Stripping Methods

Stripping voltammetry methods are the most efficient electrochemical techniques for trace analysis. The unusually high sensitivity and selectivity are based on the fact that the analyte is accumulated before it is determined and that both accumulation and determination are electrochemical processes for which progress can be controlled.

In comparison to conventional polarographic work, determinations by stripping voltammetry are generally more sensitive by a factor of 10^3 to 10^5, so that the detection limits are between 10^{-9} to 10^{-11} mol/L and in some cases even 10^{-12} mol/L.

The term stripping stands for the fact that, during the determination, the accumulated analyte is removed from the working electrode. This process can be followed voltammetrically, potentiometrically, or chronopotentiometrically, this is expressed by the terms stripping voltammetry, stripping potentiometry, and stripping chronopotentiometry.

Accumulation always takes place at constant potential (E_{acc}, accumulation potential) at a stationary mercury drop, mercury film, graphite or noble metal electrode for a controlled period (t_{acc}, accumulation time). The analyte is deposited electrolytically as a metal, as a sparingly soluble mercury compound or adsorptively as a complex compound.

The accumulated analyte species is removed (stripped) from the working electrode – the real determination step – by an oxidation or a reduction process.

In order to differentiate the stripping voltammetric method in which the determination takes place by oxidation of the accumulated product, the term anodic stripping voltammetry (ASV) is used.

In the other case where the determination step occurs by reduction of the accumulated analyte species, the method is known as cathodic stripping voltammetry (CSV).

With adsorptive accumulation of the analyte the method is known as adsorptive stripping voltammetry (AdSV).

