Stripping Voltammetry

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The recent publicity about potentially toxic concentrations of lead in the environment has increased interest in the detection of trace concentrations. Such measurements can be made electrochemically using stripping voltammetry. This article sets forth the principles of stripping voltammetry, and discusses some applications.

The concentration detection limits for such classic electrochemical techniques as d.c. polarography and cyclic voltammetry are only about 10^{-5} M due to charging and other background currents. Therefore, these techniques are of limited use for quantitative concentration measurement. The discrimination against the charging current, inherent in techniques such as differential pulse voltammetry and more recently (Osteryoung) square wave voltammetry, extends the detection limits down to 10^{-7}–10^{-8} M. However, the detection limits of these techniques can be lowered further (to 10^{-10} M–10^{-11} M, i.e., sub parts per billion (ppb)) by using them as part of a stripping experiment (1,2). The ability to quantitate low concentrations is becoming increasingly important as more is learned about the environmental and physiological effects of trace amounts of metal/metalloid ions and organic compounds.

The crucial part of a stripping experiment is the preconcentration (or deposition) step, in which analyte atoms/molecules are deposited onto or into the electrode from the solution. Stirring the solution increases the efficiency of this process. The concentration of the analyte on or in the electrode is therefore much higher than the concentration in the solution (up to a 1000-fold increase). The length of the preconcentration time determines the analyte concentration, which in turn determines the detection limit of the technique. Following a period of inactivity allowing homogeneous distribution of the analyte and restoration of quiescent solution conditions, the analyte is electrolytically removed in the stripping step.

The response due to a given analyte in the stripping step is proportional to the concentration of that analyte in the solution. The conversion of the response to a concentration can be achieved using a calibration curve, but the method of standard additions is generally used. In this method, a known amount of the analyte is added to the solution and the experiment is repeated. For each sample, two or more standard additions are often made.

Stripping techniques differ in their methods of accumulation (e.g., electrolytic vs. adsorptive) and methods of detection (voltammetry vs. potentiometry). Some of these are discussed briefly below.

a) Anodic Stripping Voltammetry (ASV)

This is probably the most well-known stripping technique, and is used for detection of metal cations, e.g., lead, cadmium, copper and zinc. The preconcentration step involves the reduction of the M^{n+} cations to the metallic state at a mercury electrode, which leads to the formation of an M/Hg amalgam. The M atoms are then reoxidized during the stripping step by scanning in a positive (anodic) direction. The peak potential in this scan is used for identification of the metal, and the peak current is proportional to the concentration.

Two types of mercury electrode are commonly used, the Hanging Mercury Drop Electrode (HMDE) and the Thin Mercury Film Electrode (TMFE) (3) (this is often formed in the preconcentration step by the deposition of small mercury droplets on a carbon electrode (4)). There are advantages and disadvantages for each of these electrodes.

1) *Analyte Concentration*–As discussed above, it is the concentration of analyte in the mercury electrode that is measured in the stripping step. This concentration depends on the surface area-to-volume ratio and the rate of stirring during the preconcentration step (see 2)). The TMFE has a larger surface area-to-volume ratio than the HMDE (5), and this leads to a higher analyte concentration for a given deposition time.

2) *Stability*–The mercury drop is inherently more unstable than the mercury film. Therefore, the stirring during the deposition step can be much faster with the TMFE. The combination of the faster stirring and the higher surface area-to-volume ratio results in greater efficiency in the deposition step for the TMFE. Hence, the time required for the deposition step is generally shorter when using the TMFE.

3) *Reproducibility*–One important requirement for any quantitative analytical technique is the ability to give reproducible results. Therefore, the surface structure of the mercury electrode must remain constant from one experiment to the next. This is relatively easy to achieve with the HMDE (indeed, the reproducibility of the mercury drop is one of the unique features of mercury drop electrodes). Since a mercury film on a carbon surface is in fact made up of discrete mercury droplets (4), the structure of the mercury layer is very dependent on the nature of the surface of the carbon electrode, and it is not always easy to obtain a reproducible surface for a solid electrode. Recently, it has been shown that a true mercury film electrode can be obtained on the surface of an iridium electrode (6), but the utility of such electrodes has yet to be fully investigated.

