PRINCETON APPLIED RESEARCH
Applied Instruments Group

APPLICATION NOTE P-2

# BASICS OF VOLTAMMETRY AND POLAROGRAPHY

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## 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 which 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 drops expose a clean, reproducible surface of constant area to the solution.

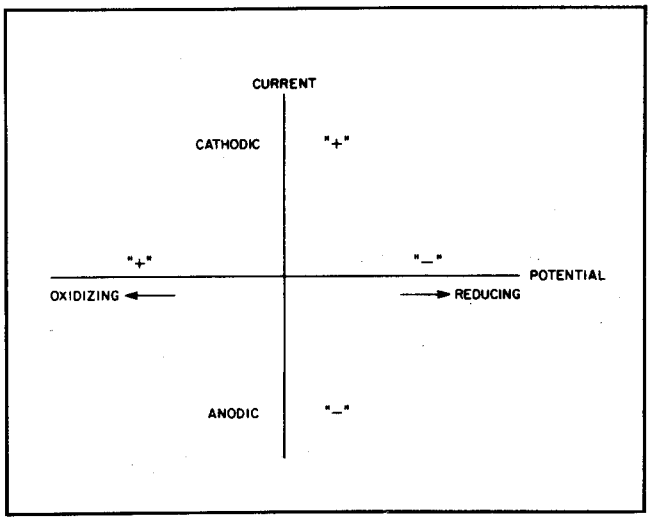



**FIGURE 1. Convention for plotting voltammograms.**

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 surface, then, is of utmost importance to the accuracy and precision of the analytical determination. The dropping mercury electrode is far superior to other electrodes in this regard. Typically, the relative standard deviation of a polarographic measurement using a DME is approximately 1%.

## Cell considerations

The EG&G 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 which 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 which is incorporated into all EG&G PARC 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 EG&G PARC 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 EG&G PARC Model 303 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. A more complete description of the Model 303 and a discussion of its operational characteristics may be found in the literature[2].

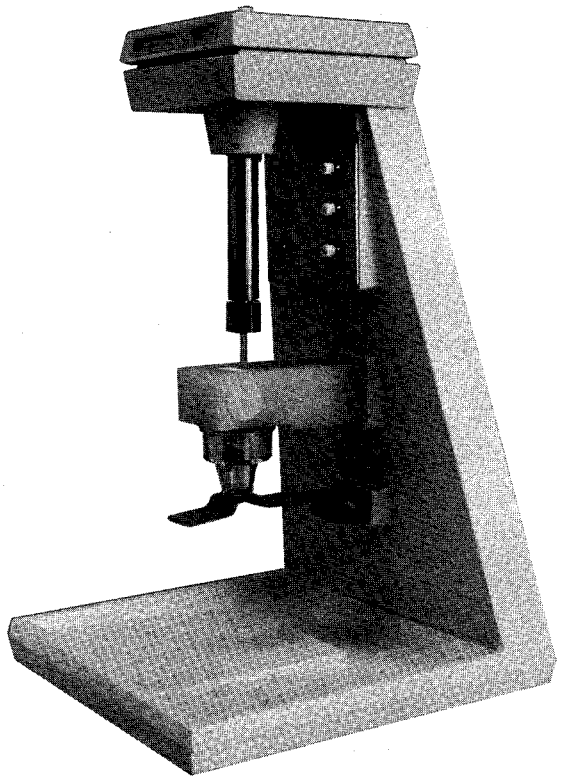


**FIGURE 2. EG&G PARC Model 303 Static Mercury Drop Electrode.**

## 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 I.

| |
|---|
| 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, DMF, DMSO—containing dissolved salts for conductivity |
| [1]TBAOH = Tetrabutylammonium Hydroxide |

**TABLE 1. Some commonly used supporting electrolytes.**

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 excessive dilution of the analytes. If, on the other hand, the analyte is present in high concentration, such as a plating bath, 10 microliters of the sample may be added to 10 milliliters 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.

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[3-11]. Elements which can be determined by voltammetry are shown in Figure 3. The half-wave potentials (defined on page 4) for some of the more common metals and ions are found in Tables 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 from reference 3 that Pb(II) is reduced in 1 *M* HCl at −0.44 V and the expected interferences are As(III) and Tl(I).

