Application Note P-2

Princeton Applied Research

Subject: Basics of Voltammetry and Polarography

INTRODUCTION

Voltammetry is the electrochemical technique in which the current at an electrode is measured as a function of the potential, or voltage, applied to the electrode. The potential is varied in some systematic manner and the resulting current-potential plot is called a voltammogram. The most common application of voltammetry is for analytical purposes.

Voltammetry can be used to analyze any chemical species that is electroactive, i.e., that can be made to oxidize or reduce. The potential of the electrode is the controlled parameter that causes the chemical species to be oxidized or reduced. The potential can be thought of as "electron pressure" which either forces a species in solution to gain an electron (reduction) or lose an electron (oxidation). As the potential of the electrode becomes more negative, it becomes more strongly reducing. Conversely, as the potential becomes more positive, it becomes more strongly oxidizing (Figure 1). Therefore, the redox reaction taking place on the electrode can be controlled by controlling the electrode potential.

The current, on the other hand, is simply a measure of electron flow. The current is due to electron transfer that takes place when an oxidation or reduction occurs on the electrode surface. This type of current is termed Faradaic. In voltammetry, the Faradaic current is proportional to concentration. The current due to a reduction (cathodic current) is, by convention, assigned a positive sign. The current due to an oxidation (anodic current) is assigned a negative sign (Figure 1).

If a voltammetric measurement is made using a dropping mercury electrode, the technique is termed polarography.[1] The dropping mercury electrode (DME), which consists of mercury flowing through a capillary and emerging from the orifice as a continual series of mercury drops, is deserving of this special consideration because it is the most useful electrode for analytical purposes. This is because the mercury drips expose a clean, reproducible surface of constant area to the solution.

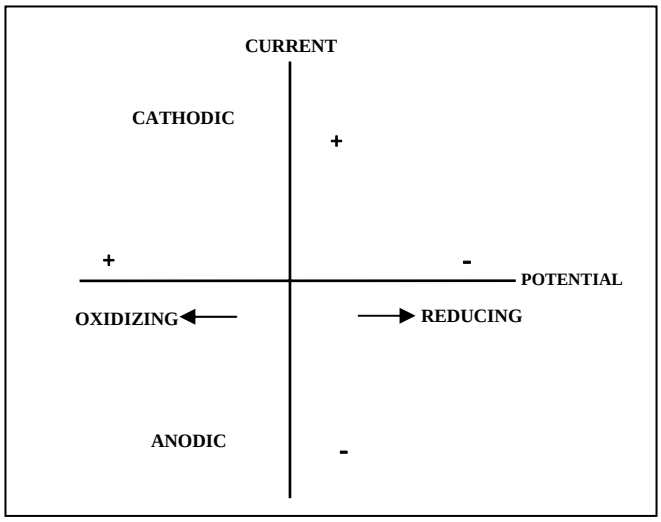

FIGURE 1: Convention for plotting voltammograms.

While electrodes such as glassy carbon, graphite or platinum can be used, great care must be exercised with such solid electrodes to insure that the surface of the electrode is not changed by the electrochemical reactions taking place. The voltammogram or polarogram is the result of electron transfer between the electrode surface and a species in solution. To be useful analytically, the current-potential plot should reflect changes that are taking place in the concentration of a species in solution and not in the nature of the electrode surface. A reproducible electrode, then, is of utmost importance to the accuracy and precision of the analytical determination. The DME is far superior to other electrodes in this regard. Typically, the relative standard deviation of a polarographic measurement using a DME is approximately 1%.

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CELL CONSIDERATIONS

The Princeton Applied Research polarographic analyzer is connected to the analytical cell. The polarographic analyzer controls the potential of the electrode and measures the current at the electrode. The cell contains three electrodes that are immersed in the solution to be analyzed. The *working electrode* is the electrode where the reaction of interest occurs. In polarography, this is the DME. The *reference electrode* provides a stable potential with which the potential of the working electrode is compared. The most common types of reference electrodes are the saturated calomel electrode and the silver/silver chloride electrode. The *counter electrode* is a conductive material that is chemically inert, such as platinum or graphite. The current in the cell is passed between the counter and working electrodes. No current passes through the reference electrode. The three-electrode potentiostatic circuitry that is incorporated into all PAR polarographic analyzers represents a major improvement over older two-electrode polarographic analyzers. Two-electrode analyzers cannot compensate for errors in potential control and current measurement caused by the resistance of the solution.

The cell should incorporate a mechanism for deaeration of the solution by purging with nitrogen. Molecular oxygen is a reducible species and will therefore contribute to the background current if allowed to remain in solution. For a more detailed discussion of the effect of oxygen on the polarographic analysis, see Princeton Applied Research Application Note D-2, "Deaeration…Why and How?". A purge time of 3-5 minutes is generally adequate. The nitrogen should be pre-saturated with the supporting electrolyte prior to purging to avoid evaporative losses and temperature changes. The cell should be blanketed with nitrogen while the polarogram is being run to avoid oxygen intrusion.

A major improvement in electrode design is incorporated into the PAR Model 303A Static Mercury Drop Electrode. The mercury reservoir, electrodes, drop knocker and deaeration system are contained in a compact, attractive unit (Figure 2). It also provides a significant increase in sensitivity when used with the polarographic analyzer.

FIGURE 2: PAR Model 303A Static Mercury Drop Electrode.

APPLICATIONS

As mentioned previously, polarography is a feasible method of analysis for any electroactive material. To perform a polarographic analysis, the following sequence is followed.

1. Sample Preparation: The sample for polarographic analysis must be in the form of a solution. If the sample is a solid, it must be dissolved. Other samples that might require special preparation would include, for example, extraction of a drug from tissue or the destruction of organic materials in blood prior to trace metal analysis.

2. Addition of Supporting Electrolyte: In most cases, an electrolyte is added to the sample before analysis. This is done to insure the conductive media which polarography requires (minimum 10^{-3} M). The particular supporting electrolyte may also dramatically affect the polarogram. It is not uncommon for electroactive materials to undergo electrochemical reactions at different potentials in different supporting electrolytes or even lose their electrochemical activity in certain media. The supporting electrolyte may be

judiciously chosen to avoid interferences. Some typical supporting electrolytes are shown in Table 1.

Another consideration is the volume of supporting electrolyte to add to the sample. This is largely determined by the analytical requirements and common sense. For example, if trace metals are being determined, a minimum volume of supporting electrolyte should be added to avoid excess dilution of the analytes. If, on the other hand, the analyte is present in high concentration, such as a plating bath, 10 µL of the sample may be added to 10 mL of supporting electrolyte

3. Polarographic Scan: The particular polarographic analyzer is set up to perform the desired measurement. This will be discussed in the following section.

4. Quantitation: Quantitation is carried out by comparing the response from the sample to the response from a standard. Quantitation may be effected by preparing a standard curve or by the method of standard additions.

Acids: HCl, HNO_3, H_2SO_4, H_3PO_4, Citric Acid

Bases: NaOH, KOH, TBAOH[1], NH_4OH

Buffers: Citrate, Tartrate, Acetate, Phosphate, Borate

Non-Aqueous Solvents: Alcohols, Acetonitrile, DFM, DMSO – containing dissolved salts for conductivity

[1]TBAOH = Tetrabutylammonium Hydroxide

TABLE 1: Some commonly used supporting electrolytes.

