$	4,90	0,51	
	$14,5 \times 10^{-9}$	7,05	0,49	
<i>Lead</i> Calibration 1	$0,965 \times 10^{-7}$	13,73	1,42	1,000
	$1,93 \times 10^{-7}$	27,65	1,43	
	$2,90 \times 10^{-7}$	41,76	1,44	
Calibration 2	$0,965 \times 10^{-7}$	13,73	1,42	0,9999
	$1,93 \times 10^{-7}$	28,24	1,46	
	$2,90 \times 10^{-7}$	42,74	1,47	
<i>Copper</i>	$3,14 \times 10^{-8}$	2,16	0,69	0,9997
	$7,86 \times 10^{-8}$	5,30	0,67	
	$12,58 \times 10^{-8}$	8,98	0,71	
	$23,58 \times 10^{-8}$	17,48	0,74	

cadmium ( $-0,68 \text{ V}$ ) and lead ( $-0,465 \text{ V}$ ), and could not be resolved completely from the former unless the experimental conditions were carefully optimized. In addition, for very thin mercury-film electrodes, where the peak resolution was at an optimum, an intermetallic compound of cadmium-thallium formed, causing the peak current for cadmium to be suppressed and that for thallium to be enhanced. However, for mercury concentrations above  $1,6 \times 10^{-4} \text{ M}$ , thallium up to 15 times the concentration of cadmium could be tolerated, and there was sufficient resolution for the peak current for cadmium to be accurately determined. Peaks for thallium did not appear on the voltammograms of the samples analysed under this programme, and it was assumed that thallium was not an interfering element.

Indium gave a stripping peak ( $E_p = -0,585 \text{ V}$  versus Ag/AgCl/saturated KCl electrode) in the chosen electrolyte that also fell midway between those of cadmium and lead. However, even for the very thin film equivalent to  $2,67 \times 10^{-5} \text{ M}$  mercury in solution, it could be resolved from metals present in concentrations 20 times higher than those of cadmium and lead. Also, there was no intermetallic interference, and calibration lines for the three metals when present together were strictly rectilinear. Again, stripping peaks for indium did not appear on the voltammograms of the samples, and it was assumed to be unimportant.

Lead, when present with either cadmium or copper in solution, did not form intermetallic compounds, even after it had been deposited into very thin mercury-film electrodes. However, a copper-cadmium intermetallic compound was readily formed in thin films. This compound stripped at an intermediate potential close to the peak potential of lead, so that the peak current for cadmium was suppressed in the presence even of traces of copper, and that for lead apparently enhanced. A linear relation between the peak current and the concentration of copper was maintained, but at a lower level than for copper alone (Table 11). This serious intermetallic interference was easily eliminated by an increase in the thickness of the TMFE. Table 12 shows that, for film electrodes equivalent to concentrations of  $2 \times 10^{-4} \text{ M}$  mercury in

DETERMINATION OF CADMIUM, LEAD, AND COPPER

TABLE 11

*Effect of copper on the peak currents of cadmium and lead when these elements are present together in solution*

Conditions:  
 Cd concn  $3,6 \times 10^{-8}$  M  
 Pb concn  $1,2 \times 10^{-8}$  M  
 Hg concn  $5 \times 10^{-6}$  M  
 Pre-electrolysis 300s at  $-1,2$  V and 750 r/min  
 DPASV Scanning rate 5 mV/s  
 Pulse amplitude 25 mV  
 Conditioning 180s at 0 V and 750 r/min

Cu concn M	Peak height, A $\times 10^{-6}$		
	Cd	Pb	Cu
Nil	15,2	10,2	0,69
$3,14 \times 10^{-8}$	13,8	11,7	4,9
$6,28 \times 10^{-8}$	12,3	12,8	8,9
$1,26 \times 10^{-7}$	10,3	14,5	16,0
$1,89 \times 10^{-7}$	8,8	16,2	24,4
$3,27 \times 10^{-7}$	7,1	20,0	42,2

TABLE 12

*Effect of mercury concentration on the peak current and potential of cadmium in the presence of copper*

Conditions:  
 Cd concn  $1,78 \times 10^{-8}$  M  
 Pre-electrolysis 300s at  $-1,0$  V and 750 r/min  
 DPASV Scanning rate 5 mV/s  
 Pulse amplitude 25 mV  
 Conditioning 180s at 0 V and 750 r/min

Hg concn M $\times 10^{-5}$	Cu concn M $\times 10^{-6}$	Cd	
		Peak current A $\times 10^{-6}$	Peak potential V
0,5	0,47	1,27	-0,86
1,0	0,47	2,74	-0,855
5,0	0,47	4,90	-0,83
10	0,47	5,88	-0,82
15	0,47	6,08	-0,81
20	0,47	6,47	-0,80
20	1,3	5,88	-0,795
20	2,0	6,86	-0,79
20	3,6	6,47	-0,80
20	6,8	6,47	-0,79
20	9,9	6,00	-0,79
20	13,0	6,37	-0,785

the electrolyte, copper in concentrations up to 700 times that of cadmium could be tolerated without interfering with the peak current or potential of cadmium.

### 3. APPLICATION OF THE METHOD

Cadmium, lead, and copper present in the range nanograms per gram were determined direct in three high-purity samples of the SAROC range of reference materials prepared by NIM. Certified international reference materials containing cadmium, lead, and copper at the relevant very low concentrations were not available. However, the United States Geological Survey (USGS) reference materials USGS-DTS 1 and USGS-BHVO 1 were chosen as monitors for cadmium and for lead respectively.

Full details of the analytical procedure are given in the Appendix.

### 4. RESULTS

The results for cadmium, lead, and copper in the three SAROCs, and for cadmium and lead in the two USGS reference materials are given in Table 13, together with estimates of precision and values from other available sources. The least-squares correlation coefficients for the calibration points on the graphs for additions were 0,9975 or better. The relation between the precision of all the results for cadmium, lead, and copper and their concentrations in the reference materials is given in Figure 20.

TABLE 13

*The determination of cadmium, lead, and copper in three SAROC and two USGS reference materials (values in nanograms per gram)*

Reference material no.	Nature of material	Cadmium					Lead					Copper			
		This work				Other values*	This work				Other values†	This work			
		$\bar{x}$	n	s	$s_r$		$\bar{x}$	n	s	$s_r$		$\bar{x}$	n	s	$s_r$
NIM-S8	Carbonatite	81	7	9.9	0,121	None	3084	5	574	0,186	None	2174	5	559	0,257
NIM-S11	Magnesite	4,1	6	0,8	0,202	None	591	4	20	0,034	None	426	6	11	0,025
NIM-S17	Quartz	1,6	6	1,2	75,0	None	266	8	9	0,032	None	170	7	12	0,069
USGS-DTS 1	Dunite	7,0	6	1,1	0,167	5,8,9,10 10,12,23 120,154	Not determined					Not determined			
USGS-BHVO 1	Hawaiian basalt	52	One result			68,76	1222	7	29	0,023	1900 2500±300 3400	Not determined			

\* From the literature<sup>24</sup>  
 † From the literature<sup>25-27</sup>  
 $\bar{x}$  = mean value, ng/g

n = number of determinations  
 s = standard deviation, ng/g  
 $s_r$  = relative standard deviation

Since small volumes of high-purity acids were used in the dissolution of the samples, the supporting electrolyte was found to be the largest contributor to the blank values for the overall procedure. Blank concentrations of cadmium, lead, and copper that were obtained by the overall procedure, including sample dissolution, are given in Table 14, together with estimates of precision, for the four batches of purified electrolyte used in the project.

### 5. DISCUSSION

For the concentration range  $10^{-3}$  to  $10^{-5}$  M in the chosen electrolyte, single-sweep and conventional polarography suggested reversible electrode reactions involving two electrons for cadmium and lead. Copper appeared to be reduced in two stages, only the reversible one-electron reduction from cuprous copper to copper being analytically useful. At the concentrations and scanning-rates applicable to DPASV, all three metals yielded data supporting two-electron electrode reactions. The effect of instrumental parameters on the peak currents and potentials of cadmium, lead, and copper followed theoretical predictions, where these could be confirmed quantitatively.

DETERMINATION OF CADMIUM, LEAD, AND COPPER

TABLE 14

Blank values for cadmium, lead, and copper obtained for the overall procedure

Batch of electrolyte no.	Blank values, $\mu\text{g/l}$								
	Cadmium			Lead			Copper		
	$\bar{x}$	$n$	$s$	$\bar{x}$	$n$	$s$	$\bar{x}$	$n$	$s$
1	0,16	4	0,025	2,1	3	0,24	2,9	2	-
2	0,09	4	0,013	7,7	4	0,76	1,5	4	0,48
3	0,08	2	-	3,8	2	-	3,1	2	-
4	0,33	3	0,025	6,7	2	-	Not determined		

Standard reference materials were not available to act as monitors for the accuracy of the lead and copper values at the low level present in the SAROC samples. The procedure returned a value of 1,22  $\mu\text{g/g}$  for lead in USGS-BHVO 1, which compared well with the concentration obtained by Heinrichs<sup>25</sup> using an electrothermal atomic-absorption spectrophotometric technique (1,9  $\mu\text{g/g}$ ). USGS-DTS 1 was chosen as the monitor for the accuracy of the cadmium determinations. The value for cadmium of 7 ng/g that was obtained falls at the lower end of the range of concentrations returned by other investigators. The recommended value of 120 ng/g for this reference material must be considered to be an outlier.

The precision for all the determinations was linearly related to the concentration of analyte metal, except for two outliers (Figure 20). The precision for two critical operations in the overall analytical procedure is given in Table 15. The lowest group of precisions for the overall procedure (Figure 20) came close to those attainable by ASV measurement alone. The adjustable micropipette used for this work was inherently precise, so that the use of small volumes of standard solutions for calibration by the method of additions contributed little to the imprecision of the overall method.

Limits of detection ( $x_L$ ) for the procedure were calculated from the following relation<sup>28</sup>:

$$x_L = \bar{x}_{bl} + k s_{bl} \dots \dots \dots (13)$$

where  $\bar{x}_{bl}$  is the mean blank value,  $\mu\text{g/l}$ ,  
 $s_{bl}$  is the standard deviation of the mean blank value,  $\mu\text{g/l}$ , and  
 $k$  is the numerical constant (= 3) chosen according to the specified confidence level.

TABLE 15

Precision of measurement for micropipetting and estimation of peak currents

Operation	Quantity measured	Precision, $s_r$
Dispensing with adjustable 50 $\mu\text{l}$ pipette ( $n = 10$ )	20 $\mu\text{l}$	0,0057
	50 $\mu\text{l}$	0,0025
Replicate scans ( $n = 5$ ) by DPASV for a single solution, and manual linear measurement of peak height to the nearest 0,5 mm	Peak height (mm) for the following metal concentrations:	
	Cd $4,5 \times 10^{-8} \text{M}$	0,014
	Pb $3,2 \times 10^{-8} \text{M}$	0,015
	Cu $1,6 \times 10^{-7} \text{M}$	0,047

From the data in Table 14, the average limits of detection for cadmium, lead, and copper were calculated to be 0,22  $\mu\text{g/l}$ , 6,6  $\mu\text{g/l}$ , and 4,0  $\mu\text{g/l}$  respectively. These values correspond approximately to 10 ng/g, 255 ng/g, and 160 ng/g respectively in the reference material for the sample mass and the dilution given in the Appendix. Reported values for cadmium in SAROCs S11 and S17 therefore fall below the average limits of detection; they were achieved by the use of a highly purified supporting electrolyte (Batch 3).

