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**THE DETERMINATION, BY DIFFERENTIAL PULSE
ANODIC-STRIPPING VOLTAMMETRY AT THE
THIN MERCURY-FILM ELECTRODE, OF
CADMIUM AND THALLIUM IN SIX NIMROC
REFERENCE MATERIALS**

by

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25th September, 1981



NATIONAL INSTITUTE FOR METALLURGY

ANALYTICAL CHEMISTRY DIVISION

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SYNOPSIS

A previously reported procedure has been extended to include the determination of thallium. In samples where thallium occurred in the presence of relatively high concentrations of cadmium, the stripping peak for cadmium was first suppressed with a non-ionic surface-active agent, Triton X-100. Cadmium and thallium were determined directly in six NIMROC reference materials without interference from iron(III), in a reducing electrolyte, which is also a complexing agent, consisting of 1 M ammonium chloride, 0,1 M citric acid, and 0,025 M ascorbic acid. Interelement interferences were eliminated by the use of a mercury-film electrode of adequate thickness. The limits of detection for cadmium were 10 ng/g and those for thallium 20 ng/g.

SAMEVATTING

'n Werkwyse waaroor daar reeds verslag gedoen is, is uitgebrei om die bepaling van tallium in te sluit. In monsters waarin tallium in die aanwesigheid van betreklik hoë kadmiumkonsentrasies voorkom, is die stroospits vir kadmium eers met 'n nie-ioniese oppervlakaktiewe middel, Triton X-100, onderdruk. Kadmium en tallium is in ses NIMROC-verwysingsmateriale regstreeks, sonder steuring van yster(III), bepaal in 'n reduserende elektroliet en komplekseerder bestaande uit 1 M-ammoniumchloried, 0,1 M-sitroensuur en 0,025 M-askorbiensuur. Tussenelementinterferensie is uitgeskakel deur die gebruik van 'n kwiklaagelektrode wat dik genoeg is. Die opsporingsgrens vir kadmium was 10 ng/g en vir tallium 20 ng/g.

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1. INTRODUCTION

In studies on pollution of the environment, cadmium has aroused interest because of its toxicity and ubiquity. Interpretation of the differences between polluted and unpolluted areas requires accurate data on cadmium in a wide range of geochemical samples, which are scanty at present.

Thallium is among the elements that occur in very low concentrations in natural silicates and are of interest in the study of geochemistry, and information on its distribution in rocks and minerals is needed to promote a better understanding of geological processes. Data for thallium in geochemical reference materials are also scanty or have not been well established.

Separation and preconcentration are usually necessary in the determination of cadmium and thallium in silicate rocks and sediments by instrumental techniques other than anodic-stripping voltammetry (ASV). For example, anion exchange has been employed before emission spectrography¹, liquid-liquid extraction before conventional atomic-absorption spectroscopy (AAS)², and fractional distillation before AAS with electrothermal atomization³.

The direct determination, by differential pulse ASV (DPASV) from a thin mercury-film electrode (TMFE), of cadmium in three South African reference materials has been described⁴. This report describes the extension of that procedure to the simultaneous determination of cadmium and thallium in six other South African reference materials. Because of the volatility of some thallium compounds, the samples were decomposed in a 15:1 mixture of hydrofluoric and nitric acids, and the excess hydrofluoric and fluosilicic acids were expelled at low temperatures. Distortion of the thallium peak in the presence of high concentrations of cadmium was eliminated by suppression of the stripping peak of the latter with Triton X-100 after it had been estimated by the method of additions.

2. EXPERIMENTAL METHODS

The three-electrode system comprised a rotating-disc electrode (Metrohm 628) with a synchronous multispeed controller and glassy-carbon tip (Metrohm EA 289/1), a platinum-rod auxiliary electrode (Metrohm EA 282/1), and an Ag/AgCl saturated KCl reference electrode (Metrohm EA 441/5) with a porous Vycor t.i.t. A PARC 174A Polarographic Analyzer and 315 Automatic Controller were combined for automated DPASV, and voltammograms were drawn on a Model RE 0074 X-Y recorder. Oxygen was removed from the sample solutions with high-purity nitrogen purified further by being bubbled through a wash bottle of vanadous sulphate followed by wash water.

The supporting electrolyte was a purified solution of 1 M ammonium chloride, 0.1 M citric acid, and 0.025 M ascorbic acid, spiked with a high-purity solution of mercuric nitrate to give a final mercury concentration of 2×10^{-4} M. The TMFE was formed *in situ* during the pre-electrolysis period, which was 300 seconds at -0.85 V, and the electrode rotated at 750 r/min. After a quiescent period of 15 seconds, the cadmium and thallium were stripped at a scanning rate of 5 mV/s with pulses having an amplitude of 25 mV. Cadmium was determined first by the method of additions. The cadmium peak was then suppressed by the appropriate addition of a non-ionic surface-active agent, Triton X-100, and thallium was determined, also by the method of additions.

At the commencement of each cycle, the rotating glassy-carbon electrode (RGCE) was conditioned electrochemically at 0 V for 90 seconds at a speed of 750 r/min. Between determinations, the tip of the electrode was conditioned mechanically by brief polishing with a slurry of α -alumina and washing, after which all the electrodes and the polarographic cell were soaked in 0.1 M high-purity nitric acid for at least 0.5 hours.

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

2.1. Voltammetry of Thallium in 1 M Ammonium Chloride, 0.1 M Citric Acid, and 0.025 M Ascorbic Acid

The effect of pre-electrolysis potential on the peak current for thallium is shown in Figure 1. When the pre-electrolysis potential was shifted anodically, a limiting potential was eventually reached at about -0.97 V, where the peak current was no longer a maximum, and beyond which it fell sharply to 0. The resulting curve (pseudopolarogram) was treated as a conventional current-potential polarogram, and the maximum or limiting peak current (I_{pmax}) at the pseudo-half-wave potential ($E_{1/2}^*$) was determined after the method of Brown and Kowalski⁵, as shown in Figure 1. When the criterion of Meites⁶ was used in determination of the slope of a reversible anodic wave,

$$E_{3/4} - E_{1/4} = \frac{0.0564}{n} \text{ V}, \dots \dots \dots (1)$$

the slope of the pseudopolarogram suggested a reversible single-electron reduction with

$$E_{3/4}^* - E_{1/4}^* = 0,051 \text{ V.}$$

Zirino and Kounaves⁷ derived (theoretically) the following relation for the reversible current-potential pseudopolarogram:

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

where

- E_d is the deposition or pre-electrolysis potential,
- E° is the standard potential for the amalgam electrode,
- I_p is the peak current at any given value of E_d ,
- I_{pmax} is the limiting peak current,
- k is a constant that includes 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
- β is RT/nF , where these have their usual notations.

For constant electrode area and rate of rotation, a plot of

$$\log \left(\frac{I_{pmax} - I_p}{I_p} \right) - \log t \text{ versus the deposition potential}$$

should therefore give a straight line of slope $n/2,303 \text{ RT}$ or $n/0,0591$ at 25°C . A plot of the pseudopolarogram for thallium is given in Figure 2. The slope is 17,0, giving a value for n of 1,00, which suggests, once more, a reversible single-electron reaction.

Figure 3 shows the effect of the mercury concentration in the supporting electrolyte (and hence the thickness of the TMFE deposited *in situ*) on the peak current and potential of thallium for mercury concentrations in the 10^{-6} M range. For the thallium concentration that had been chosen there was a critical concentration range and mercury-film thickness over which the peak current increased from zero to a maximum value. This increase was marked by an accompanying anodic shift in peak potential. Such trends are normal for a metal that is highly soluble in mercury, and were observed also for cadmium and lead in an earlier investigation⁴.

Figure 4 illustrates the dependence on the scanning rate of the peak current and peak width at half-peak height for cadmium and thallium. Peak currents gave a parabolic response with their maxima at about 10 mV/s . The form of these curves agrees with that shown by Copeland *et al.*⁸ for the differential pulse stripping of lead from a TMFE, and confirms the results obtained previously for lead and copper under similar conditions⁴. For scanning rates faster than 1 mV/s , the peak widths at half-peak height for cadmium and thallium increased linearly with increase in the scanning rate. The peak potential of thallium shifted anodically as a function of the log of the scanning rate (Figure 5), a result that agreed with the relation expressed by Batley and Florence⁹ for the stripping-peak potential (E_p) at a thin-film electrode as follows:

$$E_p = E_{1/2} + \left(\frac{2,3RT}{nF} \right) \log \left(\frac{\sigma nF l v}{D_M RT} \right), \dots \dots \dots (3)$$

where

- $E_{1/2}$ is the polarographic half-wave potential (V),
- D_M is the diffusion coefficient of metal ion (cm^2/s),
- σ 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).

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From this equation it can be predicted that, if the stirrer speed and the thickness of the mercury film are constant, the greatest shifts in E_p should occur with singly charged ions. This prediction was found to be in agreement with experimental results, since the slope for thallium (single-electron reaction) in Figure 5 was approximately twice those determined for cadmium, lead, and copper (two-electron reactions) in an earlier study¹⁰.

2.2. Resolution of the Stripping Peaks for Cadmium and Thallium

For the determination of very low concentrations of cadmium and thallium in solution (below 10^{-6} M for cadmium), a corresponding TMFE, equivalent to about 2.7×10^{-5} M mercury in solution, is required so that acceptable limits of detection can be realized. Under these conditions, the stripping peaks for cadmium and thallium were not completely resolved. However, intermetallic interference was absent and thallium had no effect on the peak current of 6×10^{-9} M cadmium until it was present at concentrations four times higher. Above this concentration ratio, the stripping peak for cadmium was hidden by the cathodic slope of the thallium peak, and the maximum peak current was proportional to the concentration of thallium present in solution (Figure 6).

TABLE I

Effect of mercury concentration on resolution of the peaks for cadmium and thallium when stripped from thin mercury films deposited in situ

Conditions:
 Cd concn 1.78×10^{-8} M
 Tl concn 1.47×10^{-7} M
 Pre-electrolysis 300 s at -1.0 V and 750 r/min
 DPASV Scanning rate 5 mV/s
 Pulse amplitude 25 mV
 Conditioning 90 s at 0 V and 750 r/min

Mercury concn M	Peak potential, V		Difference in peak potentials V	Peak current $A \times 10^{-5}$	
	Cd	Tl		Cd	Tl
1.0×10^{-5}	-0.658		} Not resolved	1.28	
2.67×10^{-5}	-0.615			2.11	
5.34×10^{-5}	-0.635	-0.585	50	0.43	2.08
8.01×10^{-5}	-0.630	-0.565	65	0.43	2.03
1.07×10^{-4}	-0.615	-0.547	68	0.86	2.00
1.33×10^{-4}	-0.612	-0.535	77	0.84	2.00
1.60×10^{-4}	-0.610	-0.523	87	0.84	1.98
2.14×10^{-4}	-0.607	-0.515	92	0.82	1.90
2.61×10^{-4}	-0.600	-0.507	93	0.86	1.84

Resolution could be improved considerably by increase of the thickness of the mercury-film electrode (i.e., of the concentration of mercury in solution) for a constant time of pre-electrolysis (Table I). With increase in the mercury concentration, and hence thickness of the TMFE, the peak potentials of cadmium and thallium shifted anodically, the displacement for thallium being almost twice that for cadmium, as could have been predicted from equation (3). The results shown in Table I confirm that the stripping peak for cadmium could be resolved in the presence of a thallium concentration almost ten times higher than that of cadmium by the addition of mercury to give a concentration of 1.07×10^{-4} M to the solution. In practice, a mercury concentration of 1.67×10^{-4} M was normally chosen, being increased to 2.5×10^{-4} M for very unfavourable ratios of cadmium to thallium i.e., 1 : 27 for United States Geological Survey (USGS) sample USGS-GSPI.