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

**TABLE 2: Half-wave potentials of some metal ions.**

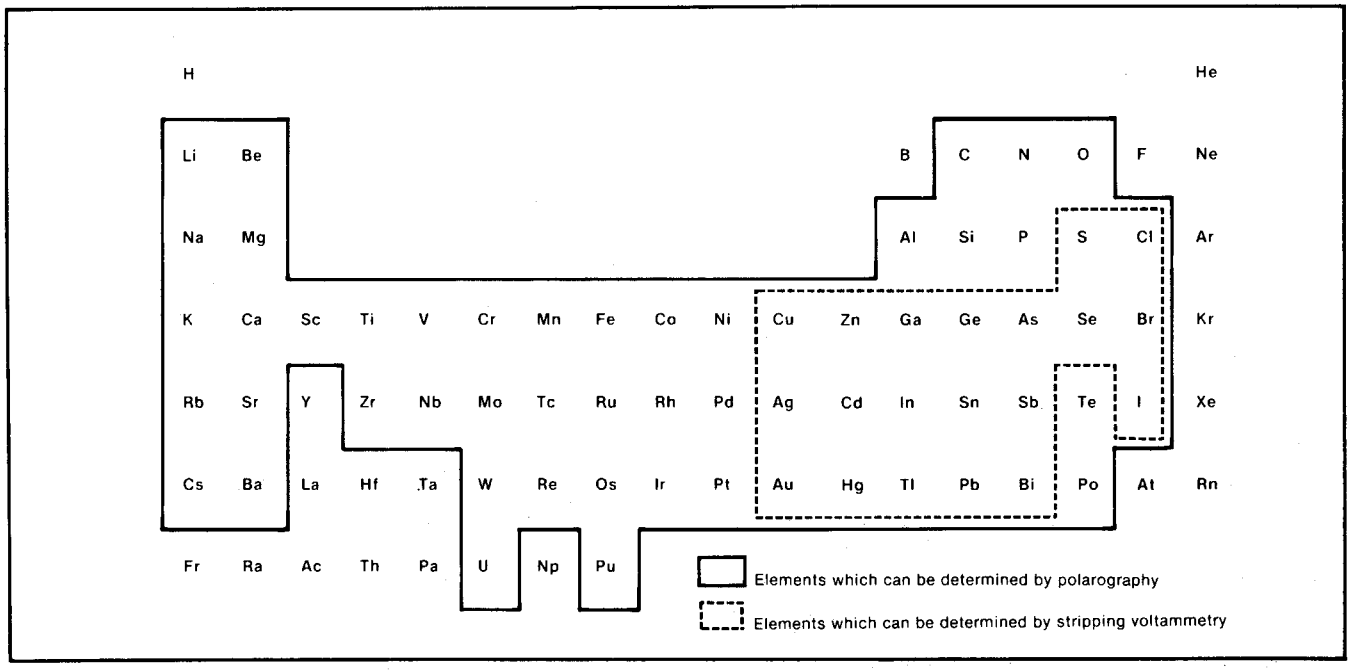



**FIGURE 3. Elements which can be determined by voltammetry.**

| ANION | SUPPORTING ELECTROLYTE | $E_{1/2}$ (V) |
|---|---|---|
| $Br^-$ | 0.1 *M* $KNO_3$ | (0.12) |
| $CN^-$ | 0.1 *M* NaOH | (−0.36) |
| $Cl^-$ | 0.1 *M* $KNO_3$ | (0.25) |
| $I^-$ | 0.1 *M* $KNO_3$ | (−0.03) |
| $IO_3^-$ | 0.1 *M* Phosphate Buffer, pH 6.4 | −0.79 |
| $NH_2OH$ | 1 *M* NaOH | (−0.43) |
| $NO_2^-$ | 2 *M* Citrate, pH 2.5 | −1.06 |
| $S^=$ | 0.1 *M* NaOH | (−0.76) |
| $SCN^-$ | 0.1 *M* $KNO_3$ | (0.18) |
| $S_2O_3^=$ | 0.2 *M* NaOAc Buffer, pH 5 | (−.40) |
| $SO_3^=$ | 0.2 *M* NaOAc Buffer, pH 5 | (−0.65) |

( ) Values in parentheses indicate that the electrode reaction is an oxidation.

**TABLE 3: Half-wave potentials of some anions.**

The reduction or oxidation of organic substances proceeds via functional groups and most references categorize organics into sections according to the functional group being reduced. For example, one would find nitro compounds in one section, carbon-halogen bond reductions in another section, and S-S bond reductions in a third section. Examples of some reducible organic functional groups are found in Table 4.

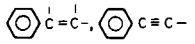
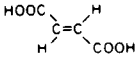
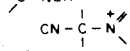
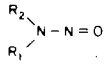
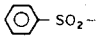
Olefin-conjugated aromatics, e.g. 
Conjugated systems such as: 
Imines, e.g. RCH=NH
Oximes, e.g. 
Nitriles, e.g. 
Diazo Compounds, e.g. 
Diazonium Salts
Nitroso Compounds, e.g. 
Sulfones, e.g. 
Sulfonium Salts, e.g. 
Nitro Compounds
Dienes
Acetylenes
Ketones
Aldehydes
Aromatic Carboxylic Acids
Halides
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. Improvements in instrumental circuitry in recent years have made polarography much more attractive to the analytical chemist. The various polarographic techniques available with EG&G PARC 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 1 *M* HCl, 0.5 *mM* 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 1 *M* HCl.

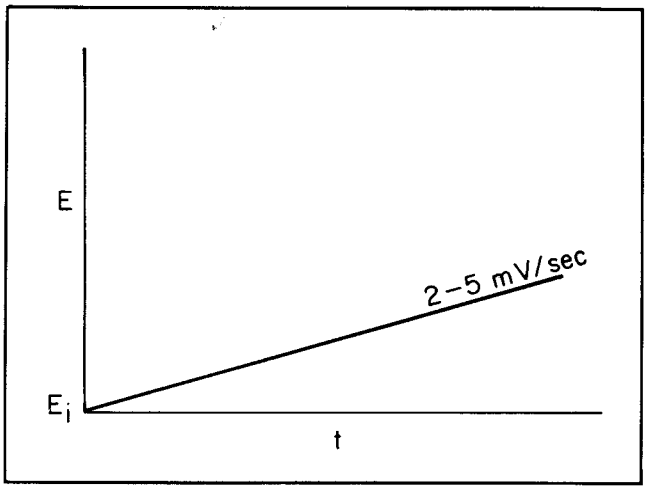



**FIGURE 4. Programming waveform for dc polarography.**

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 303 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.