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DETERMINATION OF CADMIUM, LEAD, AND COPPER

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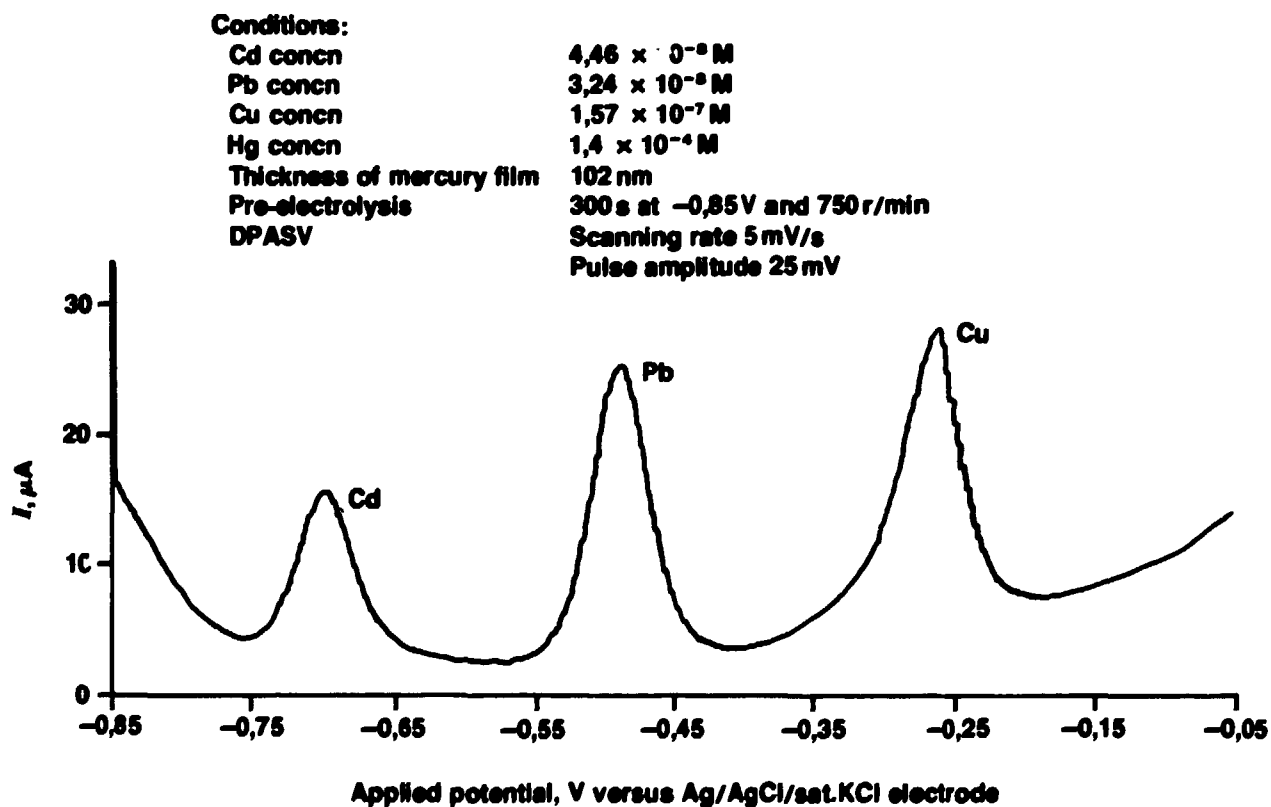


FIGURE 1. Anodic-stripping voltammogram for cadmium, lead, and copper in 1,0 M ammonium chloride, 0,1 M citric acid, and 0,025 M ascorbic acid

DETERMINATION OF CADMIUM, LEAD, AND COPPER

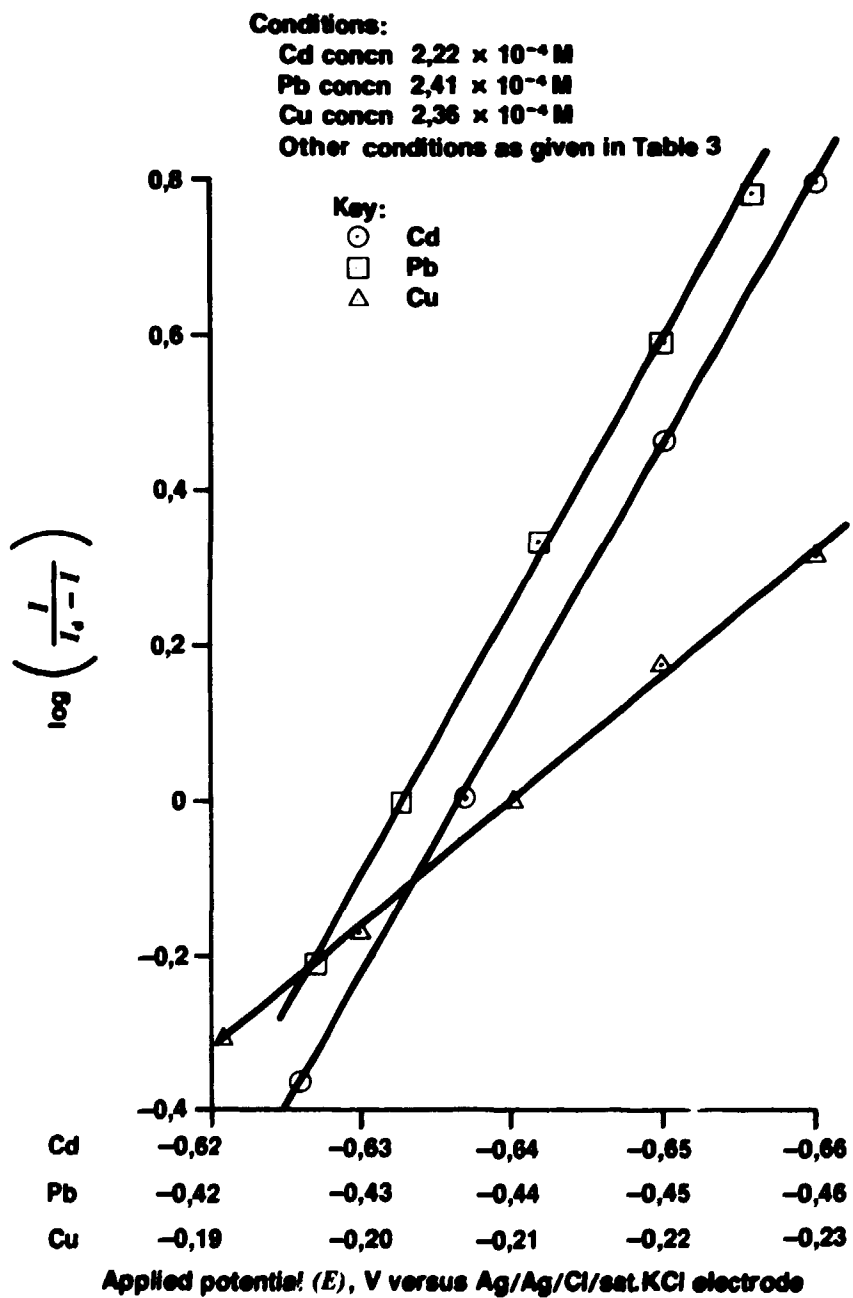


FIGURE 2. Plots of  $\log I/(I_a - I)$  versus  $E$  for cadmium, lead, and copper in 1 M ammonium chloride, 0,1 M citric acid, and 0,025 M ascorbic acid



DETERMINATION OF CADMIUM, LEAD, AND COPPER

Conditions:

Cd concn  $1,78 \times 10^{-10}M$

Hg concn  $1,25 \times 10^{-10}M$

Standard DPASV conditions as given in Section 2

Key:

○ Peak current ( $I_p$ )

◇ log slope

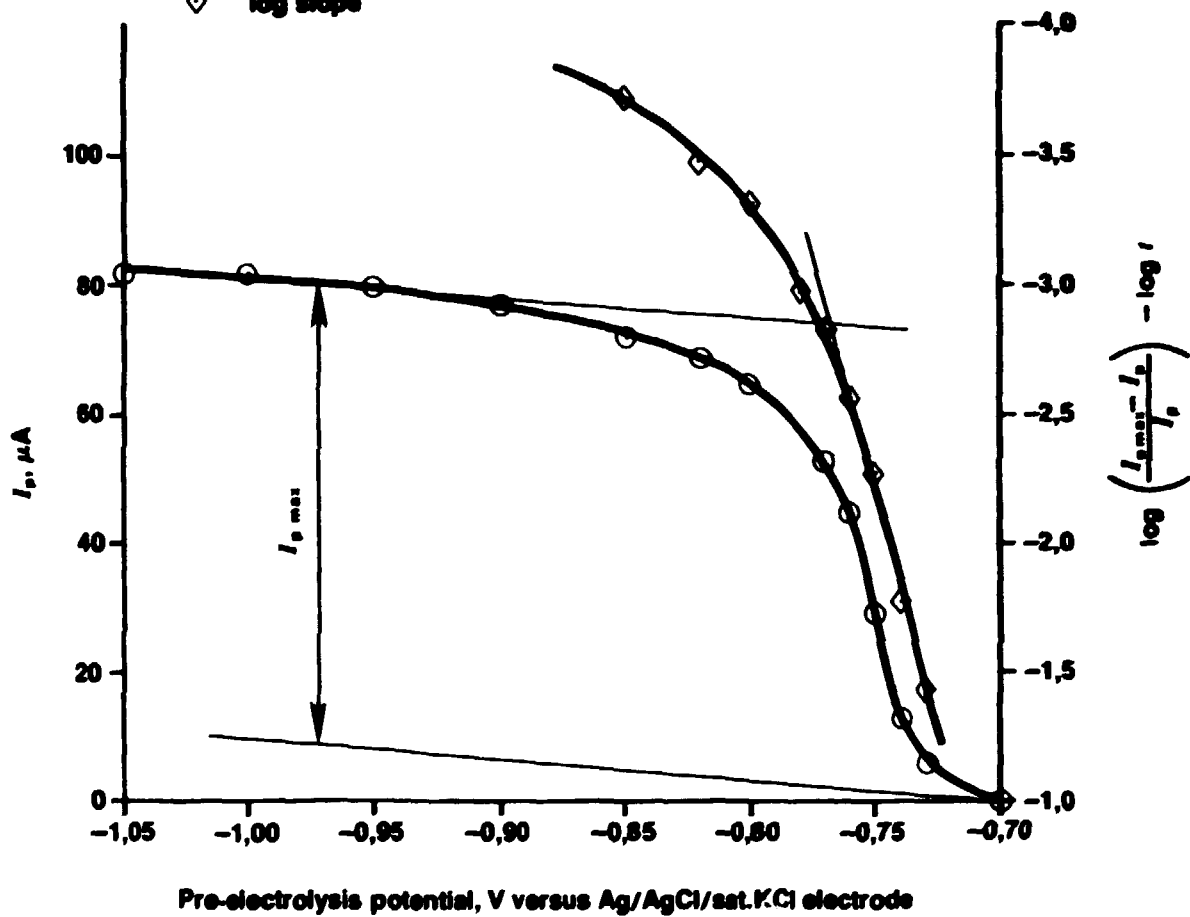


FIGURE 3. Effect of pre-electrolysis potential on the peak current of cadmium and the plot of log slope versus  $E$

