

Anodic Stripping Voltammetry

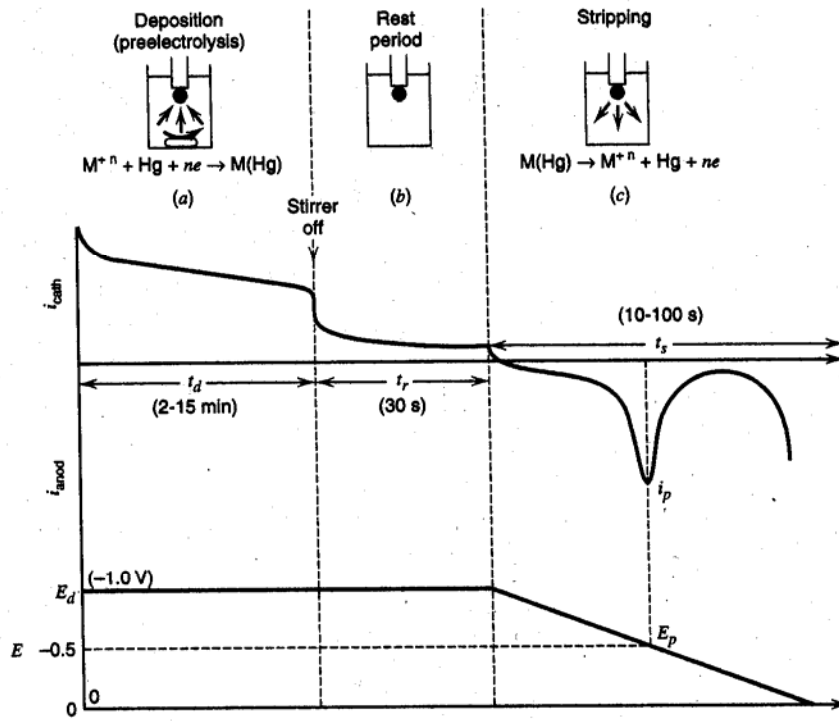


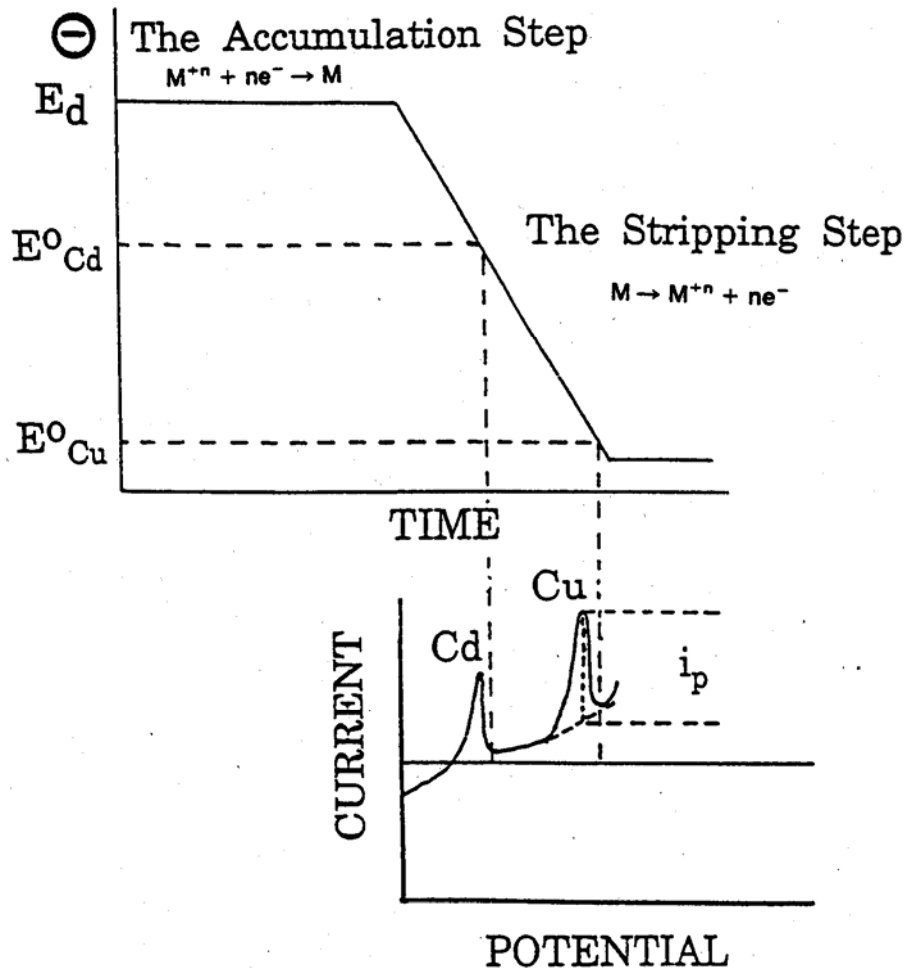
Figure 11.8.1 Principle of anodic stripping. Values shown are typical ones used; potentials and E_p are typical of Cu^{2+} analysis. (a) Preelectrolysis at E_d ; stirred solution. (b) Rest period; stirrer off. (c) Anodic scan ($v = 10\text{--}100$ mV/s). [Adapted from E. Barendrecht, *Electroanal. Chem.*, 2, 53 (1967), by courtesy of Marcel Dekker, Inc.]