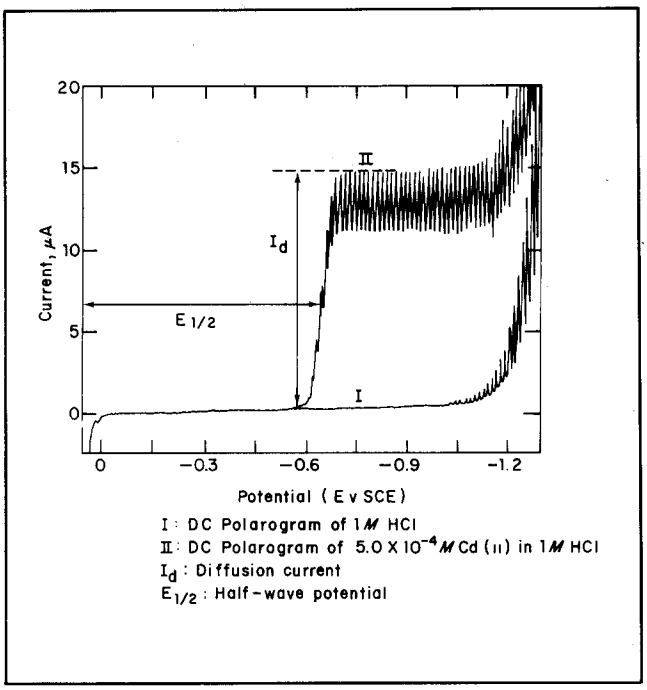



**FIGURE 5. Polarograms of (a) 1 *M* hydrochloric acid containing 0.5 m*M* cadmium ion, and (b) 1 *M* hydrochloric acid alone.**

The analytical detection limit for dc and sampled dc polarography is about 1 ppm. The net current which 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.

## *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 pulse 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 milliseconds (ms) 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 ms 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.

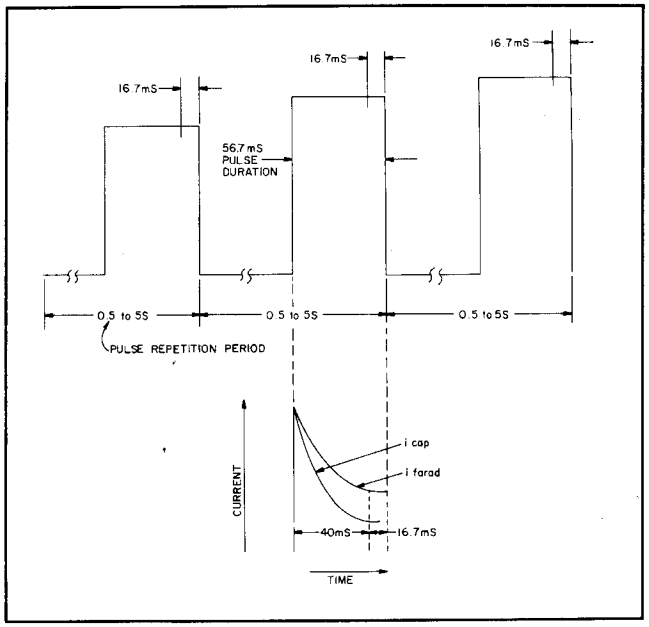



**FIGURE 6. Potential waveform and resulting current for pulse polarography.**

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 which 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 ms 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 0.2 *M* 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 mer-

curic 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 until the potential is pulsed to the appropriate value. Since the current is measured only 40 ms 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.

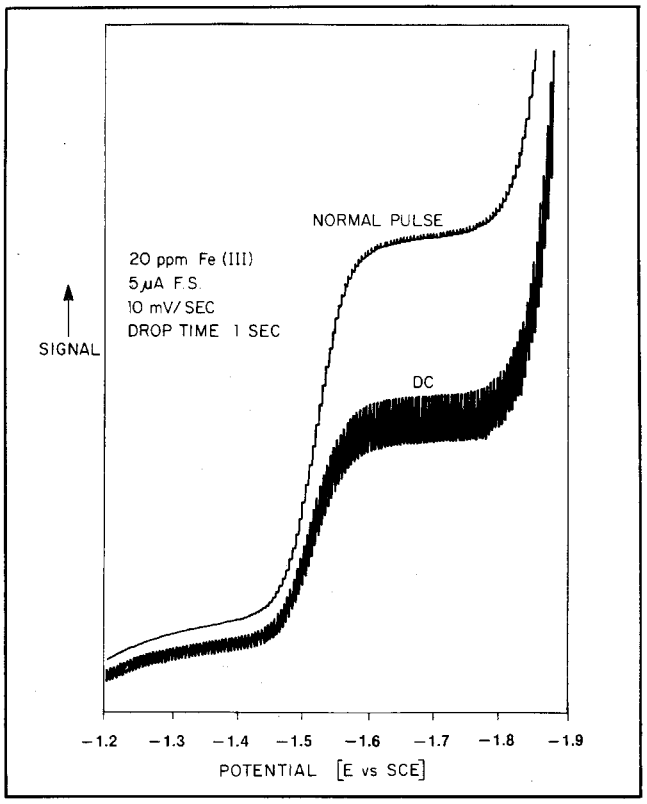



**FIGURE 7. Normal pulse and dc polarograms for iron in ammonium tartrate buffer, pH 9.**

*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 ms as in normal pulse. The current is measured twice— once before applying the pulse and once during the last 17 ms of the pulse. The first current is instrumentally subtracted from 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), no 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.

