Stripping voltammetry analyses

Dr. Md. Monirul Islam

Department of Chemistry

University of Rajshahi

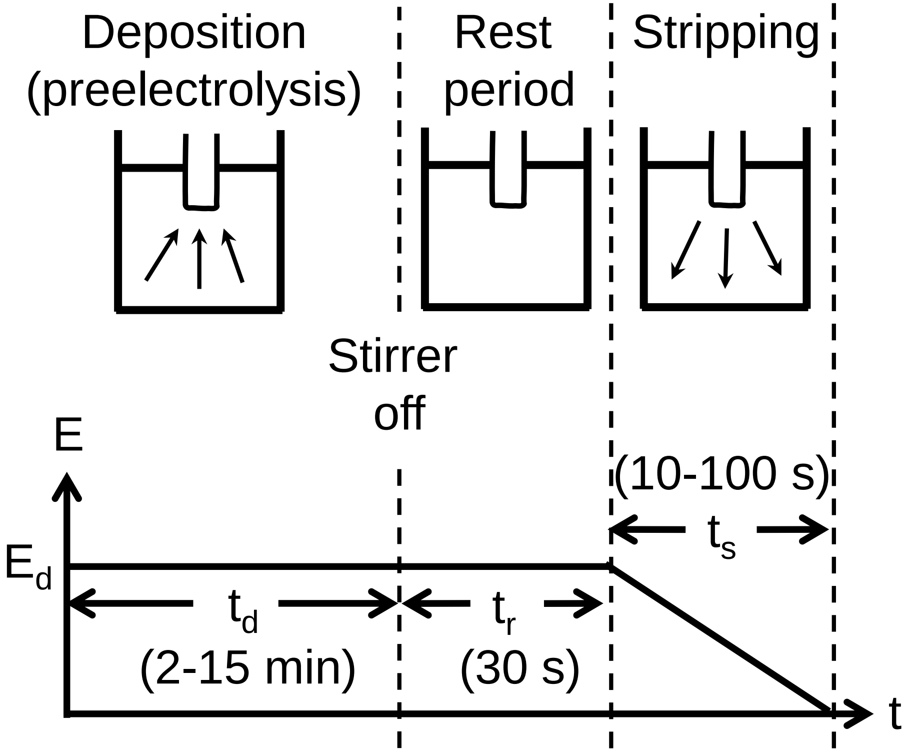
Outlines

- ❑ Stripping analysis
    - ▪ Anodic stripping voltammetry (ASV)
    - ▪ Potentiometric stripping voltammetry (PSV)
    - ▪ Adsorptive stripping voltammetry (AdAV)
    - ▪ Cathodic stripping voltammetry (CSV)

Stripping Analysis

Stripping analysis is an extremely sensitive electrochemical technique for trace analysis that involves

- *Preconcentration* of analyte species onto a solid electrode surface or into Hg (liquid) at negative or positive potentials
  - Stirring the solution: mass transfer
  - Only a fraction of analyte is deposited: accumulation process
  - Depends on c, stir rate, deposition time, electrode surface and potential
- Selective *oxidation* or *reduction* of each analyte species during anodic or cathodic potential sweep.
- Preconcentration of analytes increase the sensitivity



Depending on the nature of deposition and stripping steps, stripping analyses are classified into following

- Anodic stripping voltammetry
- Potentiometric stripping voltammetry
- Adsorptive stripping voltammetry
- Cathodic stripping voltammnetry

Anodic stripping voltammetry

- In this technique, metals are pre-concentrated by cathodic deposition into mercury electrode (a thin film or hanging mercury drop) at a controlled time and potential.
- The deposition potential, 0.3-0.5 V negative than E^0 of least reduced metal ions.
- Metal ions reached to Hg electrode by diffusion and convection are reduced and concentrated as amalgams