DETERMINATION OF CADMIUM, LEAD, AND COPPER

Conditions:  
 Pb concn  $3,24 \times 10^{-6}$  M  
 Hg concn  $1,25 \times 10^{-6}$  M  
 DPASV as given in Section 2

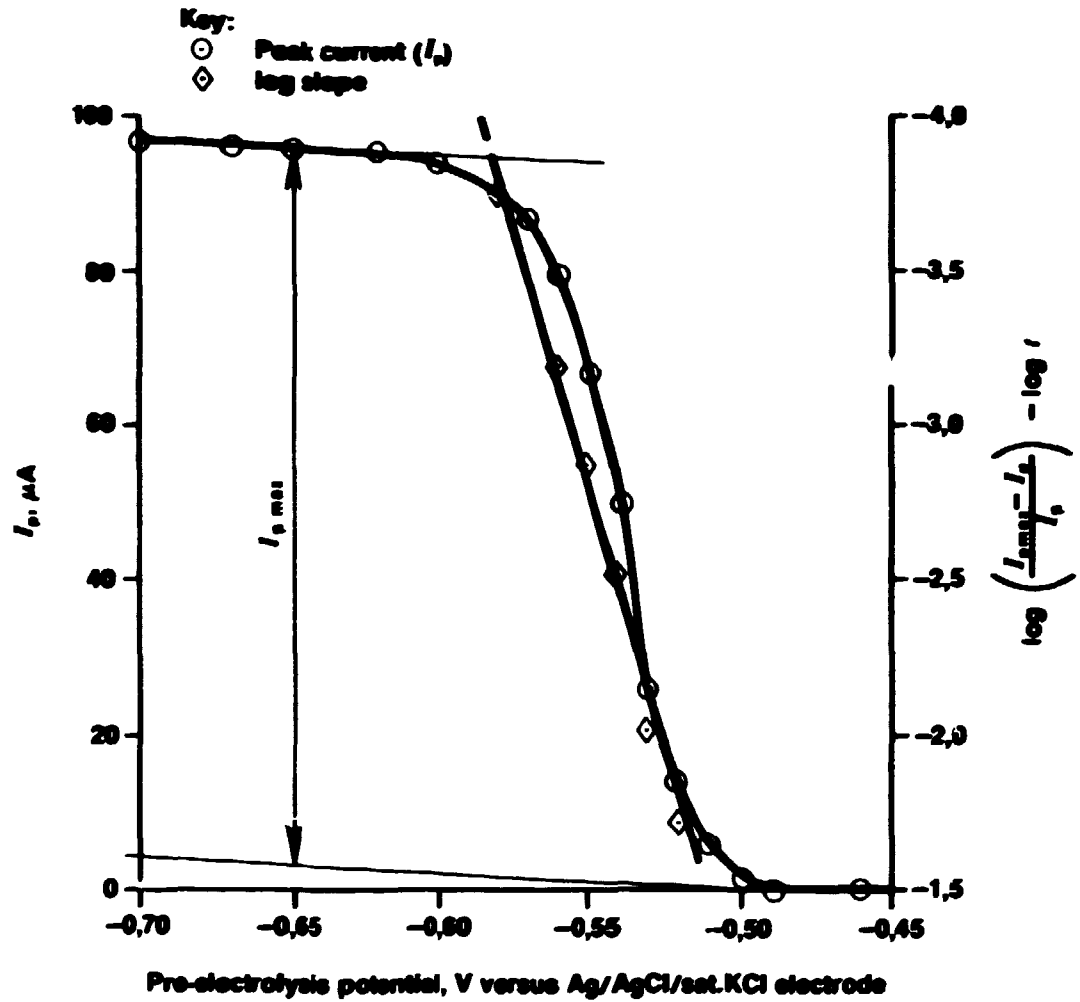


FIGURE 4. Effect of pre-electrolysis potential on the peak current of lead and the plot of log slope versus  $E$

DETERMINATION OF CADMIUM, LEAD, AND COPPER

Conditions:  
 Cu concn  $1.57 \times 10^{-7}$  M  
 Hg concn  $1.5 \times 10^{-4}$  M  
 Standard DPASV conditions as given in Section 2

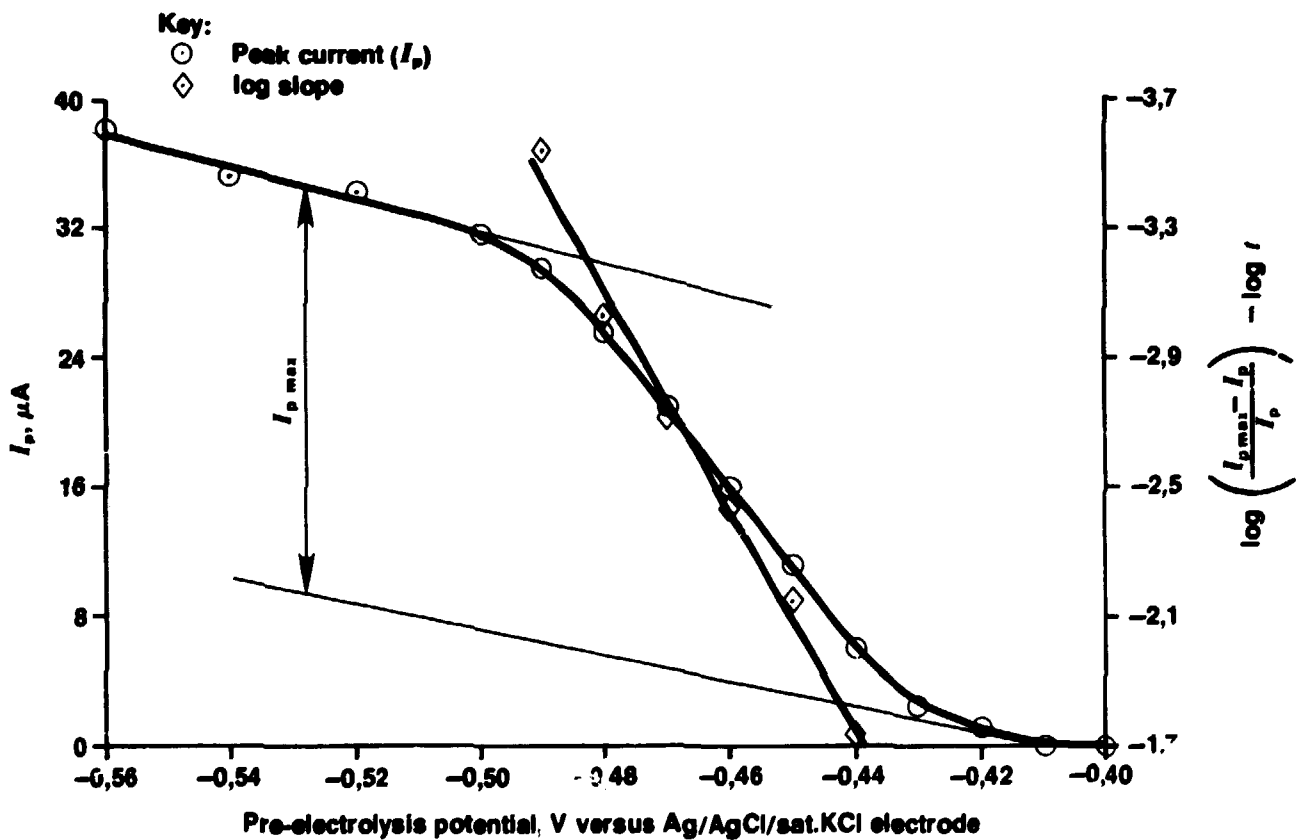


FIGURE 5. Effect of pre-electrolysis potential on the peak current of copper and the plot of log slope versus  $E$

DETERMINATION OF CADMIUM, LEAD, AND COPPER

Conditions:

Supporting electrolyte 1 M  $\text{NH}_4\text{Cl}$ , 0,1 M citric acid, and 0,025 M ascorbic acid

Pre-electrolysis  
d.c. ASV

300 s at  $-1,0\text{V}$  and 750 r/min  
20 mV/s

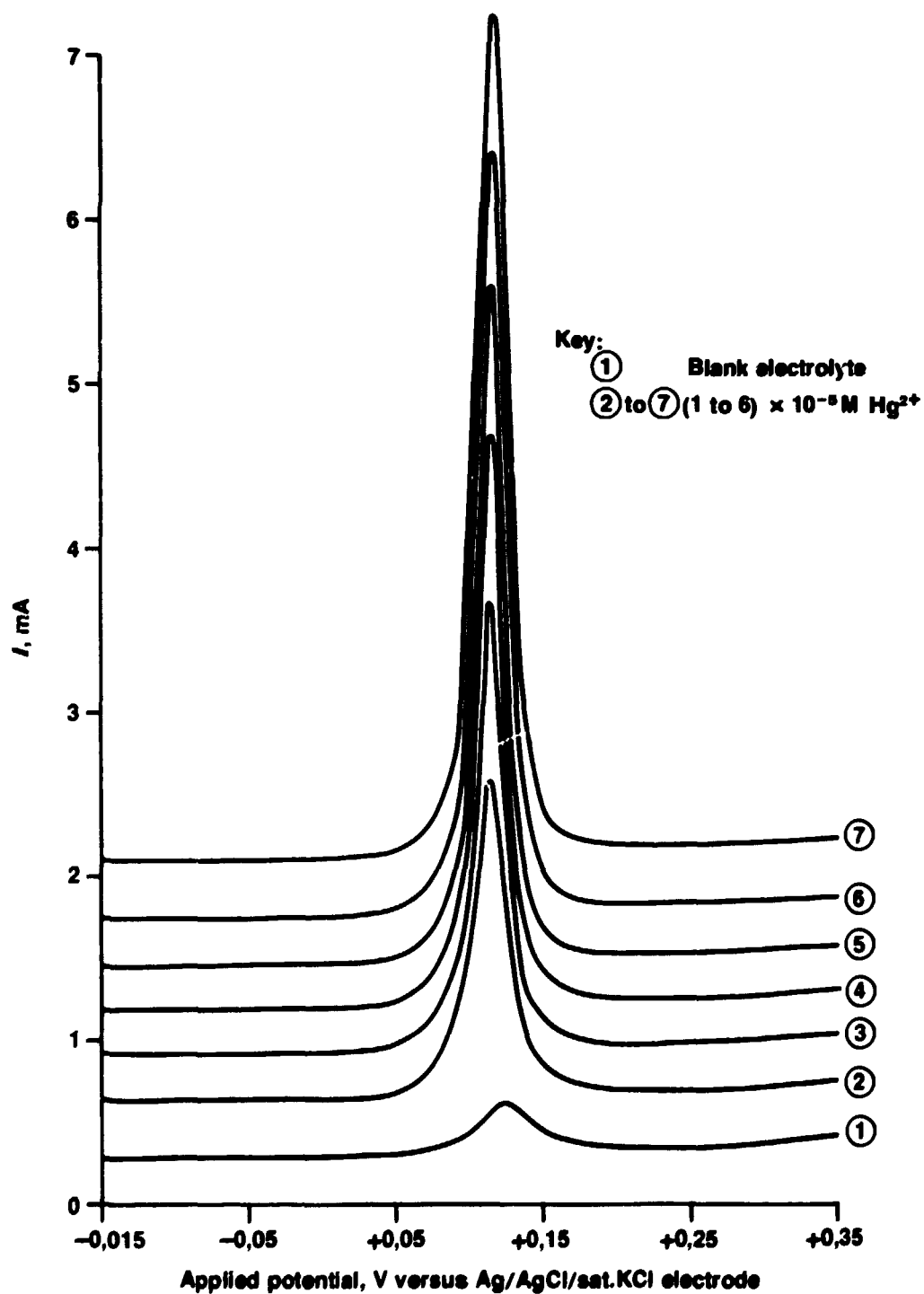


FIGURE 6. Anodic-stripping voltammetry of mercury at a rotating glassy-carbon electrode

