

THE TRACE ANALYSIS OF WATER FOR SELECTED METALLIC  
ELEMENTS EMPLOYING SQUARE-WAVE POLAROGRAPHY

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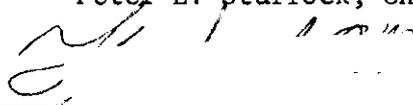
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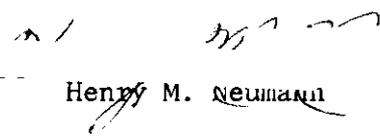
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THE TRACE ANALYSIS OF WATER FOR SELECTED METALLIC  
ELEMENTS EMPLOYING SQUARE-WAVE POLAROGRAPHY

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## SUMMARY

The subject of this investigation has been the application of a newly designed square-wave polarograph for the determination of very low concentrations of metals.

A study of solution conditions was conducted in order to find the optimum pH, electrolytes, and electrolyte concentrations for single and multi-element analysis.

With the employment of the dropping mercury electrode (DME), concentrations lower than  $10^{-8}F$  could be detected for copper (II), lead (II), and cadmium (II). Concentrations below  $10^{-7}F$  could be detected for antimony (III), arsenic (III), manganese (II), nickel (II), tin (IV), and zinc (II), while concentrations below  $2 \times 10^{-7}F$  could be detected for bismuth (III), cobalt (II), and iron (III). Even lower concentrations of these metals could have been detected if the electrochemical cell had been made of some material other than glass, with less tendency for metal adsorption.

The use of the hanging mercury drop and the thin mercury film disk electrodes (primarily employing anodic stripping voltammetry) for the analysis of very low concentrations of metals was also investigated. The mercury film rotating disk electrode allowed more rapid, sensitive, and reproducible determinations than did the hanging mercury drop electrode. The procedure employed for the determination of low concentrations of metals with the disk electrode required careful control of all instrumental and chemical parameters. In less than 15 minutes

analysis time, concentrations below  $10^{-9}$  F could be determined for metals amenable to stripping analysis.

Results are reported for the analysis of EPA water reference standards employing the rotating disk and dropping mercury electrodes.

## CHAPTER I

## INTRODUCTION

The monitoring of trace metals in water is of particular concern since metals are vital for the functioning of many biological processes and also, if present in sufficient levels may be harmful or fatal to both plant and animal life.

Even with the recent advances in analytical instrumentation, the analysis of very low concentrations of metals in varying water matrices is still time consuming and difficult. There is a considerable need for the improvement of existing analytical techniques and the development of new ones so that more sensitive and reproducible analytical determinations can be made.

Over the past forty years numerous publications have appeared on the employment of polarography for the determination of metals. However, this technique has not gained routine acceptance for the trace analysis of metals in water because of its limited sensitivity. In addition, the technique has been characterized as being very time consuming.

More recent polarographic techniques have greatly improved the sensitivities for the determination of metals; however, these techniques have not been commonly used due to the lack of commercial instrumentation. The objective of this investigation is to study

the suitability of square-wave polarography, one of the more recent and promising techniques, using a newly designed instrument.

## CHAPTER II

## THEORY

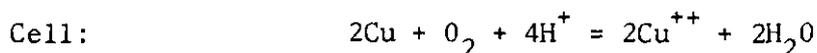
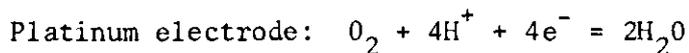
Electrolysis

The principles of electrolysis are given in this section since this technique is the basis for many other electrochemical techniques, including polarography. Basically, electrolysis can be defined as the imposition of an externally applied voltage through a cell containing an electrolyte solution causing a non-spontaneous cell reaction to occur, in which species are oxidized at the anode and reduced at the cathode.

As an illustrative example consider the cell arrangement in Figure 1 which contains a copper sulfate solution in dilute sulfuric acid medium saturated with oxygen.

Galvanic Cell

If the switch is opened so that no voltage is applied from the power supply, a finite current is passed through the cell until an equilibrium state is attained. The reactions at the two electrodes and the overall spontaneous reaction for this particular cell are



Following the conventions recommended by the International Union of Pure and Applied Chemists (I.U.P.A.C.) a shorthand representation of

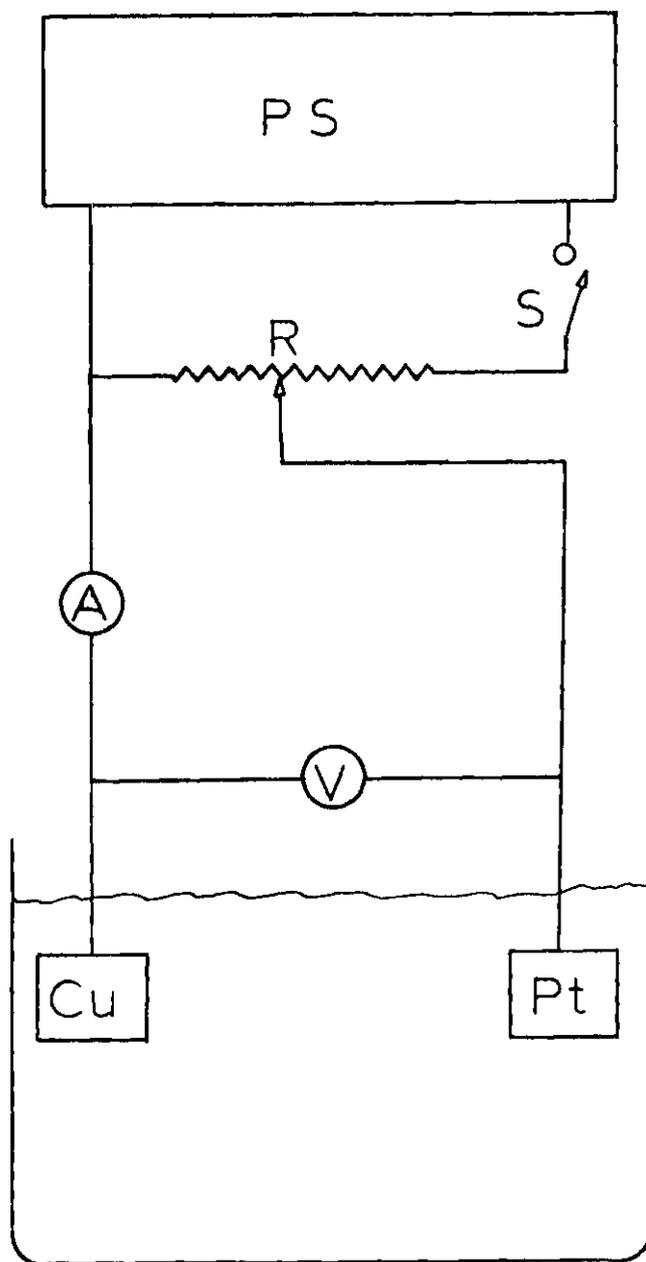
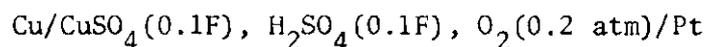


Figure 1. Electrolysis Cell ( $\text{Cu}(\text{II}) - 0.1\text{F}$ ;  $[\text{H}^+] - 0.2\text{F}$ ;  $[\text{SO}_4^{2-}] - 0.2\text{F}$ ;  $\text{O}_2 - 0.2\text{atm}$ ; PS is the power supply; S is an on-off switch; Rv is the variable resistance;  $\text{A}$  is an ammeter,  $\text{V}$  is a voltmeter; and the concentrations are given in formula weights per liter (F).)

the cell may be given as



where a solid line indicates contact between phases and a comma is used to separate different species that exist in the same phase. The cell voltage is calculated by subtracting the potential of the left electrode from the potential of the right electrode or

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} \quad (2-1)$$

If a reaction is spontaneous, then the difference between the free energy of the products must be less than that of the reactants. If the change in free energy (products minus reactants), is equal to zero then the system is at equilibrium. The equation for the determination of the change in free energy for a cell reaction is given below

$$\Delta G = -nFE_{\text{cell}} \quad (2-2)$$

where  $\Delta G$  is equal to the change in free energy of the cell reaction,  $n$  is equal to the number of electrons transferred,  $F$  is equal to the faraday constant (23,060 calories/volt), and  $E_{\text{cell}}$  is the potential of the cell. A positive value of  $E_{\text{cell}}$  corresponds to a spontaneous reaction.

The potential of a half reaction, such as the right (platinum) electrode is found by employing the Nernst equation

$$E = E^{\circ} + \frac{RT}{nF} \ln \frac{(\text{activity Ox})}{(\text{activity Red})} \quad (2-3)$$

where  $E$  is the potential of the half-cell relative to the standard hydrogen electrode, and  $E^{\circ}$  is the standard electrode potential where the species involved are at unit activity. Also  $R$  is the gas constant (8.316 volt-coulombs/degree),  $T$  is equal to the absolute temperature (degrees Kelvin), and  $F$  is equal to the value of the faraday ( $9.649 \times 10^4$  coulombs). The terms (activity Ox) and (activity Red) represent the activities of the oxidizable and reducible species at the electrode surface (molar concentrations are normally employed except for gases which are expressed as partial pressures in atmospheres). Usually, the Nernst equation is simplified for use at  $25^{\circ}\text{C}$  to the form

$$E = E^{\circ} + \frac{0.059}{n} \log \frac{[\text{Ox}]}{[\text{Red}]} \quad (2-4)$$

where square brackets denote molar concentrations. For the particular cell previously described:

$$E_{\text{right electrode}} = E_{\text{Pt}} = 1.23 + \frac{0.059}{4} \log \frac{(p\text{O}_2) [\text{H}^+]^4}{1}$$

$$E_{\text{Pt}} = 1.23 + \frac{0.059}{4} \log \frac{(0.2)(0.2)^4}{1} = 1.18\text{v}$$

$$E_{\text{left electrode}} = E_{\text{Cu}} = 0.34 + \frac{0.059}{2} \log (0.1) = 0.31\text{v}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 0.87\text{v}$$

Since  $E_{\text{cell}}$  is a positive value the reaction will occur spontaneously; thus the copper electrode will dissolve and oxygen will be produced.

### Electrolytic Cell

If the switch is closed (see Figure 1) and a voltage ( $E_{\text{appl}}$ ) is applied to the cell in the opposite direction to the cell voltage such that  $E_{\text{appl}}$  just equals  $E_{\text{cell}}$ , no current will flow. If  $E_{\text{appl}}$  is larger than  $E_{\text{cell}}$ , the cell reaction is reversed from the spontaneous direction. Thus copper (II) ions in solution will be plated out on the copper electrode (cathode) and oxygen will be produced on the platinum electrode (anode). The cell voltage in electrolytic processes is often called the back emf.

Since the concentration of reducible species decreases as electrolysis proceeds it can be seen by inspection of equation (2-4) that the reversible back emf increases progressively. Thus the potential applied must be steadily increased. The  $E_{\text{appl}}$  required for an electrolytic process can be approximated by the following equation

$$E_{\text{appl}} = E_{\text{cell}} + iR + E_{\text{conc overpotential}} \quad (2-5)$$

The  $iR$  term in this equation is called the "iR drop" and is equivalent to the voltage that is needed to compensate for the cell resistance. The  $E_{\text{conc overpotential}}$  term is known as the concentration overvoltage. This phenomenon can be depicted by viewing what is taking place at the cathode. Copper ions in solution are being plated onto the cathode, thus creating a concentration gradient between the vicinity of the electrode surface and the bulk of the solution. Copper ions are transported by the diffusion, convection, and migration processes. As the voltage is increased, the current response is approximately linear until the ion transport begins to lag. The current no longer increases

as a function of voltage because the system is limited by the rate of the ion transport unless the reduction potential of another species is reached. Thus the effective back emf is greater than the reversible back emf because the molar concentration of the species in the bulk of the solution was substituted into the Nernst equation instead of the unknown concentration at the electrode surface. Thus the difference between the effective back emf and the reversible back emf constitutes the concentration overpotential, which is made up of two composite components: the anodic and cathodic concentration overpotentials. There are several measures to reduce the concentration overpotential such as raising the temperature, stirring, and increasing the electrode area (decreasing the current density).

Kinetic Overpotential. With thorough stirring and a very small  $iR$  drop, in many cases the  $E_{\text{appl}}$  agrees with theoretical reversible electrode potentials. However, in some cases where there is no appreciable concentration overpotential and  $iR$  drop, a much higher voltage is required than the reversible emf. This additional voltage required is known as the kinetic overvoltage, designated by the Greek letter,  $\eta$ . This overpotential is called kinetic because it is due to a kinetically slow step which limits the overall electrode reaction. The mechanisms involved with the establishment of this overpotential are not fully understood but kinetic overpotentials are usually encountered when diatomic gases are produced in the electrode reaction. The magnitude of the kinetic overpotentials depend on factors such as the electrode material and the nature of the electrode surface. High kinetic overpotentials for gases are commonly observed on soft metals, especially

mercury, which is one of the major reasons for the extensive use of mercury in electrochemistry.

The decomposition potential,  $E_d$ , which consists of anodic and cathodic portions of  $\eta$  and  $E_{\text{cell}}$  is defined in equation (2-6)

$$E_d = E_a - E_c + \eta_a - \eta_c \quad (2-6)$$

where  $\eta_a$  is always positive and  $\eta_c$  is always a negative value. A more accurate estimation of  $E_{\text{appl}}$  can thus be given in the following equation

$$E_{\text{appl}} = E_d + iR + E_{\text{conc overpotential}} \quad (2-7)$$

Parameters which affect the contributing terms, and hence affect  $E_{\text{appl}}$ , are temperature, pH, and the presence of complexing agents.

### Classical Polarography

Consider an electrolysis cell such as in the example (Figure 1) except that two inert (platinum) electrodes are used for the electrolysis of the solution. The current-voltage curve will have the form shown in Figure 2 (curve A). If the potential applied is less than the decomposition potential, very little current will flow. At higher potentials, the current is given by Ohm's law,  $i = (E_{\text{appl}} - E_d)/R$ , if there is adequate stirring. The decomposition potential  $E_d$ , is usually defined as the zero-current intercept from the back extrapolation of the current versus voltage curve.

If the cathode is a microelectrode and the solution is no longer stirred, the current-voltage curve will have the form as curve B in Figure 2. As shown the current rises linearly very rapidly but then

levels off to a limiting value because, as was discussed earlier, the rate of the species reaching the electrode governs the current. The electrode is said to be "polarized" because the current is dependent upon the diffusion rate of reducible species to the electrode surface and is independent of the applied potential.

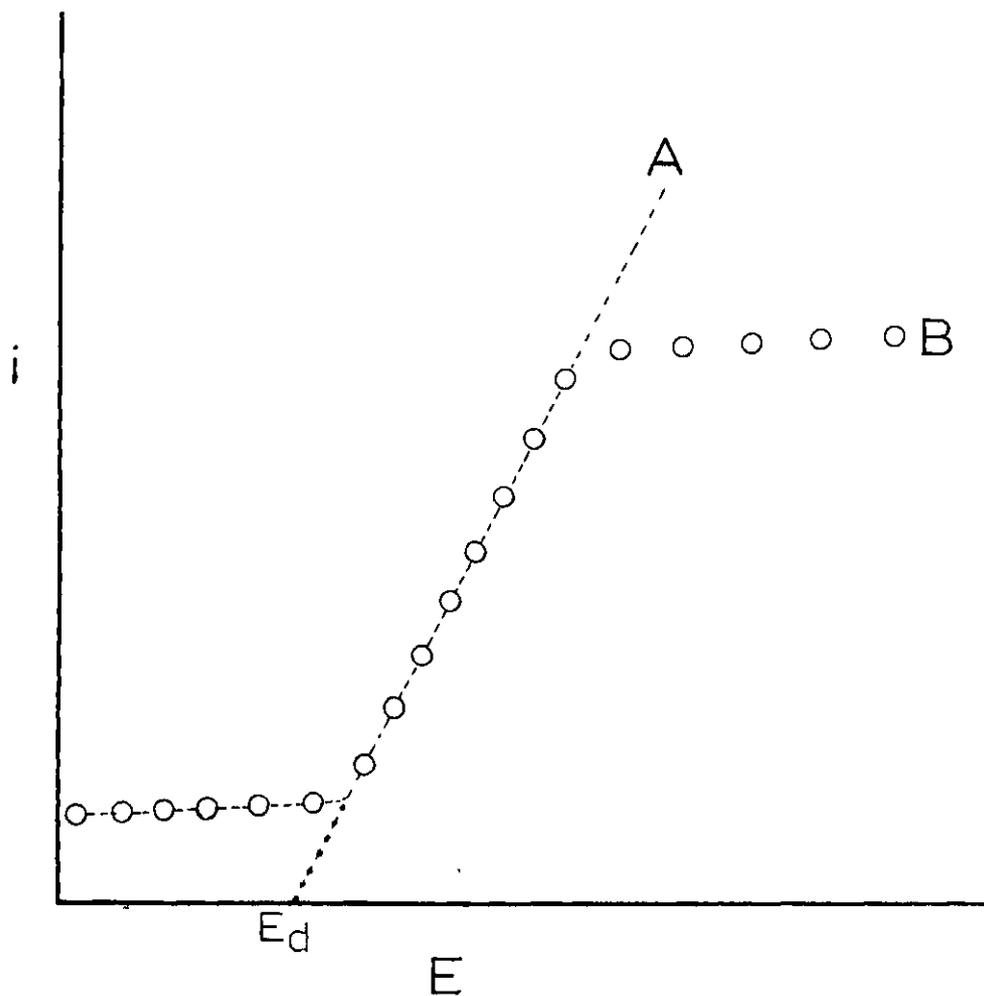


Figure 2. Current-Voltage Relationships for Electrolytic Processes (----- line represents curve A; oooooo line represents curve B).

Early attempts to use solid electrodes as the microelectrode failed, because of the problems of oxide formation on the surface, adsorption effects, etc. However, when Heyrovsky used the dropping mercury electrode (DME) as the microelectrode very reproducible results were obtained. The dropping mercury electrode consists of fine-bore tubing attached to a mercury reservoir. Under the force of gravity, new drops continuously emerge from the tip of the capillary thus allowing a fresh electrode surface to be presented to the sample solution every few seconds. Other advantages that this electrode affords are the high kinetic overpotentials of hydrogen on mercury (that is especially valuable for the study of substances that reduce at fairly negative potentials) and the very reproducible diffusion controlled limiting current which is directly proportional to the concentration of the electroactive species.

Consider a cell containing  $5 \times 10^{-4}F$  cadmium (II) and  $10.0 \times 10^{-4}F$  lead (II) ions in 1F potassium chloride medium in which one compartment contains a DME and in another compartment there is a non-polarizable electrode such as the saturated calomel electrode (SCE). Connecting the two compartments is a salt bridge which gives a conducting connection without allowing the two solutions to mix. The removal of dissolved oxygen is accomplished by bubbling an inert gas through the solution (see Chapter III). If the potential of the DME is scanned from 0.0v to -1.2v (versus SCE) and the current corresponding to each momentary voltage value is measured and plotted versus the voltage, the graph that is obtained is called a polarogram (see Figure 3).

As the cadmium and lead ions are being reduced at the cathode

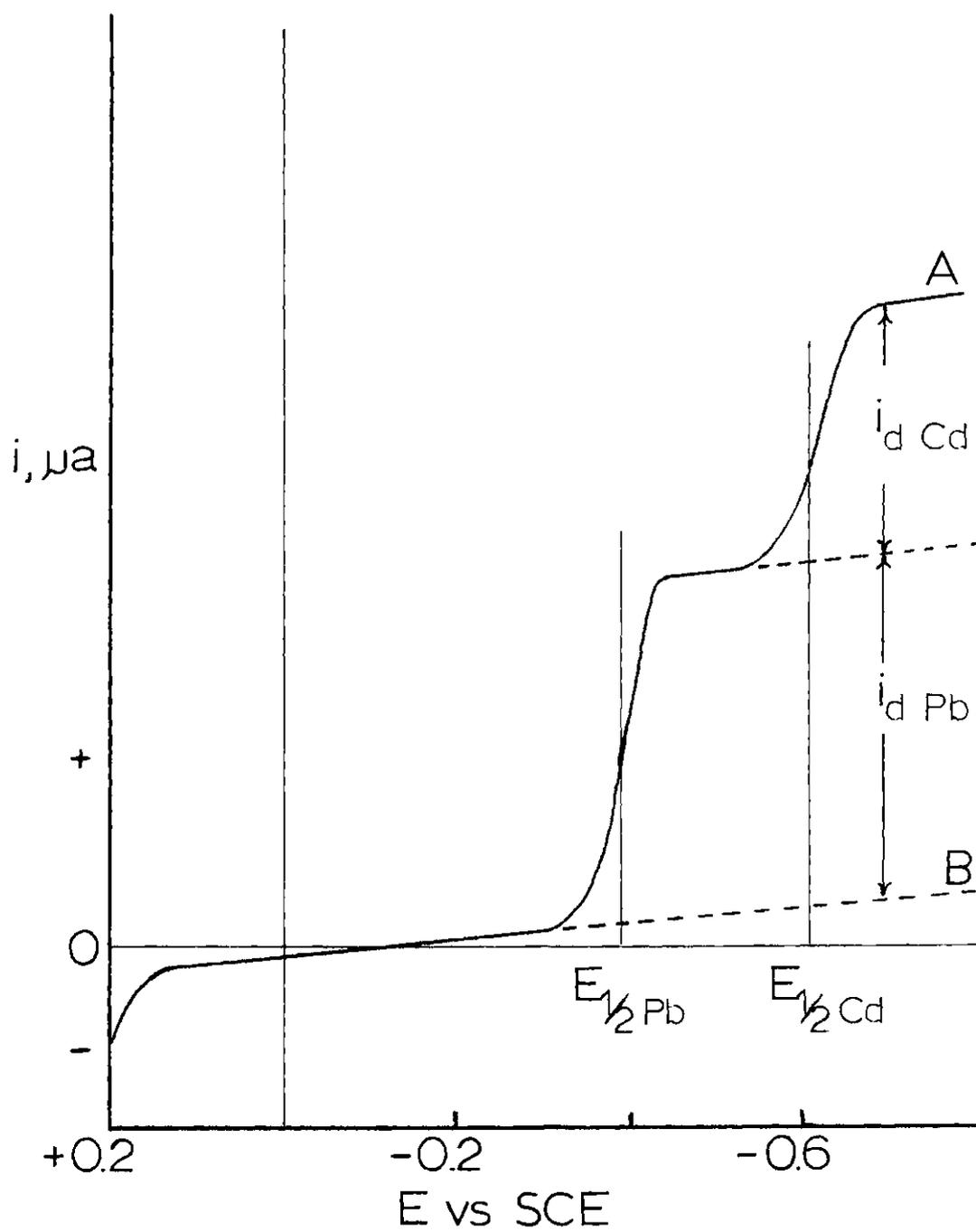


Figure 3. DC Polarogram of  $10 \times 10^{-4} \text{F Pb (II)}$  and  $5 \times 10^{-4} \text{F Cd (II)}$  in 1F Potassium Chloride

(DME), at the anode mercury is oxidized in the presence of the chloride ions to form calomel,  $\text{Hg}_2\text{Cl}_2$ . The potential of the anode remains constant since the chloride concentration is not appreciably changed, thus voltages in polarography are usually in reference to the saturated calomel electrode.