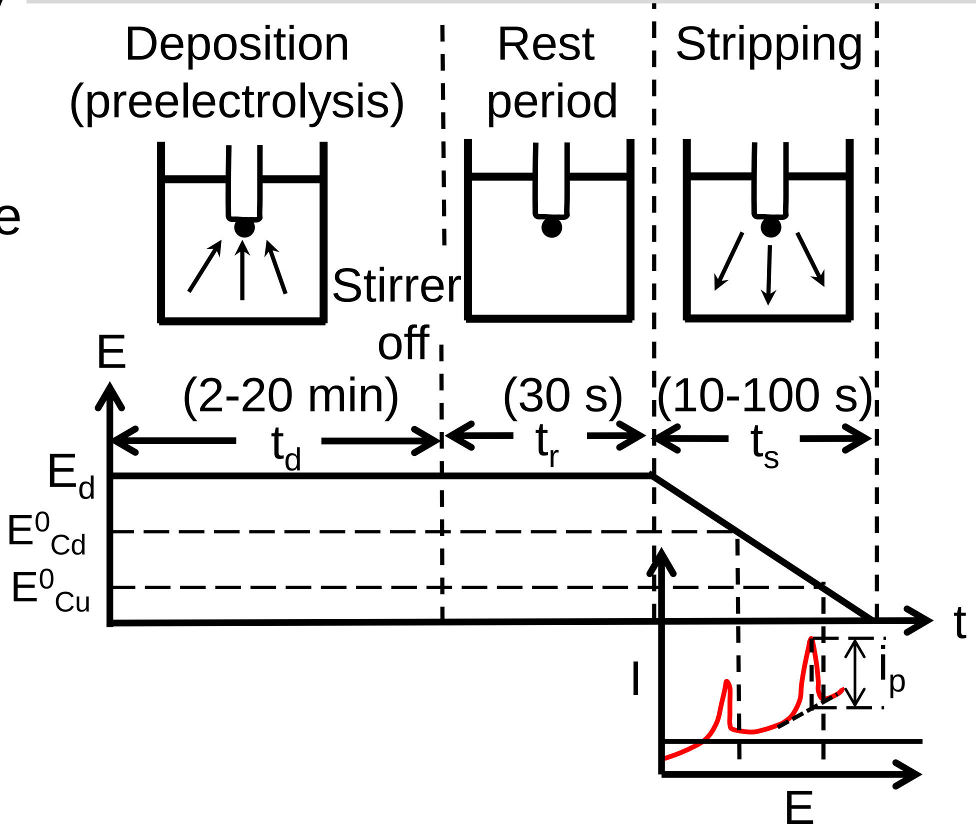
$$M^{n+} + ne^- + Hg \rightarrow M(Hg)$$

- Deposition time: < 0.5 min for 10^{-7} M to 20 min for 10^{-10} M.
- $C_{Hg} = \frac{i_l t_d}{nFV_{Hg}}$

After finishing deposition, the forced convection is stopped and potential is scanned anodically either

- Linearly or potential-time (pulse) wave form for stripping deposited metal as reoxidation

$$M(Hg) \rightarrow M^{n+} + ne^- + Hg$$



Stripping voltammetric peak, i_p

- I_p reflects the time-dependent concentration gradient of metals in mercury electrode during potential scan.
- Peak potential E_p serves to identify the metal in sample.
- I_p depends on
  - Various parameters of the deposition and stripping steps
  - Characteristics of metal ions
  - Electrode geometry

  For example, for a mercury film electrode, the peak current is given by

$$i_p = \frac{n^2F^2v^{\frac{1}{2}}AlC_{Hg}}{2.7RT}$$

And for hanging mercury drop electrode

$$i_p = 2.72 \times 10^5 n^{\frac{3}{2}} A D^{\frac{1}{2}} v^{\frac{1}{2}} C_{Hg}$$

Concentration profile during stripping

- For very thin film mercury electrode, diffusion in the film can be ignored and the peak current is directly proportional to scan rate

