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ELECTROMETRIC DETERMINATION OF METALS IN WASTE WATERS CONTAININ--ETC(U)
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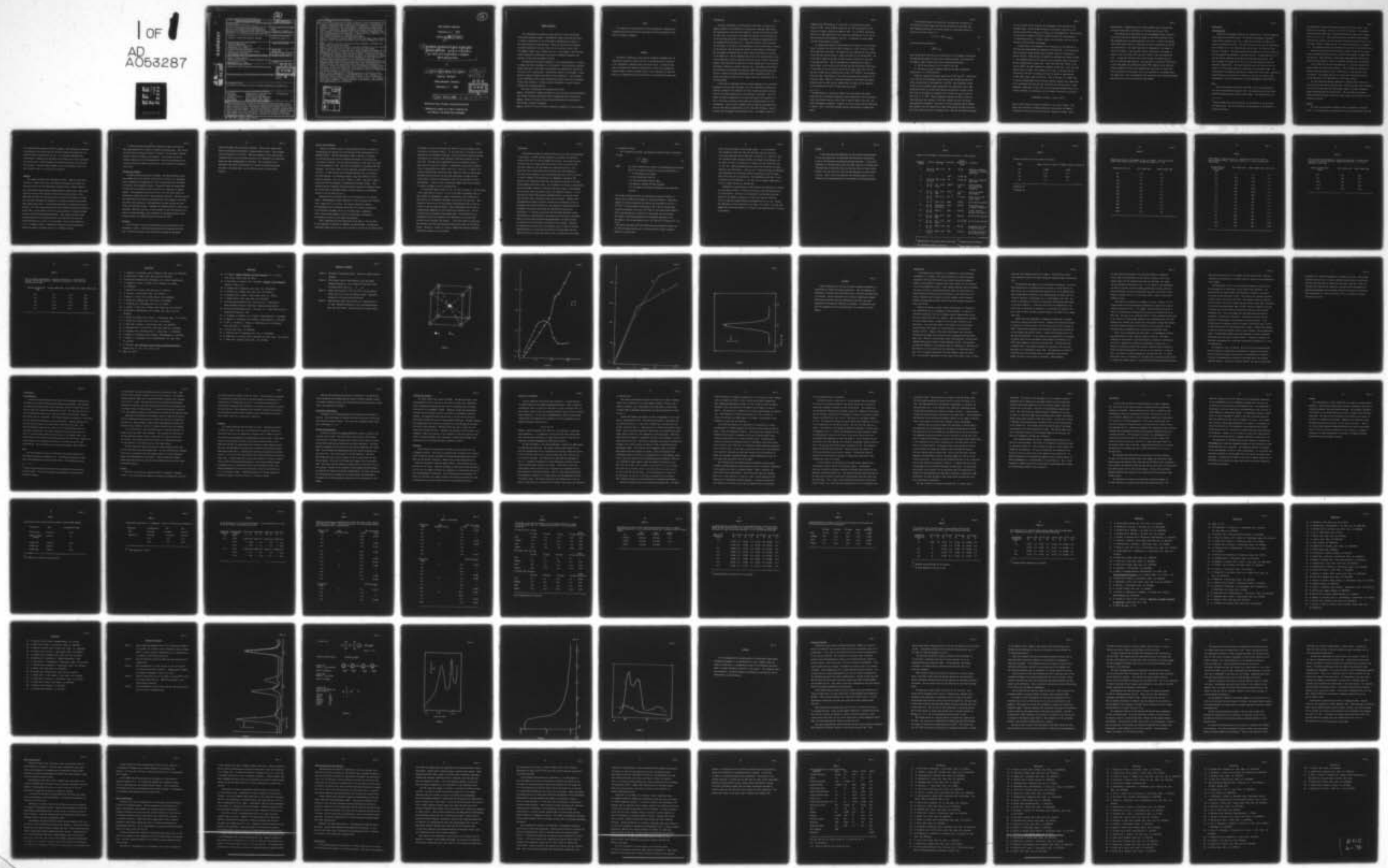

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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The investigation was pursued as one aspect of a water extractable constituents research program. Knowledge was needed concerning the effect of organic consituents on the electrometric determination of metals in such waste waters as bilge discharge. Hence the electrodics of organics, including surfactants and their effect on the reactions of metal ions--for example, copper, lead, cadmium, and zinc--was studied. The relatively recent technique of differential pulse anodic stripping voltammetry was explored as the prime electrometric method, (OVER)

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#20) (Cont'd) The application of anodic stripping to trace determinations in a variety of samples has been documented in the literature. This distinctive technique suffers from some of the common interferences and complications inherent in all work at low concentrations. Interferences unique to this method -- intermetallic compound formation and surface active substances -- were examined in the differential pulse anodic stripping voltammetric mode with an hanging mercury drop electrode. A review was also undertaken to compile relevant literature on stripping analysis.

The report incorporates the following three parts:

Part A. Intermetallic compound formation of zinc and copper using differential pulse anodic stripping voltammetry with an hanging mercury drop electrode.

Part B. Effects of organic surface activating substances on differential pulse anodic stripping voltammetry.

Part C. Review of the use of anodic stripping voltammetry for trace analysis.

The individual abstracts for Parts A, B, and C are cited below:

Part A. The value of differential pulse anodic stripping voltammetry for the simultaneous analysis of copper and zinc is depreciated by the formation of an intermetallic compound within the mercury phase. A study has been made to determine the limiting concentrations at which the intermetallic compound begins to have an adverse effect on the calibration of these two metals at an hanging mercury drop electrode in the differential pulse mode.

Part B. A major complication in the use of anodic stripping voltammetry is *interference* by *surface* activating substances. This investigation was undertaken to evaluate this interference and to eliminate the surfactants if necessary. Several surfactants were tested by employing an hanging mercury drop electrode with the differential pulse mode, and their degradation by ultraviolet radiation was examined. An adsorptive technique is suggested for the trace measurement in ideal samples.

Part C. In an investigation of the applicability of differential pulse anodic stripping voltammetry to the determination of zinc, cadmium, lead, and copper in water waste, a comprehensive review of the literature was undertaken to compile information essential to the project. The following topics were considered: stripping analysis, interferences, applicability and reproducibility, and purification.

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ELECTROMETRIC DETERMINATION OF METALS IN WASTE WATERS CONTAINING SURFACTANTS: SUITABILITY OF DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY AT AN HANGING MERCURY DROP ELECTRODE.

BY

(10) TIMOTHY A. GETEK ~~AND~~ WILLIAM E. SCHMIDT

(11) Mar 78

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GENERAL ABSTRACT

The investigation was pursued as one aspect of a water extractable constituents research program. Knowledge was needed concerning the effect of organic constituents on the electrometric determination of metals in such waste waters as bilge discharge. Hence the electrodics of organics, including surfactants and their effect on the reactions of metal ions -- for example, copper, lead, cadmium, and zinc -- was studied. The relatively recent technique of differential pulse anodic stripping voltammetry was explored as the prime electrometric method.

The application of anodic stripping to trace determinations in a variety of samples has been documented in the literature. This distinctive technique suffers from some of the common interferences and complications inherent in all work at low concentrations. Interferences unique to this method -- intermetallic compound formation and surface active substances -- were examined in the differential pulse anodic stripping voltammetric mode with an hanging mercury drop electrode. A review was also undertaken to compile relevant literature on stripping analysis.

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Part C. Review of the use of anodic stripping voltammetry for trace analysis.

Part A

BRIEF

An evaluation of the formation of Zn-Cu intermetallic compound in an hanging mercury drop electrode has been made utilizing differential pulse anodic stripping voltammetry.

ABSTRACT

The value of differential pulse anodic stripping voltammetry for the simultaneous analysis of copper and zinc is depreciated by the formation of an intermetallic compound within the mercury phase. A study has been made to determine the limiting concentrations at which the intermetallic compound begins to have an adverse effect on the calibration of these two metals at an hanging mercury drop electrode in the differential pulse mode.

INTRODUCTION

Part A

One major interference in differential pulse anodic stripping voltammetry (DPASV) is the formation of intermetallic compounds (IMC) within the hanging mercury drop electrode (hmde) or the thin film electrode (TFE). The IMC, which is produced in the deposition sequence of the analysis due to the alloying properties of the metals, alters the stripping behavior of the amalgam during the anodic scan. Hence the faradaic current measured for the metals in the IMC is not proportional to the concentration of cations in the solution, and the analytical utility of this method is diminished. One investigator eliminated the Cu and Zn IMC by the addition of gallium to the sample (1). The Ga combines with the Cu in the mercury phase to give a Ga-Cu IMC which is easily oxidized during the scan to positive potentials. However, this method may be used only in acidic medium due to the extensive hydrolysis of gallium in neutral solutions (2). Some workers have adopted the procedure of determining the copper by DPASV and separately measuring Zn with a cathodic scan using differential pulse voltammetry (DPV) (3). Others have simply excluded zinc and copper from their calibrations due to the IMC problem.

A novel idea to eliminate IMC has recently appeared in the literature. Adopting a twin electrode thin-layer cell first developed by Reilley and coworkers, DeAngelis and coworkers (4) used a double electrode to deposit the zinc and copper separately onto two different electrodes. Since the copper is removed exhaustively at one electrode before the deposition of zinc at the other electrode, these metals are stripped without the IMC interference. Another line of thought involves diluting the sample below the zinc and copper concentrations at which this IMC is formed. Several articles have recommended this procedure (5,6). For example, Kemula (7) suggested that IMC formation is a function of concentration and gave a limit of $10^{-5}\underline{M}$. Below $10^{-5}\underline{M}$ no nickel and zinc IMC were observed in the results for anodic stripping voltammetry (ASV). For $10^{-8}\underline{M}$ the same author (8) found no IMC complications for a solution containing Zn, Cd, Pb and Cu, which concurred with Stromberg's view (9). A tabulation of recent DPASV and ASV reviews appears in Table 1.

In comparing the aqueous concentrations of the metals to the electrodes used, it appears that the Zn-Cu IMC is formed at a lower quantity of metal in the TFE than in the hmde. The reason for this relation has been equated (1,10) with the surface area vs. volume of mercury in the TFE and hmde. Due to the small volume in the TFE, the IMC is quite noticeable in this type of working electrode. This correspondence is substantiated in Table 1; those workers (1,2,4,5,6,10,11,12) who used the TFE experienced difficulties in the 0.001 to 10.0 ppm aqueous concentration range, while those (13-15) who used an hmde had no problems below 10 ppb (10^{-7}-$10^{-8}\underline{M}$).* One divergence from this basic relationship is the study by Copeland and coworkers (1) employing an hmde. However, it should be pointed out that their tests dealt primarily with the TFE, and any remarks about the hmde were not supported by any organization of data in that particular review.

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* The IMC quantity in the mercury phase is not only governed by cation concentration in the aqueous sample but also by deposition time and potential limit, equilibration period, area of TFE or mercury sphere, scan rate, and other instrumental parameters. However, it is still clear from the tabulation in Table 1 that a correlation between IMC and concentration in sample does exist.

One extensive study of the Zn-Cu IMC, including the calculation of its solubility product (K_{sp}), was done by Stromberg and Gorodovykh (16). They considered the IMC in the mercury phase to be sparingly soluble for one mole of Zn and n moles of Cu

$$\mathrm{Zn} + n\mathrm{Cu} = \mathrm{ZnCu}_{n\ (solid)} \tag{A}$$

and wrote the K_{sp} expression

$$c_1^o c_2^{on} = K_{sp} \tag{B}$$

where c_1^o and c_2^o are the Zn and Cu concentration in the amalgam, respectively. By measuring the height of the Zn and Cu peaks using ASV, and varying only the aqueous copper concentration, they concluded the following:

1) The Zn and Cu exist in an 1:1 ratio in the IMC.

2) The value of $c_1 c_2^n$ in aqueous solution and under experimental conditions is 17×10^{-14} g-ion^2/L^2.

Consider a sample having equal quantities of Zn^{2+} and Cu^{2+}. Application of eq. (B) and the experimental $c_1 c_2^n$ predicts IMC interference when the cation concentration is approximately 4×10^{-7}M. This represents roughly 24 ppb in 10 mL of sample, which agrees with the observation that no IMC difficulties exist in an hmde whose aqueous concentration is under 10 ppb. Later work by stromberg and coworkers (17) verified the K_{sp} of the Zn-Cu IMC to be ca. 5×10^{-8}. There is general acceptance of the 1:1 ratio for Zn-Cu IMC since other analysts (5,10) have reached the same conclusions using different techniques. This point is further substantiated by Kamenov and coworkers (18) who reported that those metals which form IMC in mercury will form alloys outside of the amalgam state, and that this behavior depends in turn on their atomic structure and consequently their position in the Periodic Table. For Zn-Cu IMC the alloy is beta-brass, which has a composition range (19) of $CuZn_{0.55}$ to $CuZn_{1.16}$ at room temperature. The structure of this alloy is similar to that of cesium chloride (20), whose packing is illustrated in Fig. 1. However, there is no conclusive evidence for the structure existing within the amalgam.

A major point to be considered is the likelihood of the formation of the Cu-Hg and Zn-Hg amalgams as opposed to the Zn-Cu IMC. It has been noted that the various metals exhibit quite different levels of saturation in mercury (21,22). These percents by weight for saturation are listed in Table 2. Upon supersaturation of the mercury by one particular metal, the metal-mercury amalgam will no longer form. Hence free metal will "float" in the mercury sphere, and make possible the formation of IMC (23). Since the least soluble metal is copper, this element will be used to calculate the concentration of the Cu^{2+} in solution that will be needed to supersaturate an hmde sphere with a mass of 0.0070 g. This is the mass of a single drop of mercury extruded when using a Princeton Applied Research Corp. (PAR) hmde with a micrometer head that has been rotated by six vertical units. Using Sidgwick's compilation of data (21), since the Russian monograph (22) is not readily available, one multiplies the % by weight of mercury for saturation

$$0.0032\%/100 \times 0.0070\ \mathrm{g} = 0.224 \times 10^{-6}\ \mathrm{g} \tag{C}$$

Hence a 10-mL aliquot of sample corresponds to 22.4 ppb of copper. This figure was calculated by assuming exhaustive electrolysis and complete utilization of the mercury drop for plating, making this number a gross approximation. Supersaturation in a TFE of graphite and ceresin wax was 20 ng for copper where the TFE has ca. 75% plating efficiency (24).

The description of IMC effects on the voltammograms denote a decrease in the zinc peak and an addition of height to the copper peak due to the IMC stripping off at the same potential (1,2,11,25). Florence (6) working with acetate buffer (pH 5.7) stated that the percent depression by the IMC was proportional to the copper molarity but independent of the amount of zinc in the sample. Other possible results of IMC may be a doubling of peaks, a rise in the base line, and even a shift of the curve anodically (12). It should be said that even at the Cu peak, it appears that not all of the IMC has been oxidized. This was shown to be true by ^{65}Zn studies (1,10) using gamma ray scintillation where ^{65}Zn remained in the electrode. However, Nikelly and Cooke (26) explained that some metal is always lost into the interior of the mercury and is not available for stripping during the anodic scan. This is evidenced by the observation that extended stripping periods did not cause any increase in peak heights.