A unique advantage of polarography is that it works equally well for metals, non-metals, ions and organics. Extensive summaries of reduction and oxidation potentials for metals, ions and organic substances may be found in a number of different references.[2-10] Elements that can be determined by voltammetry are shown in Figure 3. The half-wave potentials for some of the more common metals and ions are found in Table 2 and 3. The listings of reduction and oxidation potentials usually include several different electrolytes for each species of interest. These listings may also be used to determine which species might interfere in a particular analysis. An interfering species is a substance that reduces or oxidizes at the same potential as the analyte. Generally, a potential difference of about 100 mV is sufficient to allow resolution of the species of interest. One could, for example, determine form reference 3 that Pb (II) is reduced in 1M HCl at -0.44 V and the expected interferences are As (III) and Ti (I). The reduction or oxidation of organic substances proceeds via functional groups and most references categorize organics into section according to the functional group being reduced. For example, one would find nitro compounds in one section, carbon-halogen bond reductions in a third section. Examples of some reducible organic functional groups are found in Table 4.

Metal	Supporting Electrolyte	$E_{1/2}$ (V)
As (III)	1M HCl	-0.43 / -0.67
Bi (III)	1M HCl	-0.09
Cd (II)	0.2M NH_4 Citrate pH 3	-0.62
Co (II)	1M NH_3 – 1M NH_4Cl	-1.22
Cr (III)	0.2M KSCN pH 3 with HOAc	-0.85
Cr (IV)	1M NaOH	-0.85
Cu (II)	0.2M NH_4 Citrate pH 3	-0.07
Fe (III)	0.2M TEA – 0.2M NaOH	-1.0
Mn (II)	1M NH_3 – 1M NH_4Cl	-1.66
Ni (II)	1M NH_3 – 1M NH_4Cl	-1.0
Pb (II)	0.2M NH_4 Citrate pH 3	-0.45
Sb (III)	6M HCl	-0.18
Sn (II)	0.2M HOAc- 0.2M NaOAc	-0.20 / -0.53
Sn (IV)	1M HCl – 4M NH_4Cl	-0.25 / -0.52
Ti (I)	1M HNO_3	-0.48
U (VI)	0.1M HCl	-0.18 / -0.94
Zn (II)	0.2M NH_4 Citrate pH 3	-1.04

TABLE 2: Half-wave potentials of selected metal ions.

Anion	Supporting Electrolyte	$E_{1/2}$ (V)
Br^-	0.1M KNO_3	(0.12)
CN^-	0.1M NaOH	(-0.36)
Cl^-	0.1M KNO_3	(0.25)
I^-	0.1M KNO_3	(-0.03)
IO_3^-	0.1M Phosphate Buffer pH 6.4	-0.79
NH_2OH	1M NaOH	(-0.43)
NO_2^-	2M Citrate pH 2.5	-1.06
S^-	0.1M NaOH	(-0.76)
SCN^-	0.1M KNO_3	(0.18)
$S_2O_3^-$	0.2M NaOAc Buffer pH 5	(-0.65)

TABLE

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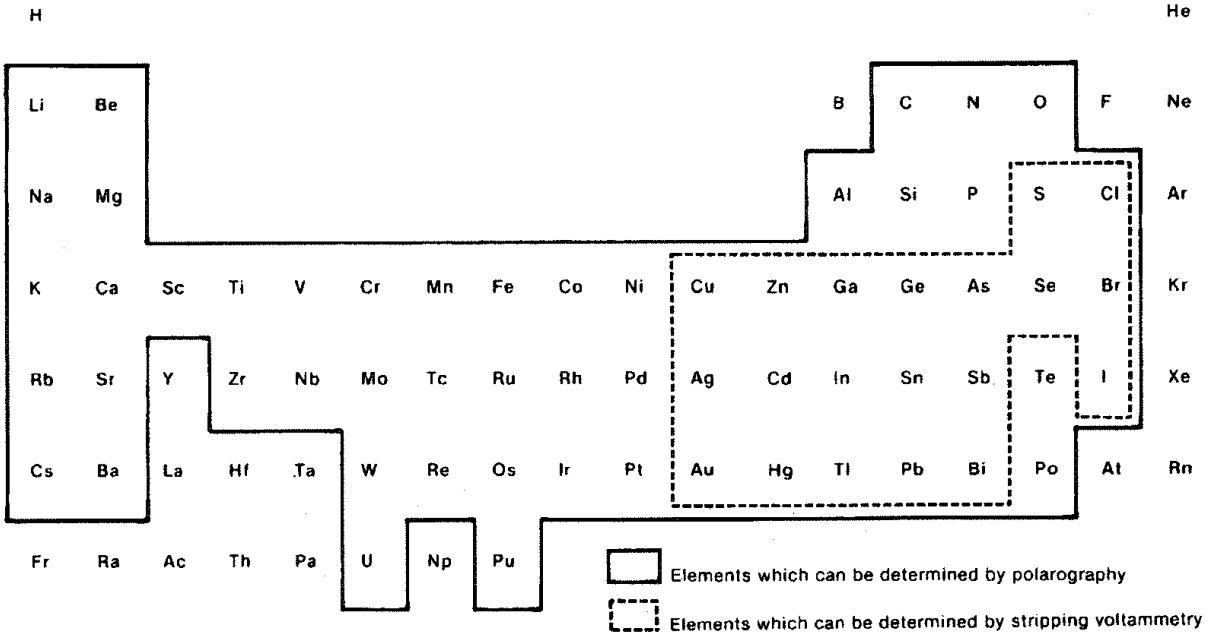

FIGURE 3: Elements determined by voltammetry.

Olefin-conjugated aromatics
Conjugated systems
Imines
Oximes
Nitriles
Diazo Compounds
Diazonium Sales
Nitroso Compounds
Dienes
Acetylenes
Ketones
Aldehydes
Aromatic Carboxylic Acids
Halides
Thiocyanates
Heterocycles
Organo-metallics

TABLE 4: Polarographic reduction of various functional groups.

POLAROGRAPHIC MODES

Polarography is an "ancient" technique by modern instrumental standards, having been discovered in 1921. analytical chemist. The various polarographic techniques available with PAR polarographic analyzers are described below.

DC and Sampled DC Polarography

The polarographic instrument scans the appropriate voltage range in which the reduction or oxidation occurs. The simplest method for applying the voltage scan is a linear "ramp" as shown in Figure 4. This is the programming waveform for dc polarography. The current is measured continuously by the polarographic analyzer. When this waveform is applied to a cell containing 1M HCl, 0.5mM Cd (II) ions and the three electrodes described previously, the dc polarogram shown in Figure 5 is obtained. At the initial potential, which is slightly positive of 0.0 V vs. SCE, the current is anodic. This is experimentally apparent by the negative value of the current. The electrode reaction at the initial potential is the oxidation of mercury. The high current from this process prevents observation of reactions at more positive potentials. As the potential is scanned in a negative direction, the oxidation of mercury ceases and at -0.6 V the reduction of Cd (II) begins. The current increases rapidly to its limiting or diffusion-controlled value and does not increase further until the reduction of the H^+ ions in the HCl begins at about -1.2 V. The potential where the Cd (II) reduction current is one-half its limiting value

is called the half-wave potential or $E_{1/2}$. The magnitude of the diffusion current above the baseline (found by running the polarogram with no Cd (II)) is proportional to the concentration of Cd (II). In this electrolyte the reduction of H^+ ions, at -1.2 V vs. SCE, limits the negative potential value to which the polarogram can be run. In other words, substances with half-wave potentials more negative than -1.2 V vs. SCE cannot be observed in 1M HCl.