In principle, a number of different potential waveforms can be used for the stripping step (e.g., differential pulse, square wave, linear sweep, staircase). In practice, the two most commonly used are differential pulse and (Osteryoung) square wave, due to their low detection limits. These limits are not only due to the discrimination against the charging current that is inherent in these techniques, but also to the "recycling" of the metal (i.e., if a metal atom is oxidized in response to a potential pulse (or forward square wave half-cycle), then it can be redeposited at the end of the pulse (or reverse square wave half-cycle) if the potential change occurs before the metal ion has diffused away from the electrode). Osteryoung square wave has the additional advantages of a faster scan rate and increased sensitivity relative to differential pulse.

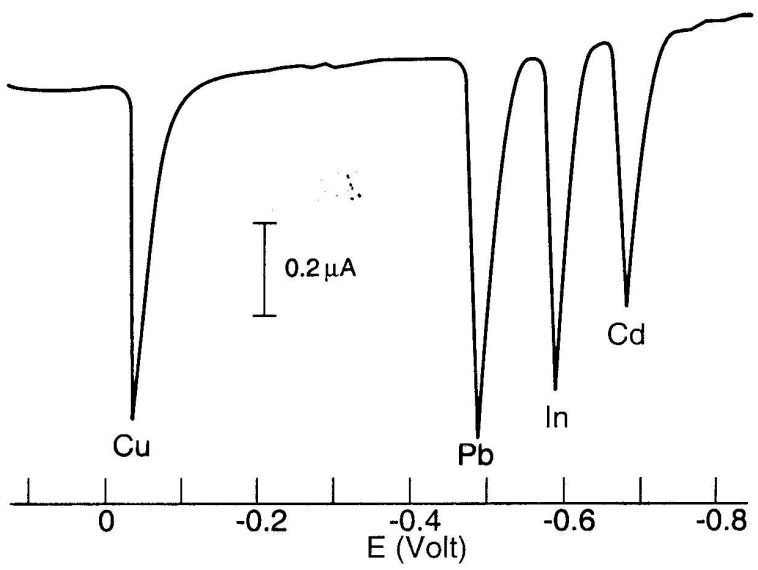
Mercury electrodes can be used only for metals (or metalloids) with oxidation potentials more negative than that of mercury, such as antimony (7), bismuth (8), cadmium (9-14), copper (9,11-13), indium (15), lead (9-14), thallium (16), tin (17) and zinc (9,11). For mercury itself and metals with more positive oxidation potentials (e.g., gold, silver, mercury), solid electrodes have to be used. Glassy carbon has been used for gold (18), silver (18) and mercury (19), gold for arsenic (20-22), selenium (23,24), mercury (18,25-27) and silver (28), and platinum for silver (29) and arsenic (20). However, multiple stripping peaks and irreproducible results often occur, due to the different interactions between the analyte metal and the electrode surface (30,31); in addition, metal electrodes adsorb hydrogen and are prone to formation of oxide films. These complications can often be minimized by careful preparation of the electrode surface (20) and optimization of the deposition potential.

The importance of ASV has increased in recent years with the increased awareness of the chronic toxic effects of metals and metal ions. Metals such as cadmium, lead and mercury are toxic in trace amounts, and metals such as copper, cobalt and zinc that are essential for living organisms in trace amounts are toxic at higher concentrations. In addition, since metals are non-biodegradable and cannot be completely excreted, there is often accumulation in vital organs. The examples in ***T1*** show that metals amenable to ASV can be detected in a variety of environmental and physiological matrices. The detection of lead in these examples should be noted in light of the recent publicity about the effects of lead accumulation in young children, and the recommendation for increased screening of lead blood levels. The major challenge for electroanalytical chemists is to produce a system that can be used for routine analysis of blood samples (i.e., there must be a considerable degree of automation).