EXPERIMENTAL

Instrumentation

A PAR 174A Polarographic Analyzer was interfaced with a PAR 315 Automated Electroanalysis Controller module. The standard instrumental settings,* unless stated otherwise, were for the PAR 174A a scan rate of +5mV/s and a modulation amplitude of 25 mV. The clock was set at 0.5 s and the operational mode indicator was in the differential pulse setting. The low pass filter was not a necessity. The display direction was opposite to the scan direction and the keyboard was depressed in the scan function. Voltage range was 1.5 V and the initial potential and output offset were both set at zero. The PAR 315 module had values of 60 s and -1.2 V for the deposition time and potential, respectively. The final potential was set at either +0.15 V or +0.20 V, but never more positive to exceed the 1.5 V potential range. The equilibration and deaeration periods were timed at 30 s and 10 min, respectively. Conditioning was not necessary nor desired; a new drop was used for each determination. The X-Y recorder was a Houston Omnigraphic, model 2200-3-3.

Cell

The electrochemical vessel was a PAR 9301 cell bottom equipped with the various electrodes and degasser (27). The working electrode was a PAR model 9323 hanging mercury drop electrode (hmde). The standard drop size

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* These settings were selected because they are similar to the ones used for ASTM studies. This will facilitate standardization of the method for analytical purposes.

was extruded by turning the micrometer head by six vertical units. This yielded on the average a volume of 5.15×10^{-4} cm^3 mercury. The standard calomel electrode (SCE) was a cracked bead Fisher electrode with a leakage rate of 0.3 to 5 μL/h. The electrolyte used in the SCE was electrolyzed saturated KCl solution, and the reference electrode was placed directly into the sample without a bridge network. The counter electrode was a platinum wire. The degassing system was automatically controlled by the PAR 315 device.

Degassing was performed with nitrogen, usually of high purity quality. Several scrubbing systems were used to remove trace amounts of oxygen from the inert N_2. These included a copper metal high temperature furnace and bubbling the N_2 through a solution of vanadous chloride over zinc amalgam.

It was found that the best deaerating gas is a specially prepared low oxygen content N_2 (Linde; Union Carbide). This nitrogen was effective in removing dissolved oxygen so that a sensitivity of 1 ppb and less could be achieved. This special gas did not require any prepurifying measures and was delivered to the PAR vessel by ¼ inch Tygon tubing.

The cell deaeration design consisted of a bulbous glass fixture that had two inlet ports form the nitrogen tank. One port allowed direct bubbling of the N_2 to be dispersed above the aqueous sample to prevent atmospheric oxygen from dissolving into the solution. The electrodes and nitrogen system were held securely in place by a hard plastic head cover that fitted the PAR cell bottom.

Stirrer

The basic stirring device supplied by PAR is a Magnestir, catalogue # 1250. It was found that the rheostat type device was heating the cell bottom causing thermal gradients within the sample. This mechanism was improved by removing the casing that held the variable element and placing only the rotatory arm and coiling under the cell. An alternative method was devised wherein a Magnestir was attached to an isolated variac which controlled the stirring rate. This arrangement also prevented warming of the solution. The stirring bar should be small enough to allow free movement on the cell base; either ½ inch or 1 cm size bar is effective.

Reagents

All reagent chemicals were ACS grade or better. 1000 ppm stock metal solutions of copper, lead, zinc, and cadmium were prepared by either dissolving the metal into the appropriate ultrapure acid or taking a Dilut-it salt solution and volumetrically standardizing the cation stock. These salts should be nitrates since chloride ion may have an adverse effect on the DPASV mode and SO_4^{2-} may precipitate with lead when a metal mixture is made. The water used throughout was purified by a millipore system that delivered ASTM reagent grade water. A saturated KCl solution was prepared and electrolyzed at -1.3 V for no less than 36 hours with a PAR electrolysis purification system (28). Acetate buffer (pH 4.5) was also purified at a mercury cathode using the PAR 173 Potentiostat/Galvanostat. This acetate buffer was made by measuring 12 mL of concentrated acetic acid into 500 mL of water and adding 50% NaOH until a pH of 4.5 was attained. This was then diluted to 1 L in a volumetric flask. A mixed metal solution of 10 ppm cations was prepared by adding a suitable aliquot to a volumetric vessel.

Gallium solutions were prepared by addition of Baker Ultrex HCl or HNO_3 (approximately 20 to 30 mL) to 0.1000 g of gallium metal. The solution was then heated to hasten dissolution of the Ga. In this manner, 1000 ppm stocks fo $GaCl_3$ and $Ga(NO_3)_3$ were prepared. It was noted that the Ga dissolved readily into the concentrated HCl, while the preparation of the nitrate solution was somewhat difficult due to the passivity of gallium in nitric acid.

Cleaning and Transfer

All glass pipets were stored in 6M HNO_3. The PAR electrolytic cells were soaked with nitric acid for no less than 1 h before use. Disposable plastic Eppendorff micropipettes were used in delivering stock and sample solutions to the voltammetric vessel. Volumetric flasks and polyethylene bottles were also leached in nitric acid prior to containment of aqueous samples. The degassing fixture and Pt wire in the cell device were also periodically soaked with acid to remove adsorbed materials. The hmde capillary was changed daily and cleansed by pulling nitric acid through the capillary bore with a water aspirator. Millipore water was used to rinse any acid residue off material surfaces. Sometimes the capillary failed to keep a drop suspended. When this occurred, it was necessary to soak the capillary overnight in concentrated HNO_3, rinse thoroughly by aspirating millipore water through the bore, and drying the glass capillary at 110°C.

Procedure

A 10 mL aliquot of acetate buffer served as the electrolyte for the voltammetric studies. The buffer was deaerated for 10 minutes with stirring. A drop of mercury was then extruded by rotating the micrometer head of the hmde, and the analysis initiated. Between runs, several hmde drops were extruded and discarded to minimize memory effects. The stripping scan was recorded on a X-Y chart. When any increments of any solution were introduced into the cell the spiked solutions were degassed for an additional minute and then voltammographed as described. Upon termination of an experiment, the buffer was discarded, the counter and working electrodes were kept in millipore water, and the SCE was stored in saturated KCl solution.

RESULTS AND DISCUSSION

Using the conditions cited in the experimental section, a series of voltammograms was recorded with electrolysis periods comprising 60 s to a maximum of 600 s. The data appearing in Table 3 and Fig. 2 correlate the electrolysis period versus stripping peak height of copper and zinc. At periods of 360-420 s, the zinc peak was reduced ca. 30%, while the copper curve was enhanced ca. 40%. This kind of phenomenon is associated with IMC formation. The acetate buffer in this experiment contained 20 ppb each of Cu and Zn. At 300 s the Zn curve decreased somewhat, but in accordance with IMC anamalies, the stripping potential (E_p) also shifted to a more positive potential - that is, from -1.007V to -1.001V. The data in Table 3 concur well with the findings of Stromberg and coworkers (29,30). They observed that the comparison between deposition period and stripping current for an IMC which is sparingly soluble in mercury exhibits a relationship similar to the one shown in Fig. 2.

Another factor that affects IMC is the concentration in the aqueous sample. Voltammograms of equal quantities of zinc and copper were recorded over a range of 0.1 to 15.0 ppm. The results tabulated in Table 4 were developed into a calibration curve (Fig. 3) to check the linearity of the analysis throughout the 0.1 to 15.0 ppm range. Apparently zinc's constant slope begins to fail at 5.0 ppm, and the analytical relationship is thus not exact above this quantity.

After confirming that some interference does exist, a test was made on the usefulness of gallium to eliminate any IMC problems. One series of experiments began with 12.5 ppm each of Zn and Cu in 10.0 mL of acetate buffer.

Increments of 5 ppm Ga (as $GaCl_3$) were added to the electrochemical cell. The results are listed in Table 5. It was noted that at 15.0 ppm Ga a peak appeared for the oxidation of gallium. This occurred only after the initial concentration of Zn and Cu were surpassed, which gives evidence for the Ga-Cu IMC. The same type of experiment with Ga was repeated using 2.0 ppm Cu and Zn in 10.0 mL of buffer. A substantial Ga peak did not appear until 2.0 ppm gallium were added to the cell. From 2.0 - 4.0 ppm Ga, the standard additions were perfectly linear (Table 6), while the copper peak decreased by about 26% and the zinc peak experienced a slight increase by 6%, which is within the experimental error of the procedures in this investigation. These two tests with gallium suggest that the IMC anomaly is greater at higher Zn and Cu concentrations.

A conspicuous anomaly occurs at 2.0 - 2.2 ppm of Zn and Cu. At this level, a split peak forms for zinc at ca.-1.0V on the DPAS voltammogram (Fig. 4). This anomaly is independent of copper concentration, and is affected in some ways by the instrumental settings, in particular the scan rate. The behavior of the Zn curve at still greater concentrations than 2.2 ppm is a shift of the zinc peak by +0.012V. These observations are the type of irregularities suggested for IMC by Kublik and coworkers (12). The use of gallium did not eliminate this doubled peak. The possibility of an instrumental defect was considered, but substitution of a strip chart recorder did not eliminate the anomaly. It has been stated by Osteryoung and coworkers (31) that instrumental fluctuations do exist in the PAR 174 module. However, no example of a double jagged peak caused by equipment failure has appeared in the literature.

CONCLUSIONS

From previous studies by notable analysts and the recent work presented in this paper, a format has been proposed to circumvent the IMC interference of Zn and Cu in ASV and DPASV with an hmde. This format utilizes dilution below the concentration limit where Zn and Cu form their IMC. The limit chosen for the instruments and conditions stated is 1 ppm. Below this level, experimental data have shown that IMC formation, if any, has little influence on the electroanalytical mode, which is contrary to Flato's remarks in his discussion of voltammetric techniques (32). Survey of the literature reveals that IMC effects are greater at the TFE and prolonged electrolysis times. For calculation of the exact concentration where IMC becomes critical to analytical functions, there is some dispute how one should treat the mercury drop in the deposition process. In considering the volume used during the plating process, one should involve only the first layers of mercury atoms near the surface. However, when establishing the volume of mercury involved in the formation of IMC, investigators have stated (33,34) that the amalgams are distributed evenly throughout the mercury drop during the equilibration period after electrolysis. It should be noted that the principal difference during electrolysis vs. equilibration is the high rate of stirring in the former. Metals are still being collected during quiescence, but their plating is controlled by the diffusion coefficients of the cations. Moreover, the deposition continues until the particular E_p for a metal is reached. This would mean for a slow scan of Zn and Cu in the ASV mode that the copper would have a longer electrolysis time in comparison to zinc which is stripped out first.

For a spherical electrode, the amalgam concentration may be calculated by (35)

$$C_R = \frac{3i_c\pi}{4\tau nFr_o^3} \qquad (D)$$

where C_R is the concentration of metal in the amalgam state (mol/cm^3).

$\frac{4\pi r_o^3}{3}$ is the volume of mercury in the drop (cm^3) where r_o is the radius of the sphere.

τ is the electrolysis time (s).

i_c is the electrolysis current (amp).

F is Faraday's constant (96 500 coulombs).

n is the number of electrons transferred in the electrode reaction.

The volume of mercury may also be calculated by using the density of mercury (13.6 g/cm^3) and the weight of the drop (0.0070 g). Using this method, the volume occupied by the mercury was calculated to be 5.15 x 10^{-4} cm^3. The electrolysis time was set at 90 s and the electrolysis current was measured to be 0.25 x 10^{-6} amp for an acetate buffer sample.* The i_c was measured for a solution of 2 ppm copper and zinc cations. The number of electrons transferred for the metals discussed is two. By using eq. (D), C_R approximates 2.26 x 10^{-7} mol/cm^3 or a quantity of 7 ng

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* For dilute solutions (10^{-6} and 10^{-7}M) the preelectrolysis currents can be taken as being proportional to the concentration if mass transport process is constant (35).

each of zinc and copper in the mercury sphere. It was calculated from Stromberg's study (16) that the IMC effect did not occur until 3.6 ng were deposited into an hmde with a volume of 2.7×10^{-4} cm^3. Note that Stromberg's hmde occupied one-half the volume of the PAR hmde, and the amount of metal in the mercury to initiate the IMC interference was ca. 50% less. Another interesting point deals with the extent of copper saturation into the mercury. From eq. (C), it was stated that an exhaustive electrodeposition of an aqueous solution containing 22.4 ppb of copper would reach the limit of saturation. From Stromberg's work (16), it was calculated for his conditions ($\tau = 30$ min) that an aqueous sample must be 24 ppb in copper and zinc to initiate IMC.

Although the concentrations for IMC formation and saturation of mercury by copper agree closely, it should be pointed out that such precision is only coincidental. This fact is illustrated by the various values presented for the weight % saturation of copper into mercury (Table 2), and the conditions assumed during electrodeposition for eq. (D). However the magnitudes of the concentrations are taken to be correct, and this does suggest that Zn-Cu IMC formation is related to the supersaturation of mercury by the metals.

SUMMARY

It has been shown experimentally for equal aqueous concentrations of zinc and copper that no substantial IMC interference exists below 1 ppm at the particular instrumental settings described. In the theory discussed, it was demonstrated that the study conducted by Stromberg and Gorodovgh (16) concurs well with the saturation limit of copper within mercury, and that above this limit the IMC phenomenon with zinc begins to occur. Hence it may be stated that IMC formation appears to be a function of the supersaturation of the mercury by the alloying metals.

TABLE 1

Review of recent DPASV and ASV studies with respect to IMC formation.

Reference Number	Cations	Deposition		Electrode	Aqueous Concentration Range	Comments
		t	E			
1	Zn Ga Cd Pb Cu Tl	120s	-1.3V	TFE	50 ppb	Used Ga as internal standard to eliminate Zn-Cu IMC.
1	"	"	"	hmde	17-200 ppb	"
11	Zn Ga Cd Pb Cu Ni	120s	-1.25V	TFE	20-120 ppb	Used Ga to eliminate Zn-Cu IMC.
5	Cd Pb Cu Zn	40-70min	-1.33V	CMGE [b]	0.3-10.0 ppm	Diluted sample below Zn-Cu IMC formation.
10	Cd Pb Cu Zn	60-300s	-1.2V	WIGE [c]	0.5-1.1 ppm	Cu must be absent from sample.
6	Cd Pb Cu Zn	300s	-1.3V	GCE [d]	<1.0 ppm	Noted no Zn-Cu IMC below 3 ppb.
7	Ni Zn	120s	-1.4V	hmde	$>10^{-5}\underline{M}$	Zn-Ni IMC was present.
12	Cd Zn Pb Cu	Information not given.		WIGE	$\sim 10^{-7}\underline{M}$	Considered K_{sp} of of metals in mercury.
13	Cd Zn Pb Cu	300s	[a]	hmde	<10 ppb	No IMC problems because Zn in excess.
14	Cu Cd Pb Zn	180-300s	-1.4V	hmde	<20 ppb	No Zn-Cu IMC reported.
15	Zn In Pb Cu	10-30min	-1.3V	hmde	$10^{-7}-10^{-8}\underline{M}$	No Zn-Cu IMC reported.
2	Zn Cd Pb Cu	180s	-1.25V	GCE	<10 ppb	Eliminated Zn-Cu IMC by multiple scans.
4	Pb Cd Tl Cu Zn	180s	-1.25V	WIGE	>20 ppm	Zn-Cu IMC eliminated by thin-layer cell.