### Half-Wave Potential

The equation that describes the current-voltage relation of a polarographic wave is

$$E = E^0 + \frac{0.059}{n} \log \frac{i_d - i}{i} + \frac{0.059}{n} \log \frac{(D_{\text{red}})^{\frac{1}{2}}}{(D_{\text{ox}})^{\frac{1}{2}}} \quad (2-8)$$

where the equation is usually written

$$E = E_{\frac{1}{2}} + \frac{0.059}{n} \log \frac{i_d - i}{i} \quad (2-9)$$

Here  $E^0$  is the standard reduction potential,  $i$  is the current at any point on the curve,  $i_d$  is the diffusion current,  $n$  is the electron change, and  $D_{\text{ox}}$  and  $D_{\text{red}}$  are the diffusion coefficients of the oxidized and reduced species, respectively. The half-wave potential,  $E_{\frac{1}{2}}$  (Figure 3), represents the inflection point of the polarograms and is the potential at which  $i = i_d/2$ . The half-wave potential is characteristic of the species being reduced and is not dependent on concentration, thus this point is a qualitative means for the identification of a particular reducible species. Equation (2-9) must be modified for metals which do not form amalgams with mercury; i.e., iron and chromium.

Equation (2-9) is not valid for solutions containing complex forming agents since the reduction is concerned with the simple aquo ion. In the presence of complex forming agents the half-wave potential is

usually shifted more negatively as described in the following equation

$$E_{\frac{1}{2}(\text{complexed})} = E_{\frac{1}{2}(\text{free})} + \frac{.059}{n} \log K_{\text{inst}} - \frac{p}{n} (0.059) \log [x] \quad (2-10)$$

where  $K_{\text{inst}}$  is equal to the instability constant of the complex,  $[x]$  is equal to the concentration of the complexing agent, and  $p$  is equal to the number of moles of  $x$  combined with one formula weight of metal in the complex.

### Polarographic Reversibility

According to equation (2-9), a plot of  $E$  versus  $\log i_d - i/i$  yields a straight line with a slope of  $+ 0.059/n$ . If this is so, the reaction is said to proceed reversibly. If the wave cannot be described by equation (2-9), the wave is called irreversible, and implies that the current is controlled by some factor other than the diffusion of species to the electrode. In the following sections some phenomena capable of causing polarographic irreversibility are discussed.

### Polarographic Limiting Current

For most chemical systems the limiting current is the sum of the diffusion current ( $i_d$ ), the migration current ( $i_m$ ), and the residual current. However, the limiting current in some systems may be governed by kinetic and catalytic currents.

Diffusion Current. Initially in a polarographic analysis the concentration of the reducible species at the electrode surface is equal to the concentration in bulk solution. When the potential applied to the electrode is greater than the decomposition potential, the concentration of electroactive species at the electrode surface decreases, thus causing a concentration gradient. The reducible species diffuse from the regions

of higher concentrations (bulk) to the regions of low concentration (electrode surface).

The flux of reducible species moving in a single direction and toward a plane surface (linear diffusion) is defined as the number of moles or reducible species that pass through a cross-sectional plane of unit area ( $1 \text{ cm}^2$ ) in length of time,  $dt$ . The flux is given by Fick's First Law

$$f(x,t) = \frac{1}{A} \frac{dN(x,t)}{dt} = D \frac{\partial C(x,t)}{\partial x} \quad (2-11)$$

where  $D$  is the diffusion coefficient ( $\text{cm}^2/\text{sec}$ ) and  $\partial C/\partial x$  is the concentration gradient.  $C(x,t)$  refers to the concentration of the reducible species at a distance  $x$  from the electrode surface at time  $t$ . The diffusion coefficient is dependent on solution characteristics, temperature, viscosity, etc. and the characteristics of the diffusible species itself such as charge and equivalent conductance.

It is very difficult to derive an equation for the exact calculation of the diffusion current of a periodically growing and falling spherical electrode. This problem was solved in an approximate manner by Ilkovic who derived the diffusion current expression by assuming that the dropping mercury electrode behaves as a plane electrode with an area increasing as a function of time and moving into the solution. Assuming also that the flow of mercury is constant and that the drop is spherical up to the moment of separation, the theoretical equation for the diffusion current is

$$i_d = 708 n D^{1/2} m^{2/3} t^{1/6} C \quad (2-12)$$

or the equation for the average current,  $\bar{i}_d$ , which minimizes the drop fluctuation by integrating over one drop time and dividing by the time interval

$$\bar{i}_d = 607 nD^{1/2} m^{2/3} t^{1/6} C \quad (2-13)$$

where  $i_d$  is the maximum diffusion current in microamperes,  $\bar{i}_d$  is the average diffusion current during the life of the drop,  $C$  is equal to the concentration of reacting species in millimoles per liter,  $D$  is the diffusion coefficient in  $\text{cm}^2$  per second,  $t$  is the drop time in seconds (usually measured at the half-wave potential), and  $m$  is equal to the rate of flow of mercury in milligrams per second).

If the drop time is too short the current is much larger than predicted and less reproducible, due to the stirring action of the rapidly falling drops. Thus the reduction of the species is not primarily controlled by the diffusion.

From the rearrangement of the Ilkovic equation (2-13), the diffusion current constant,  $I$ , is obtained.

$$I = 607 nD^{1/2} = i_d / C m^{2/3} t^{1/6} \quad (2-14)$$

This constant allows the comparison of diffusion currents with the employment of different capillaries, media, mercury height, etc.

Migration Current. The migration current is due to the attraction or repulsion of the electroactive species to and from the surface of an electrode. This current is undesirable because it is not directly proportional to the concentration of the oxidizable or reducible species

as is the diffusion current. The migration current is virtually eliminated by the addition of a relatively large amount of "supporting electrolyte," a salt which is not electroactive within the potential ranges of the voltage scans. Thus if the concentration of the electroactive species is approximately milliformal and the supporting electrolyte concentration is one formal, then the contribution of the electroactive species to migration is negligible.

Residual Current. If the reducible species lead (II) and cadmium (II) ions were excluded from the solution and a polarogram obtained, the curve would correspond to curve B (Figure 3). The residual current is partially made up of the faradaic current due to the small amount of undesirable impurities present, but the major portion of the residual current is due to the capacitance current which results from the charging of the mercury drop and the electrical double layer around its surface. The capacitance current may be either positive or negative depending on the potential at the electrode surface. At a potential more positive than about  $-0.5\text{v}$  (versus SCE), the mercury drop is positively charged with respect to the solution; thus, chloride ions will be attracted forming an inner Helmholtz layer. Because of this negatively charged layer of chloride ions, an electrical double layer is said to exist. Beyond this layer exists an outer Helmholtz layer, which is composed of a tightly held layer of hydrated chloride ions. Beyond this layer is the diffuse layer which has a net positive charge. If the potential applied is more negative than approximately  $-0.5\text{v}$  (versus SCE), then the mercury surface acquires a net negative charge and chloride ions will be repelled. Thus the charging current is now

positive (cathodic) as the electrons go to the electrode surface. The potential at which the mercury surface is uncharged is known as the electrocapillary maximum, which has a value of approximately  $-0.5\text{v}$ , but which depends on the nature and concentration of the ions in the solution. The interfacial tension is greatest at this potential since less work is required for the growth of the drop if the surface carries a charge. A continuous flow of current results, because as a drop emerges from the capillary it must be charged to the proper potential. The larger the difference between the actual potential of the electrode surface and the electrocapillary maximum the greater will be the capacitance current.

The trace impurities present that cause part of the residual current can come from the following sources: reagents, water, mercury, glassware, deaerating gas (and lines), dissolved oxygen, and dust. For a complete discussion on these sources of impurities and how they were minimized in this work see Chapter III.

The sensitivity of the polarographic method is limited by the residual current, of which the charging current usually makes up the greatest portion. Modern instrumentation can measure currents as low as  $10^{-12}$  amperes, which corresponds to concentrations of roughly  $1 \times 10^{-9}\text{F}$  for reversibly reduced species. However, the charging current is approximately  $4 \times 10^{-8}$  amperes, if the difference in the applied potential and the potential of the electrocapillary maximum is approximately 200 millivolts (1). Thus the limit of detection for classical polarography is about  $1 \times 10^{-5}$  formula weights per liter of reversible species. If the capacitance did not vary with potential, the capacitance

current would change linearly and would not constitute such a problem. A linear compensator, a device developed by Ilkovic and Semerano (2), would effectively "buck out" the capacitance current. However, the capacitance is dependent on potential, thus this device is not very effective in compensating for the charging current; consequently, the polarograms are distorted. Kelley and Miller were able to determine approximately  $2 \times 10^{-7}$  F lead employing the linear compensator and a "curve follower" (3). One fairly simple means of correcting for residual current is to run a blank (a solution containing only supporting electrolyte). This background is subtracted from the polarogram of the solution containing electroactive species. However, it is very difficult to have exactly the same solution conditions on different polarographic scans; also the instrument performance may have varied between the two polarograms. Another disadvantage of this method is the time involved for an analysis.

Differential polarography, a technique where two cells are employed simultaneously (one usually being the blank) is essentially the same as running a separate blank, except that the current of the blank is subtracted electronically from the sample solution current. The difficulty of having the same solution conditions also exists with this method, especially since the blank and the sample are run in separate cells. Since different electrodes are used for the two cells, it is especially difficult for all parameters to be the same. Another disadvantage of this method is the far more complex circuitry needed.

Many other techniques have been employed to enable a separation of the faradaic and capacitance currents or to increase the  $i_d/i_c$  ratio.

These techniques will be reviewed later in this chapter.

Kinetic and Catalytic Currents. In some cases the limiting current is not governed by the rate of diffusion of electroactive species but rather by the rate of production of an electroactive species. In this case the current is termed the kinetic current.

A catalytic current is observed when the following occurs in a solution containing species A and B. If the potential applied is such that A is reduced but B is not, and the reduction product is then re-oxidized by B, and the concentration of A regenerated is greater than the concentration diffusing, then an increase in current is observed which is not diffusion controlled.

Adsorption Waves. Anomalous behavior will result if either the reduction product or the diffusing species is adsorbed onto the electrode surface. If a wave is observed, the limiting height is proportional to the amount of adsorbed reactant. Adsorption waves are usually observed when certain organic compounds (e.g., methylene blue, thiols, and others) and arsenic (III) compounds are in solution. Sometimes the adsorption of certain species on the surface of the drop may not yield a wave but may decrease the diffusion current by lowering the effective surface area and affecting the rate of electron transfer.

Polarographic Maxima. Sometimes a large erratic hump or sharp peak is superimposed upon the polarographic wave usually just where the current is reaching the limiting value. This phenomenon is not completely understood but is thought to be due to the tangential streaming motion of solution past the drop surface (4-7).

Maxima are usually suppressed by the addition of an organic

surfactant (about 0.005%) to the solution.

#### Determination of Concentration from Diffusion Current Data

The polarographic method is employed for the determination of electroactive constituents in the  $10^{-2}F$  to  $10^{-5}F$  concentration range with a reproducibility of approximately  $\pm 1\%$ . Lower levels of species can be determined if the residual current can be effectively eliminated.

The determination of the concentration of species from diffusion current data can be performed in a number of ways. The methods commonly employed are the absolute method, the pilot ion or internal standard technique, the calibration curve technique, and the standard addition method. A brief description follows; a more complete discussion of these methods is given by Taylor (8).

Absolute Method. The concentration of electroactive species can be determined if the other terms of the Ilkovic equation (2-12) are known; however, an accurate value for the diffusion coefficient is not usually available. If the same solution conditions exist (pH, temperature, electrolyte concentration, etc.) the diffusion current coefficient,  $I$ , can be determined for a solution containing a known concentration of the species of interest. If only approximate concentrations are of interest, published values of  $I$  can be used and experimentally determined values for  $m$  and  $t$  must be obtained for each capillary employed.

The principal advantage of this method is that time-consuming standard additions are not made or calibration curves do not have to be constructed. Thus the method is simple and direct but not as accurate as the comparative techniques.

Pilot Ion Method. A solution containing an unknown concentration of a reducible species such as copper can be determined by adding a known concentration of the second substance and measuring the two diffusion currents. The second substance, e.g., lead, is known as the pilot ion. The ratio of the diffusion currents is

$$\frac{i_{d \text{ Pb}}}{i_{d \text{ Cu}}} = \frac{I_{\text{Pb}} \times C_{\text{Pb}}}{I_{\text{Cu}} \times C_{\text{Cu}}} \quad (2-15)$$

The concentration of copper in the solution is thus equal to

$$C_{\text{Cu}} = \frac{i_{d \text{ Cu}} C_{\text{Pb}} I_{\text{Pb}}}{i_{d \text{ Pb}} I_{\text{Cu}}} \quad (2-16)$$

The method is accurate and an added advantage is that the method is independent of the capillary characteristics; thus several capillaries may be employed. However, solution conditions must be exactly the same for the sample solution and the "spiked" sample. Also if a sample solution contains more than one reducible species, it may be difficult to find a pilot ion whose wave does not overlap the other waves.

Calibration Curve Technique. In this technique the diffusion current (or wave height) is plotted versus concentration for solutions with known concentrations of the species of interest ranging from the blank to solutions with high concentrations. All parameters must be kept constant (other than the concentration). The method is simple and accurate because many times as the concentration is increased, there may be some curvature in the plot. However, it is very difficult to have the same solution conditions for both samples and standards. The

topic of matrix effects will be discussed more fully in the next chapter since this is one of the major problems encountered in analytical chemistry.

The Standard Addition Technique. In this technique a known volume and concentration of the species of interest is added to a definite volume of sample solution of unknown concentration. Polarograms are obtained for the solution of unknown concentration and for the "spiked" solution. Since the terms in the Ilkovic equation for these two solutions are the same except for concentration, the expressions for the diffusion currents of the two solutions A and A' are

$$i_{dA} = KC_A \quad (2-17) \quad i_{dA'} = K \frac{C_A V + C_{A'} v}{V + v} \quad (2-17a)$$

where K is the proportionality constant,  $C_A$  and  $C_{A'}$  are the concentrations of the solutions A and A', respectively. Also V is the volume of the unknown solution and v is the volume added.

Usually fairly concentrated known solutions are added to the unknown so that only very small volumes are needed, thus not appreciably changing the total volume or the solution conditions. With this technique matrix effects are minimized since whatever happens to the sample also happens to the standard addition. Very precise results can be obtained with the method, and improved precision can be obtained if several standard additions are made.

### Other Electrodes

#### Introduction

In this section the other electrodes which were employed in this

study will be described. These electrodes were either mercury or mercury coated to take advantage of the high kinetic overpotential of hydrogen on mercury and on account of the solubilities of the various metals in mercury. Results will be given in subsequent chapters.

The major problem associated with the use of stationary electrodes is the difficulty in obtaining a reproducible "active" surface area. This difficulty is usually due to the fouling of the electrode surface by impurities or oxide formation. Thus reproducible limiting currents may be difficult to obtain. However, much larger currents are usually observed with stationary electrodes especially if stirring is employed.

### Stripping Analysis

A major advantage of stationary electrodes is their applicability to stripping analysis. Recently, there have been several excellent reviews of stripping analysis since this technique has become of increasing importance as a trace analytical technique (9-12).

If the potential applied is more negative than the half-wave potential of a particular reducible ion, then plating of the species on the stationary electrode occurs. This plating step, called the "pre-electrolysis step" may be classified as either stoichiometric or non-stoichiometric depending on whether it is carried to completion. After this step, the deposited species are stripped off anodically by sweeping the potential to more positive values. As the metal ions are returned to solution, a current peak occurs, the height of which is directly proportional to the concentration of the metal in the mercury. This step may also be either stoichiometric or non-stoichiometric. The

two non-stoichiometric steps in succession are probably the most commonly employed combination in stripping analysis, with a reproducible fraction of the reducible constituent being plated onto the electrode in the first step.

There is considerable improvement in the sensitivity and the limit of detection with the employment of stripping analysis as compared to classical polarography, because the diffusion current to capacitance current ratio is larger. However, the plating time, rate of stirring (if employed), and surface area must be carefully controlled in order to obtain reproducible results.

The stripping analysis technique cannot be employed for the determination of metals that do not form a mercury amalgam, e.g., chromium and iron. Another serious problem encountered in stripping analysis is the formation of intermetallic compounds in the mercury which increases as the concentration of certain metals is increased in the amalgam. Recently, a number of articles have appeared on this subject due to the increased use of stripping analysis as an analytical technique (13-21). In this study the zinc-copper intermetallic complex was observed. If copper ions are added to a solution containing zinc ions in which an anodic stripping voltammogram had already been obtained, a decrease in the zinc peak is observed for increasing concentrations of copper. Laboratories which perform many routine analyses for these particular metals usually employ calibration curves in which the concentration of zinc is plotted versus peak height of the zinc wave for solutions of given copper concentrations (22). Other steps that can be taken to lessen this effect are to either increase the thickness of the

mercury layer or to plate a smaller fraction of the species onto the electrode. Plating at a potential negative enough to reduce copper, but not zinc, allows the determination of the copper concentration in solutions in which the copper concentration is not otherwise known. In order to determine the zinc concentration in the same solution a potential which is negative enough to plate both metals is applied. The zinc concentration can then be determined from the previously described calibration curves.

#### Hanging Mercury Drop (HMDE) and J-Tube Electrodes

The hanging mercury drop electrode employed in this study was one in which a drop of mercury of known volume is squeezed out of the capillary by the turning of a micrometer screw.

The advantage of this electrode over many others is that fresh and reproducible surfaces may be rapidly obtained. However, one serious problem commonly observed with the use of the HMDE is that solution sometimes creeps up the walls of the capillary, thus restricting the column of mercury (23) and suddenly increasing the capillary resistance, resulting in distorted polarograms. This effect can be lessened somewhat by treating the glassware with a hydrophobic agent and/or by the employment of a capillary of special design (24).

The only differences between the hanging mercury drop and the J-tube electrode assemblies are the size and shape of the capillaries. The HMDE capillary is straight and approximately 0.2 millimeters in diameter whereas the J-tube electrode capillary, with a diameter of approximately one millimeter, is shaped as its name implies. The mercury droplet sits on top of the orifice of the capillary; thus the

drop is more stable than the mercury droplet suspended from the HMDE. Other advantages of the J-tube electrode over the HMDE are that larger drops can be employed, and the creeping of solution up the sides of the capillary is not as serious.

### Rotating Disk Electrodes

With most rotating or stirring electrodes the development of theoretical equations for the description of limiting currents has been very difficult due to the hydrodynamic complexities of the systems. Although some theoretical equations have been derived, these equations depend on the use of the Nernst diffusion layer model which is very difficult to determine experimentally.

However, accurate theoretical equations can be written for the rotating disk electrode because of the reproducible convection in this system. For this reason the RDE is becoming of increasing importance.

When the disk is rotated in solution, liquid adhering to the center of the disk is thrown outwards by centrifugal force to the periphery. Thus fresh solution from the bulk streams to the center of the electrode where it is also swept outwards as shown in Figure 4 (25).

It has been determined experimentally that the layer of deposited metals on the surface of the electrode is of uniform thickness, leading to the conclusion that the thickness of the diffusion layer is constant over the surface of the disk (27).

The equation developed by Levich which describes the limiting current is

$$i_L = 0.62 n F A C D^{2/3} \omega^{1/2} \nu^{-1/6} \quad (2-14)$$

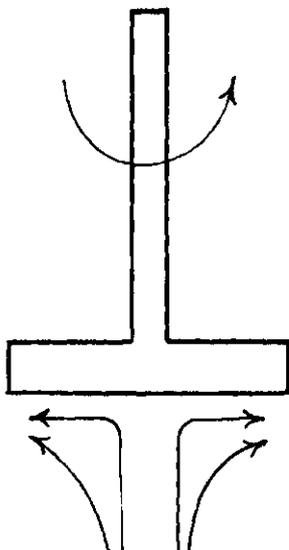


Figure 4. Solution Convection at the Rotating Disk Electrode (25)

where  $i_L$  is the limiting current in milliamperes,  $\omega$  is the angular velocity of the electrode and is equal to  $2\pi$  times the revolutions per second,  $\nu$  is the kinematic viscosity ( $\text{cm}^2/\text{sec}$ ),  $C$  is the concentration of the relevant species (formula weights/liter), and all other parameters have the same definitions as previously stated. When the electrode is used in stripping analysis, the time required in the pre-electrolysis step is greatly decreased because of the stirring of the solution due to the rotation of the electrode.

Platinum RDE. The rotating disk electrodes used in this study were of platinum and graphite. Oxide films and adsorbed hydrogen are serious problems encountered with the use of bare platinum electrodes since the kinetics of the electron-transfer processes are affected by these surface films. A surface free of oxides and hydrogen can be

obtained by cleaning the electrode by various recommended methods (28, 29). After cleaning the platinum surface a mercury film was applied. However, obtaining a homogeneous, reproducible mercury film on the electrode is difficult.

Graphite RDE. Graphite is becoming a more widely employed electrode material for several reasons. Low to moderate cost, the availability of high purity material, the wide operating potential range (approximately +1.3 to -1.3 versus SCE at pH 1-7), and the lack of oxide formation are several factors leading to the increased use of this material. Graphite electrodes are usually impregnated with wax to lower the residual current. Of the various waxes which have been used, Ceresin wax is the most widely employed (31).

Due to the thin film of mercury on the electrode, the concentration of reduced species in the amalgam is higher than with the HMDE thus more sensitive results can be obtained with the same plating time. However, oxide formation, adsorption, the changing of the surface with time, intermetallic compound formation, etc. are more of a problem than with the HMDE.

The results of the investigation of various procedures for obtaining reproducible results employing the RDE are presented in Chapter VI.

#### Square-Wave Polarography

If a small, square-wave voltage is superimposed on the usual slowly changing ramp voltage, periodic diffusion processes result at the electrode surface. These periodic changes in diffusion correspond to an alternating current. The capacitance current decays more rapidly

than the faradaic current, which is controlled by the relatively slow process of diffusion in re-establishing the concentration profile. Thus an effective separation of the faradaic and capacitance currents is attained if the current is measured shortly before each change in the half-cycle of the square-wave voltage. This greatly increases the sensitivity of the technique as compared to classical polarography.

The difference in the currents of the two successive half-cycles is plotted versus the dc potential which yields a curve whose shape as shown in Figure 5 is similar to the derivative of the normal polarogram. The current returns to the base-line value (usually zero) after each wave, thus allowing a better separation of reducible components and a better background.

