APPLICATION NOTE S-6

By William M. Peterson and Ronald V. Wong

Fundamentals of stripping voltammetry

THE DEMAND for the detection and quantitation of trace components in complex samples has come from the public and private sector alike.[1,2] Heightened awareness of the often detrimental effects of trace elements in media such as foodstuffs, drinking water, and commercial wastewater effluents has led to stringent public legislation and industrywide quality assurance programs which have been directed toward monitoring components of a sample at sub-ppm levels. Although a number of sensitive and reliable analytical techniques (e.g., optical and atomic flame spectrometry, neutron activation analysis, and spark spectroscopy) have been used for trace analysis, factors such as the high cost of instrumentation, extensive sample preparation, and limited selectivity reduce the efficacy of these analytical techniques when they are applied to multicomponent trace analysis in complex sample matrices.

The technique of stripping voltammetry has been used in trace analysis with relative ease and success in a variety of analytical applications. With minimal sample preparation, this electrochemical technique is routinely capable of identifying and quantitating trace components from 10^{-5} to 10^{-9} M with excellent sensitivity and selectivity.[2] Stripping analysis

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has received an unusual degree of interest, since it is the most sensitive electroanalytical technique currently available. This report describes the principle of analysis and discusses the analytical aspects of stripping voltammetry.

Principle of analysis

Voltammetry is an electrochemical technique in which the current-potential behavior at an electrode surface is measured. The potential is varied in some systematic manner to cause electroactive chemical species to be reduced or oxidized at the electrode. The resultant current is proportional to the concentration of the chemical species. For a more detailed treatment of electrochemical principles and polarography, see Ref. 3-7.

Stripping voltammetry is very similar to polarography, with a small, but significant, change in procedure. Stripping voltammetry is a two-step technique in which the first step consists of the electrolytic deposition of a chemical species onto an inert electrode surface at a constant potential. This preconcentration step can involve either an anodic or cathodic process. An example of an anodic process is the deposition of a halide onto a hanging mercury drop electrode in the form of an insoluble film of mercurous chloride. However, the most common use of stripping voltammetry involves a cathodic process in which a metal ionic species is reduced from the solution onto a mercury electrode, result-

ing in the formation of an amalgam. The second step consists of the application of a voltage scan to the electrode which causes an electrolytic dissolution, or stripping, of the various species in the amalgam or film back into solution at characteristic potentials.

The remarkable sensitivity of stripping voltammetry is attributable to the preconcentration that takes place during deposition. For preconcentration to take place, the deposited material obviously must adhere to the electrode surface. Although there are exceptions, mercury is generally the electrode of choice. Stripping voltammetry can be used to determine those chemical species that will be retained by the mercury, by formation of either an amalgam or an insoluble mercurous salt.

Stripping voltammetry is primarily a trace analytical technique. It can be used to make routine analytical determinations at the sub-ppm level, although this requires a high degree of care with regard to laboratory technique and sample handling. Stripping voltammetry is not recommended for samples whose concentration exceeds 1 ppm. This fact does not present a problem for the analyst, since polarography can easily detect these concentration levels. Analytes that can be determined by stripping voltammetry can also be determined polarographically at higher concentrations, although the converse is not necessarily true.

Electrodes for stripping voltammetry

Unlike polarography, the dropping mercury electrode is not used in stripping voltammetry. The electrode must be stationary. The ideal working electrode should have a reproducible surface, a reproducible area, and a low residual current. Solid electrodes such as gold, platinum, glassy carbon, wax-impregnated graphite, and carbon paste demonstrate such qualities and have been used successfully. Although solid electrodes give a sensitive response, they generally can be used for the analysis of only one species. When a solid electrode is employed in the analysis of several species, it is nearly impossible to obtain the required homogeneity of the deposited materials prior to the stripping step.

The most practical electrode for stripping voltammetry employs mercury as the electrode surface. Because of their general versatility and convenience, the hanging mercury drop electrode (HMDE) and the thin-film mercury electrode (TFME) will be described.