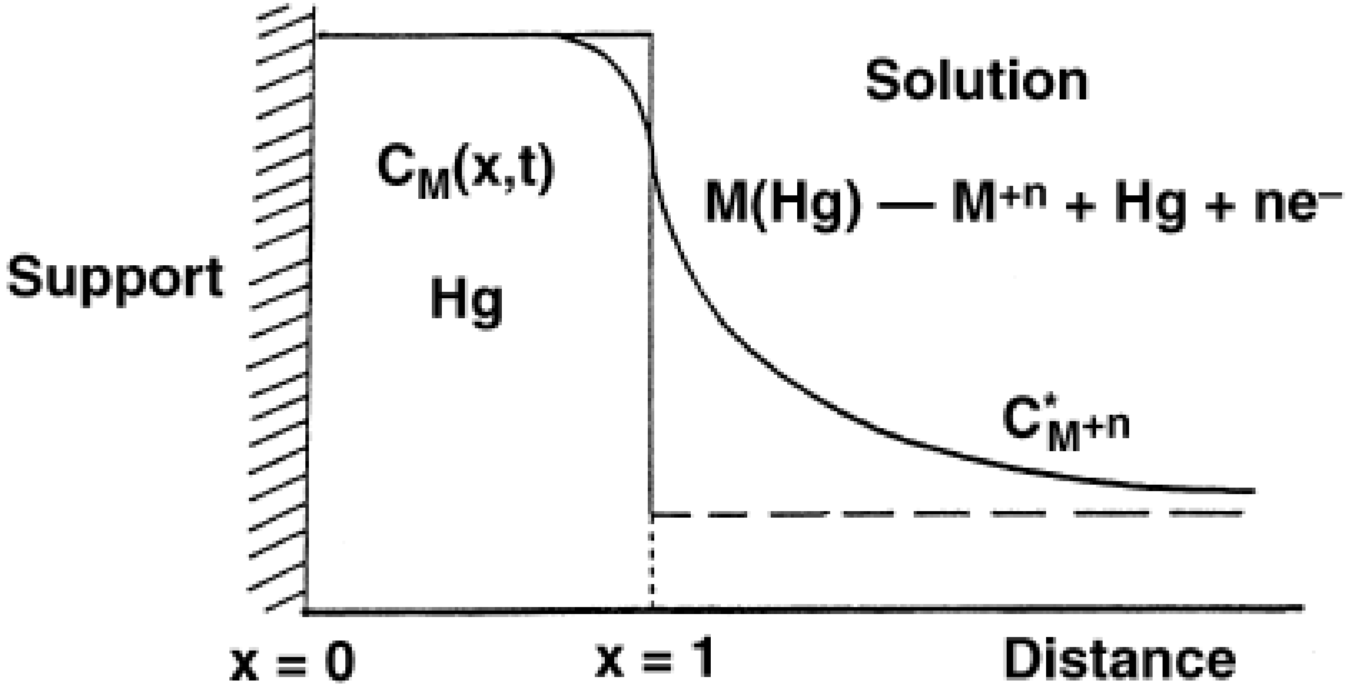


Fig. Concentration gradient of the metal in the mercury film electrode and nearby solution during the stripping step

Comparative stripping voltammograms

- Surface to volume ratio for film electrode is higher than drop electrode
- Offer more efficient preconcentration and higher sensitivity
- Thin film electrode provides sharper peaks in stripping voltammograms
- Multicomponent analysis is very convenient at thin film electrode for improved peak resolution