2.3. Suppression of the Peak Current for Cadmium with Triton X-100

Surface-active agents that are electrochemically inactive have been employed for selective inhibition of the electrochemical reduction of certain metals at the dropping-mercury electrode. In this way, electrode processes have been studied, the concentrations of the surface-active agents determined, or analyte metals estimated direct in the presence of large excesses of interfering matrix elements. Recent examples of the last application are the determination of thallium in the presence of lead¹¹, cadmium¹², and indium¹³ after suppression of the polarographic currents of the matrix metals with a variety of surface-active substances. The effect of naturally occurring substances on the determination, by stripping voltammetry, of trace metals in environmental samples^{14,15} was the first indication noted of interference from surface-active agents. In 1978, Neeb¹⁶ reported briefly on the determination, by inverse voltammetry, of zinc in the presence of excess cadmium by depression of the cadmium peak with Triton X-100. Lukaszewski *et al.*¹⁷ recently used anodic-stripping voltammetry to determine thallium and lead in cadmium salts after suppressing the cadmium peak with surface-active agents.

In this work, the non-ionic surface-active agent Triton X-100 was used to depress the peak current of cadmium at unfavourable ratios of cadmium to thallium. By use of purified supporting electrolyte alone, it was first confirmed that, in the DPASV mode, tensammetric adsorption and desorption peaks did not appear over the relevant potentiometric stripping range (-0,85 to -0,45 V) in the presence of Triton X-100, and that, over the same region, the base-line current for the blank electrolyte was not appreciably depressed. Also, initial semi-quantitative tests, in which the surface-active agent was added before pre-electrolysis or just prior to anodic stripping, indicated that the surface-active agent mainly influenced the pre-electrolysis (deposition stage) of cadmium. Therefore, for the investigations that follow, the sample solution was spiked before pre-electrolysis with aliquot volumes of a stock solution with a Triton X-100 concentration of 0,02 per cent (m/m). The voltammetric procedure that was followed is that described in Section 2. The mercury concentration in the solutions was $2,5 \times 10^{-4}$ M and, during pre-electrolysis, the deposition current was recorded and its average value computed. At the very low concentrations of analyte elements present, this current was attributed to the reduction of mercuric ions so that the thin-film electrode could be formed. The average thickness of this film, l (cm), was calculated from the equation given by Batley and Florence¹⁸, as follows:

$$l = (10^{-6} i W t) / (\pi n F d r^2), \dots\dots\dots (4)$$

where

- i is the average deposition current for the mercuric ion (μ A),
- W is the atomic mass of mercury (200,6),
- t is the pre-electrolysis time (seconds),
- n is the number of electrons involved in the reduction (2),
- d is the density of mercury (13,6g/cm³), and
- r is the radius of the surface of the electrode (0,24 cm).

Substitution in equation (4) gives

$$l = (4,23 \times 10^{-10}) i t, \dots\dots\dots (5)$$

or

$$l = (1,27 \times 10^{-7}) i \dots\dots\dots (6)$$

for a fixed pre-electrolysis time of 300 seconds.

Figure 7 shows the effect of the concentration of Triton X-100 on the thickness of the TMFE, calculated as described, under constant voltammetric conditions. The following regions can be distinguished:

- (1) the region with very low concentrations of surface-active agent (less than 2×10^{-5} per cent), where the deposition of mercury was governed by the condition of the mechanically-prepared surface of the RGCE,
- (2) a central region (2 to 20×10^{-5} per cent Triton X-100), which is still unaffected by the surface-active agent, where deposition was controlled by the electrochemically-conditioned surface of the electrode, and
- (3) a region with concentrations higher than 20×10^{-5} per cent Triton X-100, where the deposition of mercury was progressively suppressed by the surface-active agent.

The thickness of the mercury-film electrode as a function of time of pre-electrolysis for two concentrations of surface-active agent is given in Figure 8. For short pre-electrolysis times (up to about 125 seconds), the initial condition of the RGCE was the rate-determining factor. In the macrophase region, where film thicknesses of more than 1 μm were deposited, the rate of deposition could be depressed in the presence of a high concentration of surface-active agent. However, under all conditions, the thickness of the TMFE still remained a linear function of the time of pre-electrolysis.

The effect of the concentration of surface-active agent on the stripping-peak currents of cadmium, thallium, lead, and copper present together in the same supporting electrolyte is shown in Figure 9. In the supporting electrolyte alone, the peak current of cadmium could be completely suppressed in the presence of 20×10^{-5} per cent Triton X-100 with no effect on the other metals present. When the test was repeated with solutions arising from the treatment of two reference materials, suppression was found to be less efficient. In the application of the method, a constant addition of surface-active agent was therefore made to give a final concentration of 50×10^{-5} per cent Triton X-100.

An insight into the mechanism of suppression can be obtained by the comparison of Figures 10 and 11. During the initial stages of pre-electrolysis, the electrodeposition of cadmium was severely curtailed in the presence of a low concentration of surface-active agent (Figure 10). After 150 seconds, when the thickness of the TFME had built up to above 1 μm , the rate of deposition of cadmium was almost the same as it had been in the absence of a surface-active agent. Suppression of the reduction of cadmium appeared to be a surface phenomenon related to the activity of the surface of the bare RGCE. The opposite effect was found for thallium (Figure 11). In the presence of a higher concentration of surface-active agent, the rate of deposition was inhibited at pre-electrolysis times longer than 100 seconds, an effect that appeared to be controlled by diffusion.

2.4. Dependence of the Peak Current for Thallium on Concentration

Figure 12 gives some calibration lines for thallium in the absence and presence of Triton X-100. Although the relation between the peak current and the concentration was rectilinear for any given set of calibration conditions, other experimental parameters, such as the initial condition of the bare RGCE, were more important than was the concentration of surface-active agent in determining the slope of the calibration line. Quantitative estimations by the method of additions are therefore essential.

Thallium was much less sensitive than was cadmium in the electrolyte chosen (1 M ammonium chloride, 0.1 M citric acid, and 0.025 M ascorbic acid), which was originally selected for the simultaneous determination of cadmium, lead, and copper. Replicate determinations of the blank solution carried out by the method of additions (thallium being added to purified supporting electrolyte containing 50×10^{-5} per cent Triton X-100) gave an average small negative value ($\bar{x} = -0.073$ ng/ml, $n = 7$, $s = 0.20$ ng/ml, where \bar{x} is the mean value, n the number of determinations, and s the standard deviation). The limit of detection for thallium was therefore 0.53 ng/ml in solution, calculated from the following relation¹⁹:

$$x_L = \bar{x}_B + 3s_B \tag{7}$$

where

- x_L is the limit of detection, ng/ml,
- \bar{x}_B is the mean blank value, ng/ml, and
- s_B is the standard deviation of the mean blank value, ng/ml.

For a sample of 0.5 g, dissolved and made up to a final volume of 20 ml (according to the procedure given in the Appendix), the limit of detection for thallium will be 21 ng/g in the reference material.

3. RESULTS

The values for cadmium and thallium in the NIMROC and two USGS reference materials are given in Table 2, together with estimates of precision and other results from the recent literature. Where available, the correlation coefficients are included as an indication of the degree of concurrence of the calibration points arising from the method of additions to the sample. The precision of all the results had an approximate linear log relation to the concentrations of thallium and cadmium in the samples (Figure 13).

4. DISCUSSION

The effect of the deposition potential on the peak current (Figures 1 and 2) suggests a reversible single-electron reaction involving the aquo-thallos ion, as was expected, since thallium has only a small tendency to form complexes.

DETERMINATION OF CADMIUM AND THALLIUM

TABLE 2

Results for the determination of cadmium and thallium in six NIMROC and two USGS reference materials (values in nanograms per gram)

Reference material	Cadmium						Thallium					
	\bar{x}	n	s	s_r	r	Other values from recent literature	\bar{x}	n	s	s_r	r	Other values from recent literature
NIM-G	90	9	4.3	0.048	0.9998 to 0.9999	130 ²	620	6	62	0.132	0.9998 to 0.9999	940 ²
NIM-S	65	9	5.2	0.080	0.9995 to 0.9998	43 ²	917	6	31	0.033	0.9975 to 0.9997	1070 ²
NIM-L	743	5	16	0.021	0.9983 to 0.9999	630 ²	344	5	26	0.076	0.9802 to 0.9999	300 ²
NIM-N	39	6	3.2	0.083	0.9862 to 0.9989	47 ²	<20	6	-	-	-	18 ²
NIM-P	28	7	3.8	0.137	0.9993 to 0.9999	32 ²	<20	6	-	-	-	16 ²
NIM-D	50	10	5.4	0.107	T.P.	44 ²	<20	8	-	-	-	17 ²
USGS-DTSI	7	6	1.1	0.157	0.9998 to 0.9999	12 ² , 10 ² , 9 ² , 8 ² , 5 ²	<20	6	-	-	-	11 ² , 6 ² , 3 ² , 0.5 ² - ¹⁰
USGS-GSPI	48	7	5.4	0.112	0.9998	63 ² , 61 ² , 60 ² , 52 ² - ²⁶ , 51 ² , 50 ² , 16 ²	1302	7	66	0.051	0.9969 to 0.9999	1550 ² , 1520 ² , 1300 ² - ¹⁰ , 1290 ² , 1280 ² , 1220 ² , 1200 ² , 1180 ²

\bar{x} = Mean value s = Standard deviation r = Correlation coefficient (least-squares regression)
n = Number of determinations s_r = Relative standard deviation T.P. = 2-point additions only

Also, the facile suppression of the stripping-peak current of cadmium with Triton X-100 was in agreement with reported conventional polarography¹². The inhibitory mechanism for stripping from a TMFE deposited *in situ* on an RGCE has not yet been elucidated.

Only Heinrichs³ has reported values for cadmium and thallium in the NIMROC reference materials. The voltammetric values for thallium in NIM-G and NIM-S have a low bias compared with those obtained by Heinrichs³ using his electrothermal AAS procedure (Table 2). A plot of the other data for cadmium and thallium obtained from the two techniques (ASV versus electrothermal AAS) gave a least-squares linear-regression line with a slope of 0.95, an intercept of 0.28 $\mu\text{g/g}$, and a correlation coefficient of 0.9961. These results are acceptable in view of the wide range of values covered: 28 $\mu\text{g/g}$ (for cadmium) to 1302 $\mu\text{g/g}$ (for thallium).

In earlier work on thallium¹¹, the limit of determination was extended to about 0.5 $\mu\text{g/g}$ by the use of ASV at the hanging mercury-drop electrode, compared with 2 $\mu\text{g/g}$ obtained by the use of ordinary polarography at the dropping-mercury electrode¹². By the use of ASV and the TMFE, the limit of detection was reduced much further (i.e., to about 20 ng/g in the sample) without serious loss in precision.