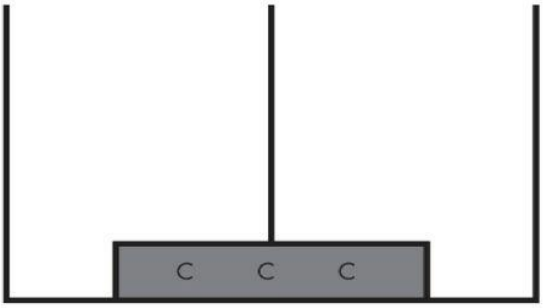
Electrode configuration

Hanging Mercury Drop Electrode

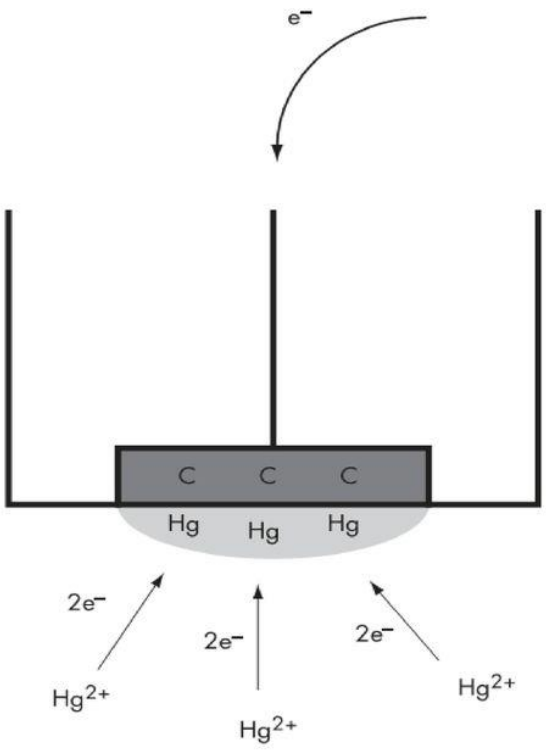
Carbon-Paste Electrode

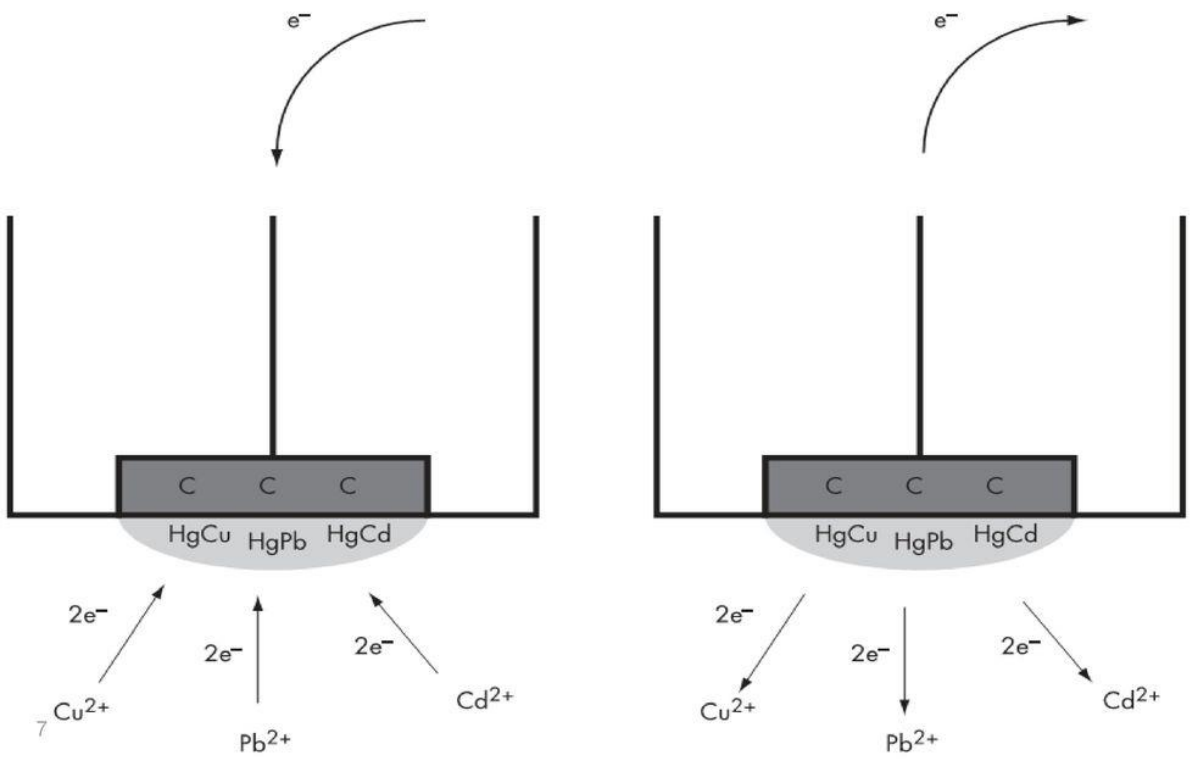
Gold Electrode

Prior to Hg deposition



Hg deposition
at –1300 mV





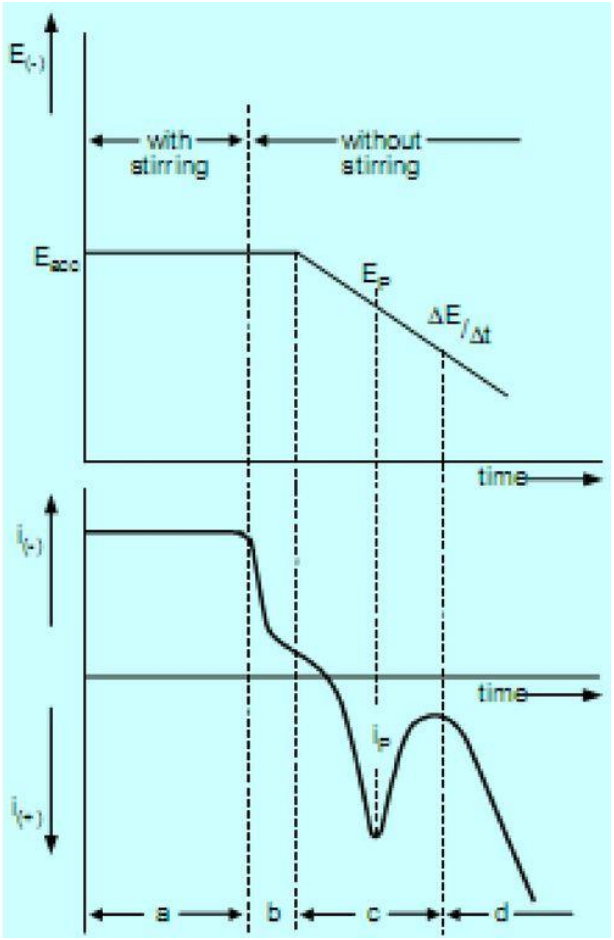
Anodic Stripping Voltammetry

Anodic stripping voltammetry (ASV) can be used to determine all metals which are soluble in mercury with the formation of amalgams or which can be deposited electrolytically at carbon or noble metal electrodes.

The mechanism for anoding stripping voltammetry can be described using the equation:

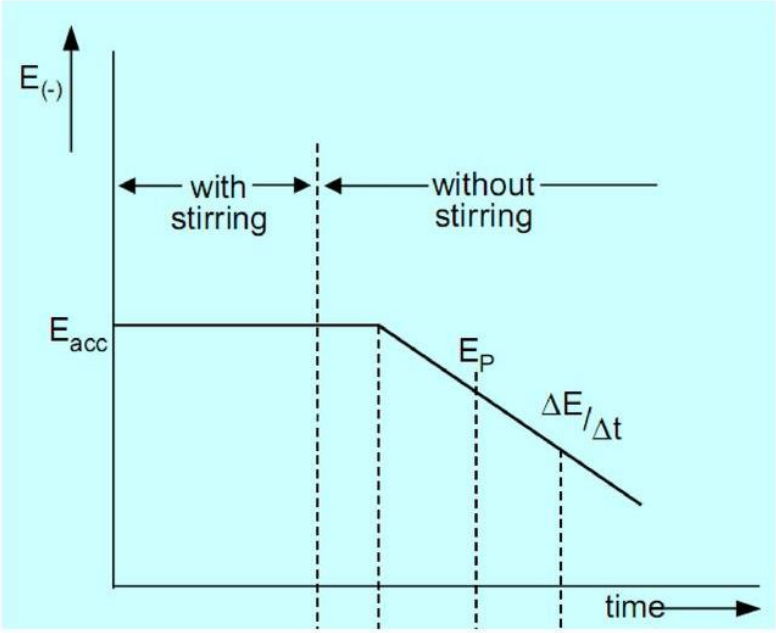
$$M^{n+} + (Hg) + ne \underset{\text{Determination (anodic)}}{\overset{\text{Deposition (cathodic)}}{\rightleftharpoons}} M(Hg)$$