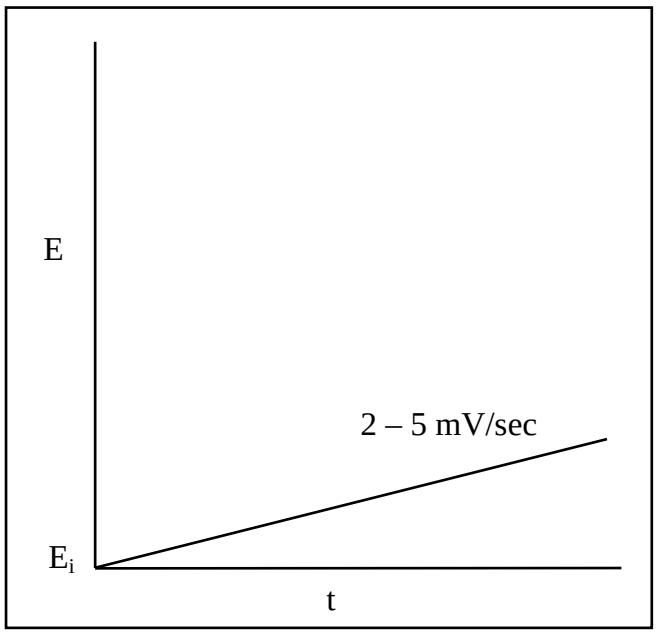

FIGURE 4: Programming waveform for dc polarography.

The current oscillations in Figure 5 are due to the changing area of the mercury drop during the drop life. This is a characteristic of the "conventional" DME, but not the Model 303A Static Mercury Drop Electrode. This undesirable feature can be remedied by using sampled dc polarography, in which the current is only measured for the last several milliseconds of the drop life. This technique results in a smooth polarogram that has the same shape as a dc polarogram. The drop time in sampled dc polarography must be mechanically controlled.

The analytical detection limit for dc and sampled dc polarography is about 1 ppm. The net current that is measured by these techniques is actually the sum of two components, the Faradaic current and the charging, or capacitance current. Faradaic current is due to the electron transfer at the electrode surface and is proportional to the concentration of the material being oxidized or reduced. Charging current is due to the capacitive nature of the electrode surface. Charging current contributes to the background current and substantially lowers the detection limit.

Although of limited analytical utility, dc and sampled dc polarography are still useful to distinguish between oxidation and reduction processes.

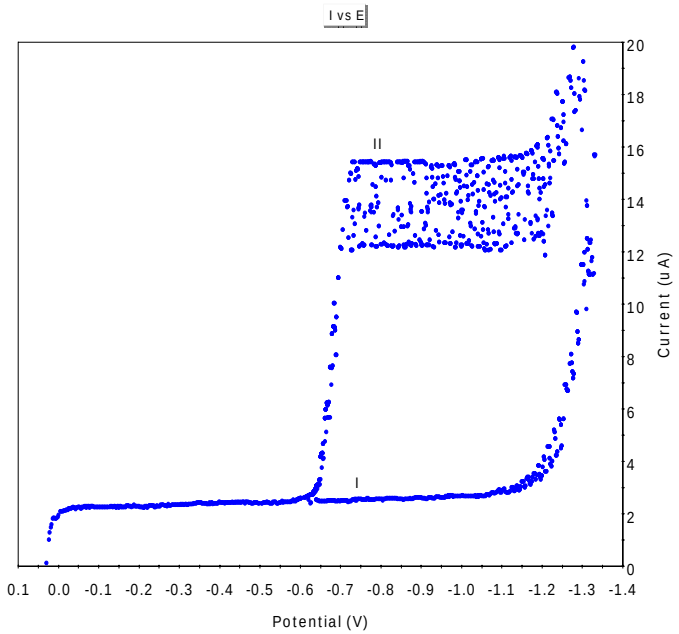

FIGURE 5: Polarograms of (I) 1M hydrochloric acid alone and (II) 1M hydrochloric acid containing 0.5 mM cadmium ion.

Pulse Polarographic Techniques

The techniques of normal pulse and differential pulse polarography have largely displaced dc polarography for analytical measurements. The pulse waveforms are designed to enhance the Faradaic current relative to the charging current, leading to significantly improved detection limits. With the pulsed techniques the drop time must be controlled, i.e., the mercury drop is dislodged by mechanically tapping the capillary. The drop knocker must be incorporated into the electrode system. The drop time is variable and is set on the polarographic analyzer. The instrument can then synchronize the drop time with the waveforms described below.

I. Normal Pulse Polarography

The programming waveform used for normal pulse polarography is shown in Figure 6. The DME is held at

the initial potential until there are only about 60 msec left in the lifetime of the drop. The potential is then stepped to a new value and held for the remainder of the drop life. During the last 17 msec of this pulse the current is measured and plotted versus the applied potential. Each new drop is stepped to a greater potential to create the voltage scan.

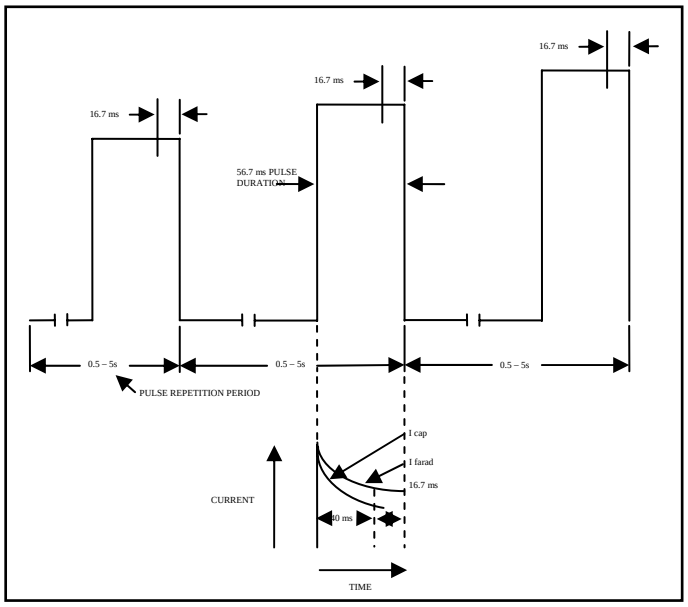

FIGURE 6: Potential waveform and resulting current for pulse polarography.

The application of the potential step produces a concomitant change in the current. This change in current comes from two sources. The first is the additional current, which must be passed to charge the double layer capacitance of the electrode to the new applied potential. The charging current decays exponentially after the initial current "spike". Simultaneously, an additional Faradaic current may be observed if the potential is stepped to a value where an oxidation or reduction reaction occurs. The Faradaic current decays from the initial "spike" at a rate that is proportional to the square root of the time.

As a result of these current decay profiles after the potential is stepped, the charging or capacitance current decays very rapidly to nearly zero but the Faradaic current (the current that is proportional to concentration) decays more slowly. The current is measured about 40 msec after the pulse is applied, at which time the current is almost purely Faradaic. A normal pulse versus a dc polarogram for Fe (III) in 0.2M ammonium tartrate buffer, pH 9, is shown in Figure 7. An improvement in detection limit of 2-10 times is observed for normal pulse over dc polarography.