The two sets of results for cadmium and thallium constitute useful geochemical data. In its behaviour in regard to crystal chemistry, thallium has close affinities with the major element, potassium, and the trace element, rubidium. It can be expected to be more abundant in rock-forming micas and potassium feldspars, and more highly concentrated in granitic than in mafic rocks. The NIMROC series of reference materials yielded a valuable relation between thallium and rubidium (Figure 14). Cadmium shows close similarities to zinc, and even to iron(II) in its distribution in rocks. A high concentration was therefore expected in NIM-L (Figure 15). This NIMROC is a valuable geochemical reference material because of its unusual concentration of trace elements.

5. REFERENCES

1. DE ALBUQUERQUE, C.A.R., and MUYSSON, J.R. The determination of p.p.b. levels of thallium in silicate rocks. *Chem. Geol.*, vol. 9. 1972. pp. 167-174.
2. ARMANNSSON, H. The use of dithizone extraction and atomic absorption spectrometry for the determination of cadmium in rocks and sediments. *Analyt. chim. Acta*, vol. 88. 1977. pp. 89-95.
3. HEINRICHS, H. Determination of bismuth, cadmium and thallium in 33 international standard reference rocks. *Fresenius Z. analyt. Chem.*, vol. 294. 1979. pp. 345-351.
4. LEE, A.F. The direct determination, by differential pulse anodic-stripping voltammetry at the thin mercury-film electrode, of cadmium, lead, and copper. Randburg, National Institute for Metallurgy, Report 2124. 1981.
5. BROWN, S.D., and KOWALSKI, B.R. Pseudopolarographic determination of metal complex stability constants in dilute solution by rapid scan anodic stripping voltammetry. *Analyt. Chem.*, vol. 51. 1979. pp. 2133-2139.
6. MEITES, L. Polarographic techniques. New York, Interscience Publishers, 1955. p. 105.
7. ZIRINO, A., and KOUNAVES, S.P. Anodic stripping peak currents: electrolysis potential relationships for reversible systems. Equation (12). *Analyt. Chem.*, vol. 49. 1977. pp. 56-59.
8. COPELAND, T.R., et al. Analytical applications of pulsed voltammetric stripping at thin film mercury electrodes. *Analyt. Chem.*, vol. 45. 1973. pp. 2172-2174.
9. BATLEY, G.E., and FLORENCE, T.M. An evaluation and comparison of some techniques of anodic stripping voltammetry. Equation (5). *J. electroanalyt. Chem. interfacial Electrochem.*, vol. 55. 1974. p. 30.
10. LEE, A.F. *op. cit.*, Figure 17.
11. MENDALIEVA, D.K., et al. Polarographic determination of thallium in the presence of lead in electrolytes containing long chain primary amine surfactants. *J. analyt. Chem. USSR*, vol. 32. 1977. pp. 123-125.
12. SHAPOVALOVA, E.N., and PROKHOROVA, G.V. Polarographic determination of thallium in the presence of large quantities of copper and cadmium. *Ind. Lab.*, vol. 44. 1978. pp. 621-622.
13. CHRISTMANN, W., et al. Determination of thallium in the presence of indium in supporting solutions containing surfactants by differential pulse polarography. *Fresenius Z. analyt. Chem.*, vol. 302. 1980. pp. 32-35.
14. BREZONIK, P.L., et al. Effect of absorption by organic compounds on the determination of trace metals by anodic stripping voltammetry. *Water Res.*, vol. 10. 1976. pp. 605-612.
15. BATLEY, G.E., and FLORENCE, T.M. Effect of dissolved organics on the stripping voltammetry of seawater. *J. electroanalyt. Chem. interfacial Electrochem.*, vol. 72. 1976. pp. 121-126.
16. NEEB, R. Polarographic and voltammetric methods for the determination of elements. *Mikrochim. Acta*, Part I. 1978. pp. 305-318.
17. LUKASZEWSKI, Z., et al. Determination of thallium and lead in cadmium salts by anodic stripping voltammetry with addition of surfactants to suppress cadmium peaks. *Talanta*, vol. 27. 1980. pp. 181-185.
18. BATLEY, G.E., and FLORENCE, T.M. An evaluation and comparison of some techniques of anodic stripping voltammetry. Equation (7). *J. electroanalyt. Chem. interfacial Electrochem.*, vol. 55. 1974. p. 31.
19. IRVING, H.M.N.H., et al. Compendium of analytical nomenclature, definitive rules 1977. Oxford, Pergamon Press, 1978. p. 133.
20. HEINRICHS, H., and LANGE, J. Trace element analysis and microanalysis of silicate and carbonate rocks by flameless atomic absorption spectroscopy. *Fresenius Z. analyt. Chem.*, vol. 265. 1973. pp. 256-260.
21. BAEDECKER, P.A., et al. Extralunar component in lunar soils and breccias. *PROCEEDINGS LUNAR SCIENCE CONFERENCE, THIRD, 1972*. Heyman, D. (ed.). Cambridge, Mass., MIT. 1972. p. 1343.
22. ROSMAN, J.K.R., and DE LAETER, J.R. Mass spectrometric isotope dilution analyses of cadmium in standard rocks. *Chem. Geol.*, vol. 13. 1974. pp. 69-74.
23. VINCENT, E.A., and BILEFIELD, L.I. Determination of cadmium in rocks by neutron activation analysis. *Geochim. cosmochim. Acta*, vol. 19. 1960. p. 63.
24. FLANAGAN, F.J. U.S. Geological Survey Standards-II. First compilation of data for the new U.S.G.S. rocks. *Geochim. cosmochim. Acta*, vol. 33. 1969. pp. 81-120.

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25. FLANAGAN, F.J. Description and analyses of eight new USGS rock standards. Washington D.C., U.S. Geological Survey, *Professional Paper 840*. 1976. p. 171.
26. LANGMYHR, F.J., *et al.* Atomic absorption spectrometric determination of cadmium, lead, silver, thallium and zinc in silicate rocks by direct atomization from the solid state. *Analyt. chim. Acta*, vol. 71. 1974. pp. 35-42.
27. MAROWSKY, G., and WEDEPOHL K.H. General trends in the behaviour of cadmium, mercury, thallium and bismuth in some major rock forming processes. *Geochim. cosmochim. Acta*, vol. 35. 1971. pp. 1255-1267.
28. SIGHINGLI, G.P. Determination of thallium in geochemical reference samples by flameless atomic absorption spectroscopy. *Atom. abs. Newsl.*, vol. 12. 1973. pp. 136-138.
29. DE ALBUQUERQUE, C.A.R., *et al.* Thallium in basalt and related rocks. *Chem. Geol.* vol. 10. 1972. pp. 41-58.
30. LAUL, J.C., *et al.* Thallium contents of chondrites. *Geochim. cosmochim. Acta*, vol. 34. 1970. pp. 909-920.
31. JONES, E.A., and LEE, A.F. The determination of thallium in ores, concentrates, and metals. Randburg, National Institute for Metallurgy. *Report 2036*. 1980. 35 pp.
32. JONES, E.A., and LEE, A.F. The determination of thallium and indium in sulphide concentrates. Randburg, National Institute for Metallurgy. *Report 2022*. 1979. 39 pp.
33. STEELE, T.W., *et al.* Analyses of the NIMROC reference samples for minor and trace elements. Randburg, National Institute for Metallurgy. *Report 1945*. 1978. 222 pp.
34. LEE, A.F. The determination, by anodic-stripping voltammetry, of zinc and lead in six NIMROC reference materials. Randburg, National Institute for Metallurgy. *Report 2083*. 1980. 33 pp.

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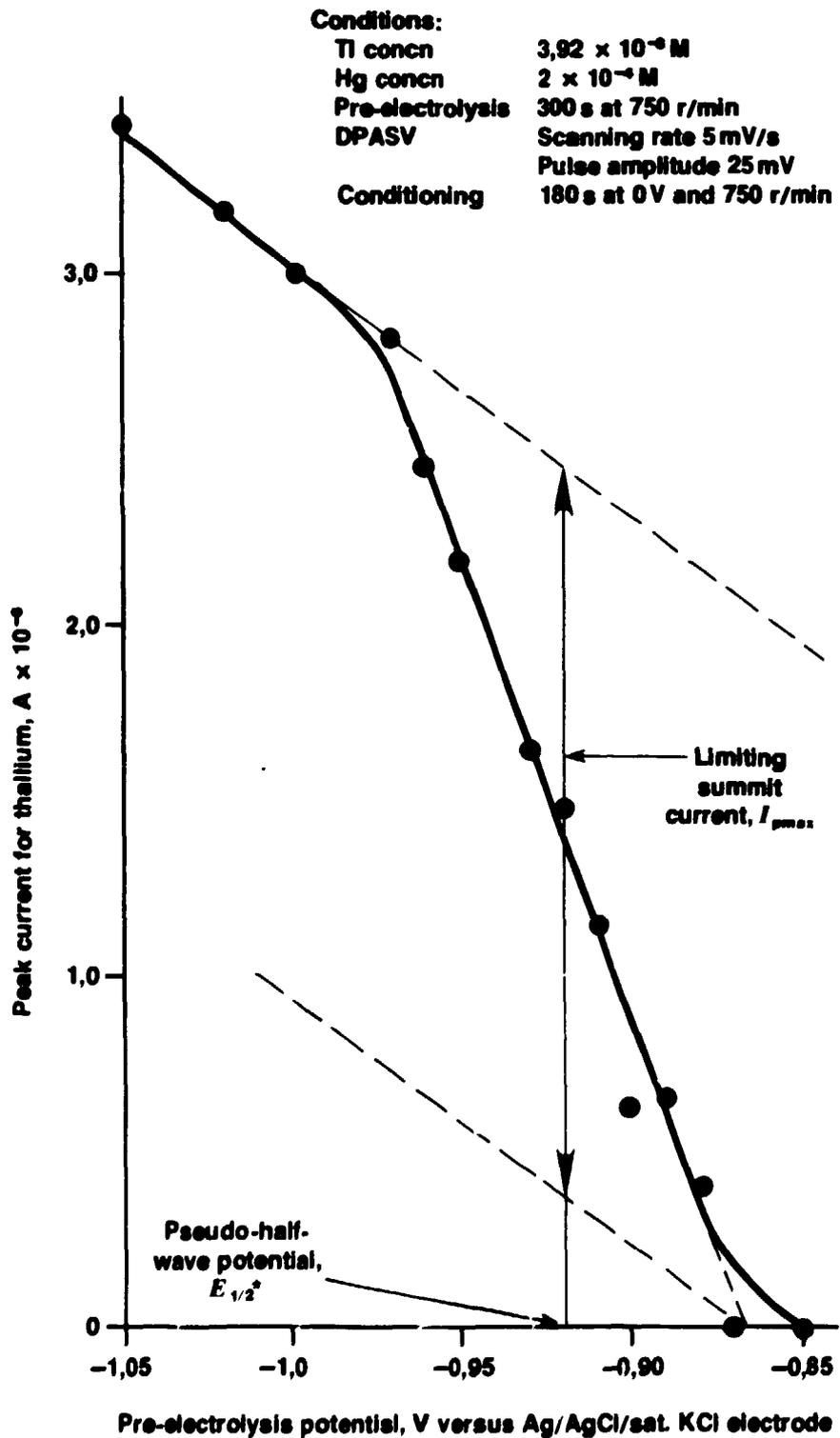