One major advantage of ASV over other techniques used for trace

F1

Stripping voltammogram for 2 x 10 $^{-7}$ M Cd(II), Cu(II), In(III) and Pb(II) in 0.1 M KNO_3 using linear potential sweep in the stripping step. 30 s deposition time, mercury film on glassy carbon rotating disk electrode (adapted from ref. 3).



analysis of metal ions is its multi-element detection capability (***F1***). However, there are two problems associated with this capability:

1) *Overlapping Peaks*–This problem can occur if there are two metal ions present with similar redox potentials. A number of methods have been proposed to overcome this. One method is the addition of a complexing agent that has different affinities for the metal ions in question (32), i.e., the peaks will be shifted by different amounts. The removal of one of the stripping peaks by careful selection of the deposition potential has also been shown to be effective (33). Mathematical procedures for deconvoluting the peaks have also been suggested (34).

2) *Intermetallic Compounds*–A high concentration of metals in the mercury electrode can lead to the formation of intermetallic compounds, either between the analyte metal and mercury or between two analyte metals (the copper-zinc combination has been studied extensively (35)). The formation of such compounds can lead to shifts in the peak potentials and depressions of the peak currents. This behavior occurs more for the TMFE than for the HMDE due to the greater concentrations of metals in the TMFE.

Another major problem that can occur for ASV techniques is the unwanted adsorption of organic molecules on the electrode surface, which can affect the peak parameters (36).

ASV experiments can be performed using BAS instruments with varying degrees of automation. Glassy carbon based TMFEs can be made using either standard voltammetry electrodes, microelectrodes or rotating disk electrodes. Rotating disk electrodes (BAS RDE-1) are generally better than stationary voltammetry electrodes due to their precise control of the rotation rate; however, use of stationary electrodes with a magnetic stirrer (such as the one in the C-2 Cell Stand) is acceptable. Stirring is not required for microelectrodes, due to the non-planar diffusion to the electrode (37). The CGME can be used as an HMDE. With the CV-27, only linear sweep voltammetry can be used in the stripping step; in addition, the coordination of the stirring and inert gas purging and the various experimental steps must be controlled manually. Differential pulse and Osteryoung square wave voltammetries are available on the CV-50W and the BAS 100B/W, both of which can control the CGME. However, only the BAS 100B/W can control the rotation rate of the RDE-1.

b) Potentiometric Stripping Analysis (PSA) (38,39)

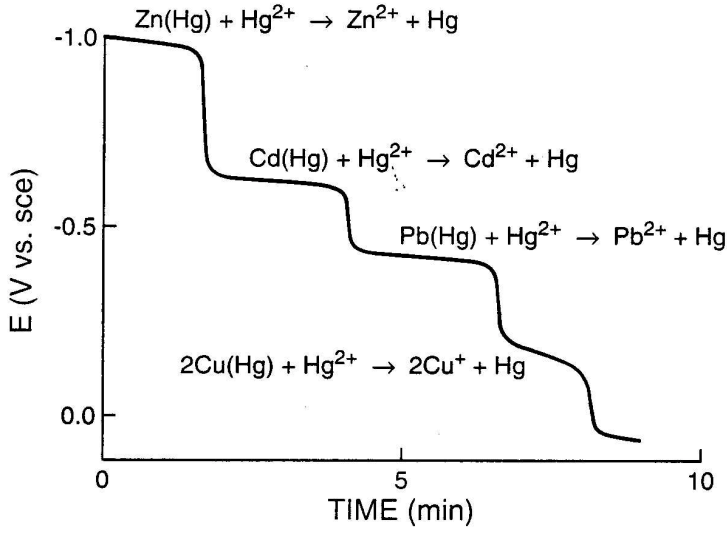
This technique is similar to ASV in that preconcentration is achieved by metal cation reduction and amalgamation with a mercury electrode. However, the detection of the metal analyte in the stripping step is achieved using chemical rather than electrochemical oxidation. Typical oxidizing reagents include oxygen, mercury(II) ions and chromium(VI) ions. (The term potentiometric stripping analysis has also been applied to experiments where the stripping step was achieved using a constant current, although these should be described as chronopotentiometric experiments.)