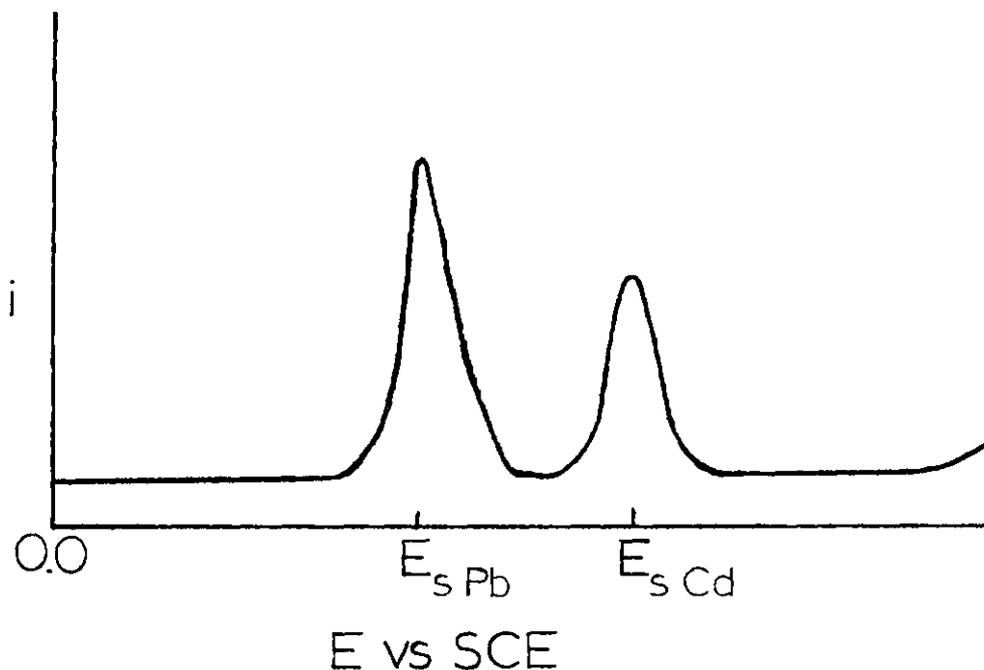


Figure 5. Square-Wave Polarogram of  $10 \times 10^{-4}$  F Lead (II) and Cadmium (II) in 1F Potassium Chloride

The analysis of a low concentration component which is reduced at a potential a little more negative than a major component is very difficult to determine in classical polarography due to the additive nature of the waves; however, as shown in Figure 10, this is much more easily accomplished with square-wave polarography.

### Capacitance Current

The electrode-solution interface behaves as a capacitor at the instant of the abrupt change in potential of each half-cycle. The capacitance current in one half-cycle follows the equation

$$i_c = \pm (\Delta E/R^*) \exp(-t/R^*C) \quad (2-15)$$

where  $\Delta E$  is the square-wave voltage,  $R^*$  is the cell resistance,  $C$  is the double layer capacitance, and  $t$  is the time measured from the beginning of the half-cycle. The plus sign corresponds to a charging process and the negative sign is indicative of discharging.

### Alternating Faradaic Current

Barker derived the following equation for the alternating component of the current for a reversible electrochemical reaction (32)

$$i = \pm \frac{n^2 F^2 C^b \Delta E}{RT(1+P)^2} \left\{ \frac{D}{\pi \tau} \right\}^{1/2} \sum_{m=0}^{\infty} (-1)^m \frac{1}{(m+\beta)}^{1/2}$$

where  $\beta = \frac{t}{\tau}$  ( $0 < t < \tau$ )

and  $P = \exp[(E-E_{1/2})nF/RT]$

Also  $E$  is the average potential during the drop life,  $E_{1/2}$  is the

half-wave potential of the particular species of interest,  $t$  is the time elapsed from the beginning of the half-cycle, and  $\tau$  is the half-period of the square-wave amplitude.  $C^b$  is the concentration in the bulk of the solution and  $D$  is the diffusion coefficient of the electroactive species in consideration. This equation holds for only small square-wave voltages, i.e.,  $\Delta E \ll RT/nF$ .

From an inspection of equation (2-16) the amplitude of the alternating current is at a maximum when  $P$  is at a minimum value.  $P$  is minimum at the half-wave potential, known as the summit potential  $E_s$ , in techniques that yield derivative type polarograms. To find the width at half-height of a peak where  $n = 2$ ,  $(E - E_{1/2})$  is calculated by setting  $i = 1/2 i_{\max}$ . For reversible species, 22.6 millivolts is obtained for  $(E - E_{1/2})$ . Since the peak is symmetrical this value is doubled; thus, the width at the half-height is 45.2 millivolts. For  $n = 1$  and  $n = 3$ , the values are 90.4 and 30 millivolts, respectively.

By comparing equations 2-15 and 2-16 it is seen that the decay of the capacitance current is proportional to  $\exp(-t/RC)$  whereas the faradaic current decays as a function of  $t^{-1/2}$ . Thus the larger the value for  $t$  and the smaller the value for  $R^*$ , the more effectively the two currents will be separated.

### Pulse Polarography

Pulse polarographic methods differ from square-wave polarography in that only one square-wave pulse is applied during the life of the drop or after a designated set time. There are three basic modes of operation: normal, derivative, and differential-pulse polarography. The differences in the three techniques are due to differences in the

applied potential before the imposition of the voltage pulse, whether pulses are constant or increasing, and the current monitoring methods.

#### Normal Pulse

At a predetermined time in the life of the drop, a square-wave pulse is applied for a duration of approximately 57 milliseconds. After the application of the pulse the potential returns to the initial potential (a ramp voltage is not applied). Then the next mercury drop is allowed to grow while a constantly applied initial potential is imposed on the electrode. At the same predetermined time a square-wave pulse of a little larger magnitude is applied. The current is measured during the last 16.7 milliseconds after the application of the pulse so that the charging current has decreased to a negligible value. To each succeeding drop a somewhat larger pulse is applied after which the potential is returned to the initial value.

The shape of the normal pulse polarogram resembles an ordinary polarogram except the currents for the same concentration of electroactive species are much larger.

#### Derivative Pulse Polarography

The only difference in this technique and normal pulse polarography is the manner in which the cell currents are processed. The measurement of the height of a peak is inherently more sensitive than the measurement of a plateau as in the normal mode and, as was discussed earlier, better resolution of the components is achievable with a derivative technique. The readout of this technique looks essentially the same as for square-wave polarography.

### Differential Pulse Polarography

In this method voltage pulses of equal magnitude are superimposed onto a slowly changing ramp voltage. The current is sampled at the end of the pulse application. The difference in the sampled currents between two succeeding drops is plotted against the potential yielding a derivative type curve.

### Square-Wave versus Pulse Polarography

Barker, who developed pulse polarography after square-wave polarography, concluded that the pulse technique was superior (33). He predicted that the detection limit for reversible species using the pulse technique was approximately four times lower than the square-wave technique ( $1 \times 10^{-8}F$  vs.  $4 \times 10^{-8}F$ ), and the limit of detection for irreversible species employing the pulse technique was approximately  $5 \times 10^{-8}F$  compared to approximately  $1 \times 10^{-6}F$  for the square-wave technique. This conclusion has been virtually unchallenged since then; thus, most of the polarographic instrumentation used today for low level determinations employs the pulse technique. The results of this study indicate that the supposed superiority of the pulse technique was probably due to the instrumentation employed rather than the inherent superiority of the technique. This section concerns the relative advantages and disadvantages of square-wave polarography as compared to the pulse technique.

In the pulse technique only one pulse is applied during the life of each drop of mercury. The current is measured for 16.7 milliseconds or some multiple thereof in order to filter out any sixty cycle line noise. In the square-wave technique the line frequency noise can be

more effectively filtered out because a continuous string of pulses are applied and thus filtering can be done effectively after sampling. The square-wave polarograph employed in this study also employed a gated integrator for current sampling rather than averaging the current with a filter network as was previously done. High frequency noise is effectively averaged out by this technique and a much larger current is obtained by integrating over a time period rather than recording an instantaneous current.

The major reason why Barker concluded the pulse technique was superior was because of the large  $iR$  drop which is encountered with the use of two electrode cells. Referring to equation 2-15 the larger the uncompensated resistance of the cell, the longer it will take the capacitance current to decay. Thus the charging current was larger for the square-wave technique due to the shorter delay time for current sampling. Since the delay time is much longer in pulse polarography, Barker could employ much more dilute supporting electrolyte solutions than he could with the square-wave technique. Thus the higher the salt concentration employed, the larger the residual current component due to trace impurities.

With the recent development of the operational amplifier polarograph employing a three-electrode cell (34), the resistance between the dropping mercury electrode and the auxiliary electrode can be minimized. Another feature incorporated in the instrument used in this study is a positive feedback loop (35, 36) which will be discussed more fully along with other instrumental aspects in Chapter IV. With the positive feedback loop the capillary resistance of the DME and the solution resistance

between the reference electrode and the DME can be compensated for. Thus with the shorter sampling times, the use of the gated integrator for current sampling, and effective compensation for resistance a much larger signal to noise ratio should be obtained with the square-wave technique.

One of the important considerations in laboratories where many analyses are performed is the analysis time per sample. The faster the scan rate for the polarogram, the less time involved for the determination. The usual scan rate employed with the pulse technique is approximately 5 mv/sec. Much faster scan rates are not possible with the pulse technique since the current is sampled only once during the drop life of four seconds. The resolution between peaks also decreases as the scan rate is increased with the pulse technique. As shown in Figure 11 scan rates of 50 mv/sec were employed with the square-wave technique (faster rates could have been used but were not available on the instrument) with excellent resolution and definition of peaks. Thus to scan the potential range from +0.1V to -1.2V (versus SCE) which is the potential range most commonly investigated takes only twenty-six seconds compared to four and one-third minutes at 5 mv/sec.

Although the square-wave technique is supposedly not as sensitive as the pulse technique for the determination of irreversible species, very low levels of these substances were determined with the instrument employed in this study (see Chapter V). However, a lower limit of detection for irreversible species can be a disadvantage depending on what elements are to be determined. Traces of oxygen and other irreversible species interfere with the determination of many reversible

metals. Thus if only the determination of reversible metals, e.g., lead, cadmium, copper, and zinc are of interest, then it would be more advantageous for the instrument to be less sensitive for irreversible species.

The other disadvantages of the square-wave technique as compared to the pulse technique which have been claimed in previous studies were investigated in this research project. The results of these findings will be given later in Chapters V-VII; only a brief discussion will be given in this section.

Usually square-wave and differential-pulse polarography are more affected by adsorption effects, particularly surfactants, than normal pulse polarography. Surfactants adsorbed onto the surface of the electrode tend to affect the rate of electrochemical transfer. Thus a thorough pretreatment of the sample when employing the square-wave technique must be performed. However, polarographic maxima do not plague the square-wave technique; thus surfactants are not needed.

Another problem that sometimes arises when employing the square-wave technique for the analysis of components below  $5 \times 10^{-7}F$  is "electrocapillary noise" with the DME (23, 37, 38). This problem arises due to fluctuations in wetting at the capillary orifice. Initially, no noise problems were encountered when working with concentration levels in this range except for one particular electrode that showed this phenomenon at potentials more negative than -1.0V. This problem can be remedied by employing another capillary or by using a capillary tip of special design as described by Cooke, Kelley, and Fisher (23). Capillary noise is also more pronounced if the capillary

is dirty. A layer of grease on the inside walls of the capillary usually intensifies the electrode noise as reported by Meites (39). Thus thorough cleaning of the DME can lessen the problem.

## CHAPTER III

## SOME GENERAL ASPECTS CONCERNING TRACE ANALYSIS

Introduction

Due to the increasing awareness of the important role of trace metals in physical, chemical, and biological systems, a new distinct field of analytical chemistry, known as "trace analysis" has emerged.

For a long time, the term "trace" in analytical chemistry meant that the concentration of a particular component was too low for quantitative determination. However, as instrumental and wet chemical methods were improved or developed, what was once considered a "trace" fell into the range of concentrations that could be determined. Thus the expression "trace analysis" has developed as a universally accepted concept for low level determinations (40-47). An analysis is called a trace analysis if the concentration of the constituent to be determined is less than approximately 0.01 percent by weight of the sample (48).

A most familiar example of how trace metals affect the physical properties of solids is the doping effect by trace metal impurities in semiconductors. Trace metals may also greatly affect the rate of a chemical reaction. Of particular interest is the role of trace metals in living organisms. Underwood (49) lists iron, copper, zinc, manganese, cobalt, molybdenum, and selenium as essential metals and barium and strontium as being probable essential elements for animals. Also of interest is the toxic effect of metals on plants and animals. As

more research is conducted, and even lower concentrations of metals are determined, probably more metals will be classified as essential. Some, as in the case of selenium, which are only considered very toxic will later be determined to be essential. Thus the monitoring of trace levels of metals in the environment will be of increasing importance.

#### Lower Limit of Detection

The lowest concentration of the species of interest that can be detected is known as the "lower limit of detection." The establishment of the lower limit of detection for a particular analytical method is based on the ability to differentiate between the signal representative of the component of interest and the blank signal.

The blank signal is composed of many contributing factors such as human errors, reagent impurities, airborne contamination, thermal electronic noise in amplifiers, sixty cycle noise, and others. Other than human errors which are minimized by good analytical technique, these factors can be generally classified as either chemical or instrumental variations. Due to the present state of electronics, the instrumental "noise" is usually much lower than the chemical variations which will be discussed later in this chapter.

The detection limit is expressed as either the absolute limit or the relative limit of detection. The absolute limit is the smallest detectable weight of the component of interest expressed in micrograms ( $\mu\text{g}$ ), nanograms (ng), etc. The lowest detectable concentration expressed in parts per million, percentages, micrograms percent, or micrograms per deciliter, etc. is the relative limit. Obviously the

relative method is far more meaningful to one not familiar with the sample size. The units used predominantly in this study are formula weights per liter or formality (F).

A literature review reveals that there is a lack of consistency in reporting the detection limits for the various analytical methods. Thus an unbiased, objective method should be employed to determine when the signal of interest can no longer be differentiated from the blank. Therefore a statistical definition for the lower limit of detection should be employed since the accuracy of a method is dependent upon the reproducibility or the precision of the method. As presented by Kaiser (50-53) a general definition for the value of the measured quantity at the lower limit of detection ( $\underline{x}$ ) applicable to any analytical technique is given by the following equations.

$$\underline{x} = \bar{x}_b = K\sigma_b \quad (3-1)$$

$$C = f(\underline{x}) \quad (3-2)$$

Referring to equation 3-1,  $\bar{x}_b$  is the mean value for a number of blank readings (at least 20) and K is the proportionality constant which is dependent on the degree of confidence required. The standard deviation ( $\sigma_b$ ) is defined by the equation

$$\sigma_b = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x}_b)^2}$$

where  $x_i$  is the  $i$ th value of  $n$  measurements of the blank.

There has been considerable disagreement over what value of K

should be employed in equation 3-1. Kaiser suggests that  $K$  should be equal to three since a strictly normal distribution cannot be pre-supposed; broader or assymmetric distributions must be taken into account. From Tschebyscheff's Theorem (assuming a normal distribution) the confidence level is at least 89 percent for  $K$  equals to three, whereas for  $K$  equals two the confidence level could be as low as 75 percent, which Kaiser points out is too low. However,  $K$  equals two is still most commonly employed. Whatever confidence level is chosen, it should be given when reporting the limit of detection for a particular method.

The analytical calibration,  $C = f(x)$ , symbolizes the correlation of the concentration ( $C$ ) as a function of the measured quantity ( $x$ ); thus, the concentration values at the lower limit of detection,  $\underline{C}$ , is accordingly determined by  $\underline{x}$ . The sensitivity of a technique, which is not synonymous with the limit of detection, is defined as the slope of this analytical calibration function.

#### Chemical Variation

The chemical impurities that can influence the blank reading can come from many sources such as reagent impurities, water, mercury, deaeration gases, airborne contamination, glassware, etc. This section will deal with the impurity problems encountered in this study and how they were or should be rectified.

#### Water

In preliminary work distilled water from a Barnstead still equipped with a Ventguard filter was used. However, as lower levels of metals were analyzed the more significant was the background due to the copper and zinc impurities in the water. Thus the distilled water was

passed through a mixed-bed deionizer to remove these trace impurities. However, inconsistent results were observed which were possibly due to the presence of flocculate deionizer particules in the water. To remove these deionizer particles, the water was then passed through a 22 centimeter column of activated charcoal on top of which was another mixed deionizer resin bed. The charcoal was precleaned by washing with hot hexane and ethanol, then by rinsing several times with dilute hydrochloric and nitric acids. The water quality was greatly improved by this pretreatment procedure. Acceptable water was also attained by passing tap water through two mixed-bed deionizers and finally through the column containing more deionizer resin particles and charcoal.

#### Container Contamination

Solutions may be affected in three ways by the container surfaces: (1) by adsorption phenomena, (2) by leaching, and (3) by the release of previously adsorbed species into the sample solution.

The adsorption of metals onto the surface of a container is dependent on the nature and concentration of ions in solution, pH values, contact time, the nature of the surface material itself, and how the surface was pretreated. Usually the adsorption of metals from acidic solutions is less than from neutral or alkaline solutions (47). In this study the pH was carefully controlled (usually pH 2.0-5.0) by the addition of buffering agents to the supporting electrolyte.

Generally, adsorption effects increase for the following sequence of materials: Teflon and other fluorine plastics, polypropylene, polyethylene, quartz, and glass (47, 54). Glass is generally regarded as unsuitable for trace analysis. However, glassware was employed in this

study, but only after the following steps were taken. Glassware was first cleaned by rinsing with several portions of hot alcoholic potassium hydroxide or hot acetone. Then the glassware was soaked in concentrated aqua regia, after which the equipment was first rinsed with the previously described pretreated water and afterwards with dilute ammonium hydroxide solution. After rinsing with dilute aqua regia, the glassware was then rinsed with copious amounts of water. When performing trace analyses, glassware should not be cleaned with chromic acid cleaning solution since adsorbed chromium is very difficult to remove (55-57). The impurities contributed by the pretreatment of the glassware with hydrophobic agents such as GE SC-87 were found to outweigh the positive effect of decreasing adsorption.

The adsorption of traces of metals after the glassware had been thoroughly cleaned was particularly noticeable. Before standard metal salt solutions were made up, the glassware was first equilibrated with a solution of the same pH, electrolyte concentration, and approximately the same concentration of the species of interest. This solution was then poured out and the standard solution was then made up in the volumetric flask. The standard solution was then transferred into a precleaned polyethylene bottle. Another procedure followed, when making up a standard solution of a particular metal, was to use the same volumetric in the future when making up solutions with this element. Dilute standard solutions, i.e., those below  $5 \times 10^{-7} F$ , were made up in precalibrated polyethylene bottles. When employing pipets, solution was first pulled through the pipet several times.

Adsorption was particularly noticeable while solutions were in

the electrochemical cell. To obviate this problem the cell was equilibrated at least one time (the number of times depended on the solution size and concentration of metals in solution to be analyzed) with a portion of the solution to be determined.

Another serious problem in trace analysis is the release of previously adsorbed metals on the container surface into the sample solution. This was especially noticeable when low standards or blank solutions were examined directly after the analysis of a solution containing a proportionately higher concentration of metals. This was very significant even after rinsing the cell and electrodes several times with water. It was found if the cell was rinsed with dilute hydrochloric and nitric acid (about 0.5F) and then with water, this problem was usually eliminated.

The leaching of impurities from container materials may also lead to a significant increase in the blank reading. Numerous analyses have demonstrated that the impurity level of containers follows the following increasing sequence: Teflon, polypropylene, polyethylene, quartz, and glass (58-63). Teflon and other fluorine plastics have been shown to be the most suitable materials for trace analysis; however, possibly due to the cost and lack of transparency of Teflon equipment polyethylene or polypropylene is more commonly used. If many analyses were to be performed employing this technique, disposable solution cells made of a plastic material such as polymethyl methacrylate (62) or polyethylene would lessen the problems mentioned above, since the degree of adsorption and impurity level in these materials is much lower than glass.

### Reagents

All stock solutions of metals (concentrations between  $10^{-3}$  and  $10^{-2}$ F) were prepared from either J. T. Baker, Mallinckrodt, or Fisher analytical reagent grade chemicals except for mercury (II) solutions which were made from triply distilled mercury. Cadmium, lead, zinc, and copper stock solutions were all titrated with a standard solution of EDTA by recommended procedures. The metal stock solutions were stored in polyethylene containers to avoid either leaching or adsorption effects.

In the past one of the chief disadvantages of polarographic techniques was the high concentration of supporting electrolyte that was required. This high concentration of supporting electrolyte made the blank value fairly large due to the impurities introduced. With the instrument employed in this study much more dilute electrolyte concentrations could be used (as low as 0.01F, but usually 0.1F) which greatly reduced the impurity level. However, as lower and lower concentrations of metals were analyzed, reagent purification became imperative. In this study controlled potential electrolysis, employing a mercury pool cathode, was used for electrolyte purification.

A nearly saturated solution of the salt was prepared from analytical reagent grade chemicals. Then, the solution was electrolyzed in a cell such as in Figure 6.