Stripping analysis is an analytical technique that involves (i) *preconcentration* of a metal phase onto a solid electrode surface or into Hg (liquid) at negative potentials and (ii) *selective oxidation* of each metal phase species during an anodic potential sweep.

Excellent technique for trace metal ion analysis!

Preconcentration leads to low detection limits!

Anodic Stripping Voltammetry



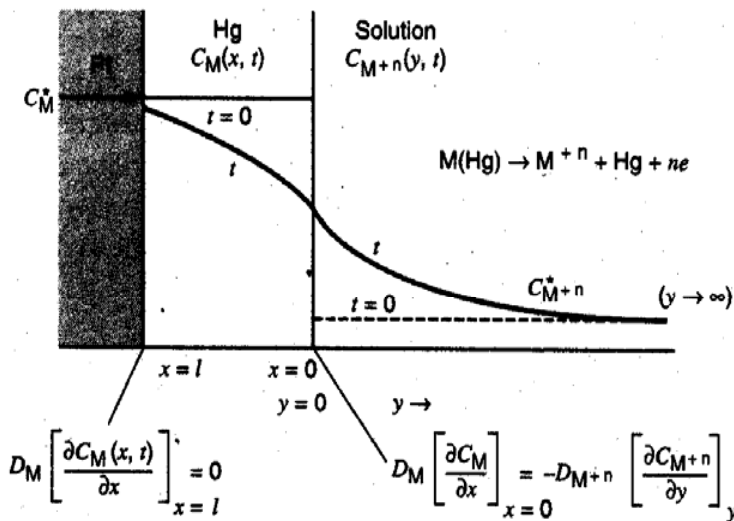
1. HMDE
2. MFE
3. Bare carbon, Au, etc.

10^{-4} to 10^{-5} Hg^{+2} added for co-metal deposition.

Electrodeposition step, E_d , carried out in a stirred solution at a potential several tenths of a volt more negative than the E° for the least easily reduced metal ion.

Figure 2.12 Anodic stripping voltammetry: the potential-time waveform (top), along with the resulting voltammogram (bottom).

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Useful for the analysis of very dilute solutions, 10^{-11} M.

