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Stripping voltammetry with collection The determination of mercury

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Stripping voltammetry with collection.

The determination of mercury

by

Robert English Allen

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I. INTRODUCTION

While stripping voltammetry (also known as inverse voltammetry with accumulation) has been shown to be a very sensitive technique for the determination of metal ions at the parts-per-billion level, it has not been extensively applied on a practical level primarily due to the lengthy time periods required for analysis. In principle, the technique involves the accumulation of the substance sought in the form of a metal or a sparingly soluble compound on the surface of an electrode in the test solution. The accumulation may proceed for a long period of time so that a significant quantity of material is deposited even though the concentration of the species in the bulk of the solution is very low. Following the accumulation the potential of the electrode is scanned in such a manner that the deposit undergoes electrochemical dissolution (stripping); and the current potential (I-E) or current-time (I-t) curve for the process at the electrode is recorded. Each curve is characterized by a sharp current peak in the potential region where the dissolution occurs. The area of the stripping peak can be related to the quantity of the original deposit and to the analytical concentration of the species sought in the test solution. The technique has a high sensitivity, especially when the accumulation is continued for a long period of time at a high rate of stirring.

It was the purpose of this work to increase the sensitivity of stripping voltammetry so that short deposition times could be used making the technique more favorable for routine analysis. The new technique uses a rotating ring-disk electrode and is called stripping voltammetry with collection.

II. LITERATURE REVIEW

A. Stripping Voltammetry

The theory and applications of stripping voltammetry for the quantitative determination of metal ions have been adequately reviewed by Barendrecht (1), Shain (2), Brainina (3), Stromberg (4), and Kemula (5) and will not be further discussed here.

B. Ring-disk Electrodes

Albery and Hitchman (6) have reviewed the theory and applications of ring-disk electrodes (RRDE). The RRDE was first developed by Frumkin and Nekrasov (7) as a means of detecting the unstable intermediates of certain electrochemical reactions. Cadle and Bruckenstein (8) and Bruckenstein and Tindall (9) studied the behavior of monolayer and submonolayer deposits of Cu and Ag on a Pt RRDE. Johnson, Napp, and Bruckenstein (10) used the RRDE to detect small amounts of Pt(II) which were produced at the Pt disk electrode during the reduction of the surface oxide. Johnson and Bruckenstein (11) detected HOBr produced by the oxidation of Br^- previously adsorbed on the Pt disk of an RRDE. The adsorption and desorption of submonolayer amounts of I^- and I_2 on the Pt disk of an RRDE was studied by Johnson (12). No references were found in the chemical literature for the quantitative analysis of solutions for species at trace levels using an RRDE.

C. Electrode Materials

Barendrecht (1), Kopanica and Vydra (13), and Alder, Fleet, and Kane (14) have reviewed the use of various electrode materials for stripping voltammetry. The three major types are bulk Hg, thin films, and inert, solid conductors.

Hanging Hg-drop electrodes (HMDE), slowly dropping Hg electrodes, and Hg-pool electrodes have been used for the determination of metal ions (usually the ions of those metals which form amalgams) in various samples (15-29). However, the deposited metal must diffuse out of the bulk of the Hg electrode during the stripping process resulting in broad peaks with poor resolution of adjacent peaks and low sensitivity (30). Intermetallic compounds have also been found when two or more metals were deposited simultaneously at a bulk Hg electrode. Such intermetallic formation results in a change in the potential for the stripping of each metal and in one or more new peaks due to the dissolution of the intermetallic species (2).

Thin Hg films on various solid substrates offer improved sensitivity and excellent resolution over bulk Hg electrodes but suffer from a general lack of reproducibility (30). Unlike the bulk Hg electrodes, the rate of diffusion of the metal out of the thin Hg film does not control the stripping process (31). Principal substrates for the film electrodes

include Pt (31-35) and several forms of carbon (30, 36-37). An obvious disadvantage of this type of electrode is that Hg itself and also metals which strip at more positive potentials than Hg cannot be determined.

Solid electrodes offer the advantages of high oxygen overvoltage, high sensitivity, and excellent resolution but have the disadvantages of low hydrogen overvoltage (relative to Hg), poor reproducibility, and non-uniform surface activity resulting in multiple peaks for a single deposited metal (13, 38). There has also been reported evidence of intermetallic compounds formed at solid electrodes when two metals were codeposited (13). However, the disadvantages can be minimized when the determination of Hg or metals more noble than Hg necessitates the use of a solid electrode. The principle solid electrodes include Pt (39-43), graphite (44-57), carbon paste (58-62), and glassy or vitreous carbon (13, 63-71). The glassy carbon electrode is praised for its hardness, high electrical conductivity, large hydrogen overvoltage, chemical inertness, and non-porous surface (30). In a study of twenty-nine different electrode materials ranging from metals to semiconductors, Alder, Fleet, and Kane (14) conclude that with the possible exceptions of Cr and tungsten carbide no other solid electrode material is as excellent as glassy carbon for anodic voltammetry.

No references were found in the chemical literature for the determination of metal ions using stripping voltammetry at a thin Au-film electrode.

D. The Determination of Mercury

There is an abundance of papers in the literature concerning the determination of Hg. Chemical Abstracts lists over 600 papers on the subject for the years 1967-1973. Because of the voluminous amount of subject matter and the numerous techniques and modifications contained therein, only representative papers describing the techniques presently in use by the majority of researchers will be cited. Reviews comparing two or more techniques for the determination of Hg have been written (72-98). Smith (72) arbitrarily classifies the techniques under the headings: activation analysis, atomic absorption and fluorescence, chromatography, colorimetry, electrometry, gravimetry, radiometry, spectrography, titrimetry, X-ray analysis, and miscellaneous. Of these, the first five are the most significant at the parts-per-million and parts-per-billion levels.

In activation analysis the sample is irradiated in a nuclear reactor at a flux of about 10^{12} to 10^{13} neutrons/cm²/sec for time periods ranging from a few minutes to several days followed by a "cooling" period (usually several days) in which the sample is allowed to decay to a level safe

enough for handling (99-102). An unusually long analysis was reported by Livingston, Smith, and Stojanovic (103) in which biological samples were irradiated for one week and "cooled" for three months before measurements were made. After irradiation, the sample is digested by one of many accepted methods followed by separation of the radioactive Hg. Separation has been achieved by ion exchange (104-108), precipitation (109-113), electrodeposition (114-119), extraction (120-122), and several other techniques. After separation, the activity of ^{197}Hg and/or ^{203}Hg is counted. Few papers report the measurement of activity without prior separation (123).

Activation analysis has the advantages of low detection limit on the order of 10^{-9} - 10^{-10} gm (124-126), capability for multi-element determinations with a single irradiation (127-131), and the capability for non-destructive analysis (132). However, because of the lengthy periods of time required for irradiation, "cooling", and separation and because of the reactor required for irradiation, the technique is not very favorable for routine analysis despite the fact that many samples can be irradiated at the same time. It has been reported that the use of laboratory sources of neutrons such as ^{252}Cf do not have the flux density to make them suitable for the determination of Hg at the ppb level in a reasonably short time (133).

Conventional atomic absorption analysis has not proved to be sensitive enough for the determination of Hg at the ppb level. While the normal detection limit is about 1-10 ppm Hg, prior separation of the Hg with dithizone or ammonium-pyrrolidinedithiocarbamate lowers the detection limit to about 0.1 ppm (134-137). Mesman and Smith (138) report a detection limit of 0.04 ppm using the extraction technique. Shirahama, Watanabe, and Mai (139) aspirated samples containing Hg together with SnCl_2 to increase the number of free Hg atoms in the flame and in so doing decreased the detection limit to 0.02 ppm. Kirkbright, West, and Wilson (140) used a nitrogen-separated nitrous oxide-acetylene flame with a microwave excited Hg electrodeless discharge lamp for the determination of Hg at 184.9 nm. They reported a detection limit of 0.02 ppm for Hg(I) and 0.05 ppm for Hg(II). However, the difficulties with which the low detection limits are obtained preclude the use of conventional atomic absorption on a practical, routine basis.

Flameless atomic absorption is based on the high volatility of most Hg compounds. The sample is digested most commonly in a mixture of KMnO_4 and H_2SO_4 , and the Hg is released into the path of a hollow cathode Hg lamp by aeration after the reduction of the ionic Hg to free Hg atoms with a reducing agent such as SnCl_2 , NH_2OH , or NH_2NH_2 (141-145). Some samples require no digestion but are simply

combusted or heated to release Hg atoms (146-152). Various techniques are used to concentrate the Hg atoms and/or remove them from interferences. The most common method is to collect the Hg atoms on a suitable material such as Au (150-155), Ag (156-159), Pt (160-163), Cu (163-165), charcoal (166), or asbestos impregnated with CdS (167). The collector is subsequently heated to release the Hg atoms into the light path of the lamp. Some researchers extract the ionic Hg as the dithizonate and pyrolyze the extract to release Hg atoms (168-179).

Detection limits for flameless atomic absorption analysis for Hg are reported to be on the order of 0.2 - 5 ppb (174-179) which is about four orders of magnitude lower than for conventional atomic absorption analysis. Dagnall, et al., (180) report that the 184.9-nm line offers 31.8 times the sensitivity of the 253.7-nm line commonly used, but the former line lies in the vacuum ultraviolet region of the spectrum and thus presents additional instrumental problems. Therefore, while certainly being sensitive enough for most work, flameless atomic absorption analysis suffers from two significant disadvantages. First, the equipment required is relatively expensive. Secondly, the method is complicated by the procedures necessary to obtain the low detection limits.

As in the case of flameless vs conventional atomic absorption analysis, flameless atomic fluorescence analysis offers a higher sensitivity than flame atomic fluorescence (181-185). However, no improvement in sensitivity is noted nor any advantages of the flameless fluorescence technique over the flameless absorption technique.

Westöö was the first to develop a gas chromatographic technique for the determination of organic Hg compounds as opposed to the determination of total Hg (186). Since then, the gas chromatographic technique has been extensively used (187-202). Because of the fact that organic Hg compounds are much more toxic than inorganic Hg compounds, this technique is of great significance. Reports concerning the detection limit of the technique vary from about 0.02 ng $(\text{CH}_3)_2\text{Hg}$ (190) to about 50 ng (200). Average detection limits appear to be on the order of 10 ppb; but because of the complicated extraction techniques involved, the method is not practical on a routine basis. Some analyses have also been done using thin layer chromatography (203-207).

By far the most popular colorimetric technique for the determination of Hg has been the one using dithizone (diphenylthiocarbazone). A sample is usually digested in a mixture of acids and/or KMnO_4 , and the Hg is extracted with an organic solvent such as CHCl_3 , C_6H_6 , or CCl_4 containing dithizone (208-218). Detection limits normally are reported

to be on the order of 0.1 - 0.5 ppm (219-222) which is obviously not sufficient for Hg at the ppb level. The method also suffers from several interferences since many of the other heavy metals form dithizonates (223). Adjustment of solution conditions to eliminate these interferences is rather complicated in many instances.

Other colorimetric procedures are known based on the complexes of Hg(II) and sodium diethyldithiocarbamate (224-226); of Hg(II), Cu(I), and I^- (227-229); of Hg(II) and I^- (230-231); of Hg(II) and Brilliant Green (232-234); and of Hg(II) and numerous other organic compounds. All of these suffer from the same disadvantages as the method using dithizone.

Ion-selective electrodes for the determination of Hg(II) have been reported for ranges of about 10^{-3} - 10^{-8} M (200 ppm - 2 ppb), but these have not been fully developed and suffer from many interferences (235-238). Another important electrometric method involves the measurement of the change in resistance of a Au (or Zn) film as a function of absorbed Hg (239-241). Samples are treated as in the flameless atomic absorption technique to release Hg vapor which is absorbed by the metal film. The technique has a detection limit of 0.05 ng and gives a linear response over the range of 1 - 10 ng with $\pm 20\%$ precision. The most notable interference is H_2S for which the technique is at least as sensitive as it is for Hg.

The use of stripping voltammetry for the determination of Hg has not been extensively explored. The utilization of Pt or Au electrodes is not satisfactory because deposited Hg amalgamates the electrodes and rapidly diffuses into the bulk of the substrates resulting in multiple peaks. In the case of Pt the anodic dissolution of the Pt-Hg intermetallic compound occurs simultaneously with the absorption of O_2 and/or the formation of the oxide on the surface of the electrode (242). Hence, the current due to the stripping of the Hg cannot be accurately determined (243). Various forms of carbon have been used successfully. Emmott (62) used a carbon paste electrode for the determination of Hg(II) in 1.8 M Li_2SO_4 over the range 0.08 - 2.5 ppm with a deposition time, t_{dep} , of 15 min. Barikov and Songina (53) determined Hg(II) down to 4×10^{-7} M at a graphite electrode in 0.1 M KNO_3 with $t_{dep} = 25$ min. Brainina, et al., (54) estimated a range of 10^{-3} - 10^{-8} M for the stripping analysis of Hg(II) and several other metals in 0.1 M KNO_3 or 1 M $KSCN$. For $t_{dep} = 60$ min, Rannev, et al., (44) found a detection limit of 0.1 ppm for Hg(II) at a graphite electrode. Kartushinskaya and Kolpakova (55) were able to determine 1 ppb Hg(II) in 0.1 M KNO_3 for $t_{dep} = 10$ min using a graphite electrode. Perone and Kretlow (56) performed anodic stripping voltammetry for the determination of Hg(II) down to 4×10^{-5} M in 0.1 M $KSCN$ on a wax-impregnated graphite electrode with $t_{dep} = 30$ min.

The use of glassy carbon has also been explored for the determination of Hg(II) by stripping voltammetry. Miwa and Mizuike (67) used the electrode in the presence of Cu(II) to determine Hg(II) down to 2.5×10^{-8} M. The effect of the Cu(II) was not explained. Kabanova and Zalogina (68) also used glassy carbon but only down to 10^{-6} M Hg(II) in 0.1 M HClO₄. Kendall (69) determined Hg(II) and several other elements at a glassy carbon electrode but required a $t_{\text{dep}} = 72.82$ min to achieve a detection limit of 0.5 ppb. An obvious disadvantage to the use of stripping voltammetry for the determination of Hg(II) is then the excessively long values of t_{dep} required for the ppb level.

A cell for the analysis of 5 - 20 μ l samples for Hg(II) by stripping voltammetry has been reported by Stulik and Stulikova (70). For $t_{\text{dep}} = 15$ min they report a detection limit of 100 pg Hg(II) using a conventional direct current stripping procedure and 10 pg (2.5×10^{-9} M for 20 μ l of solution) using a second harmonic alternating current (AC) stripping procedure. Stulikova and Vydra (71) also used the second harmonic AC technique to strip the Hg deposit and were thus able to determine 5×10^{-10} M Hg(II) in 0.1 M KSCN for $t_{\text{dep}} = 10$ min. While t_{dep} can be short when the AC technique is used, there is an additional sophistication required in the electronic instrumentation which complicates the technique.

This work reports the use of an RRDE with a glassy carbon disk and a Pt ring for the determination of Hg(II) down to 2×10^{-10} M in 50 ml of solution using stripping voltammetry with collection. When a Au film was used on the disk electrode to enhance the deposition of Hg, t_{dep} was never required to exceed 10 min.

III. DEVELOPMENT OF STRIPPING VOLTAMMETRY WITH COLLECTION

A. Definition of Terms and Notation

The following terms and notation are used uniformly throughout this dissertation:

RRDE = rotating ring-disk electrode

I = electrode current (μA)

I_1 = limiting current at an electrode (μA)

E = electrode potential (V vs SCE)

E_{dep} = deposition potential (V vs SCE)

t = time (min)

t_{dep} = deposition time (min)

Q = charge passed due to an electrochemical process (μC)

$$= \int I dt$$

n = number of electrochemical equivalents per mole

F = 96,487 coulombs per electrochemical equivalent

R_1 = radius of the disk electrode of an RRDE (cm)

R_2 = radius of the insulating gap of an RRDE (cm)

R_3 = radius of the ring electrode of an RRDE (cm)

ω = angular velocity (rad/sec)

ν = kinematic viscosity (centipoise $\cdot\text{cm}^3/\text{gm}$)

D_X = diffusion coefficient of species X (cm^2/sec)

C_X^b = bulk concentration of species X (moles/l)

N = collection efficiency of an RRDE

ϕ = rate of scan of electrode potential (V/min)

d = disk electrode when used as a subscript

r = ring electrode when used as a subscript

$\alpha = (R_2/R_1)^3 - 1$

$\beta = (R_3/R_1)^3 - (R_2/R_1)^3$

B. Description of the Technique

The electroanalytical technique known as stripping voltammetry applied at a single electrode has been demonstrated to be useful for the determination of many species present in aqueous solutions at very low concentrations. The technique has been applied to the analyses of very dilute solutions (below 10^{-8} M) in biological, semiconductor, metallurgical, and environmental research and for the determination of impurities in highly purified chemicals (1). As an example of the applicability of the technique for trace analysis, Malkov, Fedoseeva, and Stromberg (37) used liquid extraction followed by stripping voltammetry for the determination of Bi down to 5×10^{-11} M.

In practice the limit to detectability by voltammetric-stripping analysis is set by the uncertainty in the determination of the current in the electrode due to processes other than the stripping of the desired species. These "background" processes include: (i) charging of the electrical double layer at the electrode-solution interface during the scan of the applied potential; (ii) oxidation and/or reduction of impurities in the solution or adsorbed

on the surface of the electrode; and (iii) electrochemical reactions of the electrode itself, e.g., formation or dissolution of oxide at a Pt electrode. The background current is usually estimated by drawing a smooth curve under the stripping peak superimposing the portions of the I-E curve on each side of the peak. This, of course, requires an estimation by the analyst and is a great source of uncertainty since the background current is usually a function of the potential of the electrode and is, therefore, not constant during the recording of the I-E curve. The problem is not solved by recording the I-E curve for the voltammetric scan when no deposition has been allowed because the background currents are not usually reproducible from one scan to the next unless the treatment of the electrode prior to the recording of the I-E curves is identical. Furthermore, a large variation of the background current with the applied potential requires the use of a low sensitivity on the recorder. As a result, long deposition times are required to obtain perceptible stripping peaks.

Herein is described the use of a rotating ring-disk electrode (RRDE) for the determination of concentrations less than the limit of detection for stripping voltammetry at a single electrode. The technique is called stripping voltammetry with collection (SVWC). In principle, SVWC requires the accumulation and stripping of the species

sought at the disk electrode according to the accepted procedures for stripping voltammetry at a single electrode. The potential of the ring electrode is fixed at a value for the convective-diffusional limited reduction or oxidation of the species sought, and the I_r-E_d or I_r-t curve is recorded during the voltammetric stripping of the deposit from the disk electrode. A fraction of the species stripped from the disk electrode is carried by convective-diffusional processes to the ring electrode where it can be either reduced or oxidized depending upon the species involved. Because the potential of the ring electrode is constant during the voltammetric stripping, the background current for the reaction at the ring is nearly constant. Consequently, the background can be compensated electronically and the I_r-E_d curve obtained using a very high sensitivity on the recorder. The collection of very small quantities of species stripped from the disk electrode still produce significant peaks on the I_r-E_d curves even when the stripping peaks on the I_d-E_d curves are nearly imperceptible against the background current.

The instantaneous current for the deposition of a chemical species from a solution onto the disk electrode of an RRDE by a convective-diffusional limited process is related to the concentration of the species in the bulk of the solution by Equation 1 according to Levich (244). The

$$I_{d,1} = 0.62 \text{ nF } \pi R_1^2 \omega^{1/2} \nu^{-1/6} D_X^{2/3} C_X^b \quad (1)$$

charge passed at the disk electrode due to the deposition during the deposition period is given by Equation 2. If

$$Q_d = \int_0^{t_{\text{dep}}} I_d dt \quad (2)$$

ω and C_X^b remain constant during t_{dep} , Equation 2 can be written as Equation 3. The charge passed at the ring

$$Q_d = I_d \cdot t_{\text{dep}} \quad (3)$$

electrode due to the collection of the species produced by the stripping process at the disk electrode is given by Equation 4. In Equation 4, N is the fraction of the species

$$\begin{aligned} Q_r &= Q_d N \\ &= 0.62 \text{ nF } \pi R_1^2 \omega^{1/2} \nu^{-1/6} D_X^{2/3} C_X^b t_{\text{dep}} N \end{aligned} \quad (4)$$

produced at the disk which is collected at the ring. N is called the collection efficiency and can be calculated from the respective radii of the ring and disk electrodes (245).

C. Verification of Experimental Parameters

1. Introduction

SVWC was performed on solutions of H_2SO_4 containing Ag(I) to verify the parameters given in Equation 4. This particular system was chosen as a model because of the relatively simple

homogeneous chemistry involved and because only two oxidation states, Ag(I) and Ag(0), were present. It was also possible to compare the results obtained by SVWC directly with those obtained by stripping voltammetry at a single electrode since Kopanica and Vydra (13) had used the latter technique at a rotating glassy carbon disk electrode for the determination of Ag(I) in acidic media. They reported that Ag(I) could be determined "with sufficient accuracy" down to 1×10^{-9} M provided that the deposition time was long enough. They did not show any I-E curves for that particular concentration.

2. Experimental

a. Instrumentation and apparatus The RRDE used was from Pine Instrument Company of Grove City, Pennsylvania. The disk was made of glassy carbon and the ring of Pt. The pertinent geometric parameters, as discussed in References 245 and 246, were as follows: $R_1 = 0.3787$ cm; $R_2 = 0.3989$ cm; $R_3 = 0.4214$ cm; $\alpha = 0.168$; $\beta = 0.211$; and $N = 0.170$. The synchronous rotator with nine speeds ranging from 400 to 10,000 rev/min was Model PIR from Pine Instrument Company. The electrochemical cell was constructed of quartz with a fritted quartz membrane separating the main compartment from the chamber for the Pt counter electrode. The main compartment was 12.5 cm high and 58 mm ID. The reference electrode was a Beckman SCE in electrical contact

with the test solution through a quartz capillary. Glassware was cleaned using hot HNO_3 followed by thorough rinsing with triply distilled water.

The electronic control circuitry was constructed using operational amplifiers according to the design in Reference 246 with the modification to the disk circuit described in Reference 247a. Rather than using a potentiometric input for the recording of I_p as indicated in Figure 1 of Reference 246, the recorder was driven with the output of a difference amplifier which measured the difference in the signals at the outputs of F-2 and A-2. All resistors used for the measurement of current were standardized by the Physics Instrument Services of Iowa State University, and all voltages were measured using a Data Technology Corporation Model 345 Digital Voltmeter calibrated by the Physics Instrument Services. The X-Y recorder used was a Plotomatic 815 from Bolt, Beranek, and Newman, Inc., of Santa Ana, California. The areas of collection peaks were determined by integration on the original curves with a Keuffel and Esser Compensating Polar Planimeter.

b. Reagents All solutions were prepared using triply distilled water prepared with a demineralization following the first distillation with the second distillation being from alkaline permanganate solution.