FIGURE 1. Effect of pre-electrolysis potential on the peak current for thallium

DETERMINATION OF CADMIUM AND THALLIUM

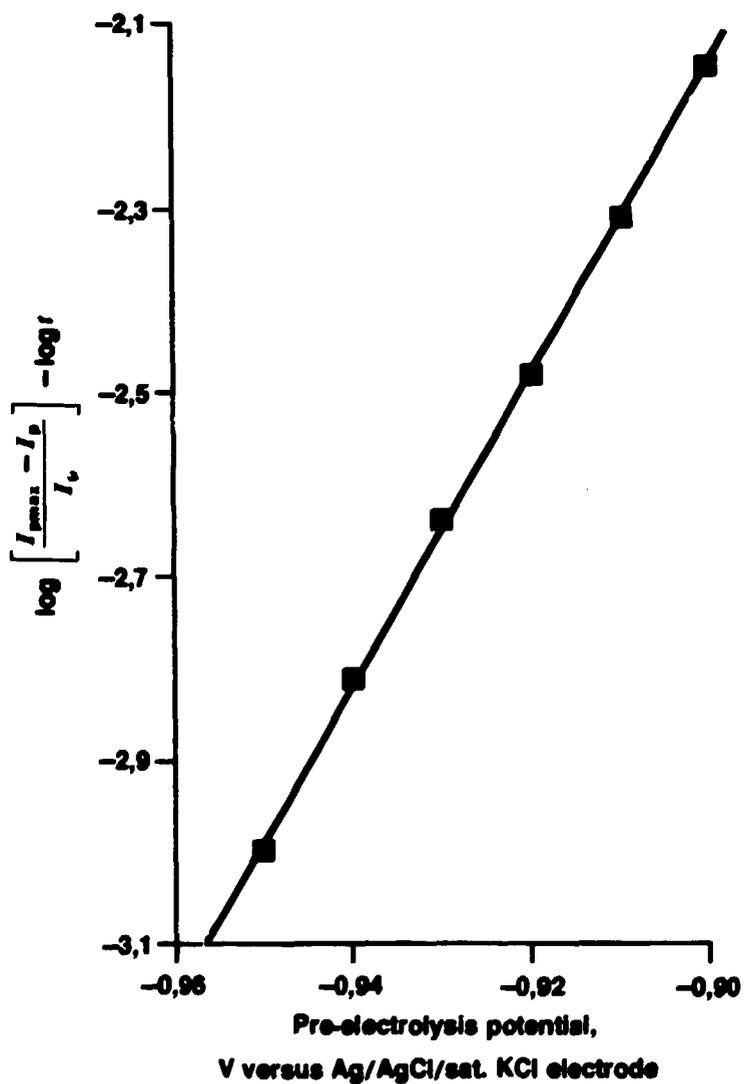


FIGURE 2. Plot of $\log \left[\frac{I_{pmax} - I_p}{I_d} \right] - \log t$ versus pre-electrolysis potential for the pseudopolarogram given in Figure 1

DETERMINATION OF CADMIUM AND THALLIUM

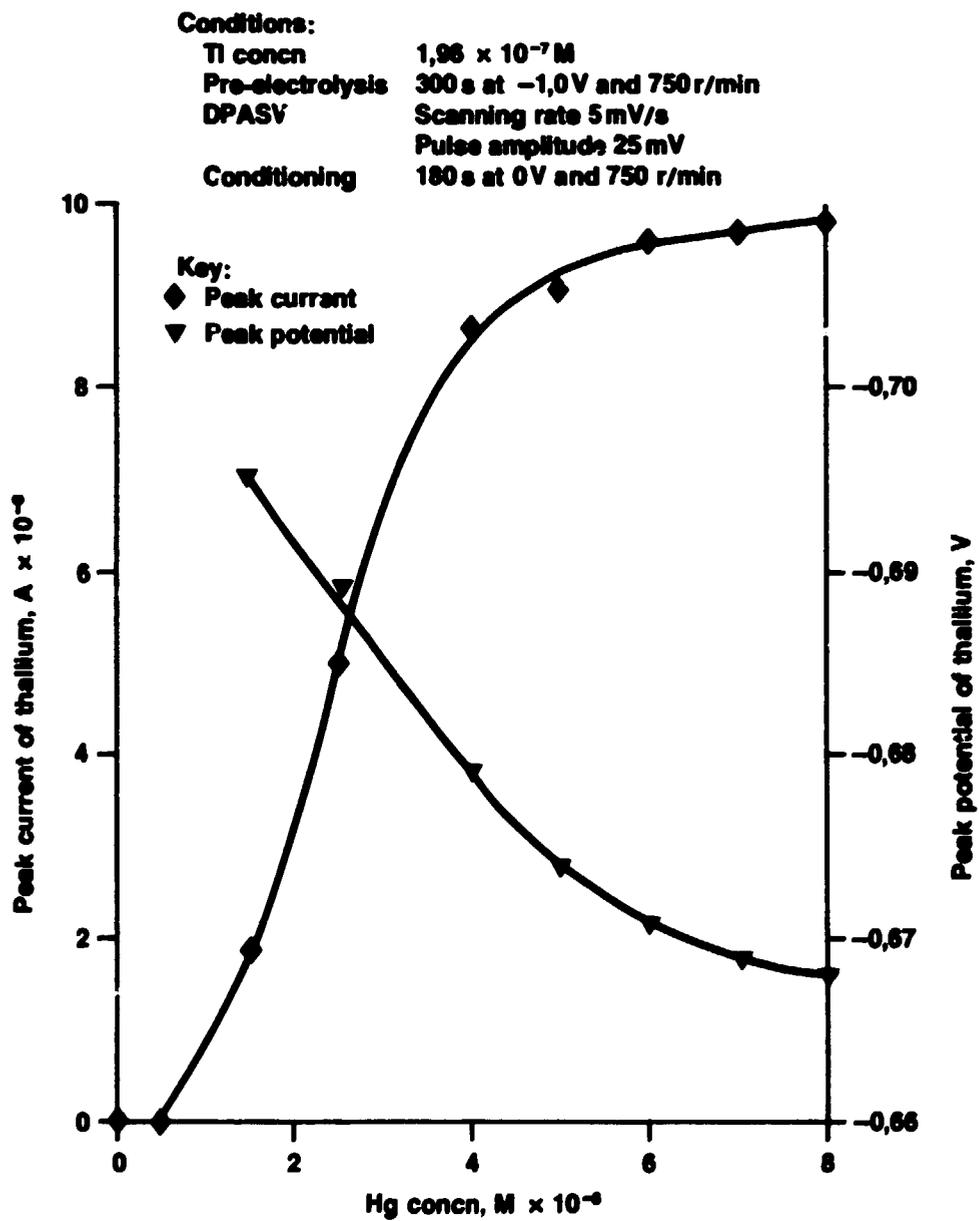


FIGURE 3. Dependence of peak current and potential for thallium on concentration of mercury in solution

DETERMINATION OF CADMIUM AND THALLIUM

Conditions:

	Cd	Tl
Analyte concn	$4,5 \times 10^{-6} \text{ M}$	$9,0 \times 10^{-6} \text{ M}$
lig concn	$1,25 \times 10^{-4} \text{ M}$	$2,67 \times 10^{-4} \text{ M}$
Pre-electrolysis	100 s at $-0,85 \text{ V}$ and 750 r/min	300 s at $-1,0 \text{ V}$ and 750 r/min
DPASV	Pulse amplitude	25 mV
Conditioning	90 s at 0 V and 750 r/min	

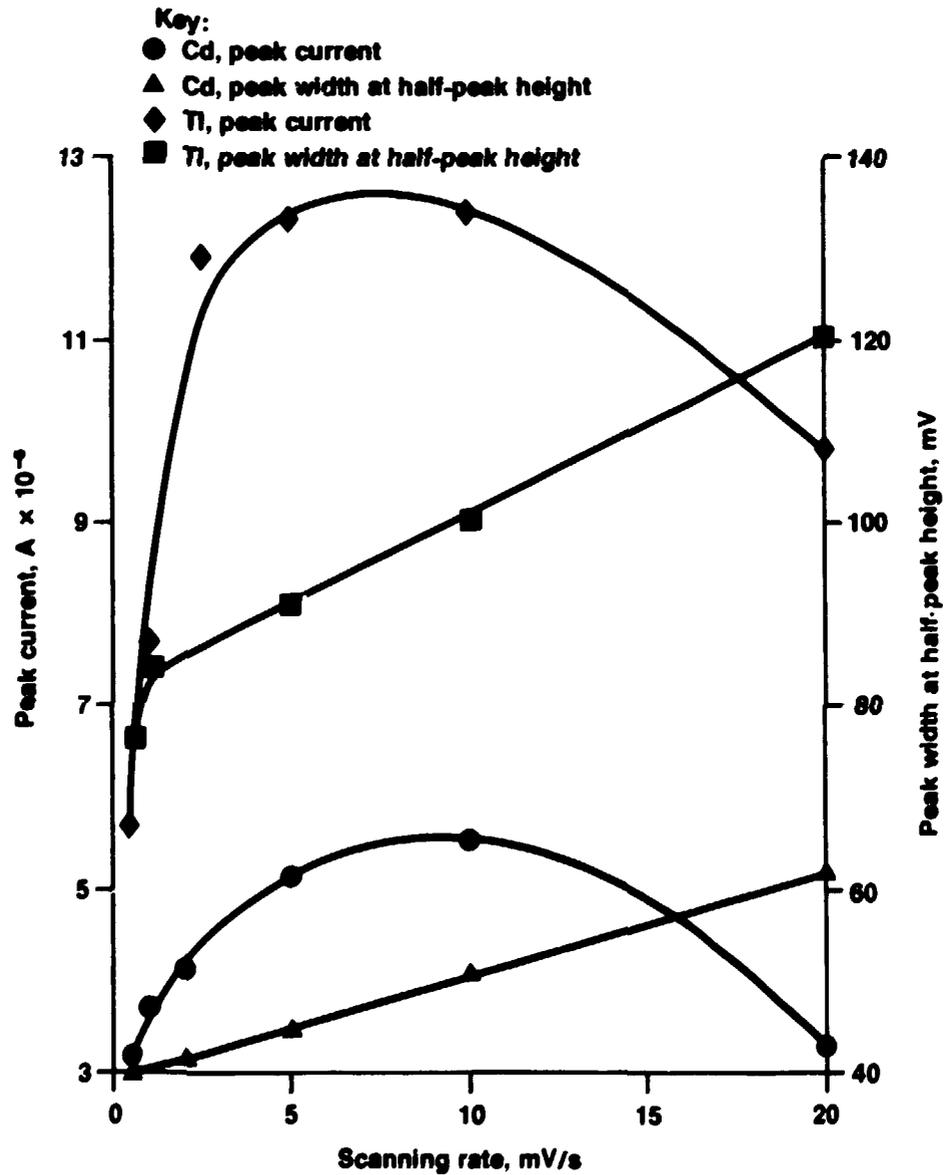


FIGURE 4. Effect of scanning rate on peak currents and peak widths at half-peak height for cadmium and thallium