Figure 11.8.3 Notation, initial conditions, and boundary conditions for theoretical treatment of MFE.

$$\text{Moles deposited} = i_d t_d / nF$$

$$C_{M+n}(0, t) = C_M(0, t) \exp[(nF/RT)(E_i - E^{o'} + \upsilon t)]$$

(Nernstian behavior)

$$C_M^* = i_d t_d / nF (4/3) \pi r_0^3 (\text{HDME})$$

$$i_p = n^2 F^2 \upsilon I A C_M^* / 2.7 RT \quad (\text{MFE})$$

$$A \times l = \text{volume (cm}^3\text{)}$$

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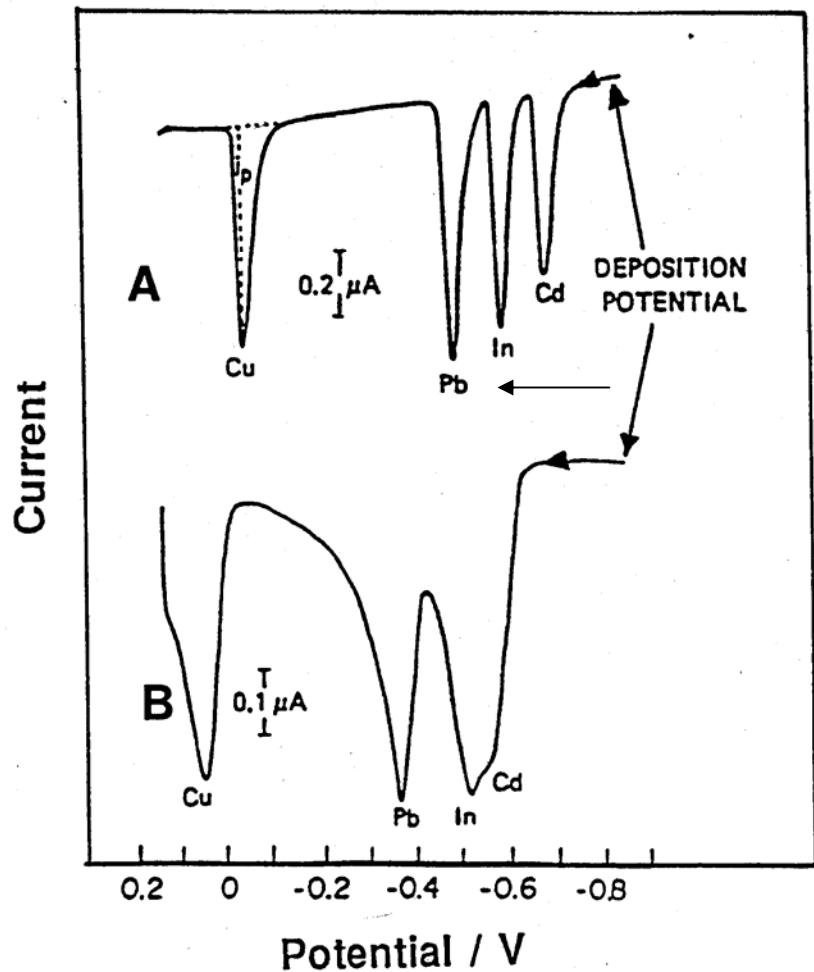
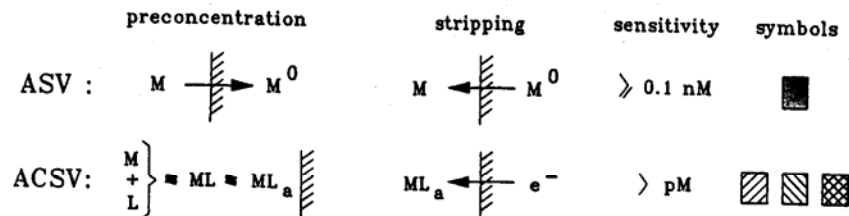


Figure 2.14 Stripping voltammograms for 2×10^{-7} M Cu^{2+} , Pb^{2+} , In^{3+} , and Cd^{2+} at the (A) mercury film and (B) hanging mercury drop electrodes. [Reproduced with permission (20).]