The supporting electrolyte was 0.1 M H_2SO_4 prepared from Mallinckrodt Reagent Grade H_2SO_4 . Test solutions of Ag(I) were prepared by the addition to the supporting electrolyte of aliquots of a 0.00100 M stock solution of AgNO_3 prepared from Baker Analyzed Reagent. The stock solution was stored in a polyethylene bottle with the exterior painted black.

c. Pretreatment of the electrode The RRDE was polished at the start of the research with Buehler Handimet 600 paper strips followed by 30 μ and 6 μ Buehler AB Metadi Diamond on nylon lubricated with Buehler Metadi Fluid. The electrode was washed carefully with detergent using a cotton swab and rinsed thoroughly with distilled water after each step in the polishing procedure. Before each day of research the electrode was polished with 1 μ diamond. To remove particles of Pt embedded in the glassy carbon during the initial stages of polishing and to prevent transfer of Pt from the ring to the disk during the last stage of polishing, the electrode was rotated at 400 rev/min as the polishing cloth was moved radially from the center of the electrode. No portion of the polishing cloth was used twice. The surface of the electrode was then cleaned by washing as described above. An I_d - E_d curve was obtained following the polishing to confirm the absence of Pt on the disk electrode. The absence of Pt was verified when a peak for the reduction of the surface oxide of Pt was not observed on the cathodic potential sweep following anodization.

The RRDE was then lowered into the test solution and deaeration with dispersed N_2 begun. E_d was cycled for 10 min between -0.40 V and $+1.20$ V at a rate of 5.0 V/min with $E_r = +0.80$ V.

d. Impurity in test solutions The supporting electrolyte was found to contain traces of Ag(I) varying from 5×10^{-10} to 5×10^{-9} M. The source of the impurity was first thought to be the silver-loaded graphite used for making electrical contact to the upper portion of the metal cylinder on which the ring electrode was mounted in the usual construction of the RRDE. This contact was directly above the cell for the rotator used. A large disk of Teflon, having an outer diameter greater than the opening of the cell, was constructed with a hole in the center just large enough for the RRDE to pass through. Rubber O-rings were placed on the RRDE above and below the disk to hold it in place. In use the RRDE was lowered into the cell so that the Teflon disk was just slightly above the opening of the cell and did not rub on the cell during rotation. With this protection it was impossible for particles from the ring contact to fall into the solution. However, no decrease in the level of the impurity of Ag(I) occurred with the use of the Teflon disk. Therefore, the contact for the ring electrode was concluded not to be the source of the impurity; but the use of the Teflon disk was continued. The H_2SO_4 was

concluded not to be the source of the trace impurity since addition of more acid directly to the test solution did not result in an increase in the level of the impurity. Several procedures were used for cleaning the glassware with no effect on the level of the impurity. The water for preparing solutions was analyzed prior to the demineralization in the procedure for purification and was found to contain about 5×10^{-8} M Ag(I). Thus, the water was concluded to be the source of the impurity. Triply distilled water from another source in the department was found to contain 2×10^{-9} M Ag(I). The presence of Ag(I) in the distilled water prior to the demineralization has been verified previously (247b).

e. Experimental procedure The procedure for the determination of Ag(I) by SVWC at the RRDE was as follows: the cyclic scan of E_d for the pretreatment of the disk electrode was halted at the desired value of $E_{d,dep}$, and E_r was stepped to the desired value for the collection of Ag(I). With the expiration of t_{dep} , E_d was scanned in a positive direction at 5.0 V/min; and the I_r-E_d curve was recorded. Since the rate of scan of E_d was constant, the I_r-E_d curve was also an I_r-t curve. The background current during the collection was estimated by drawing a smooth curve which superimposed the I_r-E_d curve on either side of the collection peak. The area of the peak was measured and Q_r calculated. The procedure was repeated for $t_{dep} = 0.00$ min, and the area of the corresponding peak determined. A

small amount of Ag was deposited at the disk electrode at $t_{\text{dep}} = 0.00$ min with the deposition occurring (i) during the cathodic portion of the cyclic scan of E_d prior to reaching the value of $E_{d,\text{dep}}$ and (ii) during the time that E_d was being scanned anodically from $E_{d,\text{dep}}$ to the value of E_d where the stripping commenced. The value of Q_r was corrected by subtracting the area of the collection peak for $t_{\text{dep}} = 0.00$ min from the area for the non-zero value of t_{dep} . For $t_{\text{dep}} = 3.00$ min the correction was approximately 3% for a rate of scan of $E_d = 5.0$ V/min. Further correction of the value of Q_r was made when preparing a calibration plot. The value of Q_r obtained for the impurity of Ag(I) in the supporting electrolyte was subtracted from the values of Q_r obtained after the intentional additions of Ag(I).

Standard additions of the stock solution of Ag(I) to the supporting electrolyte were made using 2.000 ml and 0.2000 ml micrometer syringes.

3. Results

I-E curves for glassy carbon electrodes in mineral acids are shown and discussed in Reference 248, and curves for Pt electrodes are discussed in Reference 10. These curves will not be further described here. I_d - E_d and I_r - E_d curves obtained using SVWC at the RRDE for 1.00×10^{-6} M Ag(I) are shown in Figure I. Ag deposited at the disk electrode was electrochemically stripped at $E_d > 0.1$ V with the peak of

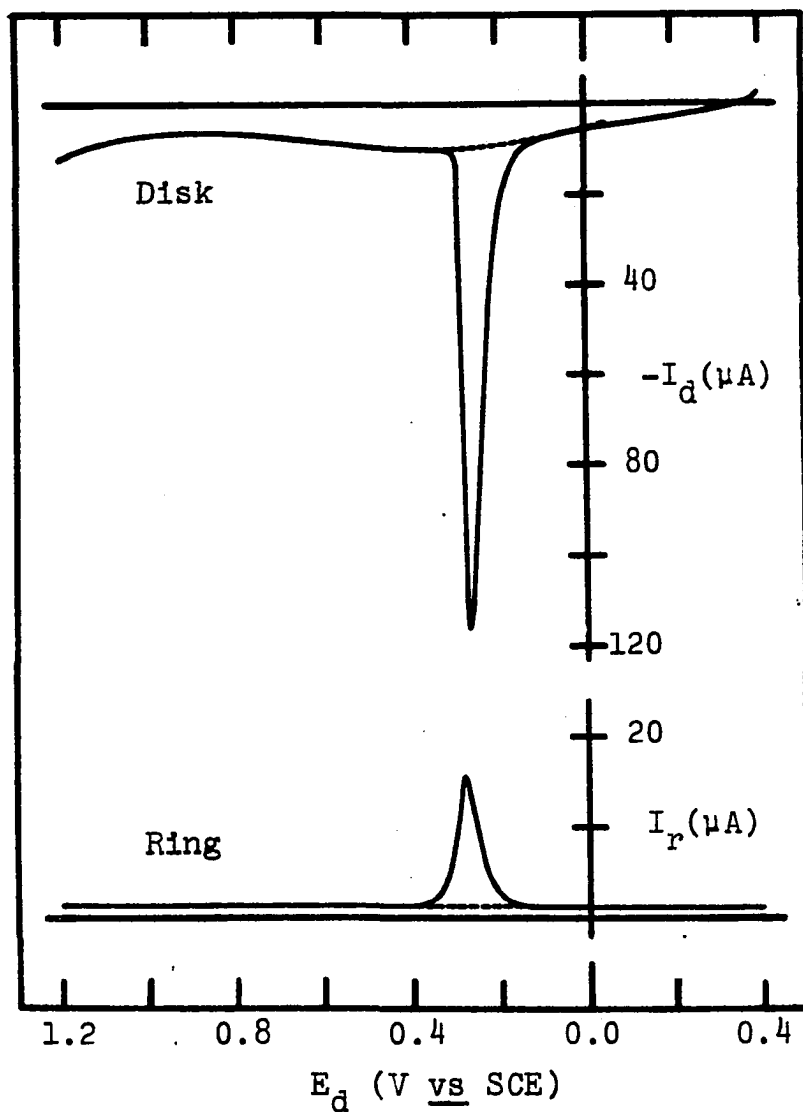


Figure I. I_d - E_d and I_r - E_d curves for SVWC in 1.00×10^{-6} M Ag(I)

$$E_{d,dep} = -0.40 \text{ V}; E_r = 0.00 \text{ V};$$

$$\omega^{1/2} = 6.47 \text{ (rad/sec)}^{1/2}; t_{dep} = 5.00 \text{ min}$$

$$\phi = 5.0 \text{ V/min}$$

the anodic current at approximately 0.25 V. In comparison to the stripping peak on the I_d - E_d curve, the collection peak on the I_r - E_d curve is slightly shifted to a more positive value of E_d . This is the result of the use of a high rate of scan of E_d and the low rate of rotation of the RRDE. A finite amount of time is necessary for a species produced at the surface of the disk electrode to be transported by convection and diffusion to the surface of the ring electrode. Consequently, the peaks for the stripping and the collection do not coincide.

For a concentration of 1.00×10^{-6} M, the contribution to Q_d and Q_r from the impurity of Ag(I) in the supporting electrolyte was negligible. From the values of the areas of the stripping and collection peaks, Q_d and Q_r were calculated to be $71.5 \mu\text{C}$ and $11.3 \mu\text{C}$, respectively. Using these values, the experimental value of \bar{N} was calculated to be 0.158 as compared to the theoretical value of 0.170. Both the stripping and collection peaks for relatively high concentrations of Ag(I), such as illustrated by Figure I, are sufficiently distinct in comparison to the background currents so that either Q_d or Q_r can be used to accurately calculate the bulk concentration of Ag(I).

To determine the I-E curve for the electrodeposition of Ag at the glassy carbon disk electrode, SVWC was performed in a 1.00×10^{-6} M Ag(I) solution for varying values of

$E_{d,dep}$ with $E_r = 0.000$ V. The values of Q_r are plotted in Figure II as a function of $E_{d,dep}$ for $\omega^{1/2} = 6.47$ (rad/sec) $^{1/2}$. The value of $E_{1/2}$ for the deposition is approximately 0.03 V. The standard reduction potential for the Ag(I)/Ag(0) couple is 0.55 V vs SCE (249). The moderate irreversibility for the deposition of Ag does not prevent the successful application of SVWC since values of $E_{d,dep}$ less than -0.3 V appear to be sufficiently cathodic that the deposition of Ag occurs at a rate limited by convective-diffusional processes. A value of $E_{d,dep} = -0.400$ V was used for all subsequent determinations.

To determine a value of E_r at which deposition of Ag at the ring electrode occurs at a rate limited by convective-diffusional processes, SVWC was repeated for the 1.00×10^{-6} M Ag(I) solution using various values of E_r . The plot of Q_r vs E_r is shown in Figure III for $\omega^{1/2} = 6.47$ (rad/sec) $^{1/2}$. The value of $E_{1/2}$ for the deposition at the Pt ring electrode is approximately 0.27 V. The deposition of Ag is more reversible at the ring electrode than at the glassy carbon disk electrode so that a value of $E_r = 0.000$ V was used for all subsequent determinations. The value of Q_r is not zero for E_r between 0.8 and 0.4 V indicating a region of deposition at underpotential. The deposition of Ag at a Pt electrode at underpotentials was investigated and discussed by Cadle and Bruckenstein (8) and Bruckenstein and Tindall (9). The phenomenon of underpotential deposition is

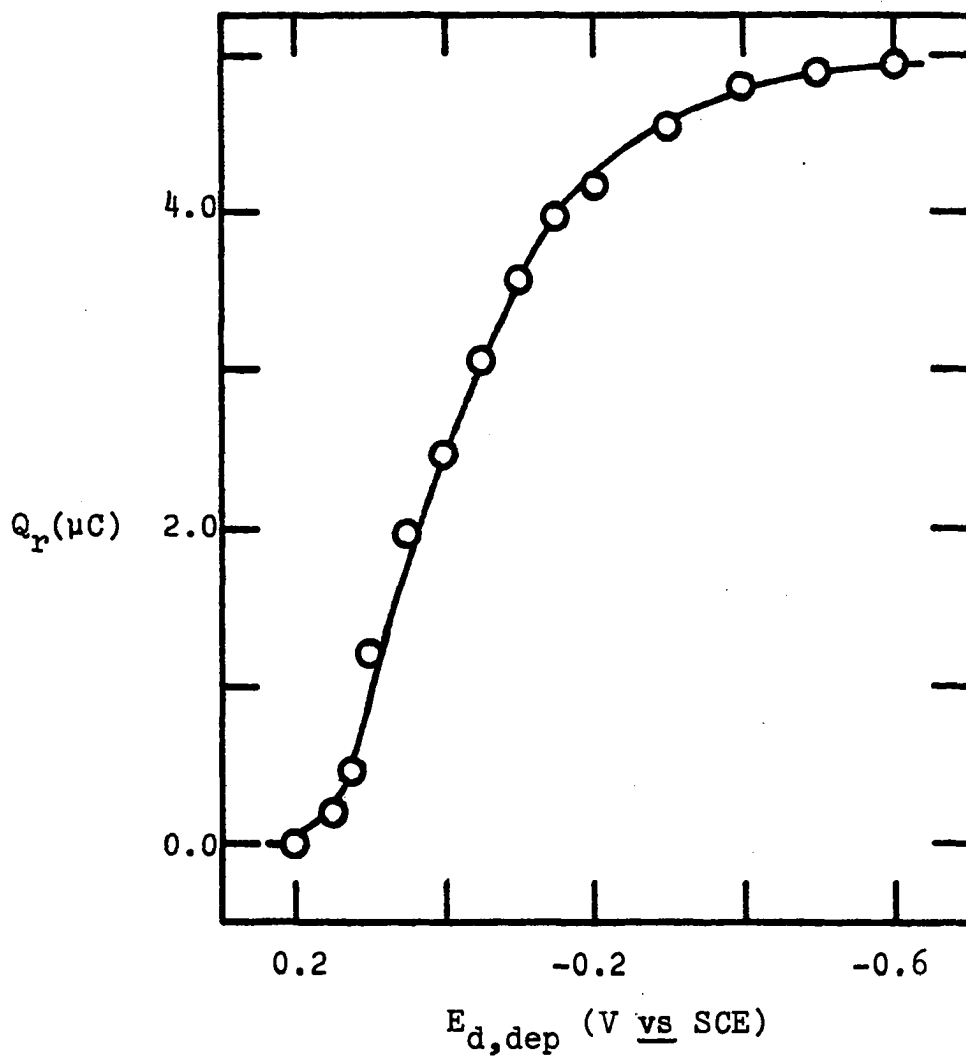


Figure II. I-E curve for the deposition of Ag at the glassy carbon disk electrode

$$C_{\text{Ag(I)}}^b = 1.00 \times 10^{-6} \text{ M}; E_r = 0.00 \text{ V};$$

$$\omega^{1/2} = 6.47 \text{ (rad/sec)}^{1/2}; t_{\text{dep}} = 2.00 \text{ min};$$

$$\phi = 5.0 \text{ V/min}$$

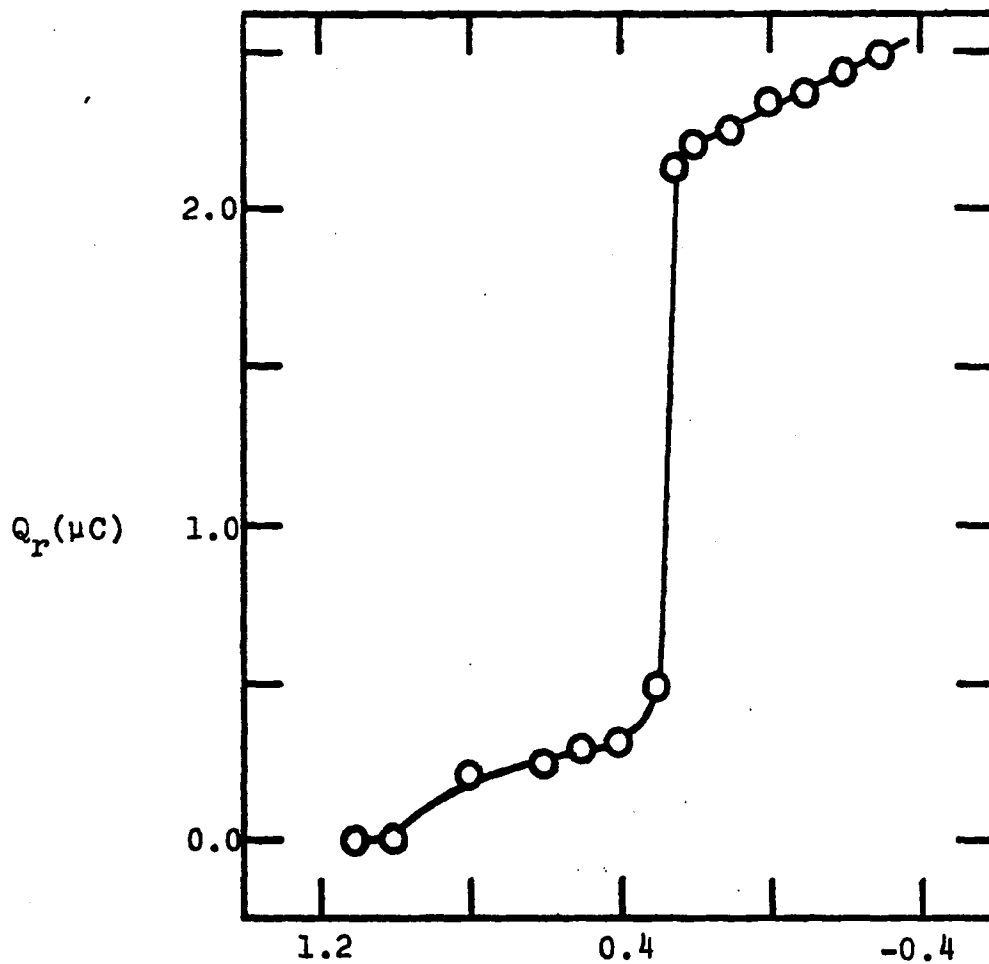


Figure III. I-E curve for the collection of Ag(I) at the Pt ring electrode

$$C_{\text{Ag(I)}}^b = 1.00 \times 10^{-6} \text{ M}; E_{d,\text{dep}} = -0.40 \text{ V};$$

$$\omega^{1/2} = 6.47 \text{ (rad/sec)}^{1/2}; t_{\text{dep}} = 2.00 \text{ min};$$

$$\phi = 5.0 \text{ V/min}$$

associated with the formation of the first layers (usually 1-2 monolayers) of metal on a solid electrode. This layer is deposited at a potential more positive than the potential at which the bulk of the metal is deposited because of the energy of stabilization resulting from the interaction of this layer with the electrode itself. It has been shown that bulk deposits do not occur until the formation of the under-potential deposit is completed.

According to Equation 4, it is predicted that Q_r is a linear function of t_{dep} . Corrected values of Q_r were obtained by SVWC in 1.00×10^{-6} M Ag(I) for $\omega^{1/2} = 6.47$ (rad/sec) $^{1/2}$ and various values of t_{dep} . The plot of Q_r vs t_{dep} is shown in Figure IV with the predicted linear relationship indicative of a convective-diffusional limited rate of mass transport.

To determine the effect on Q_r of changes in the value of $\omega^{1/2}$, SVWC was performed in 1.00×10^{-6} M Ag(I) for values of $\omega^{1/2}$ from 6.47 to 32.4 (rad/sec) $^{1/2}$. The corrected values of Q_r are shown plotted vs $\omega^{1/2}$ in Figure V. The plot is a straight line intersecting the origin in agreement with Equation 4. The linearity of the plot is in agreement with the conclusion that the deposition of Ag on the disk electrode at $E_{\text{d,dep}} = -0.400$ V occurs at a rate limited by convective-diffusional processes.

Q_r is not predicted to be dependent on the rate of scan of E_d used during the process of electrochemically stripping

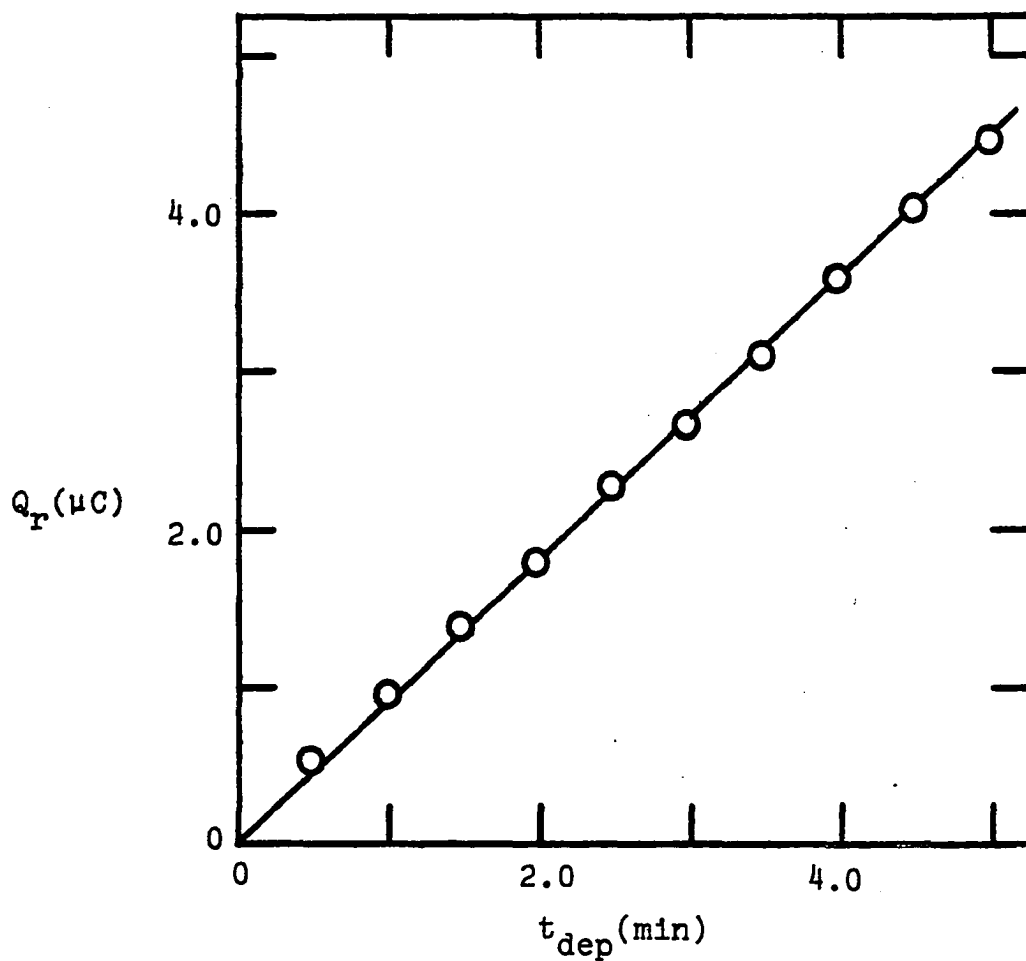


Figure IV. Plot of Q_r vs t_{dep}

$$C_{\text{Ag(I)}}^b = 1.00 \times 10^{-6} \text{ M}; E_{\text{d,dep}} = -0.40 \text{ V};$$