The output from a PSA experiment is a potential vs. time curve (***F2***), although this output can be differentiated to give a peak-shaped response. The metals are oxidized in order of their redox potentials (starting with the most easily oxidizable). Once the concentration of a metal in the mercury electrode has decreased to zero, the potential sharply changes to the redox potential of the next most easily oxidized metal. The time length of each plateau is the time required for the chemical oxidation of each metal, which is proportional to its concentration.

For concentrations of ppb or greater, the apparatus for PSA is simpler than that required for ASV. Only one negative potential is required, and the output can be sent to strip chart recorder. However, at lower concentrations (sub ppb), the amount of analyte deposited in the mercury electrode decreases, and hence the time required to oxidize each metal decreases from tens of seconds to milliseconds. For these concentrations, the potential vs.

F2

Potential stripping analysis potential-time curve for 1.5 x 10^{-6} M Cd(II), Cu(II), Pb(II) and Zn(II) in 0.5 M NaCl. 3 min deposition time, mercury drop electrode (adapted from ref. 38).



T1

Examples of metal/metalloid ions in various matrices detected using stripping techniques.

Abbreviations: AC = Alternating Current, DP = Differential Pulse, LS = Linear Sweep, SW = Square Wave, ASV = Anodic Stripping Voltammetry, AdSV = Adsorptive Stripping Voltammetry, CSV = Cathodic Stripping Voltammetry, PSA = Potentiometric Stripping Analysis, AUE = Gold Electrode, HMDE = Hanging Mercury Drop Electrode, TMFE = Thin Mercury Film Electrode

Analyte	*Matrix*	*Technique*	*Reference*
Antimony	Sea Water	LSASV/TMFE	7
Arsenic	Polluted Water	DPASV/AUE	22
Bismuth	Blood & Urine	DPASV/HMDE	8
Cadmium Copper Lead Zinc	Biological Materials	DPASV/HMDE	9
Cadmium Lead	Blood	PSA/TMFE	10
Cadmium Copper Lead Zinc	Rain	DPASV	11
Cadmium Copper Lead	Sea Water	DPASV/TMFE	12
Cadmium Copper Lead Zinc	Soil	SWASV/HMDE	13
Cadmium Lead	Urine	DPASV/TMFE	14
Cobalt Nickel	Biological Materials	AdSV/HMDE	9
Cobalt Copper Iron Molybdenum Nickel Uranium Vanadium	Sea Water	AdSV/HMDE	57
Cobalt Nickel	Soil	AdSV/HMDE	13
Indium	Sea Water	LSASV/TMFE	15
Mercury	Sea Water	DPASV/AUE	27
Selenium	Biological Materials	DPCSV	9
Thallium	Urine	ACASV/TMFE	16
Tin	Sea Water	LSASV/TMFE	17

time curve must be recorded on a PC, or a longer deposition time is used. Use of a PC is generally favored, and detection limits down to 10^{-10} M have been reported for a PC-controlled system.

Two other advantages of PSA over ASV are: 1) there is no current during the stripping step; hence, there is no charging current; and 2) oxygen can be used as the oxidizing agent (this removes the need for deoxygenation which is usually required for ASV experiments).

c) Cathodic Stripping Voltammetry (CSV) (40-43)

The method of preconcentration for this technique is the formation of an insoluble film on the surface of a mercury electrode (a silver electrode has been used for some analytes). This film consists of a mercury salt of the analyte anion A^{n-} (i.e., oxidation of the mercury electrode is required for film formation). In the cathodic stripping step, the film is reduced, regenerating A^{n-} (in solution) and mercury. Since the preconcentration occurs only on the surface of the mercury electrode, either the HMDE or a mercury pool electrode is preferable to the TMFE. In addition, the presence of mercury(II) ions in the solution (to generate the TMFE) can lead to irreproducible results for CSV due to the formation of insoluble mercury(II) salts in solution.