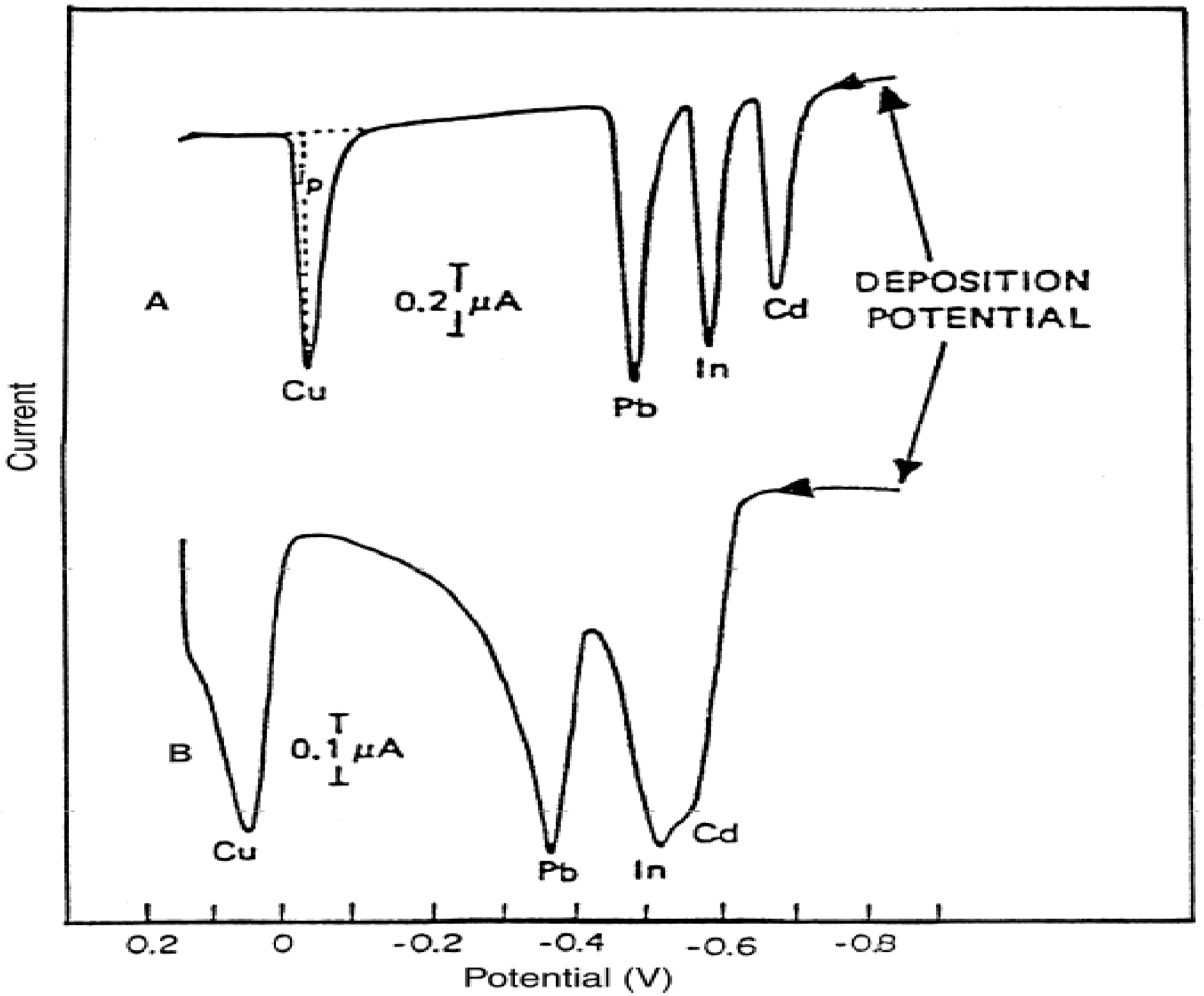


Fig. Stripping voltammograms for $2x10^{-7}$ M Cu^{2+}, Pb^{2+}, $In^{2+}$and Cd^{2+} at mercury film (A) and hanging mercury drop (B)

Potentiometric stripping analysis

- In this technique, potentiostatic control is disconnected following preconcentraion and the concentrated metals are reoxidized by and oxidizing agent (such as O_2 or Hg(II)) or at constant current.

$$M(Hg) + oxidant \rightarrow M^{n+}$$

- A stirred solution is used during stripping step and variation of working electrode potential is recorded and a stripping curve
- When the oxidation potential of a given metal is reached, the potential scan is slowed down as the oxidant (or current) is used for its stripping.
- t_m of a given metal is quantitative measure of the sample, $t_m \infty C_{M^{n+}} t_d / C_{ox}$