$$E_r = 0.00 \text{ V}; \omega^{1/2} = 6.47 \text{ (rad/sec)}^{1/2};$$

$$\phi = 5.0 \text{ V/min}$$

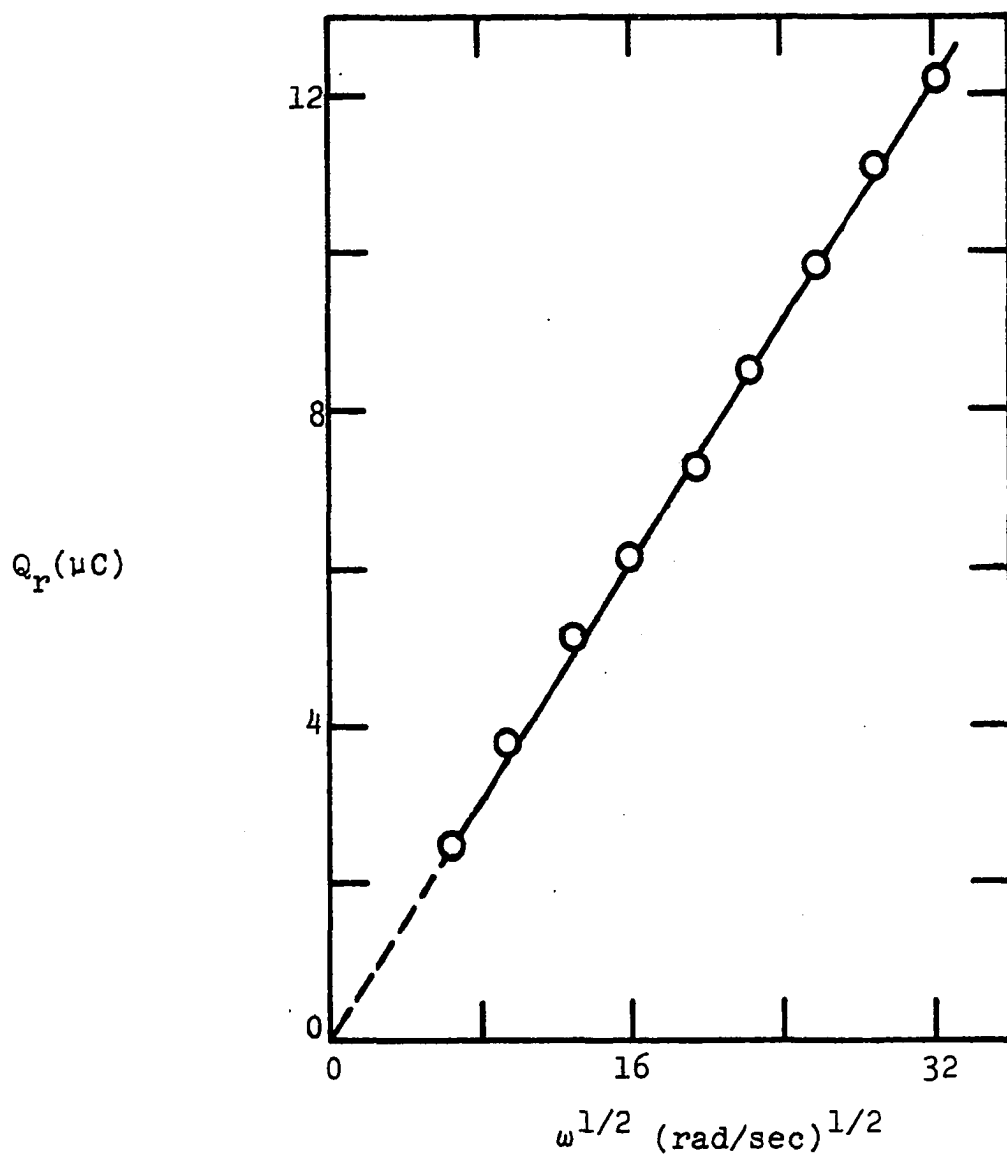


Figure V. Plot of Q_r vs $\omega^{1/2}$

$$C_{\text{Ag(I)}}^b = 1.00 \times 10^{-6} \text{ M}; E_{d,\text{dep}} = -0.40 \text{ V};$$

$$E_r = 0.00 \text{ V}; t_{\text{dep}} = 1.00 \text{ min};$$

$$\phi = 5.0 \text{ V/min}$$

the deposit of Ag from the disk electrode. Corrected values of Q_r for SVWC in 1.00×10^{-6} M Ag(I) are tabulated in Table I as a function of ϕ . The results are consistent with Equation 4.

Table I. Effect of ϕ on Q_r

ϕ (V/min)	Q_r (μC)
2.0	0.84
3.0	0.84
4.0	0.84
5.0	0.84
7.0	0.84
9.0	0.84

SVWC was performed for values of $C_{\text{Ag(I)}}^b$ ranging from 1.00×10^{-10} to 1.00×10^{-6} M. The values of concentration were calculated on the basis of standard addition, and values of Q_r were corrected as described earlier. The plot of Q_r vs $C_{\text{Ag(I)}}^b$ on a log-log scale is shown in Figure VI. Each value plotted represents the average of three determinations at that concentration. The average deviation of the values is not reflected in the size of each point on the plot. The plot is linear in agreement with Equation 4. The determinations of Q_r for $C_{\text{Ag(I)}}^b$ less than 10^{-9} M were performed at a time when the blank was advantageously low (approximately 5×10^{-10} M).

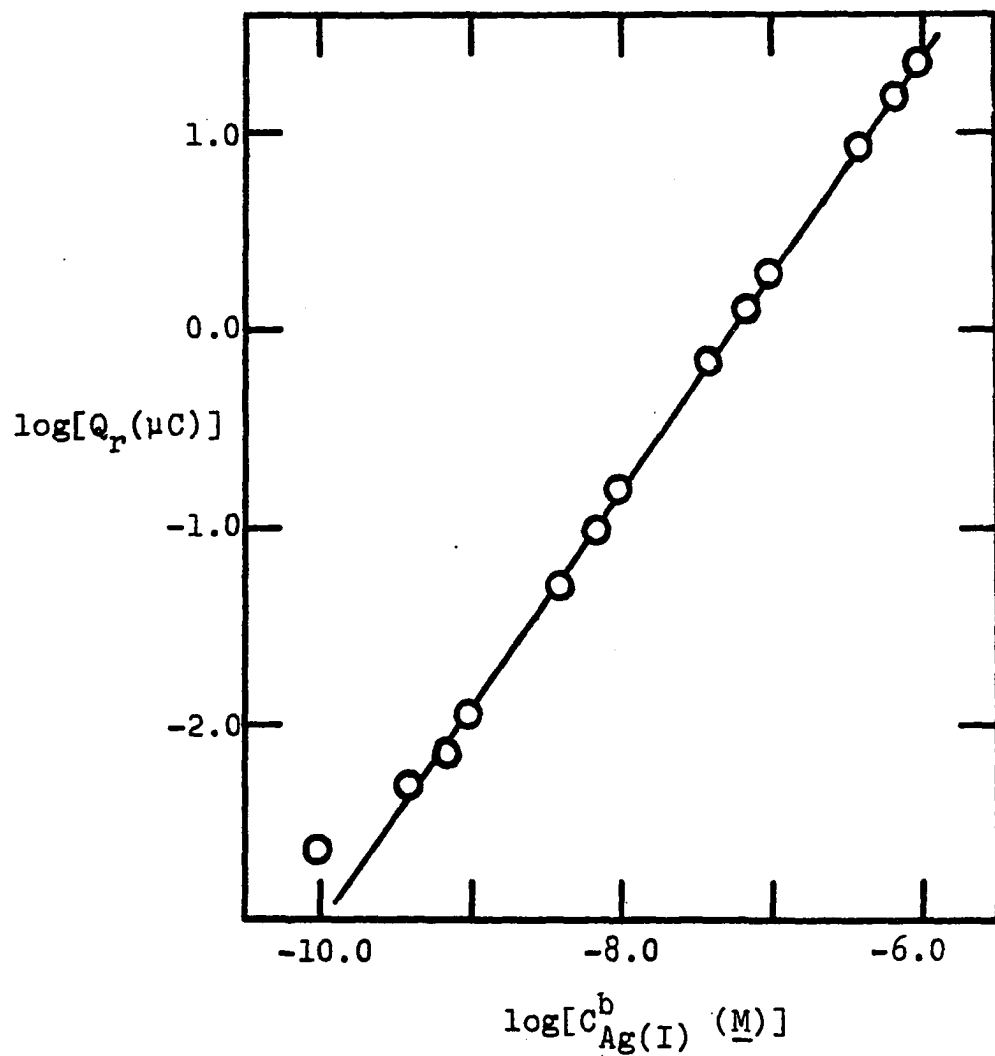


Figure VI. Log-log plot of Q_r vs $C_{\text{Ag(I)}}^b$

$$E_{d,\text{dep}} = -0.40 \text{ V}; E_r = 0.00 \text{ V};$$

$$\omega^{1/2} = 6.47 (\text{rad/sec})^{1/2}; \phi = 5.0 \text{ V/min}$$

Several days after completion of the calibration curve shown in Figure VI, supporting electrolyte was prepared for which the blank was approximately 2×10^{-10} M. Values of Q_r for five determinations of the blank had an average relative deviation of 25%. Values of Q_r for five determinations following the addition of an amount of the stock solution of Ag(I) to give a 1.00×10^{-10} M Ag(I) solution excluding the blank had an average relative deviation of 7.4%.

The value of the diffusion coefficient for Ag(I) in 0.1 M H_2SO_4 was calculated using Equation 4 and the data shown in Figure VI. The value was 1.29×10^{-5} cm^2/sec . This value is in good agreement with the value of 1.30×10^{-5} cm^2/sec determined by Johnson (250) in 0.1 M KNO_3 from values of $I_{d,1}$ at a rotating disk electrode for the deposition of Ag(I).

D. Comparison of SVWC

with Conventional Stripping Voltammetry

The effect of the background current to limit the application of conventional stripping voltammetry at a single electrode was discussed in Part B of this chapter. The possibility of applying SVWC at an RRDE for the determination of concentrations lower than amenable to conventional stripping voltammetry is illustrated by the I_d-E_d and I_r-E_r curves shown in Figure VII. These curves were obtained for 6.0×10^{-9} M Ag(I). The large anodic peak on the I_d-E_d curve

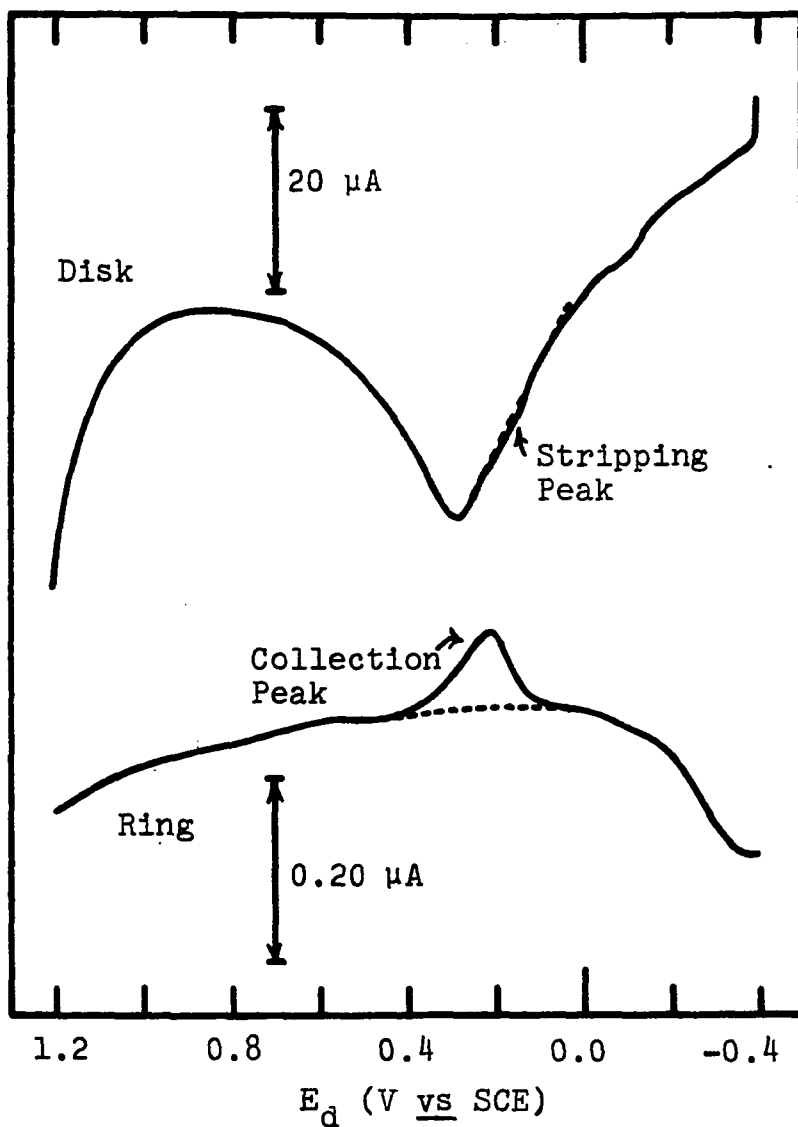


Figure VII. I_d-E_d and I_r-E_d curves for SVWC in 6.0×10^{-9} M Ag(I)

$$E_{d,dep} = -0.40 \text{ V}; E_r = 0.00 \text{ V};$$

$$\omega^{1/2} = 6.47 \text{ (rad/sec)}^{1/2}; t_{dep} = 10.0 \text{ min};$$

$$\phi = 5.0 \text{ V/min}$$

is due to background processes at the disk electrode and not the dissolution of the Ag deposit. The small shoulder at about 0.2 V is due to the stripping of the Ag deposit. Even though the sensitivity is relatively high for the recording of the curve, no possibility exists of accurately determining the area of the stripping peak. The background current at the ring electrode is much more independent of E_d than the background current at the disk electrode. Consequently, the I_r-E_d curve was recorded at a very high sensitivity. The collection peak is very distinct, and integration of the peak can be done accurately.

The rapid change of the background on the I_r-E_d curve from -0.4 to 0.0 V is thought to be due to the presence of residual amounts of O_2 in the supporting electrolyte. O_2 is reduced at the Pt ring electrode for $E_r = 0.00$ V. However, for E_d more negative than 0.00 V it is also likely that O_2 is reduced at the glassy carbon disk electrode even though the reduction is so irreversible that the voltammetric wave at the disk cannot be discerned from the charging current. Because of the reduction at the disk electrode, the ring electrode is shielded somewhat from the O_2 in the bulk of the solution. When E_d becomes more positive than 0.00 V, the reduction of O_2 at the disk decreases thus allowing more O_2 to reach the ring electrode and resulting in an increase in I_r .

The change in the background is also due in part to the electronic instrumentation. Proper alignment of the electronic circuit is described in Reference 246 and involves adjustment of resistor R_4 so that E_r does not change while E_d is varied. The alignment is very essential, particularly if it is desired to measure very small currents at the ring electrode. Even with maximum care in alignment, it was not possible to prevent a small change in E_r (1-3 mv) while scanning E_d in the vicinity of 0.0 V. This small fluctuation results in some charging phenomena which contribute to the background current shown in Figure VII.

E. Conclusions

The applicability of an RRDE for decreasing the already dramatically low detection limits for analyses based on stripping voltammetry has been demonstrated. There are at least two additional advantages of SVWC at an RRDE over the conventional method at a single electrode.

First, the time of analysis is greatly decreased because Q_r can be determined accurately even though the quantity of deposit accumulated is very small. This allows the use of SVWC for routine analyses without the need for irritatingly long deposition periods.

Secondly, the difficulties in the simultaneous determination of two or more metallic species resulting from the formation of intermetallic compounds at the electrode surface

may be largely circumvented. This follows since the maximum coverage of the electrode by the deposit need never approach a monolayer; and therefore, the chance of inter-element reactions is greatly reduced or eliminated.

IV. PRELIMINARY INVESTIGATION OF THE DETERMINATION OF MERCURY USING SVWC

A. Introduction

In the early 1970's what were termed to be intolerably high levels of Hg were found in certain food fishes commercially available for human consumption in the USA. After the deaths of several people in Japan from Hg poisoning (Minimata disease) in the 1950's as a result of eating seafood contaminated with Hg waste discharged from a nearby caustic soda plant, there was an increasing public concern about the amounts of Hg to be found in the environment. Therefore, it was no surprise that the presence of Hg in fish samples in this country prompted an outcry that the entire environment was being contaminated with Hg. However, subsequent analyses of fish specimens preserved in museums from as long ago as 1880 (251-252a) showed comparable levels of Hg to those caught in the 1970's.

It is obvious that in order to obtain a clear picture of the extent of the pollution of the environment by Hg accurate information about natural background levels of Hg as well as levels indicative of pollution are essential. Because of the fact that Hg compounds are extremely toxic to almost all living organisms and the fact that almost all organisms accumulate these compounds, the levels of concern are the parts per million to parts per trillion levels. Hg, however,

has long been one of the most difficult elements to determine at these levels by any method of analysis; but because of the early success with SVWC, it was thought that this technique would be viable for the determination of Hg. Primary considerations were the very high sensitivity, the short analysis time, and the simplicity of operation. Therefore, an investigation of the feasibility of SVWC for the determination of Hg was initiated.

B. Experimental

1. Instrumentation and apparatus

See Chapter III, Part C, Section 2(a).

2. Reagents

A stock solution of Hg(II) was prepared by dissolving triply distilled Hg in cold concentrated HNO₃ (Mallinckrodt Reagent Grade) followed by dilution with water to give a solution of 1.00×10^{-3} M Hg(II) and 0.10 M HNO₃. The stock solution was stored in an opaque, polyethylene bottle. Standard additions of the stock solution were made using 2.000 and 0.2000-ml micrometer syringes. All other reagents were the same as described in Chapter III, Part C, Section 2(b).

3. Pretreatment of the electrode

See Chapter III, Part C, Section 2(c).

4. Experimental procedure

The procedure for the application of SVWC for the determination of Hg(II) in 1.0 M H₂SO₄ was as follows. During deaeration of the supporting electrolyte, E_d was scanned in a cyclic manner at 5.0 V/min between -0.40 and +1.00 V with E_r = +0.80 V and $\omega^{1/2} = 6.47 \text{ (rad/sec)}^{1/2}$. The deaeration was stopped, and the N₂ was allowed to pass over the top of the solution to prevent O₂ from re-entering the supporting electrolyte. The desired aliquot of Hg(II) was added to the solution, ω was changed to the desired value, and the solution was allowed to mix. The negative scan of E_d was stopped at the chosen value of E_{d,dep}, and the deposition of Hg at the disk electrode was continued for the desired t_{dep}. E_r was switched to the appropriate value for the collection of the stripped Hg species approximately 2 min before E_d was scanned to allow I_r to decay to a steady-state value. At the expiration of t_{dep} the cyclic scan of E_d was begun in the positive direction, and the I_r-E_d curve was recorded for the anodic half of the first and second scans. The collection peak for the second scan was considered to be the blank, i.e., the value of Q_r corresponding to t_{dep} = 0.00 min.

C. Verification of Experimental Parameters

It was determined that Hg can be electrolytically deposited and stripped at the glassy carbon disk electrode of

the RRDE in 1.0 M H_2SO_4 containing 1.00×10^{-5} M $\text{Hg}(\text{II})$. The potential of the stripping peak on the I_d - E_d curve was approximately 0.45 V. The species stripped from the disk was redeposited at the Pt ring electrode at $E_r = 0.00$ V. Figure VIII is a plot of Q_r as a function of $E_{d,\text{dep}}$. The value of $E_{1/2}$ for the deposition process at the disk electrode is approximately -0.23 V, and it was concluded that the deposition was limited by convective-diffusional mass transport for $E_{d,\text{dep}} \leq -0.50$ V. The standard reduction potential for the $\text{Hg}(\text{II})/\text{Hg}(\text{O})$ couple is +0.54 V vs SCE (249). It is obvious that the deposition of Hg at the glassy carbon disk is very irreversible.

It was determined that the species produced by the voltammetric stripping of the Hg at the glassy carbon disk electrode could be oxidized or reduced at the ring electrode. Figure IX is a plot of the area of the peak on the I_r - E_d curve at $E_d = 0.45$ V as a function of E_r . The $E_{1/2}$ for the cathodic process at the ring electrode is approximately 0.32 V, and the $E_{1/2}$ for the anodic process is approximately 0.91 V. The limiting cathodic and anodic values of Q_r are virtually equal in magnitude. Hence, it was concluded that more than 95% of the deposited Hg is stripped at the glassy carbon electrode as $\text{Hg}(\text{I})$. Reactions consistent with the data in Figures VIII and IX are given by Equations 5-8.