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[a] Appropriate for the metals under examination.

[b] Composite mercury-graphite

[c] Was impregnate graphite electrode.

[d] Glassy carbon electrode.

TABLE 2

Percent saturation of various metals in mercury.

Metal	Weight % metal in mercury [a]	Weight % metal in mercury [b]
Cu	0.0032	0.006
Zn	2.15	6.4
Cd	4.92	10.0
Pb	1.3	1.2

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[a] reference 21.

[b] reference 22.

TABLE 3

Electrolysis time vs. peak height of zinc and copper. 10.0 mL of acetate buffer with 20 ppb of Zn and Cu. Deposition potential of -1.2V.

Deposition time (s)	Zinc height (μA)	Copper height (μA)
60	1.0	0.7
90	1.4	1.0
120	1.7	1.2
150	2.0	1.5
180	2.3	1.7
240	2.8	2.2
300	3.0	2.7
360	2.8	3.1
420	1.9	4.4
480	1.6	4.6
540	1.6	5.2
600	1.6	5.8

TABLE 4

Peak heights of copper and zinc vs. concentration of Cu^{2+} and Zn^{2+} in aqueous acetate buffer. Deposition potential of -1.2V and a deposition time of 60s.

Concentration of Cu^{2+} and Zn^{2+} (ppm)	Zinc height (μA)	Copper height (μA)	Ratio Zn/Cu
0.1	4.1	3.7	1.1
0.6	25.4	23.4	1.1
1.1	46.9	43.2	1.1
1.6	67.6	63.4	1.1
2.1	88.7	84.6	1.2
2.2	109	90.8	1.3
2.3	123	98.0	1.2
2.4	125	102	1.2
2.5	132	107	1.2
2.6	137	111	1.2
3.1	156	127	1.2
3.6	172	145	1.2
5.0	230	193	1.6
7.5	283	258	1.1
10.0	308	350	0.88
15.0	322	386	0.83

TABLE 5

Zinc and copper peak heights vs. gallium concentration. Acetate buffer contains 12.5 ppm Cu^{2+} and Zn^{2+}. Deposition potential of -1.2V and a deposition time of 60s.

Gallium concentration (ppm)	Zinc height (μA)	Copper height (μA)
0.0	322	386
5.0	348	282
10.0	356	187
15.0	374	118
20.0	383	92.0

TABLE 6

Zinc and copper peak heights vs. gallium concentration. Acetate buffer contains 2.0 ppm Cu^{2+} and Zn^{2+}. Deposition potential of -1.2V and a deposition time of 60s..

Gallium concentration (ppm)	Gallium height (μA)	Zinc height (μA)	Copper height (μA)
0.0	0.0	73.4	70.4
1.0	4.0	73.2	58.4
2.0	12.0	73.6	52.0
3.0	24.0	78.4	48.8
4.0	36.0	76.4	46.0

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Captions to Figures

Figure 1 Structure of beta-brass (ZnCu). Similar to cesium chloride packing.

Figure 2 Electrolysis time vs. peak heights of zinc and copper. Deposition potential -1.2V; 20 ppb Zn^{2+} and Cu^{2+} in 10.0 mL acetate buffer (pH 4.5). Zn Cu.

Figure 3 Equal concentrations of Zn^{2+} and Cu^{2+} in 10.0 mL acetate buffer (pH 4.5) vs. their stripping currents. Deposition potential -1.2V; electrolysis period 60s.

Figure 4 Characteristic split peak for zinc at a concentration ca. 2.1 ppm. Deposition potential -1.2V, electrolysis period 60s, scan rate +5mV/s. Electrolyte pH 4.5 acetate buffer.