Hanging mercury drop electrode

The HMDE is the best working electrode for stripping voltammetry because of its extremely reproducible surface. All of the characteristics of the dropping mercury electrode[8] which make it the most suitable electrode for routine analytical determinations also apply to the HMDE. The entire stripping voltammetry experiment is performed on one mercury drop. That drop is then dislodged and a new drop is dispensed for the next experiment. Because the electrode is "replaced" for each experi-

ment, the condition of the electrode surface is not a variable in the analysis. This is not true for solid electrodes.

It is imperative that the HMDE used in stripping voltammetry should be able to dispense a mercury drop with an area that is reproducible to within 1%. The measured current in an electrochemical experiment is proportional to the electrode area. Since the current from a standard is compared to the current from the sample, an error in the surface area of the drop will lead directly to an error in the calculated sample concentration. Stripping voltammetry with an HMDE is a much more convenient technique to implement since the advent of "automatic" HMDEs in which the drop is dispensed with the push of a button.[8]

The perennial problem of the HMDE is in maintaining the drop on the end of the capillary. Simply stated, the mercury drop can fall off, in which case the experiment must be aborted. The ability to hold a drop is a function of the mechanical construction of the electrode, and has been effectively addressed in modern electrode designs.

The performance characteristics of the HMDE can often be improved by siliconizing the interior bore of the capillary. Siliconizing is performed by coating the bore with a material such as dimethyldichlorosilane. Siliconizing enhances the hydrophobic nature of the capillary and minimizes the deleterious effects of minor imperfections in the surface of the glass.

Thin-film mercury electrode

A TFME is prepared by depositing a film of mercury onto a glassy carbon electrode. Although other electrode materials may be used, glassy carbon usually gives excellent results. The TFME is generally used only for anodic stripping voltammetry. Such electrodes are most useful where maximum sensitivity is required. The TFME exhibits high sensitivity because only an extremely small amount of mercury is incorporated into the film, resulting in the formation of a very concentrated amalgam during the deposition step. The stripping peaks that are obtained with a TFME tend to be sharper than those observed with an HMDE. The TFME can be prepared by placing the glassy carbon electrode in a well-stirred solution of 2.5-ppm reagent-grade $Hg(NO_3)_2$ made slightly acidic with nitric acid at -0.4 v vs SCE for 5 min. Once the TFME is generated, it must be protected from oxygen to prevent oxidation of the film. Also, because the layer of deposited mercury is extremely thin, the use of the TFME should be limited to analyte concentrations less than 10^{-7} M.

The TFME can also be prepared in situ by adding 2-5-ppm Hg^{2+} directly to the sample solution and depositing mercury and the analyte simultaneously.[9] The experiment is begun with a completely clean electrode, usually glassy carbon. The mercury and deposited analyte are removed from the surface either mechanically or electrolytically following completion of the experiment.
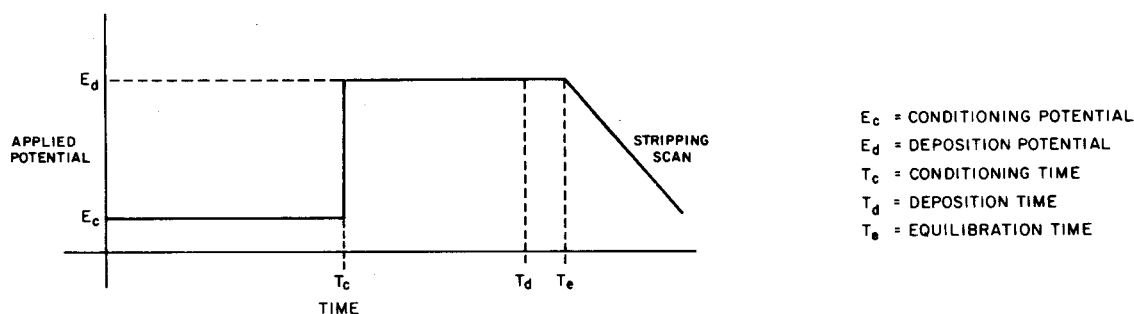
Figure 1 *Potential waveform for stripping voltammetry.*