DETERMINATION OF CADMIUM, LEAD, AND COPPER

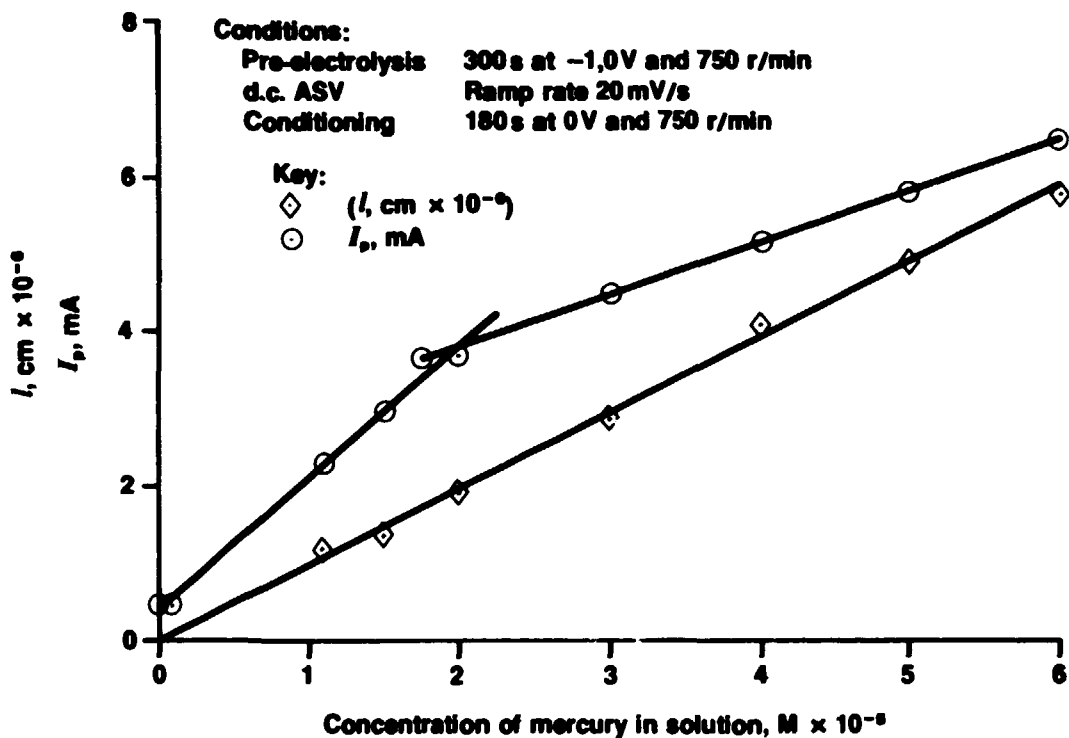


FIGURE 7. Dependence of peak current and film thickness on concentration of mercury in solution (linear-ramp stripping)

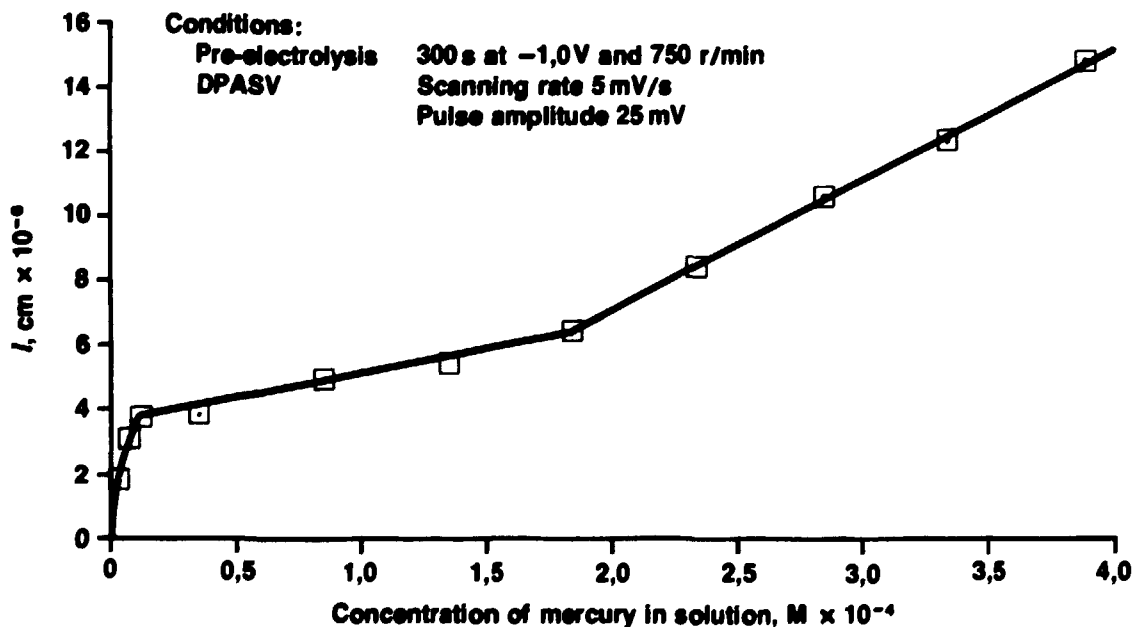


FIGURE 8. Dependence of the thickness of the thin mercury-film electrode on the concentration of the mercury in solution (differential pulse mode)

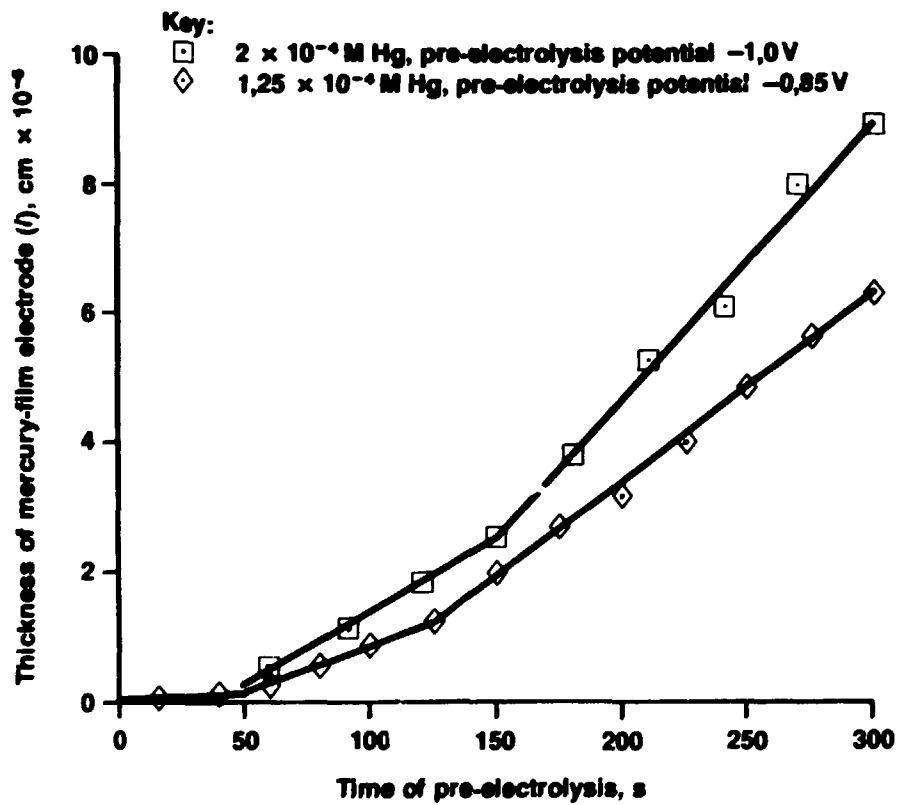


FIGURE 9. Dependence of film thickness on time of pre-electrolysis

DETERMINATION OF CADMIUM, LEAD, AND COPPER

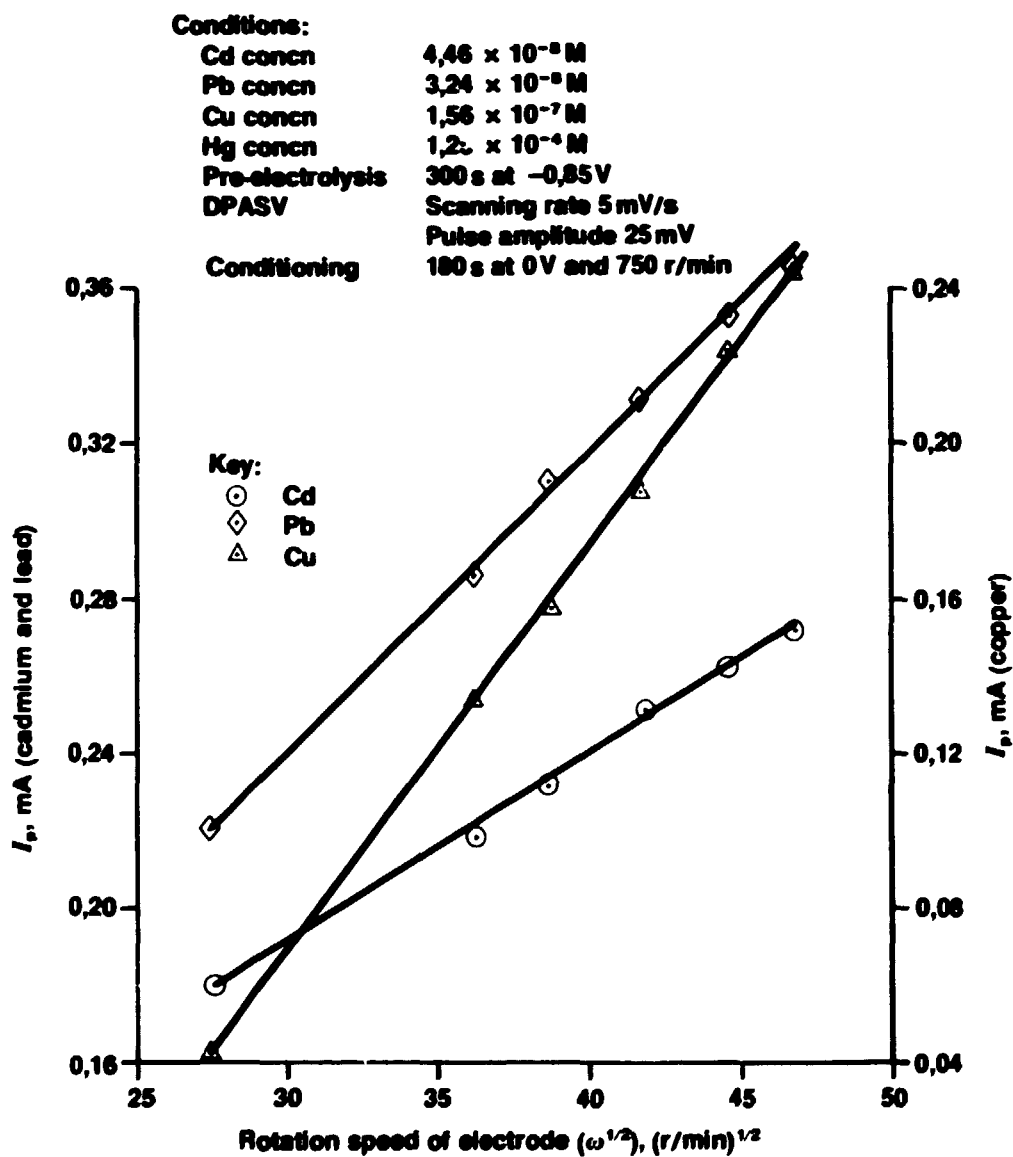


FIGURE 10. Dependence of peak current on rotation speed of thin mercury-film electrode