DETERMINATION OF CADMIUM AND THALLIUM

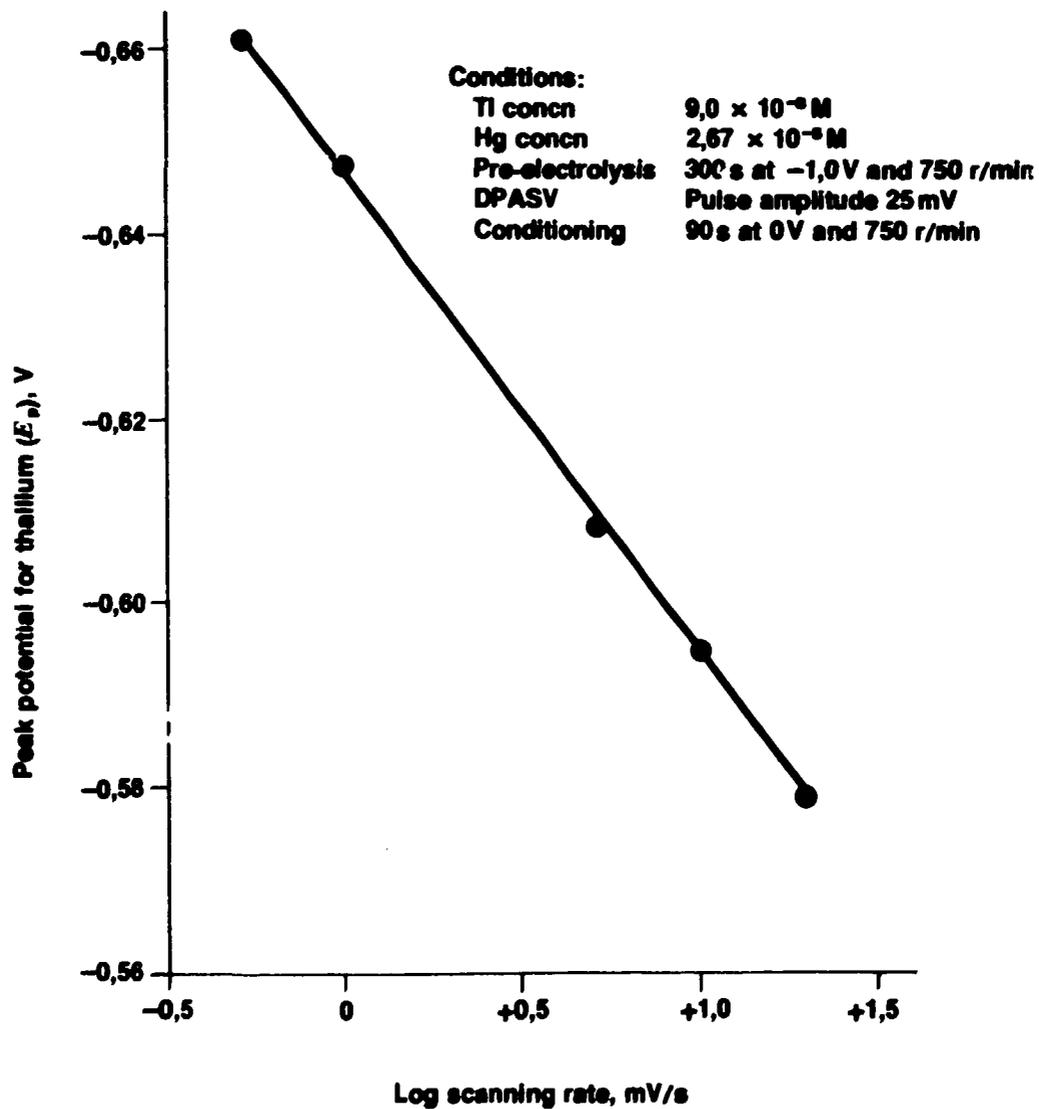


FIGURE 5. Dependence of peak potential for thallium on scanning rate

DETERMINATION OF CADMIUM AND THALLIUM

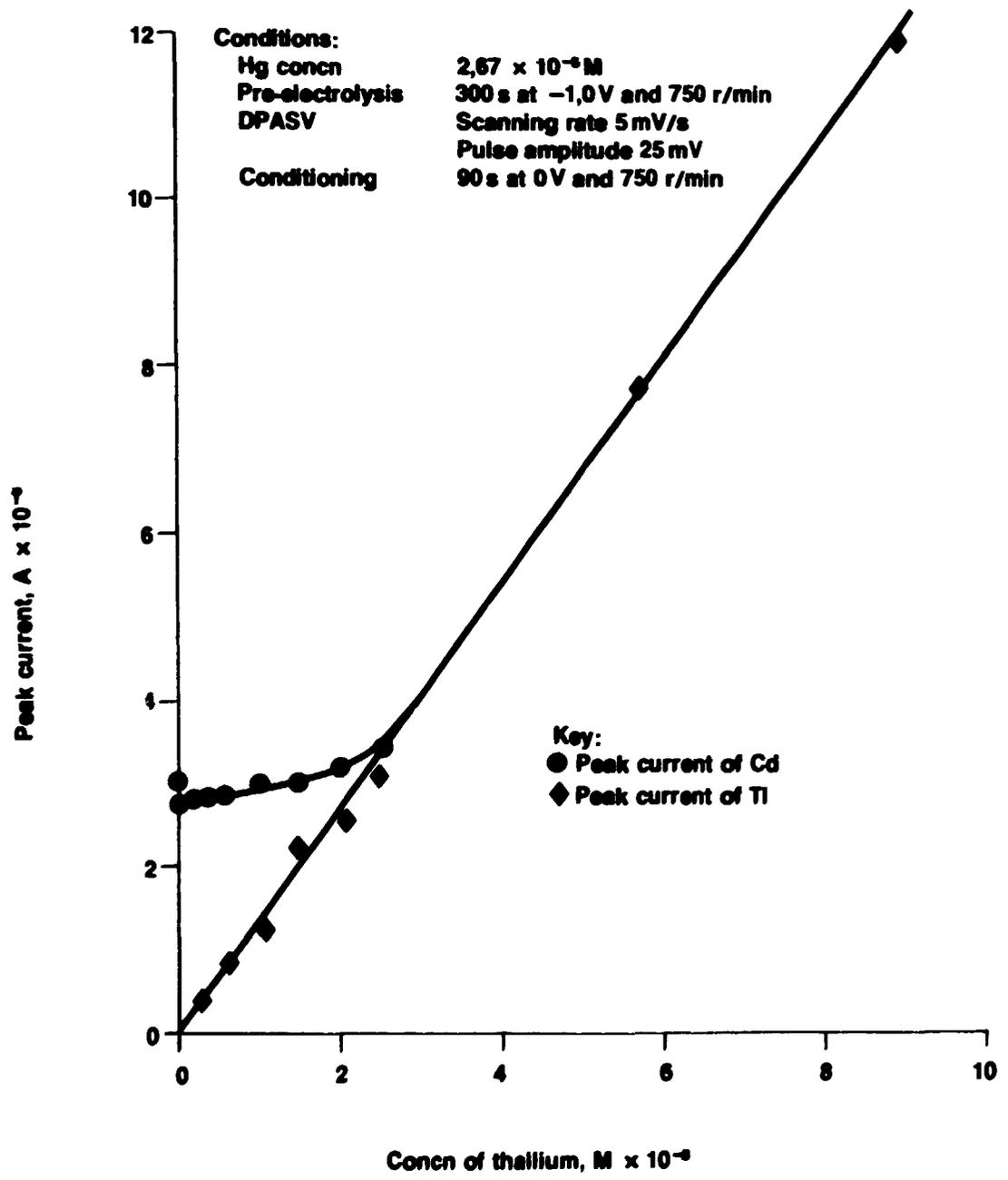


FIGURE 6. Effect of thallium concentration on the peak current for $6 \times 10^{-9} \text{ M}$ cadmium

DETERMINATION OF CADMIUM AND THALLIUM

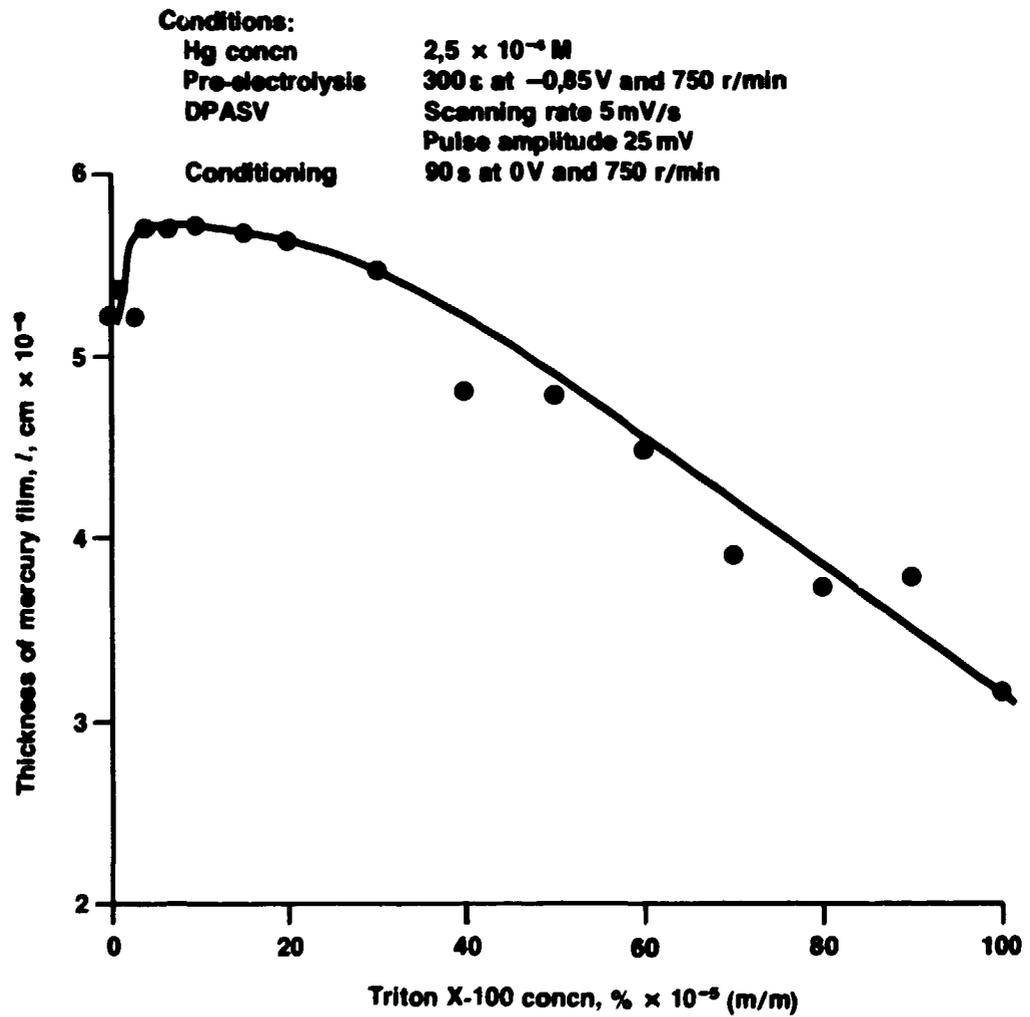


FIGURE 7. Effect of Triton X-100 on the deposition of the thin mercury-film electrode