The solution was deaerated by passing nitrogen through the solution to remove oxygen, and then the gas dispersion tube was raised above the solution to keep a purge over the salt solution. The potential was set at a negative enough potential to reduce the commonly

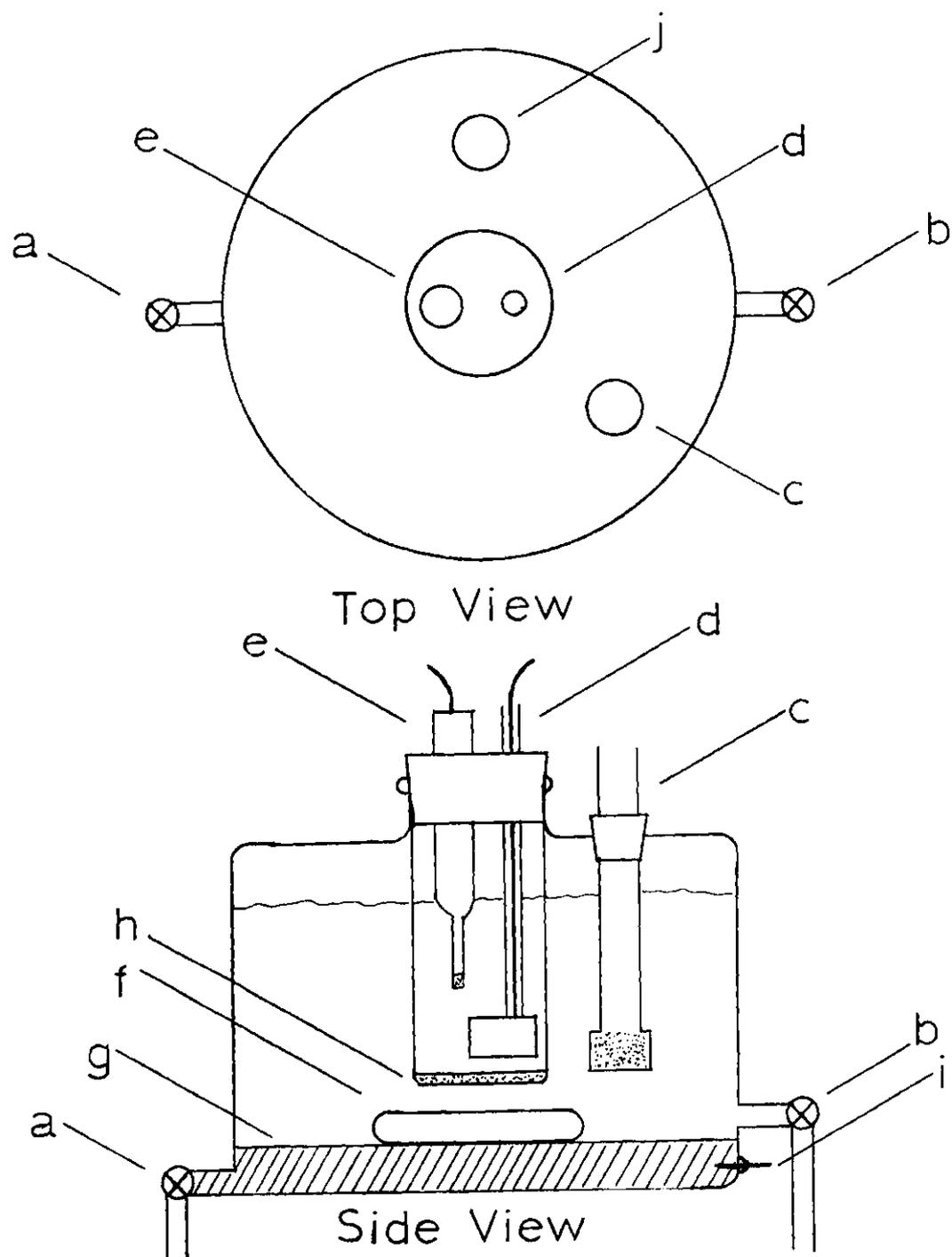


Figure 6. Electrolysis Cell for Reagent Purification (a - stopcock a (to drain the mercury); b - stopcock b (to drain the solution); c - gas dispersion tube; d - counter electrode; e - SCE (with a long salt bridge); f - magnetic stirring bar; g - mercury pool; h - fritted disk; i - electrical contact (platinum wire); j - addition port).

occurring impurities, usually at -1.3 volts (dependent on pH). The solution was stirred by using a large, magnetic Teflon-coated stirring bar, which floated on top of the mercury, with the cell resting on a magnetic stirring plate.

While maintaining the potential of the electrode the solution was drained out of stopcock B while pushing down the piston type inner cell in order to maintain electrical contact. Solutions were usually electrolyzed for at least 24 hours, then the solution was stored in polyethylene bottles or either dried down with a rotoevaporator and then the salt was stored in reagent bottles.

The mercury employed in this study was Bethlehem triply distilled mercury. In most instances the impurity level in the mercury was fairly low; however, an occasional lot would be received which contained a relatively high level of metal impurities. The mercury was purified by imposing a potential positive enough on a mercury pool electrode so that commonly occurring impurities were anodically stripped out of the mercury.

As was pointed out in Chapter II, oxygen produces two broad irreversible peaks at approximately -0.2 and -1.0 volts. If there is dissolved oxygen in a solution in which a mercury film or hanging drop electrode is used as the working electrode, a coating of mercury oxide is likely to form which lowers the effective surface area of the electrode and affects the electrochemical reaction rate. Thus oxygen is usually removed by bubbling an inert gas, such as nitrogen, through the solution. Many times, however, the deaeration process introduces impurities such as traces of oxygen and organics from the nitrogen, and

metal impurities, especially rust, from the gas lines. Thus the nitrogen gas was first passed through a quartz tube containing copper turnings heated to approximately 500°C, so that any oxygen would combine with the copper to form copper oxide. When a new tube was first employed, copper and cadmium impurities increased as the deaeration time was increased. To rectify this, the nitrogen stream, after having passed through the hot copper turnings, was first bubbled into a trap containing a saturated solution of sodium ethylenediaminetetraacetate (pH 10) and then into a trap containing water. The Tygon tubing leading from the last trap to the cell was packed with activated charcoal to help remove any other impurities including water vapor.

#### Airborne Contamination

Airborne contamination may contribute a significant level of impurities to the solution to be analyzed. These contaminants which are in the form of dust, volatile compounds, aerosols, and vapors come from ceilings, floors, paint, fumes from engines, personnel, clothing, etc. Essentially everything in the laboratory can be considered a source of contamination. Sample pretreatment procedures such as dissolution, digestion, and evaporation are probably the most affected by airborne contamination because of the use of muffle furnaces, fume hoods, ovens, and hot plates. In addition, the longer preparation times for these procedures increases the period of exposure to the laboratory atmosphere.

The recent development of high-capacity air filters (64) has brought about an effective means of removing particulate matter from air so that whole rooms or "clean rooms" may be made virtually dust

free (65). Generally most clean rooms described in the literature have walls, ceilings, and floors sealed, and construction materials which are known to significantly contribute to air contamination are not used (43). Clean rooms are flushed with either a vertical or horizontal laminar flow of filtered air and some employ air locks to separate the room from the rest of the building.

As a less expensive means of greatly reducing airborne contamination plastic, Plexiglas, or polyethylene glove boxes which are purged with purified air or some inert gas such as nitrogen may be employed.

#### Other Considerations

In order to depict some of the other aspects of trace analysis several of the other considerations in the analysis of a water sample will be discussed.

Assuming that a representative sample has been obtained, the sample should be stored in a container consisting of a material which has no significant level of impurities and does not exhibit adsorption effects. It has been found that water samples can be stored in polyethylene bottles at pH 2 (with the addition of nitric acid) without any significant change in trace metal concentration.

The trace metals to be determined exist in a so-called sample matrix. The matrices concerned may include biological material, organic compounds, and inorganic materials which may vary widely in their relative concentrations. The matrix may be used as the medium or supporter for the determination of the trace metals if it does not interfere with the determination of the elements. Many times substances such as surfactants are present which may seriously affect the

determination even when present in minute amounts. Many other types of interferences may plague the analysis. Thus if the sample matrix interferes with the determination of the trace elements, the sample must be pretreated before analysis can be performed. The method of pretreatment depends upon the particular sample matrix.

An example of a type of water sample which usually requires pretreatment is a river water sample containing considerable quantities of biological matter.

The volume required for a polarographic analysis varies with size and geometry of the cell. Cells with a total capacity as small as 0.01 milliliters have been made (66); however, little applied use of these cells have been made. Since large electrodes were used, the particular cell employed in this study required 20 milliliters of solution. A reasonable cell size for routine analysis (for stripping analysis or for work with the DME) is one requiring three milliliters total volume. If a 0.5 milliliter portion of a sample is digested by the procedure recommended in Chapter VII and the residue is taken up in three milliliters of supporting electrolyte medium, the concentration of the metals which was initially very low will be further decreased by a factor of six. This is one of the major problems encountered in fields of microanalysis such as clinical chemistry where commonly encountered sample portions are in the order of 100 microliters. If a large sample size is available and a larger portion such as 100 milliliters is digested, then a 33-fold increase in the concentration of the metals has been accomplished. Other commonly employed methods of enrichment and separation are extraction techniques, precipitation,

volatilization, controlled potential electrolysis, and ion exchange chromatography.

The standard addition technique was found to yield more accurate results than the calibration curve technique. The principal reason for this is that the matrix for the sample and the spiked sample solution is almost the same since very little dilution has occurred (typically five microliters to 25 milliliters of solution). It is well established that the signal usually differs for an equal concentration of a metal in different matrices. Other reasons for selecting the standard addition technique are given in Chapter V.

As was pointed out earlier, the total analysis time is of considerable concern in trace analytical determinations since generally the longer the time required for the analysis the greater the probability of the inclusion of significant levels of impurities.

Other important considerations are the complexity (chemical and instrumental) of the method and the number of manipulations which greatly magnify the probability of human error.

The trace analysis of metals will be of increasing difficulty as the demand for the determination of lower concentrations of metals increases, the sample sizes become wider in range, and the complexity and novelty of the samples increase.

## CHAPTER IV

## INSTRUMENTATION AND EQUIPMENT

Instrumental Description

The square-wave polarograph employed in this study was designed and built by the Chemistry Department electronics shop. The instrument is of solid state circuitry. A number of the features of a previously designed instrument (67) were incorporated in this polarograph. A general discussion of the aspects of this square-wave polarograph is presented with the functional diagrams.

Potential Control

The polarograph contains three internally generated potential inputs that are combined and imposed along with two feedback signals, one of which may or may not be present, onto the summing point of the potentiostat (see Figure 7). These three internally generated potential inputs are: (1) the initial potential, (2) the DC ramp, and (3) the square-wave functions.

Initial Potential. The initial potential is a DC voltage level within the adjustable potential range of  $0 \pm 2$  volts with a ten-turn potentiometer. A polarity switch and a voltage divider switch on the front panel of the instrument selects whether the voltage is  $\pm 1$  volt or  $\pm 2$  volts.

DC Ramp. The sweep generator located on printed circuit card one (PC 1), is an active integrator consisting of amplifier 1 (A1), a five

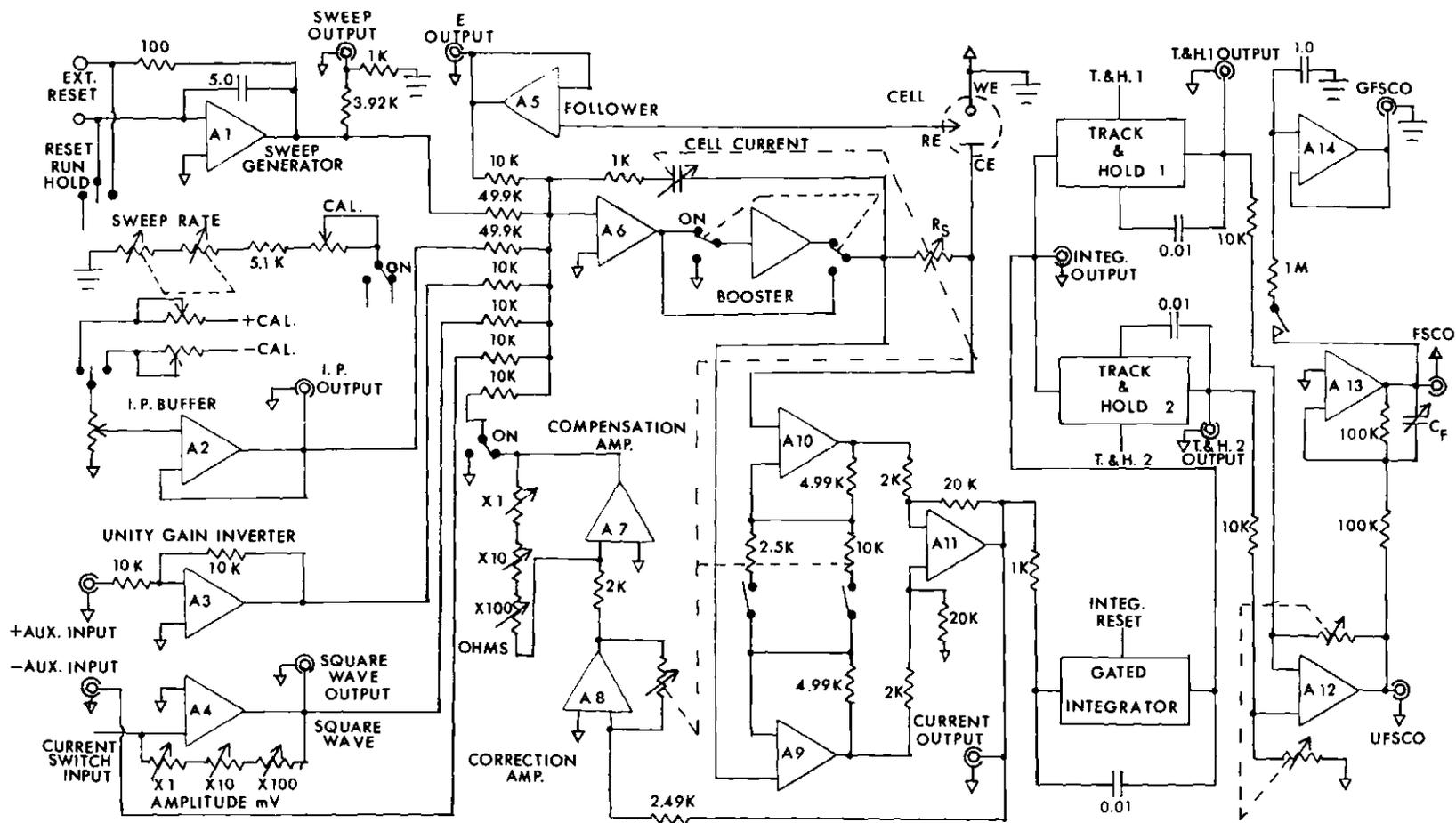


Figure 7. Square-Wave Polarograph Functional Diagram (All resistances are in ohms and capacitances are in microfarads. Abbreviations employed: GFSCO - gated, filtered, sampled cell current; UFSCO - unfiltered sampled cell current; Integ. - integrator; Aux. - auxiliary; Ext. - external; I.P. - initial potential; WE - working electrode; CE - counter electrode, RE - reference electrode.)

microfarad feedback capacitor, and selectable input resistances which produce linear voltage ramps when a DC voltage is applied to the input. A polarity switch is used to generate sweeps of either polarity and the sweep rate is selected by a switch in a 1-2-5 sequence from 1 to 50 millivolts per second.

Square-Wave. The square-wave generator produces a continuous 50 percent duty cycle pulse, of a polarity, amplitude (0 to 100 millivolts), and frequency (15 to 1000 Hertz), determined by front panel controls. The frequency and polarity conditions are determined by the digital logic which feeds a signal at the proper frequency to one of two controlled current sources on PC 5.

Cell Voltage Control Loop. The potentiostat or the cell voltage control loop is of three electrode design with the test (DME) electrode connected to signal ground (34). The cell voltage control amplifier A6 produces an algebraic sum of up to seven inputs and drives the cell or the booster (depending on whether the booster is "in" or "out"). With the booster "out" A6 can supply up to  $\pm 10$  volts and  $\pm 20$  milliamperes to the cell. The negative feedback loop for A6 is through a voltage follower (A5) which has a high input impedance. Since the reference electrode (RE) only connects to the input of A5, no current goes to the reference electrode; thus, the current must flow through the DME. The voltage at the cell voltage output (output of A5) is equal to the algebraic sum of the external and internal inputs to the control amplifier. This output is equal to the reference to working (ground) electrode potentials in the cell. The booster (Figure 7) is driven by the control amplifier A6 and has an output capability of  $\pm 25$  volts

and  $\pm 2$  amperes to the cell. The voltage gain of the circuit is approximately four. The additional voltage and current provided for the cell with the booster decreases the cell current decay time, thus allowing a better separation of the capacitance and faradaic currents.

Positive Feedback. In Chapter II the importance of effectively lowering the cell resistance to a minimum value was pointed out. Referring to equation 2-15 the capacitance current decays as a function of the RC time constant. Thus the lower the resistance, the faster the capacitance current decays. The cell resistance is composed of the internal resistance,  $R_i$  and the external resistance,  $R_e$ .  $R_i$  consists of the capillary resistance (DME), and the cell resistance between the reference electrode and the DME (68). The capillary resistance is constant whereas the solution resistance between the reference and the working electrode varies as a function of the surface area of the electrode.  $R_e$  is the solution resistance between the auxiliary electrode and the working electrode and as was discussed in Chapter II is virtually eliminated by the use of the three electrode cell.

With the employment of a positive feedback system (35, 36) compensation for the internal resistance can be attained (Figure 8). The input to the compensation circuit is the output of the cell current amplifier (A11). The cell current amplifier produces a voltage proportional to the cell current. The conversion factor (milliamperes/volts) is selected by the cell current switch on the front panel (0.2 to 500 ma/v). When the cell current switch is rotated, one of three resistors is placed in series with the cell. The voltage across a resistor is proportional to the cell current and is monitored by the

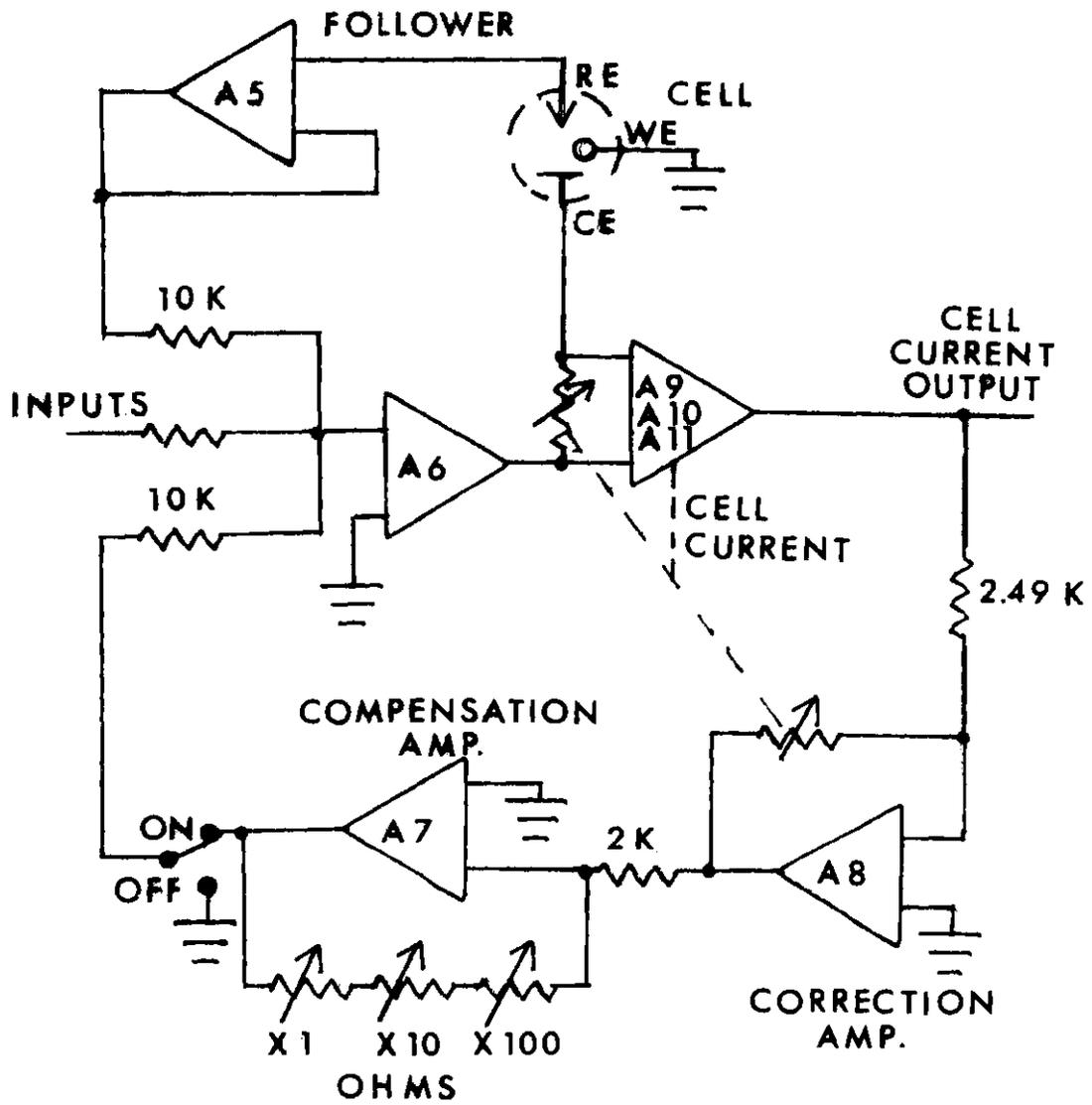


Figure 8. Positive Feedback Loop

differential amplifier (A11).

The compensation or positive feedback network can be employed to compensate for up to 999 ohms of resistance in most of the current ranges by the relative positioning of three thumbwheel switches on the front panel. The positive feedback required depends on the cell geometry, the nature of the supporting electrolyte, and its concentration. To ascertain the optimum feedback for a particular solution the cell current was monitored on an oscilloscope as a function of time and the compensation was adjusted to just before the circuit oscillated. Figure 9 shows the effect of compensation in lowering the capacitance current. However, one major difficulty is that the degree of compensation attainable is limited by the propagation delay of the feedback circuit. For example, if the compensation is optimized at about 0 volts, and a cathodic sweep initiated, the double-layer capacitance decreases with increasingly negative electrode potential, and a point will be reached at which the cell control loop becomes unstable. Thus many times the scan must be stopped at -0.5 volts and the compensation decreased before the scan is completed.

#### Control Logic

The control signals are derived from a timing chain which is fed from a Colpitts type oscillator operating at 400 kilohertz. Another modification which helped reduce the beat frequency and harmonic noise due to the oscillator frequency was to derive the timing and control clock logic from the 60 Hertz line frequency.

The transistor-transistor logic (TTL) controls the generation of the square-wave and the operation of the gated integrator and the track

and hold circuits. The logic also generates the cycle trigger which energizes a solenoid that dislodges the mercury drop of the DME every four seconds. The square-wave, integrator, and track and hold controls are enabled continuously.

The transitions at each half-cycle of the square-wave are used to initiate either a 400 to 800 microsecond delay. The delay is used to allow the capacitance current to decay to a negligible value before current measurement. After the delay the gated integrator is switched to the integrate mode and the cell current signal is integrated until five microseconds after switching the track and hold module to the hold mode, to eliminate errors which may be caused by resetting the integrator and simultaneously switching the track and hold modules to the hold mode. Then the integrator is held in the reset mode for either 395 or 795 microseconds after which it is switched again to the integrate mode and the cycle is repeated continuously.

#### Differential Current Measurement

The integrator gain depends on the integration time constant and the integration time; thus, each particular combination of frequency and delay time produces a different effective gain. A gain in the cell current signal of up to 250 is provided by the integration process which also greatly reduces the sample and hold error due to high frequency noise.

The track and hold modules are used to store the integrated cell current values before each transition of the square-wave. The difference in these values is then amplified to produce the differential sampled cell current output. If a square-wave is not applied to the

cell then the sampled cell current is about zero. If a positive square-wave is applied to the cell, track and hold module 1 (T & H 1) stores the value of the baseline current (the current without the square-wave voltage applied) while T & H 2 stores the value of the cell current with the square-wave applied. If a negative square-wave pulse is applied the track and hold modules reverse their roles.