E_{acc} = Accumulation potential;
$\Delta E/\Delta t$ Potential scan rate;
E_P Peak potential;
i_P Current peak;
a: Accumulation time;
b: Rest period;
c: Determination step;
d: Anodic dissolution of the mercury electrode



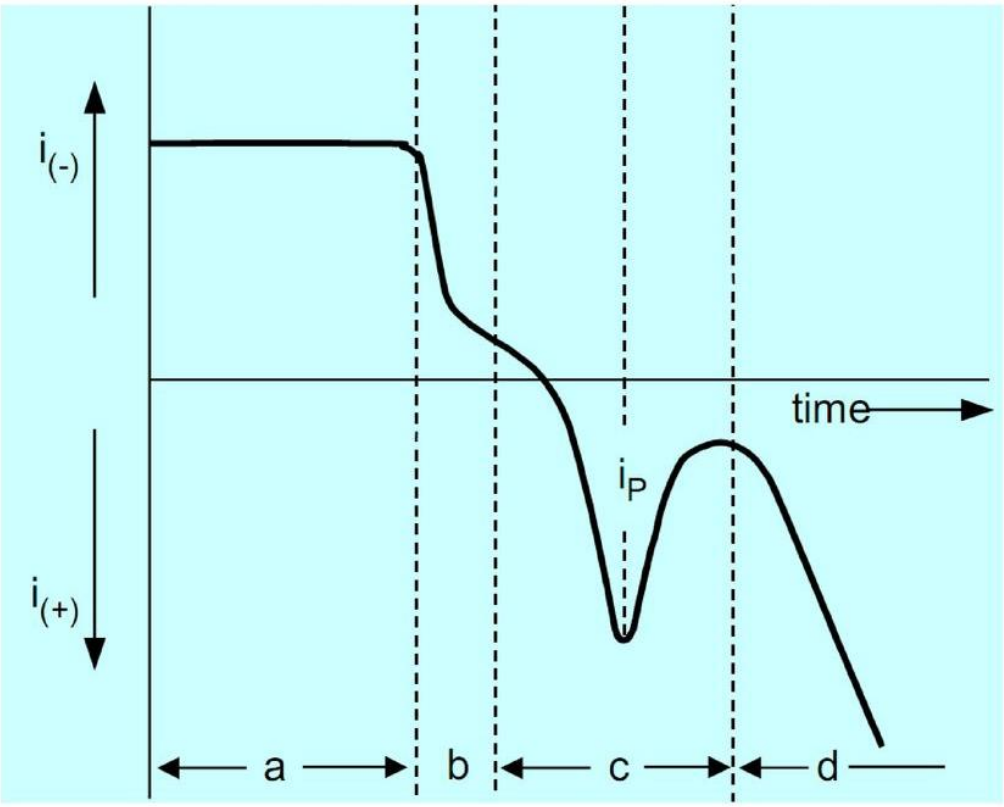
The upper part of the figure is the accumulation time, in which the analyte is deposited onto the working electrode at a constant potential and with the sample solution being stirred continuously throughout accumulation.

As deposition is always incomplete, the working conditions must be strictly controlled if reproducible measurements are to be achieved. These include the accumulation time, accumulation potential, the shape, size and arrangement of the stirrer, the stirring speed (rotation), the sample volume and the surface area of the electrode (surface of the mercury drop or film).