DETERMINATION OF CADMIUM AND THALLIUM

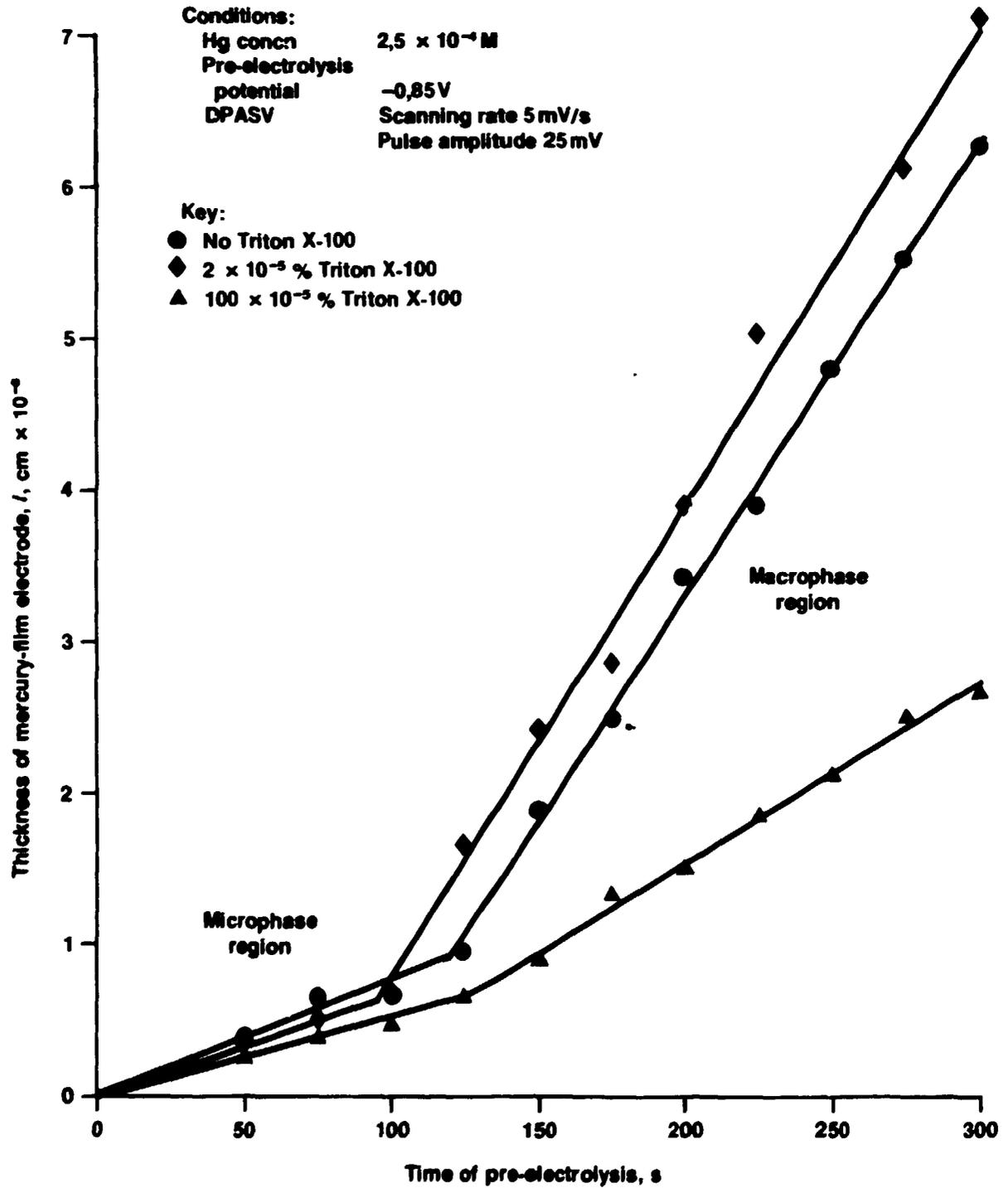


FIGURE 8. Dependence of thickness of mercury-film electrode on time of pre-electrolysis in the absence and presence of a surface-active agent

DETERMINATION OF CADMIUM AND THALLIUM

Conditions:

Cd concn	$2,93 \times 10^{-6} \text{ M}$
Tl concn	$7,35 \times 10^{-6} \text{ M}$
Pb concn	$3,24 \times 10^{-6} \text{ M}$
Cu concn	$4,87 \times 10^{-6} \text{ M}$
Hg concn	$2,5 \times 10^{-6} \text{ M}$
Pre-electrolysis	300 s at $-0,85 \text{ V}$ and 750 r/min
DPASV	Scanning rate 5 mV/s Pulse amplitude 25 mV
Conditioning	90 s at 0V and 750 r/min

Key:

- ▼ Cd (blank electrolyte)
- Cd (NIMROC NIM-L)
- Cd (NIMROC NIM-D)
- Tl
- ◆ Pb
- ▲ Cu

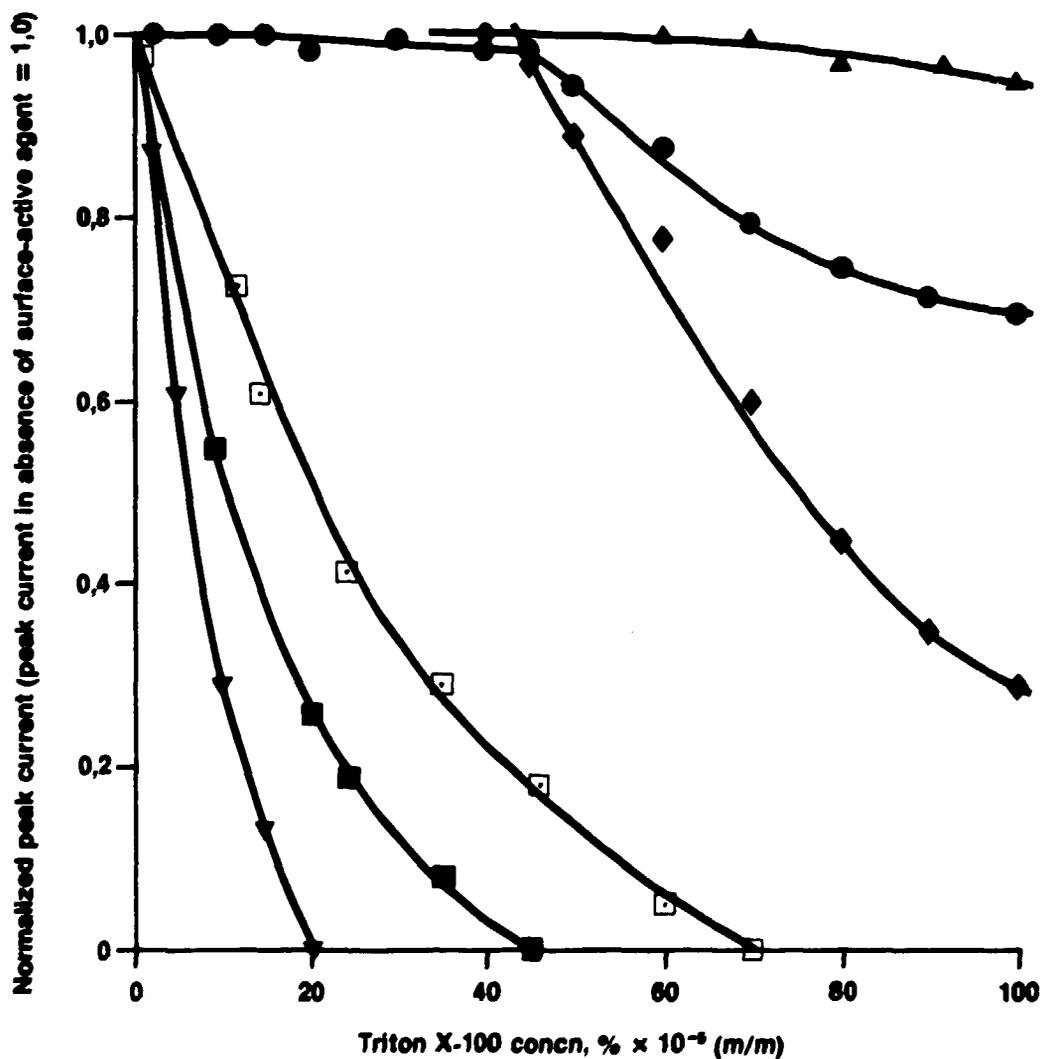


FIGURE 9. Depression of stripping-peak currents for cadmium, thallium, lead, and copper by Triton X-100

DETERMINATION OF CADMIUM AND THALLIUM

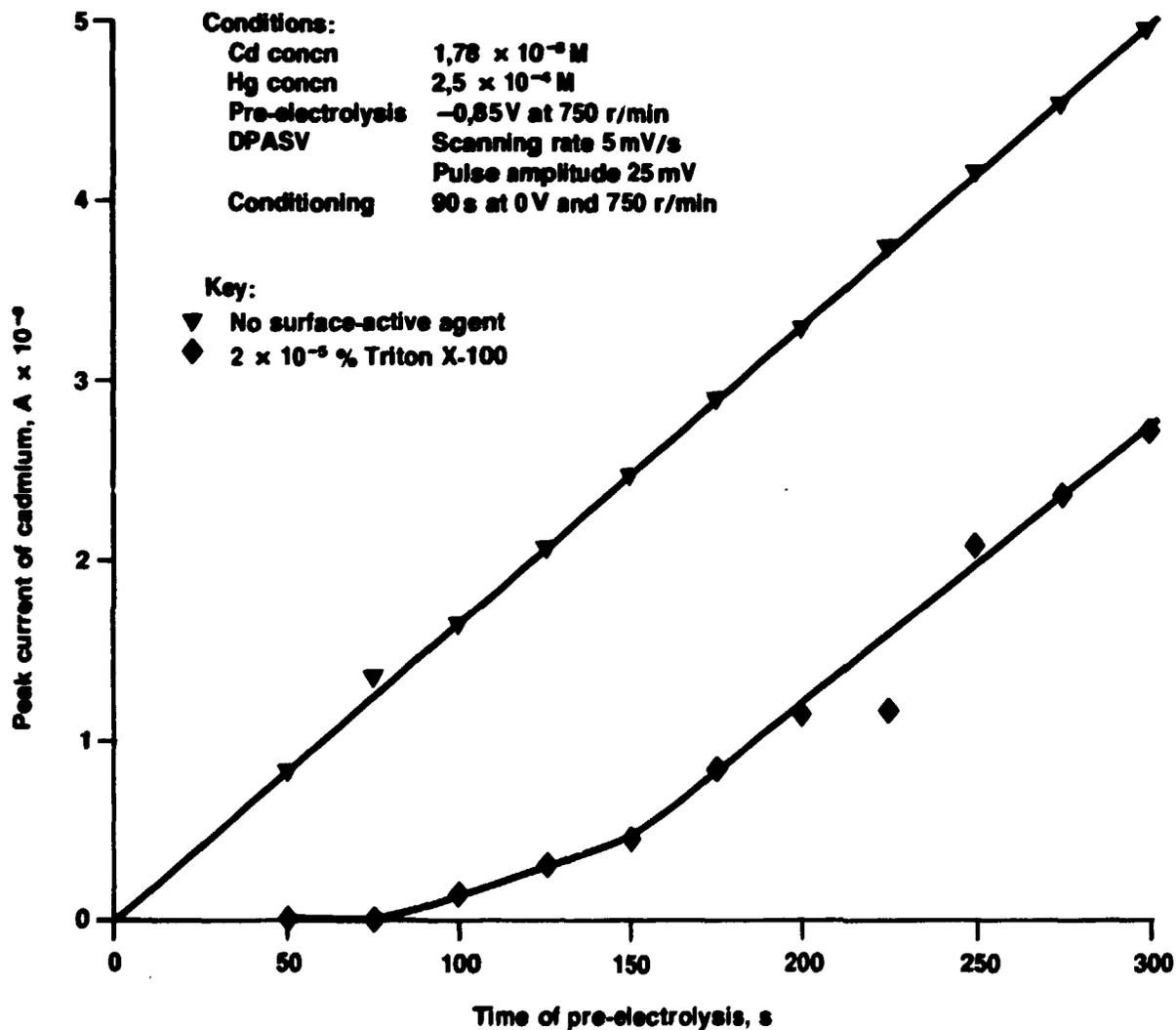


FIGURE 10. Dependence of the peak current for cadmium on time of pre-electrolysis in the absence and presence of a surface-active agent