CSV has been used for the detection of inorganic anions such as halide ions, selenide and sulfide ions, and oxyanions such as $[MoO_4]^{2-}$ and $[VO_3]^{2-}$. Some organic compounds (e.g., thiols (43,44) and nucleic acid bases (45-47) (**T2**)) also form insoluble mercury(II) salts, and are therefore suitable for CSV.

d) Adsorptive Stripping Voltammetry (AdSV) (48,49)

In the three previous techniques, preconcentration was achieved by reduction or oxidation. In the preconcentration step for AdSV, no charge is transferred, and accumulation is achieved via the inherent tendency of particular molecules to adsorb to a mercury surface (e.g., due to hydrophobicity) (however, it should be noted that there is a potential dependence for the preconcentration step, and the optimum preconcentration potential needs to be determined experimentally). This technique has been promoted extensively for organic molecules (e.g., chlorpromazine (50,51), dopamine (52,53), bilirubin (54), triazine-containing pesticides (55) and polychlorinated biphenyls (56) (**T2**)). It should be noted that the organic molecules listed in **T2** are pharmaceuticals and agrochemicals. The ability to detect trace concentrations of such molecules has become increasingly important in recent years, due to the increased efficacy of many pharmaceuticals and the increased knowledge of the toxic effects of trace amounts of many agrochemicals.

AdSV can also be used for detection of transition metal cations, through the formation of insoluble complexes (e.g., dimethylglyoxime complexes of nickel(II) and cobalt(II) (9,13,48,57) (**T1**)).

The stripping step in AdSV can be anodic or cathodic, so the direction of the potential scan should be specified. However, this has led to some confusion in the literature, since AdSV with a cathodic stripping step has sometimes been referred to as CSV. It is important to

T2

Examples of organic molecules detected using stripping techniques.

Abbreviations: AdSV = Adsorptive Stripping Voltammetry, CSV = Cathodic Stripping Voltammetry, AGE = Silver Electrode, CPE = Carbon Paste Electrode, GCE = Glassy Carbon Electrode, HMDE = Hanging Mercury Drop Electrode, PTE = Platinum Electrode, WIGE = Wax Impregnated Graphite Electrode

Analyte	*Method*	*Reference*
Adriamycin (antibiotic)	AdSV/CPE	60
Benzodiazepines Diazepam Nitrazepam (sedatives)	AdSV/HMDE	43
Bilirubin	AdSV/HMDE	54
Butylated hydroxyanisole (anti-oxidant)	AdSV/CPE	61
Captopril (vasodilator)	CSV/HMDE	62
Catecholamines Catechol L-Dopa Dopamine Norepinephrine	CSV/HMDE	63
Chlorambucil (anti-tumor)	AdSV/WIGE	64
Chlorhexidine (bactericide)	AdSV/WIGE	65
Chlorpromazine (antipsychotic)	AdSV/WIGE	50
Chlorpromazine	AdSV/CPE	51
Chlorprothixene (CNS depressant)	AdSV/GCE	66
Cimetidine (H2 antagonist)	AdSV/HMDE	67
Clozapine (sedative)	AdSV/GCE/CPE	68
Cocaine Intercaine Procaine	AdSV/HMDE	69
Cyanuric chloride	CSV/HMDE	70
Cysteine Glutathione	CSV/HMDE	71
Cysteine Penicillamine	AdSV/HMDE	72
Daunorubicin (Anti-tumor)	AdSV/HMDE/CPE	73
Digitoxin Digoxin (cardiac agents)	AdSV/HMDE	74
Diltiazem (cardiac agent)	AdSV/HMDE	75
Dopamine	AdSV/PTE	52,53
Erythromycin (antibiotic)	AdSV/HMDE	76
Estriol Estradiol (estrogens)	AdSV/HMDE	77
Felypressin	AdSV/HMDE	78
5-Fluorouracil	CSV/HMDE	79
5-Fluorouracil	AdSV/HMDE	64
Food Coloring (Carmoisine Red 2G Quinoline Yellow Tartrazine)	AdSV/HMDE	80
Heme	AdSV/HMDE	81
Mercaptans	CSV/HMDE	43,44
Methotraxate (anti-tumor)	AdSV/HMDE	82,83
NAD^+	AdSV/HMDE	84
Nitro-containing pesticides DNOC Dibutone	AdSV/HMDE	55

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distinguish whether the preconcentration step is electrolytic (oxidation of mercury followed by a mercury salt film formation in CSV) or non-electrolytic (adsorption on the electrode surface in AdSV).