As will be explained later, normal pulse polarography is not as sensitive as differential pulse polarography. Its greatest analytical utility is for those reactions which tend to "poison" the electrode. For example, sulfide ion (S^{2-}) reacts with mercury at the proper potential to form mercuric sulfide on the surface of the mercury drop. Since reactions of this type occur on the surface, the surface tends to become less reproducible, leading to a loss of precision in the current measurement. This is especially true with dc, sampled dc or differential pulse polarography, where the potential is "ramped". With normal pulse polarography, the initial potential can be set at a potential where the surface reaction does not occur. The filming reaction does not take place **u**ntil the potential is pulsed to the appropriate value. Since the current is measured only 40 msec after the application of the pulse, the electrode surface, and therefore the measured current, is very reproducible. In fact, "poisoning" of the surface is rare with a DME (S^{2-} can be determined with excellent precision at a DME), but can be extremely serious for a solid electrode.

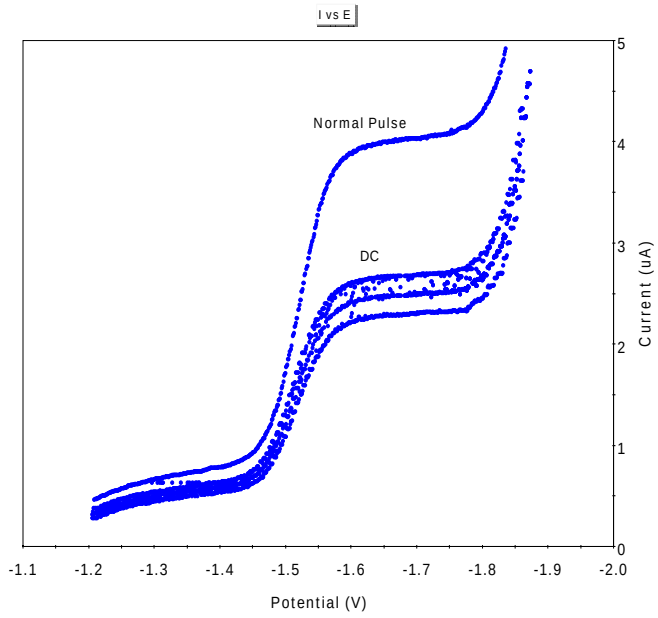

FIGURE 7: Normal pulse and dc polarograms for iron in ammonium tartrate buffer, pH 9.

II. Differential Pulse Polarography

A still greater improvement in sensitivity is made by using the programming waveform shown in Figure 8. The technique using this waveform is called differential

pulse polarography and combines a linear voltage ramp with pulses of a fixed magnitude. The pulses (magnitude 5-250 mV) are repeated once during each drop lifetime and last about 60 msec as in normal pulse. The current is measured twice – once before applying the pulse and once during the last 17 msec of the pulse. The first current is instrumentally subtracted form the second current. The differential pulse polarogram is thus a plot of current difference versus applied potential. The use of the pulse minimizes the effect of charging current, as in normal pulse polarography. When both potentials, i.e., the potential before and the potential after the pulse is applied, lie either before or after the rising portion of the polarographic wave (see Figure 5), not change in the measured Faradaic current will be observed. However, when at least one of these potentials is on the rising portion of the polarographic wave, a significant Faradaic current will be measured using the differential pulse technique. The measurement of current difference gives the differential pulse polarogram a peak shape which is analogous to the derivative of the dc polarogram. A comparison of a differential pulse and a dc polarogram is shown in Figure 9. Notice the slope of the dc polarogram baseline versus the baseline of the differential pulse polarogram. With differential pulse polarography, the peak current is a quantitative measure of concentration and peak potential is analogous to $E_{1/2}$. Notice, however, that peak potential and $E_{1/2}$ are not identical because the finite pulse height that is used results in a differential instead of a true derivative.

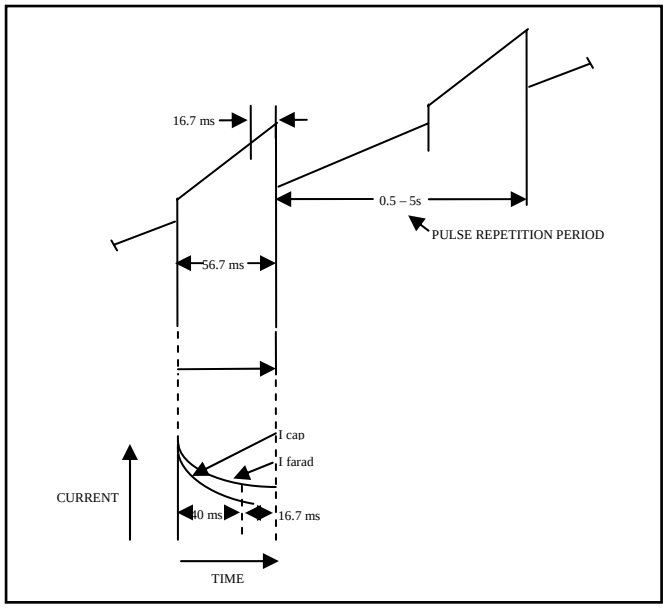

FIGURE 8: Differential pulse excitation waveform and resulting current-time behavior.

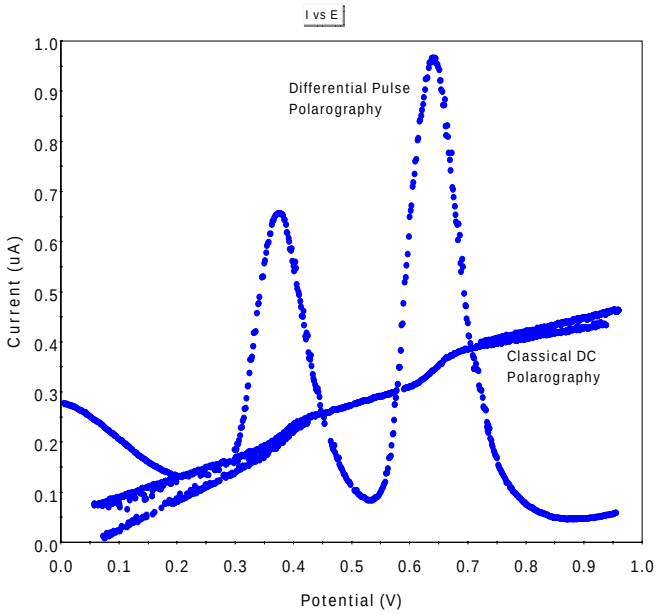

FIGURE 9: Differential pulse polarography.

The pulse height is a parameter that can be varied in differential pulse polarography to improve the sensitivity. As the pulse height increases (Figure 10) the peak potential increases in an almost linear manner. As this polarogram of Fe (III) and Mn (II) indicates, the pulse height also causes resolution to decrease and quantitation becomes more difficult for closely spaced peaks. One can manipulate sensitivity with pulse height, making the differential pulse technique a very potent analytical tool.