DETERMINATION OF CADMIUM AND THALLIUM

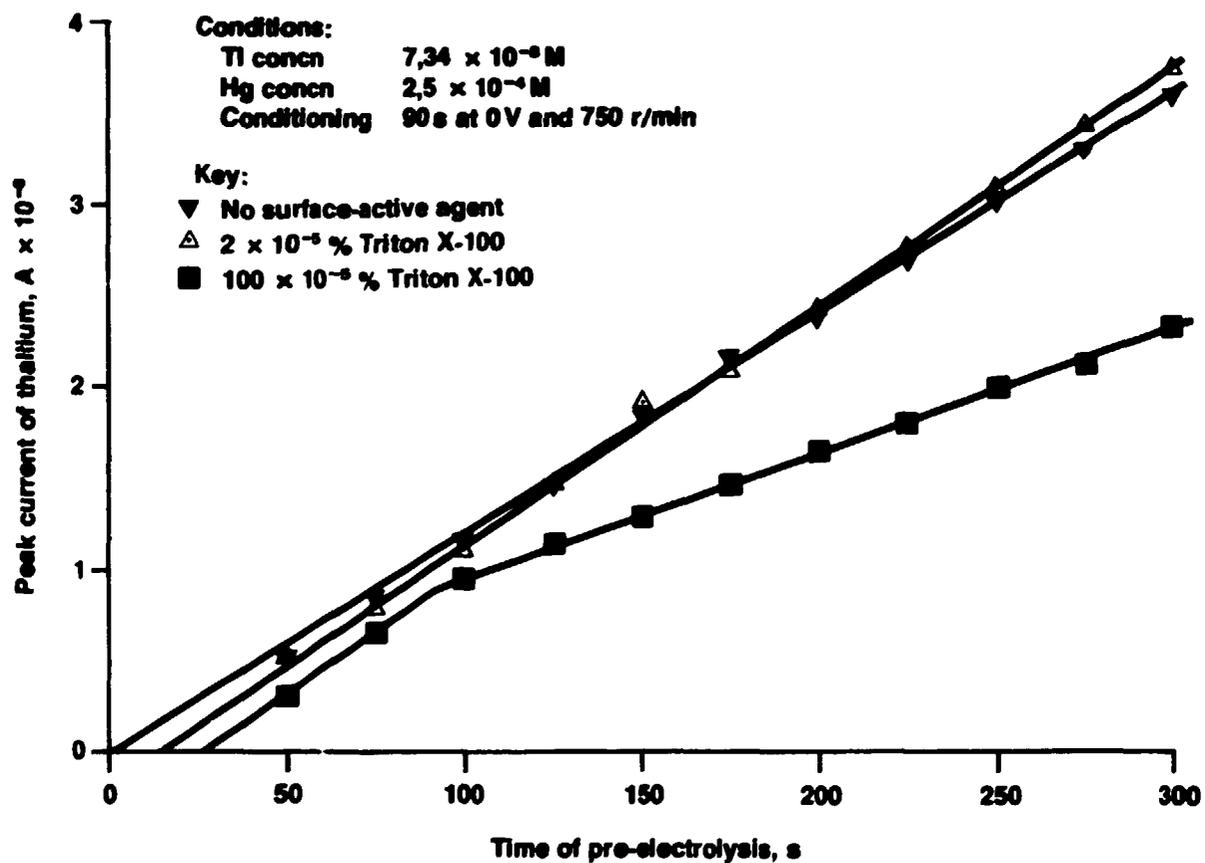


FIGURE 11. Dependence of the peak current for thallium on time of pre-electrolysis in the absence and presence of a surface-active agent

DETERMINATION OF CADMIUM AND THALLIUM

Conditions:

Hg concn $1,67 \times 10^{-4}$ M
 Pre-electrolysis 300 s at $-0,85$ V and 750 r/min
 DPASV Scanning rate 5 mV/s
 Pulse amplitude 25 mV
 Conditioning 90 s at 0 V and 750 r/min

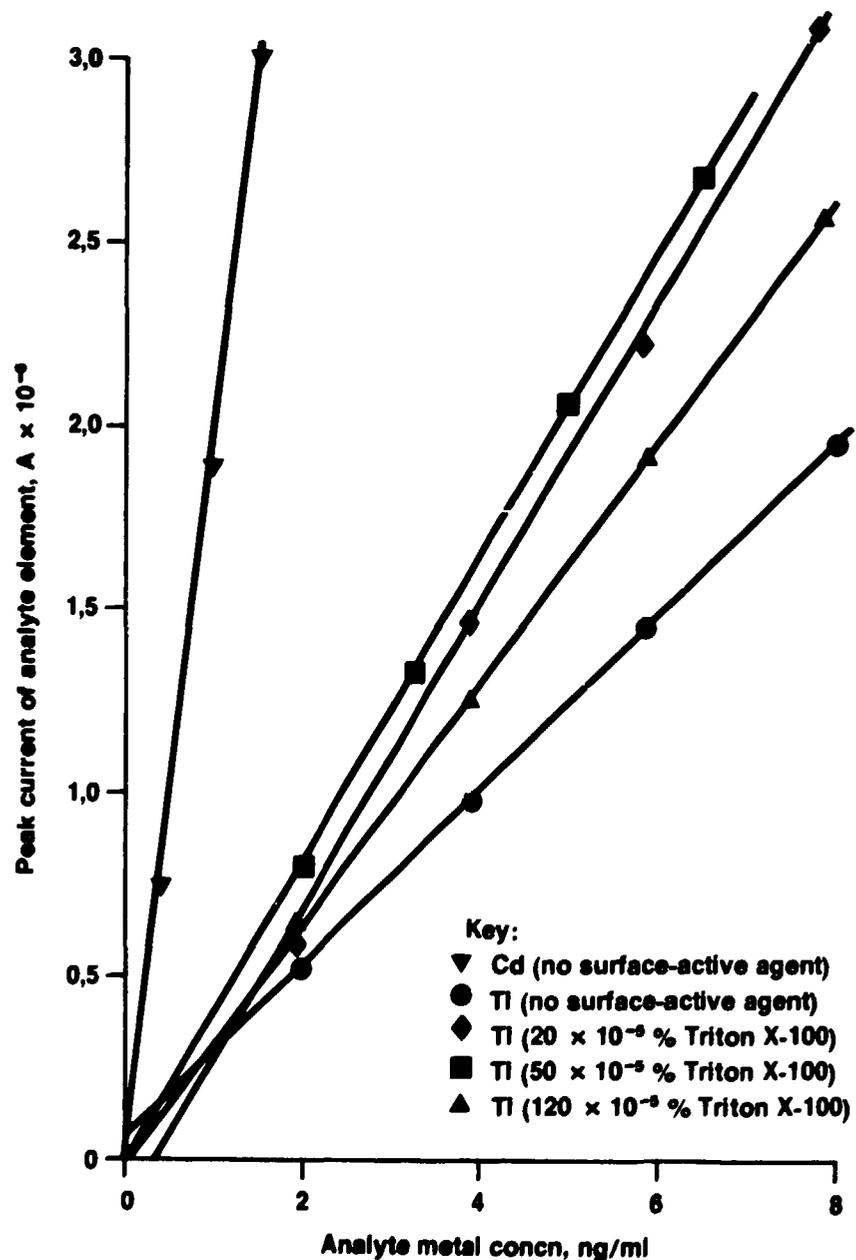


FIGURE 12. Dependence of the peak currents for cadmium and thallium on concentration in the absence and presence of a surface-active agent

DETERMINATION OF CADMIUM AND THALLIUM

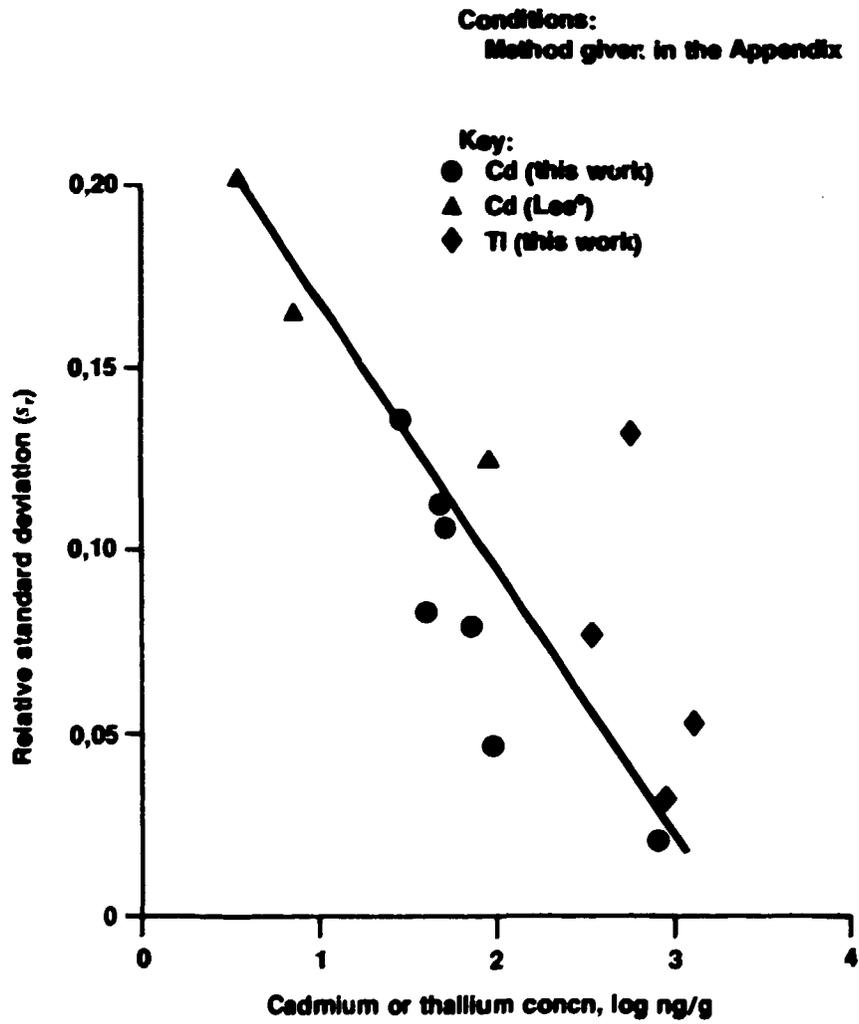


FIGURE 13. Relation between precision of results and concentration of cadmium or thallium in reference materials