E_c = CONDITIONING POTENTIAL
E_d = DEPOSITION POTENTIAL
T_c = CONDITIONING TIME
T_d = DEPOSITION TIME
T_e = EQUILIBRATION TIME

I. SAMPLED DC POLAROGRAM FOR LEAD AND CADMIUM

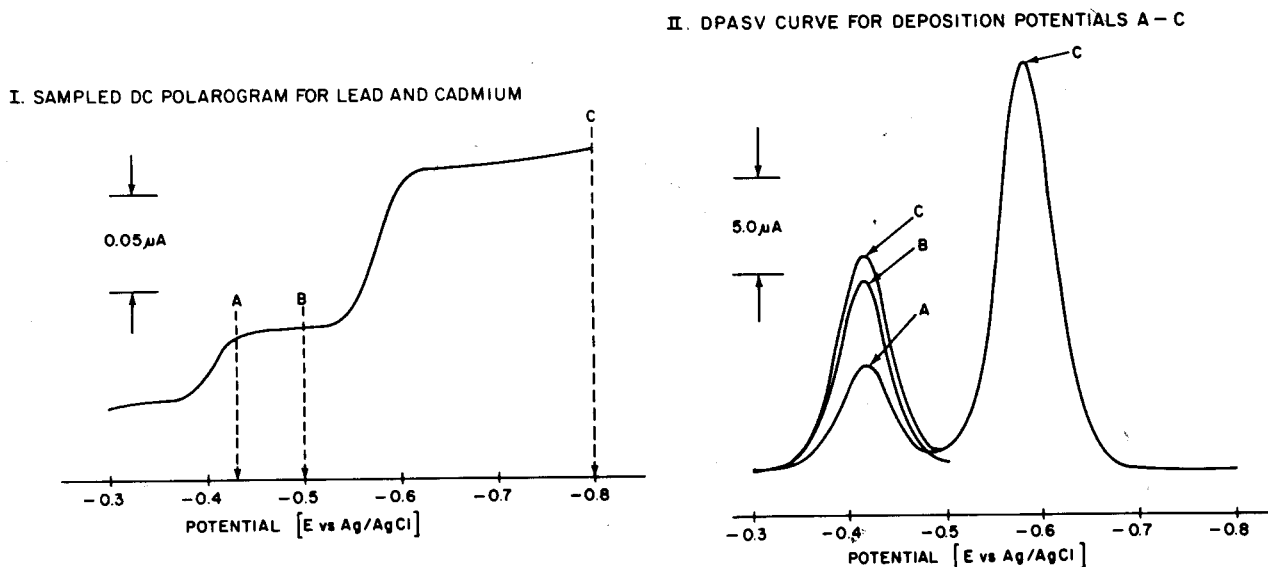II. DPASV CURVE FOR DEPOSITION POTENTIALS A – C

Figure 2 *Effect of deposition potential on stripping voltammogram.*

Because the same electrode surface is used for repetitive analyses, the condition of the surface is a major consideration. Steps must be taken to ensure that the surface of the TFME is as reproducible as possible prior to each analysis. Procedures that have been used successfully include physically cleaning the surface with a tissue, applying a conditioning potential (see next section), or cycling the potential between empirically determined values. Failure to guarantee a consistent surface may give rise to irreproducible results, since the current due to a particular analyte concentration is dependent upon a reproducible electrode surface. This problem, of course, is not a consideration with the HMDE since a new mercury drop is used for each determination.

The TFME is recommended only when maximum sensitivity is required. Because of the care required to obtain consistent results, the TFME cannot be considered appropriate for routine analytical purposes. In fairness, it should be noted that the TFME can provide unmatchable sensitivity. Metals have been determined in seawater using a TFME at concentrations on the order of 1 part per trillion.[10]

Stripping voltammetry

A general waveform for stripping voltammetry is shown in *Figure 1*. The waveform is a plot of potential applied to the working electrode vs time, and consists of several discrete steps.