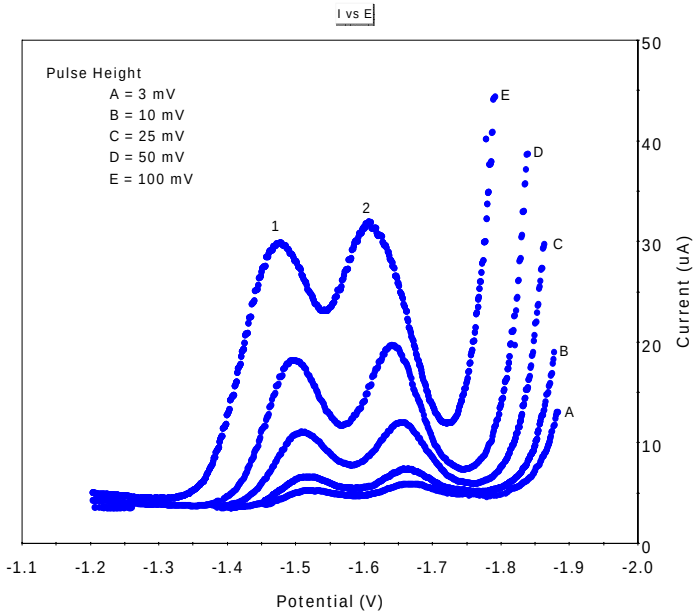

FIGURE 10: Effect of pulse height on peak height and resolution. 1: 20 ppm Fe (III) 2: 20 ppm Mn (III).

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A comparison of the sensitivities of the various polarographic techniques can be seen in Figure 11. The polarograms were obtained on a solution of 1 ppm Pb^{2+} and Cd^{2+} in 0.1M HNO_3. The current range, drop time and scan rate were the same for the four curves. The pulse height for the differential pulse polarogram was 50 mV.

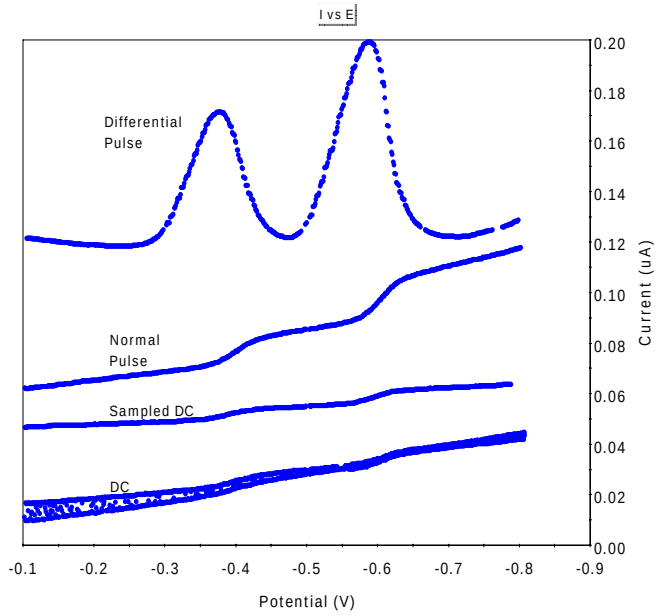

FIGURE 11: Comparison of polarographic modes. 1 ppm Pb^{2+} and Cd^{2+} in 0.1M HNO_3.

It is also possible to distinguish between Faradaic and capacitive currents in other ways, such as ac and square wave polarography, but these will not be discussed here.[11,12]

ANALYSIS BY DIFFERENTIAL PULSE POLAROGRAPHY

Direct Analysis

To illustrate the different approaches to polarography analysis, several examples will be presented. The vast majority of polarographic analyses involve a simple addition of the supporting electrolyte to the sample, followed by the polarographic scan. For example, the analysis of a lead-tin solder plating bath is performed in this way. The species of interest are lead and stannous (Sn^{2+}) ion. The analysis is carried out by adding 100 µL of the plating bath with a micropipette to 10 mL of an acetate buffer, pH 4.5. The polarogram obtained is shown in Figure 12.

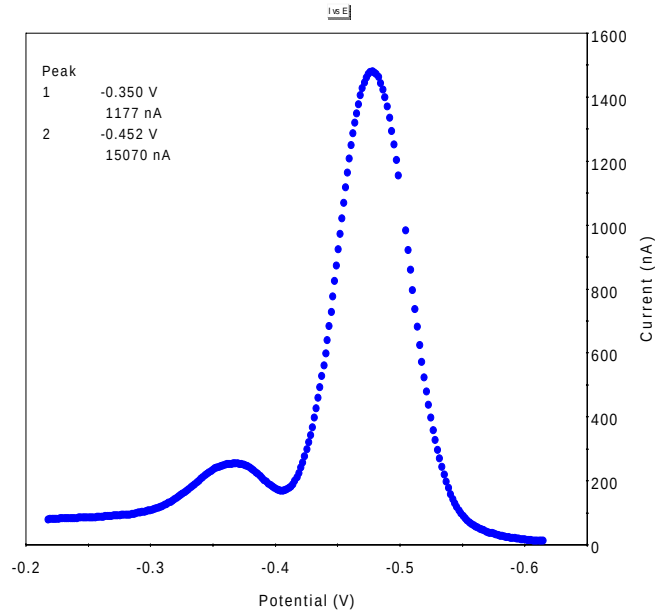

FIGURE 12: Analysis of a solder bath for Pb and Sn (II). Supporting electrolyte: acetate buffer, pH 4.5.

Chemical Pretreatment

Figure 13 illustrates the determination of 1 ppm Cu (II) I the presence of several thousand ppm Fe (III). Since Fe (III) is usually reduced at potentials more positive than Cu (II), most electrolytes present problems when the solution contains a large excess of Fe (III) compared to Cu (II). The reduction current due to Fe (III) swamps the current form the Cu (II) reduction. However, by reducing Fe (III) to Fe (II) with hydroxylamine (hydrochloride or sulfate), the analysis becomes trivial because the Fe (II) is no reduced before the Cu (II) reduction potential.

Extraction

A different sample preparation technique is illustrated by the work done on Levamisole, a veterinary pharmaceutical compound. This analysis uses an extraction technique to remove and concentrate the Levamisole form a milk matrix. After extraction form milk and evaporation of the solvent, the residue was taken up in 0.1 M tetramethylammonium iodide and the polarographic scan was performed. The peak in Figure 14 is for 30 ppb Levamisole in milk.

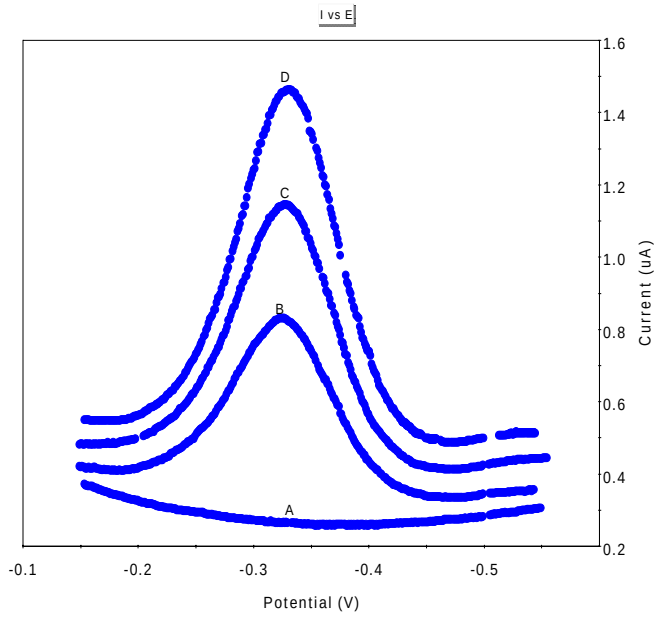

FIGURE 13: Differential pulse polarography of copper in the presence of iron saturated hydroxylamine HCL. A: Blank; B: Sample; C: Sample + 1 ppm Cu^{2+}; D: Sample + 2 ppm Cu^{2+}.