Recently there has been interest in improving the specificity of the working electrodes used for detection by chemically modifying the electrode surface (58,59). For example, an electrode could be made specific for a particular metal ion by attaching to the electrode surface a complexing agent which has high specificity for that metal ion. The attachment can be achieved through adsorption, covalent bonding, immobilization within a polymer coating or bulk modification of the electrode material.

As with any quantitative analytical technique, the success of SV techniques depends on the reproducibility of the results; i.e., all experimental conditions should be constant for all experiments. These conditions include the electrode surface (reproducibility is easier to achieve using the HMDE), the rate of stirring (a rotating disk electrode is often preferred due to the precise control of the stirring rate) and the deposition time (microprocessor control of the potential and the stirring is favorable). Good laboratory practices are also required to minimize sample contamination. Therefore, all glassware should be thoroughly cleaned, and any solutions used should be pre-electrolyzed to remove trace metal ion impurities. All sample preparations and experiments should be performed in a clean atmosphere at a constant temperature.

The examples given in ***T1*** and ***T2*** show the wide range of metal ions and organic molecules that can be detected in trace amounts using stripping techniques. However, many of these applications have been developed in academic and industrial research laboratories, and it remains to be seen whether stripping techniques will be used for routine analysis of any of these systems.

T2 (cont.)

Novobiocin (antibiotic)	AdSV/HMDE	76
Nucleic acid bases Adenine Guanine Cytosine Uracil Thymine	CSV/HMDE	45 - 47
Organic halides (drug dissolution tests)	CSV/HMDE	85
Penicillin (antibiotic)	AdSV/HMDE	86
9,10 Phenanthrene-quinone Oxoapomorphine	AdSV/CPE	87
Riboflavin	AdSV/HMDE	88
Sex hormones Methyltestosterone Testosterone Progesterone	AdSV/HMDE	89
Streptomycin (antibiotic)	AdSV/HMDE	76
Tetracycline Chlortetracycline Doxycycline Oxytetracycline (antibiotics)	AdSV/HMDE	90
Thioacetamide Thiourea Thionicotinamide Ethionamide Thiosemicarbazide	CSV/AGE	91
Thioamides	CSV/HMDE	92,93
Thiobarbiturates	CSV/HMDE	94
Thiouracil	CSV/AGE	95
Thiourea Phenylthiourea Napthylthiourea (pesticides)	CSV/HMDE	96
Thiourea Napthylthiourea Diphenylthiourea	AdSV/HMDE	97
Triazine-containing pesticides Ametryne Prometryne	AdSV/HMDE	55
Trichlorobiphenyl (industrial waste)	AdSV/HMDE	56
Tricyclic anti-depressants Desipramine Imipramine Trimipramine	AdSV/GCE/CPE	98
Vitamin K1	AdSV/CPE	99

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Riboflavin	AdSV/HMDE	88
Sex hormones Methyltestosterone Testosterone Progesterone	AdSV/HMDE	89
Streptomycin (antibiotic)	AdSV/HMDE	76
Tetracycline Chlortetracycline Doxycycline Oxytetracycline (antibiotics)	AdSV/HMDE	90
Thioacetamide Thiourea Thionicotinamide Ethionamide Thiosemicarbazide	CSV/AGE	91
Thioamides	CSV/HMDE	92,93
Thiobarbiturates	CSV/HMDE	94
Thiouracil	CSV/AGE	95
Thiourea Phenylthiourea Napthylthiourea (pesticides)	CSV/HMDE	96
Thiourea Napthylthiourea Diphenylthiourea	AdSV/HMDE	97
Triazine-containing pesticides Ametryne Prometryne	AdSV/HMDE	55
Trichlorobiphenyl (industrial waste)	AdSV/HMDE	56
Tricyclic anti-depressants Desipramine Imipramine Trimipramine	AdSV/GCE/CPE	98
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