1. *Conditioning:* Conditioning is a term that denotes electrolytic cleaning of the electrode surface. A specified potential is applied to the electrode for a controlled time in order to remove contaminants or materials not removed during the stripping step from the electrode surface. Conditioning is not required with a hanging mercury drop electrode because a new drop is used for each determination. On the other hand, conditioning is a necessity with a thin-film mercury electrode because the same electrode surface will be used in subsequent determinations. When the TFME is used to determine metals, the conditioning potential should be positive with respect to the half-wave potentials of the analyte to ensure the oxidation of the metals back into solution. If the TFME is being formed in situ, the conditioning potential may be set positive of the oxidation potential of mercury to provide a clean electrode surface for the deposition step. The solution

is stirred during conditioning. A typical conditioning time is 60–120 sec.

2. *Deposition:* The deposition potential is applied to the working electrode to cause the material of interest to be deposited onto the surface of the working electrode. The solution is generally stirred during deposition to maximize analyte-electrode contact. The selection of the deposition potential depends upon whether the material to be determined is oxidized or reduced. For a reducible metal, the deposition potential should be negative with respect to the half-wave potential of the metal. For oxidizable materials, the deposition potential should be selected so that it is positive with respect to the half-wave potential.

The choice of the deposition potential can provide some selectivity in the measurement (see *Figure 2*). In considering a dc polarogram of lead and cadmium as a comparison, this figure shows the first plateau as the diffusion-limited current due to the reduction of lead; the second plateau is due to the diffusion-limited current of both lead and cadmium. Deposition at potential *A* yields stripping peak *A* for lead. There is no contribution to the stripping voltammogram from the cadmium in solution since deposition at this potential reduces lead only. Deposition at potential *B* yields stripping peak *B*. The peak is somewhat higher, but there still is no contribution from the cadmium in solution. Finally, deposition at potential *C* yields two stripping peaks on curve *C*. The peak at about -0.6 v corresponds to cadmium since deposition at potential *C* is negative enough to reduce cadmium and lead simultaneously. As is obvious from Figure 2, the deposition potential is most appropriately chosen by running a polarogram of a concentrated solution (10–20 ppm) of the analyte.
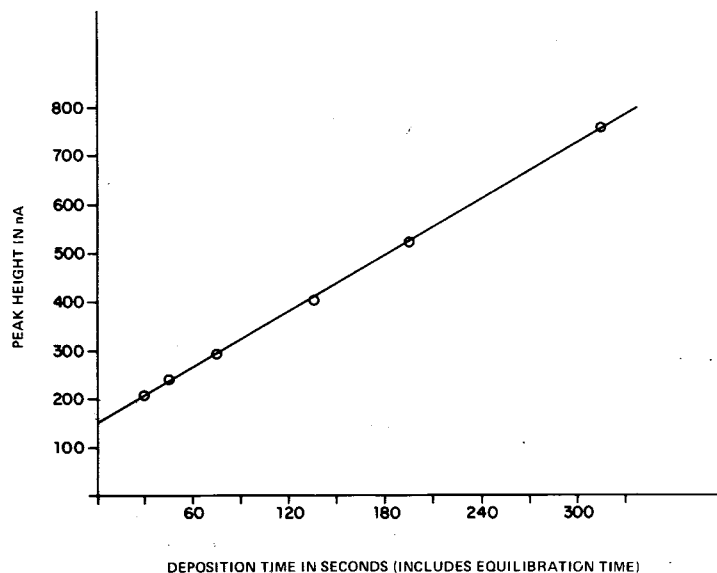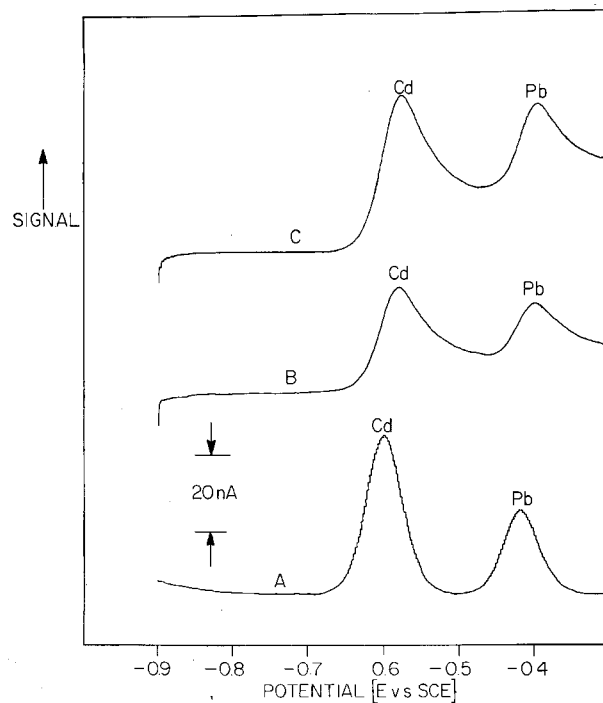