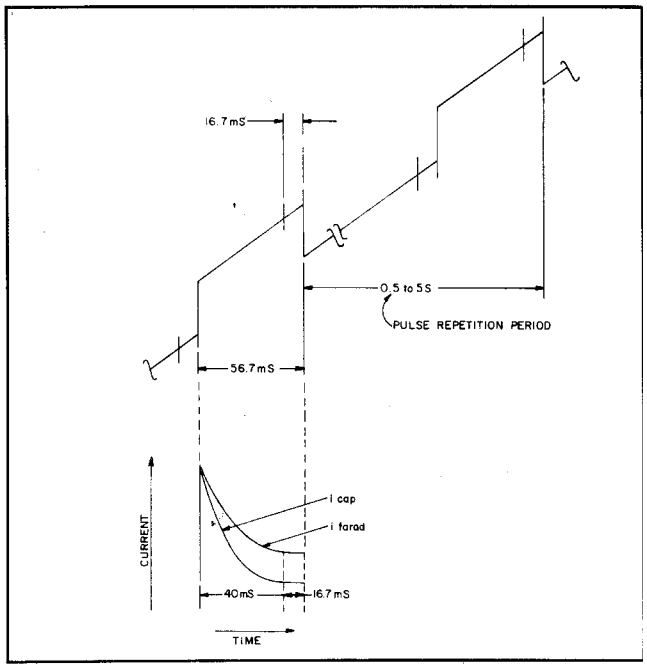



**FIGURE 8. Differential pulse excitation waveform and resulting current-time-behavior.**

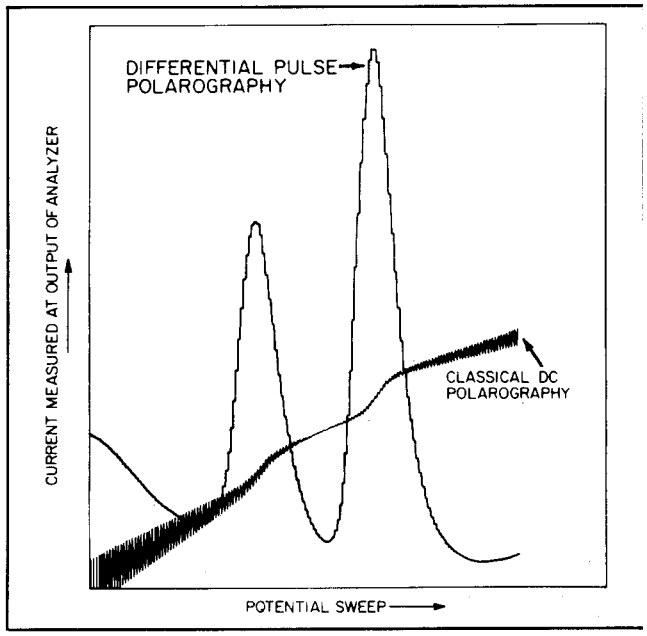



**FIGURE 9. Differential pulse polarography.**

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.