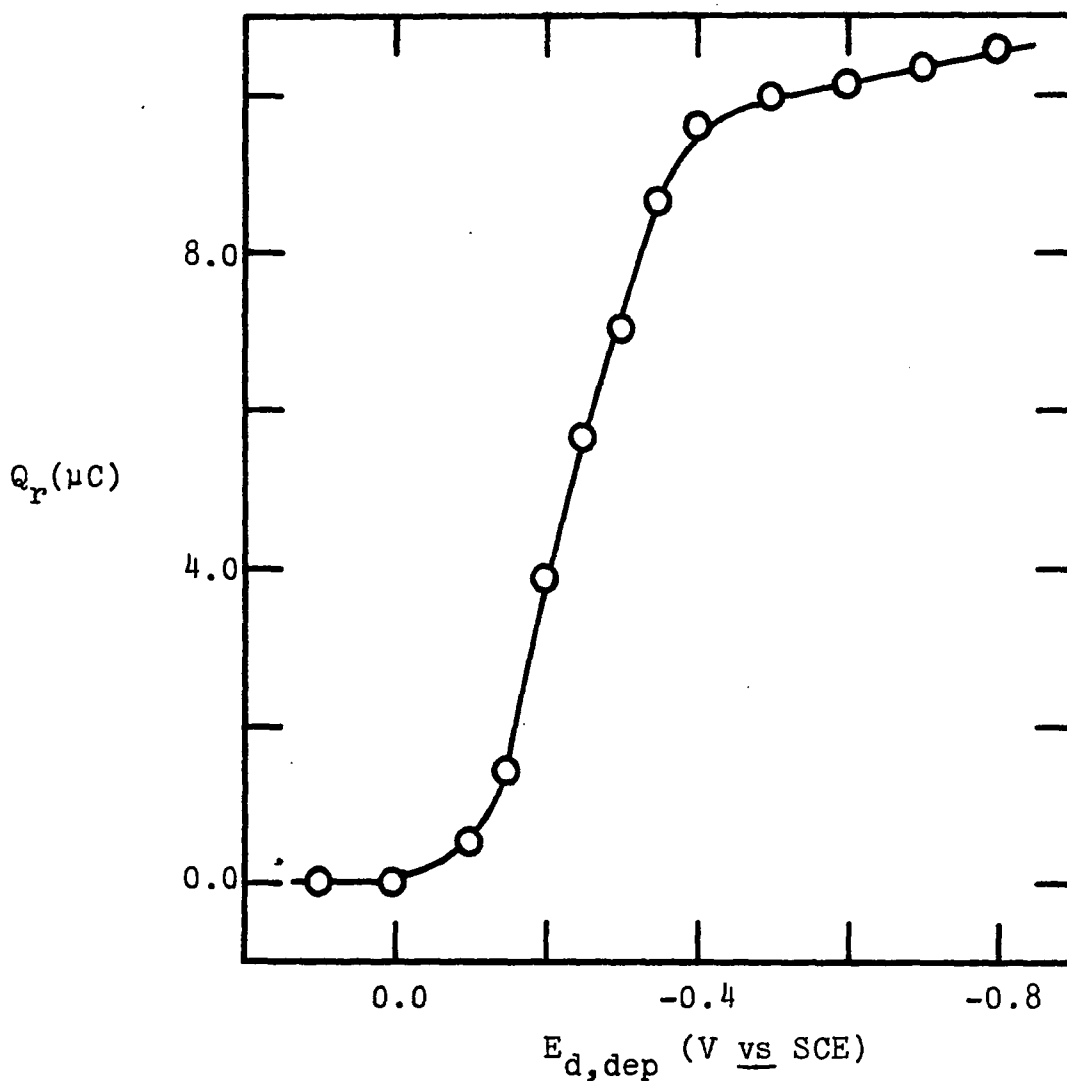


Figure VIII. I-E curve for the deposition of Hg at the glassy carbon disk electrode

$$C_{\text{Hg(II)}}^b = 1.00 \times 10^{-5} \text{ M}; E_r = 0.00 \text{ V};$$

$$\omega^{1/2} = 6.47 \text{ (rad/sec)}^{1/2}; t_{\text{dep}} = 1.00 \text{ min};$$

$$\phi = 5.0 \text{ V/min}$$

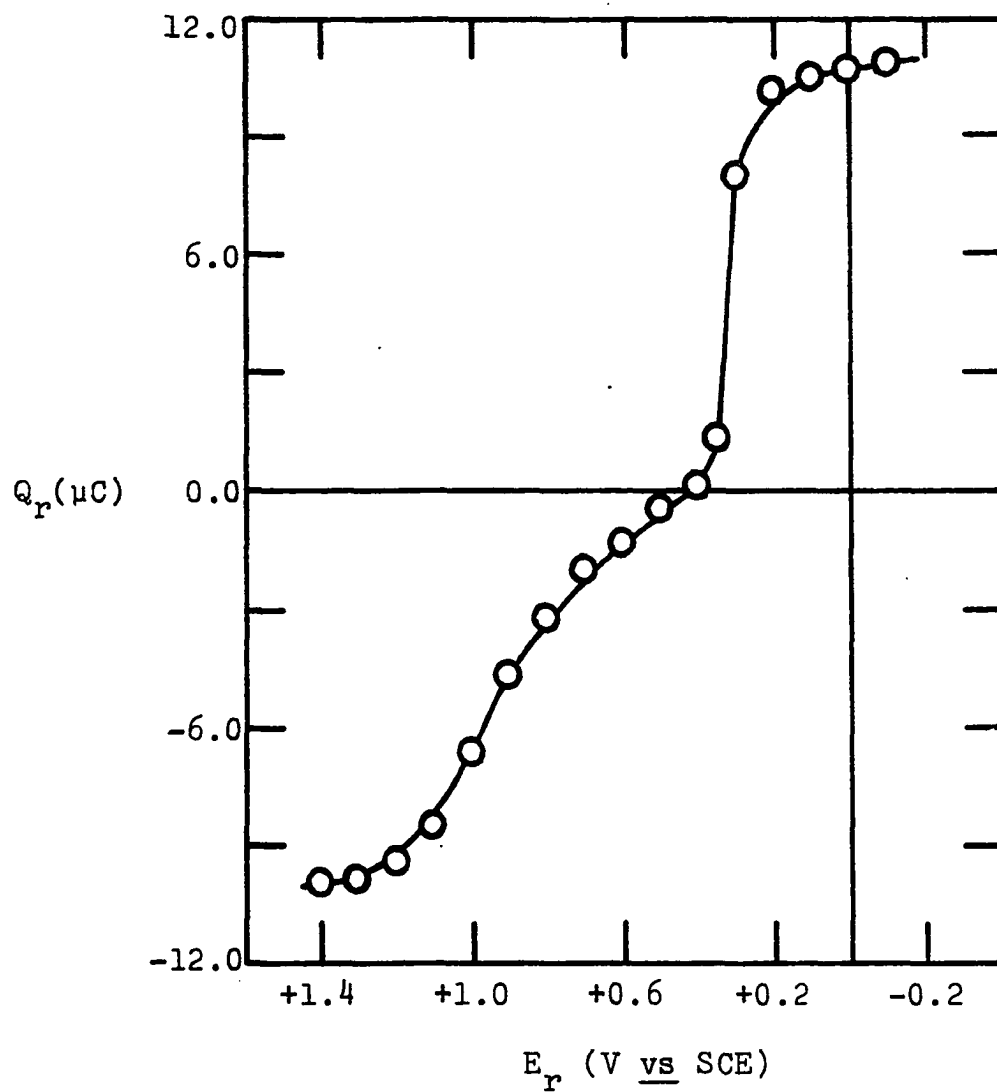


Figure IX. I-E curve for the collection of the Hg(I) at the Pt ring electrode

$$C_{\text{Hg(II)}}^b = 1.00 \times 10^{-5} \text{ M}; E_{d,\text{dep}} = 0.00 \text{ V};$$

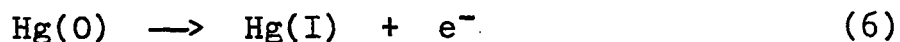
$$\omega^{1/2} = 6.47 \text{ (rad/sec)}^{1/2}; t_{\text{dep}} = 1.00 \text{ min};$$

$$\phi = 5.0 \text{ V/min}$$

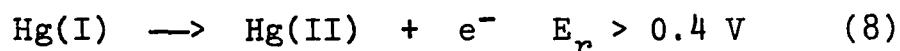
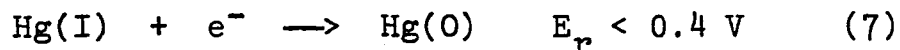
Deposition at the disk electrode:



Stripping at the disk electrode:



Collection at the ring electrode:



The fact that the Hg is stripped as Hg(I) which can be oxidized to Hg(II) at the ring electrode makes it possible to use SVWC for the determination of Hg(II) in the presence of Ag(I). This is not possible using stripping voltammetry at a single electrode without the use of complexing agents because the stripping peaks for Hg and Ag have significant overlap. I_d-E_d and I_r-E_d curves for $E_r = 0.00 \text{ V}$ and 1.20 V are shown in Figure X for a $1.0 \text{ M H}_2\text{SO}_4$ solution containing $1.00 \times 10^{-6} \text{ M Hg(II)}$ and $3.00 \times 10^{-7} \text{ M Ag(I)}$. Both Ag(I) and Hg(I) are reduced at the ring electrode at $E_r = 0.00 \text{ V}$, but only Hg(I) is oxidized at the ring electrode for $E_r = 1.20 \text{ V}$. The value of Q_r at $E_r = 1.20 \text{ V}$ can be used for the determination of Hg, and the difference between Q_r at $E_r = 0.00 \text{ V}$ and $Q_r = 1.20 \text{ V}$ can be used for the determination of Ag.

A linear plot of Q_r vs t_{dep} with a zero intercept is expected on the basis of Equation 4 for the collection of the

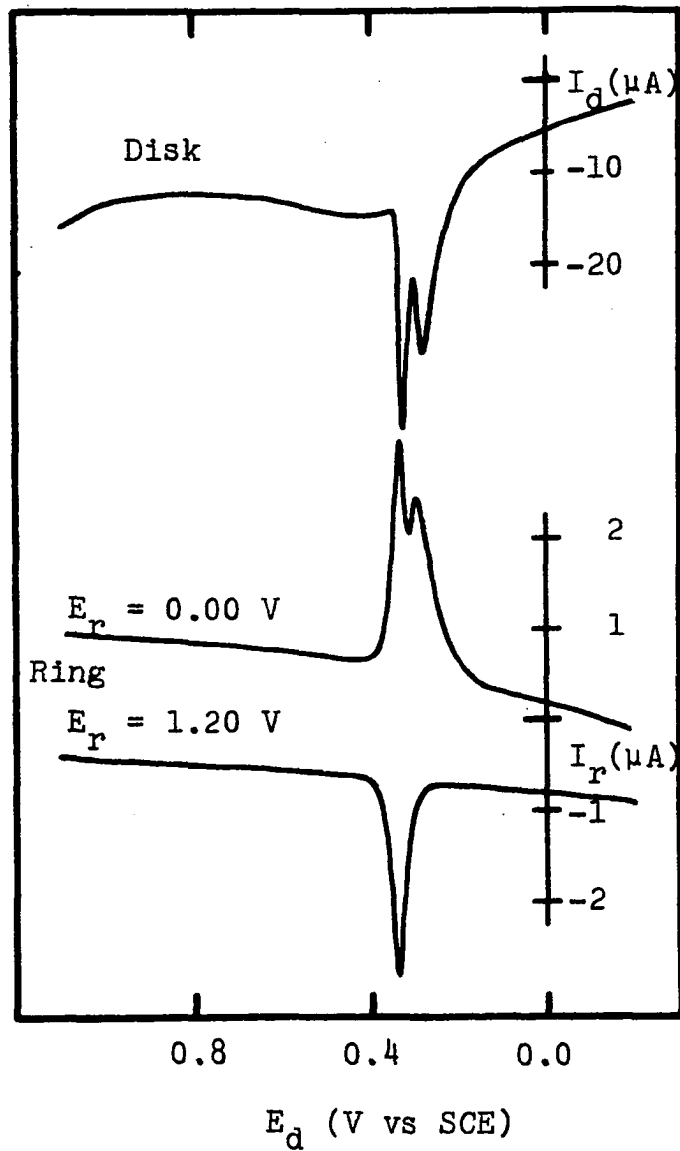


Figure X. I_d - E_d and I_r - E_d curves for SVWC in a mixture of Hg(II) and Ag(I)

$$C_{\text{Hg(II)}}^b = 1.00 \times 10^{-6} \text{ M}; C_{\text{Ag(I)}}^b = 3.0 \times 10^{-7} \text{ M};$$

$$E_{d,\text{dep}} = -0.60 \text{ V}; \omega^{1/w} = 6.47 \text{ (rad/sec)}^{1/2};$$

$$t_{\text{dep}} = 2.00 \text{ min}; \phi = 5.0 \text{ V/min}$$

stripped Hg species. Such was obtained for $C_{\text{Hg(II)}}^b \geq 1.00 \times 10^{-5} \text{ M}$ for t_{dep} ranging from 0 to 20 min for $E_{\text{d,dep}} = -0.50 \text{ V}$. The plot was not linear, however, for $C_{\text{Hg(II)}}^b < 1.00 \times 10^{-5} \text{ M}$ as illustrated by the curve in Figure XI for $1.00 \times 10^{-6} \text{ M}$ Hg(II). Apparently, the electrodeposition of Hg at a glassy carbon disk electrode at $E_{\text{d}} = -0.50 \text{ V}$ is limited by convective-diffusional processes only after a finite amount of Hg has been deposited. For $C_{\text{Hg(II)}}^b \geq 1.00 \times 10^{-5} \text{ M}$ Hg(II) the time required for the deposition of the requisite amount of Hg was much less than all values of t_{dep} resulting in no observation of curvature in the plot of Q_r vs t_{dep} . Attempts to deposit Hg at $E_{\text{d,dep}} < -0.50 \text{ V}$ were not successful for solutions containing less than $1.00 \times 10^{-5} \text{ M}$ Hg(II) due to the interference of H_2 formed at the surface of the electrode.

The values of Q_r obtained day-to-day for $E_{\text{d,dep}} = -0.50 \text{ V}$ and $C_{\text{Hg(II)}}^b = 1.00 \times 10^{-6} \text{ M}$ varied dramatically. Because of the omnipresence of indeterminate amounts of Cu(II) and other cations in reagents, SVWC was performed in 1.0 M H_2SO_4 containing $1.00 \times 10^{-6} \text{ M}$ Hg(II) and $1.00 \times 10^{-6} \text{ M}$ Cu(II). An anodic peak on the $I_{\text{d}}-E_{\text{d}}$ curve for the stripping of the deposit of Cu was observed at approximately 0.00 V . A plot of Q_r vs t_{dep} for the redeposition of Hg(I) stripped from the disk electrode at $E_{\text{d}} = 0.4 \text{ V}$ is shown in Figure XII. (For comparison, the data from Figure XI is replotted in this figure.) The dramatic increase in values of Q_r due to the

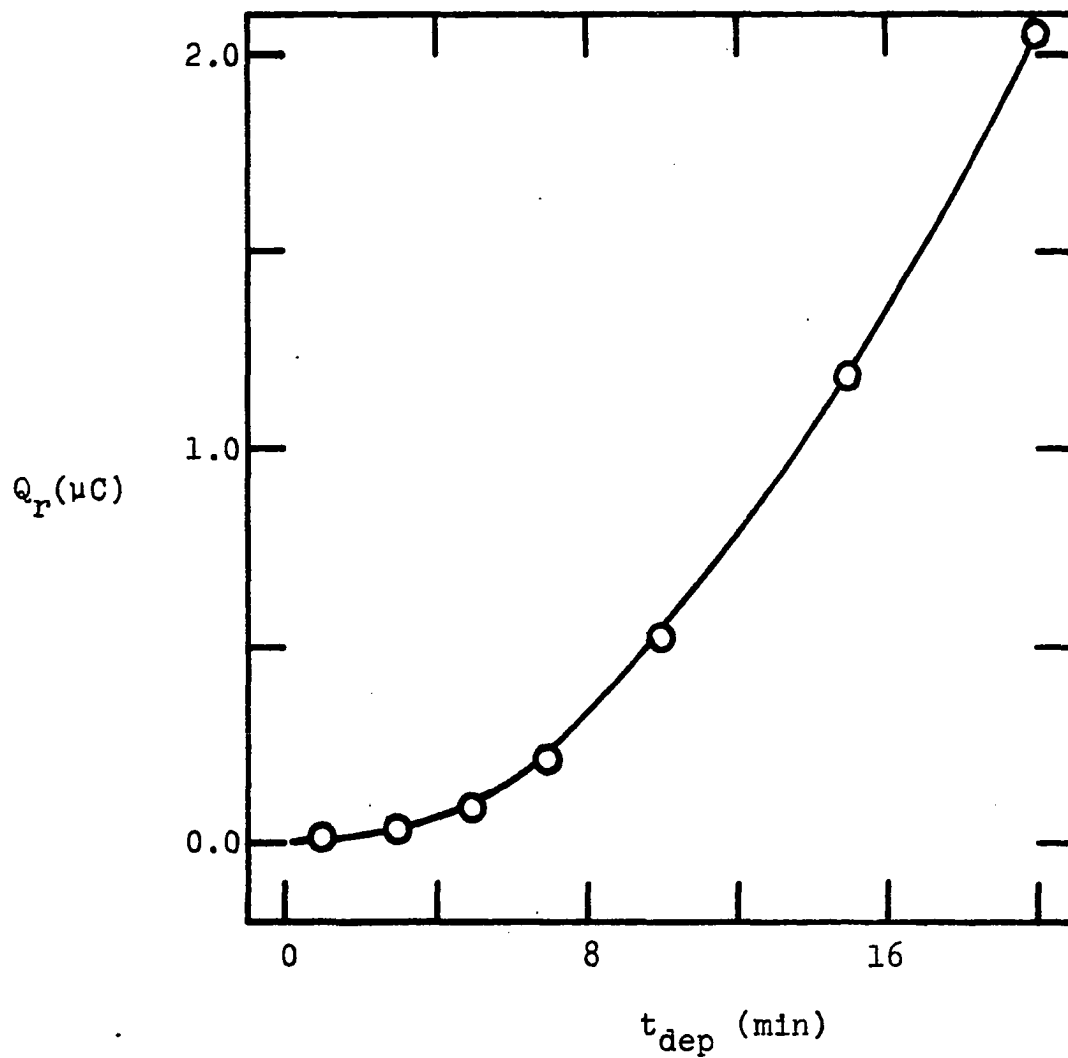


Figure XI. Plot of Q_r vs t_{dep}

$$C_{\text{Hg(II)}}^b = 1.00 \times 10^{-6} \text{ M}; E_{d,\text{dep}} = -0.50 \text{ V};$$

$$E_r = +1.20 \text{ V}; \omega^{1/2} = 6.47 \text{ (rad/sec)}^{1/2};$$

$$\phi = 5.0 \text{ V/min}$$

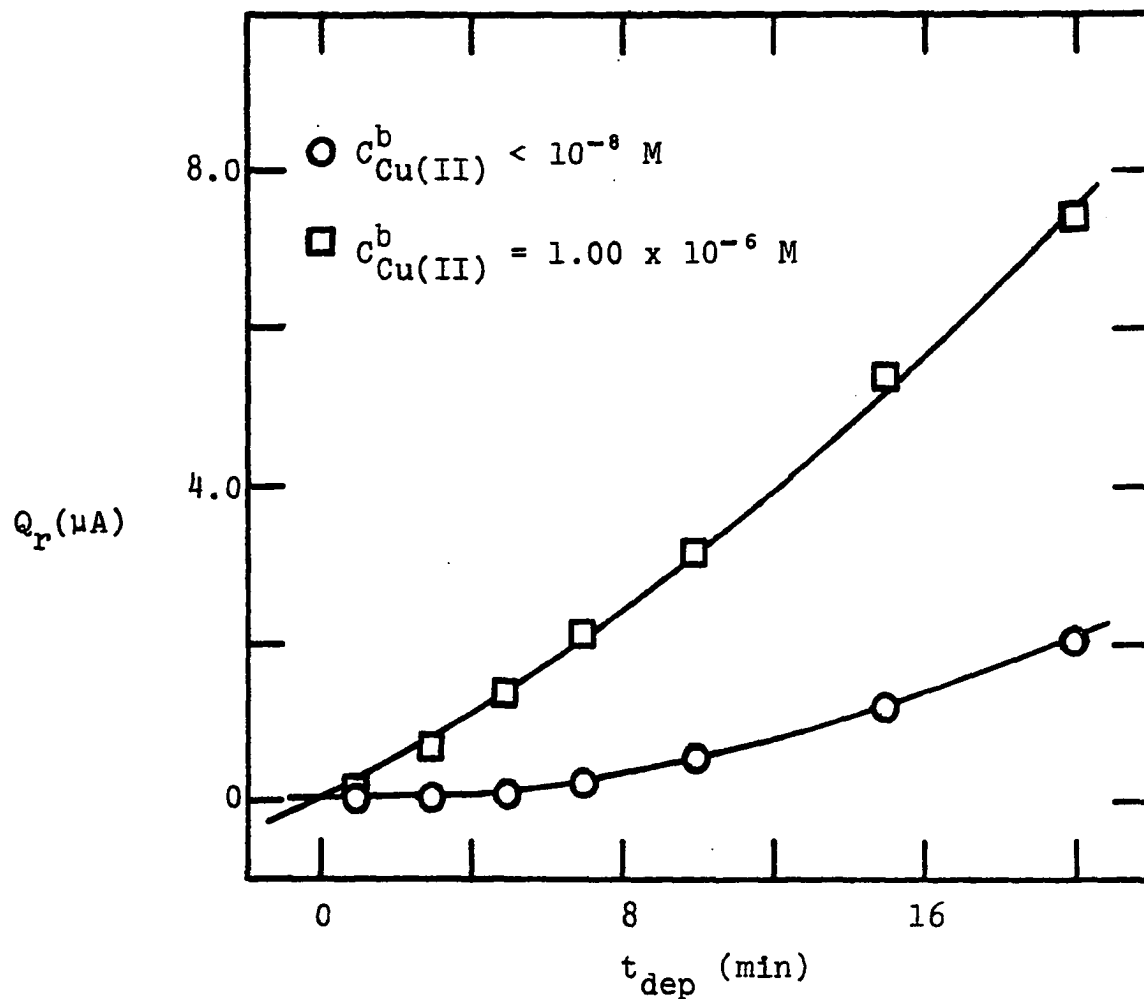


Figure XII. Plot of Q_r vs t_{dep} for SVWC of Hg(II) in the presence of Cu(II)

$$c_{\text{Hg(II)}}^b = 1.00 \times 10^{-6} \text{ M}; E_{\text{d,dep}} = -0.50 \text{ V};$$

$$E_r = +1.20 \text{ V}; \omega^{1/2} = 6.47 \text{ (rad/sec)}^{1/2};$$

$$\phi = 5.0 \text{ V/min}$$

presence of Cu(II) was concluded to result from the greater reversibility for the electrodeposition of Hg(II) at a film of Cu in comparison with that at a bare glassy carbon electrode. The effect of Cu(II) on the determination of Hg(II) by stripping voltammetry at a single electrode was previously noted by Miwa and Mizuike (67), but no explanation for the phenomenon was given. It was concluded that the day-to-day variations in Q_p noted above were due to fluctuations of the level of trace metal impurities in the supporting electrolyte.

D. Conclusions

The electrodeposition of Hg(II) on glassy carbon was concluded to be controlled by convection and diffusion only after a finite amount of Hg had been deposited. Therefore, the use of glassy carbon for the determination of Hg(II) by SVWC was deemed unfeasible since with the desired value of $t_{\text{dep}} = 10$ min, the prerequisite amount of Hg deposit would not be deposited if the concentration of Hg(II) were less than 5×10^{-6} M (1 ppm).

The use of a Cu film on the glassy disk for the determination of Hg(II) by SVWC was also concluded to be unworkable. Under the conditions desired for the deposition of Hg, it was found that the minimum amount of Cu(II) required for the Cu film was 5×10^{-7} M. However, at this level of Cu(II) the minimum measurable concentration of Hg(II) was found to be

about 5×10^{-8} M which was approximately two orders of magnitude greater than the level desired.

It was predicted that the same effect as that produced by the Cu film would result from the presence of a film on the glassy carbon electrode of any metal which readily forms an amalgam.

V. THE USE OF GLASSY CARBON WITH A THIN GOLD FILM
FOR THE DETERMINATION OF MERCURY BY SVWC

A. Introduction

If analytical advantage is to be taken of the increased reversibility for the electrodeposition of Hg at a metal film electrode, it is desirable (i) that the film be semi-permanent; (ii) that its preparation not involve doping of the test solution; (iii) that the film be completely reproducible; and (iv) that the film be thin enough so that the problems of bulk electrodes are avoided. The use of a Cu film is not satisfactory because Cu is stripped at potentials more negative than those for the stripping of Hg. Hence, test solutions would have to be doped with Cu(II) prior to the analysis. The use of a Pt film was concluded to be unsatisfactory because the electrolytic dissolution of the Hg-Pt intermetallic compound is known to occur simultaneously with the formation of the Pt oxide (243). Johnson, Napp, and Bruckenstein (10) determined that a small quantity of an unidentified, soluble electroactive species is produced at a Pt electrode simultaneous to the anodic formation of the surface oxide. That species reacts at the ring electrode at potentials used for the collection of the stripped Hg species, and the ring current resulting only from the Hg cannot be quantitatively determined. Furthermore, a portion of the film would be removed as soluble Pt(II) during electrochemical

reduction of the Pt oxide on the cathodic scan of E_d (10). After several cyclic scans the Pt film would have to be renewed.

A thin film of Au electrodeposited on the glassy carbon disk of the RRDE was determined to have the desired properties of high affinity for Hg and inertness toward electrochemical oxidation during the anodic stripping of Hg.

B. Experimental

1. Instrumentation and apparatus

See Chapter III, Part C, Section 2(a).