The track and hold circuits are switched to the track mode and track the integrator output the last 2.5 percent of a square-wave half-cycle with the track mode being enabled on alternate half-cycles for the two modules. The value of the integrator output is held by the track and hold unit until the next square-wave cycle.

The difference in the voltage stored in the track and hold circuits is amplified by the sampled current amplifier by a selected value of 1 to 100. A low-pass active filter following the differential sampled current amplifier reduces noise due to the track and holds and other sources.

When a new drop emerges from the DME, the current increases rapidly as a function of time until the area of the mercury drop does not increase appreciably. Thus if the current is measured during this early life of the mercury drop, large fluctuations in the baseline are incurred. To avoid this, the output of the difference amplifier is sampled by a relatively slow track and hold circuit. The circuit is switched to the hold mode during the first two seconds of the four-second cycle. Prior to incorporating the slow track and hold circuit, the square-wave, the integrator, and the track and hold functions were disabled during the first two seconds and for the latter two seconds

were enabled. However, due to the relatively short time constants in the track and holds, critical zero adjustments were required to prevent their outputs from drifting during the two-second interval while in the hold mode. This modification eliminated these problems by allowing the high speed track and holds to operate continuously and using a low speed track and hold to "gate" the sampled cell current output.

#### Power Supplies

All power supplies, except for a regulated +24 volt supply used to power the lamps and relays, employed in the square-wave polarograph are standard commercial power supplies.

Two Sorensen model QSA-28-2 power supplies provide power ( $\pm 30$  volts) for the booster amplifier and the current amplifiers. Active current limit circuits are contained in these supplies and an external overvoltage protection module is adjusted to trip at 33 volts.

A Lambda model LZS-30 supply provides +5 volts at up to 0.9 amperes to the control logic. A Hybrid System Model C-500-15 supply provides  $\pm 15$  volts at 0.5 amperes to the analog circuits.

#### Digital Panel Meter (DPM)

An API Instruments Model 4304,  $3\frac{1}{2}$  digit DPM was incorporated in the instrument in order to monitor the initial potentials, cell voltage, cell current, and sampled cell current signals.

Four pairs of pushbutton switches on the front panel of the instrument allow a readout of the four functions and the range of the functions in volts or millivolts.

#### Drop Kicker Circuit and Assembly

The drop kicker driver consists of a monostable multivibrator

and a power switching circuit to produce 0 to +24 volt pulses to the solenoid assembly. Once every four seconds the monostable multivibrator is triggered by a positive transition of the logic signal. The multivibrator pulse width and hence the energy applied to the solenoid is adjusted by a rear panel potentiometer.

A hammer driven by the solenoid laterally strikes the capillary detaching the mercury drop. A Tacussel Electronics Model MP03 drop knocker assembly is employed for this purpose.

#### Other Equipment Employed

All of the other equipment employed is commercially available and will be briefly discussed in the following sections.

#### Measuring Stand and Electrochemical Cell Assemblies

A type CPR-3-B Tacussel measuring stand served as the cell holder and the faradaic cage. The faradaic cage made of two half-cylinders of perforated steel was used to shield the electrochemical cell system from picking up electromagnetic radiation noise. An electronic temperature controller and pump included in the assembly were not usually used.

The electrochemical cell employed is also manufactured by Tacussel. The jacketed cell is made of Pyrex glass and consists of a top half which has five holes in the top for the electrodes and a tapered bottom half which contains the solution to be analyzed.

A medium porosity gas dispersion tube was employed for the deaeration of solutions in the cell. It was found that much less time was required for deaeration if the fritted portion is sealed down to the end so that nitrogen gas bubbles are only emitted from the bottom

of the bubbler.

### Electrodes

As was discussed earlier, a three-electrode cell consisting of a reference, counter, and working electrode was employed in this study. The following commercially available electrodes were employed.

DME. A 2 to 5 second Sargent-Welch capillary was connected by Tygon tubing to a Pyrex reservoir containing mercury. The capillary was cleaned by first pulling spectral grade acetone, concentrated nitric acid, and then pretreated water through by vacuum. The Tygon tubing was cleaned by first washing with acetone, then with 2F hydrochloric acid, and finally with water. The Pyrex reservoir was cleaned by the same procedure as in Chapter III.

Hanging Mercury Drop Electrode (HMDE). The Beckman 39016 hanging mercury drop electrode assembly was used. This unit was used also with the J-shaped capillary tubes for the sitting drop electrode employed in this study.

Rotating Disk Electrode. The Beckman Rotating Electrode System consisted of the variable speed drive assembly (3-100 revolutions per second), the electrode assembly, and the vitreous carbon and platinum electrode tips was employed for research involving the rotating disk electrode.

Reference Electrode. The most commonly used reference electrode employed in the electrochemical cell was the porous ceramic junction Fisher Dri-Pak calomel electrode. If perchloric acid is employed to digest biological samples or if a perchlorate electrolyte is used, a double salt bridge system is needed to prevent the blocking

of the salt bridge by the formation of sparingly soluble potassium perchlorate.

Counter Electrode. The counter electrode simply consists of a square, thin piece of platinum (surface area about 2 cm<sup>2</sup>) sealed into the end of a hollow glass tube inside of which electrical contact is made to the lead from the instrument.

#### Oscilloscope

A Tektronix Model RM 31A oscilloscope with a type H plug-in unit was employed for the monitoring of various instrumental functions such as voltage, cell current, and the integrator output.

#### Recorder

A Hewlett-Packard 7004A X-Y recorder was used for the recording of all polarograms.

#### pH Meter

pH measurements were made with a Corning Model 7 pH meter after calibrating the instrument with 0.05 F potassium acid phthalate or saturated bitartrate buffer solution.

## CHAPTER V

EXPERIMENTAL RESULTS EMPLOYING THE  
DROPPING MERCURY ELECTRODEOptimization of Instrumental Parameters

The first phase of this research project was to determine the optimum instrumental parameters while employing the DME as the working electrode. The optimum instrumental parameters for functions such as frequency, square-wave amplitude, sweep rate, etc., are given in the following sections.

Frequency

Poole (69) mentioned previously that in employing phase selective AC polarography the background (blank value) for many supporting electrolytes differs with change in frequency. In order to study this effect a 0.2 F sodium sulfate-0.01 F sodium tartrate solution (pH 4) containing  $1.0 \times 10^{-6}$  F cadmium (II) was studied. The timing circuit card based on the 60 Hertz line frequency (with 15 and 30 Hertz being the only selections) and the other timing circuit card (with 20, 50, 100, 200, 500, and 1000 Hertz frequency selections) were both employed.

Obviously, if the current is integrated during a square-wave half-cycle after a predetermined delay time, the lower the frequency the longer the cell current is integrated. Thus, a larger integrated current value is obtained (if all other instrumental parameters are the same) at 15 Hertz than at any of the other frequencies employed.

Therefore, in order to obtain a signal of measurable size at higher frequencies, the recorder sensitivity or the differential sampled cell current gain must be increased.

A low, broad wave between 0.0 and -0.5 volts was observed when analyzing very low levels of metals. This phenomenon was reported previously by Liddle and Buchanan (70, 71) who also employed square-wave polarographic techniques. The difference in the maximum and the minimum heights of this peak was measured versus the peak height of the cadmium wave. To insure that the solution contained no oxygen the cell was deaerated for ten minutes. Also the solution was changed often to avoid losses in cadmium due to adsorption effects. From this and similar other investigations the ratio of the cadmium peak height to the background value was largest at 30 Hertz. For example the ratio obtained in this particular study for 30 Hz was nearly twice the ratio obtained at 200 Hertz.

#### Square-Wave Amplitude

The larger the square-wave amplitude applied to the electrode, the larger the measured cell current signal. However, as Osteryoung (72) reported for pulse polarography, the peak width increases as a function of increasing square-wave voltage. For reversible species the peak width at the half-height approaches the theoretical values (see page 32) when small voltage pulses are employed. However, since very low concentrations of metals were being determined, a relatively large square-wave voltage pulse was applied (usually 50 mv) which resulted in peaks approximately 60 mv wide at the half-height (for  $n=2$ ). Obviously, if the resolution between two peaks is poor, then a lower

square-wave voltage should be employed.

The square-wave polarity depended on the directions of the voltage scan. If the scan was in a cathodic direction the potential step function was always a negative stepping function. Conversely if an anodic scan was employed, as in stripping analysis, the potential step function was always positive or in the same direction as the voltage ramp function.

#### Sweep Rate

Generally, one of the disadvantages of analysis employing the DME versus the stripping techniques is the usually much longer time required to complete the voltage scan. If the sweep rate is much faster than 5 mv/sec (with the DME) there is a problem in obtaining reproducibility and there is usually a reduction in peak height.

#### Compensation and Delay Time

Obviously, the shorter the delay time the larger the sampled current signal obtained. However, when employing a supporting electrolyte concentration of less than 0.1 F, the capacitance current (background) is usually significant even with positive feedback compensation. Thus an 800  $\mu$ sec delay time rather than a 400  $\mu$ sec delay time was employed at 500 and 1000 Hz.

Figure 9 shows the effect of compensation in reducing the background for a 0.03 F sodium sulfate solution containing  $1 \times 10^{-6}$  F cadmium (II). With a supporting electrolyte concentration of approximately 0.1 F, employing 800  $\mu$ sec delay time, and compensation optimized, the background observed is much smaller than in Figure 9.

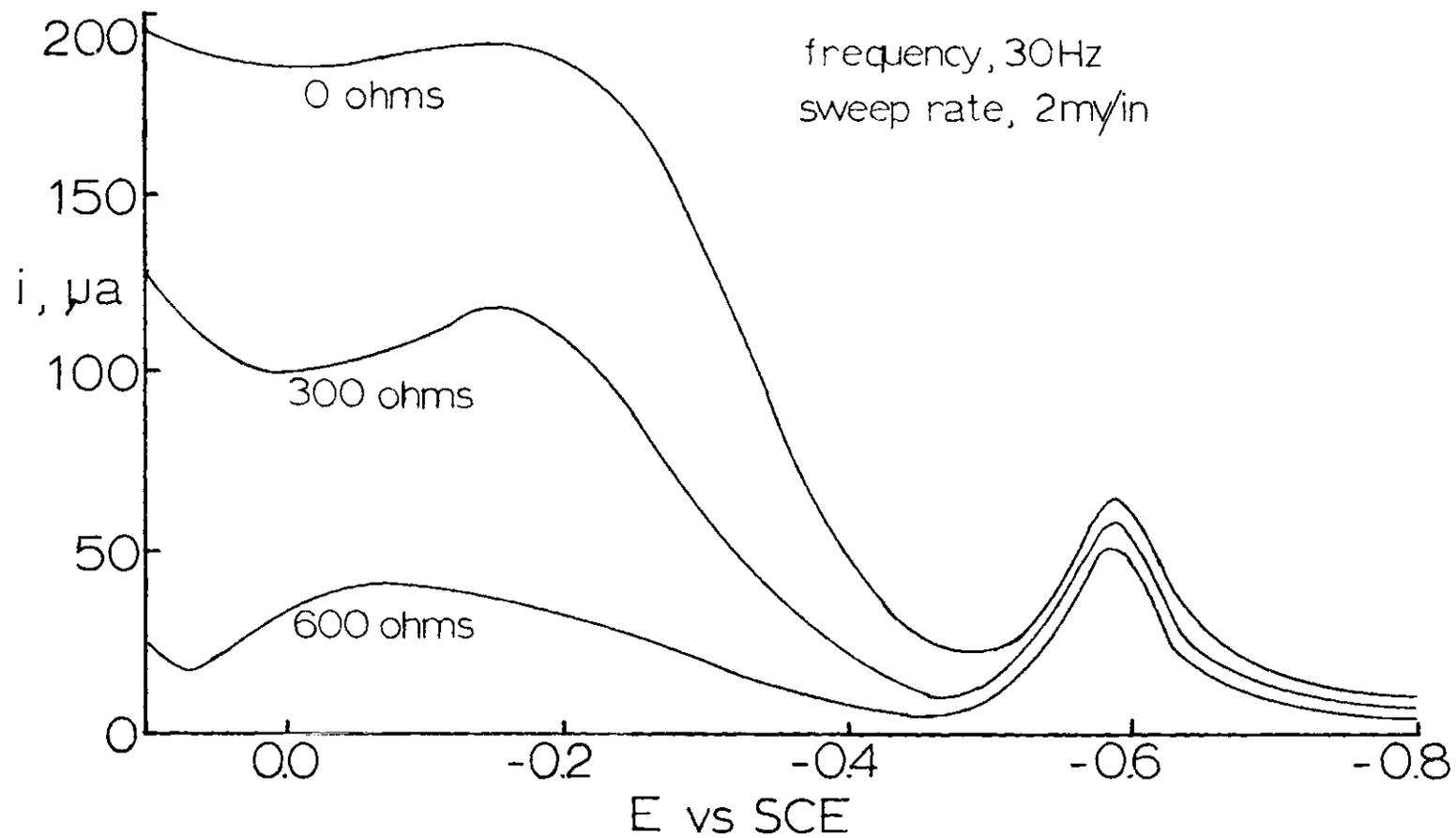


Figure 9. The Effect of Positive Feedback Compensation in Reducing the Background Current ( $0.03F Na_2SO_4$  supporting electrolyte with  $10^{-6}F Cd(II)$  added.)

### Solution Optimization

The second phase of this study was to determine the most suitable supporting electrolytes for the determination of single and multi-component systems. After a review of the recommended supporting electrolytes for the determination of selected metal ions (73-75), a study of these electrolytes was first undertaken. Many electrolytes which are recommended for classical polarographic techniques, where higher concentrations of the metals are present, are not suitable for very low level determinations because of background interferences or the high level of impurities introduced with the high concentration of supporting electrolyte.

The choice of supporting electrolyte and its concentration is of primary importance since these factors affect the characteristics of the reduction wave of a component in a variety of ways, as will be discussed in the following sections.

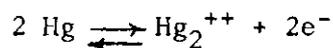
#### Choice of Supporting Electrolyte

The diffusion current coefficient,  $I$ , varies with the supporting electrolytes employed. Thus, with equal concentrations of a component, a much larger peak height may be observed in one electrolyte than in another. This may be because the species may diffuse much slower in one medium than in another due to the relative size of the complex formed. Also the effective charge of the complexed species may vary from one medium to another. In addition, the electrochemical reduction rate and thus the reversibility of the reaction may be influenced by the ions which are formed.

Another important consideration in choosing a particular

supporting electrolyte is the selectivity obtainable. The half-wave potential for a metal (as shown in Table 1) is greatly influenced by the supporting electrolyte. Use of an electrolyte which allows freedom from interfering reduction waves may be at the expense of sensitivity. Many electrolytes such as 0.1 F potassium chloride medium (pH 7) allow the sequential determination of copper, lead, cadmium, zinc, and manganese in parts per billion levels. Another electrolyte such as oxalate medium may be better for the determination of trace levels of copper; however, all of the other elements cannot be determined in parts per billion levels in the oxalate medium.

Mercury Dissolution Wave. One of the major interferences in the determination of metals which are easily reduced, is the mercury dissolution wave. This wave is due to the anodic current resulting from the following reaction:



The standard potential of this reaction is +0.553 volts (versus SCE). However, solutions containing ions that form insoluble salts or complex ions with the Hg (I) or Hg (II) ions shift the anodic wave of mercury to more negative potentials.

It was observed that the longer a solution was deaerated the more significant was the mercury anodic wave. This is probably because the nitrogen bubbles impinging on the DME caused the detachment of very small mercury droplets, thus greatly increasing the surface area of mercury exposed to the solution. After a five minute deaeration process, the mercury dissolution wave was quite significant. It was

found, however, if the DME was raised above the solution during de-aeration (allowing the normal droplets to fall by force of gravity into the solution) the mercury anodic wave was much less of a problem. Also the longer the solution is in contact with the mercury droplets on the bottom of the cell, the greater the mercury anodic wave.

pH. Another important solution parameter which must be controlled is pH. The half-wave potentials for certain elements are greatly affected by the pH of the medium. For example, the half-wave potentials for the iron (III)/iron (II) complex in 0.5 F tartrate media range from -0.17v at pH 5.8 to -1.2v at pH 9.4 (76). The reversibility of the reduction wave may also be greatly affected by pH. Another important reason for pH control is the hydrogen reduction wave; the higher the hydrogen ion concentration, the more positive will be the potential at which hydrogen will be produced. Thus, for the submicroformal determination of manganese, acidic media cannot be used.

#### Elemental Analysis

Table 1 represents the compiled findings for some of the electrolytes employed for the determination of several elements. The first column represents the oxidation state of the element. The second column gives most of the supporting electrolytes employed; the third column shows the corresponding summit potentials ( $E_s$ ) for the metallic elements in these supporting electrolytes. The final column contains a description of the reversibility for the polarographic wave, general comments concerning the use of the particular electrolyte for the determination of the indicated element, and the approximate lower limit of detection for the given electrolyte medium. The lower limit of detection in most cases

is estimated by measuring the peak heights at low concentrations and then extrapolating back to where the analytical signal to noise (background) ratio is three to one. An estimate of the lower limit of detection is not given if it is felt that a reasonable approximation cannot be obtained.

It should be pointed out here that even lower levels of these metals probably could have been detected if the electrochemical cell had not been made of glass. If a standard addition is made to a glass cell containing a very low concentration of the metal of interest, some or almost all of the metal ions added may be adsorbed. Another important factor which should be considered is that the instrument was designed for work with much larger electrodes than the DME. If the instrument had been designed for work with very small electrodes, more sensitive current measurements would have been possible. The expression "NA" in columns three and four means that a microformal concentration of the metallic species in the particular supporting electrolyte listed does not yield an observable wave, or that the medium is not acceptable as compared to the other electrolytes listed.

#### Antimony

The antimony wave is not very well defined in non-complexing media such as nitric and sulfuric acids, but as the chloride content is increased the reduction wave for antimony becomes more well defined as shown in Table 1. This is because the reduction of the tetrachloroantimonate (III) ion ( $\text{SbCl}_4^-$ ) is easier than the reduction of the antimonyl ion ( $\text{SbO}^+$ ). As Poole (77) pointed out earlier, the chloride concentration and the acidity must be fairly high to obtain reversible

waves for this element. Antimony (V) does not give a very reversible polarographic wave thus antimony should be in the +3 state for analysis.

The limiting factors for the determination of antimony are the mercury dissolution interferences and the impurity level that is usually present when such a high level of supporting electrolyte concentration is employed. However, even with these difficulties, the detection limit employing 0.5 F hydrochloric acid or a sulfuric-hydrochloric acid mixture is about  $5 \times 10^{-8}$  F antimony.

One of the advantages of this method for the analysis of antimony, other than the low detection limit, is the very good separation of the antimony and arsenic waves. Submicroformal amounts of both elements can be determined on one polarographic scan. Bismuth and copper may interfere in the determination of antimony; however, several electrolytes allow an effective separation of these elements.

#### Arsenic

Arsenic, just as antimony, is determined in the +III oxidation state employing a complexing electrolyte. Arsenic does not have a very reversible wave in any electrolyte medium, but due to the flat background, very low levels of arsenic can be determined. The optimum electrolyte which was employed for the determination of arsenic was 0.5 F hydrochloric acid which gave a broad but large wave with a summit potential of -0.44 volts and another wave which is of very little quantitative use at approximately -0.9 volts.

Other electrolytes such as tartrate media, sulfuric, and nitric acids did not give very useful waves for the analysis of submicroformal concentrations of arsenic. The background and the peak height

found for the arsenic (III) to elemental arsenic wave ( $E_s = -0.44v$ ) appeared to be as large as reported in another published report (78); however, it was determined that the practical limit of detection is approximately  $5 \times 10^{-8}$  F arsenic (III).

One of the major advantages of employing a polarographic method for the determination of arsenic is the separation of the arsenic and antimony reduction waves.

One of the problems encountered in the analysis for arsenic is that arsenic is very difficult to remove from glassware. Volumetric flasks, the solution cell, and the auxiliary electrode were cleaned with aqua regia and the reference electrode had to be cleaned with dilute hydrochloric acid to remove adsorbed arsenic.

Lead ( $E_s = -0.43v$ ), tin ( $E_s = -0.44v$ ), and thallium ( $E_s = -0.49v$ ) all interfere with the determination of arsenic in 0.5 F hydrochloric acid medium. Use of 0.1 F sulfuric acid medium allows an effective separation of the arsenic reduction wave ( $E_s = -0.69v$ ) from the other elements. After the arsenic is thus determined in 0.1 F sulfuric acid, 1 F sodium hydroxide solution can be employed for the determination of lead and thallium since tin and arsenic are polarographically inactive in this medium. In 0.5 F sodium citrate medium tin (IV) gave a fairly well-defined wave ( $E_s = -0.13v$ ); while the lead summit potential is  $-0.53v$ .

### Bismuth

Although the reported diffusion current constant is larger for bismuth in hydrochloric acid media than any of the other commonly employed electrolytes, this electrolyte is not amenable for the

analysis of submicroformal concentrations of bismuth (III) due to the interference of the mercury dissolution wave.

A 0.25 F solution of sodium tartrate with the pH adjusted to 4.4 with hydrochloric acid was probably the best of the various electrolytes employed for the determination of bismuth. Copper may interfere with the determination for bismuth in this medium if the copper concentration is much higher than the bismuth concentration. The detection limit of bismuth (III) is approximately  $1 \times 10^{-7}$ .

#### Cadmium

Due to the increasing awareness of the toxicity of cadmium, the analysis of cadmium in the environment is of great concern. In this study the sequential analysis of cadmium, lead, copper, and zinc employing the same supporting electrolyte was of particular interest. For this reason a large number of supporting electrolytes were investigated. Only the electrolytes of particular interest are given in Table 1.

The cadmium (II) ion gave a reversible wave for virtually every electrolyte medium employed. The summit potential of cadmium in most supporting electrolyte media lies in a polarographic region where the background is usually fairly flat. Thus, very low levels of cadmium can be detected (approximately  $5 \times 10^{-9}$  F).

Indium (III) ion is the only somewhat common interference in polarographic cadmium analyses. In the absence of complexing agents, indium is irreversibly reduced at the DME. Therefore, a much larger indium concentration would have to be present to interfere with the determination of cadmium. Thus, the concentration of indium can be determined by subtracting the cadmium peak height from the total peak

height in 0.1 F potassium chloride  $E_{sIn(III)} = -0.56v$ ), or some other complexing electrolyte, after the cadmium concentration has been determined in a non-complexing electrolyte.

A relatively large concentration of lead may interfere somewhat; however, as Figure 10 shows there is good separation between the two components even when the lead concentration is approximately one thousand times the cadmium concentration.