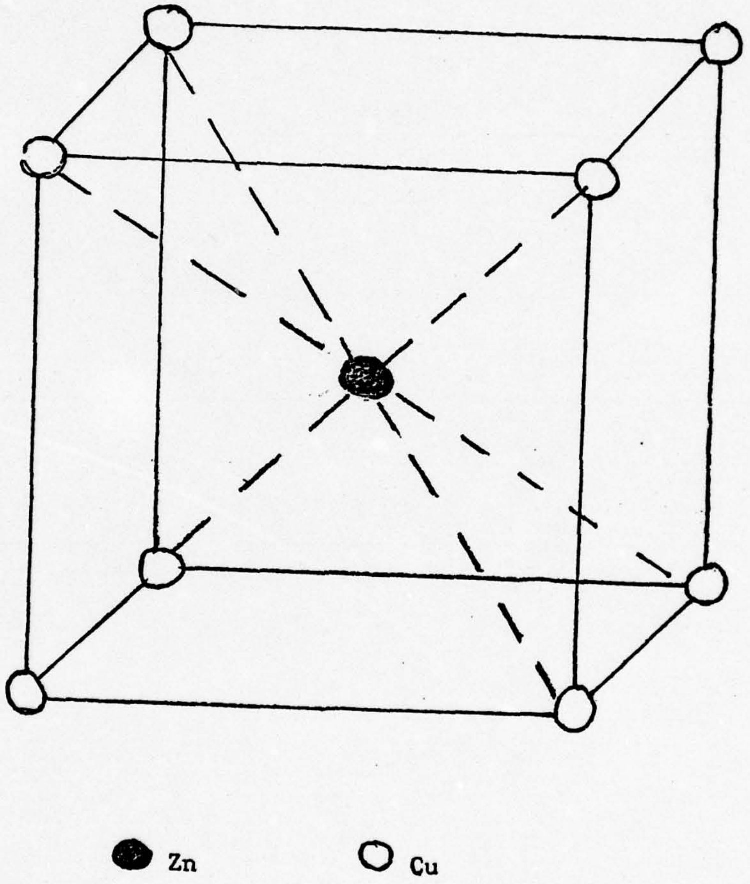

FIGURE 1

Part A

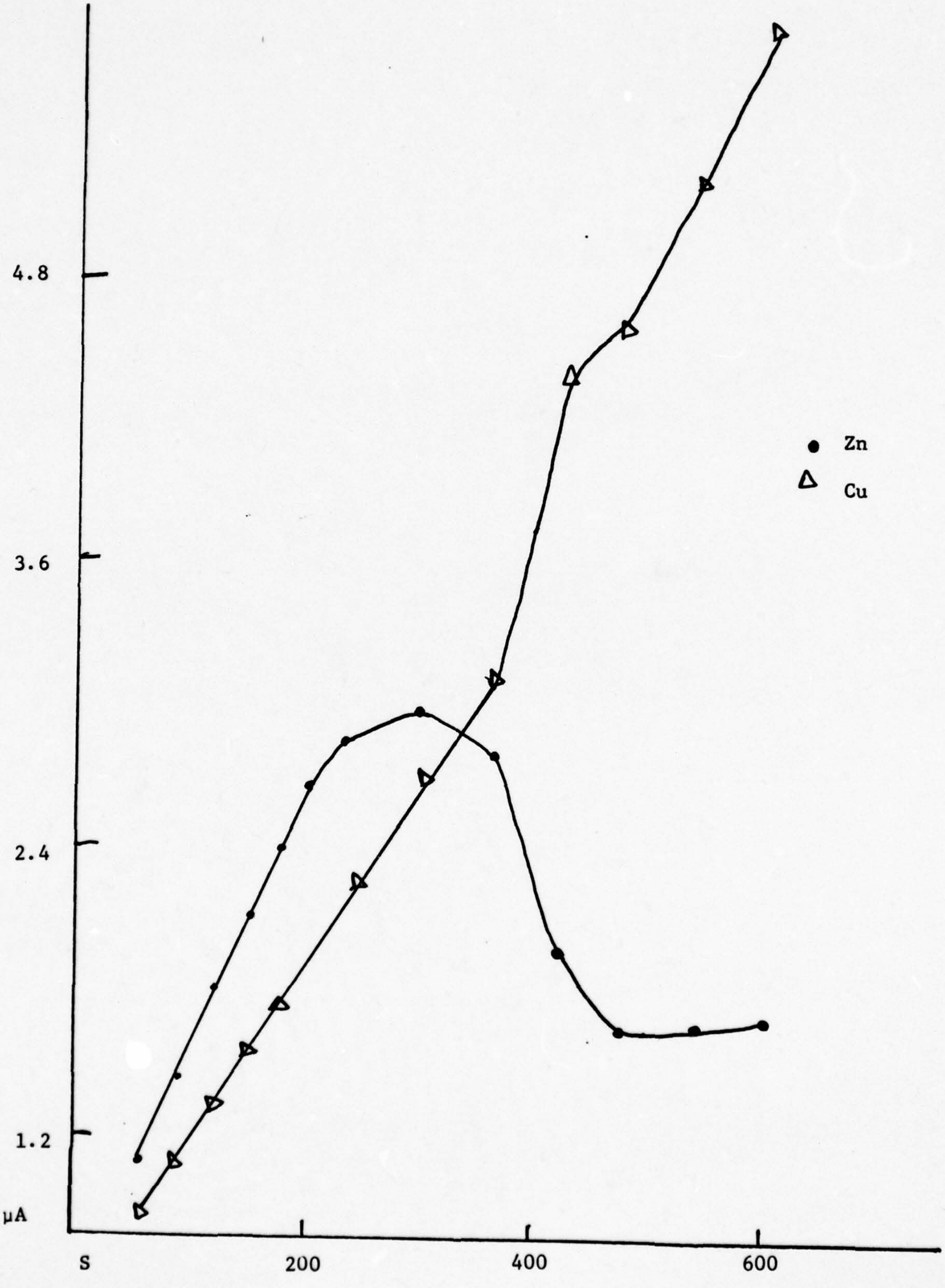

FIGURE 2

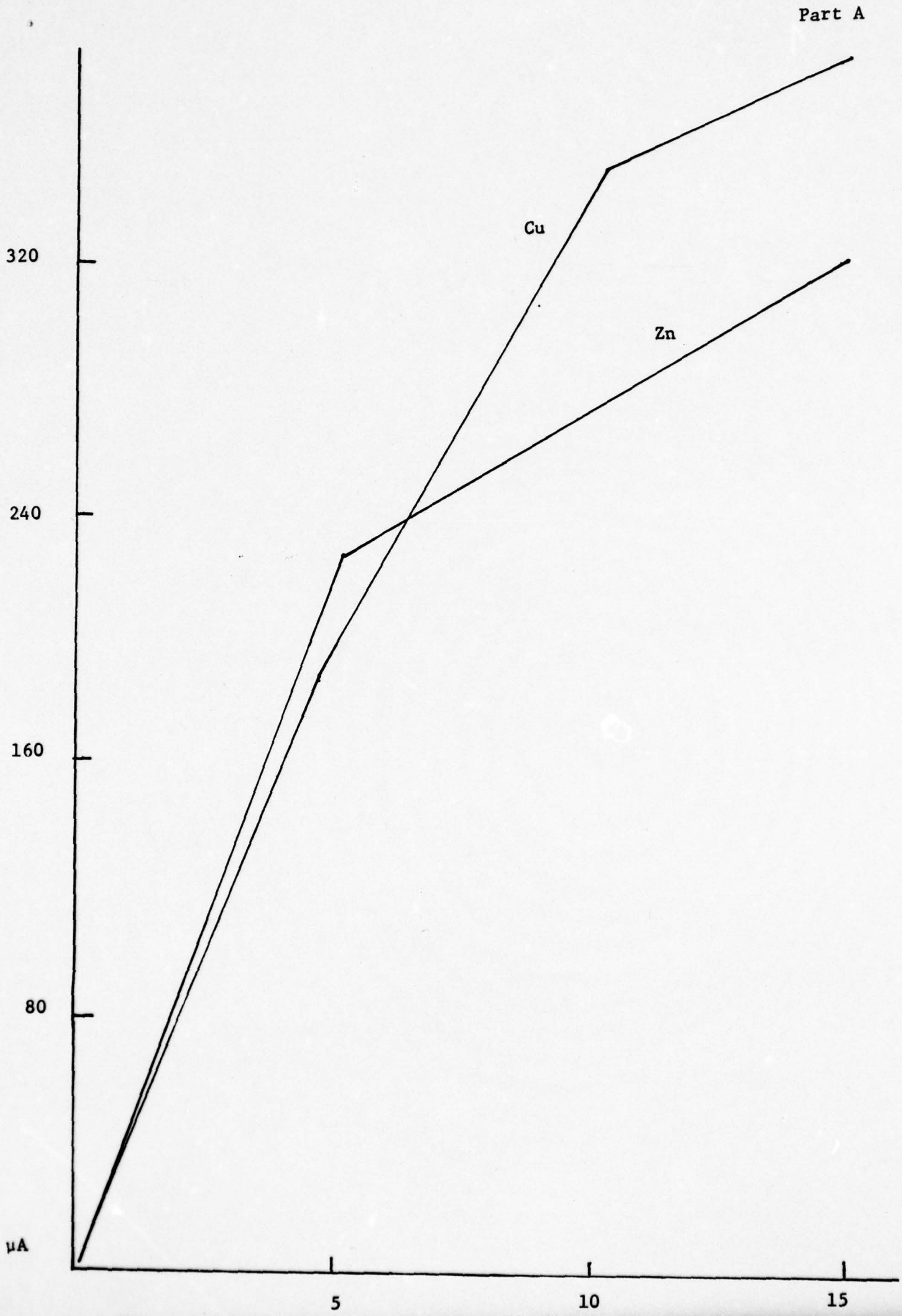

FIGURE 3

Part A

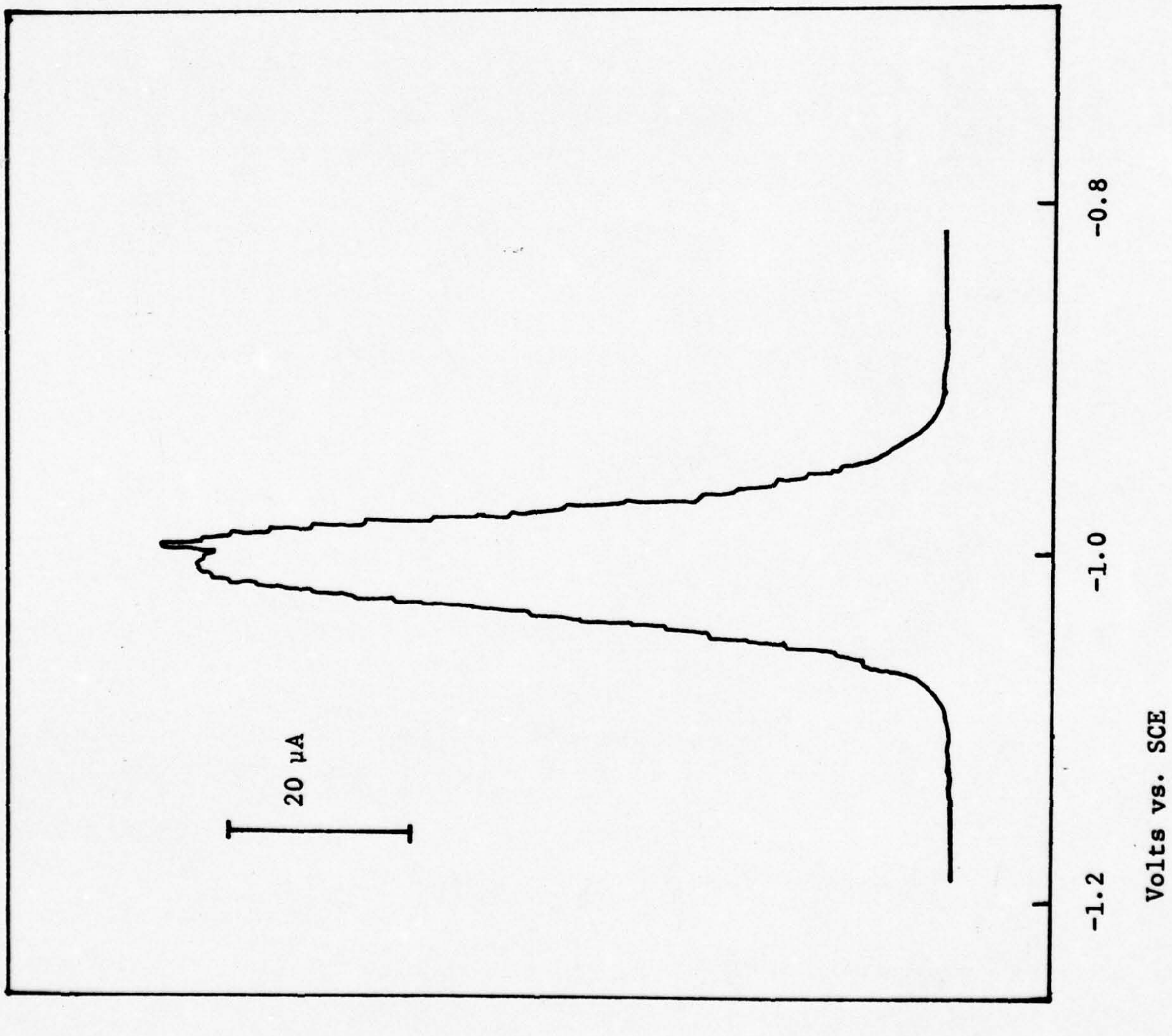

FIGURE 4

Part B

ABSTRACT

A major complication in the use of anodic stripping voltammetry is interference by surface activating substances. This investigation was undertaken to evaluate this interference and to eliminate the surfactants, if necessary. Several surfactants were tested by employing an hanging mercury drop electrode with the differential pulse mode, and their degradation by ultraviolet radiation was examined. An adsorptive technique is suggested for the trace measurement of surfactants in ideal samples.

In performing trace analysis, it is important to keep interfering contaminants to a minimum. One major interference in anodic stripping voltammetry (ASV) and differential pulse anodic stripping voltammetry (DPASV) is the presence of organics that either adsorb onto the electrode or are electrochemically active. Those organic compounds that are adsorbed are known as surface activating substances (SAS) and their effects on electroanalytical methods have been documented in the literature (1-8). Organic compounds such as gelatin have been commonly used to suppress maxima in polarography and their addition has been standard procedure in many cases (9-12).

Organics are known to produce adverse complications to voltage-current measurements due to a phenomenon called streaming. It was first observed by Antweiler (13) that streaming around an hanging mercury drop electrode (hmde) gives rise to a maximum. This streaming may be initiated by three different means. Maxima of the first kind originate in the depolarizer. The cause that leads to this anomaly is the non-uniform current density that results in a non-uniformity of the interfacial potential (14-17). Maxima of the second kind develop from convection arising from the rapid flow of mercury into a dropping mercury electrode (dme) (18). Maxima of the third kind result from adsorption of hydrocarbon compounds which induce surface tension gradients (19,20). Polarographic currents are enhanced at the potential where the surfactant is adsorbed (21). The observation of this third type of interference is complicated due in part to the stringent requirements of purity needed to study the effect (5). An additional complication is that contact with rubber, cork, or filter paper may leach unwanted SAS into the sample. Even momentary contact with polyethylene bottles and Tygon tubing may introduce these interferences (22).

The problem of SAS appears to be an adsorptive phenomenon. For stripping analysis with a stationary mercury electrode, sorption affects the peak current (i_p) by inhibiting metal deposition due to the adsorbed layer and by hindering the oxidation of the amalgam during the anodic scan (6). A similar situation is experienced in d.c. polarographic work (23). The extent of adsorption is related to the molecular configuration and charge of the SAS in question. It has been found that the adsorbability of an alkane type of surfactant is augmented, in accordance with Traube's rule, by a factor of three for every methylene added to the length of the organic chain (24).

Studies have been undertaken to examine the orientation of organic molecules on mercury electrodes (25-31). Frumkin (32) stated that benzene is oriented in relation to the π electrons and gives an area coverage of 35 $Å^2$. Benzene type structures such as aniline realign their orientation as they approach the mercury surface. Laviron (33) observed this to be the case with benzidine. In the instance of the adsorption of a monolayer of benzoic acid, the area occupied by one molecule is calculated to be 26 $Å^2$, which suggests a vertical orientation (34). This may mean that a specific part of the organic structure is attracted to the electrode depending on its hydrophillic nature (35). The compaction of particular structures onto the electrodes seems to be dependent upon molecular weight and shape of the tenside (7,31,36-39). This dependence has been inferred by Holmqvist (40) from his studies of polyglycols If the metal to be measured is in the form of a chelate, and it has a charge opposite to the adsorbed SAS around the electrode, the complex can pass unhindered through the layer. If the charges of the depolarizer and SAS are the same, the metal ligand system must overcome a potential energy difference, and their polarographic $E_{\frac{1}{2}}$ values are shifted to more negative voltages (10,41), or in the case of ASV, a delay in the metal's oxidation occurs.

The kinetics of adsorption is assumed to be fast. However, for low concentrations of SAS the adsorption equilibrium is reached slowly and is limited by diffusion (2,42). For example, this equilibrium was shown to take 15 to 30 minutes in unstirred dilute solutions of surfactants for an hmde (43). The lack of any surfactant effect at short sdsorption times could be the result of the SAS being retained by the preceding mercury drop (35). Gundersen and Jacobsen (44) analyzed data from several reviews and observed that SAS adsorption depends on concentration of the surfactant, and no interferences are exhibited below a particular concentration level.

Due to the interferences that SAS produce in voltammograms, methods have been devised to remove them from aqueous solutions. One simple technique is the addition of activated charcoal to adsorb the surfactants (24,45-47). Digestion of samples with fuming HNO_3 or $HClO_3$ (48), or addition of hydrogen peroxide (49), usually oxidizes organic substances. A more interesting manipulation is the use of ion floatation to bring the SAS to the surface to permit skimming the colligend off (50). A popular purification mode is irradiation of the sample with ultraviolet light (51-57) to oxidize the organic matter. A related UV method involves generating ozone and delivering O_3 directly to the sample for ASV analysis (58). With any technique for purification, the method should be rapid and non-contaminating to the sample.

The measurement of SAS in the enviroment becomes more critical with the increased use of surfactants in many products and operations. One adverse effect of large tenside concentrations in seawater is the build up of SAS on gill epithelium of fish. This affects the exchange interfaces of gases, water, and various ions (59). The numerous methods of analysis for SAS include titration of anionic SAS with cationic types (60), fluorometry (53), ultraviolet spectroscopy (60), IR (60), and even a membrane electrode to measure the critical micelle concentration (CMC) of certain cationic detergents (61). Ciocan and Anghel (62) have performed potentiometric titrations to analyze for surfactants. Some groups have used the suppression of oxygen maxima in polarography to measure organics. These include Dolezil and Kopanica (63) who attained a sensitivity level of 10^{-6} to $10^{-5}\underline{M}$ and Vavruch (47) who measured SAS in sugars. Schwarz (64) analyzed for SAS in natural and effluent waters by also utilizing the O_2 suppression method. Polarographic studies have been undertaken to obtain qualitative information about the CMC of tensides (65,66). Titrametric analysis combined with polarography has given SAS concentration estimations to a level of $10^{-4}\underline{M}$ (67.68).

The adsorptive nature of SAS has been used for their quantification. One such analytical scheme uses the suppression of maxima of the second kind to estimate surfactant concentration to a sensitivity of $10^{-9}\underline{M}$ (24). A familiar electroanalytical technique to determine SAS is the Kalousek commutator method. This mode of analysis records the current output when potentials are switched repeatedly by a regular cycle (69). The Kalousek commutator has been used to measure sorptive characteristics of particular SAS (70) and surfactants in seawater at less than 1 ppm (59). Zutic and coworkers (25) compared the commutator technique with an instrument that measures polarographic mercury maxima influenced by various oil fractions. This determination of the fractions gave rise to a procedure to measure petroleum pollutants.

EXPERIMENTAL

Instrumentation

A Princeton Applied Research Corp. (PAR) 174A Polarographic Analyser was interfaced with a PAR 315 Automated Electroanalysis Controller. The standard instrumental settings,* unless stated otherwise, were for the PAR 174A a scan rate of +5mV/s and a modulation amplitude of 25 mV. The clock was set at 0.5 s and the operational mode indicator was in the diff. pulse setting. The low pass filter was not a necessity. The display direction was opposite to the scan's and the keyboard was depressed in the scan function. Voltage range was 1.5 V and the initial potential and output offset were both set at zero. The PAR 315 module had values of 60 s and -1.2 V for the deposition time and potential, respectively. The final potential was set at either +0.15 V or +0.20 V, but never more positive to exceed the 1.5 V potential range. The equilibration and deaeration periods were timed at 30 s and 10 min, respectively. Conditioning was not necessary nor desired; a new drop was used for each determination. The X-Y recorder was a Houston Omnigraphic, model 2200-3-3.

Cell

The electrochemical vessel was a PAR 9301 cell bottom equipped with the various electrodes and degasser (27). The working electrode was a PAR model 9323 hanging mercury drop electrode (hmde). The standard drop size

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* These settings were selected because they are similar to the ones used for ASTM studies. This will facilitate standardization of the method for analytical purposes.

was extruded by turning the micrometer head by six vertical units. This yielded on the average a volume of 5.15×10^{-4} cm^3 mercury. The standard calomel electrode (SCE) was a cracked bead Fisher electrode with a leakage rate of 0.3 to 5 µL/h. The electrolyte used in the SCE was electrolyzed saturated KCl solution, and the reference electrode was placed directly into the sample without a bridge network. The counter electrode was a platinum wire. The degassing system was automatically controlled by the PAR 315 device.

Degassing was performed with nitrogen, usually of high purity quality. Several scrubbing systems were used to remove trace amounts of oxygen from the inert N_2. These included a copper metal high temperature furnace and bubbling the N_2 through a solution of vanadous chloride over zinc amalgam.

It was found that the best deaerating gas is a specially prepared low oxygen content N_2 (Linde: Union Carbide). This nitrogen was effective in removing dissolved oxygen so that a sensitivity of 1 ppb and less could be achieved. This special gas did not require any prepurifying measures and was delivered to the PAR vessel by ¼ inch Tygon tubing.

The cell deaeration design consisted of a bulbous glass fixture that had two inlet ports form the nitrogen tank. One port allowed direct bubbling of the N_2 to be dispersed above the aqueous sample to prevent atmospheric oxygen from dissolving into the solution. The electrodes and nitrogen system were held securely in place by a hard plastic head cover that fitted the PAR cell bottom.

Stirrer

The basic stirring device supplied by PAR is a Magnestir, catalogue # 1250. It was found that the rheostat type device was heating the cell bottom causing thermal gradients within the sample. This mechanism was improved by removing the casing that held the variable element and placing only the rotatory arm and coiling under the cell. An alternative method was devised wherein a Magnestir was attached to an isolated variac which controlled the stirring rate. This arrangement also prevented warming of the solution. The stirring bar should be small enough to allow free movement on the cell base; either ½ inch or 1 cm size bar is effective.

Reagents

All reagent chemicals were ACS grade or better. 1000 ppm stock metal solutions of copper, lead, zinc, and cadmium were prepared by either dissolving the metal into the appropriate ultrapure acid or taking a Dilut-it salt solution and volumetrically standardizing the cation stock. These salts should be nitrates since chloride ion may have an adverse effect on the DPASV mode and SO_4^{2-} may precipitate with lead when a metal mixture is made. The water used throughout was purified by a millipore system that delivered ASTM reagent grade water. A saturated KCl solution was prepared and electrolyzed at -1.3 V for no less than 36 hours with a PAR electrolysis purification system (28). Acetate buffer (pH 4.5) was also purified at a mercury cathode using the PAR 173 Potentiostat/Galvanostat. This acetate buffer was made by measuring 12 mL of concentrated acetic acid into 500 mL of water and adding 50% NaOH until a pH of 4.5 was attained. This was then diluted to 1 L in a volumetric flask. A mixed metal solution of 10 ppm cations was prepared by adding a suitable aliquot to a volumetric vessel.

1000 ppm SAS solutions were prepared by weighing out the appropriate active ingredient and standarizing the stocks in 100-mL volumetric flasks. If excessive foaming occurred, the diluted surfactants were allowed to stand before any aliquots were removed.

Ultraviolet Spectroscopy

A Beckman Acta III spectrophotometer was utilized for attaining UV spectra. Since wavelengths of interest were 350 nm and below, the D_2 lamp was employed during the studies. The cells were rectangular quartz vials with a pathlength of 1 cm.

Ultraviolet Degradation

In order to perform the *in situ* degradation of SAS, a specially constructed cell was used. The lower half of the cell was a 10-mL quartz vial attached to an upper concave glove of Pyrex by five rings of various glasses which permitted the sealling of the Pyrex and quartz. The Pyrex globe was designed so that it may be fitted with the PAR head cover model 9300. The electrodes and degassing fixture were placed cautiously into the quartz cell. Due to the snug fit, the SCE required a PAR model 9332 bridge tube with a plastic sleeve so that it may be bent into the aqueous sample. The source of UV light was a Hanovia 140 W ultraviolet lamp. The quartz cell was cooled by allowing water to rush over the outside surface. Because of the low power of the filament in the UV source, the lamp did not require any special thermostating. The source was placed 10 cm from the quartz cylinder and the light pathway was surrounded by aluminum foil to obtain maximum concentration of the ultraviolet on the sample.