2. Reagents

The reagents used were the same as described in Chapter IV, Part A, Section 2(b). Additionally, a stock solution of Au(III) was prepared by dissolving Au metal obtained from Pine Instrument Company in a minimum of aqua regia and diluting with water and HNO_3 to produce a solution of 2.17×10^{-3} M Au(III) and 1.0 M HNO_3 .

3. Pretreatment of the electrode

See Chapter III, Part C, Section 2(c).

4. Experimental procedure

The procedure for the electrodeposition of Au at the glassy carbon disk electrode of the RRDE in 1.0 M H_2SO_4 was as follows: During deaeration of the supporting electrolyte,

E_d was scanned in a cyclic manner at 5.0 V/min between -0.40 V and +1.10 V with $E_r = +0.80$ V and $\omega^{1/2} = 6.47$ (rad/sec) $^{1/2}$. The scan of E_d was stopped at 1.10 V, and an aliquot of the Au(III) stock solution was added to give a solution 1.00×10^{-5} M in Au(III). The solution was allowed to mix. E_d was scanned to 0.000 V and held there for the desired value of t_{dep} . E_r was held at +0.80 V during this time since the Au film was not needed at the Pt ring electrode. With the expiration of t_{dep} , E_d was scanned to +1.10 V; and the electrode was removed from the solution and rinsed thoroughly with water. The remainder of the procedure for the application of SVWC for the determination of Hg(II) in 1.0 M H_2SO_4 using the thin Au film was the same as that for the determination using the bare glassy carbon-disk electrode described in Chapter IV, Part A, Section 2(d). The only difference was that the positive limit of E_d was changed to 1.10 V from 1.00 V.

C. Verification of Experimental Parameters

Electrodeposition of Au at the glassy carbon disk electrode at $E_{d,dep} = 0.000$ V was determined to occur by a process limited by convective-diffusional mass transport. A plot of $I_{d,l}$ vs $\omega^{1/2}$ was linear as predicted by Equation 1. The diffusion coefficient of Au(III) in 1.0 M H_2SO_4 was calculated from this plot to be 1.00×10^{-5} cm 2 /sec. The quantity of Au electroplated at the disk electrode was

calculated from the time integral of the current predicted by the Levich equation over the period t_{dep} . The equivalent number of monolayers of Au deposited was calculated assuming that the packing density for bulk Au was the same as for the Au film. A value of 1.50 \AA was found for the covalent radius of Au (252b).

The electrolytic dissolution of the Hg deposit from the Au film was determined to occur on the positive scan of E_d at values less than those for the formation of Au oxide or the stripping of the Au. For E_d more negative than +1.15 V, it was found that all the Hg was stripped from the Au film, no oxide of Au was formed, and no Au was lost on repeated cycles of E_d . The Au film was determined to be stable indefinitely.

Figure XIII shows I_r - E_d curves which were obtained at the RRDE with the equivalent of 2 monolayers of Au on the glassy carbon electrode. The curves were obtained using $E_r = 0.00 \text{ V}$ with the positive limit of E_d set at +1.10 V and varying the negative limit of E_d from -0.20 V to +0.60 V in 0.20 V increments. The concentration of Hg(II) was sufficiently large so that a substantial amount of Hg was deposited even though the cycle was not stopped at a value of $E_{d,\text{dep}}$. For a negative limit of $E_d \leq 0.20 \text{ V}$ a stripping peak for bulk Hg was obtained during the anodic scan of E_d at 0.34 V. The cathodic ring current observed for values of

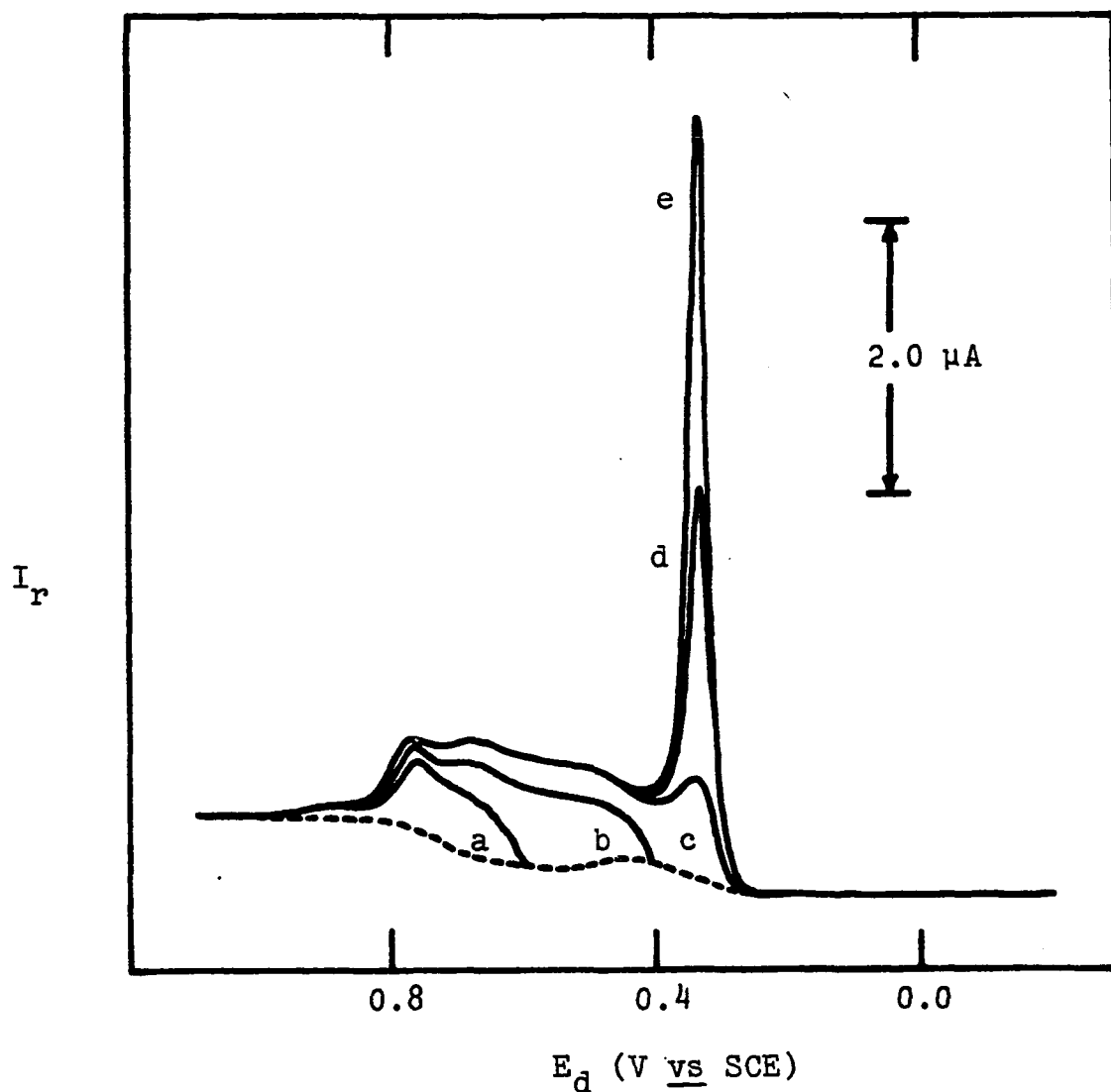


Figure XIII. I_r - E_d curves for SVWC of Hg(II) using a Au-film glassy carbon-disk Pt-ring RRDE

$$C_{\text{Hg(II)}}^b = 5.0 \times 10^{-6} \text{ M}; E_r = 0.00 \text{ V};$$

$$\omega^{1/2} = 16.2 \text{ (rad/sec)}^{1/2}; \phi = 2.0 \text{ V/min};$$

negative limit of E_d : (a) +0.60 V;

(b) +0.40 V; (c) +0.20 V; (d) 0.00 V;

(e) -0.20 V

$E_d > 0.4$ V was concluded to correspond to the reduction of the ionic Hg species produced by the electrolytic dissolution of more than one Hg-Au intermetallic species since several peaks were observed for the stripping of the Hg from the Au film. The I_r - E_d curve shown for the negative scan of E_d exhibits the effects of shielding of the flux of Hg(II) from the bulk of the solution at the ring electrode for values of $E_d < 0.8$ V. These results are consistent with the conclusions that Hg is deposited at the Au film at underpotential between 0.4 and 0.6 V with the resulting formation of several intermetallic species and that bulk Hg is deposited for $E_d < 0.4$ V after the intermetallic species are formed. Bruckenstein, et al., (8-9, 253-257) have discussed deposition at underpotential.

The I_d - E_d curve obtained on the positive scan of E_d for $C_{\text{Hg(II)}}^b = 1.00 \times 10^{-6}$ M and the corresponding I_r - E_d curves for $E_r = 0.00$ V and +1.20 V are shown in Figure XIV. Collection peaks on the I_r - E_d curves were obtained simultaneously to the appearance of the stripping peak for bulk Hg at $E_d = 0.34$ V for both values of E_r . This observation is consistent with the conclusion that bulk Hg on the disk electrode is stripped as Hg(I). A collection wave for $E_d > 0.4$ V was obtained only for $E_r = 0.00$ V. Hence, it was concluded that Hg(II) is the only product of the electrolytic dissolution of the Hg-Au intermetallic species.

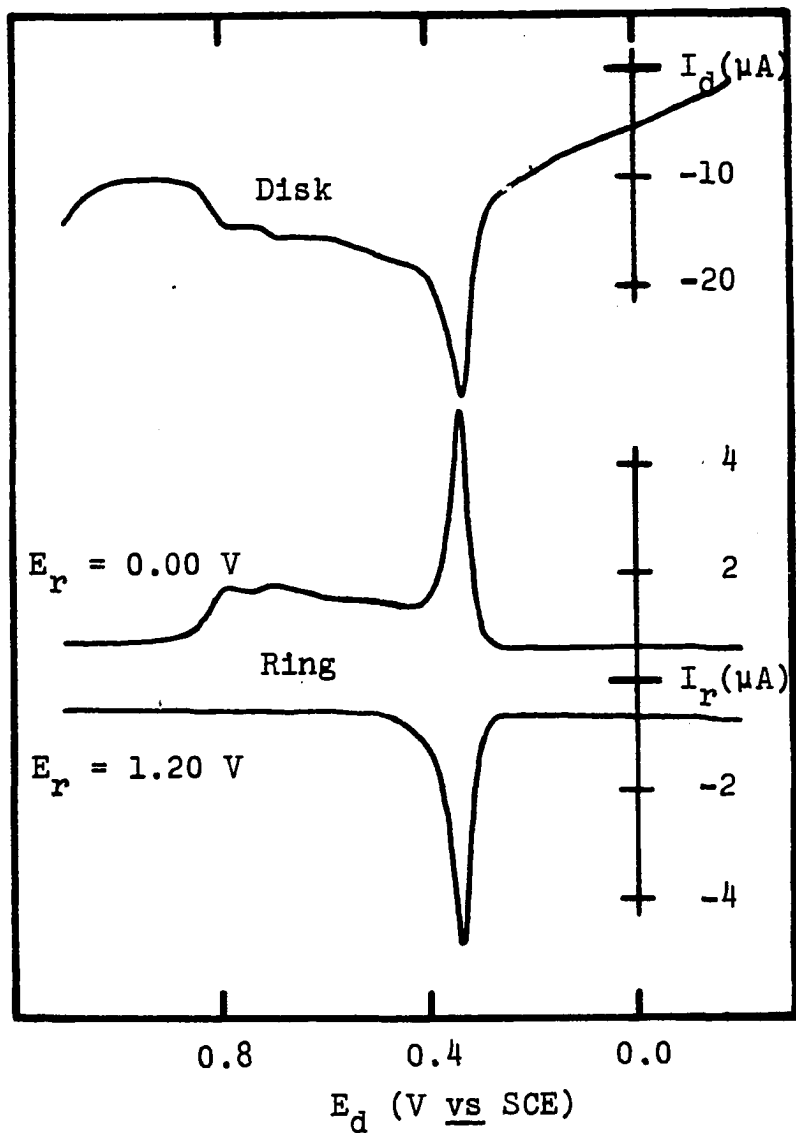


Figure XIV. I_d - E_d and I_r - E_d curves for SVWC of Hg(II) using the Au-film glassy carbon-disk Pt-ring RRDE

$$C_{\text{Hg(II)}}^b = 1.0 \times 10^{-6} \text{ M}; E_{d,\text{dep}} = -0.20 \text{ V};$$

$$\omega^{1/2} = 16.2 \text{ (rad/sec)}^{1/2}; t_{\text{dep}} = 2.0 \text{ min};$$

$$\phi = 5.0 \text{ V/min}$$

Multiple stripping peaks for a single element are not desirable in the quantitative application of stripping voltammetry. Thus, it was hoped that the use of the single peak at $E_d = 0.8$ V would be adequate for the determination of Hg(II) by SVWC at an RRDE. Bulk Hg is not formed at the Au film until the formation of the Hg-Au intermetallic species is complete. Hence, the appearance of a single peak can be assured by the precise control of ω , t_{dep} , or the quantity of sample taken.

To determine the optimum thickness of the Au film, I_r-E_d curves for $C_{Hg(II)}^b = 1.00 \times 10^{-6}$ M were compared for various quantities of Au deposited at the disk electrode. These curves are shown in Figure XV. For the total absence of Au, no collection peak was obtained. For a quantity of Au equivalent to 0.1 monolayer a small collection peak was obtained for the stripping of bulk Hg, and a collection wave was obtained for the dissolution of the Hg-Au species. Apparently, the quantity of Hg deposited was more than sufficient to amalgamate the small quantity of Au present so that bulk Hg was also formed. As the quantity of Au was increased to the equivalent of 2 monolayers, the collection peak corresponding to the stripping of bulk Hg disappeared; and the collection wave for the dissolution of the Hg-Au species developed into a well defined peak. The values of Q_r for 1 and 2 monolayers were the same. A Au film equivalent to 2 monolayers was used for the remaining studies.

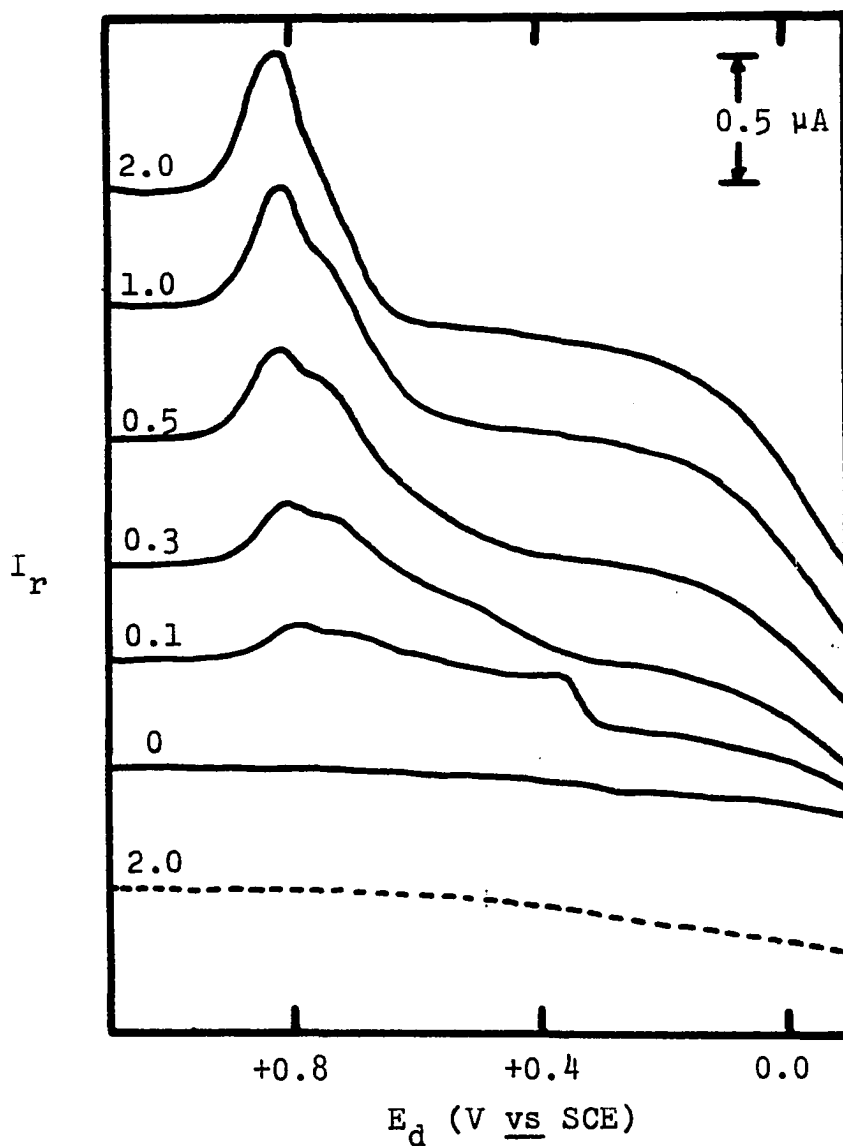


Figure XV. I_r - E_d curves for SVWC of Hg(II) using various thicknesses of Au at the disk of the RRDE

$$C_{\text{Hg(II)}}^b = 1.0 \times 10^{-6} \text{ M}; E_{d,\text{dep}} = -0.20 \text{ V};$$

$$E_r = 0.00 \text{ V}; \omega^{1/2} = 6.47 \text{ (rad/sec)}^{1/2};$$

$\phi = 5.0 \text{ V/min}$; monolayer equivalents of Au

indicated in figure; ---- $C_{\text{Hg(II)}}^b = 0.0 \text{ M}$

The I_r-E_d curve is also shown for 2 monolayer equivalents of Au for $C_{\text{Hg(II)}}^b = 0.00$ M. In this case no collection peaks were obtained proving that no stripped Au species contributed to the currents previously attributed to the stripped Hg species.

Values of Q_r for the single collection peak obtained on the I_r-E_d curve at $E_d = 0.8$ V are shown plotted in Figure XVI as a function of $E_{d,\text{dep}}$. For $t_{\text{dep}} = 2.0$ min and $C_{\text{Hg(II)}}^b = 5.0 \times 10^{-8}$ M no bulk Hg was deposited. The curve in Figure XVI, in essence, an I-E curve for the electrolytic formation of the Hg-Au species. The $E_{1/2}$ for the process is about 0.52 V which is 0.75 V more positive than for the deposition of Hg at the glassy carbon disk without the Au film (Figure VIII). This shift in $E_{1/2}$ corresponds to a free energy of -34 kcal/mole which is consistent with the conclusion that the Hg-Au species is formed by the deposition of Hg at under-potential. The rate of deposition of Hg was concluded to be limited by convective-diffusional processes for $E_{d,\text{dep}} \leq 0.3$ V. A value of $E_{d,\text{dep}} = 0.300$ V was chosen for all subsequent experiments.

It is predicted on the basis of Equation 4 that Q_r for the collection peak at $E_d = 0.8$ V should be a linear function of $\omega^{1/2}$ and t_{dep} so long as the limiting amount of the Hg-Au species has not formed, i.e., small values of Q_r . This was verified for $Q_r \leq 1.6$ μC using the Au film of 2 monolayer

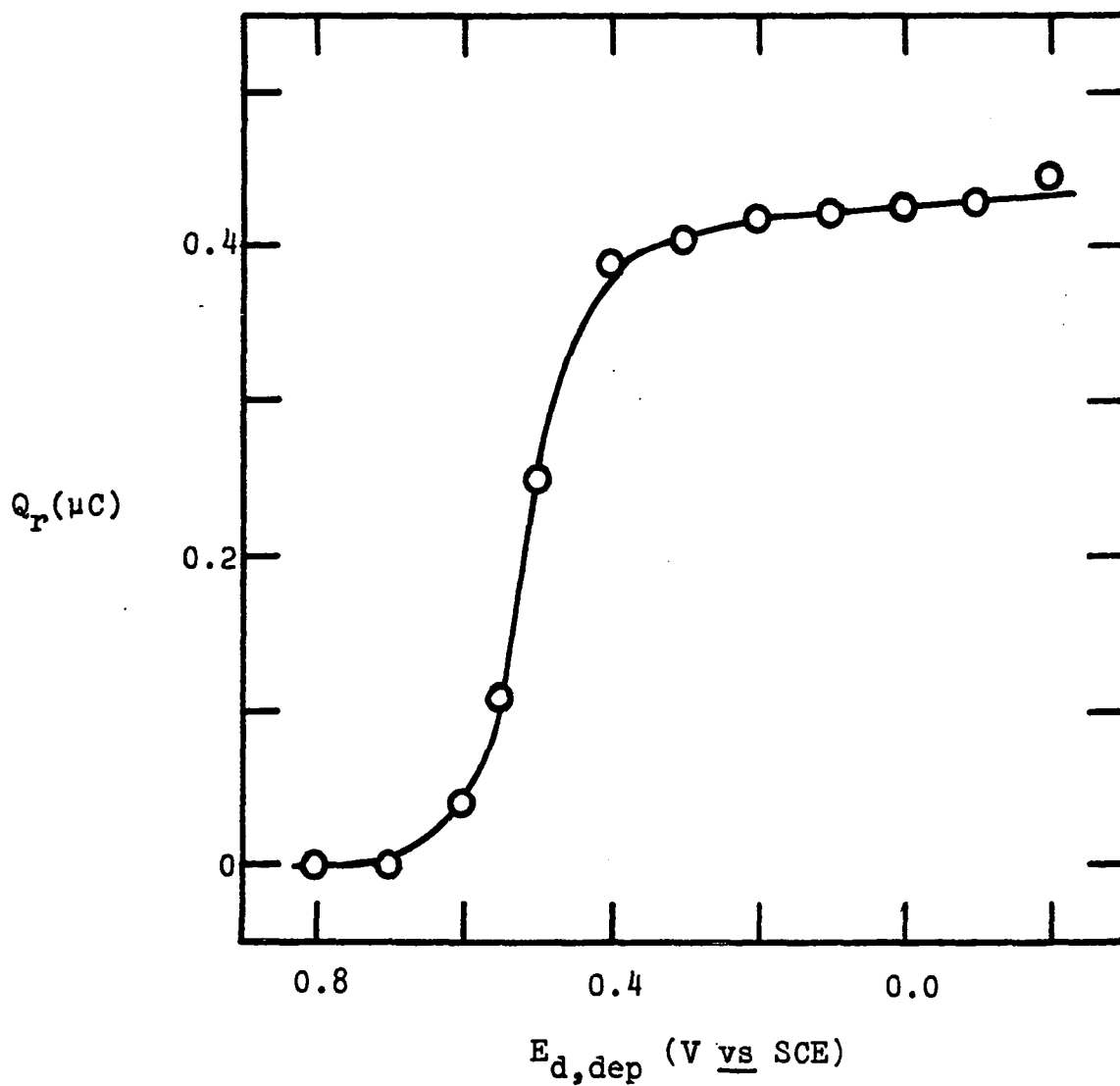


Figure XVI. I-E curve for the deposition of Hg at the Au-film glassy carbon-disk electrode

$$C_{\text{Hg(II)}}^b = 5.00 \times 10^{-8} \text{ M}; E_r = 0.00 \text{ V};$$

$$\omega^{1/2} = 6.47 \text{ (rad/sec)}^{1/2}; t_{\text{dep}} = 2.00 \text{ min};$$

$$\phi = 5.0 \text{ V/min}$$

equivalents as shown in Figure XVII, Curve I, and Figure XVIII, Curve I. The limiting value of Q_r for each of these curves is approximately $2 \mu\text{C}$. On the basis of $Q_r = 2 \mu\text{C}$ the stoichiometry of the Hg-Au species was calculated to be 1 Hg : 33 Au atoms. Repeated measurements of the limiting value of Q_r under these conditions gave virtually the same result. A possible explanation for the lack of a simple stoichiometry is that the Au film exists in patches rather than as a uniform film 2 atoms thick. A non-uniform film would not be unexpected since the non-uniform activity of solid electrodes had been noted previously (13, 38). Since the covalent radii of Au and Hg are almost equal (1.50 Å and 1.49 Å, respectively (252b)), a uniform monolayer of Hg on a uniform film of Au 2 atoms thick would result in a stoichiometry of 1 Hg : 2 Au atoms. If the same amount of Au were in a film 10 atoms thick, the stoichiometry would be 1 Hg : 10 Au atoms. The ratio 1 Hg : 33 Au atoms found indicates that the 2 monolayer equivalents of Au deposited on the glassy carbon electrode do not exist as a film 2 atoms thick but most likely in patches of varying thickness.