- Qualitative information rely on potential measurements $E = E^0 + \frac{RT}{nF} \ln \frac{[M^{n+}]}{[M(Hg)]}$

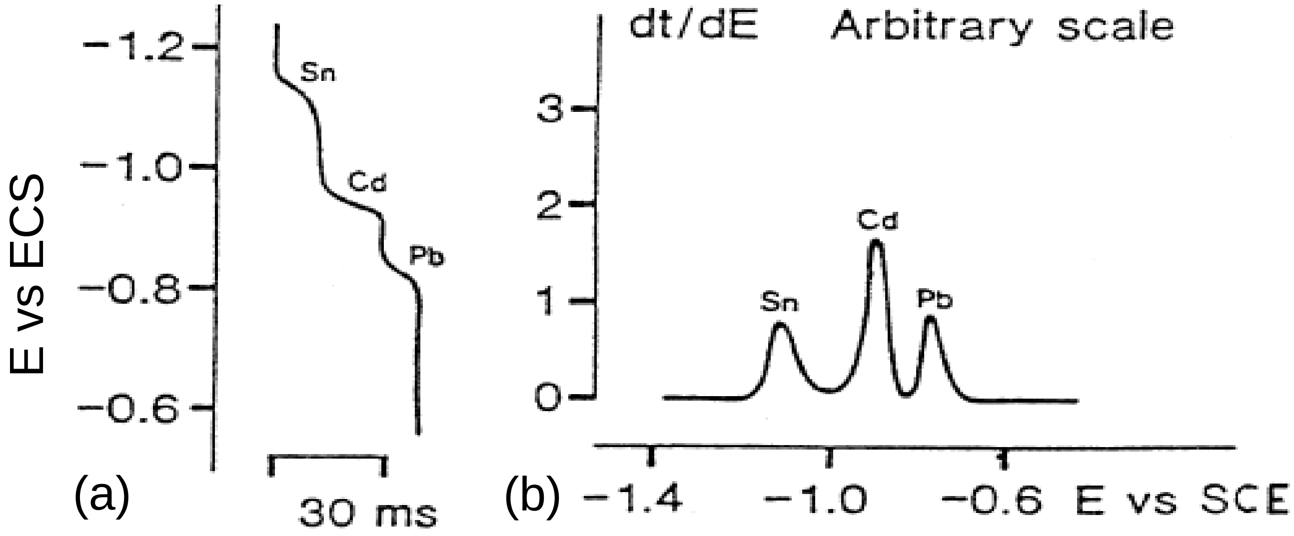


Fig. Stripping voltammograms for a solution containing 100 μg L^{-1} Sn, CD and Pb; 80 s accumulation at -1.4 V. (a) original and (b) differential displays

Adsorptive stripping voltammetry and Potentiometry

- In this technique, metals are adsorbed on the electrode surface through metal complex formation.
- The formation of metal complex is done at constant potential
- The stripping of metal complex is followed by
  - — Linear potential scan
  - — Potential-time (pulse) waveform
  - — Potentiometric analysis
- The detection limit is extremely (10^{-10} to 10^{-10} M for very important metal such as Cr, U, V, Fe, Al and Mb)
- For Pt it is 10^{-12} M
- Beside the trace metal, organic compounds can also be analyzed.