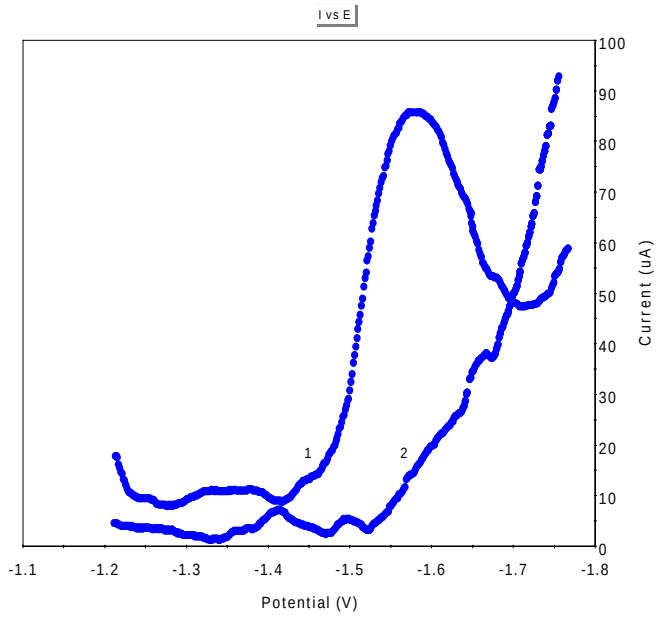

FIGURE 14: Analysis of levamisole in milk by differential pulse polarography. 1: milk control; 2: milk control + 30 ppb levamisole.

Derivatization

Sample preparation can also involve conversion of a non-reducible species to one that is reducible. The determination of aluminum illustrates this very well. The reduction potential of Al (III) is very negative and thus difficult to carry out directly. The analysis is easily performed, however, by formation of the Al (III) – Solochrome Violet RS complex. This dye reduces at about -0.45 V in the same buffer. Figure 15 shows that one may determine levels of aluminum as low as 50 ppb in this manner. This method has been applied to aluminum analyses in such diverse matrices as deodorants and explosives.

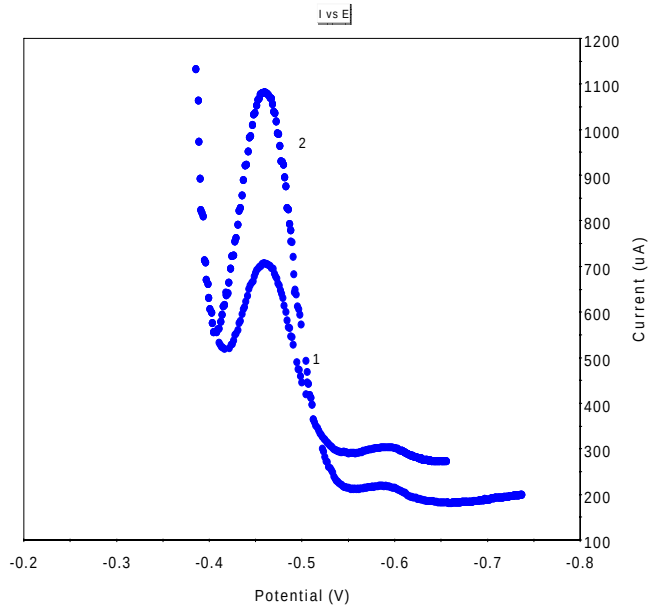

FIGURE 15: Al-SVRS complex in 0.1M acetate buffer by differential pulse polarography. 1: 50 ppb; 2: 125 ppb.

Supporting Electrolyte

The choice of supporting electrolyte may sometimes be the most important factor in a successful polarographic analysis. The determination of maleic and fumaric acids, for example, is impossible in acidic solutions because the peak potentials of the two isomers are nearly identical. In a phosphate buffer containing 1 M NH_4Cl at pH 8.2, these two isomers have well-separate peak potentials and analysis is straightforward as shown in Figure 16.

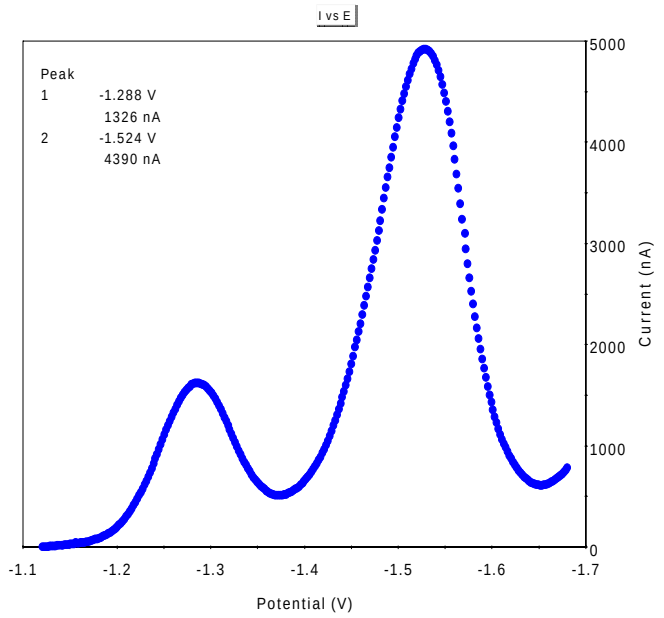

FIGURE 16: Differential pulse polarography of maleic acid (1) and fumaric acid (2) in malic acid.

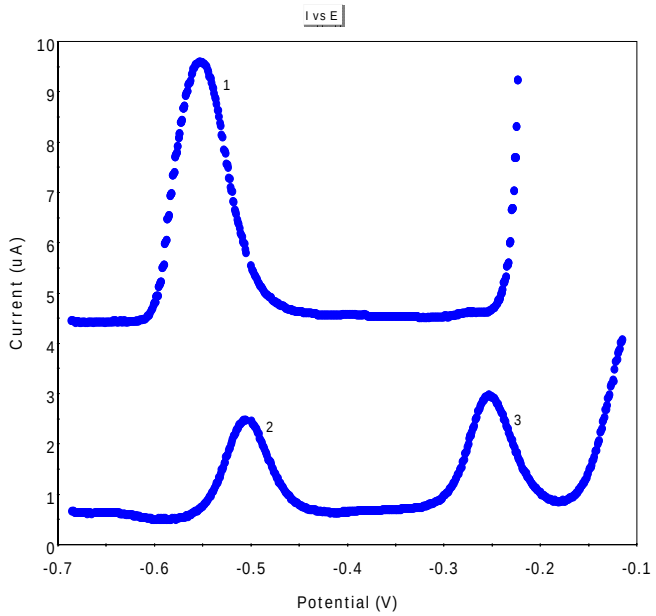

FIGURE 17: Sulfide, thiosulfate and sulfite in 0.025M NaOH and 0.025M acetate buffer. 1: 6.4 ppm S^{2-}; 2: 16 ppm SO_3^{2-}; 3: $S_2O_3^{2-}$.

pH Effects

The effect of pH in an analysis can be very important and adjustment of solution pH can often be used to analyze several species in a single solution. A mixture of S^{2-}, $S_2O_3^{2-}$ and SO_3^{2-} is often found in paper mill process liquors. In a 0.025 M NaOH solution, only S^{2-} shows a differential pulse peak, as shown in Figure 17. After adding acetic acid to bring the sample to pH 5, the S^{2-} is eliminated form the solution as H_2S while deaerating with nitrogen and separate peaks for $S_2O_3^{2-}$ and SO_3^{2-} are observed.