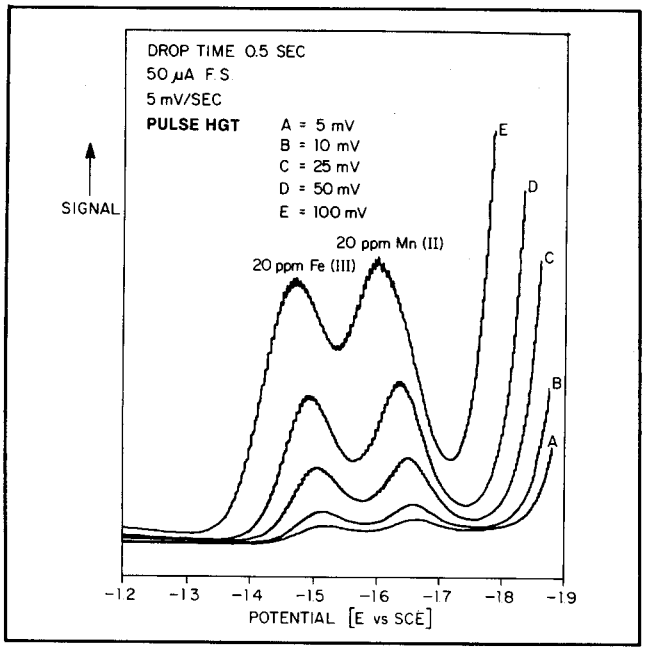



**FIGURE 10. Effect of pulse height on peak height and resolution.**

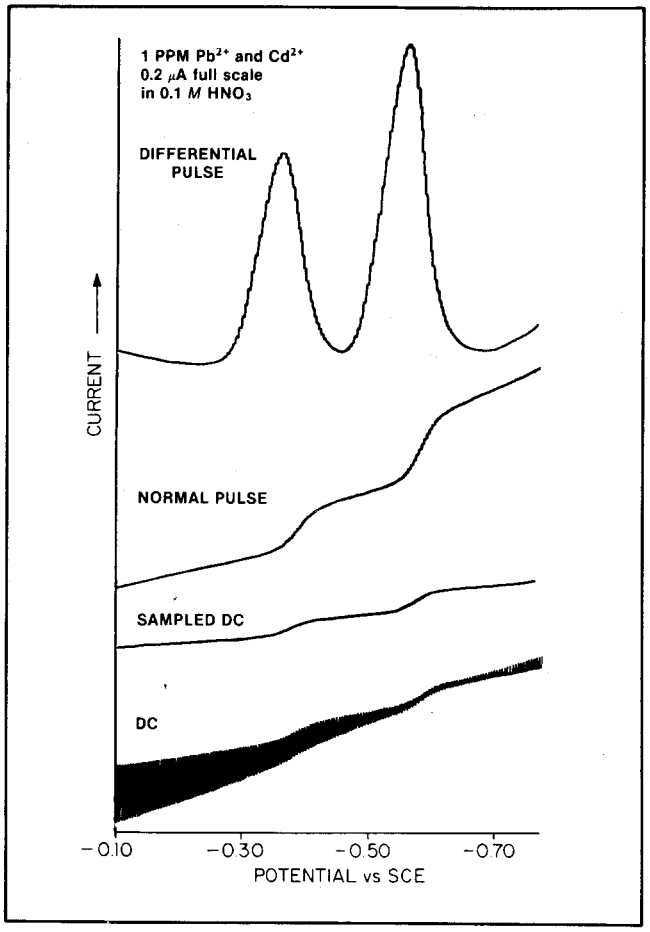



**FIGURE 11. Comparison of polarographic modes.**

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 0.1 *M* $HNO_3$. 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.

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[12-13].

## Analysis by differential pulse polarography

### *Direct Analysis*

To illustrate the different approaches to polarographic 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 microliters of the plating bath with a micropipet to 10 milliliters of an acetate buffer, pH 4.5. The polarogram obtained is shown in Figure 12.

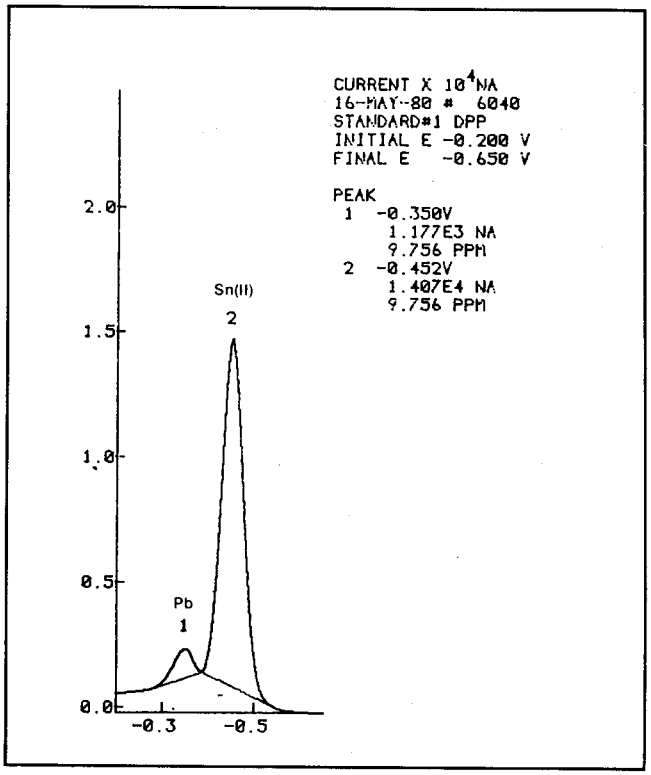



**FIGURE 12. Analysis of a solder bath for Pb and Sn(II). Supporting electrolyte: acetate buffer, pH 4.5.**

## *Chemical Pretreatment*

Figure 13 illustrates the determination of 1 ppm Cu(II) in 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 from 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 not reduced before the Cu(II) reduction potential.

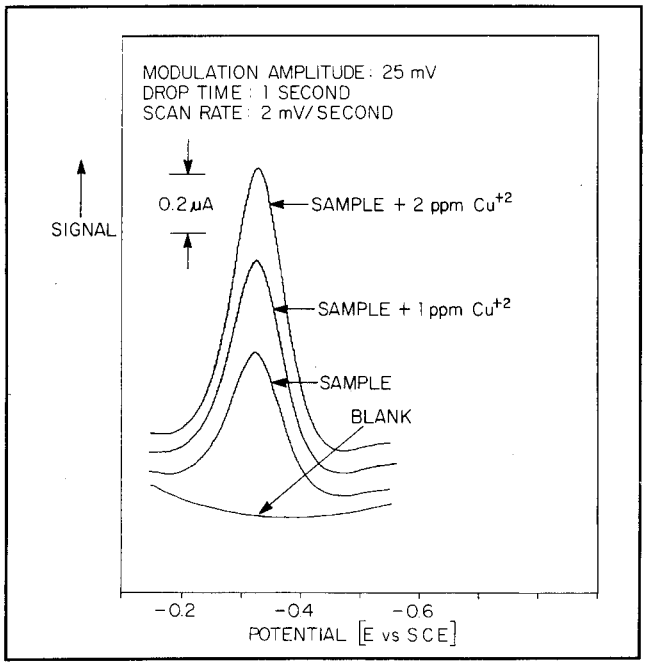



**FIGURE 13. Differential pulse polarography of copper in the presence of iron in saturated hydroxylamine•HCl.**

## *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 from a milk matrix. After extraction from 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.