Figure 4 *Comparison of dc and differential pulse anodic stripping voltammetry at an HMDE—5 ppb Cd in 0.1 M acetate buffer (Pb impurity); deposition time: 20 sec; equilibration time: 30 sec. Curve A: Differential pulse— 25-mv pulse height, 2-mv/sec scan rate. Curve B: Direct current—20-mv/sec scan rate. Curve C: Direct current— 50-mv/sec scan rate.*

The deposition time must be carefully controlled. The deposition time is an important experimental parameter that is unique to stripping voltammetry. If more sensitivity is required, the analyst simply increases the deposition time. This increases the degree of preconcentration, making a greater amount of deposited analyte available at the electrode during the stripping step. The influence of deposition time on peak height is illustrated in *Figure 3*.

3. *Equilibration:* During equilibration, the deposition potential is applied to the working electrode, but stirring is halted. This allows convection currents from the stirring to decrease to a negligible level and also allows time for the amalgam to stabilize.

4. *Stripping:* An excitation waveform is applied from the polarographic analyzer which electrolyzes the deposited material back into the solution. The current is measured vs the applied potential. The materials deposited in the electrode will strip at potentials very close to their polarographic half-wave potentials. The measured current at these potentials is proportional to the concentration of the analyte in the original sample. Either a dc or a differential-pulse waveform may be used during the stripping step (see *Figure 4*). Curve *A* shows the stripping peak for cadmium with a differential-pulse waveform. Curves *B* and *C* show the same stripping peak with a dc waveform at different scan rates. As in polarography, a significant increase in sensitivity is observed when the differential-pulse waveform is used.
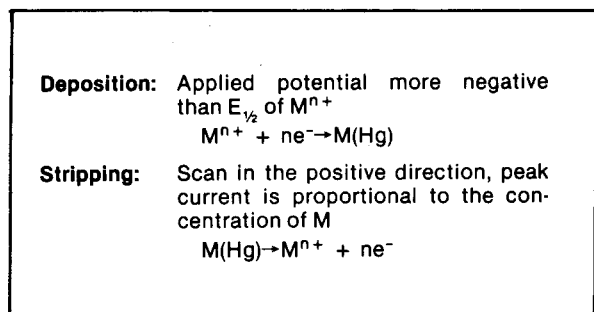

Figure 3 *Influence of deposition time on peak height.*

Deposition:	Applied potential more negative than $E_{1/2}$ of M^{n+}
	$M^{n+} + ne^- \rightarrow M(Hg)$
Stripping:	Scan in the positive direction, peak current is proportional to the concentration of M
	$M(Hg) \rightarrow M^{n+} + ne^-$

Figure 5 *Anodic stripping voltammetry.*

Deposition:	At a relatively positive potential where Hg^+ ions can be produced
	$Hg \rightarrow Hg^+ + e^-$
	then
	$2Hg^+ + 2X^- \rightarrow Hg_2X_2$ (insoluble film)
Stripping:	Scan in the negative direction, peak current is proportional to the concentration of X^-
	$Hg_2X_2 + 2e^- \rightarrow 2Hg + 2X^-$

Figure 6 *Cathodic stripping voltammetry.*

There are two types of stripping voltammetry — anodic stripping voltammetry (ASV) and cathodic stripping voltammetry (CSV). Although very similar in concept, they are used to determine completely different types of materials.