Complexation

The complexing ability of some supporting electrolytes can also be used to distinguish between the different oxidation states of a metal (Figure 18). In most electrolytes a single differential pulse peak is found for a mixture of Fe (II) and Fe (III), but in a 0.1 M Na2P2O7 buffer, pH 9, the Fe (III) is complexed more strongly by the pyrophosphate than the Fe (II). The differential pulse polarogram shows two well separated peaks for the Fe (II) / Fe (III) mixture.

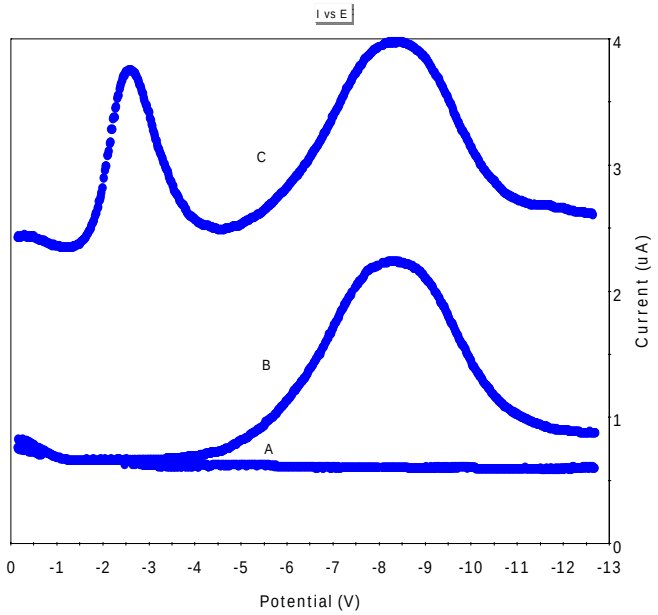

FIGURE 18: Differential pulse polarography of a Fe(II)/Fe(III) mixture. A: Blank; B: Blank + 25 ppm Fe(III); C: Blank + 25 ppm Fe(III) + 10 ppm Fe(II).

QUANTITATION

As with many other analytical techniques, quantitation in polarography may be carried out by calibration curve or standard addition techniques. In polarography it is not uncommon to obtain linear calibration curves over 3-4 orders of magnitude. To illustrate the linearity of calibration curves one normally observes in polarography, the calibration curve for Cr (III) in a 0.2 M KSCN – 0.2 M HOAc buffer is shown in Figure 19. When extended form concentrations of 0.1 ppm to 10 ppm, the calibration plot exhibits excellent linearity and a zero intercept.

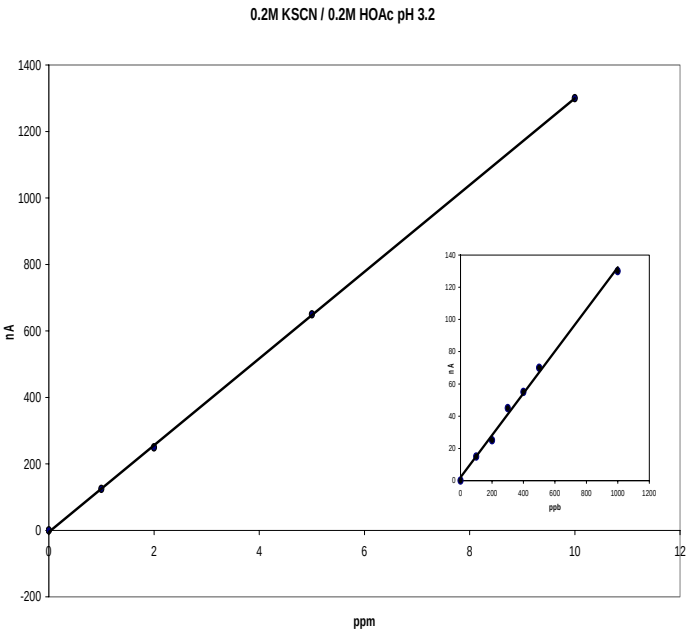

FIGURE 19: Chromium (III) peak current vs. concentration, differential pulse polarography.

ANODIC AND CATHODIC LIMITS

The DME is the electrode of choice for analytical voltammetry because of the reproducibility of the electrode surface.

However, since mercury is itself oxidized at potentials between 0 and +0.3 V vs. SCE, analytes that react positively of these potentials cannot be determined due to the excessively high current form the mercury oxidation. In these instances, another electrode material must be used. Alternative electrodes include platinum, gold, graphite and glass carbon. Glassy carbon is generally the best choice because of its inertness, hardness, nonporosity and ability to be polished to a very smooth finish.

The cathodic, i.e., negative, limit in the polarogram is determined by the reduction of cations in the supporting electrolyte. Acidic solutions, for example, are limited by the reduction of hydrogen ions, which occurs at approximately -1 V vs. SCE. The "breakdown" of sodium hydroxide solutions takes place at about -1.8 V vs. SCE, corresponding to the reduction of sodium ions. The most negative potentials can be attained by using tetraalkylammonium salts as the supporting electrolyte.

Mercury can be used to determine virtually every reducible metal. Also, the majority of organic functional groups are reducible and lend themselves well to analysis with a DME.

LINEAR SWEEP VOLTAMMETRY

The term linear sweep voltammetry is used to describe an analytical technique involving a solid electrode, i.e., not a DME, a linear dc "ramp" waveform (see Figure 4), and a rapid scan rate (20-100 mV/sec). It is most useful for determining oxidizable organics with a glassy carbon electrode (see Figure 20). A linear sweep voltammogram is "one-half" of a cyclic voltammogram. Cyclic voltammetry is an electrochemical technique that is used to examine the kinetics of electrode processes. *Cyclic voltammetry is not used for analytical determinations.* The peak height of a linear sweep voltammogram is proportional to concentration. The analytical sensitivity of linear sweep is approximately 1 ppm. The peak current is proportional to the square root of the scan rate.

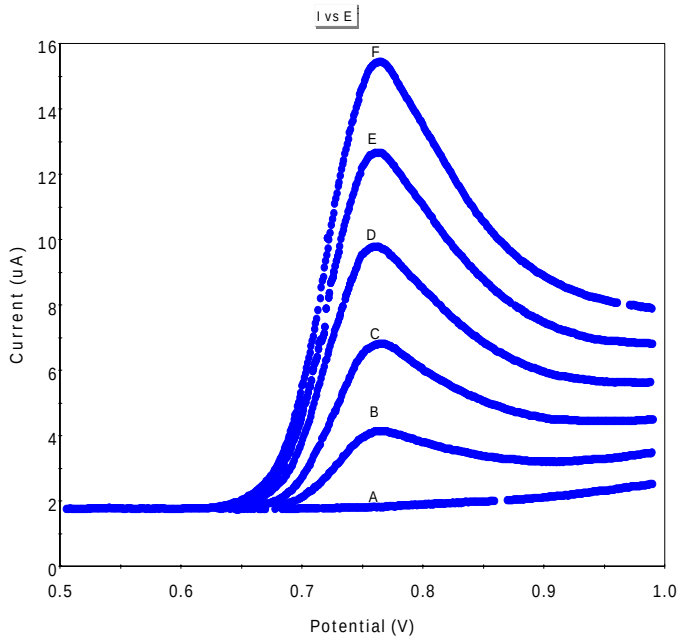

FIGURE 20: Linear sweep voltammetry of butylated hydroxyanisole in 0.12 M H2SO4 in 1:1 ethanol/benzene. A: Blank; B: 8.26 ppm; C: 16.4 ppm; D: 24.5 ppm; E: 32.6 ppm; F: 40.5 ppm.