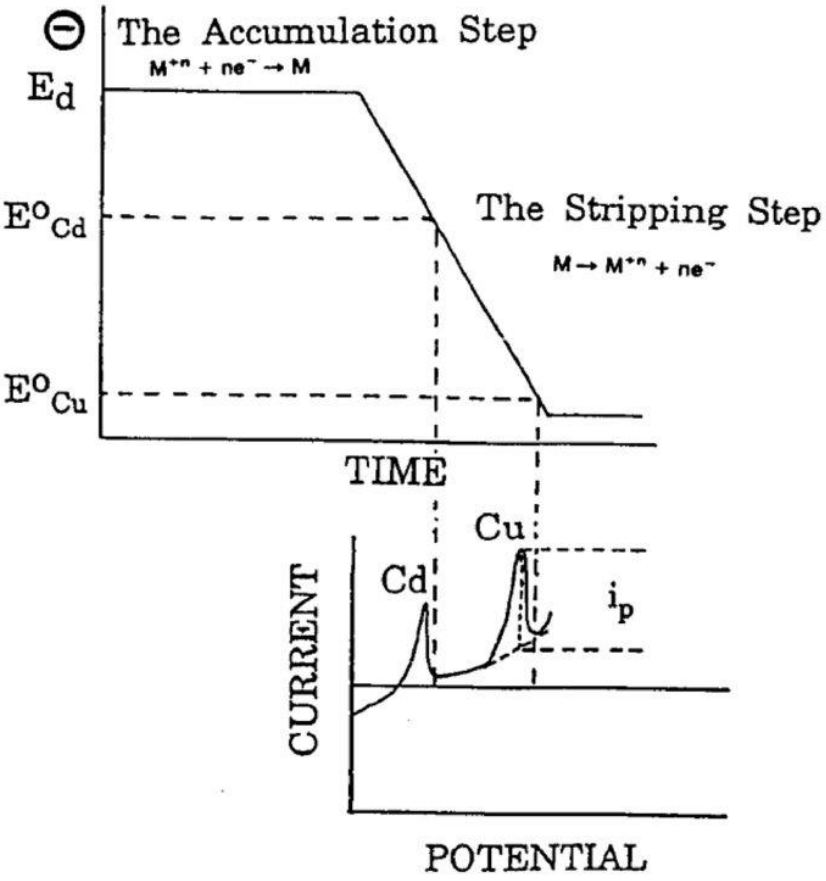
In the lower part of the figure, section b is the rest period. During this period the sample solution is no longer stirred, this means that the cathodic current drops because of lack of convection.

As small amounts of the analyte are deposited even from an unstirred solution, this period must also be controlled. Several seconds pass before the solution comes to a standstill and the deposited metal is well distributed in the mercury drop. This is why the rest period is defined as being 5 s to a maximum of 30 s.



In a mercury film the distribution process is complete after only a few seconds. Section c is defined by the potential scan rate ($\Delta E/\Delta t$ = const.), which is the rate at which the anodic stripping voltammogram is recorded. The measured signal is the peak current i_P, which, in Section d, changes into the anodic current for the dissolution of the mercury electrode.

The preconcentration is done by cathodic deposition at a controlled time and potential. The deposition potential is usually 0.2–0.4V more negative than E° of the the metal having the lowest E° (for the metal ion to be determined).



Amount of accumulated metal in the amalgam

The following equation is used to calculate the amount of metal deposited:

$$C_{M(Hg)} = \frac{i_{acc} * t_{acc}}{V_{Hg} * n * F}$$

$C_{M(Hg)}$: Concentration of the metal (accumulated analyte) in the amalgam

i_{acc}: Electrolysis current during accumulation

t_{acc} : Accumulation time

n : Electrons transferred during reduction of the analyte

F : Faraday constant

V_{Hg} : Volume of the hanging mercury drop

In case the anodic stripping analysis is done using a hanging mercury drop, then the volume of the drop is given by:

$$V_{Hg} = \frac{4}{3}\pi r^3$$

While if a thin film mercury electrode (TFME) is used, the volume of the mercury film is given by the relation:

V_{Hg} = Area of film * thickness of film

The electrolysis current, i_{acc} , is determined by the mass transport of the analyte and the potential at which accumulation takes place. To achieve high accumulation rates the solution should be stirred and the accumulation potential should be in the diffusion current range.

The accumulation time depends on the concentration of the analyte in the sample solution and must be chosen in a way that the measured signal remains linear throughout as large a concentration range as possible.

Deposition is never fully complete at voltammetric working electrodes. Complete deposition may be achieved with very small sample volumes (< 0.1 mL) and long electrolysis times, which is in fact not necessary for ASV.

Under normal working conditions with 5 to 20 mL sample solution and about 1 min accumulation time at a mercury drop with a surface area of a few mm^2 only a few tenths of a percent are deposited.

The transport of the analyte to the electrode surface takes place by diffusion and is supported by convection if the solution is stirred during accumulation (which is usually the case). This means that the electrolysis current, i_{acc} , not only depends on the diffusion conditions, but also on the hydrodynamic conditions which are based on laminar or turbulent flow (at high stirring speeds or when working with a rotating electrode). At a constant stirring speed or number of revolutions, the amount of metal deposited at the cathode is proportional to both the accumulation time and the analyte concentration in the sample solution.

$M(Hg) \alpha t_{acc} * [M^{n+}]$

ASV Using a HMDE

For ASV using a hanging mercury drop electrode, the determination is based on the anodic dissolution of the accumulated analyte, and the process produces a peak current which is proportional to the potential scan rate and the radius of the mercury drop, r^2.