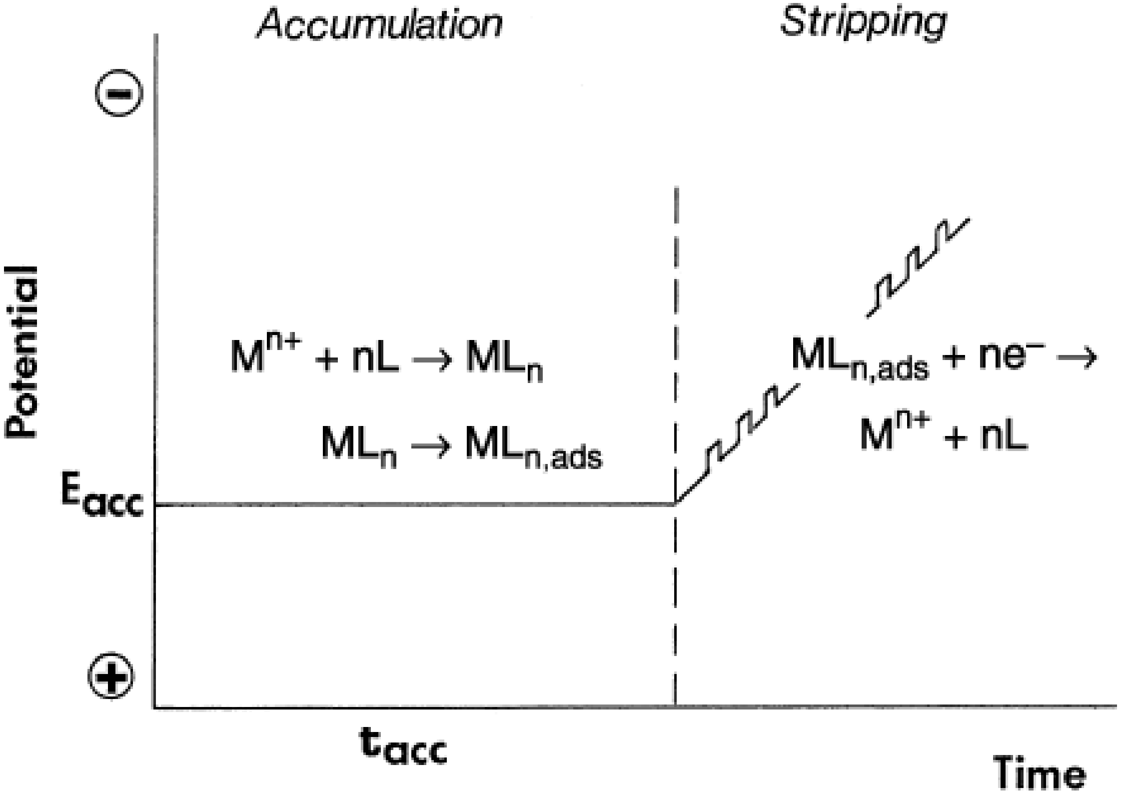
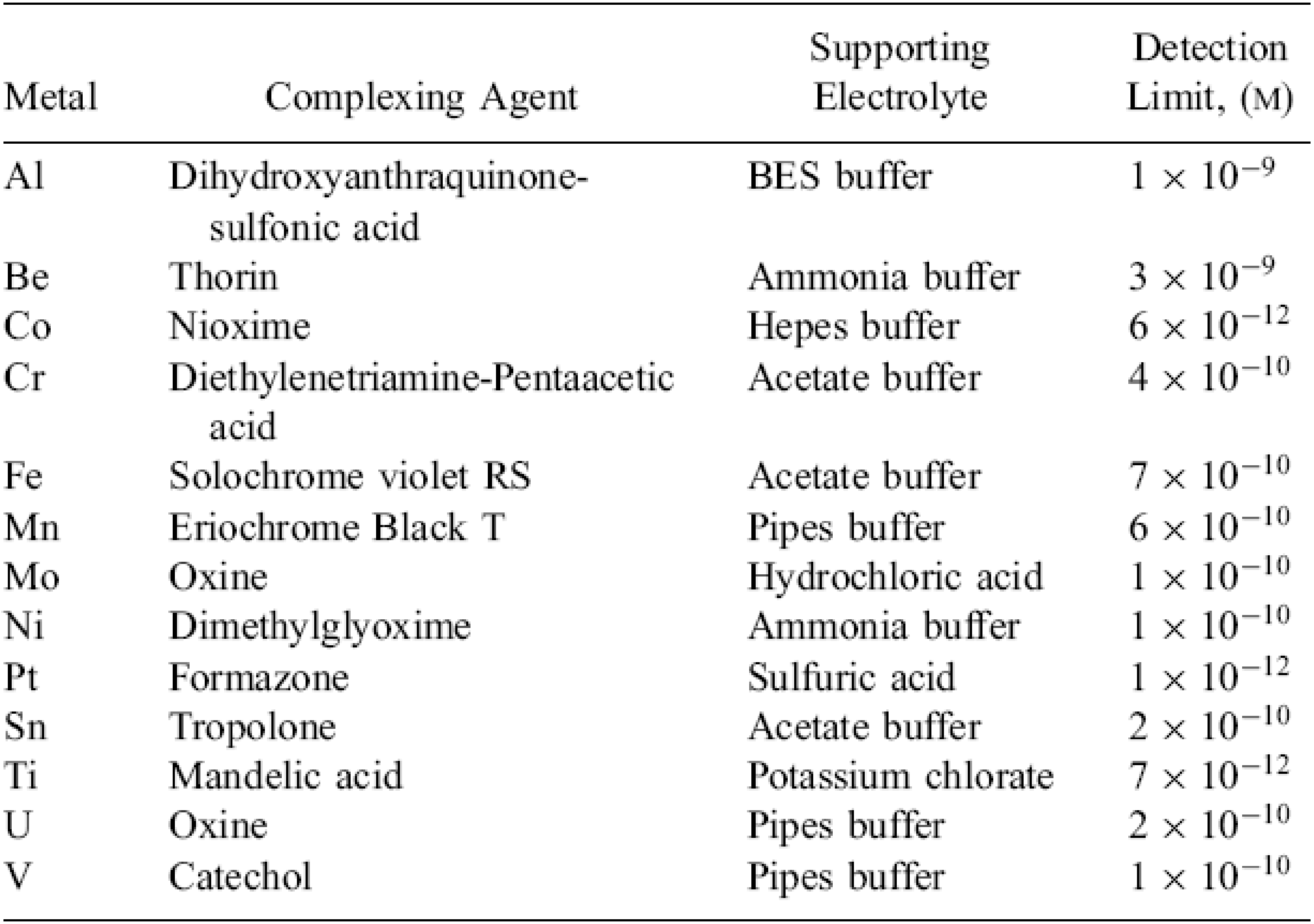