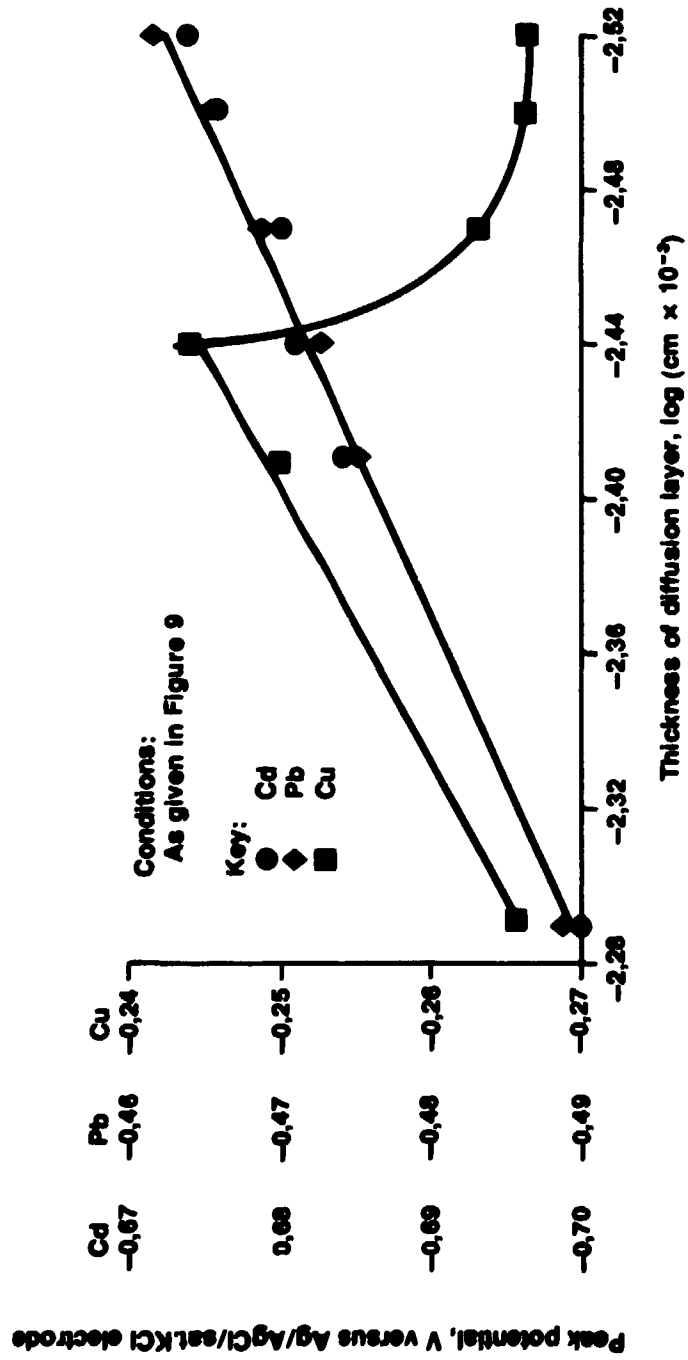


FIGURE 11. Dependence of peak potential on thickness of diffusion layer



DETERMINATION OF CADMIUM, LEAD, AND COPPER

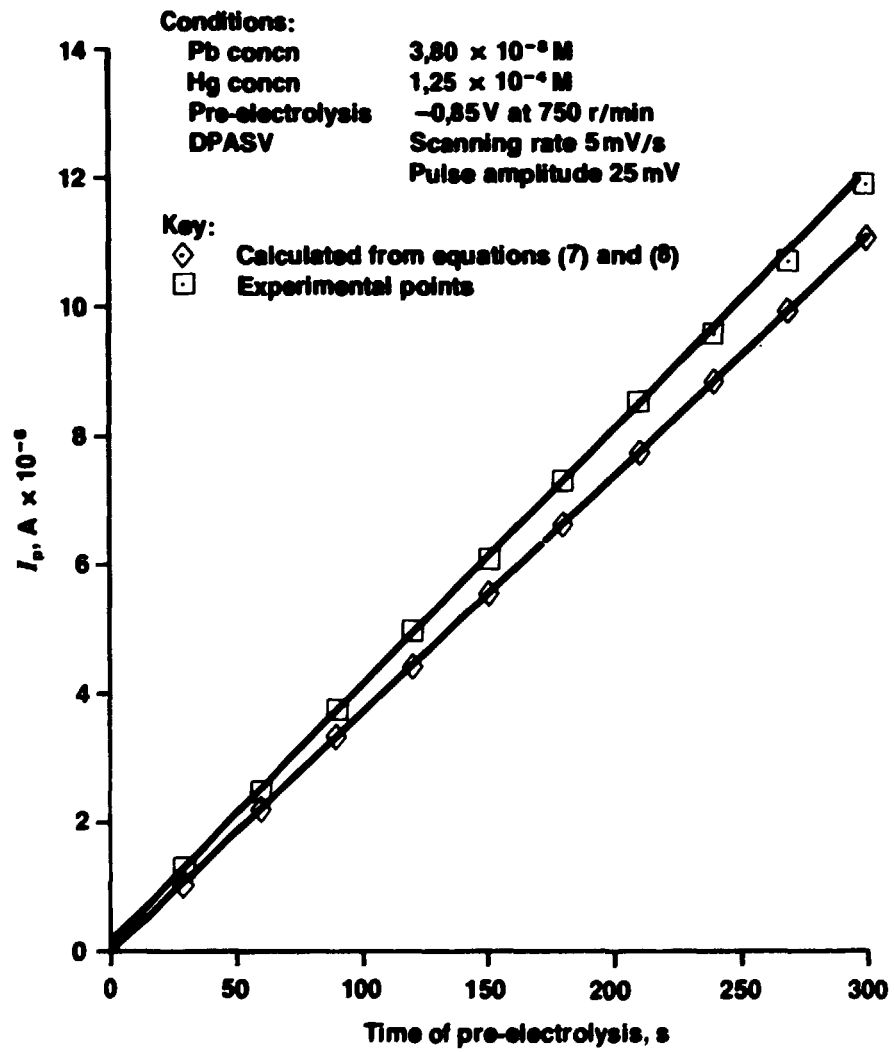


FIGURE 12. Dependence of peak currents for lead on time of pre-electrolysis

DETERMINATION OF CADMIUM, LEAD, AND COPPER

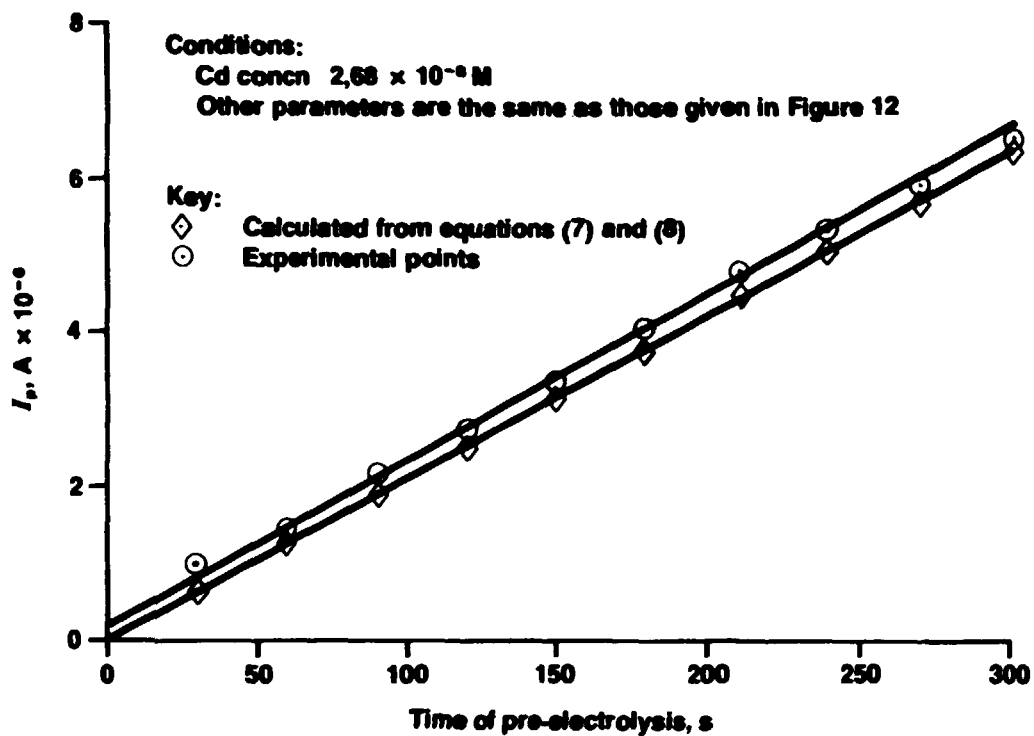


FIGURE 13. Dependence of peak currents for cadmium on time of pre-electrolysis

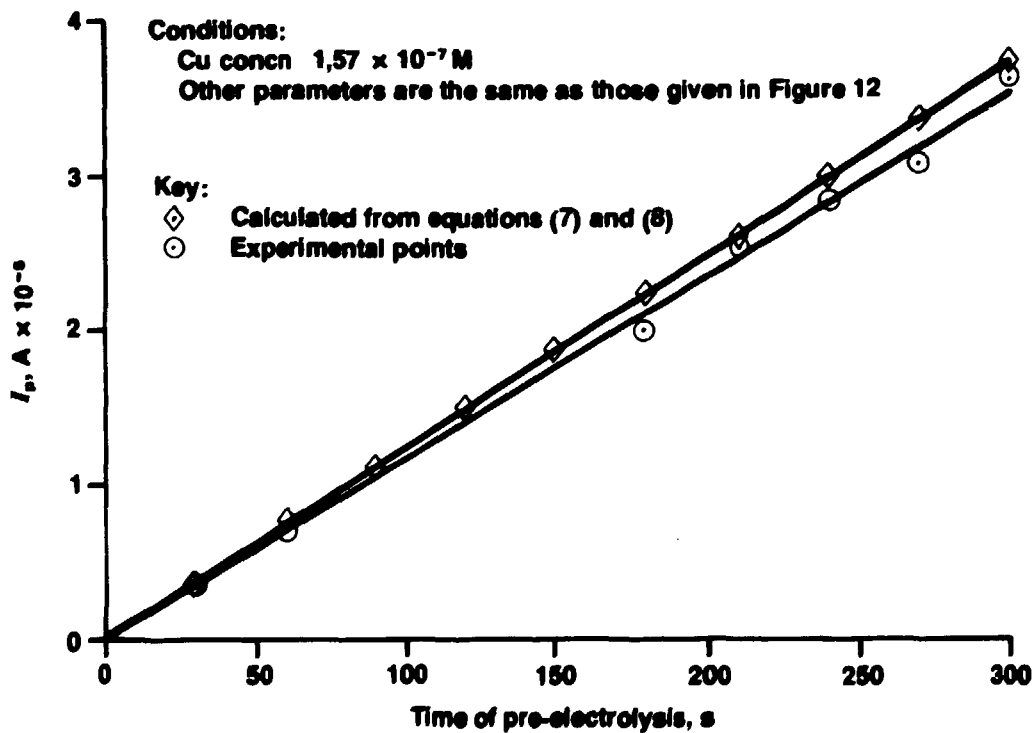