Probably the greatest problem when performing analyses on solutions containing low concentrations of cadmium is the adsorption of cadmium in the electrochemical cell and the later release of the previously adsorbed cadmium ions into the solutions. Thus, the cell should be rinsed with dilute (0.5 F) hydrochloric and nitric acids and several times with water after the analysis of a solution containing cadmium.

### Cobalt

Although cobalt is generally not known to exhibit very reversible polarographic behavior, fairly well-defined waves were obtained in this study. When the principal cobalt species in solution is the hexaquo cobalt (II) ion, poor waves with a reduction potential of  $-1.4v$  are obtained. As the concentration of a complexing agent such as chloride ion is increased, the reduction potential shifts to more positive values (79). Thus the cobalt chloro complex is easier to reduce than the hexaquo cobalt (II) ion.

To find an electrolyte which would yield separation between cobalt and nickel was of particular interest. Solutions 0.1 F and 1 F in potassium thiocyanate were first employed; however, poor results

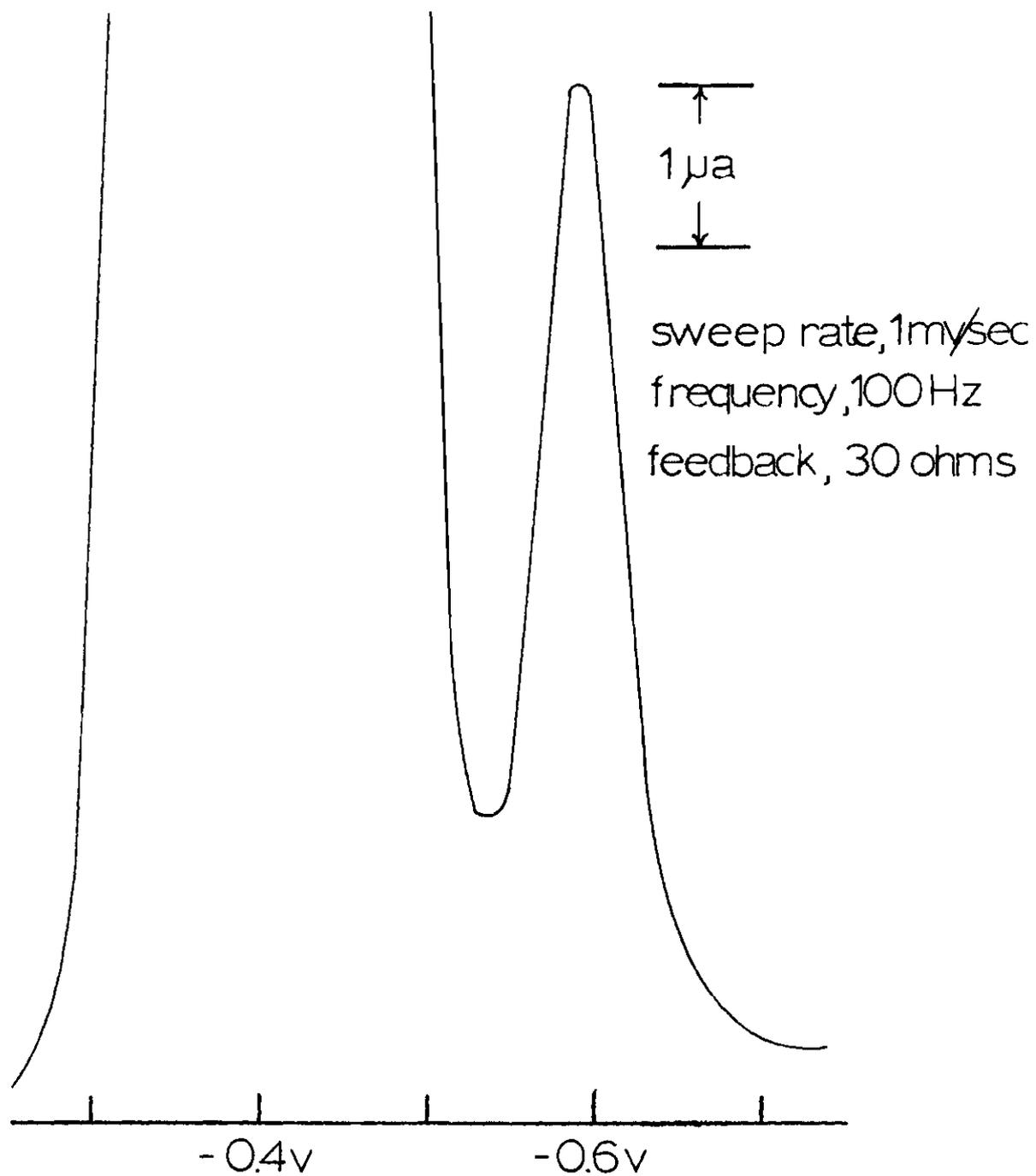


Figure 10. Square-Wave Polarogram of  $2 \times 10^{-3}$ F Pb (II) and  $6.6 \times 10^{-6}$ F Cd (II) in 0.3F  $\text{KNO}_3$  (pH 3.5)

were obtained because the mercury dissolution wave almost completely smothered the nickel wave, and neither of the waves was very reversible. As shown in Table 1, 0.1 F ammonium chloride-0.1 F ammonium hydroxide was an excellent electrolyte for the simultaneous determination of cobalt, manganese, and nickel.

The cobalt reduction wave in 0.1 F potassium nitrate with 0.01 F ethylenediamine was fairly well defined with a summit potential of -0.47v; however, the nickel wave is not very well defined in this medium. Lead impurity is a problem with the employment of this electrolyte since the lead summit potential is -0.56v. However, in the absence of lead interference, this is an excellent medium for the determination of cobalt (II), with a detection limit of about  $2 \times 10^{-7}$  F.

### Copper

Copper produces well-defined polarographic waves in a number of supporting electrolytes as shown in Table 1. Copper (II) ion in non-complexing media produces a single wave corresponding to the direct reduction to the elemental state. The same is true with complexing agents such as tartrate, oxalate, and citrate ions which form more stable complexes with the copper (II) ion than the copper (I) ion. However, in the presence of complexing agents such as chloride ion and ammonia which form more stable complexes with the copper (I) ion, the copper (I) ion is stabilized so that a step-wise reduction of the copper (II) ion occurs. Thus, two closely spaced reduction waves (or a doublet) of almost equal magnitude are observed.

There are two major interferences in the determination of copper. One is the mercury dissolution wave and the other is the iron (III) to

iron (II) reduction wave. By the use of electrolytes which do not form insoluble salts or complexes with mercury, very low levels of copper can be determined. At copper concentrations below  $1 \times 10^{-7}$  F, the DME must be removed from the cell during deaeration to lower the mercury dissolution background. Oxalate media are excellent for the determination of copper because the copper reduction wave is shifted to more negative potentials while the mercury dissolution wave is not. Thus, relatively flat backgrounds are obtainable in oxalate media.

Tartrate media is excellent for the sequential determination of copper, bismuth, lead, cadmium, and zinc; however, iron may be an interference. In non-complexing media the iron (III) to iron (II) reduction wave occurs at a potential more positive than the anodic mercury dissolution wave; thus, iron does not interfere. Copper yields such well-defined waves in so many electrolytes, that the determination of copper in the presence of iron is not really a problem; however, the determination of iron in the presence of copper is more of a problem. Since iron is not soluble in mercury, copper can also be determined by means of a stripping technique without iron interference.

### Iron

The iron (III) to iron (II) reduction potential in non-complexing media is somewhat more positive than the anodic mercury dissolution wave ( $E_s$  approximately +0.4v); thus, appropriate complexing agents are necessary in order to observe the iron (III) to iron (II) reduction wave. These complexing agents must form strong complexes with the iron (III) ions but not form insoluble salts or complexes with mercury (I) or mercury (II) ions or the mercury dissolution wave will still overlap the

iron (III) to iron (II) wave.

Generally, the pH of the solution has a large effect on the half-wave potential and the reversibility of the iron (III) to iron (II) reduction wave. For example, the half-wave potential for this reduction varies from -0.17v (pH 5.8) to -1.2v (pH 9.4) in 0.5 F sodium tartrate medium (76). The major interference in the determination of iron from the iron (III) to iron (II) wave is copper. Although oxalate, citrate, tartrate, ascorbate, and acetate media were employed there was little or no separation of the copper and iron waves. For example, only one reduction wave was observed when using a solution containing 0.1 F potassium nitrate and either 0.001 F, 0.01 F, or 0.1 F potassium oxalate (pH 4). When standard additions of iron were made to the supporting electrolyte the peak height increased and the peak widened after each addition until a half-width of approximately 90 millivolts was reached. When standard additions of copper were made to the same solution, the peak width at half-height became narrower. If copper interference is not present, nitrate-oxalate medium (pH 4) is excellent for the determination of iron. If copper is present, another electrolyte (non-complexing) can be employed for the determination of copper. The peak height for known concentrations of copper can be plotted versus the peak height in oxalate media. Thus, from the concentrations of copper found in the non-complexing media, the corresponding peak height in oxalate media can be found. This value is then subtracted from the total peak height and then standard additions of iron (III) solution are added to determine the iron concentration.

Alternatively the concentration of iron can be determined from

the iron (II) to elemental iron reduction wave. This wave is generally not as well defined as the iron (III) to iron (II) reduction wave and the lower limit of detection is only about  $3 \times 10^{-7}$  F. Two electrolytes which yield reversible waves for copper, iron, cadmium, lead, and zinc are 0.1 F ammonium hydroxide-0.1 F ammonium tartrate and 0.1 F ammonium hydroxide-0.1 F ammonium oxalate. The summit potentials for these elements in the former electrolyte are -0.15 and -0.38v (Cu), -0.47 and -1.42v (Fe), -0.7v (Cd), -0.54v (Pb), and -1.2v (Zn). The summit potentials for the same elements in the latter electrolyte are -0.18 and -0.38v (Cu), -0.29 and -1.56v (Fe), -0.7v (Cd), -0.53v (Pb), and -1.24v (Zn).

#### Lead

Due to the very reversible behavior of lead in a variety of supporting electrolytes and the great concern for monitoring lead levels in the environment, a considerable amount of research was conducted involving the analysis of this heavy metal.

Depending upon the electrolyte employed, it was generally noticed that the reversibility and the peak height for lead were diminished if the pH was much higher than 5. It was also observed that ions (such as sulfate, monohydrogen phosphate, and carbonate) which form insoluble precipitates with lead lower the peak height for lead as their concentrations are increased even if the ion products are not greater than the respective solubility products of the lead precipitates.

A number of the supporting electrolytes employed for the determination of lead are given in Table 1. Probably the optimum electrolyte found for the determination of lead was chloride media (about 0.5 F).

Thallium, arsenic, and tin may interfere with the determination of lead in some electrolytes; however, lead yields such reversible waves in so many media that separation of the lead wave from these interferences is not a considerable problem.

Buchanan et al. (71) previously reported that a supporting electrolyte of sodium perchlorate with sodium fluoride (pH 3) yielded a much flatter background for the determination of lead. When a potassium nitrate-sodium fluoride electrolyte at pH 7 was investigated in this study, no significant improvement in the background or in the sensitivity for lead was observed. However, as the pH was lowered, the lead and zinc peaks increased tremendously. At pH 3 very high blank values for lead and zinc were obtained. It was observed that the longer the solution was in contact with the electrochemical cell the larger the lead and zinc peaks became. When a standard addition of lead, zinc, cadmium, and copper ions was made to a reagent blank, no significant increase in the lead and zinc peaks was observed and no cadmium or copper waves were seen. It was discovered at a later date that the DME glass capillary contained high levels of lead and zinc.

### Manganese

It was found that manganese should be in the (II) oxidation state to yield the most reversible waves for the determination of manganese. Due to the negative half-wave potential for the manganese (II) reduction wave the pH must be above 7 or the hydrogen wave will seriously interfere. At fairly negative potentials a problem sometimes encountered with the DME is that the drop grows more rapidly due to the low surface tension; hence, it falls before the end of the four-second cycle.

Obviously, this phenomenon is dependent upon the natural drop time of the capillary itself.

The optimum electrolyte for the determination of manganese was found to be 0.1 F ammonium chloride -0.1 F ammonium hydroxide which yielded a fairly well-defined wave with a relatively flat background. The lower limit of detection in this supporting electrolyte medium is approximately  $8 \times 10^{-8}$  F manganese (II).

Hamamoto (80) reported that the diffusion current was not a linear function of the manganese (II) concentration at low concentrations when employing alkali chloride supporting electrolytes. It was found in this study, however, that a linear relationship was obtained when the peak height was plotted versus the concentration of manganese (II) ranging from the blank (0.1 F ammonium chloride-0.1 F ammonium hydroxide) to  $5 \times 10^{-6}$  F, thus confirming Lingane's contention that a strict linear relation is obtained if proper correction for the residual current is achieved (81).

### Nickel

Nickel, in non-complexing media, exists chiefly as the hexaquo-nickel (II) complex which yields an irreversible reduction wave at about -1.1v. If complexing media such as chloride are employed, the nickel reduction wave occurs at a more positive potential than -1.1v because the nickel chloro complexes are more easily reduced than is the hexaquo-nickel (II) ion (82).

It was of particular interest in the investigation of nickel to find an electrolyte which could be used for the simultaneous determination of both cobalt and nickel since these two elements usually occur

together. A 0.1 F ammonium chloride-0.1 F ammonium hydroxide medium afforded good separation between the two waves, and the reduction waves for the two elements were fairly well defined. A series of standard additions containing cobalt, nickel, and manganese were made to the supporting electrolyte corresponding to concentrations ranging from the blank to  $5 \times 10^{-6}$  F for these metals. A linear relationship was obtained when the peak height versus concentration was plotted for each of these elements.

### Thallium

The thallium (I) ion produces reversible waves in almost all commonly employed supporting electrolytes. The half-wave or summit potential for the reduction of thallium (I) ion to thallium metal does not change appreciably with changes in supporting electrolyte media since the thallos ion displays little tendency to form complexes. This property of thallium (I) ion allows its separation from many possible interferences such as lead, tin, and arsenic.

A 0.1 F potassium chloride (pH 4) medium allows separation of the thallium ( $E_S = -0.46\text{v}$ ) and lead ( $E_S = -0.39\text{v}$ ) waves if their concentrations are about equal. Arsenic and tin yield irreversible waves in this medium and would have to be present in quite large concentrations to interfere.

Lead interference can also be obviated by employing 1 F sodium hydroxide solution in which arsenic and tin are polarographically inactive.

In 0.2 F sodium acetate-0.1 F potassium chloride medium (pH 5.0) copper, lead ( $E_S = -0.4\text{v}$ ), thallium ( $E_S = -0.46\text{v}$ ), cadmium, and zinc are

all determined on the same polarographic scan. Then disodium EDTA solution is added to the previous solution to make approximately 0.005 F EDTA, in which only thallium and copper can be determined. This electrolyte was found to be the best for the analysis of unknown solutions in which one of the two elements (lead and thallium) is present in a concentration higher than the other. The pH must be maintained above approximately pH 4.7 in order to insure complexation of the lead; however, the pH should not be greater than approximately 7.

The detection limit for thallium (I) employing the DME is approximately  $5 \times 10^{-8}$  F; a lower concentration can be determined if stripping analysis techniques are employed.

### Tin

Tin was analyzed in solution in the (IV) oxidation state since the tin (II) ion is rapidly oxidized by oxygen to tin (IV).

In hydrochloric acid media the tin (IV) to tin (II) reduction wave is not as well defined as the tin (II) to elemental tin reduction wave. Also, many times the anodic mercury dissolution wave overlaps the tin (IV) to tin (II) wave. Apparently the chloride concentration must be high in order to obtain well-defined waves for the tin (II) to elemental tin reduction since 0.1 F hydrochloric acid did not yield nearly as large or as well-shaped waves as compared to 0.5 F hydrochloric acid. The electrolyte of choice for the determination of tin (IV) employed in this study was 1 F ammonium chloride-0.25 F hydrochloric acid medium ( $E_s = -0.46v$ ); however, lead, thallium, or arsenic may seriously interfere in the determination of tin in chloride media.

To obviate interference by lead, thallium, or arsenic, 1 F acetic

acid-1 F ammonium acetate medium can be employed, yielding a fairly well-defined wave for tin (IV) ( $E_s = -0.6v$ ). Another electrolyte which afforded separation of the tin wave from the other interfering elements is 0.5 F sodium citrate (pH 4.5). The observed wave is due to the tin (IV) to tin (II) reduction ( $E_s = -0.13v$ ), because of the stability of the tin (II)-citrate complex. The reduction of tin (II)-citrate complex does not yield an observable wave.

### Zinc

Zinc exhibited well-defined polarographic waves in many supporting electrolytes as shown in Table 1. Two important reasons for employing a polarographic technique for the analysis of zinc are the wide separation of the zinc and cadmium waves (zinc and cadmium are usually present together), and the lack of sensitivity of most other methods for the determination of zinc.

The pH must be controlled because if it is too low the reduction of hydrogen ion interferes with the determination of zinc. It was found in this study that the initiation of the hydrogen wave depended on the electrolyte medium employed. It was noticed that in some electrolytes the hydrogen wave would interfere with the determination; whereas, in others at the same pH the hydrogen wave would not cause interference.

Another important observation concerning zinc is that generally the lower the electrolyte concentration, the larger the peak. Liddle (83) found that the peak height for  $10^{-4}$  F zinc increased from 3.5 centimeters for 1 F potassium nitrate to 23.5 centimeters for 0.01 F potassium nitrate.

The optimum electrolyte found in this study was 0.01 F potassium chloride (pH 7), which yielded well-defined waves with a flat background.

Table 1. Characteristics of Selected Metal Ions in Various Supporting Electrolytes

Metal Ion	Supporting Electrolyte	$E_s$	Remarks
$M^{+n}$		vs SCE	(1) Reversibility: vp (very poor), p (poor), f (fair), fw (fairly well), w (well defined) (2) General comments (3) Approximate detection limit (F and parts per billion (ppb)).
Sb (III)	(1) 1F HCl	-0.15v	(1) w (2) The major interferences are the mercury dissolution wave, Bi (III), and relatively high concentrations of Cu (II) (3) $7 \times 10^{-8}$ F or 8.5 ppb.
	(2) 1F HNO <sub>3</sub>	-0.30v	NA
	(3) 0.5F H <sub>2</sub> SO <sub>4</sub> -0.01F KCl	-0.21v	(1) p (2) The poorly defined wave does not allow very low determinations (3) $4 \times 10^{-7}$ F or 49 ppb.
	(4) 1F HNO <sub>3</sub> -0.02F KCl	-0.17v	(1) p (2) The peak is larger and better defined than 1F HNO <sub>3</sub> (3) $3 \times 10^{-7}$ F or 37 ppb.
	(5) 0.5F H <sub>2</sub> SO <sub>4</sub> -0.05F HCl	-0.14v	(1) fw (2) The mercury dissolution wave is not a considerable problem (3) $8 \times 10^{-8}$ F or 9.7 ppb.
	(6) 0.24F sodium tartrate, pH 4.4 (with HCl)	NA	NA (a wave was not observed for $8 \times 10^{-7}$ F Sb (III)).

Table 1. Continued

Metal Ion	Supporting Electrolyte	$E_s$	Remarks
Sb (III)	(7) 0.5F HCl	-0.14v	(1) w (2) The mercury dissolution wave is less of a problem than 1F HCl (3) $5 \times 10^{-8}$ F or 6.1 ppb.
As (III)	(1) 1F HCl	-0.44v	(1) f (2) Pb (II), Sn (IV), and Tl (I) are interferences; however, the baseline is fairly flat (3) $8 \times 10^{-8}$ F or 6.0 ppb.
	(2) 0.5F H <sub>2</sub> SO <sub>4</sub> -0.5F HCl	-0.45v	(1) vp (2) An ill-defined As (III) wave is obtained in this medium (3) $8 \times 10^{-7}$ F or 60 ppb.
	(3) 1F HNO <sub>3</sub> -0.02F KCl	NA	NA
	(4) 0.1F H <sub>2</sub> SO <sub>4</sub>	-0.69v	(1) vp (2) This electrolyte allows separation from common interferences (3) $8 \times 10^{-7}$ F or 60 ppb.
	(5) 0.25F sodium tartrate (pH 4.4)	NA	NA
	(6) 0.5F HCl	-0.44v	(1) f (2) The peak appears to be at least as sharp as in 1F HCl, and the impurity level is lower in 0.5F HCl (3) $5 \times 10^{-8}$ F or 3.7 ppb.
Bi (III)	(1) 0.5F HCl	-0.06v	(1) w (2) The mercury dissolution wave severely interferes if the acid concentration is increased to 1F; the summit

Table 1. Continued

Metal Ion	Supporting Electrolyte	$E_s$	Remarks
			potential in 1F HCl is -0.09v and the mercury dissolution interference is even more severe (3) $8 \times 10^{-7}$ or 167 ppb.
	(2) 0.05F $H_2SO_4$	-0.04v	NA
	(3) 0.25F sodium tartrate pH 4.4 (adjusted with HCl)	-0.24v	(1) fw (2) This electrolyte allows a fairly effective separation of the copper and mercury dissolution interferences (3) $1 \times 10^{-7}$ F or 21 ppb.
Cd (II)	(1) 0.1F $KNO_3$ (pH 3.5)	-0.58v	(1) w (2) Excellent supporting electrolyte for simultaneous Pb (II), Cu (II), Zn (II), and Cd (II) analysis (3) $1 \times 10^{-8}$ F or 1.1 ppb.
	(2) 0.1F $Na_2SO_4$ (pH 3.5)	-0.59v	(1) w (2) Excellent supporting electrolyte for the determination of Cd (II) (3) $1 \times 10^{-8}$ F or 1.1 ppb.
	(3) 0.1F KCl (pH 3.5)	-0.60v	(1) w (2) Chloride media is excellent for the determination of Cd (II), Pb (II), Cu (II), and Zn (II) (3) $6 \times 10^{-9}$ F or 0.7 ppb.
	(4) 0.1F $KH_2PO_4$ (pH 4)	-0.59v	(1) w (2) This is an excellent supporting electrolyte because of its pH buffering.