Anodic stripping voltammetry

Anodic stripping voltammetry is used to determine the concentration of trace metals. ASV consists of a deposition potential that is more negative than the half-wave potential of the metals to be determined, and an anodic (positive-going) scan to oxidize the reduced metal back into solution (see *Figure 5*). During deposition, an amalgam is formed by the elemental metal and the mercury on the electrode. Anodic stripping voltammetry can only be used to determine those metals that exhibit appreciable solubility in mercury (see *Table 1*).

Cathodic stripping voltammetry

Cathodic stripping voltammetry is used to determine those materials that form insoluble salts with mercurous ion. In CSV, the mercury working electrode is not inert, but takes an active part in the formation of the deposit (see *Figure 6*). The application of a relatively positive potential to a mercury electrode in the presence of such a material will result in the formation of an insoluble film on the surface of the mercury electrode. Stripping in CSV consists of a cathodic (negative-going) scan to re-
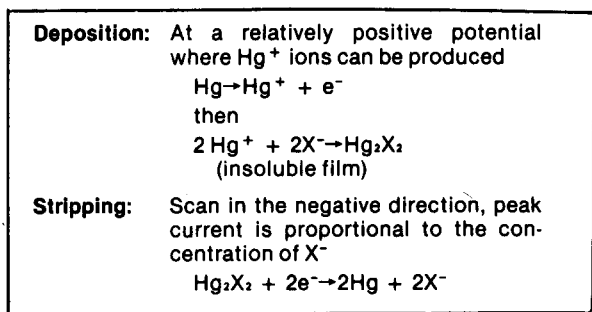
duce the deposited salt back into solution. Materials that can be determined by cathodic stripping voltammetry are shown in *Table 2*. Because CSV involves the formation of a film on the surface of an electrode and not a homogeneous amalgam as in ASV, it is not unusual for calibration curves in a CSV analytical procedure to display nonlinearity at higher concentrations. Even though the curves may be nonlinear, they are generally quite reproducible and can be used with confidence. Alternatively, at these higher concentrations the analyst may prefer to make the determination polarograpically.

Good laboratory practice and contamination

Since stripping voltammetry is an extremely sensitive technique for trace analysis, the problem of sample contamination is always present. All of the principles of good analytical practice—careful sample preparation and handling, proper attention to reagent purity and glassware cleanliness, proper preparation and storage of standards—must be observed for reproducible results. Glass cells should be soaked 1 hr (or overnight, if possible) with reagent-grade 6 M nitric acid and rinsed with deionized water prior to use. Polypropylene or PTFE cells are preferable to glass to reduce the problem of contamination and adsorption on the walls of the cell. The reagents used for the preparation of the standards and supporting electrolyte should be of the highest purity possible (Ultrex, Aristar, Suprapur). Even when reagent-grade chemicals are used for the preparation of the supporting electrolytes, low-level heavy metal contamination can become a significant factor at the high (1 M) concentrations that are sometimes used in polarographic analysis.

Table 1

Metals that can be determined by anodic stripping voltammetry

Antimony	Indium
Arsenic (Ref. 11)	Lead
Bismuth	Mercury[a] (Ref. 20)
Cadmium	Silver[a]
Copper	Thallium
Gallium	Tin
Germanium	Zinc
Gold[a]	

[a]Must be determined on solid electrode, such as glassy carbon or gold.

Table 2

Species that can be determined by cathodic stripping voltammetry

Arsenic (Ref. 12)	Sulfide
Chloride	Mercaptans (RSH)
Bromide	Thiocyanate (SCN)
Iodide	Thio compounds
Selenium (IV)	

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CURRENT X 10²NA
16-APR-81 *    17
STANDARD#1 DPS
INITIAL E -1.200 V
FINAL E    0.150 V