Cleaning and Transfer

All glass pipets were stored in 6<u>M</u> HNO_3. The PAR electrolytic cells were soaked with nitric acid for no less than 1 h before use. Disposable plastic Eppendorff micropipettes were used in delivering stock and sample solutions to the voltammetric vessel. Volumetric flasks and polyethylene bottles were also leached in nitric acid prior to containment of aqueous samples. The degassing fixture and Pt wire in the cell device were also periodically soaked with acid to remove adsorbed materials. The hmde capillary was changed daily and cleansed by pulling nitric acid through the capillary bore with a water aspirator. Millipore water was used to rinse any acid residue off material surfaces. Sometimes the capillary failed to keep a drop suspended. When this occurred, it was necessary to soak the capillary overnight in concentrated HNO_3, rinse thoroughly by aspirating millipore water through the bore, and drying the glass capillary at 110°C.

Procedure

A 10 mL aliquot of acetate buffer served as the electrolyte for the voltammetric studies. The buffer was deaerated for 10 minutes with stirring. A drop of mercury was then extruded by rotating the micrometer head of the hmde, and the analysis initiated. Between runs, several hmde drops were extruded and discarded to minimize memory effects. The stripping scan was recorded on a X-Y chart. When any increments of any solution were introduced into the cell the spiked solutions were degassed for an additional minute and then voltammographed as described. Upon termination of an experiment, the buffer was discarded, the counter electrode and working electrodes were kept in millipore water, and the SCE was stored in saturated KCl solution.

RESULTS AND DISCUSSION

Various commercial surfactants were aliquoted to a 10.0-mL portion of acetate buffer and the DPAS voltammograms recorded. Table 1 shows the concentration levels at which the SAS begins to have an adverse effect on the relative current output and stripping potential (E_p) of the four metals under examination. In all of the voltammorgrams in which the SAS caused complicaitons, the magnitude and initiation of the i_p depression and E_p movement followed in the order of

$$\mathrm{Zn} > \mathrm{Cd} > \mathrm{Pb} > \mathrm{Cu}.$$

However, copper experienced very little or no i_p depletion or potential shift whatsoever. It is important to note that this order follows from zinc with the most negative E_p to copper with the least. This order of appearance on DPAS voltammogram is illustrated in Fig. 1.

As seen from Table 1, the various SAS begin to affect the DPASV signal at different concentrations. The dodecyl sodium sulfate (DSS) did not show any interferences up to a concentration of 20 ppm, whereas the Triton X-114, which has a more complex structure than DSS, shows complications at a level of 0.20 ppm. The structures of these SAS are diagrammed in Fig. 2. A plausible explanation of these differential effects could involve the hydrocarbon structure of the SAS. Triton X-114, which has a phenyl group, shows an affinity for π electrons to be adsorbed onto the hmde parallel to the mercury surface. DSS is a long chain compound with an hydrophillic component, the sulfate group, and an hydrophobic portion, the dodecyl chain. The surface coverage by the sulfate anion is not as great as that which can be provided by an aromatic ring; hence the difference in adsorbability.

The observed interferences caused by the SAS on the anodic scanning signals are a depression of the peak height, movement of E_p to a more positive potential, and a broadening of the peak widths, in this order. A typical DPAS voltammogram demonstrating the SAS interferences is shown in Fig. 1.

Another SAS anomaly that appears on DPAS voltammograms is an unknown peak at approximately +0.15V. This peak was observed to some degree for all surfactants tested. In the case of Aliquat 221, this peak was very strong, as noted in Fig. 3. These waves at ca. +0.15V were unique in their shape. Their occurrence began with a sharp rise in the differential pulse signal which resulted in a non-uniformity of the pulse steps. When this peak reached its maximum, it gradually returned to the baseline or it overlapped the mercury wave. This type of phenomenon was noted by Jacobsen and Lindseth (71) in their studies of effects of SAS on differential pulse polarography (DPP). They used the term tensammetric peak to describe these waves which were sorptive in nature. They stated further that tensammetric waves in DPP are not accompanied by d.c. polarographic steps. Table 2 lists the results of the differential pulse voltammetry (DPV) and d.c. voltammetry (DCV) applied to DSS and Dowfax 2A1 (formerly called Benax 2A1) on an hmde. For a cathodic scan from 0.0 to -1.5V, no peaks were observed for the DSS; however, for Dowfax 2A1 a wave did occur at -1.312V in the DPV and DCV modes. As the concentration of Dowfax 2A1 was increased, the wave at -1.312V also increased, but not linearly. This calibration defect was also pointed out by Jacobsen and Lindseth.

Another interesting feature was observed with Dowfax 2A1. For DPASV with 10 ppm SAS at a deposition potential of -1.2V, the E_p for zinc, cadmium, lead, and copper are -0.844, -0.564, -0.410, and +0.010V, respectively. Upon changing the deposition voltage to -1.3V, the E_p for the four metals returned to what they would be if no SAS were in the sample, as seen in Table 3. The destruction of Dowfax 2A1 in various aqueous media is difficult (72). This anomaly at a deposition potential of -1.3V, at which the adverse interferences on DPASV appear to be absent, could become a novel technique to remove SAS from solution.

Since SAS interferences are considered to be adsorptive in origin, the adsorption of several tensides were tested on various sizes of mercury drops. These are organized in Table 4. The Triton X-114, Aliquat 221, and Dowfax 2A1 were added by increments to 10.0 mL of acetate buffer using a series of hmde sizes of 4, 6, and 8 vertical units. An hmde drop extruded by rotating the micrometer head of a PAR hmde by six vertical units has a volume of 5.15×10^{-4} cm^3. No conclusive evidence supports adsorption effects from the SAS. In all cases, except for Triton X-114, the difference is too small to correlate any noticeable change in the concentration at which the individual surfactants begin to cause interferences on the current output and the surface area of the hmde.

After observing all the complications and anomalies caused by SAS on DPASV, standard additons were performed to check if analytical information can be gained with a SAS in an aqueous sample. Table 5 evaluates the various SAS linear relationships. Only Triton X-114 does not interfere when it is in the solution at a level of 1 ppm. As for Aliquat 221 and Dowfax 2A1, no calibration could be achieved. It should be noted that upon addition of the metal cation, the E_p remains where it was shifted by the original amount of surfactant.

During the course of this work, it was ascertained that the movement of the E_p of the current signals of the various metals may be used as an analytical technique to measure for SAS concentration. This possibility was examined by observing the E_p movement caused for cadmium by Triton X-114. The X-Y recorder scale (X axis) was changed by a factor of 10 and the voltage range on the PAR 174A was set at 3.0V. This gave an x-coordinate breadth of 0.3V. The deposition voltage and final voltage were changed to -0.75 and -0.45V respectively on the PAR 315 module. The scan rate was reduced to +2mV/s. The results of the cadmium E_p shifts and additions of Triton X-114 are graphed in Fig. 4. Several SAS estimations were made using this graph, and experimental results are very close to the actual Triton X-114 concentrations being measured, as read from Table 6. As the Triton X-114 concentration rises above 800 ppb, the analytical measurement becomes difficult due to the small E_p shift with further increments of SAS. The calibrated region lies between 200 and 800 ppb. Above and below this region very little precision and accuracy may be achieved. Although the range of analysis for Triton X-114 is limited, the monitoring capability of this technique may still be valuable.

At this juncture, the elimination of the SAS became imperative for the analysis of metal cations in the aqueous sample. A preliminary study was initiated by placing a solution of 500 ppm Triton X-114 into the specially constructed quartz cell. The material was then irradiated with an UV source over a period of hours and UV spectroscopic data were taken over this time span. Fig. 5 shows the UV adsorption spectrum for 50 ppm Triton X-114 in water, and a spectrum after approximately 16 h of irradiation with ultraviolet light. The reduction in the peaks at 220 and 198 nm, where the 220 nm peak represents the phenyl group in Triton X-114 (60), is ca. 77%. This demonstrated that this method of degradation is effective for this particular SAS. It was observed that during the irradiation period the SAS solution became less turbid and finally clarified. A yellow-orange precipitate was also noted at the bottom of the quartz vial. This precipitate may have been the non-oxidized hydrophobic portion of the organic surfactant since it was soluble in acetone and insoluble in water and 6$\underline{M}$ HNO_3.

Attention was now directed towards the degradation of various SAS by UV irradiation and the measurement of the percent decomposition by DPASV. The same quartz cell was retained for the DPASV studies, and the electrodes and degassing fixture were placed in their positions in the PAR cell cover. Table 7 reveals the different i_p and E_p for the four metals after various times of UV irradiation of an initial concentration of 10.0 ppm Triton X-114 in 10.0 mL of acetate buffer. The E_p were unique for the cases of lead and copper, because they became more negative after prolonged UV exposure than the original solution without SAS. After a nine hour span, standard additions were performed on the UV irradiated sample of Triton X-114 and acetate electrolyte. The linearity and standard deviation of the calibrations for the four metals are tabulated in Table 8. It appears that the linear relationship for the irradiated SAS sample is quite good. By calculating the E_p shift of the cations, it was determined that the concentration of Triton X-114 had diminished from 10.0 ppm to 0.50 ppm, a reduction of 95%. Furthermore, the major decrease in SAS concentration occurred after only 6 h of ultraviolet irradiation.

The next tenside to be tested was Aliquat 221, a cationic type of surfactant. The results of UV treatment for 3 h are shown in Table 9. Apparently the UV light had no noticeable effects on the interferences caused by the 10 ppm Aliquat 221 in 10.0 mL acetate buffer. This fact could be due to the comple structure of this quartenary ammonium compound. The "coco" group has numerous chemical components in its make-up (Fig. 2), and the UV light may be affecting some of these constituents while leaving other functional side chains intact. At this point, 100 uL of 30% H_2O_2 were introduced into the quartz cell to aid in the oxidation of the Aliquat 221. This method proved fruitless because of the oxygen being produced from the decomposition of H_2O_2. This excess oxygen could not be completely removed from the aqueous sample by the inert N_2, and hence any voltammetric analysis was prohibited.

The surfactant Dowfax 2A1 was next examined by delivering 20 ppm to 10.0 mL of acetate buffer. The extent of irradiation by ultraviolet light is tabulated in Table 10. After an elapse of only 2 h, almost 100% of the Dowfax 2A1 was destroyed. The percent destruction was evaluated by the return of the E_p for the metals to the original values without SAS. It should be pointed out that Dowfax 2A1 begins to have an adverse effect on DPAS voltammograms at a concentration of 7.5 ppm (Table 1). Thus, it was necessary to oxidize only 62.5% of the initial 20 ppm Dowfax 2A1 to remove all complications caused by this surfactant.

CONCLUSIONS

In this study the surface activating ability of organic compounds has been shown to have adverse effects on DPASV analysis by inhibiting oxidation of amalgams. Other interferences may result, as shown by other investigators, from the precipitation of metals with the SAS, as in the case of DSS and cadmium (44). Since the masking capability of surfactants is a function of the electronegativity of the metal, specific SAS could be used to suppress overlapping waves as has been done for several cations and complexes (23,73). Jacobsen and Tandberg (74) demonstrated that particular tensides make polarographic inactive indium oxalate complexes reducible at a working electrode. The SAS appears to affect the voltammograms by adsorption onto the mercury layer at a potential of +0.15V. Kemula (75) stated that this error may be a product of a large capacitance effect on the mercury double layer by the SAS. Other possibilities may be a chloride interference on the copper wave (76) or Hg^{2+} being formed at the mercury electrode (77).

For improving the sensitivity of the adsorption E_p shift technique, the use of a thin film electrode (TFE) could augment the calibration range. However Batley and Florence (78) noted that the TFE suffers less interference than the hmde, and postulated that the hmde surface may be able to flex and display fresh surface area to give current surges. Perone (79) has already measured methylene blue content by the observation of the adsorption peaks in ASV studies.

The degradation of organics by ultraviolet irradiation appears to be quite effective for removing these SAS form aqueous solutions. The addition of H_2O_2 to aid in the oxidation of the hydrocarbon substances is not recommended for trace voltammetric studies since the excess O_2 is difficult to purge from the electrochemical cell. The elimination of surfactants is not only important in electroanalytical work, but also in atomic absorption spectroscopy (80,81). UV degradation requires several hours, but prior treatment of samples a day before analysis could well make this purification mode rapid, systematic, and clean. For ultimate trace analysis, the _in situ_ decomposition of organics is recommended to remove the possibility of contamination during pipetting and transfer. No deterioration of the electrodes or purging system was observed during UV irradiation. However, it is worthwhile to state that a SCE should be the reference electrode and not a Ag/AgCl, since AgCl is sensitive to UV.

The dispersion of surfactants has become ubiquitous throughout our environment, and a rapid and inexpensive method for their analysis not only becomes desirable but a necessity. Few analytical methods are reliable for the determination of SAS at a trace concentration. It is possible that adsorption phenomena in ASV and DPASV may be the device to monitor these pollutants. Further work is needed in this area to improve sensitivity of the method and to explore the origin and nature of molecular interaction at the mercury electrode.

SUMMARY

The interferences of SAS on DPASV have been shown to be concentration dependent. These adverse complications include i_p depression, E_p shifts to positive potentials, and peak width broadening. The adsorptive phenomenon is discussed as a plausible analytical method to estimate trace surfactant quantities. The limit of the calibration is determined by the amount of E_p shift for increments of SAS added. Degradation by ultraviolet light was highly successful for anionic and non-ionic surfactants. However, for the quartenary ammonium complex difficulty arose due to the variable nature of the "coco" group incorporated in its structure. *In situ* UV irradiation for DPASV measurements is desirable to eliminate possible contamination during transfer processes.

TABLE 1

Concentration level of SAS where they begin to affect DPASV signals.

Surfactant	Type	Concentration (ppm)
Triton X-114	non-ionic	0.20
Dodecyl sodium sulfate	anionic	[a]
Aliquat 221	cationic	0.40
Dowfax 2A1	anionic	7.5
Dowfax 3B2	anionic	10.0

---

[a] No effects up to 20 ppm in concentration.

TABLE 2

Differential pulse and d.c. voltammetric scans of Triton X-114 and Dowfax 2A1.

Surfactant	Concentration	DPV	DCV
DSS	0.25 ppm	no waves	no waves
Dowfax 2A1	10.0 ppm	0.8 uA [a]	0.07 uA
	12.5	4.2	0.11
	15.0	4.2	0.12

---

[a] Wave appears at -1.312 V.