FIGURE 14. Dependence of peak currents for copper on time of pre-electrolysis

DETERMINATION OF CADMIUM, LEAD, AND COPPER

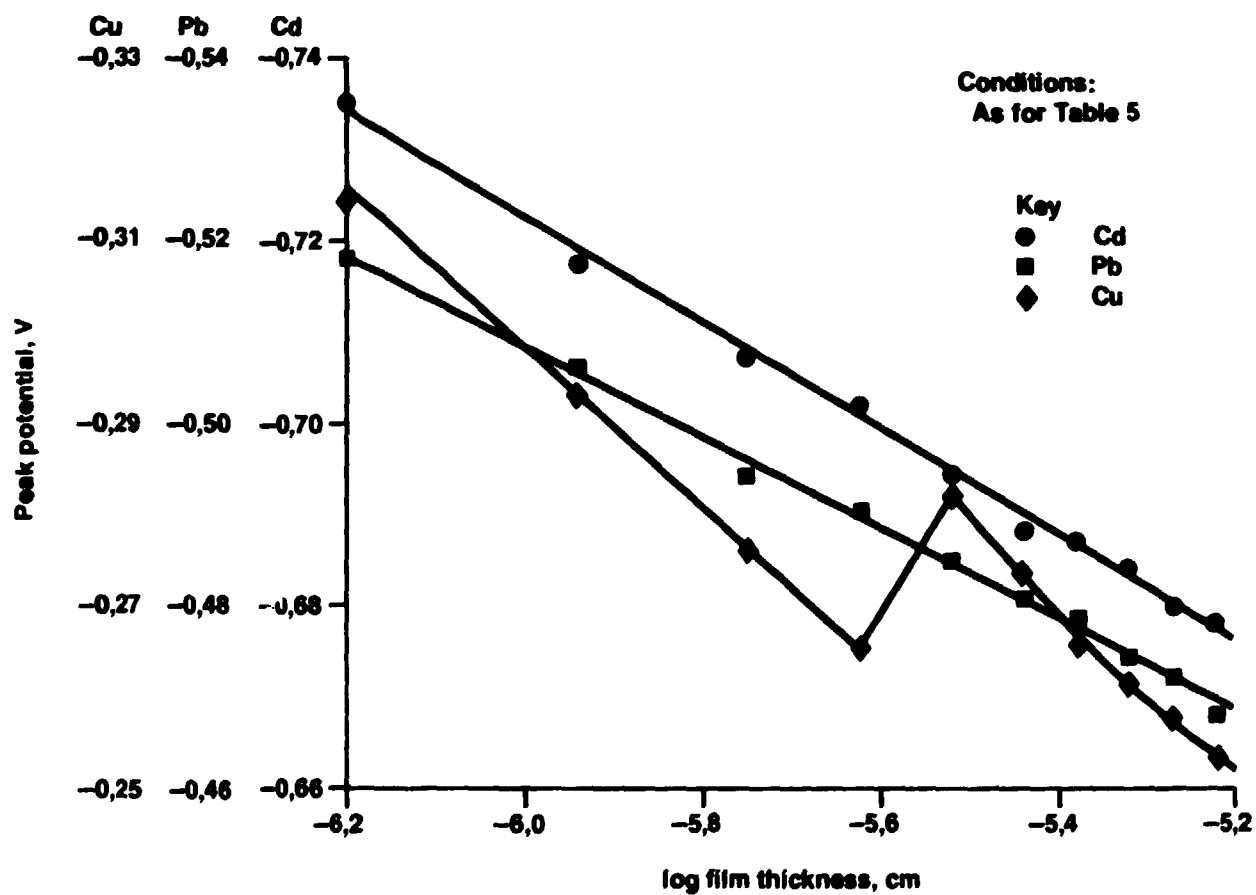


FIGURE 15. Dependence of peak potentials for cadmium, lead, and copper on the thickness of the thin mercury-film electrode

DETERMINATION OF CADMIUM, LEAD, AND COPPER

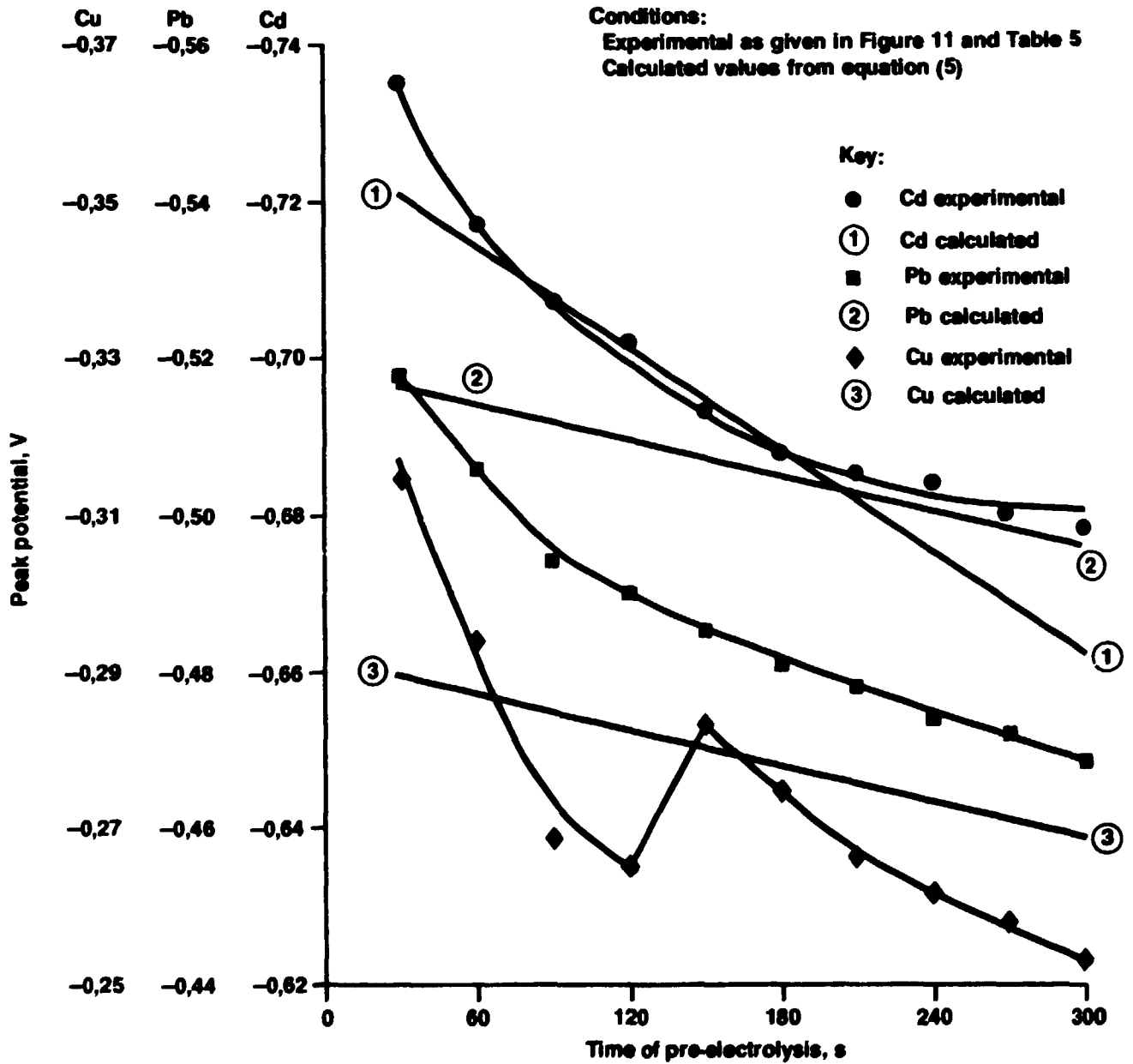


FIGURE 16. Dependence of peak potentials for cadmium, lead, and copper on time of pre-electrolysis