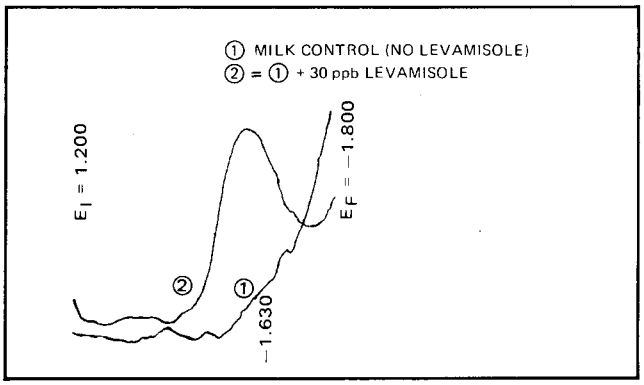



**FIGURE 14. Analysis of levamisole in milk by differential pulse polarography.**

## *Derivatization*

Sample preparation can also involve conversion of a non-reducible species to one which 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.

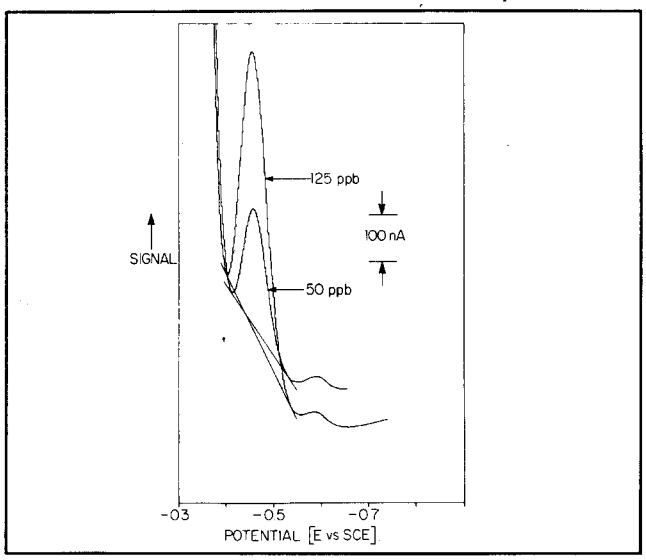



**FIGURE 15. Al•SVRS complex in 0.1 *M* acetate buffer by differential pulse polarography.**

## *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-separated peak potentials and analysis is straightforward as shown in Figure 16.

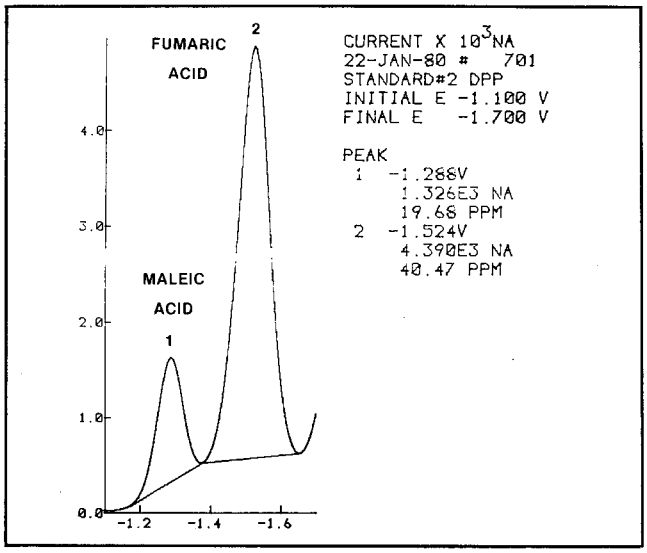



**FIGURE 16. Differential pulse polarography of maleic acid and fumaric acid in malic acid.**

### *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 from the solution as $H_2S$ while deaerating with nitrogen and separate peaks for $SO_3^{2-}$ and $S_2O_3^{2-}$ are observed.

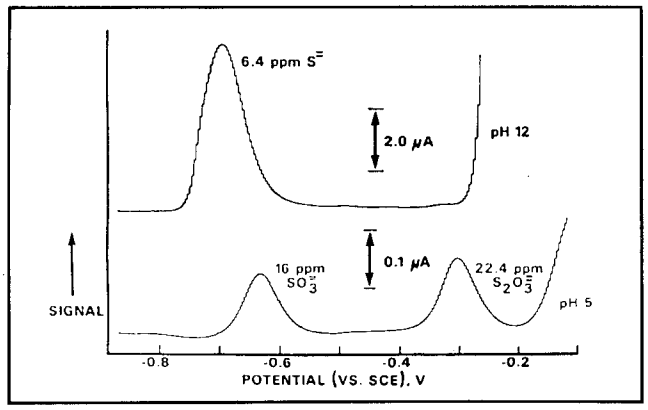



**FIGURE 17. Sulfide, thiosulfate, and sulfite in 0.025 *M* NaOH and 0.025 *M* acetate buffer.**

### *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* $Na_2P_2O_7$ 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.