$$i_p = \left(2.72 \times 10^5\right) n^{3/2} A D_{M(Hg)}^{1/2} \nu^{1/2} C_{M(Hg)} r^2 t_{acc}$$

i_P , Peak current , n : Electron transfer during oxidation of the analyte

$D_{M(Hg)}$: Diffusion coefficient of the metal deposited in the amalgam

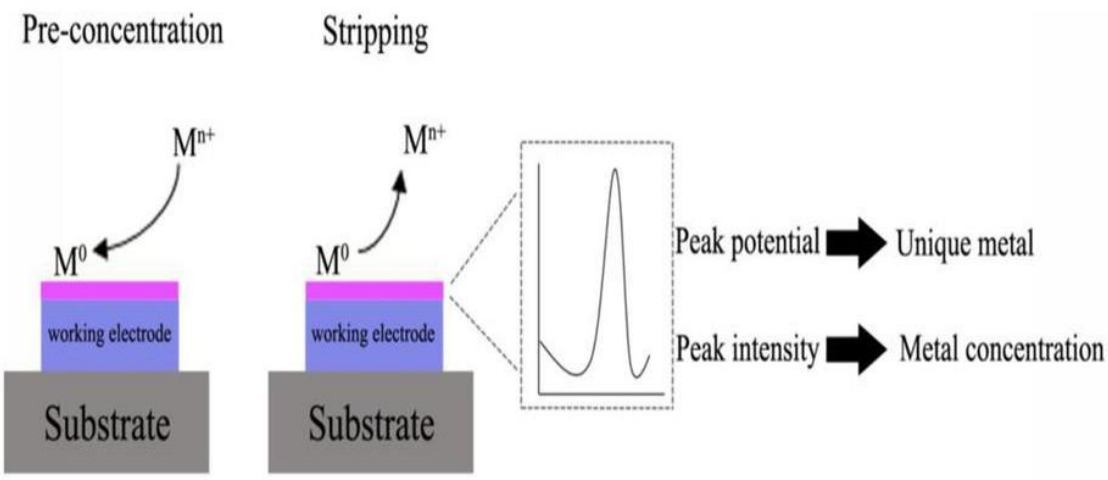
$C_{M(Hg)}$: Concentration of the metal (accumulated analyte) in the amalgam , v : Scan rate , r : Radius of mercury drop, and t_{acc} is the accumulation time

ASV using a thin film mercury electrode (TFME)

The following equation applies for the peak current obtained with the TMFE; it can be seen that the peak current is proportional to the scan rate and surface area A_F of the mercury film, in addition to accumulation time.

$$i_p = kn^2 A_F \nu t_{acc} C_{M(Hg)}$$

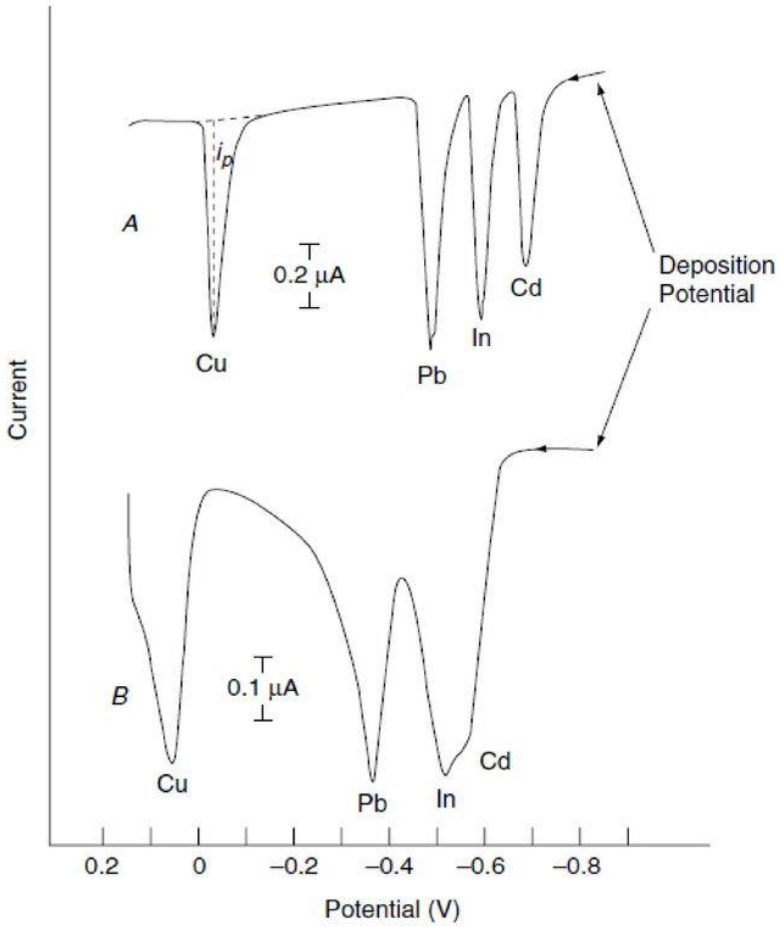
i_P Peak current, k Constant, n Electron transfer during the oxidation of the analyte, A_F Surface area of mercury film, *v* Scan rate, t_{acc} Accumulation time $C_{M(Hg)}$ Concentration of metal (accumulated analyte) in the amalgam



Measurements with mercury film electrodes produce higher signal currents and narrower peak shapes, but also have relatively high background currents.