A further indication of the complex nature of the Hg-Au species can be seen in Figure XVII and Figure XVIII. Figure XVII shows a plot of Q_r vs $\omega^{1/2}$ for two values of t_{dep} , and Figure XVIII shows a plot of Q_r vs t_{dep} for two values of $\omega^{1/2}$. The data in both these figures was obtained using the

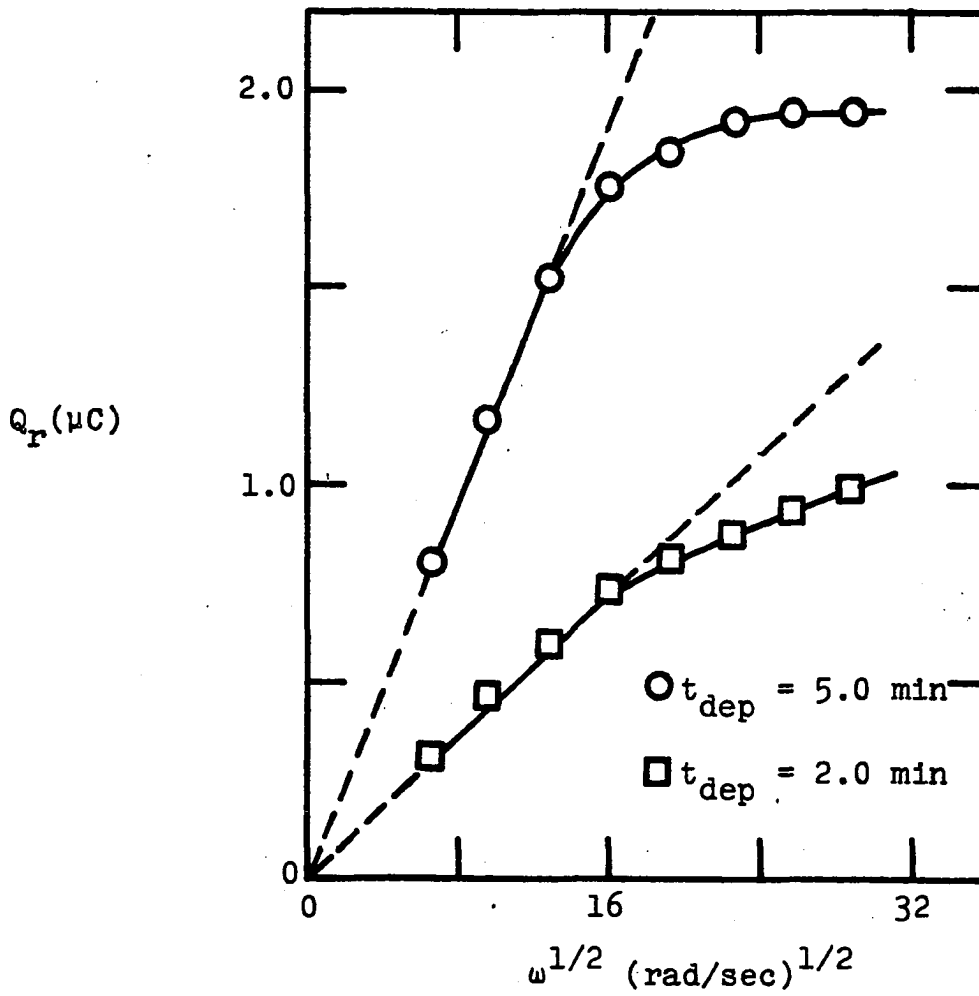


Figure XVII. Plot of Q_r vs $\omega^{1/2}$

$$C_{\text{Hg(II)}}^b = 5.00 \times 10^{-6} \text{ M}; E_{d,\text{dep}} = +0.30 \text{ V}$$

$$E_r = 0.00 \text{ V}; \phi = 5.0 \text{ V/min}$$

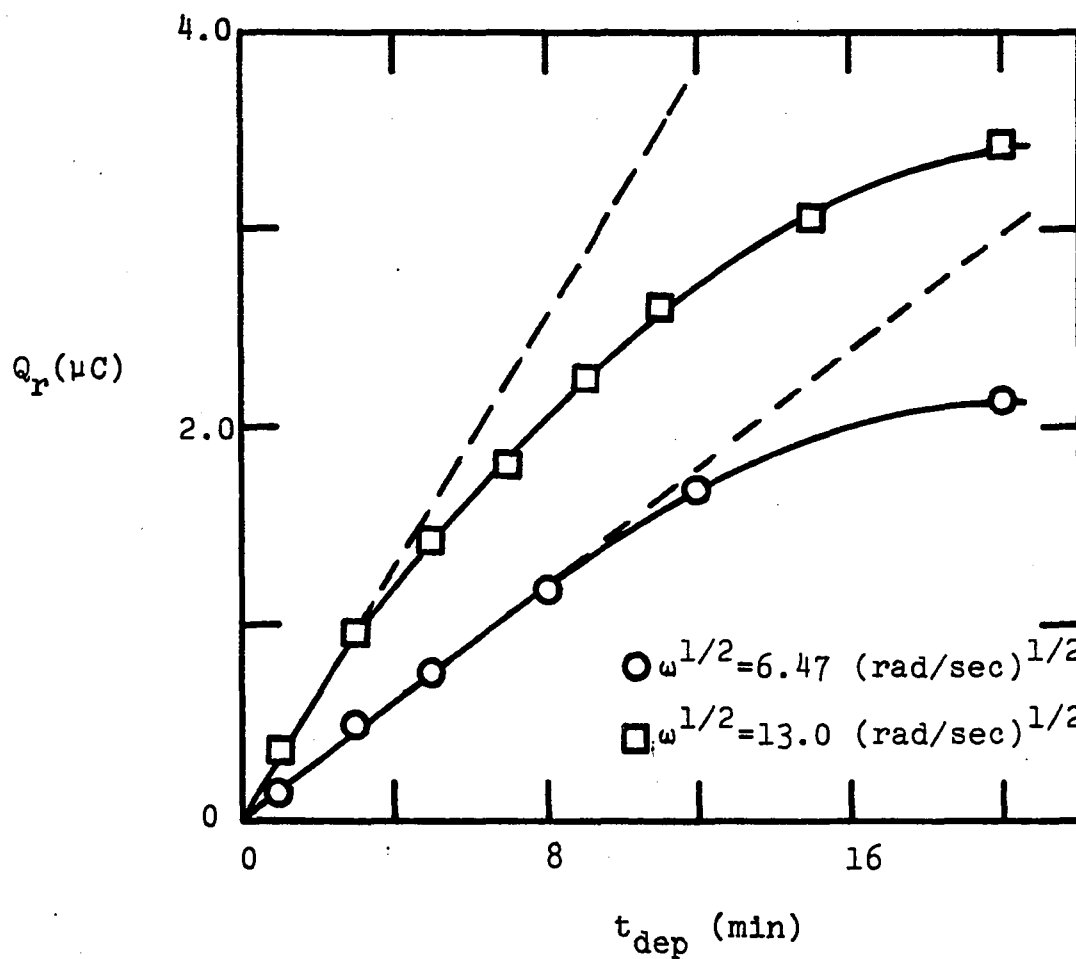


Figure XVIII. Plot of Q_r vs t_{dep}

$$C_{\text{Hg(II)}}^b = 5.00 \times 10^{-8} \text{ M}; E_{d,\text{dep}} = +0.30 \text{ V};$$

$$E_r = 0.00 \text{ V}; \phi = 5.0 \text{ V/min}$$

collection peak at $E_d = +0.8$ V. The fact that two different limiting values of Q_r were obtained is an indication of the diffusion of Hg into the bulk of the Au film. There would be a concentration gradient of Hg from the Au-solution interface to the Au-glassy carbon interface. As more Hg is deposited at the Au-solution interface, the gradient gives a driving force so that more Hg diffuses toward the Au-carbon interface resulting in a greater limiting value of Q_r . This argument is substantiated by the data in Figure XVII since more Hg is deposited for $t_{\text{dep}} = 5.0$ min than for $t_{\text{dep}} = 2.0$ min and by the data in Figure XVIII since more Hg is deposited for $\omega^{1/2} = 13.0$ (rad/sec) $^{1/2}$ than for $\omega^{1/2} = 6.47$ (rad/sec) $^{1/2}$. This data leads to the distinct possibility that a Au-ring Au-disk RRDE could be used for the determination of Hg(II) by SVWC if conditions were maintained so that the limiting value of Q_r were never reached. For the Au-film glassy carbon-disk Pt-ring RRDE, the determination of Hg(II) by SVWC was not seriously affected for $\omega^{1/2} \leq 13.0$ (rad/sec) $^{1/2}$, $t_{\text{dep}} \leq 10.0$ min, and $C_{\text{Hg(II)}}^b \leq 5.0 \times 10^{-8}$ M.

A calibration curve was prepared (Figure XIX) relating Q_r for the collection peak at $E_d = 0.8$ V to $C_{\text{Hg(II)}}^b$ for the range 5.00×10^{-10} M to 5.00×10^{-8} M (0.10 - 10.0 ppb). The values of $C_{\text{Hg(II)}}^b$ were calculated on the basis of the technique of standard additions. Values of Q_r were corrected

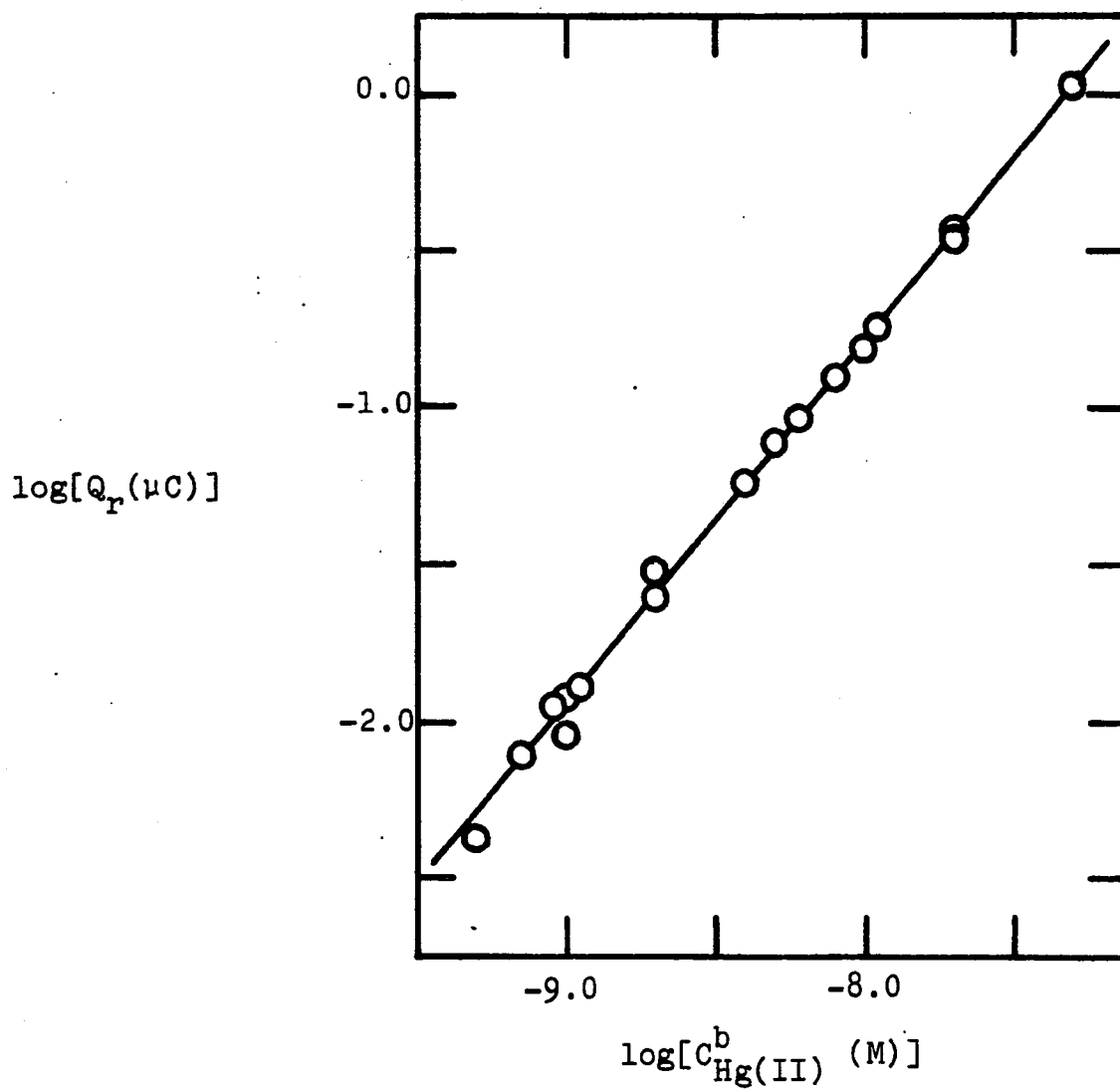


Figure XIX. Log-log plot of Q_r vs $C_{\text{Hg(II)}}^b$

$$E_{d,\text{dep}} = +0.30 \text{ V}; E_r = 0.00 \text{ V};$$

$$\omega^{1/2} = 9.71 (\text{rad/sec})^{1/2}; t_{\text{dep}} = 10.0 \text{ min};$$

$$\phi = 5.0 \text{ V/min}$$

for the blank measured at $C_{\text{Hg(II)}}^b = 0.00 \text{ M}$. Each point represents the average of 3 determinations with the average relative deviation at $5.0 \times 10^{-10} \text{ M Hg(II)}$ calculated to be 7.5%. For that determination only $28 \times 10^{-12} \text{ gm}$ of Hg were deposited and stripped at the Au-film glassy carbon disk electrode. On the basis of the results obtained in this study it was concluded that the detection limit for the determination of Hg(II) in $1.0 \text{ M H}_2\text{SO}_4$ by SVWC is approximately 0.01 ppb. Figure XX shows the I_r - E_d curve for the blank, for the $1.1 \times 10^{-9} \text{ M}$ solution, and for the $6.0 \times 10^{-9} \text{ M}$ solution under the conditions described for the calibration curve.

D. Interference Study

1. Introduction

Since it was known that several metal ions other than Hg(II) were electroactive at a Au electrode, it was necessary to determine which of these would interfere with the determination of Hg(II) using SVWC at the Au-film glassy carbon-disk Pt-ring RRDE. To facilitate the study of many cations in the interference study, an electrochemical detector described by Johnson and Larochelle (258) was used with a liquid chromatograph described by Seymour, Sickafoose, and Fritz (259). The electrochemical detector was a tubular Pt electrode packed with Pt chips and was reported to be

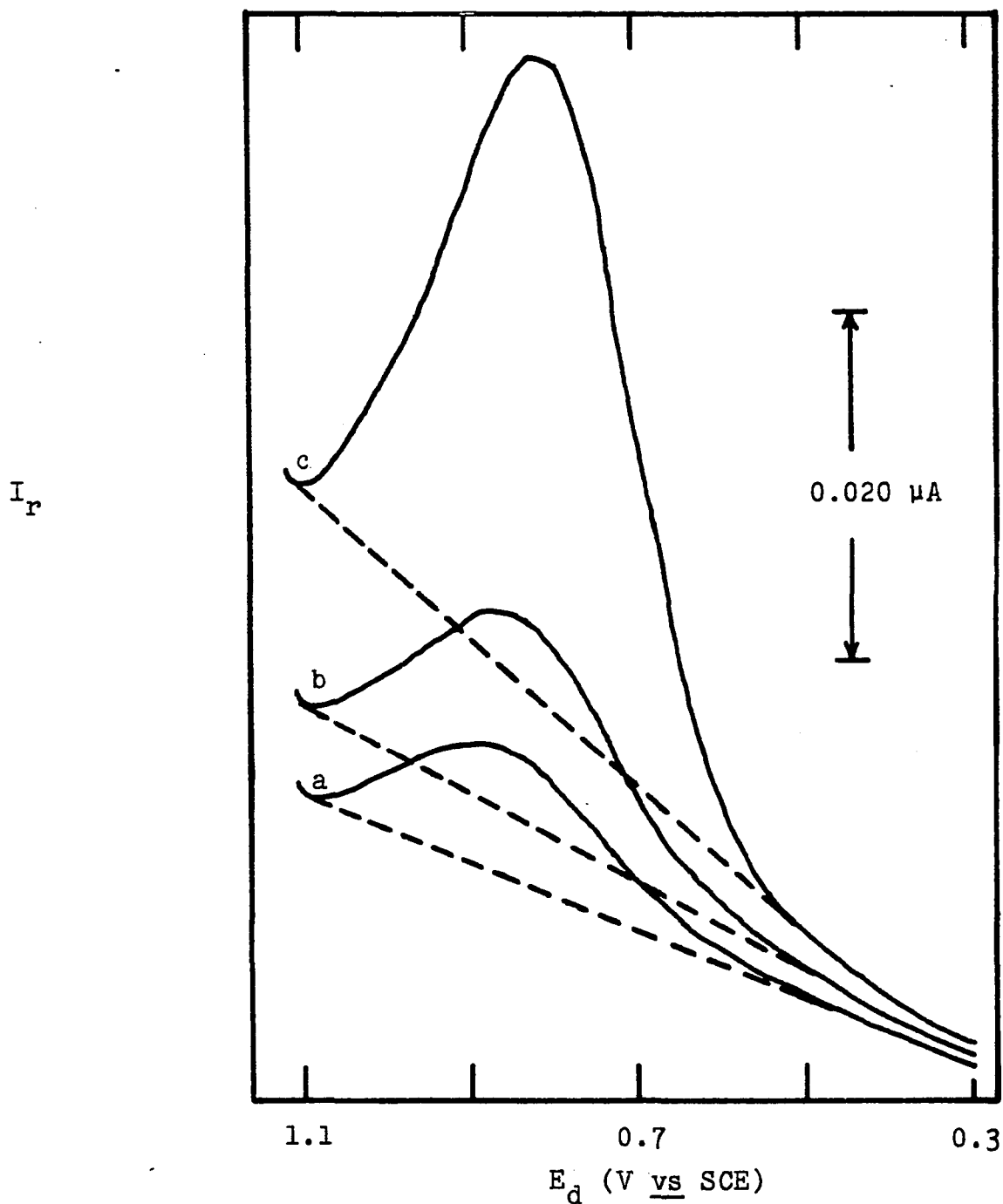


Figure XX. I_r - E_d curves for SVWC of Hg(II)

$E_{d,dep} = +0.30$ V; $E_r = 0.00$ V; $\phi = 5.0$ V/min

(a) blank; (b) 1.0×10^{-9} M Hg(II);

(c) 6.0×10^{-9} M Hg(II)

coulometric, i.e., 100% of the electroactive species in a stream of supporting electrolyte was electrolyzed as it passed through the detector. The chromatographic technique was employed because (i) it was much faster than SVWC since it required no changing of solutions in an electrochemical cell and no deaeration of the supporting electrolyte; (ii) it was desired to characterize the liquid chromatographic technique as a means of determining Hg(II); and (iii) the information obtained was entirely pertinent to the use of the Au film for the determination of Hg(II) using SVWC.

2. Experimental

a. Instrumentation and apparatus The liquid chromatograph was constructed according to the design described in Reference 258. The cation exchange resin (3 mm x 9 cm bed, 180-250 mesh) was Amberlite IRA-200 from the Rohm and Haas Company. The column was necessary in order to retard the movement of the Hg(II) so that the peaks for Hg(II) and O₂ would not overlap. The detector was a Au tube (1.5 cm x 2 mm ID) from Pine Instrument Company packed with approximately 80-mesh Au filings. Wads of 30 gauge Au wire were used in each end of the detector to hold the filings in place. The detector was enclosed in a Teflon shroud.

The electronics used were the 3 electrode potentiostat of a 4 electrode potentiostat similar to that described in Chapter III, Part C, Section 2(c), an analog integrator

constructed from an operational amplifier, a Leeds and Northrup Speedomax strip chart recorder, and a Systron Donner Model 7050 digital voltmeter.

b. Reagents The supporting electrolyte was prepared by dissolving sufficient CaCO_3 (Baker Analyzed) in a stoichiometric amount of HClO_4 followed by the addition of HClO_4 and water to give a solution of 0.50 M $\text{Ca}(\text{ClO}_4)_2$ and 0.50 M HClO_4 . A 0.00100 M stock solution of $\text{Hg}(\text{II})$ was prepared by dissolving $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (Baker Analyzed) in 0.50 M HClO_4 . Solutions of various cations for the interference study were prepared as listed in Table II.

c. Experimental procedure To test the interference of each cation, X, an injection (0.50 ml) of each of the following solutions was made into the stream of 0.50 M $\text{Ca}(\text{ClO}_4)_2 - 0.50 \text{ M HClO}_4$:

Solution A - 0.00100 M $\text{Hg}(\text{II})$

Solution B - 0.00100 M $\text{Hg}(\text{II})$ + 0.00100 M X

Solution C - 0.00100 M $\text{Hg}(\text{II})$ + 0.0100 M X

Solution D - 0.00100 M $\text{Hg}(\text{II})$ + 0.100 M X

The electrolyte was flowing at a rate of 0.50 ml/min, and the Au detector was potentiostated at +0.20 V vs SCE. The SCE was filled with saturated NaCl to avoid the formation of insoluble KClO_4 in the fibrous tip of the electrode. The areas of the reduction peaks obtained from Solutions B, C,

and D were divided by the peak from Solution A and multiplied by 100 to get the percent recoveries which are recorded in Table II.