PEAK
1  -0.860V
   1.328E2 NA
   25.00 PPB
2  -0.564V
   6.380E1 NA
   25.00 PPB
3  -0.428V
   5.540E1 NA
   25.00 PPB
4  -0.036V
   3.420E2 NA
   25.00 PPB
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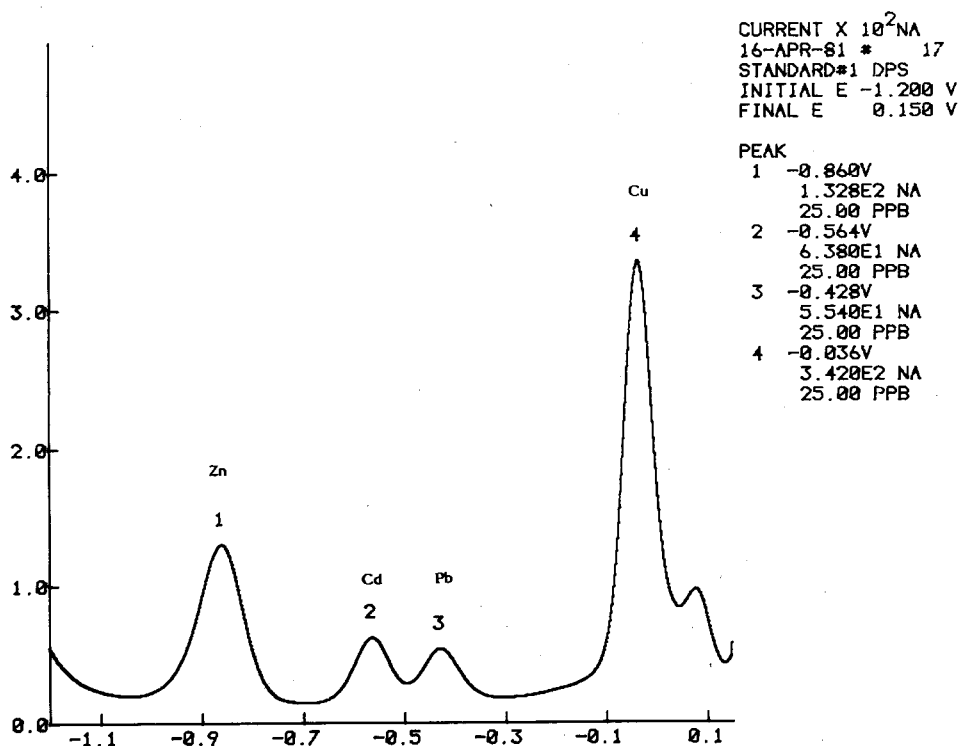
Figure 7 Differential-pulse anodic stripping voltammogram of 25 ppb zinc, cadmium, lead, and copper.

The use of a blank sample and the method of standard addition is recommended. By this analytical method, the limit of detection is nearly always governed by the magnitude of the blank value and not by instrumental sensitivity. Purification of the supporting electrolyte can be accomplished by controlled potential electrolysis or ion exchange. Standard solutions should be stored at a concentration no more dilute than 10^{-3} M. Dilute standards and samples must be prepared on a daily basis and utilized promptly since nonspecific adsorption of trace components can occur upon standing in their respective vessels. In some cases, it may be necessary to perform all sample handling and analyses in a filtered environment such as a laminar-flow hood. Only triple-distilled or better analytical-grade mercury should be used for HMDE operation (Bethlehem Apparatus Co.).

Procedure

A general procedure for stripping voltammetry is presented below:

1. Aliquot the sample and the electrolyte into the cell. The cell and solution to be run are prepared in exactly the same way for stripping voltammetry as they are for polarographic measurements. Additional care to avoid extrinsic contamination should be undertaken here as mentioned earlier. The temperature and stirring of the sample solutions must be kept as constant and as reproducible as possible. A reagent blank analysis should be performed in order to correct for possible contamination.

2. Immerse electrodes into the sample solution.

3. Deaerate with stirring. Purging the solution with purified nitrogen gas for 2–10 min will eliminate interference from oxygen. The nitrogen gas should be passed through a scrubbing tower filled with supporting electrolyte in order to allow the nitrogen stream to be saturated with the electrolyte solution to eliminate the possibility of pH changes or volatilization in the cell.