TABLE 3

E_p of the metals vs. the deposition potential. 10.0 ppm Dowfax 2A1 in 10.0 mL acetate buffer; electrolysis period 60s.

Deposition Potential (V)	Concentration of Metals (ppm)	(V) Zn E_p	(μA) i_p	(V)Cd E_p	(μA) i_p	(V)Pb E_p	(μA) i_p	(V)Cu E_p	(μA) i_p
-1.2	0.25	-0.844	0.24	-0.564	1.0	-0.410	1.8	+0.010	10.4
	0.50	"	0.48	"	2.1	"	3.6	"	22.4
	0.75	"	0.70	"	3.1	"	5.7	"	28.3
-1.3	0.25	-1.012	0.92	-0.584	1.9	-0.410	2.3	+0.008	11.3
	0.50	"	6.2	"	3.2	"	2.9	"	23.2
	0.75	"	23.2	"	11.0	"	9.7	"	33.5

TABLE 4

Effects of drop size on concentration at which SAS begin to have adverse interferences on DPASV. Deposition potential -1.2V; electrolysis period 60s, electrolyte pH 4.5 acetate buffer.

Triton X-114 (ppm)	hmde (vertical units)	Cd^{2+} (0.50 ppm) i_p (µA)	E_p (V)
0.1	4	13.0	-0.584
0.2		12.6	"
0.3		9.0	-0.582
0.4		3.2	-0.544
0.1	6	16.0	-0.584
0.2		15.4	"
0.3		12.4	-0.582
0.4		4.4	-0.554
0.1	8	13.6	-0.584
0.2		14.2	"
0.3		13.0	"
0.4		5.3	-0.568
0.5		3.8	-0.538
Aliquat 221 (ppm)		Cd^{2+} (0.25 ppm)	
0.3	4	5.3	-0.592
0.4		5.3	"
0.5		5.3	"
0.6		2.6	-0.578

TABLE 4 (continued)

Aliquat 221 (ppm)	hmde (vertical units)	Cd^{2+} (0.25 ppm)	
		i_p (μA)	E_p (V)
0.3	6	7.8	-0.586
0.4		7.8	"
0.5		7.8	"
0.6		3.6	-0.576
0.2	8	7.8	-0.580
0.4		7.8	"
0.5		7.2	"
0.6		3.0	-0.572
Dowfax 2A1 (ppm)		Cd^{2+} (0.25 ppm)	
1.0	4	6.2	-0.586
3.5		6.2	"
6.0		6.2	"
8.5		2.7	-0.580
2.5	6	7.4	-0.582
5.0		7.4	"
7.5		3.5	"
10.0		1.2	-0.552
2.5	8	14.4	-0.584
5.0		15.0	"
7.5		4.4	-0.570
10.0		2.6	-0.552

TABLE 5

Evaluation of the SAS interferences on the standard additions of metals in acetate buffer (pH 4.5). Electrolysis potential -1.2V; electrolysis period 60s.

A) Triton X-114, 1.0 ppm

	0.5 ppm	1.0 ppm	1.5 ppm	2.0 ppm	Slope Deviation
Zinc	2.8 uA	5.1	7.5	9.8	0.02
Cadmium	4.8	9.5	14.3	18.4	0.20
Lead	2.0	2.6	3.3	3.8	0.05
Copper	27.6	53.4	77.6	100.4	0.70

B) Aliquat 221, 10.0 ppm

	0.4 ppm	0.6 ppm	0.8 ppm	1.0 ppm	Slope Deviation
Zinc	[a]	[a]	[a]	[a]	—
Cadmium	3.4	5.0	7.3	8.4	0.27
Lead	3.8	5.3	7.0	8.9	0.10
Copper	16.4	12.0	15.1	17.9	2.24

C) Dowfax 2A1, 10.0 ppm

	0.25 ppm	0.50 ppm	0.75 ppm	1.0 ppm	Slope Deviation
Zinc	0.2	0.5	0.8	1.1	0.00
Cadmium	1.5	2.2	3.0	4.2	0.14
Lead	2.0	4.0	5.0	7.4	0.29
Copper	13.7	21.0	28.1	40.5	1.60

---

[a] No stripping peak was observed.

TABLE 6

Determination of Triton X-114 using stripping potential shift of cadmium. Deposition potential -1.2V; electrolysis period 60s. Electrolyte pH 4.5 acetate buffer.

E_p	SAS measured	SAS in buffer	percent error
-0.592 V	0.31 ppm	0.30 ppm	3.3
-0.539 V	0.63 ppm	0.55 ppm	13.6
-0.528	1.20 ppm	1.20 ppm	—

TABLE 7

i_p measurement and E_p movement for an irradiated solution of 10.0 mL acetate buffer and 10.0 ppm Triton X-114 vs.. hours of UV irradiation. Concentration of metals 0.25 ppm; electrolysis potential -1.2 V; electrolysis period 60s.

Time of UV irradiation (h)	(V) Zn	(μA)	(V) Cd	(μA)	(V) Pb	(μA)	(V) Cu	(μA)
	E_p	i_p	E_p	i_p	E_p	i_p	E_p	i_p
—[a]	-1.016	9.9	-0.592	7.0	-0.418	3.9	+0.006	11.4
—	-0.872	0.2	-0.484	1.4	-0.296	0.4	+0.012	8.4
0.5	-0.872	0.3	-0.470	1.0	-0.296	0.4	+0.014	7.2
2.5	-0.890	0.9	-0.524	1.2	-0.396	0.9	+0.006	9.6
4.0	-0.904	1.3	-0.558	1.8	-0.412	3.0	+0.004	12.1
5.0	-0.908	1.6	-0.566	2.0	-0.420	3.7	+0.006	13.6
6.0	-0.912	1.6	-0.568	2.2	-0.420	4.0	+0.006	13.1
9.0	-0.916	1.6	-0.576	2.1	-0.424	3.8	+0.010	9.9

---

[a] Recorded without the Triton X-114 in solution.

TABLE 8

Standard additions of metals in 10.0 mL acetate buffer and 10.0 ppm Triton X-114 after nine hours of UV irradiation.

	0.25 ppm	0.50 ppm	0.75 ppm	Slope	Slope Deviation
Zinc	7.9 uA	15.9	24.5	33.2	0.058
Cadmium	6.0	11.9	17.0	22.0	0.058
Lead	4.3	7.5	26.5	11.6	0.058
Copper	9.4	18.6	26.5	34.2	0.115

TABLE 9

UV irradiation for a 10.0-mL aliquot acetate buffer with 10.0 ppm Aliquat 221. Deposition potential -1.2V; electrolysis period 60s.

Ultraviolet Irradiation (h)	(V) Zn	(μA)	(V) Cd	(μA)	(V) Pb	(μA)	(V) Cu	(μA)
	E_p	i_p	E_p	i_p	E_p	i_p	E_p	i_p
— [a]	-1.014	8.4	-0.594	5.6	-0.420	3.1	+0.002	8.9
—	[b]		-0.542	1.0	-0.396	1.0	+0.012	5.4
1.0	[b]		-0.552	1.0	-0.400	0.8	-0.010	4.3
2.0	[b]		-0.546	0.9	-0.396	0.7	-0.006	4.0
3.0	[b]		-0.540	0.7	-0.392	0.7	-0.004	5.2

---

[a] Recorded without Aliquat 221 in solution.

[b] No waves appeared at the E_p of zinc.

TABLE 10

UV irradiation for a 10.0-mL aliquot acetate buffer with 10.0 ppm Dowfax 2A1. Deposition potential -1.2V; electrolysis period 60s.

Ultraviolet Irradiation (h)	(V) Zn E_p	(μA) i_p	(V) Cd E_p	(μA) i_p	(V) Pb E_p	(μA) i_p	(V) Cu E_p	(μA) i_p
— [a]	-1.014	7.2	-0.594	4.6	-0.420	2.4	+0.002	6.9
—	-0.872	0.2	-0.560	0.9	-0.412	1.4	+0.002	7.1
1.0	-0.960	0.4	-0.576	1.1	-0.416	1.4	+0.002	6.5
2.0	-1.014	6.4	-0.594	3.8	-0.420	2.2	+0.002	5.9

---

[a] Recorded without Dowfax 2A1 in solution.

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Part B

Captions to Figures

Figure 1	Typical DPAS voltammogram (curve A) of 0.50 ppm Zn (-1.008V), Cd (-0.584V), Pb (-0.408V), and Cu (+0.024V) in pH 4.5 acetate buffer. Curve B, which is underneath curve A, resulted from the addition of 0.50 ppm Triton X-114.
Figure 2	Various surfactants tested on DPASV and their structures and compositions.
Figure 3	DPAS voltammogram of 1.0 ppm Aliquat 221 and 0.25 ppm Cu^{2+} in 10.0 mL acetate buffer (pH 4.5). Copper peak at +0.002V and unknown "tensammetric" wave at ca. +0.1V.
Figure 4	Graph of ppm Triton X-114 vs. E_p shift of 0.5 ppm Cd^{2+} in 10.0 mL acetate buffer (pH 4.5). Deposition potential -1.2V; electrolysis period 60s.
Figure 5	UV spectrograph of 50 ppm Triton X-114 (A), and same solution after 16 h of UV irradiation (B).

Part B

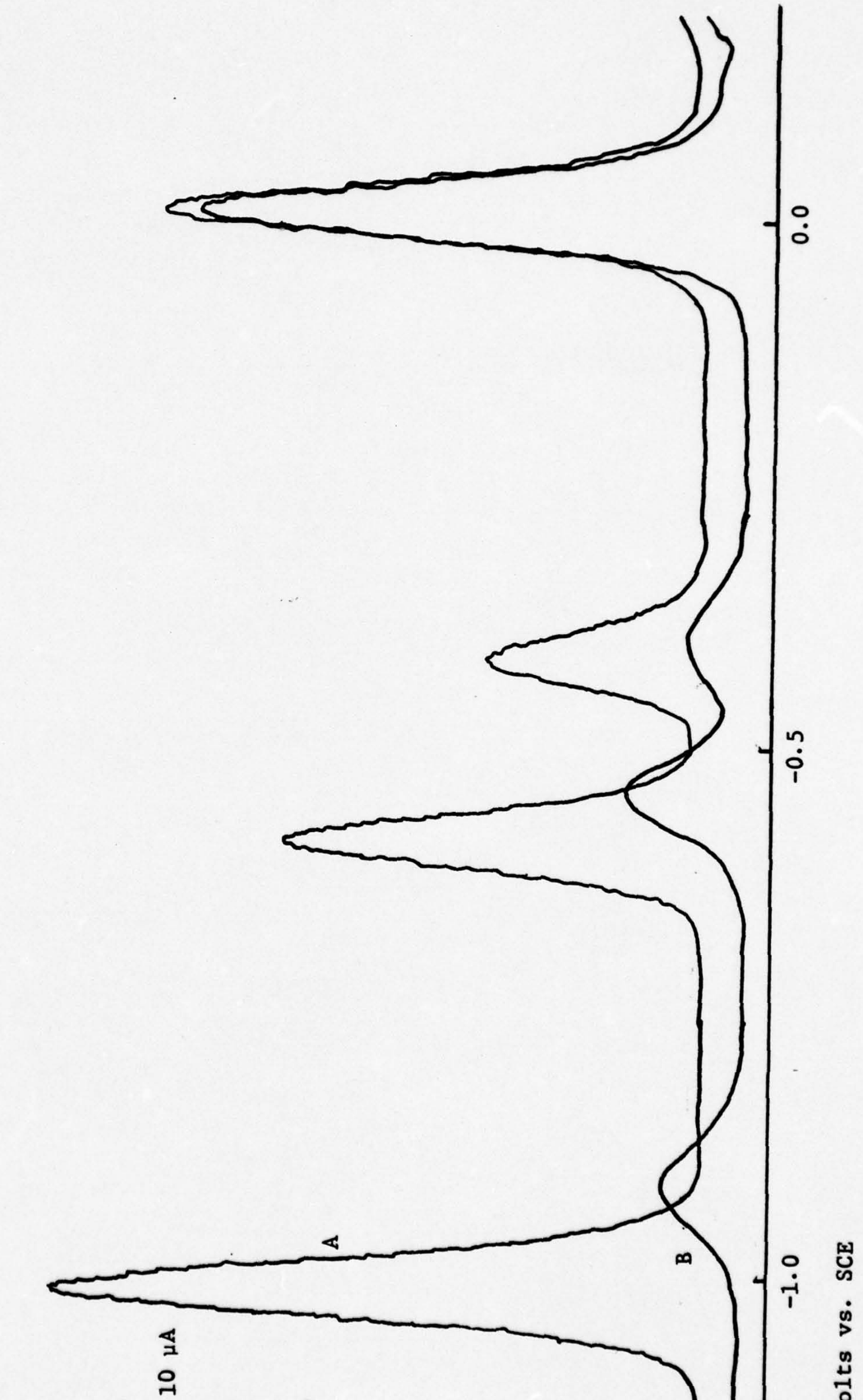
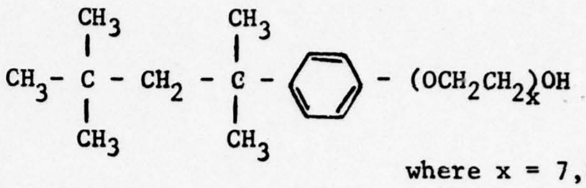


FIGURE 1

Part B

Triton X-114



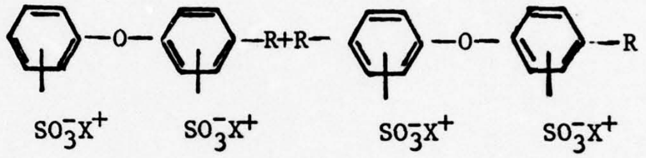
where x = 7,8

Dodecyl Sodium Sulfate

$CH_3(CH_2)_{11}OSO_3Na$

Dowfax 2A1
Where R = C_{12} branched

and X^+ is sodium.



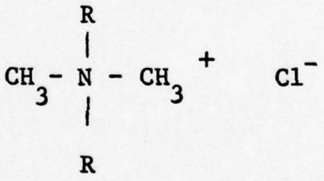
Dowfax 3B2
Where R = C_{10} linear

and X^+ is sodium.