CONCLUSION

This brief introduction to polarography illustrates the versatility of the technique, which allows the analytical chemist to determine the concentrations of metals, ions and organics. In polarography, the substance of interest is reduced or oxidized at a DME and the resulting current provides quantitative information about the substance in solution. Of the different polarographic techniques developed, differential pulse polarography is the most sensitive, enabling one to reach typical detection limits of 20 ppb, and possibly lower for some analytes. A comparison of the sensitivities of some polarographic and voltammetric techniques is found in Figure 21. More detailed descriptions of polarography and its applications are readily available from references cited.

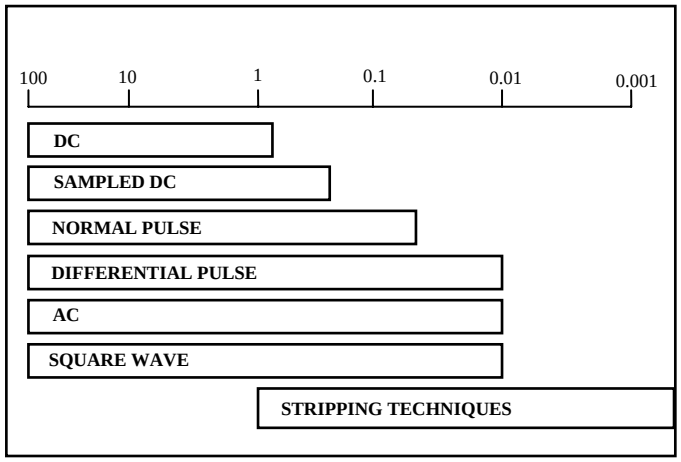

FIGURE 21: Relative sensitivities of polarographic techniques.

The analytical aspects of stripping voltammetry are not discussed in this Application Note. Details of this technique may be found in Application Note S-6 "Fundamentals of Stripping Voltammetry", available from Princeton Applied Research.

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Preparation of the most common buffers used in polarographic determinations

1. ***Acetate buffer*** **(0.1M, pH 4.5):** Dissolve 8.2 g of anhydrous sodium acetate (13.6 g sodium acetate trihydrate) in 800 mL deionized water and adjust to pH 4.5 with glacial acetic acid. Dilute to 1L.

2. 2. ***Ammonia/Ammonium Chloride buffer*** **(0.1M pH 9.4):** Dissolve 5.4 g NH_4Cl in 900 mL deionized water. Adjust to pH 9.4 with concentrated NH_4OH. Dilute to 1 L with deionized water.

3. ***Ammonium Citrate buffer*** **(0.2M, pH 3):** Dissolve 42.5 g of citric acid (monohydrate) in 750 mL deionized water. Adjust to pH 3 with NH_4OH. Dilute to 1 L.

4. ***Ammonium Tartrate buffer*** **(0.2M, pH 9):** Dissolve 30 g tartaric acid $[HOOC(CHOH)_2COOH]$ in 500 mL deionized water. Adjust to pH 9 with NH_4OH. The tartaric acid will precipitate near pH 4 but will redissolve near pH 6. Dilute to 1 L.

5. ***Sodium Tartrate buffer*** **(0.1M, pH 5):** Dissolve 15 g tartaric acid in 500 mL deionized water and adjust the pH to 5 by adding NaOH. Dilute to 1 L.

6. ***Phosphate buffer*** **(0.2M, pH 6.8):** Dissolve 24 g monosodium phosphate in 500 mL deionized water and adjust to pH 6.8 with phosphoric acid. Dilute to 1 L.

7. ***Thiocyanate buffer*** **(0.2M sodium thiocyanate, 0.2M acetic acid, pH 3.2):** Dissolve 16.2 g sodium thiocyanate (NaSCN) in 500 mL deionized water. Add 11.5 g glacial acetic acid. Dilute to 1 L.

8. ***Triethanolamine-Sodium Hydroxide*** **buffer (0.3 M triethanolamine, 0.2 M NaOH):** Dissolve 40.3 mL (45 g) triethanolamine and 8 g NaOH in deionized water and dilute to 1 L.

9. ***Britton-Robbinson buffer,*** **Stock solution: 0.04M acetic, phosphoric and boric acid, pH 2.87:** Add 17.5 mL of 0.2M NaOH to 100 mL of the stock solution. pH 7: add 52.5 mL of 0.2M NaOH to 100 mL stock solution.

10. ***Lithium Hydroxide/Lithium Chloride buffer*** **(0.1M LiOH/0.1M LiCl):** Dissolve 2.4 g of LiOH and 4.3 g of LiCl in deionized water and dilute to 1 L.

11. ***Hydrochloric Acid*** **1M HCl:** Add 82.5 mL of conc. HCl to 900 mL deionized water. Dilute to 1 L with deionized water. 0.1M HCl: Add 100 mL of the 1M HCl to 900 mL deionized water.

12. ***Nitric Acid*** **1M HNO_3:** Add 63 mL conc. HNO_3 to 900 mL deionized water. Dilute to 1 L. 0.01M HNO_3: Add 100 mL of the 1M HNO_3 to 900 mL deionized water. Or, add 6.3 mL conc. HNO_3 to 900 mL deionized water and dilute to 1 L.

13. ***Sulfuric Acid*** **1M H_2SO_4:** Add 55.5 mL H_2SO_4 to 900 mL deionized water. Dilute to 1 L. 0.1M H_2SO_4: Add 100 mL of the 1M H_2SO_4 to 900 mL deionized water. Or, add 6.3 mL conc. HNO_3 to 900 mL deionized water.

14. ***Sodium Hydroxide*** **1M NaOH**: Dissolve 40 g NaOH in 750 mL deionized water. Allow solution to cool and dilute to 1 L with deionized water. 0.1M NaOH: Dissolve 4 g NaOH in 750 mL deionized water. Dilute to 1 L.

15. ***Potassium Nitrate*** **(1M KNO_3)**
    i. Dissolve 101.1 g of KNO_3 in 800 mL of
    ii. deionized water. Dilute to 1 L.

16. ***Potassium Chloride*** **(1M KCl):** Dissolve 74.6 g of KCl in 800 mL of deionized water. Dilute to 1 L.

17. ***Tetraalkylammonium salts*** are often used in methanol, acetonitrile or dimethylformamide at 0.1M and 0.01M concentrations. Weigh out the salt and add the solvent. Examples:
    Tetrabutylammonium hydroxide
    Tetrabutylammonium fluoroborate
    Tetrabutylammonium iodide
    Tetrabutylammonium bromide
    Tetrabutylammonium perchlorate

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Tetramethyl analogs are also readily available. These compounds can be purchased form a laboratory supply house or Southwester Analytical Chemicals P.O. Box 485, Austin, TX 78764

18. ***Mercury***

Instrument mercury, purified by triple distillation, is available form Bethlehem Apparatus Co. In., Front and Depot Streets, Hellertown, PA 18055.