4. Generate a new mercury drop on the HMDE or from the TFME. Dislodge the used mercury drop and form a new drop for the HMDE. If a TFME is to be used, then follow instructions for preparation as specified previously. The TFME must be conditioned after each use in order to remove contaminants from the film and to assure reproducible operation. A conditioning potential of 0.0 v vs SCE for 60 sec is generally suitable for removing such contaminants from the mercury film without oxidizing the mercury.

5. Deposit with stirring. Stirring may be used to speed up the preconcentration process and shorten the deposition time. The concentration of metals deposited on the electrode is dependent upon the stirring rate, deposition time, bulk concentration, and electrode area. Generally, the deposition time required is dependent on the sample concentration, but 30–300 sec deposition time is normally sufficient for most determinations in the range of 1–50 ppb.

6. Equilibrate without stirring. An equilibration time of 30 sec allows for the stirring convection currents in the cell to settle down and assures minimal current fluctuation from this source.

7. Strip without stirring. A slow (2–5 mv/sec) differential-pulse scan or a more rapid (10–100 mv/sec) dc scan is applied to the electrode. The scanning range must span the potential region where the chemical species of interest are electrolyzed back into solution. Measure the current of peaks corresponding to the analytes that are present. *Figure 7* is a differential-pulse anodic stripping voltammogram of 25 ppb copper, lead, cadmium, and zinc.

8. Add an aliquot of standard. In order to minimize errors due to the sample matrix and stirring variations from cell to cell, the method of standard addition is recommended. In this method, one first records the voltammogram of an exactly known volume of the unknown solution; then a known volume of a standard solution of the substance being determined is added and a second voltammogram is recorded. Sufficient standard solution should be added so that the measured current is approximately 10 times the sample current.[5] Calculate the concentration of the original sample as follows:

$$C_u = \frac{i_1 v C_s}{i_2 v + (i_2 - i_1)V} \qquad (1)$$

where

i_1 = sample peak height
i_2 = standard addition peak height
v = volume of standard solution added
V = volume of original sample
C_s = concentration of standard solution
C_u = concentration of original sample

If the volume of added standard v is small compared to the volume of the original sample V, Eq. (1) simplifies to:

$$C_u = \frac{i_1 v C_s}{(i_2 - i_1)V} \qquad (2)$$

Use of a 10-mL sample and a 10- to 100-μL micropipet for the standard addition allows the valid use of Eq. (2).

Remarks

Anodic stripping voltammetry at a TFME can be complicated by intermetallic formation inside the mercury film. When metals such as Zn and Cu are present in high concentrations, there is a tendency for a Zn-Cu intermetallic to be formed when these metals are deposited into the mercury film. Other metals may also participate in intermetallic formation. When such intermetallics are present, the stripping peaks for the constituent metals may be shifted, severely depressed, or absent completely. Frequently, this type of interference can be overcome by adjusting the deposition time to reduce the concentration of metals in the amalgam or by setting the deposition potential to a value where only the species of interest is deposited and detected. The use of the differential-pulse waveform is advantageous since deposition times can be kept short so that

minimal amounts of metals are incorporated into the TFME. The formation of intermetallics is rarely a problem with a hanging mercury drop electrode. If the concentration of metals in the sample is high enough to allow intermetallic formation in an HMDE (solution concentration > 10 ppm), then the sample can easily be analyzed using differential-pulse polarography.

The HMDE used with the differential pulse waveform is the most versatile electrode-technique combination. Not only is the sensitivity high for trace determinations, but the tendency for intermetallic formation is minimized in all but the most concentrated solutions.

Any polarographic analyzer can perform stripping voltammetry. To avoid time-consuming steps and to assure reproducibility of experimental parameters, it is a distinct advantage if the instrument can automatically sequence through the steps detailed in the section on stripping voltammetry. Commercial instrumentation is available that can perform stripping voltammetry completely unattended.

Additional information on stripping voltammetry can be found in Ref. 6 and 13 to 19. Anodic stripping voltammetry procedures utilizing a hanging mercury drop electrode are detailed in Ref. 21–27. References 28–31 describe similar procedures using a thin-film mercury electrode. Several determinations using cathodic stripping voltammetry are contained in Ref. 32–37.

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