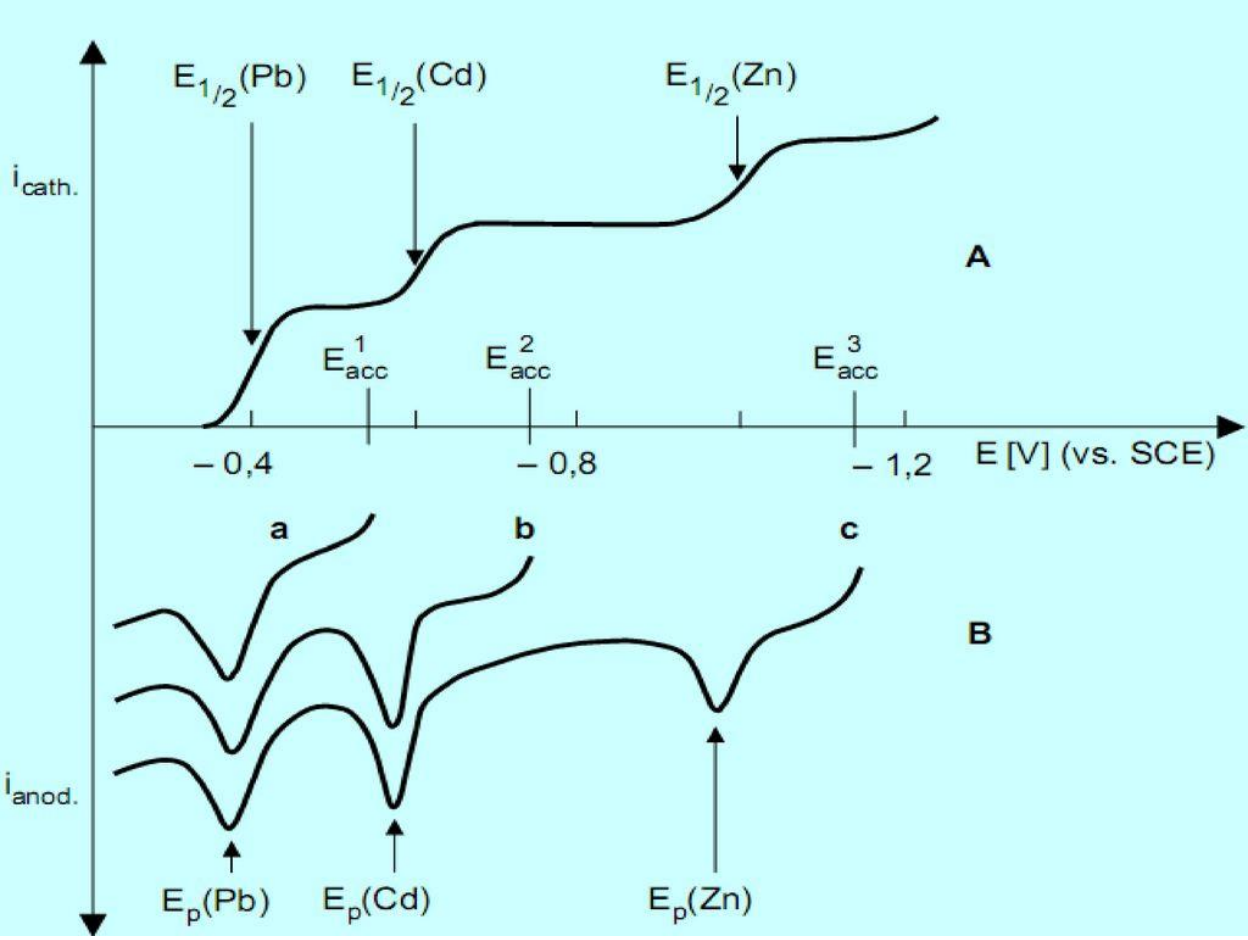
Good results (with lower background currents) can be achieved with the hanging mercury drop electrode, if the voltammogram is recorded at a slow scan rate and with very small drops. The advantage of a small mercury drop is (similar to the film) the relatively small diffusion area, from which (during anodic dissolution) the analyte can diffuse very rapidly to the surface for exchange. As the mercury drop is easy to handle and can be renewed reproducibly by dropping (tapping), the hanging mercury drop electrode is used more frequently in practice than the mercury film electrode.

Stripping voltammograms for 2 * 10^{-7}M Cu^{2+}, Pb^{2+}, In^{3+}, and Cd^{2+} at the mercury film (*A*) *and hanging mercury drop (B) electrodes*