Table 1. Continued

Metal Ion	Supporting Electrolyte	$E_s$	Remarks
Cd (II)	(5) 0.1F $\text{NH}_4\text{Cl}$ -0.1F $\text{NH}_4\text{OH}$	-0.69v	(1) w (2) An excellent supporting electrolyte with a buffered pH.
	(6) 0.1F $(\text{NH}_4)_2$ tartrate-0.1F $\text{NH}_4\text{OH}$	-0.73v	(1) w (2) A fairly good medium for the determination of Cu (II), Fe (III), Pb (II), Cd (II), and Zn (II).
	(7) 0.09F sodium acetate pH 4.75 (with $\text{HNO}_3$ )	-0.59v	(1) w (2) An excellent supporting electrolyte with pH buffering (3) $1 \times 10^{-8}\text{F}$ or 1.1 ppb.
	(8) 0.09F $\text{KNO}_3$ with 0.01F borax (pH 7.2)	-0.58v	(1) w (2) The higher pH has no apparent affect on the reversibility of the Cd (II) wave.
	(9) 0.09F $\text{KNO}_3$ with 0.01F tartrate (pH 4)	-0.58v	(1) w (2) Probably the best supporting electrolyte found for the simultaneous determination of Pb, Cd, Cu, and Zn (3) $8 \times 10^{-9}\text{F}$ or 0.9 ppb.
Co (II)	(1) 1F KSCN	-1.10v	(1) p (2) The background is not very good for the determination of Co (II) and Ni (II) (3) $8 \times 10^{-7}\text{F}$ or 47 ppb.
	(2) 0.1F KSCN	-1.10v	(1) p (2) A little better background is observed with 0.1F KSN as compared to 1F KSCN (3) $8 \times 10^{-7}\text{F}$ or 47 ppb.

Table 1. Continued

Metal Ion	Supporting Electrolyte	$E_s$	Remarks
Co (II)	(3) 0.1F $\text{KNO}_3$ with 0.01F ethylene diamine	-0.47v	(1) fw (2) The Ni (II) wave is not very well defined and Pb (II) ( $E_s = -0.56\text{v}$ ) may interfere (3) $3 \times 10^{-7}\text{F}$ or 18 ppb.
	(4) 0.1F $\text{NH}_4\text{Cl}$ -0.1F $\text{NH}_4\text{OH}$	-1.18v	(1) fw (2) The optimum electrolyte found for the simultaneous determination of Co (II), Ni (II), and Mn (II) (3) $2 \times 10^{-7}\text{F}$ or 12 ppb.
Cu (II)	(1) 0.1F $\text{KNO}_3$ (pH 3.5)	+0.01v	(1) w (2) Excellent for the determination of Cu (II) in the presence of Fe (III) (3) $2 \times 10^{-8}\text{F}$ or 1.3 ppb.
	(2) 0.1F $\text{KH}_2\text{PO}_4$	-0.01v	(1) w (2) The mercury dissolution wave limits the determination of sub-microformal levels (3) $2 \times 10^{-7}\text{F}$ or 13 ppb.
	(3) 0.1F $\text{KCl}$ (pH 3.5)	-0.15v	(1) fw (2) The mercury dissolution wave limits the determination of Cu (II) (3) $8 \times 10^{-8}\text{F}$ or 5.2 ppb.
	(4) 0.09F sodium acetate pH 4.75 with $\text{HNO}_3$	-0.01v	(1) w (2) The mercury dissolution wave limits the determination of Cu (II).
	(5) 0.1F $\text{KNO}_3$ with 0.01F borax (pH 7.2)	-0.03v	(1) fw (2) The reversibility of the copper wave is affected by the relatively high pH (3) $5 \times 10^{-8}\text{F}$ or 3.2 ppb.

Table 1. Continued

Metal Ion	Supporting Electrolyte	$E_s$	Remarks
Cu (II)	(6) 0.1F $\text{NH}_4\text{Cl}$ -0.1F $\text{NH}_4\text{OH}$	-0.15v -0.38v	(1) w (2) The first wave (Cu (II) $\rightarrow$ Cu (I)) is smothered by the mercury dissolution wave.
	(7) 0.1F $(\text{NH}_4)_2$ tartrate-0.1F $\text{NH}_4\text{OH}$	-0.15v -0.38v	(1) w (2) This electrolyte allows separation from relatively small concentrations of Fe (III) (3) $8 \times 10^{-8}$ or 5.2 ppb.
	(8) 0.1F $(\text{NH}_4)_2\text{C}_2\text{O}_4^-$ 0.1F $\text{NH}_4\text{OH}$	-0.18v -0.38v	(1) w (2) This electrolyte allows effective separation from the Fe (III) $\rightarrow$ Fe (II) wave (3) $8 \times 10^{-8}$ F.
	(9) 0.09F $\text{KNO}_3$ with 0.01F tartrate (pH4)		(1) w (2) This is an excellent supporting electrolyte for the simultaneous determination of Pb (II), Cu (II), Cd (II), and Zn (II) (3) $2 \times 10^{-8}$ F or 1.3 ppb.
	(10) 0.1F $\text{KNO}_3$ with $10^{-3}$ F $\text{K}_2\text{C}_2\text{O}_4$ (pH 4)	-0.12v	(1) w (2) 0.01F $\text{K}_2\text{C}_2\text{O}_4$ (pH 4) provides better pH buffering (3) $8 \times 10^{-9}$ F or 1 ppb.
Fe (III)	(1) 0.1F sodium pyrophosphate (pH 3.7)	NA	NA (no wave was observed for $1 \times 10^{-6}$ F Fe (III) in this supporting electrolyte.
	(2) 0.5F sodium tartrate pH 12	NA	NA

Table 1. Continued

Metal Ion	Supporting Electrolyte	$E_s$	Remarks
Fe (III)	(3) 0.1F $\text{NH}_3\text{Cl}$ -0.1F $\text{NH}_4\text{OH}$ with ascorbic acid (0.01F)	NA	NA
	(4) 0.1F $(\text{NH}_4)_2$ tartrate-0.1F $\text{NH}_4\text{OH}$	-0.47v -1.42v	(1) fw (2) This electrolyte allows a somewhat effective separation between the copper and iron waves (3) $2 \times 10^{-7}\text{F}$ or 11.2 ppb.
	(5) 0.1F $(\text{NH}_4)_2\text{C}_2\text{O}_4$ 0.1F $\text{NH}_4\text{OH}$	-0.29v -1.56v	(1) fw (2) This electrolyte allows an effective separation between Fe (III) and Cu (II).
	(6) 0.2F $\text{KNO}_3$ with 0.01F $\text{K}_2\text{C}_2\text{O}_4$ (pH 4)	-0.14v	(1) fw (2) Probably the best electrolyte for the determination of Fe (III) if Cu (II) is absent (3) $1 \times 10^{-7}\text{F}$ or 5.6 ppb.
	(7) 0.1F $\text{KNO}_3$ -0.1F $\text{K}_2\text{C}_2\text{O}_4$ (pH 4)	-0.21v	(1) fw (2) The copper wave overlaps the iron wave in this medium also.
	(8) 0.1F $\text{KNO}_3$ -0.1F $\text{K}_2\text{C}_2\text{O}_4$ with 0.008F EDTA pH 4	-0.18v	(1) p (2) Neither copper nor iron are masked by the addition of EDTA at pH 4.
Pb (II)	(1) 0.1F $\text{KNO}_3$ (pH 3.5)	-0.39v	(1) w (2) Excellent for the simultaneous determination of Cd (II), Cu (II), Zn (II), and Pb (II) (3) $1 \times 10^{-8}\text{F}$ or 2.1 ppb.

Table 1. Continued

Metal Ion	Supporting Electrolyte	$E_s$	Remarks
Pb (II)	(2) 0.1F $\text{Na}_2\text{SO}_4$ (pH 4)	-0.40v	(1) w (2) Even if milliformal acetate or tartrate media is added, the lead peak is still relatively smaller than in most other electrolytes.
	(3) 0.1F $\text{KH}_2\text{PO}_4$ (pH 4)	-0.40v	(1) w (2) The peak height for $4 \times 10^{-7}\text{F}$ (Pb (II)) is about one-half the peak height in 0.1F $\text{KNO}_3$
	(4) 0.1F $\text{KNO}_3$ with $10^{-3}\text{F}$ sodium acetate (pH 6.6)	-0.41v	(1) fw (2) The reversibility of the Pb (II) wave is affected by the higher pH.
	(5) 1F NaOH	-0.76v	(1) fw (2) This electrolyte allows separation between Pb (II) and Tl (I).
	(6) 0.09F $\text{KNO}_3$ with 0.01F sodium tartrate (pH 4)	-0.41v	(1) w (2) An excellent electrolyte for the determination of Cd (II), Cu (II), Pb (II), and Zn (II) (3) $8 \times 10^{-9}\text{F}$ or 1.7 ppb.
	(7) 0.09F $\text{KNO}_3$ with 0.01F borax (pH 7.2)	-0.42v	(1) fw (2) The reversibility for the Pb (II) wave is definitely affected by the higher pH.
	(8) 0.09F sodium acetate pH 4.75 with $\text{HNO}_3$	-0.41v	(1) w (2) This electrolyte affords pH buffering (3) $1 \times 10^{-8}\text{F}$ or 2.1 ppb.

Table 1. Continued

Metal Ion	Supporting Electrolyte	$E_s$	Remarks
Pb (II)	(9) 0.1F $\text{KNO}_3$ -0.05F NaF (pH 3.0)	-0.39v	(1) w (2) Glassware cannot be used if this electrolyte is employed.
	(10) 0.1F KCl (pH 3.5)	-0.40v	(1) w (2) Chloride media is probably the best for the determination of Pb (II); the peak height for Pb (II) increases as the chloride concentration is increased (3) $5 \times 10^{-9}$ F or 1ppb.
Mn (II)	(1) 0.1F KCl with 0.02F $\text{NH}_4\text{OH}$	-1.49v	(1) fw (2) The pH must be above seven in order to observe the Mn (II) wave (3) $5 \times 10^{-7}$ F or 27 ppb.
	(2) 0.1F KSCN	-1.50v	(1) f (2) This electrolyte is not recommended for the determination of Mn (II) (3) $2 \times 10^{-6}$ F or 110 ppb.
	(3) 0.1F $\text{NH}_4\text{Cl}$ -0.1F $\text{NH}_4\text{OH}$	-1.51v	(1) fw (2) The optimum electrolyte found for Mn (II) (3) $8 \times 10^{-8}$ F or 4.4 ppb.
Ni (II)	(1) 0.1F KSCN	-0.71v	(1) fw (2) A $10^{-6}$ F Ni (II) solution in this medium appears as a shoulder on the background (3) $8 \times 10^{-7}$ or 47 ppb.
	(2) 1F KSCN	-0.17v	(1) fw (2) The mercury dissolution wave does not allow the determination of sub-microformal concentrations.
	(3) 0.1F $\text{KNO}_3$ with 0.01F ethylene diamine	-0.65v	(1) p (2) A broad wave is obtained for Ni (II) in this medium (3) $1 \times 10^{-6}$ F or 59 ppb.

Table 1. Continued

Metal Ion	Supporting Electrolyte	$E_s$	Remarks
Ni (II)	(4) 0.1F $\text{NH}_4\text{Cl}$ -0.1F $\text{NH}_4\text{OH}$	-0.93v	(1) fw (2) The reversibility of Ni (II) in this electrolyte is almost equal to that of Cd (II) or Pb (II) (3) $8 \times 10^{-8}\text{F}$ or 4.7 ppb.
Tl (I)	(1) 0.5F HCl	-0.48v	(1) w (2) This electrolyte is excellent for the determination of Tl (II) if As (III), Pb (II), or Sn (IV) impurities are not present.
	(2) 0.1F KCl	-0.46v	(1) w (2) Relatively high concentrations of Pb (II) interfere (3) $5 \times 10^{-8}\text{F}$ or 10 ppb.
	(3) 1F KCl with 0.008F sodium EDTA (pH 4)	-0.47v	(1) w (2) pH is too low to effectively mask the Pb (II) interference; however, if the pH is too high (>11.0) the reversibility of the Tl (I) wave is affected.
	(4) 0.09 $\text{KNO}_3$ with 0.01F tartrate (pH 4)	-0.46v	(1) w (2) Pb (II) interferes in the determination of Tl (I) in this medium.
	(5) 0.2F sodium acetate-0.1F KCl (pH 4.75)	-0.46v	(1) w (2) Lead interferes with the determination of Tl (I) in this electrolyte.
	(6) 0.2F sodium acetate-0.1F KCl (pH 4.75) with EDTA added (0.005F)	-0.47v	(1) w (2) Lead interference is masked by the addition of EDTA; Cu (II) can also be determined with the employment of this electrolyte (3) $5 \times 10^{-8}\text{F}$ or 10 ppb.

Table 1. Continued

Metal Ion	Supporting Electrolyte	$E_s$	Remarks
Tl (I)	(7) 1F NaOH	-0.48v	(1) w (2) The Pb (II) wave occurs at -0.76v.
Sn (IV)	(1) 0.1F HCl	-0.42v	(1) p (2) The peak height and reversibility of the wave is much improved if a higher concentration of HCl is employed (3) $3 \times 10^{-7}$ F or 36 ppb.
	(2) 0.5F HCl	-0.44v	(1) w (2) The interferences are Pb (II), Tl (I), and As (III) (3) $5 \times 10^{-8}$ F or 6 ppb.
	(3) 1F HOAc-1F $\text{NH}_4\text{Ac}$	-0.60v	(1) fw (2) This electrolyte allows the Sn (II) $\rightarrow$ Sn $^{\circ}$ reduction wave to be effectively separated from Tl (I), Pb (II), and As (III).
	(4) 0.5F sodium citrate (pH 4.5)	-0.13v	(1) f (2) The mercury dissolution wave interfered with the determination of low levels of Sn (IV).
	(5) 1F $\text{NH}_4\text{Cl}$ -0.25F HCl	-0.46v	(1) w (2) If As, Tl, or Pb ions are not present, this electrolyte is excellent (3) $4 \times 10^{-8}$ F or 4.8 ppb.
Zn (II)	(1) 0.1F $\text{KNO}_3$ (pH 3.5)	-0.99v	(1) fw (2) The only commonly occurring interference is Ni (II) (3) $2 \times 10^{-8}$ F or 1.3 ppb.
	(2) 0.1F $\text{Na}_2\text{SO}_4$ (pH 4)	-1.00v	(1) fw (2) Ni (II) may interfere (3) $2 \times 10^{-8}$ F or 1.3 ppb.

Table 1. Continued

Metal Ion	Supporting Electrolyte	$E_s$	Remarks
Zn (II)	(3) 0.1F $\text{KH}_2\text{PO}_4$	-1.00v	(1) fw (2) The pH is buffered when this electrolyte is employed (3) $2 \times 10^{-8}$ F or 1.3 ppb.
	(4) 0.09F $\text{KNO}_3$ with 0.01F borax (pH 7.2)	-1.00v	(1) fw (2) The hydrogen wave does not interfere at pH 7.2 (3) $2 \times 10^{-8}$ F or 1.3 ppb.
	(5) 0.1F $\text{KNO}_3$ with 0.05F NaF (pH 3)	-0.99v	(1) fw (2) Glassware should not be employed with this electrolyte. The hydrogen wave interferes also.
	(6) 0.1F $\text{KNO}_3$ with $10^{-3}$ F $\text{K}_2\text{C}_2\text{O}_4$ (pH 4)	-1.01v	(1) f (2) If the oxalate concentration is increased to 0.01F, a zinc wave is not observable if the zinc concentration is $2 \times 10^{-7}$ F (3) $1 \times 10^{-7}$ F or 6.5 ppb.
	(7) 0.09F NaAc pH 4.75 (with $\text{HNO}_3$ )	-1.00v	(1) fw (2) This is an excellent supporting electrolyte for determination of Zn (II) (3) $2 \times 10^{-8}$ F or 1.3 ppb.
	(8) 0.01F KCl (pH 7)	-1.00v	(1) w (2) The peak height for Zn (II) decreases as the chloride concentration is increased (3) $1 \times 10^{-8}$ F for 0.7 ppb.

## CHAPTER VI

EXPERIMENTAL RESULTS EMPLOYING FIXED  
AREA ELECTRODESHanging Mercury Drop Electrode

The hanging mercury drop electrode was employed for both forward scan investigations (no pre-plating) and stripping analysis for cadmium and lead only. Many of the supporting electrolytes used for the analysis of cadmium and lead with the DME were the electrolytes of choice in investigations with the HMDE.

The objective of the study with the HMDE was to compare it with the DME and the RDE to determine its suitability for low-level determinations.

The sitting drop electrode (J-tube electrode) was also employed; however, most of the low-level quantitative determinations utilized the HMDE since it is more commonly employed. The investigation of the hanging mercury drop and the sitting drop electrodes demonstrated that more reproducible results can be obtained and lower levels of trace metals can be determined with the sitting drop electrode since it produces a larger and more stable mercury droplet. As mentioned in Chapter II, the creeping of solution up the capillary walls is also a less severe problem with the J-tube electrode.

If the mercury was tightly filled (i.e., all air pockets removed from the electrode system) in the hanging drop electrode, more reproducible results were obtained since the droplet characteristics

were consistent. The stability of the suspended droplet was also affected by the quality of the filling of the electrode. However, even with a tightly filled electrode it was difficult to obtain reproducible results. The cell current was monitored versus time on an oscilloscope, and it was observed that the decay time for the current-potential curve varied from one drop to another. Many times, especially when the electrode was first used, the decay times were very long. Usually considerable compensation (positive feedback) was required in order to obtain a decay time of less than one hundred microseconds. It was observed that if the cell was slightly overcompensated and then the compensation was switched off, and adjusted again on the same droplet, much less compensation was required and the decay time was much shorter. This phenomenon was attributed to the sudden application of the positive feedback voltage which forced some of the solution on the inside walls of the capillary to be expelled or by lowering the resistance of the mercury column in the capillary tip. Gross overcompensation of the electrode resulted in loss of potential control. Sometimes this resulted in the formation of calomel. Very reproducible results were obtained if the decay time for each droplet was adjusted to the same value.

It was felt that if reproducible results could be obtained employing the forward scan (no pre-plating), the incorporation of pre-plating would further improve the reproducibility and sensitivity since a much larger peak height to background ratio would be obtained. In Table 2 are the results which show the reproducibility and sensitivity achievable with the HMDE with no pre-plating.

The three sample solutions listed in Table 2 were reagent blanks

Table 2. Experimental Parameters and Results with HMDE

Experimental Parameters					
	Electrode Size	1 Microliter ( $\mu$ l)			
	Supporting Electrolyte	0.1F $\text{KNO}_3$ (not pre-electrolyzed)			
	Scan Rate	5 mv/sec			
	Square-wave Amplitude	50 mv			
	Frequency	30 Hz			
Metal Ion	Concentration Added (in ppb)	Peak Height (in scale division)			
		Solution 1	Solution 2	Solution 3	Average
Pb (II)	0	20	20	25	21.7
	13.6	60	62	65	62.3
	27.2	107	114	116	112.3
Cd (II)	0	0	0	0	0
	7.4	40.6	40	40.5	40.4
	14.8	78.6	79.2	78.6	78.8

to which standard additions were made. Sample number three (blank 3) had an initial higher blank reading because a different batch of potassium nitrate supporting electrolyte was employed. If a larger sized mercury droplet, such as 2  $\mu\text{l}$  is employed even larger peak heights can be obtained. Droplets up to 3  $\mu\text{l}$  in volume are stable. After the analysis of sample number three with the final standard addition added, the potential was set at -1.2v, and the electrode was plated for four minutes. After only four minutes plating time, the components were anodically stripped off yielding peaks approximately four times the size of the forward scans.

During the deaeration process, nitrogen bubbles from the gas dispersion tube should not be allowed to impinge directly on the capillary orifice because this may force solution up the capillary. When employing a stripping technique with the hanging mercury drop, stirring must be utilized after each standard addition to achieve homogeneity. If bubbling is employed for stirring, less reproducible results will be obtained if bubbles of nitrogen are allowed to form on the electrode surface.

When concentration versus peak height was plotted for solutions of concentrations  $8 \times 10^{-9}$  F,  $3.2 \times 10^{-8}$  F,  $8 \times 10^{-8}$  F, and  $2.8 \times 10^{-7}$  F (lead (II) and cadmium (II)), a linear plot was obtained. Employing a 1  $\mu\text{l}$  drop size and no pre-plating, the lower limit of detection for lead was  $3 \times 10^{-9}$  F, and for cadmium it was  $4 \times 10^{-9}$  F. With the use of the previously described square-wave polarograph and stripping techniques employing the HMDE, the lower limit of detection for these metals is well below  $10^{-9}$  F.

### Thin Mercury Film Rotating Disk Electrodes

Earlier investigators found that mercury plated electrodes were non-reproducible and required much longer pretreatment procedures than other electrodes, such as HMDE, which were employed for stripping analysis (84, 85). It has been suggested that the cause of the earlier lack of reproducibility for these electrodes was the interaction of the mercury film and the substrate material (86).

In spite of these earlier difficulties, a wide variety of electrode materials and experimental procedures have been investigated because of the sensitivity of thin-film electrodes. A major reason for the increased sensitivity with these electrodes is that the mercury surface to volume ratio is much greater as compared to the hanging mercury drop electrode. The combination of electrode rotation with the use of thin-film mercury electrodes offers an even more sensitive technique. Obviously, the transport of reducible species to the electrode surface is much greater with the employment of stirring or rotation than with the normal process of diffusion. Referring to equation 2-14, if the metals are plated while the electrode is rotated, the limiting current is directly proportional to the square root of the rotation rate. Thus, the higher the rotation rate of the electrode the greater the amount of metals deposited per unit time (within the limits of laminar flow).

After the plating of the metals at a desired potential, the potential is scanned linearly in a positive direction, and for each metal a characteristic potential is reached at which the metal is anodically stripped out. As the metal ions return to solution, a peak is observed which is proportional to the concentration of the metal in

the mercury film (87).

If the potential is scanned anodically while continuing electrode rotation, the peak heights for the components are observed to be diminished with respect to the peak heights obtained when the electrode is scanned quiescently. This phenomenon is theoretically predicted because the concentration of the oxidized species at the electrode surface is greatly diminished due to stirring. Also the background noise is much greater with electrode rotation than if the electrode is immobile.

#### Platinum

After cleaning the platinum surface of the electrode by the procedures recommended in Chapter II, the electrode was coated with mercury. Three generally recommended procedures for the coating of the platinum electrode with mercury were investigated. One procedure consisted of the deposition of mercury from an acidic mercuric nitrate solution onto the platinum surface (88-90). A second procedure involved immersing the tip into a mercury pool with the potential applied (91, 92). The final procedure investigated was abrading the platinum surface while the platinum tip is submerged in mercury (93). However, none of these techniques yielded very reproducible surfaces. If the platinum surface is not completely covered, the background current is very high due to the production of hydrogen on the platinum surface. Even when the electrode was completely covered with mercury, the peaks were generally much broader and not as well defined as those obtained with graphite. Thus, most of the research conducted with the RDE employed the graphite (vitreous carbon) disk electrodes.

## Graphite

Graphite has become widely employed as the substrate material for thin-film mercury electrodes due to the reasons given in Chapter II, and the reproducible results which have been obtained.

Wax Impregnation. In most of the previously reported work in which graphite was employed as the electrode material, the electrode was usually wax impregnated to lower the residual current. After reviewing the types of waxes used for this purpose and the procedure for impregnation (94, 95), it was concluded that a very inexpensive paraffin wax (Gulfwax) should be investigated first. This wax did not impregnate the vitreous carbon material very well, and cracking of the wax on the electrode surface allowed the seepage of the solution into the electrode.