Fig. Accumulation and stripping steps in adsorptive stripping measurements of a metal ion in presence of an appropriate chelating agent.

Common adsorptive stripping schemes for measurements of trace metals



Metal	Complexing Agent	Supporting Electrolyte	Detection Limit, (M)
Al	Dihydroxyanthraquinone-sulfonic acid	BES buffer	1×10^{-9}
Be	Thorin	Ammonia buffer	3×10^{-9}
Co	Nioxime	Hepes buffer	6×10^{-12}
Cr	Diethylenetriamine-Pentaacetic acid	Acetate buffer	4×10^{-10}
Fe	Solochrome violet RS	Acetate buffer	7×10^{-10}
Mn	Eriochrome Black T	Pipes buffer	6×10^{-10}
Mo	Oxine	Hydrochloric acid	1×10^{-10}
Ni	Dimethylglyoxime	Ammonia buffer	1×10^{-10}
Pt	Formazone	Sulfuric acid	1×10^{-12}
Sn	Tropolone	Acetate buffer	2×10^{-10}
Ti	Mandelic acid	Potassium chlorate	7×10^{-12}
U	Oxine	Pipes buffer	2×10^{-10}
V	Catechol	Pipes buffer	1×10^{-10}

Common adsorptive stripping schemes for measurements of trace metals

Example for adsorptive striping analysis

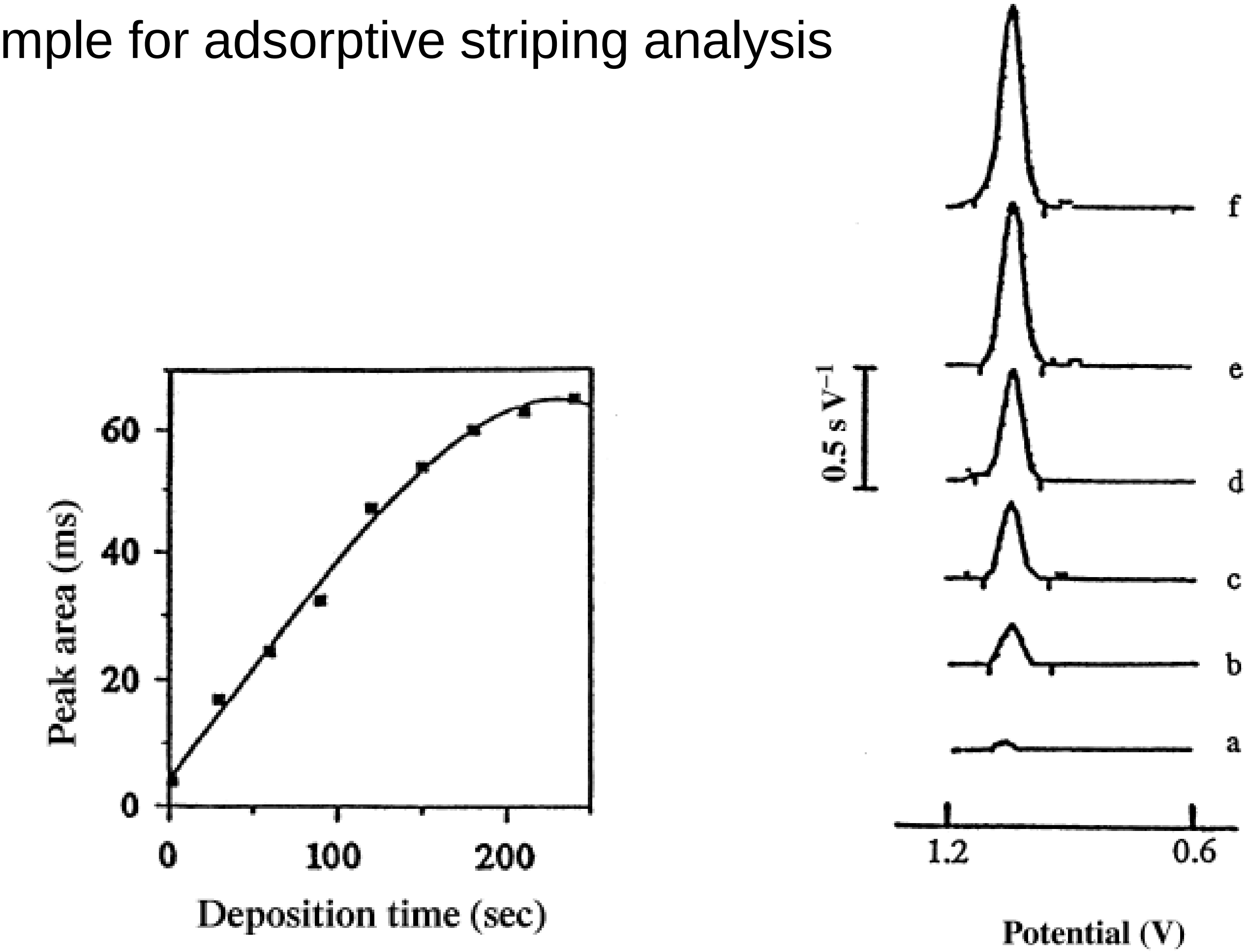


Fig. Adsorptive stripping potentiograms for 0.5 ppm calf-thymus DNA following different adsorption times of 1-150 s (curves a-f)

Cathodic stripping voltammetry

- This technique is just mirror image of ASV
- It involves anodic deposition of the analytes followed by stripping in a negative-going potential scan

$$A^{n-} + Hg \underset{\text{stripping}}{\overset{\text{deposition}}{\rightleftharpoons}} HgA + ne^{-}$$

- Resulting reduction peak current provides the desired quantitative information
- It is used for measuring a wide range organic and inorganic compound capable of forming insoluble salts with mercury
- Thiols, penicillins, halides ions, cyanides, sulfide.
- The deposition and stripping steps involves the reaction at silver disk electrode