DETERMINATION OF CADMIUM, LEAD, AND COPPER

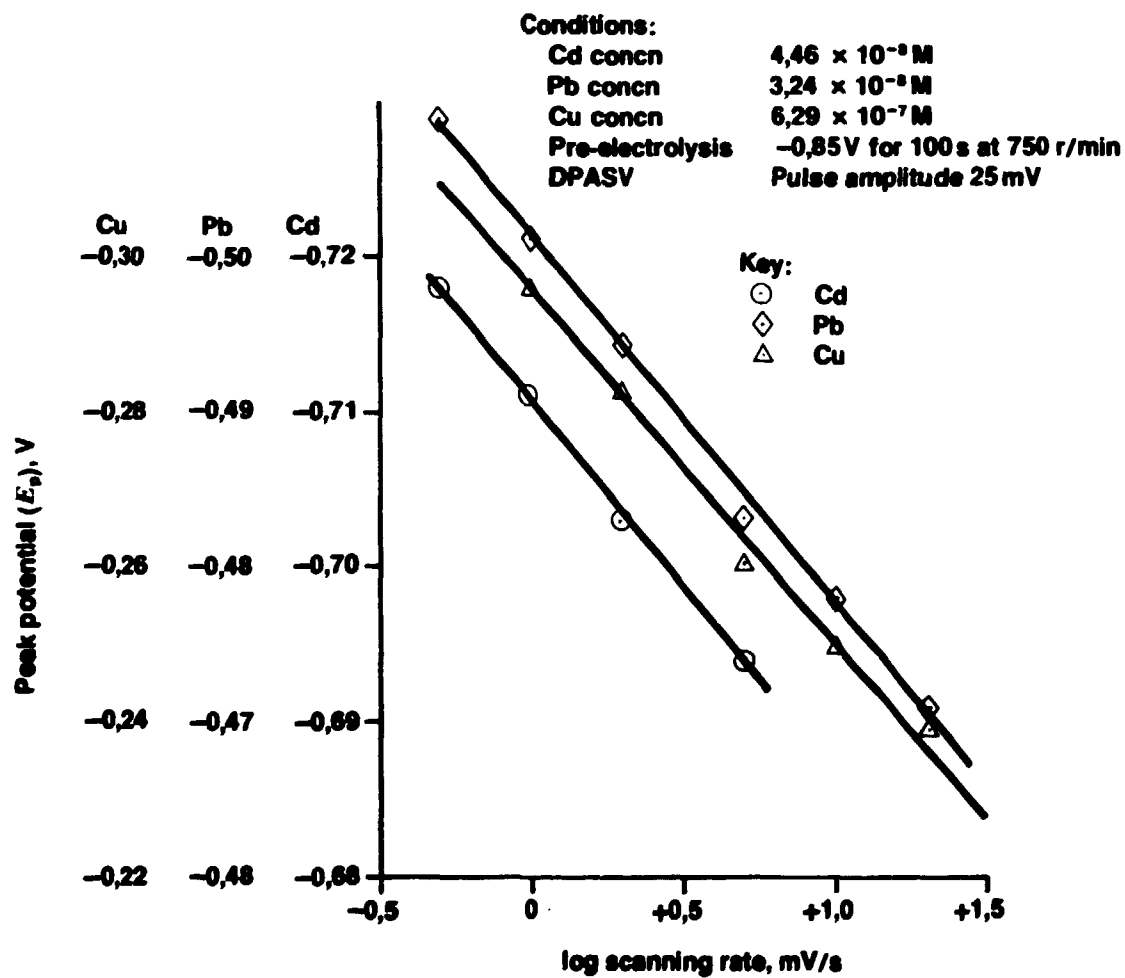


FIGURE 17. Dependence of peak potentials for cadmium, lead, and copper on scanning rate

DETERMINATION OF CADMIUM, LEAD, AND COPPER

Conditions:  
 Cd concn  $1,79 \times 10^{-8} \text{ M}$   
 Pb concn  $3,24 \times 10^{-8} \text{ M}$   
 Cu concn  $1,57 \times 10^{-7} \text{ M}$   
 Pre-electrolysis 300 s at  $-1,0 \text{ V}$  and 750 r/min

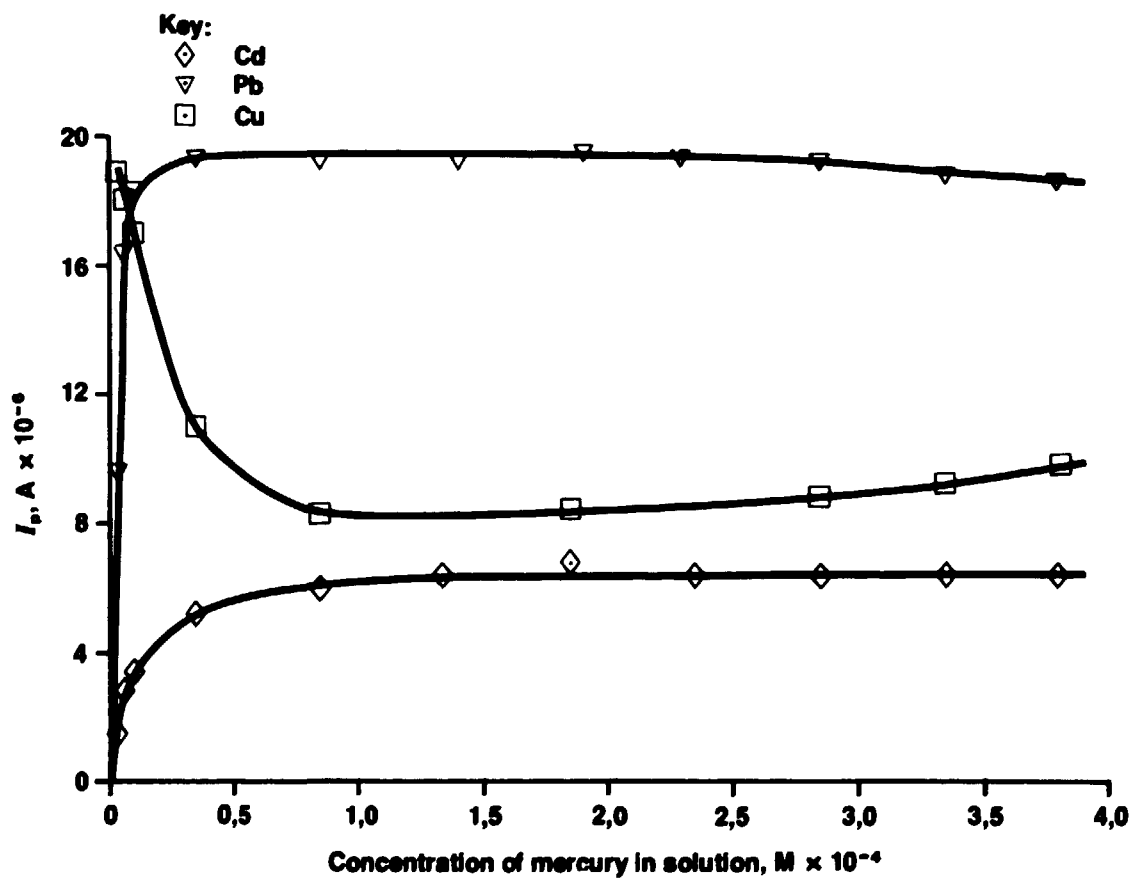


FIGURE 18. Dependence of peak currents for cadmium, lead, and copper on the concentration of mercury in solution

DETERMINATION OF CADMIUM, LEAD, AND COPPER

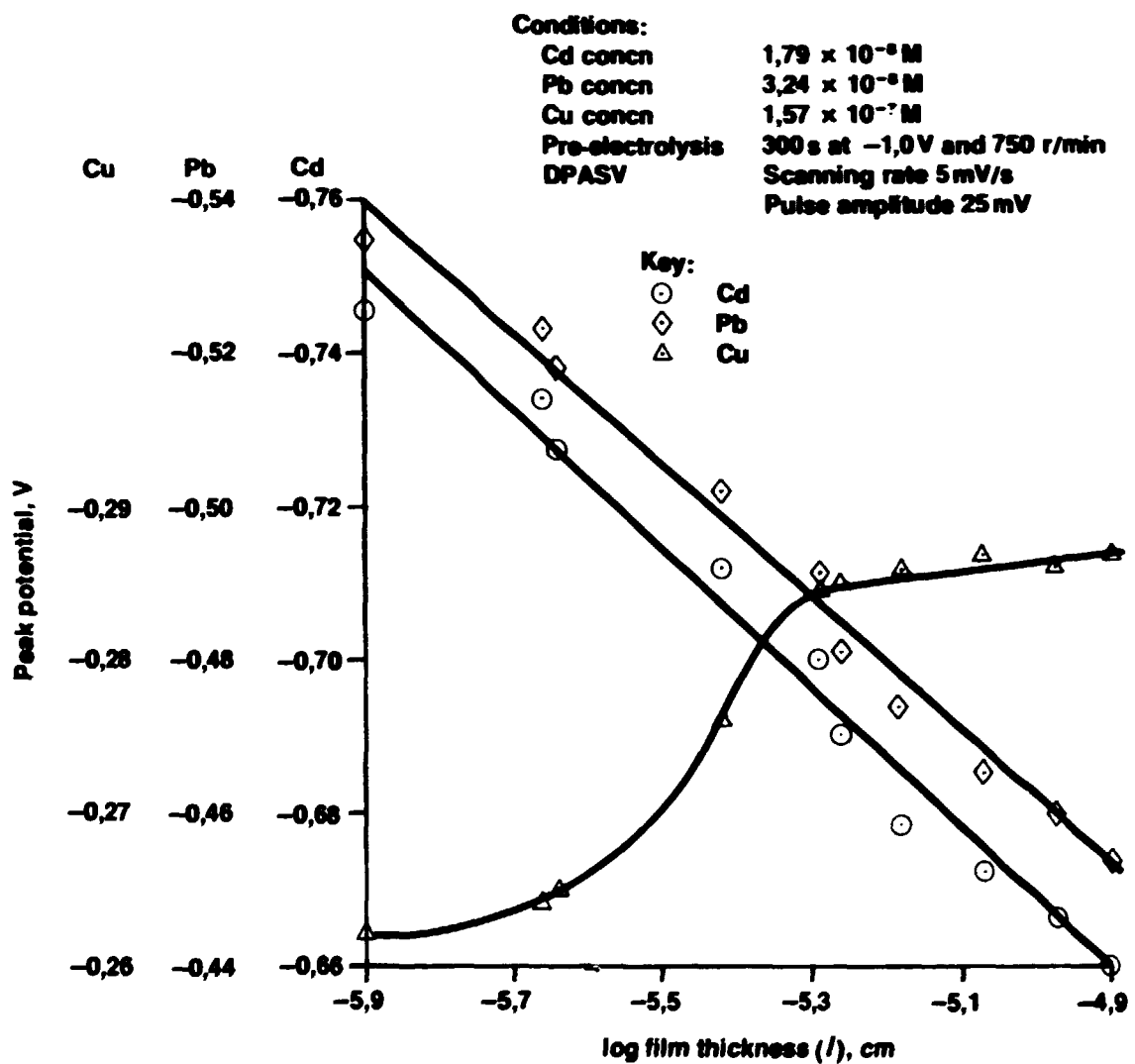


FIGURE 19. Dependence of peak potentials for cadmium, lead, and copper on the thickness of the thin mercury-film electrode