Table II. Results of the interference study

Cation	% Recoveries			Compound tested	Comments
	Sol. B	Sol. C	Sol. D		
Fe(III)	130	214	-	Fe(NO ₃) ₂ ·9H ₂ O	1,6
Cu(II)	100	100	100	Cu(NO ₃) ₂ ·3H ₂ O	2,6
Cd(II)	100	100	99	Cd(NO ₃) ₂ ·4H ₂ O	2,6
Tl(I)	100	100	100	TlNO ₃	3,6
Al(III)	100	100	100	Al(NO ₃) ₃ ·9H ₂ O	1,6
Pb(II)	100	100	107	Pb(NO ₃) ₂	2,6
U(VI)	100	100	100	UO ₂ (NO ₃) ₂ ·6H ₂ O	1,6
Co(II)	100	100	100	Co(NO ₃) ₂ ·6H ₂ O	1,6
Cr(III)	100	100	100	Cr(NO ₃) ₃ ·9H ₂ O	4,6
Ag(I)	150	357	-	AgNO ₃	1,6
Zn(II)	100	100	99	Zn(NO ₃) ₂ ·6H ₂ O	4,6
Ni(II)	100	100	99	Ni(NO ₃) ₂ ·6H ₂ O	2,6
Bi(III)	100	100	107	Bi(NO ₃) ₃ ·5H ₂ O	1,7
Se(IV)	109	122	-	Se	5,9,12
Mn(II)	100	100	99	MnSO ₄ ·H ₂ O	2,6
V(V)	158	-	-	V ₂ O ₅	4,8,12
As(III)	98	94	-	As ₂ O ₃	1,8
Mo(VI)	107	-	-	H ₂ MoO ₄	1,8,12
Pt(IV)	259	-	-	Pt	3,11,12
Sb(III)	-	-	-	Sb	4,10,13
Sn(IV)	-	-	-	SnCl ₄ ·5H ₂ O	2,6,13
Cr(VI)	346	-	-	Na ₂ Cr ₂ O ₇ ·2H ₂ O	1,6,12

Table II (Continued)

-
- Comments:
- (1) Baker Analyzed
 - (2) Mallinckrodt
 - (3) Source unknown
 - (4) Matheson, Coleman, and Bell
 - (5) Abbott Laboratories
 - (6) Dissolved in 0.5 M HClO₄
 - (7) Dissolved in 1.0 M HClO₄
 - (8) Dissolved in 8 M NaOH and acidified to 0.5 M HClO₄
 - (9) Dissolved in hot HNO₃ and diluted to 0.5 M HClO₄
 - (10) Dissolved in hot H₂SO₄ and diluted to 2.0 M H₂SO₄
 - (11) Dissolved in minimum aqua regia and diluted to 1 M HNO₃
 - (12) Manual integration by planimeter (all others by electronic integrator)
 - (13) No peaks observed due to interfering anions present
-

3. Results

Of the cations investigated Fe(III), Ag(I), Se(IV), As(III), V(V), Mo(VI), Pt(IV), and Cr(VI) were found to cause serious interference. Although no data was obtained, it was strongly suspected that Sb(III) would interfere in a manner similar to As(III), Te(IV) in a manner similar to Se(IV),

and Ce(IV) in a manner similar to Cr(VI). Of these only Ag(I), Se(IV), As(III), Pt(IV), Sb(III), and Te(IV) are of primary concern since these cations are known to be reduced to the respective metals at a Au electrode whereas the others are just reduced to lower oxidation states. Those cations which are reduced to the metals must be separated from Hg(II) before the application of SVWC if their stripping peaks overlap the stripping peak for Hg.

The following anions form slightly soluble compounds with Hg(II) and/or Hg(I) and are thus expected to cause some interference: Cl^- , Br^- , I^- , S^{-2} , IO_3^- , and SCN^- . It was shown in a manner like that used for the cations above that up to the 0.5 M level SO_4^{-2} and PO_4^{-3} do not interfere. Obviously, NO_3^- and HClO_4 do not interfere.

E. Conclusions

It was concluded that the use of SVWC with a thin Au film on the disk of a rotating glassy carbon-disk Pt-ring electrode was practical for the determination of Hg(II) in acidic media at the ppb level. The determination was shown to have a low detection limit (0.01 ppb), a relatively short analysis time (about 35 minutes excluding the preparation of a calibration curve), high precision (7.5% relative deviation at the 0.1 ppb level), and few interferences. These factors make the technique more favorable for the determination of

Hg(II) than many of the more commonly used techniques discussed in Chapter II, Part D.

VI. ANALYSIS OF SAMPLES USING SVWC

A. Introduction

The determination of Hg in biological samples presents two important considerations. First, the determination is of great significance because of the widespread occurrence of Hg compounds and the toxicity of Hg compounds to all living organisms. Secondly, the analysis of biological samples presents the analyst with a very complex matrix which provides a good test of the merit of any analytical technique. Therefore, an attempt was made to determine Hg in two National Bureau of Standards reference materials (orchard leaves and bovine liver) to determine the applicability of SVWC to the determination of these materials.

B. Experimental

1. Instrumentation and apparatus

The instrumentation and apparatus were the same as described in Chapter III, Part C, Section 2(a).

2. Reagents

Baker Analyzed HNO_3 was distilled in glass before using. After distillation the acid was deaerated with N_2 to remove volatile oxides of N_2 . Dilute solutions of HNO_3 were prepared by dissolving the appropriate amount of the distilled acid in water. All other reagents were the same as described in Chapter IV, Part B, Section 2.

3. Pretreatment of the electrode

The entire pretreatment procedure was the same as described in Chapter V, Part B, Section 4, except that a Au film equivalent to 20 monolayers was deposited at the ring electrode. For the deposition of the Au at the ring, $t_{\text{dep}} = 14$ min was required for $\omega^{1/2} = 13.0$ (rad/sec)^{1/2} with all the other parameters being the same as for the deposition at the disk electrode.

4. Ion exchange resin

Dowex 50X8 analytical grade cation exchange resin (100-200 mesh) obtained from Bio-Rad was used to separate Hg(II) from interfering species. The resin was a strong acid cation exchange type with a capacity of 5.1 meq/gm of dry resin and a resin bed density of 0.33 gm/ml of resin. A bed of resin 6.5 cm long was prepared in a 1.0 cm ID column and washed with 500 ml of 4 M HNO₃ in 50 ml portions. Prior to the passing of each sample through the column, the resin was washed with 50 ml of 0.20 M HNO₃ which had previously been passed through another column of the same resin to remove the Hg(II) impurity found in the reagent grade HNO₃.

5. Experimental procedure

A weighed sample was placed in a 10 ml erlenmeyer flask to which a 24/40 standard taper joint had been attached. Concentrated HNO₃ (2.50 ml for sample sizes from 0.10 to 0.50 gm) was added slowly to prevent foaming. The flask was

attached to a 50 cm West condenser filled with glass beads and heated to gentle boiling until a clear solution was obtained or for 30 minutes. About 25 ml of H₂O was washed through the condenser into the flask. The cooled sample was transferred to a larger erlenmeyer flask where it was diluted so that $C_{\text{HNO}_3}^b \leq 0.2 \text{ M}$.

The sample was then passed through the ion exchange column at a rate of 5-10 ml/min. A suction flask and aspirator were used to maintain the rate of flow. After the sample had passed, the sample flask was washed with small portions of 0.20 M HNO₃ which were passed through the column. The column was then washed with additional 0.20 M HNO₃ until the total volume of washing was 200 ml.

Hg(II) was eluted from the resin with 3.0 M HNO₃ into a 50 ml volumetric flask. A 50 ml volume of the eluent was sufficient to elute all the Hg(II). The flask was filled to the mark with the eluent, and the solution was mixed thoroughly. The total volume of eluate was placed in a 125 ml erlenmeyer flask and boiled for 5 min under reflux. After the solution cooled, it was placed in the electrochemical cell, the RRDE was immersed into the liquid, and the potentiostat was turned on with $E_d = +1.10 \text{ V}$ and $E_r = +1.00 \text{ V}$. E_d was scanned to +0.30 V and stopped, at which time E_r was stepped to +0.30 V. With the expiration of t_{dep} , E_d was scanned to +1.10 V while $I_r - E_d$ was recorded.

E_r was then stepped back to +1.00 V, and E_d was allowed to cycle twice between +0.30 V and +1.10 V before the next deposition was begun. This procedure was repeated for as many I_r - E_d curves as were required for a particular solution. After the last curve was recorded, E_d was stopped at +1.10 V, E_r was stepped to +1.00 V, and the potentiostat was turned off. The cell was emptied, washed with triply distilled water, and allowed to drain. The procedure was repeated for a blank containing the same amount of HNO_3 as the sample. The peaks for the two runs were integrated, and the concentration of $Hg(II)$ in the sample was determined by comparing the difference in the two areas against a calibration curve.

C. Results and Discussion

1. SVWC of $Hg(II)$ in the presence of O_2

To decrease the time required for an analysis and to prevent the loss of $Hg(II)$ from solution due to volatilization, it was desired to perform SVWC for the determination of $Hg(II)$ without deaerating the sample solutions to remove dissolved O_2 . It was found that the reduction of O_2 at the Pt ring electrode at $E_r = 0.00$ V produced so much current that the current follower in the potentiostat became current limited when a high sensitivity was used. This prevented the use of the Pt ring for the collection of the stripped Hg

species. However, after a 20 monolayer equivalent of Au was deposited on the Pt ring electrode, a collection potential of +0.30 V could be used, and the current due to the reduction of O_2 was diminished to the point that it was unnecessary to deaerate the solutions before SVWC was performed. Figure XXI shows an I_d-E_d curve and an I_r-E_d for a solution of 4×10^{-10} M Hg(II) in 3.0 M HNO_3 saturated with O_2 . The stripping peak is not perceptible on the I_d-E_d curve, but the collection peak is very well defined on the I_r-E_d curve. It is apparent from this figure that O_2 does not interfere with the determination of Hg(II) using SVWC under the conditions used.

2. Verification of interferences

To determine if the suspected interferences actually affected the collection peaks for Hg, curves were obtained for samples containing 1.0×10^{-7} M Hg(II) and 1.0×10^{-5} M of one of the following ions: Se(IV), As(III), Sb(III), Ag(I), and Fe(III). The results are shown in Figure XXII. It is apparent that with the exception of Fe(III) all the ions interfere. The mechanism for the interference seems to be that the ions are preferentially adsorbed and/or deposited on the Au film thus shielding the Hg(II) from the active sites. The interference was very irreversible, except in the case of Ag(I), and the Au films had to be renewed after each curve in Figure XXIII was obtained.

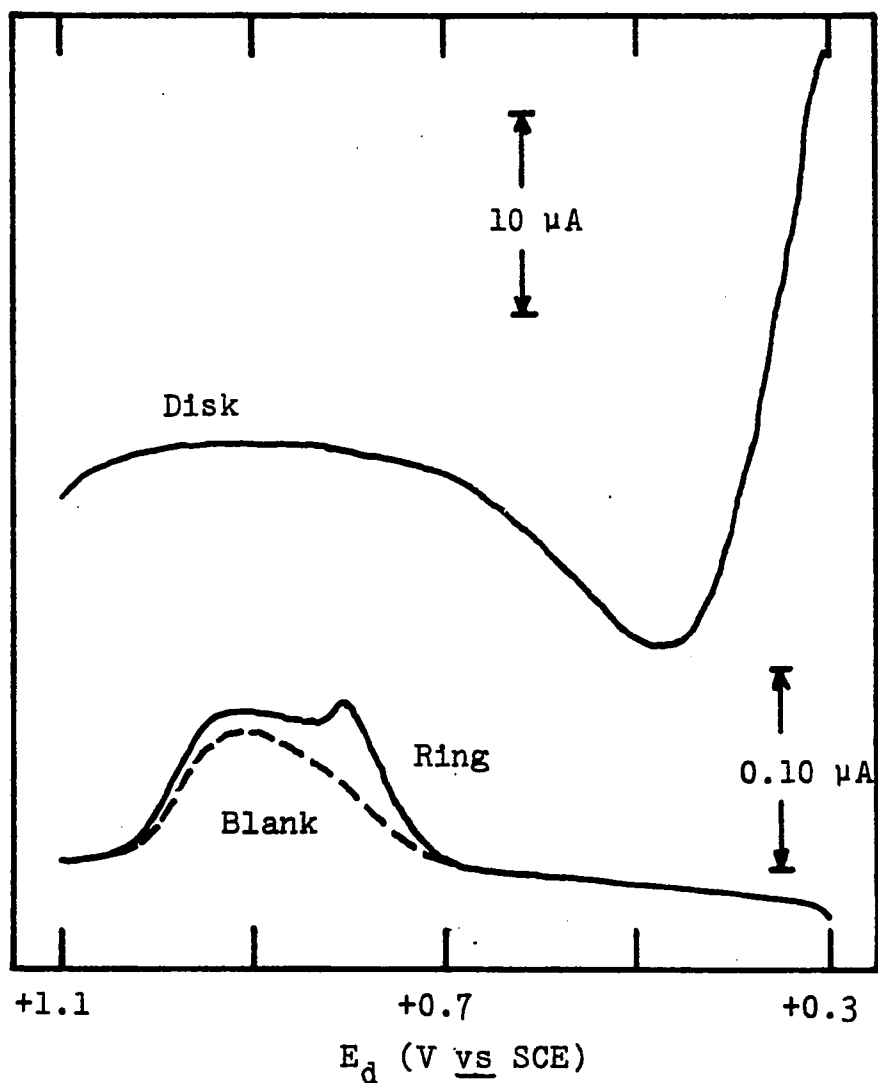


Figure XXI. I_d - E_d and I_r - E_d curves for SVWC of Hg(II) in the presence of O_2

$C_{\text{Hg(II)}}^b = 4.0 \times 10^{-10} \text{ M}$ in 3.0 M HNO_3 saturated with O_2 ; $\omega^{1/2} = 13.0 \text{ (rad/sec)}^{1/2}$;

$E_{d,\text{dep}} = +0.30 \text{ V}$; $E_r = +0.30 \text{ V}$;

$t_{\text{dep}} = 5.0 \text{ min}$; $\phi = 5.0 \text{ V/min}$

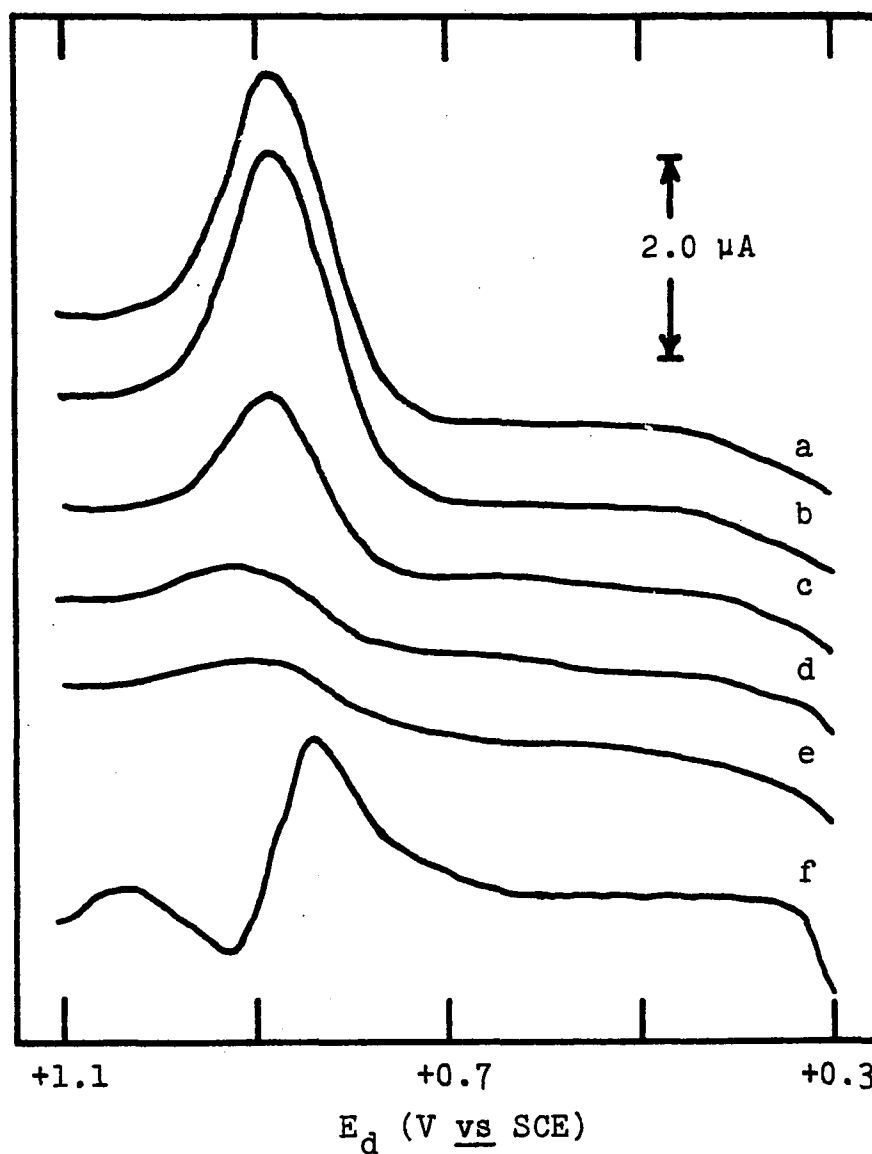


Figure XXII. I_r - E_d curves for SVWC of Hg(II) in the presence of various ions

$C_{\text{Hg(II)}}^b = 1.00 \times 10^{-7} \text{ M}$; $C_{\text{ion}}^b = 1.00 \times 10^{-5} \text{ M}$;
 $E_{d,\text{dep}} = +0.30 \text{ V}$; $E_r = +0.30 \text{ V}$; $\omega^{1/2} = 13.0$
 $(\text{rad/sec})^{1/2}$; $t_d = 2.0 \text{ min}$; (a) Hg(II);
 (b) Hg(II) + Fe(III); (c) Hg(II) + As(III);
 (d) Hg(II) + Sb(III); (e) Hg(II) + Se(IV);
 (f) Hg(II) + Ag(I)

Pt(IV), V(V), Cr(VI), and Mo(VI) were not tested since these ions were not expected to be found in biological samples. Te(IV) was not tested since it was expected to behave like Se(IV). Any As(V) or Sb(V) present would be expected to behave like the respective trivalent ions.

3. Separation of interferences

The separation scheme used was based on the data given by Strelow, et al., (260) part of which is reproduced in Table III. No distribution coefficients were given for

Table III. Distribution coefficients in HNO₃

Cation	0.1N	0.2N	0.5N	1.0N	2.0N	3.0N	4.0N
Hg(II)	4700	1090	121	16.9	5.9	3.9	2.8
Fe(III)	>10 ⁴	4100	362	74	14.3	6.2	3.1
Ag(I)	156	86	36	18.1	7.9	5.4	4.0
Se(IV)	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
As(III)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Te(IV)	40.3	19.7	8.5	5.0	2.4	0.6	0.2
Mo(VI)	11.6	6.3	0.9	0.2	0.1	0.1	0.1
V(V)	20.0	10.9	4.9	2.0	1.2	0.8	0.6

Sb(III) or Sb(V). Using this data a separation scheme was devised in which Hg(II) was adsorbed from 0.2 M HNO₃. Washing with 0.2 M HNO₃ removed most of the interferences from the column leaving only Hg(II) and Fe(III) behind. Any Sb originally present in the sample is oxidized in the digestion process to Sb(V) which has no cationic chemistry (261) and thus is not likely to adsorb on the resin.

A 200 ml sample of 0.20 M HNO₃ containing 1×10^{-7} M Hg(II) was passed through the column at a flow rate of 12 ml/min. This was followed by 200 ml of 0.20 M HNO₃ to wash the column. Periodic analysis of the effluent showed no increase in Hg(II) concentration over the blank occurred during the wash cycle. The Hg(II) was eluted from the resin with 3.0 M HNO₃, and the elution curve obtained is shown in Figure XXIII. It is evident that 50 ml of the eluent was sufficient to elute all the Hg(II). Elution was also tried with 2.5 M HNO₃ and successful elution of Hg(II) resulted except that about 70 ml of eluent was required for complete elution of the Hg(II). It was decided to use 3.0 M HNO₃ as the eluent for all subsequent experiments.

The separation scheme was considered to be successful when the collection peak for Hg(II) for a sample of orchard leaves did not decrease with successive depositions and stripping cycles. Since this sample contained Se, As, and possibly Ag, an unsuccessful separation of the Hg from these

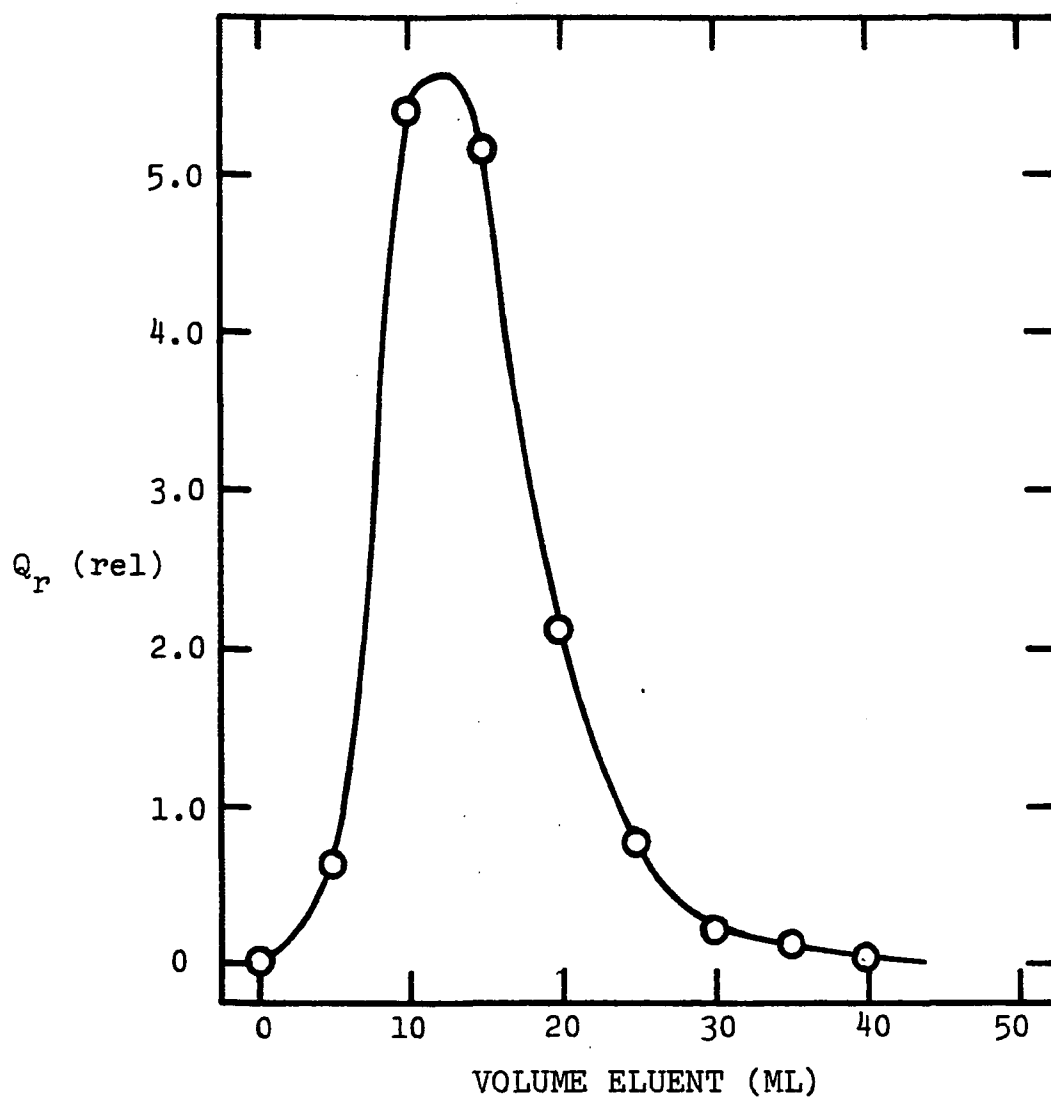


Figure XXIII. Elution curve for Hg(II) from Dowex 50X8 cation exchange resin using 3.0 M HNO₃

$E_{d,dep} = +0.30V$; $E_r = +0.30 V$; $t_{dep} = 5.0$ min;

$\omega^{1/2} = 13.0$ (rad/sec)^{1/2}; $\phi = 5.0$ V/min;

2.0 μg of Hg(II) were sorbed on the resin

elements would have resulted in successive decreases in Q_r , with each cycle due to the irreversible adsorption and/or deposition of these elements on the Au film.