DETERMINATION OF CADMIUM AND THALLIUM

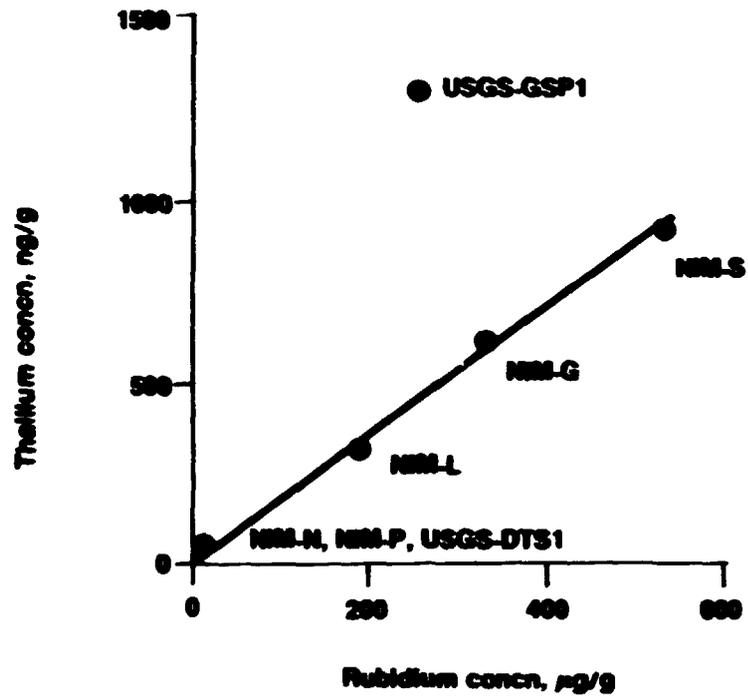


FIGURE 14. Relation between thallium and rubidium⁸⁷ in the NIMROC and two USGS reference materials

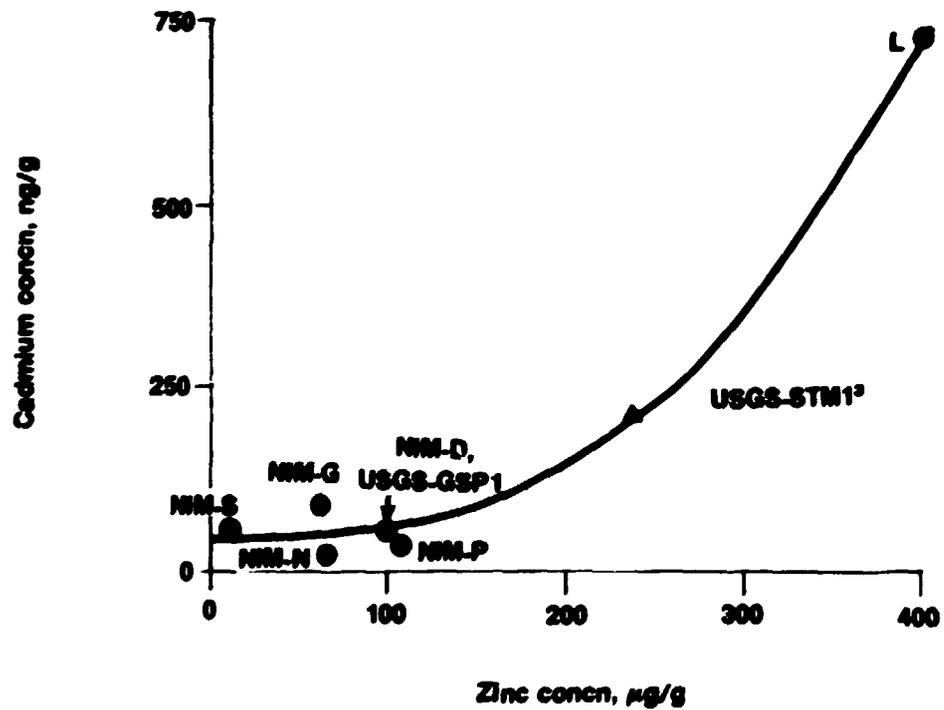


FIGURE 15. Relation between cadmium and zinc⁶⁶ in the NIMROC and two USGS reference materials

APPENDIX

THE DETERMINATION, BY DIRECT DIFFERENTIAL PULSE ANODIC-STRIPPING VOLTAMMETRY
AT A MERCURY-FILM ELECTRODE, OF CADMIUM AND THALLIUM IN SILICATE REFERENCE
MATERIALS
(LABORATORY METHOD NO. 48/7)

1. OUTLINE

The sample is dissolved in a 15:1 mixture of hydrofluoric and nitric acids in a closed Teflon cup at ambient temperature, or supported in a pressure vessel at 150 °C. The solution is then brought to dryness twice with concentrated nitric acid to expel fluoride ions. The residue is dissolved in a mixture of ammonium chloride, citric acid, and ascorbic acid, transferred to a 20 ml volumetric flask, and diluted to volume. Cadmium is then determined in an aliquot volume of the solution by use of differential pulse anodic-stripping voltammetry (DPASV) at the thin mercury-film electrode (TMFE) and the method of additions. The cadmium wave is then suppressed with Triton X-100, and thallium is determined in the same aliquot volume by use of the same technique.

2. APPLICATION

The procedure was found to be successful with all the NIMROC reference materials and with two similar United States Geological Survey (USGS) reference materials. It should be applicable to similar geochemical reference materials in which the concentrations of cadmium and thallium are above the detection limits of 10 ng/g and 20 ng/g respectively.

The accuracy, as established by two controls (USGS-DTS1 and USGS-GSP1) was acceptable. The precision varied with the metal concentration in the sample from a relative standard deviation of 0,15 at a concentration of 10 ng/g for cadmium or 350 ng/g for thallium down to 0,025 at 750 ng/g for cadmium or 1300 ng/g for thallium. The analytical time for the sequential determination of cadmium and thallium in one sample by the method of multiple-standard additions was approximately 2 hours.

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. Baker Chemicals, Ultrex, 49 per cent.
- (2) *Nitric Acid*
B.D.H. Aristar, 70 per cent.
- (3) *Water*
Triply distilled, and stored in a polythene bottle.
- (4) *Triton X-100, 0,03 per cent (m/m) Solution*
Dilute 60 mg of Merck reagent 12298 with triply distilled water to 200 ml.
- (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 nitric acid (prepared from B.D.H. Aristar reagent). Take the solution down to fumes to oxidize any Hg(I). Dissolve the residue in water and make up to 100 ml.

DETERMINATION OF CADMIUM AND THALLIUM

- (6) **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 (chemically 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 pyrrolidone dithiocarbamate (APDC). Agitate gently for 10 minutes to 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 a further 5 ml of 1 per cent APDC solution to the aqueous layer, and repeat the extraction. Again discard the organic layer, and wash the aqueous electrolyte twice, each time with 50 ml of chloroform. Discard the final (organic) phase. Remove the entrained chloroform from the electrolyte by bubbling nitrogen through the warm solution until it is free from any smell of the solvent or APDC extractant.
- (7) **Standard Solution of Cadmium**
From the pure metal, prepare a stock solution of cadmium containing 1 g per litre in 10 per cent nitric acid. By further dilution with 10 per cent nitric acid, prepare a dilute solution containing 20 mg of the metal per litre. (This solution is stable for at least 2 weeks.) Finally, by further dilution with triply distilled water, prepare daily a working solution containing 1,0 mg of cadmium per litre.
- (8) **Standard Solution of Thallium**
Dissolve 1,305 g of thallos nitrate in water and dilute to exactly 500 ml with 10 per cent nitric acid to give a solution containing 1 g of thallium per litre. Prepare, by a single-stage dilution with water, a dilute intermediate solution containing 50 mg of thallium per litre. (This solution is stable for at least 2 weeks.) Finally, prepare daily a working solution containing 4 mg of thallium per litre.

5. PROCEDURE

- a. Weigh accurately about 0,25 g of sample into a Teflon cup, moisten with 0,2 ml of nitric acid, slowly add 3 ml of hydrofluoric acid, and swirl.
- b. Cover, and warm gently on a hot-plate for 10 minutes. Alternatively, for materials insoluble at that temperature, digest overnight in a pressure vessel at 150°C.
- c. Cool, remove from the pressure vessel, and take the contents of the cup to moist solids. Add 2 ml of nitric acid and again take to moist solids. Repeat once more, this time taking the contents just to dryness.
- d. Dissolve the residue in a few millilitres of electrolyte and transfer to a 20 ml grade-A volumetric flask with further small volumes 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 μ l of 5×10^{-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 under the following conditions. Pre-electrolyse at $-0,85$ V for 300 seconds at 750 r/min. Allow a quiescent period of 15 seconds. Scan anodically to $-0,5$ V at 5 mV/s, a pulse amplitude of 25 mV, and current density of 0,2 or 0,5 mA for full-scale deflection. Sequentially, add 15 μ l aliquot volumes of cadmium solution (1,0 mg/l) to give final cadmium concentrations of 1 μ g/l, 2 μ g/l, 3 μ g/l, and 4 μ g/l in the total electrolyte solution. Record voltammograms between additions.
- g. Add 25 μ l of Triton X-100 0,03 per cent solution (final concentration 5×10^{-5} per cent), and mix with nitrogen for 3 minutes.
- h. Record voltammograms for thallium under the following conditions. Pre-electrolyse at $-0,85$ V for 300 seconds at 750 r/min. Allow a quiescent period of 15 seconds. Scan anodically to $-0,45$ V at 5 mV/s, a pulse amplitude of 25 mV, and a current density of 0,2 or 0,5 mA for full-scale deflection. Sequentially, add 30 μ l aliquot volumes of thallium solution (4,0 mg/l) to give final thallium concentrations of 8 μ g/l, 16 μ g/l, 24 μ g/l, and 32 μ g/l in the total electrolyte solution. Record voltammograms between additions.
- i. Condition electrochemically the rotating glassy-carbon electrode for 90 seconds before each pre-electrolysis step by holding at 0 V and 750 r/min.
- j. After each determination of cadmium and thallium (10 voltammograms), renew the surface of the glassy-carbon electrode by polishing briefly with a slurry of α -alumina on a plastic cloth (Metrohm EA 276A). 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.

DETERMINATION OF CADMIUM AND THALLIUM

- k. 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 μ l of 5×10^{-2} M mercuric nitrate solution, and de-aerate for 15 minutes.
 - (ii) Record a voltammogram for cadmium and thallium by pre-electrolysing for 300 seconds at -1.0 V and 750 r/min. After 15 seconds quiescence, scan anodically to -0.45 V at 5 mV/s, a pulse amplitude of 25 mV, and current density of 0.2 mA for full-scale deflection.
 - (iii) Spike the blank solution with aliquot volumes of working solutions of cadmium and thallium to give final concentrations of 1.0 μ g/l for cadmium and 4.0 μ g/l for thallium. Record the voltammogram of the spiked blank solution. Repeat this spiking step twice.
- l. Plot graphs of peak height versus concentration for cadmium and thallium in the sample and blank solutions. Determine the concentrations of the 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

Cadmium or thallium in sample, ng/g = $(A-B)(C/D)$.

where

- A is the concentration of metal in the sample solution (μ g/l),
- B is the concentration of metal in the blank solution (μ g/l),
- C is the volume of the sample or the blank solution, i.e., 20 ml, and
- D is the mass of sample taken for analysis, i.e., 0.25 g.