DETERMINATION OF CADMIUM, LEAD, AND COPPER

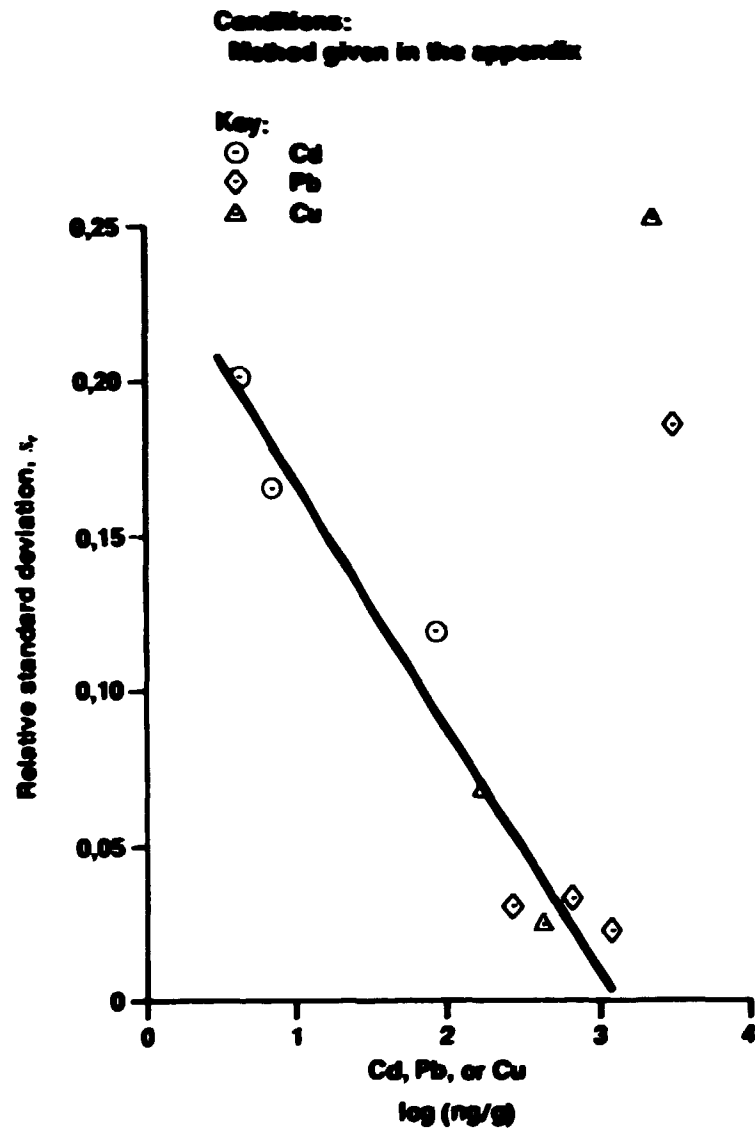


FIGURE 20. Relation between precision of results and concentration of metals in samples



E.1. Cadmium  
E.1. Lead  
E.1. Copper

## APPENDIX

### THE DETERMINATION, BY DIRECT DIFFERENTIAL PULSE ANODIC-STRIPPING VOLTAMMETRY AT A MERCURY-FILM ELECTRODE, OF CADMIUM, LEAD, AND COPPER IN GEOCHEMICAL REFERENCE MATERIALS (LABORATORY METHOD NO. 48/6)

#### 1. OUTLINE

The sample is dissolved in a mixture of hydrofluoric and perchloric acids in a closed Teflon cup in a pressure vessel either at ambient temperature or at 150°C. The solution is brought slowly to dryness in the same apparatus, and the residue is dissolved in a mixture of ammonium chloride, citric acid, and ascorbic acid. Cadmium, lead, and copper are then determined sequentially in the same aliquot volume of solution by differential pulse anodic-stripping voltammetry at a thin mercury-film electrode, the method of additions to the sample being used.

#### 2. APPLICATION

The procedure was applied to three SAROC samples of high purity (carbonatite, magnesite, and quartz) and two United States Geological Survey (USGS) samples, DTS 1 and BHVO 1. It should be applicable to the determination of acid-soluble cadmium (above 10 ng/g), and lead and copper (above 150 ng/g) in samples of similar high purity.

The accuracy of values returned for the USGS control samples was acceptable. The precision was related to the concentration of the metal in the sample, varying from a relative standard deviation of 0.2 at 50 ng/g to 0.03 above a metal concentration of 50 ng/g. Excluding sample dissolution, the analytical time is about 3 hours for one sequential determination of cadmium, lead, and copper.

#### 3. SPECIAL APPARATUS

- (1) *PARC 174A Polarographic Analyzer with 315 Automatic Controller*
- (2) *PARC Model RE 0074 X-Y Recorder*
- (3) *Metrohm 628 Rotating-disc Electrode with E 289/1 Glassy-carbon Tip*
- (4) *Metrohm EA/441/5 Ag/AgCl/sat.KCl Reference Electrode and Metrohm EA 282/1 Platinum-rod Auxiliary Electrode*
- (5) *Parr Type 4745 Pressure Vessels and 23 ml Type A255 Teflon Cups and Covers*
- (6) *Microlitre Pipette*  
Adjustable, up to 50 µl volume.
- (7) *Nitrogen-purification Train*  
Wash bottles containing vanadous chloride solution and wash water.

#### 4. REAGENTS

- (1) *Hydrofluoric Acid*  
J.T. Barker Chemicals, Ultrex, 49 per cent.
- (2) *Perchloric Acid*  
Merck Suprapur, about 70 per cent.
- (3) *Water*  
Triply distilled, and stored in a polythene bottle.
- (4) *Electrolyte of 1,0 M Ammonium Chloride, 0,1 M Citric Acid, and 0,025 M Ascorbic Acid*  
Dissolve 53,5 g of A.R.-grade ammonium chloride and 21 g of A.R.-grade citric acid monohydrate in about 600 ml of triply distilled water, and add 4,5 g of ascorbic acid (chemical pure). Dilute to 1 litre and purify as follows. Transfer the solution to a large separating funnel, and add slowly, with swirling, 25 ml of an 8 per cent aqueous solution of ammonium pyrrolidine dithiocarbamate. Agitate gently for 10 minutes to clear the milky solution and complex the metallic impurities. Add 50 ml of Merck A.R.-grade chloroform, and shake for 20 minutes. Separate, and discard the chloroform layer. Add 5 ml of 1 per cent ammonium pyrrolidine dithiocarbamate solution to the aqueous layer, repeat the extraction, and again discard the chloroform layer. Wash the aqueous

electrolyte twice by shaking each time with 50 ml of chloroform. Discard the final (organic) phase. Remove the dissolved and entrained chloroform from the electrolyte by bubbling nitrogen through the warm solution until it is free from any smell of the solvent.

(5) **Mercuric Nitrate Solution,  $5 \times 10^{-2}M$**

Dissolve 1.0 g of mercury (triply distilled) in 6.5 ml of 10 per cent (v/v) nitric acid solution (prepared from B.D.H. Aristar reagent). Take the solution down to fumes to oxidize any Hg(I). Dissolve the residue in triply distilled water, transfer to a 100 ml volumetric flask, and dilute to the mark.

(6) **Standard Solutions of Cadmium, Lead, and Copper**

From the pure metals, prepare separate stock solutions of cadmium, lead, and copper containing 1 g per litre of 10 per cent nitric acid. By a series of dilutions with further nitric acid, prepare intermediate solutions containing 20 mg of metals per litre. (These solutions are stable for at least 2 weeks.) Finally, by further dilution with triply distilled water, prepare daily working solutions containing cadmium (1.0 mg/l), lead (5.0 mg/l), and copper (5.0 mg/l).

## 5. PROCEDURE

- a. Weigh 0.50 g of sample into a Teflon cup, and add a little water to form a slurry and so slow down the subsequent reaction. Add 0.1 ml of perchloric acid, and then 3 ml of hydrofluoric acid.
- b. Cover the cup with a small watch-glass until the reaction has moderated. For materials insoluble at room temperature, cover the cup with a Teflon lid, enclose in a pressure vessel, and hold overnight in an oven at 150°C.
- c. Allow to cool, remove the cup from the pressure vessel, and take the contents slowly to dryness. Transfer to a sand-bath and fume briefly.
- d. Dissolve the residue in about 5 ml of electrolyte and transfer to a 20 ml grade-A volumetric flask with three portions of electrolyte. Dilute to volume and mix.
- e. Using a clean, dry pipette, transfer 15.0 ml of solution to a dry polarographic cell, and add 50  $\mu$ l of  $5 \times 10^{-2}M$  mercuric nitrate solution. De-aerate with purified nitrogen for 15 minutes, and then maintain an inert atmosphere above the surface of the electrolyte.
- f. Record voltammograms for cadmium, lead, and copper under the following conditions.
  - (i) For cadmium, pre-electrolyse at -0.85 V for 300 s at 750 r/min. Allow a quiescent period of 15 s. Strip to -0.55 V at 5 mV/s, a pulse amplitude of 25 mV, and current density of 0.5 mA for full-scale deflection. Sequentially, add 15  $\mu$ l aliquot volumes of cadmium solution (1 mg/l) to give final cadmium concentrations of 1.2  $\mu$ g/l, 3  $\mu$ g/l, and 4  $\mu$ g/l in the total electrolyte solution. Record voltammograms between additions.
  - (ii) For lead, pre-electrolyse at -0.65 V for 100 s at 750 r/min. Allow a quiescent period of 15 s. Strip to -0.45 V at 5 mV/s, a pulse amplitude of 25 mV, and current density of 2.0 mA for full-scale deflection. Add sequential volumes of 30  $\mu$ l of lead solution (5 mg/l) to give lead concentrations of 10, 20, 30, and 40  $\mu$ g/l in the total electrolyte solution. Record voltammograms between additions.
  - (iii) For copper, pre-electrolyse at -0.45 V for 100 s at 750 r/min. Allow a quiescent period of 15 s. Strip to -0.05 V at 5 mV/s, a pulse amplitude of 25 mV, and current density of 2.0 mA for full-scale deflection. Add sequential volumes of 45  $\mu$ l of copper solution (5 mg/l) to give final copper concentrations of 15  $\mu$ g/l, 30  $\mu$ g/l, 45  $\mu$ g/l, and 60  $\mu$ g/l. Record voltammograms between additions.
- g. Condition electrochemically the rotating glassy-carbon electrode for 90 s before each pre-electrolysis step by holding at 0 V and 750 r/min.
- h. After each determination (15 voltammograms), renew the surface of the glassy-carbon electrode by polishing briefly with a slurry of  $\alpha$ -alumina on a plastic cloth (Metrohm EA 276 A). Wash the electrodes and polarographic cell thoroughly with distilled water, and soak in 0.1 M nitric acid for at least 30 minutes before the next determination. When the electrodes are not in use, hold them in 0.1 M nitric acid.
- i. Prepare blank solutions and record their voltammograms as follows.
  - (i) Repeat steps a to d of the procedure, but omit the sample. Pipette 15.0 ml of blank solution into a dry polarographic cell, add 15  $\mu$ l of  $5 \times 10^{-2}M$  mercuric nitrate solution, and de-aerate for 15 min.
  - (ii) Record a voltammogram for cadmium, lead, and copper by pre-electrolysing for 300 s at -1.0 V and 750 r/min. After 15 s of quiescence, strip to -0.1 V at 5 mV/s, a pulse amplitude of 25 mV, and current density of 1.0 mA for full-scale deflection.

## DETERMINATION OF CADMIUM, LEAD, AND COPPER

- (iii) Spike the blank solution with aliquot volumes of working solutions of cadmium, lead, and copper to give final concentrations of  $1 \mu\text{g/l}$  for cadmium and  $5 \mu\text{g/l}$  for lead and copper. Record the voltammogram of the spiked blank solution. Repeat for two more additions.
- j. Plot graphs of peak height versus concentration for cadmium, lead, and copper in sample and blank solutions. Determine the concentrations of metals from the intercepts on the  $x$ -axes. Alternatively, determine the intercepts using least-squares linear-regression analysis and a programmed desk-top computer.

### 6. CALCULATION

$$\text{Cadmium, lead, or copper in sample, ng/g} = (A - B) \frac{C}{D}$$

where

$A$  is the concentration of metal in the sample solution ( $\mu\text{g/l}$ ),

$B$  is the concentration of metal in the blank solution ( $\mu\text{g/l}$ ),

$C$  is the volume of the sample or the blank solution, i.e., 20 ml, and

$D$  is the mass of the sample taken for analysis, i.e., 0.5 g.