"

Aliquat 221
Where R represents the
fatty acids of:

caprylic	5%
capric	6%
lauric	52%
myristic	19%
palmitic	9%
stearic	2%
oleic	7%



$$\left[CH_3-\overset{\displaystyle R}{\underset{\displaystyle R}{N}}-CH_3\right]^+ \quad Cl^-$$

FIGURE 2

Part B

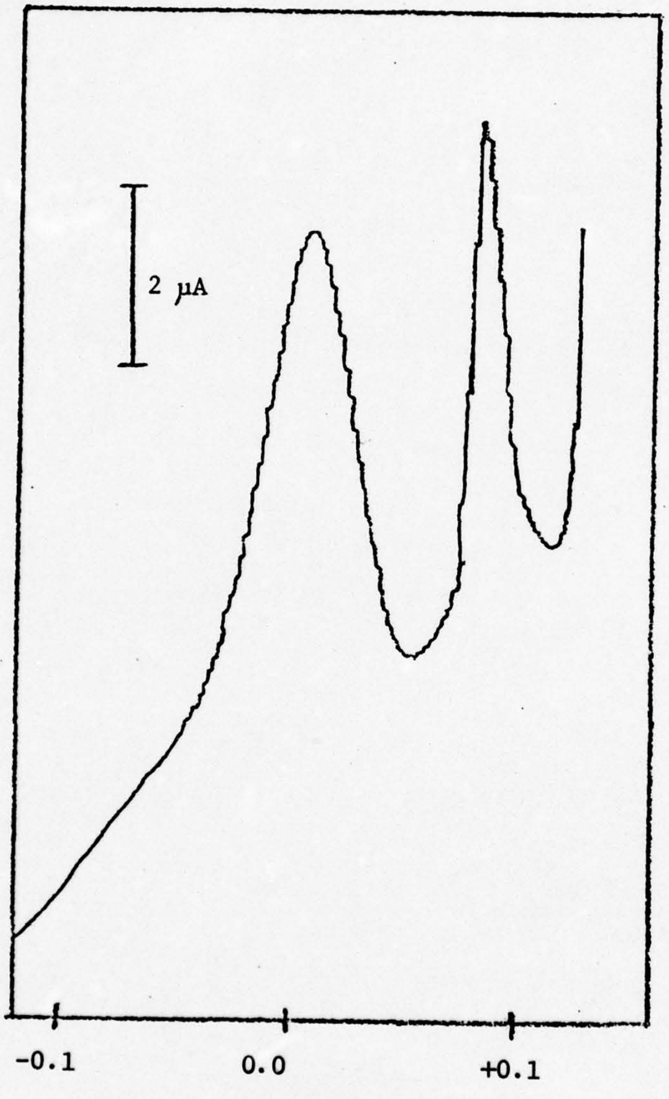


FIGURE 3

Part B

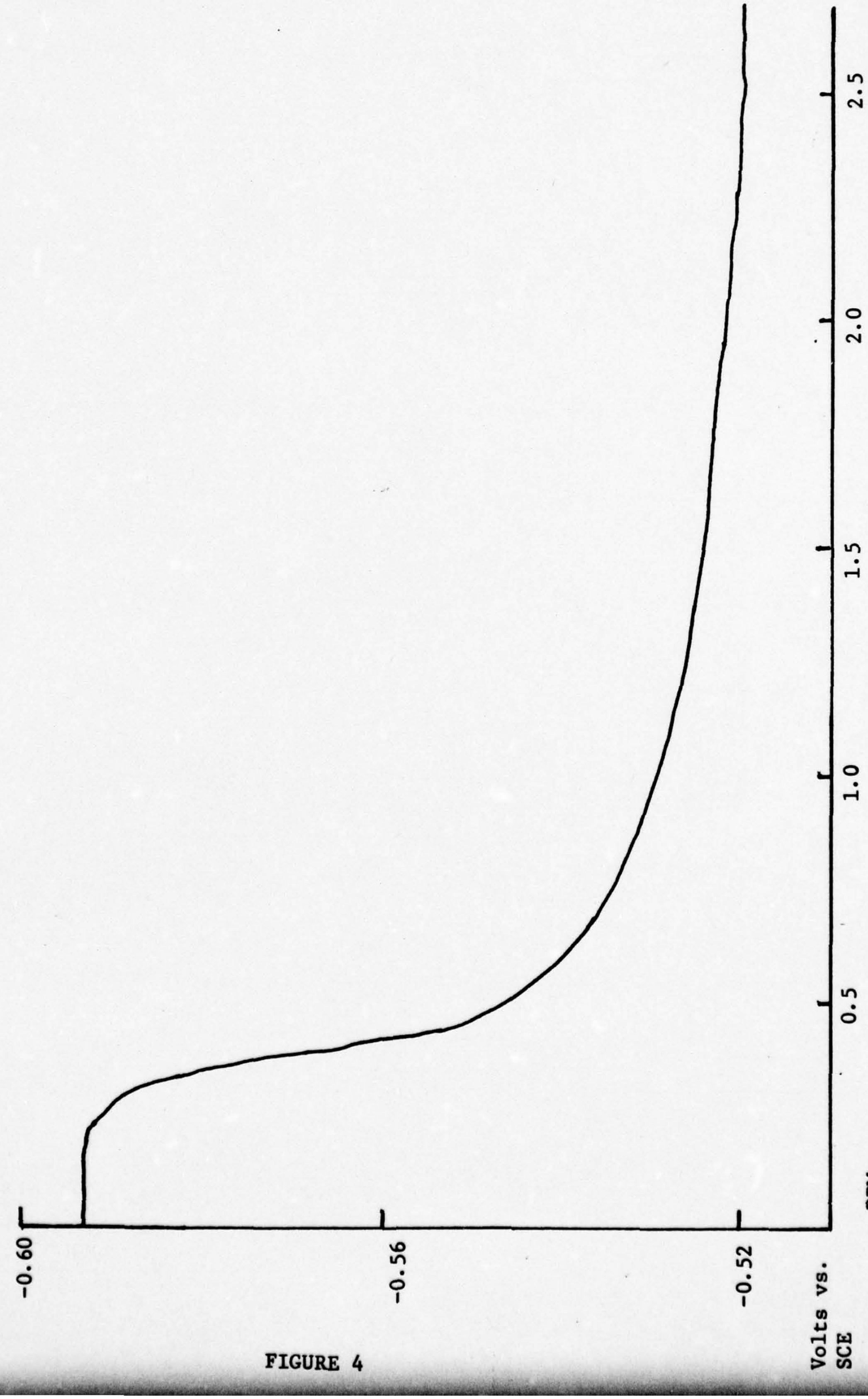


FIGURE 4

Part B

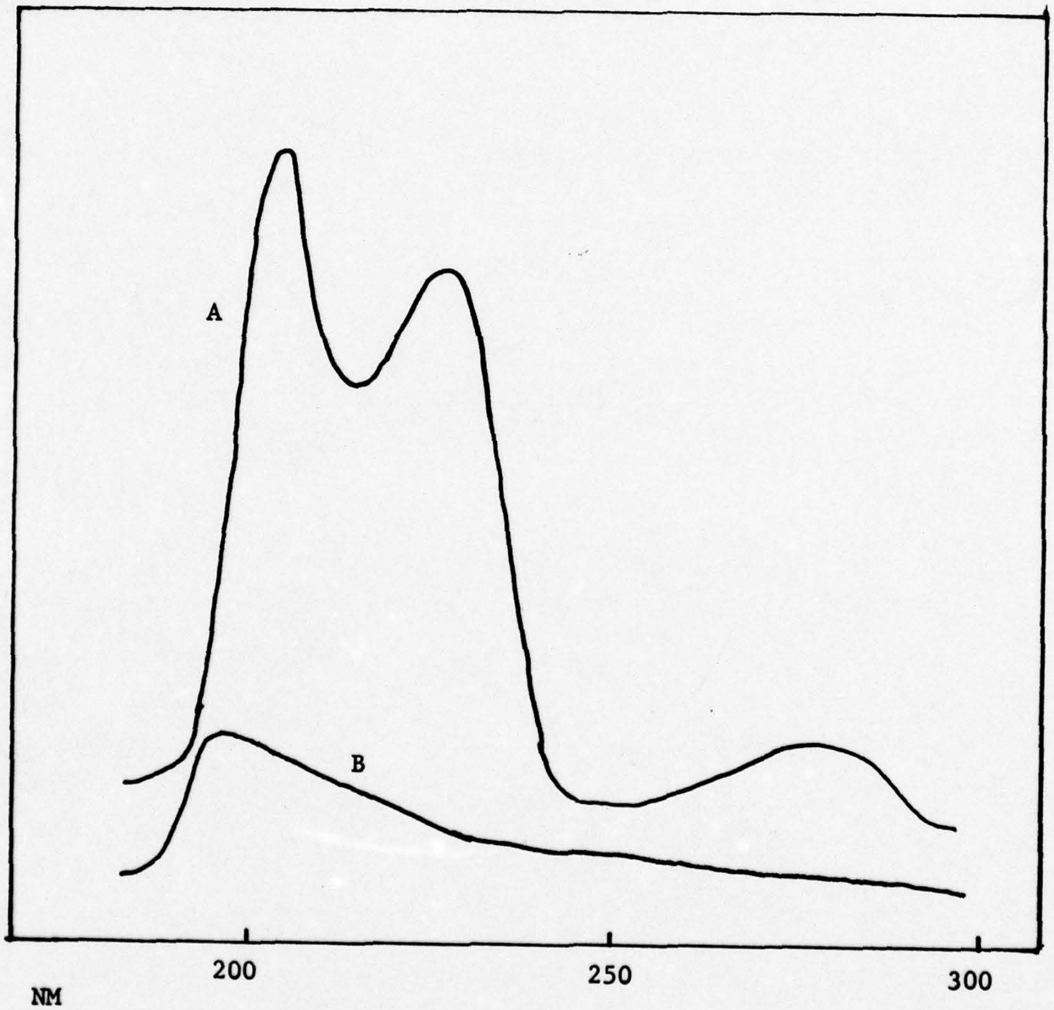


FIGURE 5

Part C

ABSTRACT

In an investigation of the applicability of differential pulse anodic stripping voltammetry to the determination of zinc, cadmium, lead, and copper in water waste, a comprehensive review of the literature was undertaken to compile information essential to the project. The following topics were considered: stripping analysis, interferences, applicability and reproducibility, and purification.

Stripping Analysis

Differential pulse anodic stripping voltammetry (DPASV) is an electroanalytical method of trace analysis that has distinct sequential steps in its manipulation. First there is the deaeration of the solution and preparation of the working electrode. The solution is then placed under an applied potential and electrodeposition occurs at the working electrode, normally a mercury cathode. After a set time, the cell is allowed to equilibrate. This usually means that the stirring is stopped for a period of 10 to 30 s before stripping. The stripping scan is to a more positive potential (anodic). The voltage ramp has a pulse superimposed on it, and the current is measured at the beginning and end of this pulse (differential). Several reviews have been written about the differential pulse and normal pulse modes in polarography and voltammetry (1-7). They concur on the basic advantages of the pulse method, which are increased sensitivity and selectivity.

Other studies have been made on various signals that may be applied to a linear voltage ramp to increase sensitivity in polarographic and voltammetric analyses. These include staircase (8), square wave (9,10), and a.c. (11-14). Experimental comparisons have been made using the various scanning ramps (6,15,16).

Many devices and techniques have been utilized to increase sensitivity in stripping analysis. These include higher temperature to enlarge the mercury drop (17,18), addition of ammonium to inflate the mercury sphere to form a larger surface area (19), the use of two electrodes to cancel background effects (20), and rapid scanning with computer interfacing (21).

The basic potentiostatic three electrode cell for anodic stripping voltammetry (ASV) consists of working, reference, and counter electrodes (6). Cell design should permit degassing with an inert gas and agitation of the solution (22,23). Instrumental parameters for optimizing stripping peaks (i_p) in ASV work have been investigated (2,24-27).

The prevalent distinction between voltammetry and polarography is in the former a stationary electrode is being utilized, such as an hanging mercury drop electrode (hmde). In polarography, the working electrode is a dropping mercury electrode (dme) and drop time is an important parameter.

DPASV and ASV require the collection of metals at a mercury cathode. Hence, a dme with a short drop time becomes impractical and undesirable. Various mechanisms and materials have been employed for designing stationary electrodes. The two primary types are the hmde and the thin film electrode (TFE).

The hmde uses a small droplet of mercury as the electrode. This droplet may be suspended from a silver or platinum wire, extruded from a barometric bore capillary by a micrometer piston, or hung by any other means whereby the electrical circuit may still be completed. One novel type of hmde used by Zirino and Healy (20) involves sealing a platinum wire into a flint glass rod. This Pt wire is then sanded down to the glass surface. The Pt cross section is plated with mercury from a saturated solution of $Hg(NO_3)_2$ at -1.5 V, and the stripping analysis proceeds as usual.

The average volume of a mercury droplet in an hmde has a magnitude of 10^{-4} cm^3. The volume can be determined by weighing the drops and assuming the density of mercury to be approximately 13.6 g/cm^3. The surface area (ca. 10^{-2} cm^2) can be easily calculated by considering the radius or volume of the spherical drop. However, some analysts (28) have developed area estimations by observing that the drop is actually an oblate spheroid due to gravitational forces.

Shain and coworkers (29,30) have performed stripping analysis with an hmde and derived equations to explain the concentration of amalgams in spherical electrodes. The stripping current for an hmde is related to the diffusion coefficients, scan rate, and concentration of the amalgam (31). The stripping potential (E_p) is independent of the bulk radius of the hmde.

Several workers (13,32) have developed dme with a long drop time so that stripping voltammetry may be synchronized with the life of the drop. Other analysts (20,33,34) have used two synchronized hmde systems whereby the background can be substracted. Hence electrolyte impurities and other interferences do not affect the voltammetric measurement.

Various TFE have been used for DPASV and ASV work. These include wax impregnated graphite electrodes (WIGE) and glassy carbon electrodes (GCE).

The WIGE is a piece of graphite rod that has been impregnated with an amorphous wax so that no solution will be lost due to the porosity of the graphite. The planar end is then filed carefully to expose the electrically conductive anode. Clem and coworkers (23) stated that the greater the amorphous content of the wax, the greater will be the long term stability. The WIGE is placed into a Hg^{2+} solution, and a potential is applied so that the merucry is reduced at the exposed carbon surface. Upon termination of the stripping analysis, the electrode is wiped clean with a tissue.

The GCE is used in much of the same manner as the WIGE, except the hard carbon surface has very low porosity and does not require any wax impregnation.

The GCE is usually sealed in a plastic holder, such as teflon, to prevent solution loss and to expose only the planar end of the carbon.

A study by Copeland and coworkers (35) demonstrated the superiority of GCE over WIGE. This superiority was substantiated by Lund and Salberg (36) by their investigation of a rotating GCE, where the mercury was plated in situ. The term in situ for TFE means that the mercury was deposited together with the metals to be determined.

The direct in situ deposition technique has been utilized for tubular thin film electrodes with real samples (37,38). Problems have been encountered in the analysis of seawater. The chloride ion from the saline solution forms a film with the Hg^{2+} and disrupts the ASV signal (37). One of the advantages of tubular electrodes is the enhanced mass transport of the cations to the TFE surface resulting in an increase in sensitivity.