$$Ag + X^{-} \rightleftharpoons AgX + e^{-}$$

$$X^{-} = Cl^{-}, Br^{-}$$

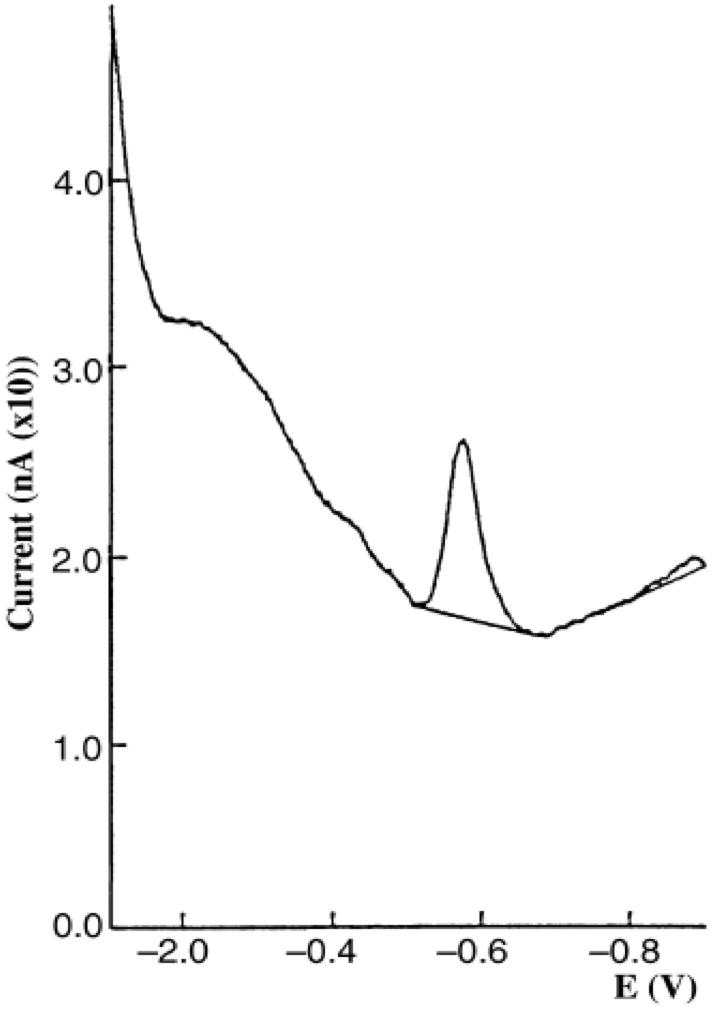
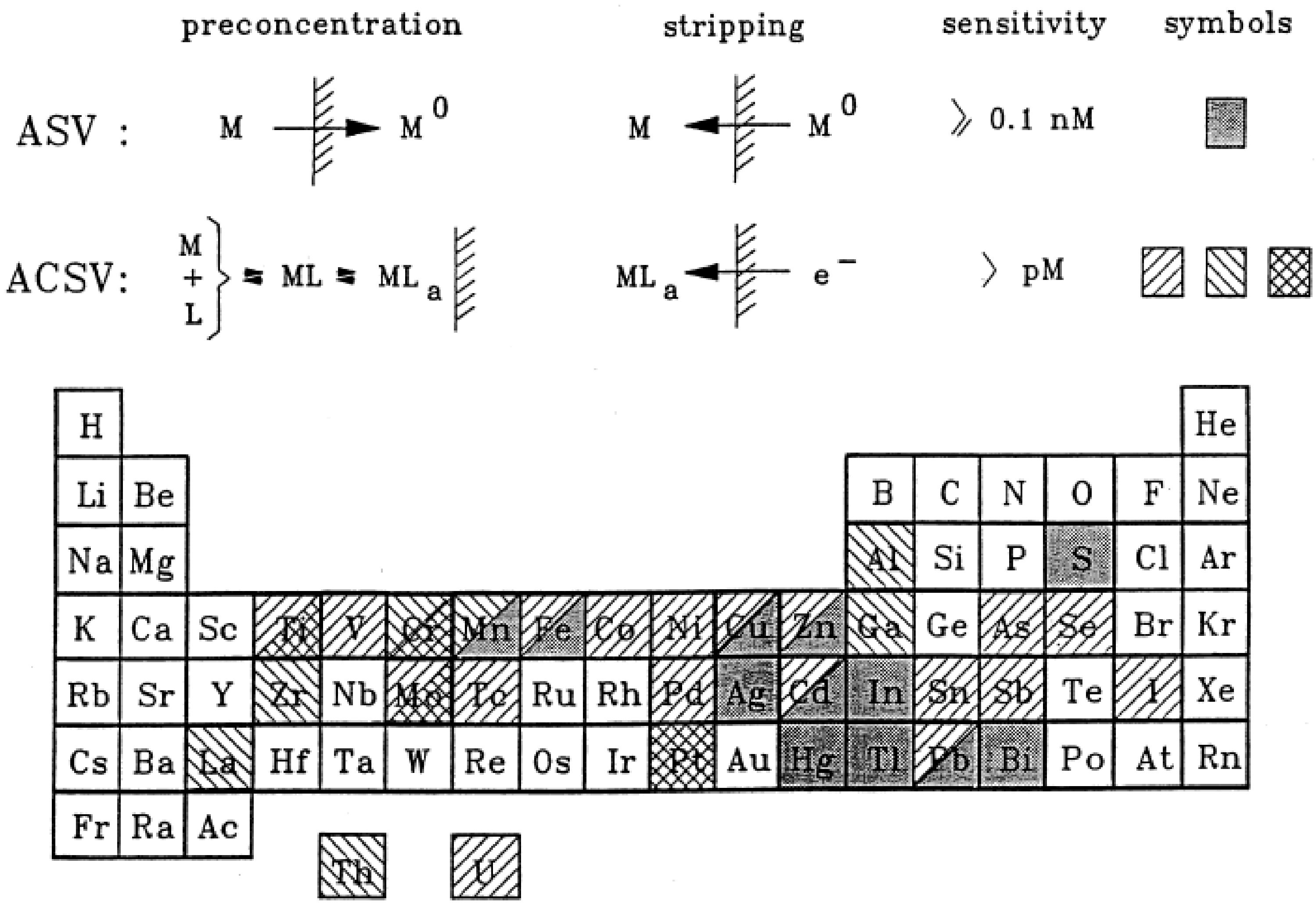


Fig. Stripping voltammograms for trace iodine in seawater

Applications of stripping analysis



- Industrial, clinical samples as well as foodstuff, beverages, gunshot residues and pharmaceutical formulations
- Environmental analysis, blood screening and so on.