It was found in the course of the work with the resin that some unidentified species was washed from the resin whenever 3.0 M HNO_3 was passed through the column. The species had an effect similar to that produced by Se(IV) in that it apparently adsorbed irreversibly on the Au films preventing the deposition of Hg. The unknown species was thought to be some organic compound, and this hypothesis was supported when it was discovered that boiling the eluate under reflux for 5 min completely eliminated the interference. Apparently, the concentration of the species was sufficiently low so that the HNO_3 in the eluate was sufficient for complete oxidation. It was concluded, therefore, that it was necessary to boil each eluate collected before SVWC was performed.

4. Digestion scheme for samples

Hoover, Melton, and Howard (262) obtained 95-102% recoveries for the determination of Hg in liver, fish, bread, and alfalfa by flameless atomic absorption using a digestion with HNO_3 although in some cases the samples were not completely dissolved. They found no improvement using $\text{HNO}_3\text{-HClO}_4$ or $\text{HNO}_3\text{-H}_2\text{SO}_4$ mixtures and even noted decreased recoveries in some instance with these mixtures of acids

because of their high boiling points. It has also been shown (263-264) that the loss of Hg from water samples during storage is negligible when the samples are acidified to pH 1 with HNO_3 . This evidence led to the digestion of samples for analysis by SVWC using concentrated HNO_3 heated just to boiling under reflux condition. This method of digestion was expected to result in complete recovery of Hg in the samples and no loss of Hg(II) to the walls of the container. When the orchard leaves were digested, only a residue of silica remained undissolved while a small quantity of fat remained when the bovine liver was digested. Similar types of residues were found by Hoover, et al.

5. Calibration curve

Figure XXIV is a calibration curve for the determination of Hg(II) by SVWC in O_2 saturated 3.0 M HNO_3 . A log-log plot of ngHg/ml vs $Q_r \mu\text{C}/t_{\text{dep}} \text{ min}$ was made to allow for any necessary variation in sample volume and/or t_{dep} . The lowest point represents 1.0×10^{-10} M in 50 ml of 3.0 M HNO_3 while the highest is for 5.0×10^{-8} M.

Several of the collection curves recorded for the calibration curve are shown in Figure XXV. The peak for $C_{\text{Hg(II)}}^b = 1.0 \times 10^{-10}$ M was barely discernible from the peak for the blank and was, therefore, concluded to represent the detection limit under these conditions. The peak for 2.0×10^{-10} M was easily measured. It is not known what

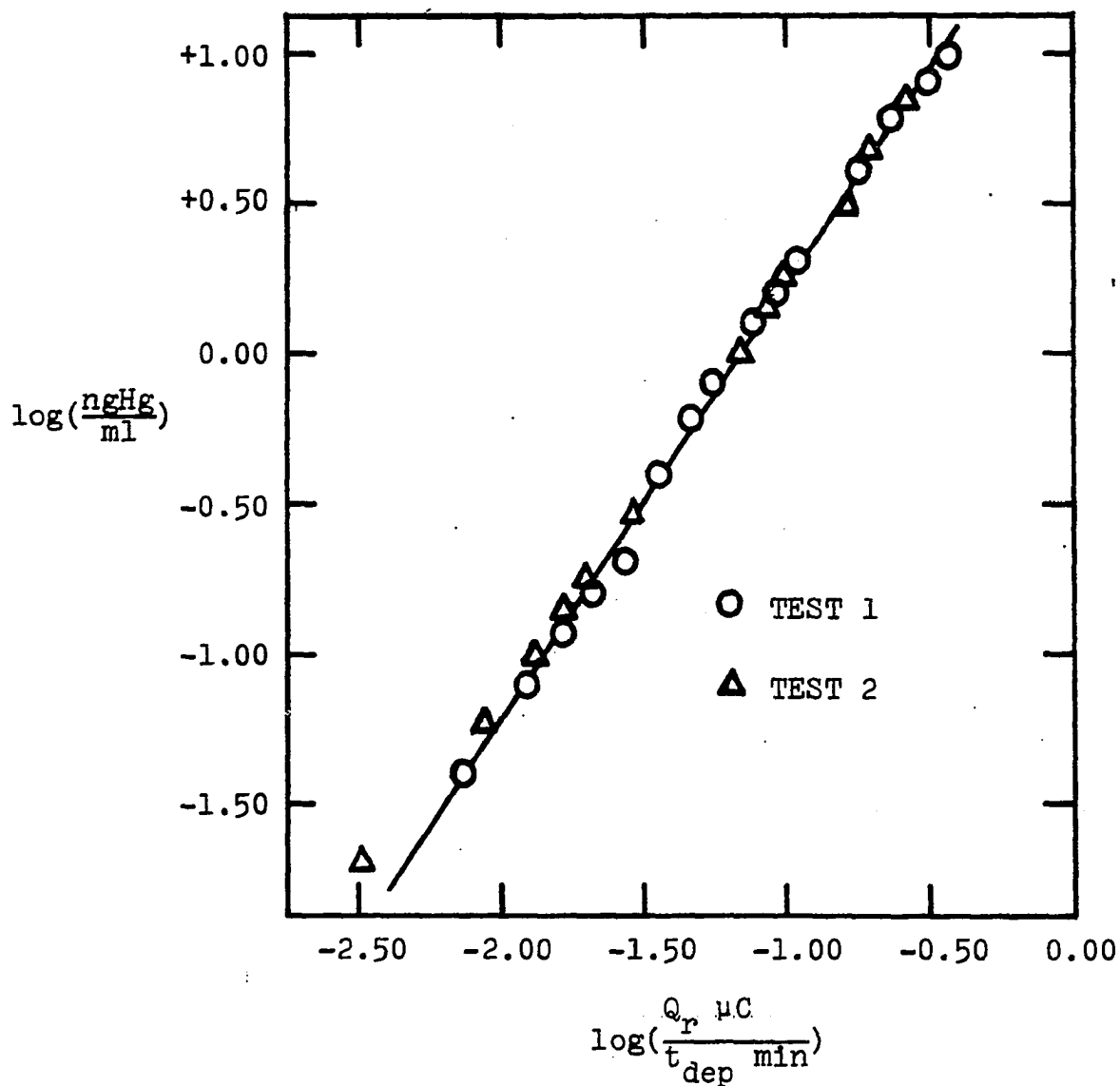


Figure XXIV. Calibration curve for the determination of Hg(II) using SVWC

$$E_{d,\text{dep}} = +0.30 \text{ V}; E_r = +0.30 \text{ V};$$

$$\omega^{1/2} = 13.0 \text{ (rad/sec)}^{1/2}; \phi = 5.0 \text{ V/min}$$

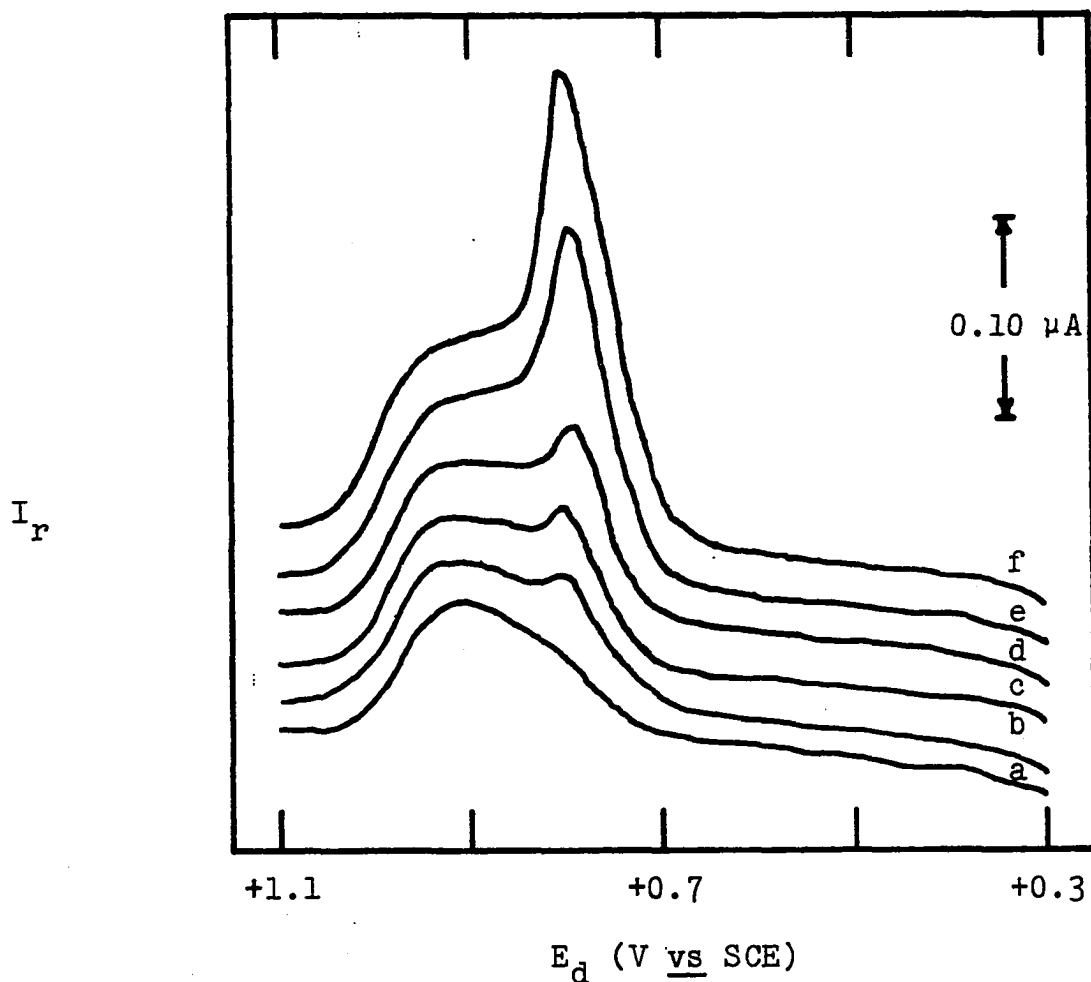


Figure XXV. I_r - E_d curves for several concentrations of Hg(II)

$$E_{d,\text{dep}} = +0.30 \text{ V}; E_r = +0.30 \text{ V};$$

$$\omega^{1/2} = 13.0 (\text{rad/sec})^{1/2}; t_{\text{dep}} = 5.00 \text{ min}$$

$$\phi = 5.0 \text{ V/min}$$

$$C_{\text{Hg(II)}}^b = (\text{a}) \text{ blank}; (\text{b}) 2.0 \times 10^{-10} \text{ M};$$

$$(\text{c}) 4.0 \times 10^{-10} \text{ M}; (\text{d}) 6.0 \times 10^{-10} \text{ M};$$

$$(\text{e}) 2.00 \times 10^{-9} \text{ M}; (\text{f}) 4.00 \times 10^{-9} \text{ M}$$

species produces the peak for the blank, but it is thought to result in part from the Ag(I) impurity discussed in Chapter III and a Hg(II) impurity in the HNO₃. The presence of the Hg(II) impurity was verified when standard additions of concentrated HNO₃ to a solution of 0.20 M HNO₃ gave increases in the collection peak for Hg(II) when SVWC was performed.

6. Determination of the reagent blank

In order to apply SVWC for the determination of Hg(II), an accurate determination of the contribution to Q_r by impurities in the HNO₃ used for the digestion of samples must be made so that this contribution can be subtracted from the values of Q_r obtained for the samples. For the reagent blank in this work, a 2.50 ml aliquot of the distilled, concentrated HNO₃ was carried through the entire procedure used for samples. The results obtained over a 2 week period are shown in Table IV with each result representing the average of 3-4 determinations of Q_r for that solution. Experiments 10-14 were done in a single day. Using the calibration curve in Figure XXIV, $Q_r = 0.346 \mu\text{C}$ was calculated to correspond to 49.9 ng of Hg.

In Table V are shown the results of an experiment in which the blank for 5 separate 50-ml aliquots of 3.0 M HNO₃ were determined by SVWC. The relative standard deviation for the 5 resulting peaks was 6%. The experiment was repeated for 5 additional 50-ml aliquots of the same 3.0 M HNO₃.

Table IV. Results for the determination of reagent blank

Experiment Number	Q_r (μC)
1	0.607
2	0.858
3	0.540
4	0.486
5	0.816
6	0.550
7	0.465
8	0.494
9	0.501
10	0.308
11	0.282
12	0.455
13	0.341
14	0.346

*Average 0.346 μC
 *Standard deviation 0.066 μC
 *Rel. standard deviation 19%

$E_{d,dep} = +0.30 \text{ V}$; $E_r = +0.30 \text{ V}$; $t_{dep} = 5.00 \text{ min}$;
 $\phi = 5.0 \text{ V/min}$; $\omega^{1/2} = 13.0 \text{ (rad/sec)}^{1/2}$

*Calculated for the Experiments Number 10-14 only.

Table V. Determination of the reagent blank for 3.0 M HNO₃

Experiment Number	Q _r (μC) without column	Q _r (μC) with column
1	0.130	0.366
2	0.126	0.390
3	0.142	0.288
4	0.137	0.289
5	0.145	0.276
Average	0.136	0.322
Standard deviation	0.008	0.052
Rel. standard deviation	6%	16%

$$E_{d,dep} = +0.30 \text{ V}; E_r = +0.30 \text{ V}; t_{dep} = 10.0 \text{ min};$$

$$\phi = 5.0 \text{ V/min}; \omega^{1/2} = 13.0 \text{ (rad/sec)}^{1/2}$$

except in this case the aliquots were passed through the ion exchange column and then boiled for 5 min before SVWC was performed. The resulting relative standard deviation was found to be 16%. The values of Q_r for the second part of the experiment were also found to be larger than for the first half of the experiment even though the column had been washed thoroughly with 100 ml of 3.0 M HNO₃ before the first aliquot was passed through. The washing of the column should have removed any residual Hg(II). It is obvious that the physical

handling of the samples and the use of the ion exchange column introduce a variable amount of Hg(II) into the samples. $Q_r = 0.136 \mu\text{C}$ corresponds to 8.3 ng of Hg which results in a value of $4.4 \times 10^{-9} \text{ M Hg(II)}$ calculated for the concentrated HNO_3 .

7. Results of analyses

The results obtained for the determination of Hg in the standard reference materials are shown in Table VI. These

Table VI. Results for the analyses of standard reference materials

Sample	Wt. Sample (gm)	Hg Expected (μg)	Hg Found (μg)	% Error
#1571 Orchard leaves	0.2500	0.0388	0.0036	-91
#1571 Orchard leaves	0.5002	0.0775	0.0236	-70
#1571 Orchard leaves	0.5000	0.0775	0.0158	-80
#1577 Bovine liver	0.5001	0.0080	0.0112	+40

$$E_{d,dep} = 0.30 \text{ V}; E_r = +0.30 \text{ V}; t_{dep} = 5.00 \text{ min};$$

$$\phi = 5.0 \text{ V/min}; \omega^{1/2} = 13.0 \text{ (rad/sec)}^{1/2}$$

results were calculated using the average blank recorded in Table IV.

The fact that the results for the analyses tended to be low prompted an experiment to determine if any Hg(II) was lost during the digestion process. The results of that experiment are shown in Table VII. In Experiment A, Hg(II)

Table VII. Investigation of the loss of Hg(II) during digestion

Experiment	Hg expected (μg)	Hg found (μg)	% Error
A	0.0200	0.0196	-2
B	0.0200	0.0126	-37
C	0.0200	0.0041	-80

$$E_{d,dep} = +0.30 \text{ V}; E_r = +0.30 \text{ V}; t_{dep} = 5.00 \text{ min};$$

$$\phi = 5.0 \text{ V/min}; \omega^{1/2} = 13.0 \text{ (rad/sec)}^{1/2}$$

was determined by SVWC in 50.0 ml of 3.0 M HNO₃ to which 10.0 μl of a 1.00×10^{-5} M Hg(II) solution had been added. For Experiment B, a 10.0 μl aliquot was added to 2.50 ml of concentrated HNO₃ and diluted with water to 200 ml. The resulting solution was then carried through the separation scheme. Experiment C was the same as B except that the 10.0 μl aliquot and the 2.50 ml of concentrated HNO₃ was heated at the boiling point under reflux for 20 min before

being diluted to 200 ml and passed through the ion exchange column. It is apparent that some Hg(II) is lost during the digestion process and also during the post-separation boiling process that is required to eliminate the organic impurities which bleed from the ion exchange resin.

D. Conclusions

If successful application of SVWC for the determination of Hg(II) is to be made, reagents must be obtained in an ultrapure state so that reagent blanks are kept to a minimum. The HNO₃ used in this work was found to contain about 5×10^{-9} M Hg(II). This concentration should be reduced to 10^{-10} M or lower for optimum use in SVWC. Exhaustive electrolysis of the reagents prior to use might achieve this level of purity.

To prevent the loss of Hg(II) during the digestion process, a total reflux apparatus should be used. Quartz would be the optimum material for the digestion apparatus as well as for all other vessels for solutions containing Hg(II) to minimize any loss of Hg(II) due to adsorption on the walls of the containers.

In addition, a resin must be used for the separation of Hg(II) from interfering species that does not present the problems found when Dowex 50X8 was used. However, since the resin used was analytical grade, stringent measures for the

cleaning of this resin or some other resin are perhaps the only solution to the problem.

Despite the difficulties encountered when the analysis of real samples was attempted by SVWC, it is thought the low detection limit, the short deposition times, and the high precision of the technique makes SVWC significant for the determination of trace metals. After the publication of the work described in Chapters III-V (265-266), there appeared in the literature an application of SVWC by Laser and Ariel (267) for the simultaneous determination of Pb(II), Cd(II), Zn(II), and Cu(II) down to 10^{-9} M in an acetate buffer of pH 4.8. They used a Hg film on both the ring and disk electrodes of a glassy carbon RRDE, and reported results comparable to those presented in this work. It is important also to note that for some metals other than Hg and for some sample matrices other than biological ones, SVWC could be applied with little difficulty. For example, SVWC could be applied to the determination of metal impurities in reagent grade acids and certain other inorganic chemicals as easily as conventional stripping voltammetry has been applied previously (1). It remains to solve the problems of digestion, separation, and sample handling to permit the application of the technique routinely to the analysis of biological samples.

VII. SUMMARY

The development of a new electroanalytical technique called stripping voltammetry with collection (SVWC) has been described. The technique makes use of a rotating ring disk electrode (RRDE) and the phenomenon of collection associated with this type of electrode. Compared to conventional stripping voltammetry at a single electrode, SVWC has been shown to have a limit of detection at least an order of magnitude lower which results in a shorter time required for the deposition of the species sought. This results primarily from the fact that there is no contribution to the faradaic current observed at the ring electrode by charging or background currents at the disk electrode.

Illustrations of the technique were given by the determination of Ag(I) down to 1×10^{-10} M in 0.1 M H₂SO₄ and the determination of Hg(II) down to 2×10^{-10} M in 3.0 M HNO₃ using a glassy carbon-disk Pt-ring electrode. In neither instance did the time of deposition exceed 10 min. Satisfactory results were obtained for the determination of Hg(II) only after 2.0 monolayer equivalents of Au were deposited at the glassy carbon disk electrode. In the absence of the Au film, Hg(II) could only be determined down to 5×10^{-6} M for $t_{\text{dep}} = 10$ min. When a thin film of Cu was used on the disk electrode, Hg(II) could be determined down to 5×10^{-8} M. The use of a 20 monolayer equivalent film

of Au on the Pt ring electrode allowed the determination of Hg(II) in solutions saturated with O₂.

Se(IV), Sb(II), As(III), Ag(I), Fe(III), Pt(IV), V(V), Cr(VI), Ce(IV), and Mo(VI) were found to be reduced at a tubular Au electrode which was being used as a detector of a forced-flow liquid chromatograph. An ion exchange separation scheme was devised to separate Hg(II) from the first four of these species since these were the only ones expected to be codeposited with Hg. Successful separation was achieved, but the use of the ion exchange resin yielded widely varying results for the determination of the reagent blank and, consequently, for the standard reference material analyzed. For 5 determinations of the reagent blank done in a single day, the relative standard deviation was 19% at a level 50 times greater than the detection limit of the technique. Apparently, there was also some Hg(II) introduced into the samples by the resin. It was also noted that some Hg(II) was lost from the samples during the digestion process. Because of the variations introduced by the ion exchange resin and the digestion process, accurate determination of Hg in neither of the standard reference materials (NBS #1571 Orchard Leaves and #1577 Bovine Liver) was possible.

VIII. SUGGESTION FOR FUTURE WORK

In order to further improve the applicability of SVWC for the determination of metal ions, it is suggested that in place of the RRDE two tubular electrodes be used in series in the effluent stream of a forced flow liquid chromatograph. The upstream electrode would be analogous to the disk of the RRDE while the downstream tube would be analogous to the ring of the RRDE. The system would utilize all the principles of SVWC as well as the same instrumentation but also have the following additional advantages: (i) O_2 would not be a problem no matter what the electrode materials since a metal would be deposited as the flowing stream of electrolyte swept the aliquot of sample containing the O_2 out of the system. (ii) Physical handling of the samples would be kept to a minimum. (iii) Separations such as that required in the determination of Hg(II) would be accomplished much faster and with greater resolution with the forced flow chromatograph than with the normal gravity flow system. (iv) The necessity of cleaning an electrochemical cell after each sample would be eliminated as would the loss of an ion from solution by adsorption on the walls of the cell. (v) Excluding digestion time, the total time for an analysis with separation of interferences would be on the order of 10 to 15 minutes. (vi) A wide range of sample volumes (ca. 50 μ l to 10 ml) could be used thus allowing the analysis of a wider range of

samples. (vii) For cases in which SVWC is not applicable or necessary, either one of the two electrodes could be disconnected and the other used as a simple detector for species in the effluent stream of the chromatograph.

A design for a two tube electrode system was submitted to Pine Instrument Company for construction. The resulting model had a downstream Pt tube (2 mm ID x 7.5 mm long) and an upstream glassy carbon tube (2 mm ID x 15 mm long) encased in series in a Teflon shroud. The reference electrode and counter electrode were placed near the outlet of the Pt tube. Attempts to use this model for SVWC were not successful because the Pt tube could not be maintained at a constant potential for collection while the glassy carbon tube was scanned to strip a deposited metal. It is felt that the problem arises from the spatial arrangement of the four electrodes and that placement of the counter electrode at a position near the inlet of the glassy carbon tube will remedy the difficulty. At present the engineering problems involved with such an arrangement have not been satisfactorily resolved, but the outlook for an adequate solution is good.

IX. BIBLIOGRAPHY

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