CONTROLLED POTENTIAL TECHNIQUES

55



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Au	Hg	Tl	Pb	Bi	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Figure 2.19 Elements measured by conventional ASV \blacksquare , adsorptive stripping schemes with reduction of the element in the complex $\begin{matrix} \text{diagonal lines} \\ \text{cross-hatch} \\ \text{dots} \end{matrix}$, reduction of the ligand $\begin{matrix} \text{diagonal lines} \\ \text{cross-hatch} \\ \text{dots} \end{matrix}$, or catalytic process $\begin{matrix} \text{diagonal lines} \\ \text{cross-hatch} \\ \text{dots} \end{matrix}$. [Reproduced with permission (39).]

Anodic Stripping Voltammetry

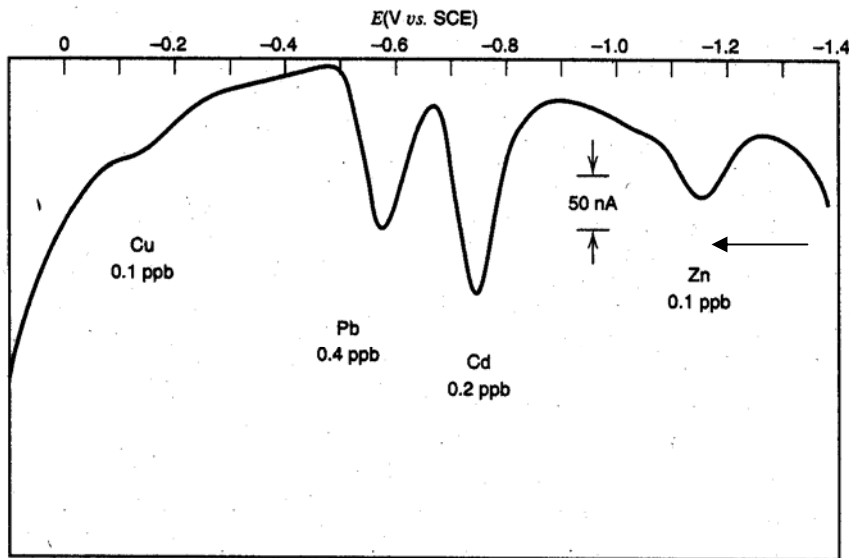


Figure 11.8.5 Anodic stripping analysis of a solution containing $2 \times 10^{-9} M$ Zn, Cd, Pb, and Cu at an MFE (mercury-plated, wax-impregnated graphite electrode). Stripping carried out by differential pulse voltammetry.

Table 2.3 Representative Applications of Stripping Analysis

Metal	Sample Matrix	Stripping Mode	Working Electrode	Ref.
Antimony	Gunshot residue	ASV	MFE	40
Cadmium	Lake water	ASV	MFE	41
Chromium	Soil	AdSV	HMDE	42
Cobalt	Seawater	AdSV	HMDE	26
Copper	Steel	ASV	HMDE	43
Iodide	Seawater	CSV		38
Iron	Wine	AdSV	HMDE	44
Lead	Blood	PSA	MFE	45
Lead	Paint	ASV		46
Mercury	Fish	ASV	Au	47
Nickel	Plant leaves	AdSV	HMDE	48
Selenium	Soil	CSV	HMDE	49
Thallium	Urine	ASV	HMDE	50
Titanium	Seawater	AdSV	HMDE	34
Uranium	Ground water	AdSV	HMDE	51
Zinc	Eye tissue	ASV	HMDE	52

ASV = anodic stripping voltammetry
 CSV = cathodic stripping voltammetry
 AdSV = adsorptive stripping voltammetry

ppb and even ppt detection limits are possible (s/n = 3) with ASV!

Anodic Stripping Voltammetry

- Very sensitive and reproducible (RSD<5%) method for trace metal ion analysis in aqueous media.
- Concentration limits of detection for many metals are in the low ppb to high ppt range (S/N=3) and this compares favorably with AAS or ICP analysis.
- Field deployable instrumentation that is inexpensive.
- Approximately 12-15 metal ions can be analyzed for by this method.
- The stripping peak currents and peak widths are a function of the size, coverage and distribution of the metal phase on the electrode surface (Hg or alternate).