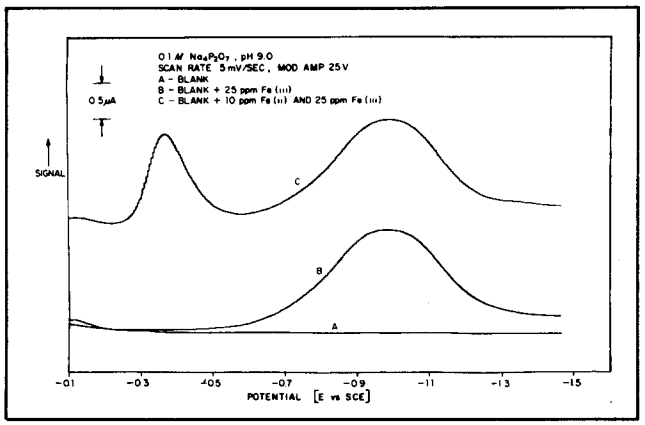



**FIGURE 18. Differential pulse polarography of a Fe(II)/Fe(III) mixture.**

## Quantitation

As with many other analytical techniques, quantitation in polarography may be carried out by standard 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 from concentrations of 0.1 ppm to 10 ppm, the calibration plot exhibits excellent linearity and a zero intercept.

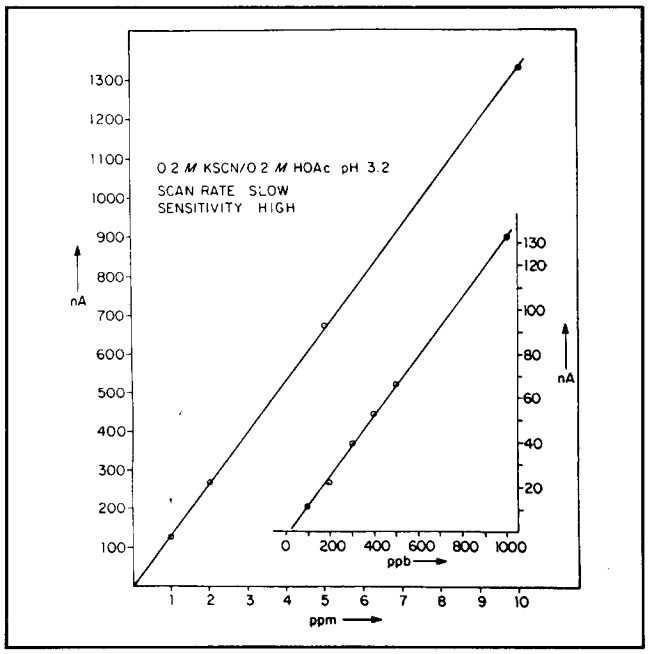



**FIGURE 19. Chromium(III) peak current vs. concentration, differential pulse polarography.**

## 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 which react positively of these potentials cannot be determined due to the excessively high current from the mercury oxidation. In these instances, another electrode material must be used. Alternative electrodes include platinum, gold, graphite, and glassy 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. For more details, request EG&G PARC Application Brief A-5 regarding Antioxidants.

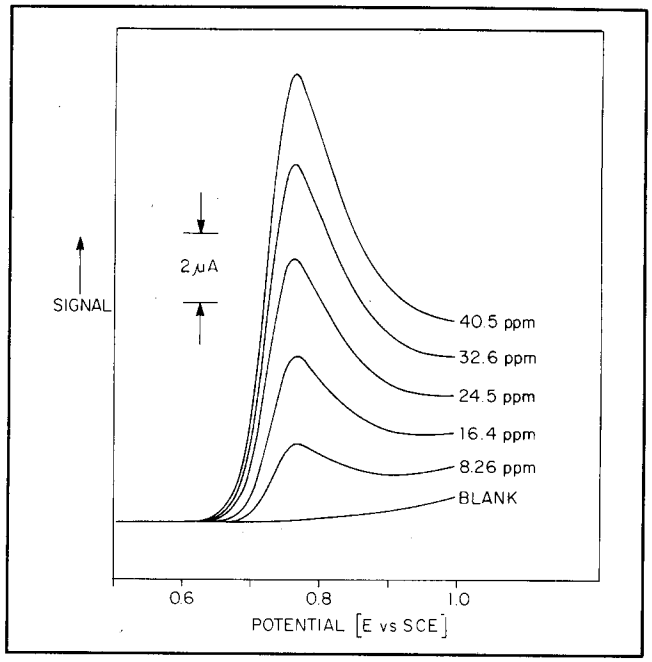



**FIGURE 20. Linear sweep voltammetry of butylated hydroxyanisole in 0.12 *M* H{SO| in 1:1 ethanol/benzene.**

## 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 even 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.

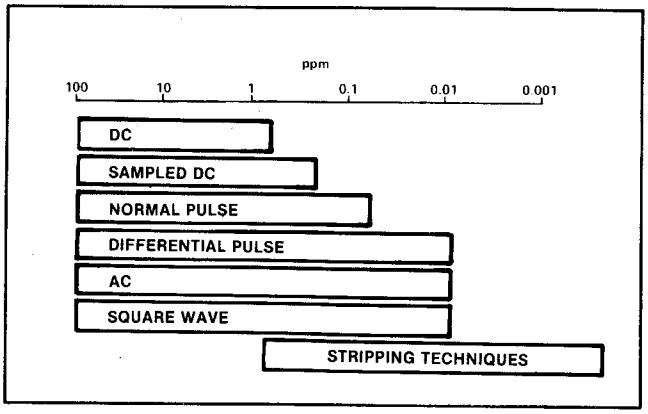



**FIGURE 21. Relative sensitivities of polarographic techniques.**

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[14]", and Application Note W-1, "Differential Pulse Stripping Voltammetry of Water and Waste Water", available from PRINCETON APPLIED RESEARCH.