Ceresin wax, because of its common use for this purpose, was then investigated. The employment of this wax contributed to the reduction of the background current as compared to the paraffin wax. If the Ceresin wax impregnated electrode was allowed to stay in the solution for several days, the background current rose steadily until current saturation of the integrator usually resulted. It was also observed, as was reported in another publication (95), that a Ceresin wax impregnated electrode is relatively insensitive for the determination of zinc.

Vitreous Carbon. In a recent publication (96) it was shown that the hardest, least porous graphite material displayed significant stripping current enhancement, as well as improved reproducibility and more durable mercury films than some of the more porous graphite materials. The investigators found that wax impregnation was not necessary and employed the vitreous carbon electrode with differential pulse

stripping analysis for the determination of lead and cadmium in natural waters, whole blood, blood plasma, and urine.

The only observable advantage for the use of the wax impregnated electrode is that the background current was somewhat lower than with the non-impregnated graphite electrodes. The advantages of the use of non-impregnated vitreous carbon electrodes are that lengthy wax impregnation procedures and the subsequent polishing of the waxed graphite surface is avoided, and larger peak heights for the components are observed. The only pretreatment of these bare electrode tips was cleaning in hot spectral grade chloroform and acetone. The electrode tip was then polished with 4/0 Emery paper and rubbed with dampened Kimwipes.

#### Mercury Coating on Graphite

The characteristics of the peaks for an anodic stripping voltammogram from a mercury film electrode are greatly affected by the mercury film. For a particular metal, the concentration range for which the plot of concentration versus peak height is linear, is dependent upon the metal's solubility in mercury and how much mercury is on the disk electrode. The amount of mercury on the electrode surface should not vary from one run to another since there will be a lack of reproducibility because the peak height of an anodically stripped out component is directly proportional to the amalgam concentration (85-87, 90).

One common procedure for the use of the mercury film electrode is to plate a fresh film for each sample solution or standard addition, and then to completely strip the electrode before replating for the next solution.

A wide concentration range (from  $5 \times 10^{-7}$  to  $1 \times 10^{-4}$  F) of

mercury (II), the plating potential, and the duration of the plating process were investigated for the mercury plating of the electrode tips. After the mercury and other metals of interest were co-deposited on the electrode surface, the potential was scanned from the plating potential (usually -1.0v) to a potential at which mercury and the other metals are stripped off. The summit potential for the mercury wave was +0.375v in 0.1 F sodium acetate (pH 4.75); thus, potentials ranging from +0.375 to +1.0v were employed for the stripping off of the mercury. It was found that for the same solution the peak heights of the various components for each succeeding voltammogram increased. Usually the peaks were broad and not very well defined for the first few scans, but after about the fourth voltage scan the peaks became larger and more well defined. Also the residual current steadily increased if the electrode had not been wax impregnated, indicating the probability of the seepage of solution into the graphite material.

Probably the largest disadvantage of this technique is the fouling of the surface in the presence of ions which form insoluble salts with mercury ions, particularly chloride ions, which are usually found in most samples. Thus if the mercury is stripped off in a solution containing chloride ions, the electrode surface may be fouled due to the formation of calomel. If mercury was physically removed (by wiping off with dampened paper towels) after its use for one solution, it was also difficult to obtain reproducibility.

It is very time consuming to plate the mercury on and remove it for each scan. For this reason, as well as the other difficulties discussed above, an alternate procedure was investigated in which the

plated electrode is used for repeated samples without stripping and replating. Impressive results have been reported by high-volume laboratories using this alternate procedure (97). For this particular technique the mercury concentration of the plating solution was varied in order to determine the amount of plated mercury required to obtain the most consistent results. High concentrations of mercury, such as  $4 \times 10^{-4}$  F mercury (II) yielded the most reproducible results. If mercury is plated from a quiescent solution containing a high concentration of mercury (II) ions, a thin layer of mercury droplets is deposited on the graphite surface (95).

When electrodes prepared in this manner were employed, along with electrode rotation for the analysis of a sample solution, a significant increase in peak heights for each successive voltammogram on the same solution was found. This effect is believed to be due to the impingement of the solution onto the surface as the electrode rotates which knocks off the larger mercury drops. The peak heights are thought to be larger because the amalgam concentration is higher. Even the addition of mercury (II) to the solutions to be analyzed did not diminish the increases in peak heights. However, if the mercury was plated overnight, and then the electrode was rotated a few minutes at the same rate as subsequently used in the plating procedure for the unknown solution, very reproducible results were obtained after the first scan. However, for very low concentrations, a significant increase in peak heights was observed between the first and second scans after the solution had been changed. Only a small increase occurred for about the next three scans, and then virtually the same peak heights were observed on succeeding runs.

This effect was probably due to the formation of mercuric oxide on the electrode surface when a new solution containing oxygen was added to the cell. Several reducing agents such as ascorbic acid and hydrazine, were added to the solution to reduce the oxygen, but their use did not produce any significant improvement. Mercury (II) ions ranging in concentration from  $10^{-7}$  to  $10^{-3}$  F were added to the solution to be analyzed in order to obtain a fresh surface. The addition of high concentrations of mercury yielded spurious results because the amount of mercury on the electrode surface was appreciably changed. The higher concentrations of mercury greatly affected the amount of plated mercury on the electrode surface. However, extremely dilute mercury (II) concentrations (such as  $10^{-7}$ ) did not appreciably change the amount of mercury on the surface, but the effect of the oxide formation problem was lessened.

The procedure finally adopted for running successive solutions is as follows. A new sample solution was introduced to the cell and deoxygenated for two to five minutes with the electrode rotating and the potential at  $-1v$ . The solution was not vigorously deaerated because the impingement of nitrogen bubbles on the surface of the electrode resulted in the loss of mercury. After sufficient deaeration the nitrogen gas stream was diverted in order to purge the cell above the solution. The potential was then scanned anodically to a potential of approximately  $-0.1v$  where the potential was held for approximately one minute to insure the complete stripping out of lead and cadmium. Then the potential was reset to  $-1v$ , the electrode rotated, and the metals of interest were plated for one to five minutes. The rotating electrode

was then stopped, positive feedback adjusted, and after a predetermined time delay (usually 30 seconds after the electrode had been stopped) the anodic stripping voltammogram was recorded.

Standard additions were usually made to the solution at this point and since very small volumes were added (approximately 5  $\mu$ l), deaeration was not necessary. The change in "sensitivity" of the electrode when solutions are changed is not of vital concern since calibration techniques (as described in Chapter II) were not employed. However, it is of vital concern if there is a significant change from one scan to another since this invalidates the method of standard addition. The initial deaeration and plating step serves as a test run. The compensation, recorder sensitivity, etc. can be adjusted using the results of this run. The same procedure was employed for the analysis of the "spiked" solutions, and from the increases in peak heights the concentration of the initial solution was determined.

Inconsistent results were obtained if the solution was deaerated while the metals were being plated because the convection is difficult to reproduce. If the electrode was rotated for approximately one minute while at a potential of about -0.1v the peaks in successive voltammograms became significantly larger. However, if rotation was not employed at these potentials very reproducible results were obtained.

If the electrode was allowed to be in contact with the solution for several days, wetting of the graphite material resulted. Usually each electrode tip was plated overnight, then rotated before use. At the end of the day, mercury was removed with dampened paper towels, and the bare electrode tip was stored dry. Another electrode tip was

then plated overnight.

Rotation Rate. The peak heights for the components of the anodic stripping voltammogram increased as a function of the square root of the rotation rate as theoretically predicted by equation 2-14.

Initially, a rotation rate of 90 rps was employed, giving results which were not very consistent. This was possibly due to the cavitation of the solution around the electrode tip and the foaming of the solution, at this high rotation rate, particularly when acetate media was employed. In order to obviate this problem and to prolong the life of the rotating assembly, 50 rps were employed.

Sweep Rate. A 50 mv/sec sweep rate was employed for most determinations. It was observed that the faster the scan rate, the larger the peak heights. For example, when a scan rate of 10 mv/sec was employed for a solution containing a known concentration of lead, the measured peak height was 16.5 scale divisions, at 20 mv/sec the peak height was 21 scale divisions, and at 50 mv/sec the peak height was 29 scale divisions. A scan rate of 50 mv/sec yielded excellent resolution of cadmium and lead peaks as shown in Figure 11. Higher scan rates should be possible, but 50 mv/sec was the highest available on the instrument. The final track and hold circuit mentioned in Chapter IV is not utilized since a fixed surface electrode is employed.

### Conclusion

A linear relationship was obtained when peak height versus concentration was plotted for solutions of lead and cadmium ranging in concentration from  $10^{-9}$  to  $10^{-7}$  F employing a five-minute plating time. Above  $10^{-7}$  F there is some curvature in the plot. To achieve linearity

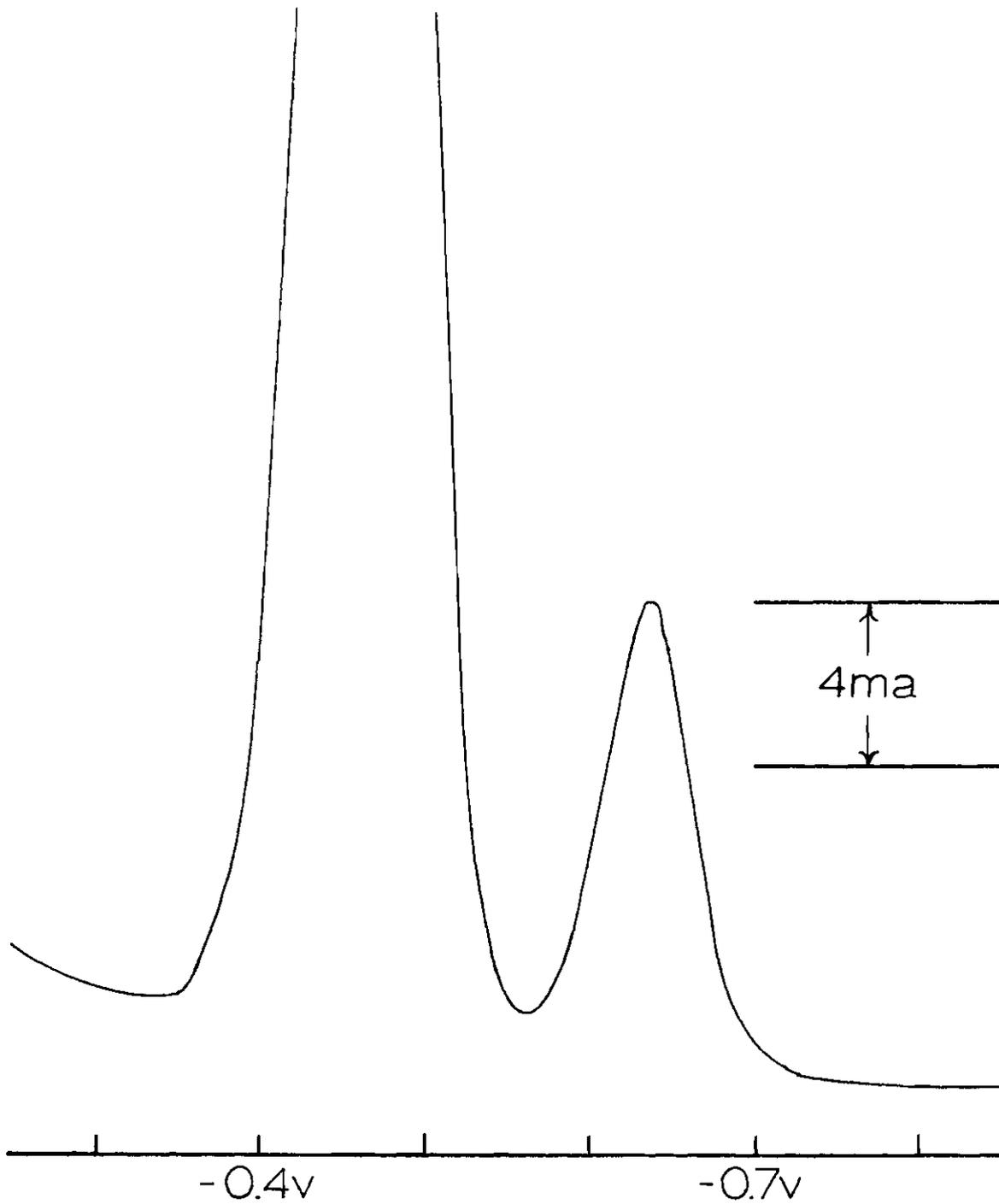


Figure 11. Anodic Stripping Voltammogram of  $4.9 \times 10^{-8}$  F Cd (II) and  $1.7 \times 10^{-7}$  F Pb (II) at 50 mv/sec Scan Rate (All parameters are the same as given in Table 3.)

for higher concentrations, shorter plating times can be employed or the rotation rate can be decreased. Since reducing analysis time was one of the objectives of this study, plating time was usually decreased. The total analysis time, including deaeration, the test run, and the voltammogram of the unknown solution and the spiked solution, is less than 15 minutes.

In Chapter VII the results of analyzing an EPA reference solution with the rotating, mercury coated, graphite electrode will be presented. A summary of the optimum instrumental and chemical parameters employed for these determinations is given in Table 3.

Table 3. Summary of Optimum Experimental Conditions (RDE)

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I. Chemical Parameters

A. Mercury Plating Procedure

1. Mercury (II) Concentration -  $4 \times 10^{-4}$  F.
2. Mercury Plating Time - overnight quiescently and then rotating at 50 rps for 10 minutes or for approximately 20 minutes at 50 rps.
3. Plating Potential - -300mv (versus SCE). If copper is to be determined, the plated copper must be stripped out first.

B. Supporting Electrolytes - 0.09F sodium acetate (pH 4.75) with  $\text{HNO}_3$  and 0.09F  $\text{KNO}_3$  with 0.01F sodium tartrate (pH 4)

C. Deaeration time - at least two minutes with electrode rotation

II. Instrumental Parameters

- A. Square-wave Voltage - 50mv
  - B. Sweep Rate - 50mv/sec
  - C. Frequency - 30 Hz
  - D. Positive Feedback - Adjusted for each scan
  - E. Electrode Rotation Rate - 50 rps
-

## CHAPTER VII

## REAL SAMPLES

Introduction

One of the major objectives in this investigation was to compare the results for the analysis of real samples, i.e., natural and industrial water samples, which were obtained employing the square-wave polarographic technique versus the results obtained by other laboratories employing competitive analytical techniques. However, the problem of obtaining rapid analyses of the same sample by another laboratory arose. It did not appear to be a meaningful evaluation of this technique if the results could not be cross-checked with another technique. In order to achieve this, sets of Environmental Protection Agency (EPA) water reference standards were obtained and these samples were analyzed employing both the DME and the mercury coated, rotating disk electrode.

The square-wave technique and other similar electrochemical techniques have been applied for several years for the analysis of very low concentrations of metals (32, 98-100). However, probably the major disadvantage with the employment of polarographic techniques is the time required for analysis. Thus one of the objectives of this study was to decrease the analysis time for water samples.

Sample Pretreatment

In general, sample pretreatment is not necessary for samples which do not contain biological or organic substances. Since there

are fairly rapid pretreatment procedures which thoroughly convert biological and organic materials to inorganic substances, it is usually wise to employ the pretreatment procedures.

The following is one of the pretreatment procedures which may be used for the analysis of complex samples. A measured portion of the sample is placed into a Vycor or Teflon coated digestion tube. Then an acid digestion mixture consisting of 24 parts (70%) perchloric acid, 24 parts concentrated nitric acid, and one part concentrated sulfuric acid is added. The tube is then placed into a bored hole in an aluminum block which sits on top of a hot plate. The time required for this procedure depends on the sample size. A large water sample such as 250 milliliters can be evaporated to a small volume before the acid digestion mixture is added.

Just before the sample is evaporated to dryness, the tube is removed from the block and cooled. The desired volume of supporting electrolyte solution is added to the residue, and the polarographic or stripping technique is performed. When using this procedure all of the precautions discussed in Chapter III should be considered.

This digestion procedure is very thorough and has been employed for the pretreatment of complex samples such as blood, tissue, etc. If the concentration of biological matter and surfactants in the sample is relatively low, nitric acid digestion is sufficient.

Environmental Sciences Associates, Inc. (ESA) which has employed electrochemical techniques for the trace analysis of metals, has developed a procedure by which low levels of lead and some other metals can be determined in whole blood and other complex samples without

Table 4. The Analysis for Lead in an EPA Water Reference Solution with the Employment of the DME\*

Solution Number	Peak Height in Scale Divisions	Peak Height After the Addition of 41.4 ppb Pb (II)	Calculated Concentration	Percent Deviation
1	34.2 SD (32.5)	48.8 SD	92 ppb	0.0%
2	33.6 SD (31.9)	48.0 SD	91 ppb	1.1%
3	34.5 SD (32.8)	49.8 SD	88 ppb	4.3%

\*The values enclosed in parentheses in column two represent the net peak heights, i.e., after subtracting the blank value.

sample pretreatment. The sample is simply added to ESA's Metexchange solution and then the lead is determined by employing a stripping technique. It is probable that this Metexchange solution or a similar solution could be employed for the analysis of other types of complex samples such as water samples, thus greatly reducing the total analysis time.

#### EPA Reference Samples

The EPA water reference standards consisted of many metals stored in concentrated form, which when diluted yielded concentrations for these metals ranging from very low to high parts per billion levels. The concentrations and stability of these metals have been checked by repeated analysis over a long period of time. The EPA Analytical Laboratory incorporated an extraction technique for preconcentration, with atomic absorption spectroscopy.

In order to show the reproducibility and sensitivity obtainable with the employment of this instrument with the DME, an EPA reference solution containing 92 parts per billion ( $4.4 \times 10^{-7}$  F) lead was analyzed. The results for three determinations are presented in Table 4.

Cadmium was determined in this EPA reference solution; however, non-reproducible results were obtained due to the adsorption of cadmium onto the surfaces of the electrochemical cell. The adsorption characteristics probably changed after the addition of the fairly acidic standard addition solutions since a non-pH buffering supporting electrolyte was employed, thus further affecting the reproducibility. Thus, an approximate concentration of 10 ppb cadmium was found, as compared

to the reported value of 16 ppb. Fairly reproducible results were obtained while employing the mercury film rotating disk electrode for the analysis of low parts per billion levels of cadmium (see Table 5). This is probably because the analysis can be performed much more rapidly than with the DME.

The results obtained for the analysis of the EPA solutions, employing the optimum experimental conditions listed in Table 3, are given in Table 5. The reported value for each analysis is usually an average of several scans.

Probably the largest source of error in the results (Table 5) was the use of such small micro pipets (1-10  $\mu$ l) for standard additions and the use of a 25 milliliter graduated cylinder to measure the total solution volume.

Table 5. The Results for the Analysis of EPA Water Standards Employing the Mercury Film RDE

Analysis Number	Metal Ion	Reagent Blank (in ppb)	Reported Concentration (in ppb)	Concentration Found (in ppb)
1	Pb (II)	1.2	28.0	27.5
2	Cd (II)	0.2	1.8	1.7
3	Pb (II)	0.7	28.0	27.1
4	Cd (II)	1.2	1.8	1.0
5	Pb (II)	1.4	22.4	21.0
6	Cd (II)	1.2	1.4	1.0
7	Pb (II)	2.8	28.0	27.1
8	Cd (II)	0.2	1.8	1.4
9	Pb (II)	1.9	9.2	11.5
10	Cd (II)	1.6	1.6	1.5
11	Pb (II)	2.2	9.2	9.8
12	Cd (II)	1.1	1.6	1.6

## CHAPTER VIII

## CONCLUSIONS AND RECOMMENDATIONS

Introduction

Based on the experimental results of this investigation, the square-wave polarograph described in Chapter IV enabled the determination of very low concentrations of reversible and irreversible metals with the employment of the dropping mercury, the hanging mercury drop, and the rotating disk electrodes.

Dropping Mercury Electrode

Linear plots of peak height versus concentration were found in the investigation of all of the metals listed in Table 1. With the DME, concentrations lower than  $10^{-8}$  could be detected for copper (II), lead (II), and cadmium (II), and concentrations below  $2 \times 10^{-7}$  could be detected for the other elements investigated. If a cell had been made of some material with less tendency to adsorb trace metals, even lower limits of detection would have been possible. Cells made of materials such as polymethyl methacrylate or polyethylene should be investigated for this purpose. The surface area of the electrodes and the gas dispersion tube in contact with solution should be minimized as much as possible so that adsorption effects are reduced. Whenever possible fused silica should be used instead of the other types of glasses. For example, the platinum counter electrode should be sealed in fused silica rather than in a Pyrex glass tube. A DME capillary made of

Teflon should also be investigated (101). Fritted glass disk dispersion tubes should not be employed for low-level determinations. Possibly polyethylene tubing with a porous Vycor tip would be more suitable for the deaeration of solutions.

#### Hanging Mercury Drop Electrode

From the investigation of the hanging mercury drop and the sitting drop electrodes, it was found that very sensitive and sometimes reproducible results could be obtained. However, the difficulty in obtaining reproducible resistances in the mercury column is the chief disadvantage of this technique. This results in distorted backgrounds, and a longer plating time is required in order to make the differences in background insignificant in comparison to the much larger anodic stripping currents obtained. If it had not been necessary to deaerate the solution after each standard addition, the same mercury droplet could have been used for successive scans and much better reproducibility would have resulted. A cell design in which gas bubbles do not impinge on the drop surface should minimize this problem.

#### Mercury Film Rotating Disk Electrode

The employment of the mercury coated RDE allows the determination of metals, amenable to stripping analysis, to concentrations well below  $10^{-8}$  F in less than 15 minutes analysis time. This time includes deaeration, the anodic stripping scan on the sample solution, and the scan after the standard addition has been made.

It was also determined in the study of the thin film rotating

disk electrodes that excellent reproducibility was obtained with the employment of vitreous carbon as an electrode substrate material. Another advantage of the employment of this material is that wax impregnation is not necessary. Better reproducibility was obtained when the same mercury coating was employed for the analysis of several solutions, instead of plating the mercury on and removing it for each scan.

#### Other Considerations

It was concluded that the employment of this square-wave polarograph is feasible for the analysis of water samples. The instrument with the use of the DME and RDE could be employed for routine analyses. The thin mercury film RDE could be utilized for the rapid analysis of very low concentrations of metals. The DME could be employed for the determination of metals which are not amenable to stripping analysis and when intermetallic compound formation is a considerable problem. The use of more than one electrochemical cell with the same instrument would reduce the total analysis time for a large number of samples.

The utilization of square-wave polarography would have the following salient features: a cross-check for other methods such as emission and atomic absorption spectroscopy, the determination of several metal ions for one voltage scan, a relatively less expensive technique (less than \$3000), and has the additional flexibility of being useful for the determination of non-metals.

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