Investigations have been performed to evaluate the optimum conditions for TFE in stripping analysis (24,35). Theory has also been developed to supplement experimental findings (3,39). Results have shown that for a TFE the maximum sensitivity is achieved when the thinnest film is deposited. The E_p depends on the thickness of the Hg film and deviation from the optimum plating quantity (2) causes reduction in i_p.

The comparative features of the hmde and TFE include their preparation, economy, and sensitivity. As already mentioned, the hmde is easily formed by placing a drop on a conducting material, whereas the TFE requires special pretreatment. The economy of an hmde, due in part to its preparation, is better than the TFE since the investment for extraneous materials (e.g. diamond dust filing paper, carbon substrate, etc.) is not necessary. The sensitivity, however, is greater in a TFE than in an hmde.

The major reason for the increase in sensitivity for the TFE involves the higher surface area to volume ratio (2,40). Hence, the electrode area for deposition is greater in a TFE, although Stulikova (41) has pointed out that the thin film is actually an aggregate of small mercury droplets on the carbon substrate. One study evaluated the electrochemically effective area of an hmde (42). Another variation between the two types of electrodes includes scan rate (v), whereby i_p is proportional to v for a TFE and $v^{\frac{1}{2}}$ for an hmde. E_p for a TFE is dependent upon the thickness of the film, while E_p is independent of the bulk size for an hmde. Comparisons have also been made using different modes with the TFE and hmde (3,24,31,43).

Various interferences are greater using the different types of working electrodes. Overlapping waves may become critical in the analysis of zinc, cadmium, lead, and copper if the TFE film thickness changes the E_p of these metals so that they are not resolved. However, in the case of an hmde, no overlap problem is predicted.

For intermetallic compounds, the problem appears to be more prevalent in a TFE due to the small volume of mercury (3,40,44). The large volume of mercury in an hmde decreases the concentration of amalgam and hence the mercury remains unsaturated (31).

Surface activating substances affect a TFE less than an hmde (43). Although the explanation is not conclusive, the hmde may be able to flex and break the surface of the adsorbed surface activating substance to give current surges.

The longevity and purification of an electrode is important for multiple trace analyses. For a TFE, the problem of purity is minor since the mercury surface is being renewed for each analysis. However, the stability of TFE, especially for a WIGE in acidic medium, is short termed. Florence and Farar (45) have reported a GCE that has been in almost continuous use for five years without repolishing.

An hmde also replenishes its surface before each analysis, except in the case of conditioning of the mercury drop. Conditioning involves maintaining a potential at which the metals to be analyzed will be oxidized from the Hg. The obvious advantage is that the volume of Hg remains the same throughout the experiment. In the case of copper, a good conditioning potential would be +0.1 V. This is at a potential where Cu will be oxidized, but the mercury will remain in the metal state. If conditioning is not used, and a capillary type hmde is being employed, several drops of mercury should be extruded and discarded from the hmde prior to the next analysis. The capillary hmde may suffer from memory effects. The amalgam formed during plating may diffuse up into the mercury thread. If the drop is suspended from a Pt or Ag wire, amalgam formation or intermetallic compound complication with the wire is likely (5,20).

Purification of capillaries for hmde is a nagging problem. Solution creep into the capillary is a major annoyance (46). Water proofing the capillary with a silane compound reduces solution creeep. However, this water proofing is not suitable for use with low pH solutions and at potentials more reducing than -0.9 V vs. SCE. To maintain the maximum sensitivity with an hmde, the capillary should be changed daily and cleansed with nitric acid, or hot chromic acid and hot H_2SO_4 should be used (28).

Major Interferences

During the course of the literature review, interferences that may affect DPASV were evaluated. The three major complications that could occur are overlapping of stripping peaks, intermetallic compound (IMC) formation of alloys, and adsorption by surface activating substances (SAS) onto the working electrode surface.

Overlapping for the peaks of zinc, cadmium, lead, and copper is not a problem in DPASV since the peaks occur at separable stripping potentials. However, if overlapping did occur, as it may in the case of tin and lead (45,47), means must be taken to overcome the problem.

If a thin film electrode is being employed as the working electrode, the E_p is dependent on the film thickness. By varying the thickness, the waves may be resolved (48).

Surfactants can cause a shift in E_p and they may be used to separate overlapped stripping peaks (51,52). Stromberg and Stromberg (27) have suggested using complexing materials to shift the E_p of the metal so that it may be resolved. Ariel and coworkers (53) used stripping and deposition in different media to alleviate overlapping in ASV.

Interferences by various metals do affect the ASV analysis of Zn, Cd, Pb, and Cu. This interference is usually IMC formation. For the four metals stated, zinc and copper exhibit a distinct IMC (51). Other analysts have observed complications between cadmium and copper (43,54). IMC problems may also arise from metals that are not being analyzed, such as Ag-Cu (55), Ag-Zn (57), Ag-Cd (56), Au-Zn (57), Co-Zn (58,59), and Ni-Zn (57,60,61,62). IMC appears to be related to amalgam concentration (51,55) and the extent of formation is independent of one metal's concentration of the IMC pair (61).

Ferric ion may also cause complications in ASV work (63), either as a contaminant in reagents or as a major component of the sample to be analyzed. In such cases, Fe^{3+} may be removed by extraction or by complexation with a ligand.

SAS in DPASV and ASV measurements are detrimental to these electroanalytical methods (51). It is generally regarded that surfactants affect the i_p by adsorbing onto the working electrode surface. This accumulation of adsorbed SAS blocks electrodeposition and hinders stripping. Investigations to circumvent these problems have been reported (51).

Other Interferences

Problems other than overlapping waves, IMC formation, and SAS adsorption do exist in stripping analysis. Halide complexation and adsorption onto a mercury electrode may cause problems in attaining analytical information. Studies by Kolthoff and Jordan (64) have provided evidence for the formation of insoluble mercurous halide films, between 50 to 500 Å thick, adhering to a mercury electrode. Copper may form a ligand with Cl^- and a stepwise reduction of this stable complex may lead to a double wave appearing in polarographic work (65). In one investigation, it was noted that below $10^{-2}\underline{M}$, there is no shift in the Cu^{2+} $E_{\frac{1}{2}}$ (66).

Pinchin and Newham (67) observed in ASV studies that copper waves, in the presence of chloride, became asymmetrical with the steeper slope on the anodic side. A distinct shoulder appeared on the cathodic side and sometimes splitting occurred.

The major Cl^- contamination in a voltammetric cell is due to either KCl or NaCl leakage from a SCE or Ag/AgCl reference electrode. These interferences may be reduced by employing an electrolyte bridge with a Vycor disc which has a low seepage rate. A cracked bead SCE has a leakage rate of ca. 3 μL/h, and is extremely effective for trace voltammetric analysis. O'Shea and Mancy (68) used a Hg/$HgSO_4$ reference electrode, and Stulikova (41) placed a $NaClO_4$ bridge between the SCE and sample solution to prevent complexation of metals with chloride.

Complexation by organic compounds has adverse effects on the E_p and i_p of particular metals. Complexation is also a function of the pH of the solution. Zirino and Yamamoto (69) stated that at the average pH of seawater (pH 8.1), the percentages of uncomplexed metal ions range from about 17% for zinc to approximately 1% for copper. Investigators (68) have made comparisons of free metal vs. complexed metal by ASV analysis. Shuman and Woodward (70) have performed complexometric titrations of metal complexes followed by ASV.

The effects on ASV of complexing materials in the sample include a cathodic shift of E_p (71). Bradford (72) substantiated this complexation effect by noting that Zn experienced a potential movement when the pH of the sample was changed from 8.3 to 5.5. Ligands may also be adsorbed onto the surface of the electrode. Anson and Barclay (73) stated that the better the bridging ligand, the more chance of it being adsorbed onto the electrode.

Reproducibility and Applicability

Reproducibility of results is important for all trace analysis work. MacLeod and Lee (75) concluded for ASV analysis that a standard deviation of less than 12% may be attributed to instrumental variability and operational error, such as pipetting. Other problems in precision may result from CO_2 equilibrium in the solution and memory effects of the mercury electrode (60). In general, the blank value, which includes impurities introduced by reagents and lab air, affect the reproducibility and limit detection of an analysis, while metal adsorption and volatilization tend to affect the accuracy (76).

Several analysts have performed comparative determinations by ASV and atomic adsorption spectrophotometry (AAS). Osteryoung and coworkers (77) pointed out that the major difference between spectroscopic and electroanalytical techniques is in discrimination between dissolved and particulate material. Huderova nad Stulik (26) noted that the apparatus utilized in ASV is cheaper and does simultaneous determinations, even in concentrated matrix solutions. The AAS was considered to be faster and broader in applications with fewer interferences.

Agreement for values measured by a.c. polarography and AAS were quite good (11). ASV and AAS comparisons also agreed well (14,63,78). It was observed that below 1 ppm, a difference in measurement did occur. This may be a result of non-labile metal complexes (63).

Purification

In measuring ultratrace concentrations of metals, the purity of the analytical apparatus and reagents is a pervasive problem. The types of contamination that affect the highly sensitive measurements are interfering metal cations, surfactants, organic matter, dissolved gases, and particulate debris. These substances may have their origin in container walls, laboratory atmosphere, transferring technique, measuring devices, chemicals, and other materials which the sample may contact. For electrochemical analysis, such as ASV these problems are magnified by the sensitivity of the operational mode.

The most important reagent to consider in the study of aqueous systems is water. For work in the ppb concentration range it is of the utmost importance that this solvent be as pure as possible from contaminants. One of the simplest methods for purification is distillation from borosilicate glass or quartz, one or more times. It has been stated, however, that there is only a slight difference between doubly and triply distilled water (79). Inorganic compounds may be added to the distillation pot to induce the oxidation of organic matter. These include distillation from $KMnO_4/KOH$ and $H_2SO_4/K_2Cr_2O_7$. Other techniques involve the use of decolorizing carbon to adsorb any carbonaceous residuals (80,81), ultraviolet oxidation (82) sometimes enhanced by the addition of a photosensitizer (83), gas chromatography (84), and even high energy radiation methods with X-rays (83) and fast neutrons (85). A purification apparatus using demineralization and millipore filters gives very satisfactory water and is readily available.

Some tests for the cleanliness of water involve color changes upon the addition of chemicals such as H_2SO_4 with $KMnO_4$, the retention of surfactant bubbles after shaking the water, and a check on ionic species by conductivity

The theorectical K for water at 25°C is $0.0549 \times 10^{-6}\ \Omega^{-1}\mathrm{cm}^{-1}$. (86,87). Resistances as high as $10^{-6}\ \Omega^{-1}\mathrm{cm}^{-1}$ have been reached using the purification techniques described.

In performing electroanalytical measurements, it is advantageous to have the sample in some sort of electrolyte to conduct the current output, although with certain operational modes this electrolyte is not needed (5). It is also important for specific metal cations and organics to be analyzed at a particular buffered pH, such as for zinc and gallium. These electrolytes and buffers must have a blank level below the concentration of the constituents being studied, and this obligates the analyst to establish a tolerance level for these materials. If this limit is not maintained, a purification process becomes necessary. These processes include extraction with chelating substances such as dithizone, recrystallization of salts (23,88), and electrolysis at a mercury cathode (30,60,67,89); the latter being the most popular method for voltammetric analyses. For organic contamination, treatment with activated charcoal (90) and roasting of salts (46) are convenient purifying procedures.

After cleaning the solutions and chemicals, uncontaminated containers must be used to store these materials. Studies have been made to determine the various contaminants that exist in container walls and various materials (79,91). A tabulation of materials and inherent metal components are listed in Fig. 1. For trace analysis work, sampling and solution vessels must be leached with a desorptive solvent prior to use, usually an aqueous acid (4,63,91,92). Another problem is the adsorption of metals onto the container wall. This is a pertinent difficulty when dealing with standarized stock solutions of low molarities. Rook and coworkers (92) studied the adsorption of metals onto teflon using radioactive tracers, and observed little indication of loss onto the vessel's surface at a concentration of one ppm. When dealing with glass containers, one method to reduce the sorptive effect is coating the glass surface with a silane compound, such as dimethyldichlorosilane (48,61). DeMars (30) equilibrated his containers several times with stock mixtures, and finally stored the fifth dilution in a leached polyethylene bottle.

Deaeration of the sample is a necessity in most voltammetric work. The simplest method for deaeration is bubbling an inert gas such as nitrogen or helium through the solution. In the more sensitive ASV measurements, the degasser must be completely free of oxygen, otherwise the baseline will be distorted and no analytical information will be retrieved. In order to further purify the inert gas, scrubbing towers are used that contain compounds to absorb the oxygen in a consuming chemical reaction. Vanadium (II) sulfate (93) and acidic chromous chloride have been utilized for such scrubbing reactions. Another possibility is a furnace containing copper metal which reacts with the O_2 before it reaches the electrochemical cell. A novel procedure presented by Benesch (94) involves addition of catalase to consume the oxygen directly in the cell. Several groups (20,66,68,95) have developed surface. The electrolyte in the reference electrode should be purified to lessen the possibility of contamination due to leakage. A bridge may be used or a cracked bead SCE is very satisfactory. The mercury in the working electrode, or plated onto the TFE, must also meet purity requirements. Multiply distilled mercury usually attains these requirements, although extraction with $KMnO_4$ in H_2SO_4 (95) and anodic dissolution followed by cathodic reduction (65) have also been utilized to remove impurities. Pure mercury will break up into small drops or spheres upon shaking (95).

TABLE 1

Metal contaminants in various substances.

SUBSTANCE	Zinc	Iron	Cobalt	Silver	Copper
Average Sea Water	10 ppb	10	0.05	0.2	10
Teflon	9.3	35	1.7	<0.3	22
Polyvinyl Chloride	7120	$2.7\text{x}10^5$	45	<5	630
Neoprene Rubber	$1.82\text{x}10^7$	U.M.	2300	<1000	N.M.
Polyethylene Hose	55	7.4	140	<300	N.M.
Quartz Distilled Water	∿1	∿1	∿0.04	<0.02	N.M.
Triply Distilled Water	∿0.5	∿1	<0.02	<0.02	N.M.
Nitric Acid	13	∿2	0.018	∿0.24	1.3
Doubly Distilled Chloroform	2.1	1.6	∿0.003	<0.005	0.29
Borosilicate Glass	730	$2.8\text{x}10^5$	81	<0.001	N.M.
Vycor	U.M.	U.M.	U.M.	U.M.	U.M.
Nalgene	28	10,400	0.07	<0.1	6.6
Kimwipe	$4.8\text{x}10^4$	1000	24	∿0.8	N.M.
Millipore Filter	2370	330	13	<0.05	N.M.
Dithizone	1150	<7000	1.2	<10	420
Sodium Hydroxide	<20	<900	5.5	<0.2	N.M.
Skin (Human)[a]	6000				700
Gasoline[b]					$5\text{x}10^6$

All data from ref. 79, except a from ref. 76 and b from ref. 75.

N.M. Not measurable

U.M. Unable to measure; below detection limit.

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6-78