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13. A. M. Bond, "Modern Polarographic Methods in Analytical Chemistry", Marcel Dekker, Inc., New York (1980).

14. William M. Peterson and Ronald V. Wong, "Fundamentals of Stripping Voltammetry", *American Laboratory*, p. 116, November, 1981. Available free of charge from EG&G PARC.

# Preparation of the most common buffers used in polarographic determinations

1. *Acetate buffer* (0.1 *M*, 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 1 liter with deionized water.

2. *Ammonia/Ammonium Chloride buffer* (0.1 *M*, 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 liter with deionized water.

3. *Ammonium Citrate buffer* (0.2 *M*, 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 liter with deionized water.

4. *Ammonium Tartrate buffer* (0.2 *M*, pH 9)
   Dissolve 30 g tartaric acid [$HOOC(CHOH)_2COOH$] in 500 ml deionized water and add concentrated ammonium hydroxide ($NH_4OH$) dropwise to pH 9. The tartaric acid will precipitate near pH 4 but will redissolve near pH 6. Dilute to 1 liter with deionized water.

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

5. *Phosphate buffer* (0.2 *M*, pH 6.8)
   Dissolve 24 g monosodium phosphate ($NaH_2PO_4H_2O$) in 500 ml deionized water and adjust to pH 6.8 with phosphoric acid ($H_3PO_4$). Dilute to 1 liter with deionized water.

6. *Thiocyanate buffer* (0.2 *M* sodium thiocyanate, 0.2 *M* acetic acid, pH 3.2)
   Dissolve 16.2 g sodium thiocyanate (NaSCN) in 500 ml deionized water. Add 11.5 ml glacial acetic acid. Dilute to 1 liter with deionized water.

7. *Triethanolamine-Sodium Hydroxide buffer* [0.3 *M* triethanolamine, $(HOCH_2CH_2)_3N$, 0.2 *M* NaOH]
   Dissolve 40.3 ml (45 g) triethanolamine and 8 g NaOH in deionized water and dilute to 1 liter.

8. *Britton-Robbinson buffer:* Stock solution; 0.04 *M* acetic, phosphoric, and boric acid
   pH 2.87: Add 17.5 ml of 0.2 *M* sodium hydroxide (NaOH) to 100 ml of the stock solution.
   pH 7: Add 52.5 ml of 0.2 *M* NaOH to 100 ml stock solution.

9. *Lithium Hydroxide/Lithium Chloride buffer* (0.1 *M* LiOH/0.1 *M* LiCl)
   Dissolve 2.4 g of LiOH and 4.3 g of LiCl in deionized water and dilute to 1 liter with $H_2O$.

10. *Hydrochloric Acid*
    1 *M* HCl: Add 82.5 ml of concentrated HCl to 900 ml deionized water. Dilute to 1 liter with deionized water.
    0.1 *M* HCl: Add 100 ml of the 1 *M* HCl to 900 ml deionized water.

11. *Nitric Acid*
    1 *M* $HNO_3$: Add 63 ml conc. $HNO_3$ to 900 ml deionized water. Dilute to 1 liter with deionized water.
    0.1 *M* $HNO_3$: Add 100 ml of 1 *M* $HNO_3$ to 900 ml deionized water. Or, add 6.3 ml conc. $HNO_3$ to 900 ml deionized and dilute to 1 liter.

12. *Sulfuric Acid*
    1 *M* $H_2SO_4$: Add (slowly!) 55.5 ml $H_2SO_4$ to 900 ml of deionized water. Dilute to 1 liter with deionized water.
    0.1 *M* $H_2SO_4$: Add 100 ml of 1 *M* $H_2SO_4$ to 900 ml deionized water.

13. *Sodium Hydroxide*
    1 *M* NaOH: Dissolve 40 g NaOH in 750 ml deionized water. Allow solution to cool, and dilute to 1 liter with deionized water.
    0.1 *M* NaOH: Dissolve 4 g NaOH in 750 ml deionized water, dilute to 1 liter with deionized water.

14. *Potassium Nitrate* (1 *M* $KNO_3$)
    Dissolve 101.1 g of $KNO_3$ in 800 ml of deionized water. Dilute to 1 liter.

15. *Potassium Chloride* (1 *M* KCl)
    Dissolve 74.6 g of KCl in 800 ml of deionized water. Dilute to 1 liter.

16. *Tetraalkylammonium salts* are often used in methanol, acetonitrile, or dimethylformamide at 0.1 *M* and 0.01 *M* concentrations. Weigh out the salt and add the solvent.
    Examples:
    tetrabutylammonium hydroxide
    tetrabutylammonium fluoborate
    tetrabutylammonium iodide
    tetrabutylammonium bromide
    tetrabutylammonium perchlorate
    tetramethyl analogs are also readily available.
    These compounds can be purchased from laboratory supply houses or Southwestern Analytical Chemicals, P. O. Box 485, Austin, TX 78764.

*Mercury*
Instrument mercury, purified by triple distillation, is available from Bethlehem Apparatus Co. Inc., Front and Depot Streets, Hellertown, PA 18055. Phone: 215/838-7034.