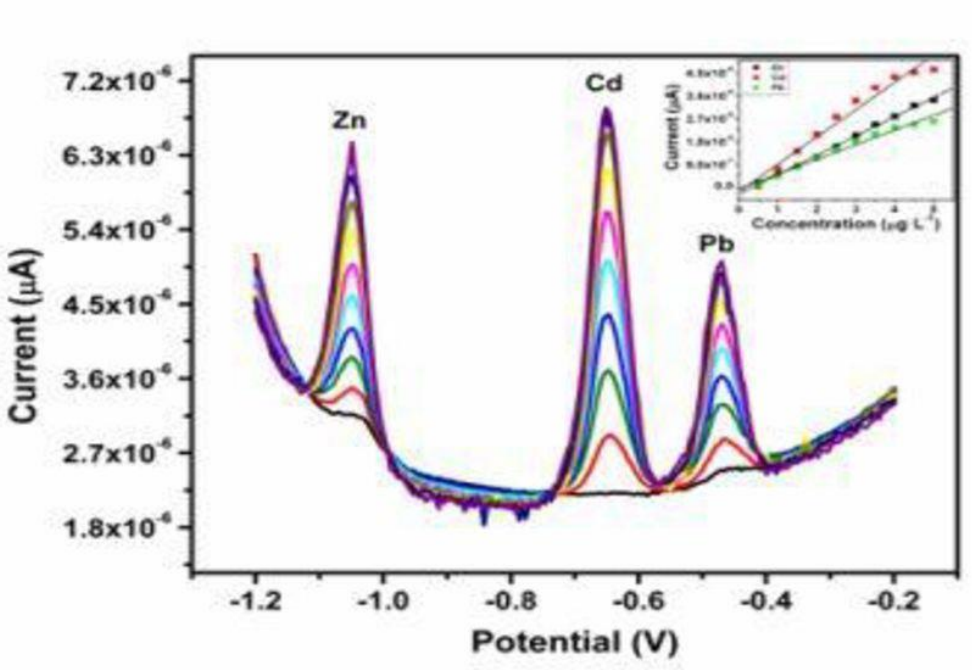
Improvement of the Selectivity of ASV

The potential-controlled recording of stripping voltammograms has the advantage that the dissolution process can be halted at a particular potential. In this way it is possible to dissolve those metals which are easier to oxidize than the analyte and whose high concentration in the amalgam interferes with the determination of the analyte. After the interruption the recording of the current-potential curve for the unimpeded determination of the (nobler) analyte is continued. Otherwise the relatively small peak of the trace element would be concealed by the signal from the excess components.



A further way of improving the selectivity of ASV determinations is based on the alteration of the electrochemical behavior of the analyte by complex formation. In many cases selected chelating agents can be used for the better separation of neighboring peaks and to suppress the signals from interfering components. If two elements that are electrochemically similar have to be determined in the same sample then a solution of a chelating agent is added that only forms a stable complex with one of the sample components. Both elements are accumulated together at a sufficiently negative potential, however they give separate peaks in the stripping voltammogram.

Quantitative Analysis

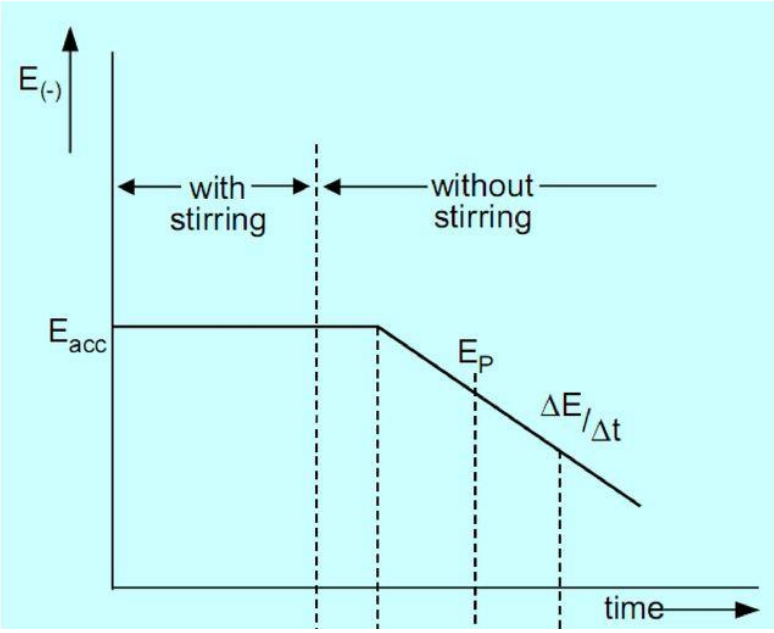


Anodic Stripping Voltammetric Techniques

The previously studied voltammetric techniques can be used for stripping of analyte species. These include (but not limited to) the following:

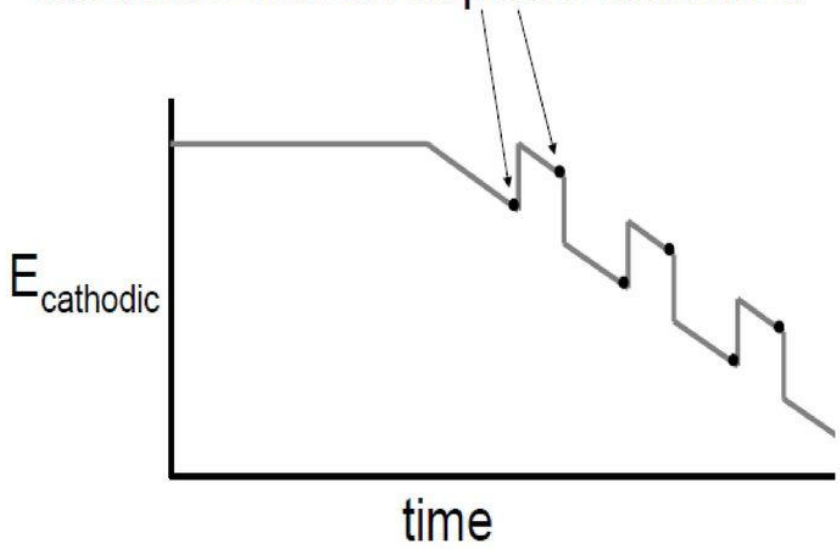
1. **Linear scan voltammetry**
2. **Differential scan voltammetry**
3. **Square wave voltammetry**

Linear Scan Anodic Stripping Voltammetry



Differential Pulse Anodic Stripping Voltammetry

- Measure current at points indicated



Cathodic Stripping Voltammetry (CSV)

-Mirror image of ASV

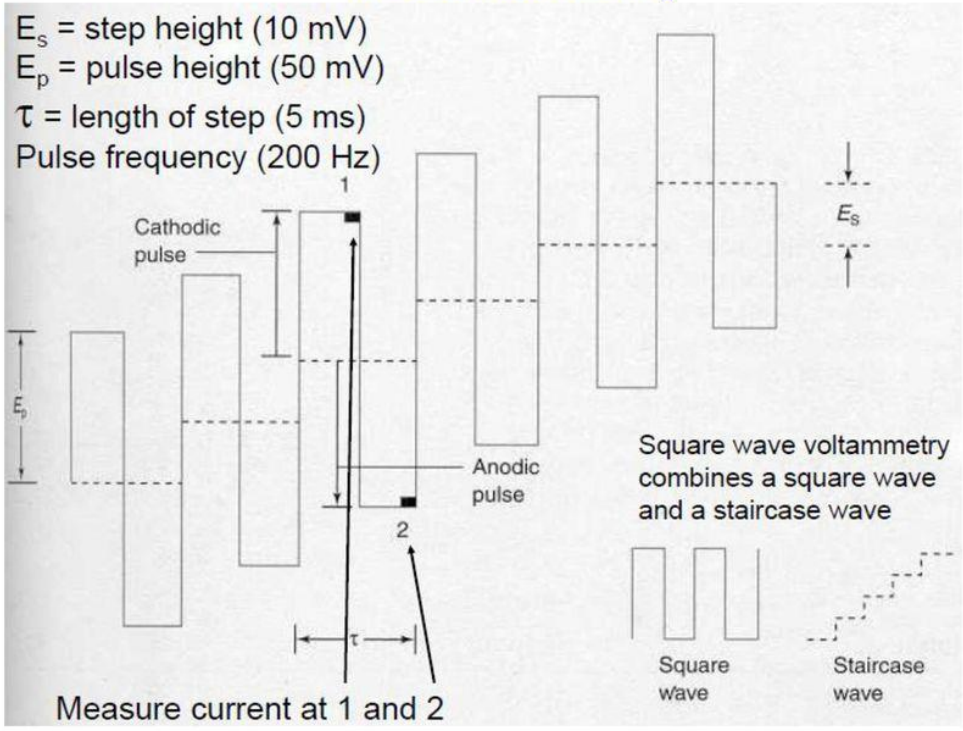
-- Involves anodic deposition of anionic analyte and subsequent stripping by a potential scan in the negative direction

$$A^{n-} + Hg \leftrightarrow A(Hg) + ne^-$$

(Deposition to the right and stripping to the left)

- Useful for measuring organic and inorganic anionic compounds that form insoluble salts with Hg (thiols, penicillin, halides, cyanides)

Square Wave Cathodic stripping Voltammetry



Evaluation:

✓ **Scale of Operation:**

Voltammetry is routinely used to analyze samples at the parts-per-million (ppm) level and, in some cases, can be used to detect analytes at the parts-per-billion (ppb) or parts-per-trillion level.

✓ **Accuracy and Precisoin:**

The accuracy of a voltammetric analysis often is limited by the ability to correct for residual currents, ppm level, accuracies of ±1–3%. Under most experimental conditions, precisions of ±1–3% .

- **Precision** is generally limited by the uncertainty in measuring the limiting or peak current. Under most experimental conditions, precisions of ±1–3% . One exception is the analysis of ultratrace analytes in complex matrices by stripping voltammetry,(precisions as poor as ±25%).
- **Sensitivity** In many voltammetric experiments, sensitivity can be improved by adjusting the experimental conditions.
- **Selectivity** Selectivity in voltammetry is determined by the difference between half-wave potentials or peak potentials, with minimum differences of ±0.2–0.3 V required for a linear potential scan, and ±0.04–0.05 V for differential pulse voltammetry.

- **Time, Cost and Equipment:** Commercial instrumentation for voltammetry ranges from less than $1000 for simple instruments to as much as $20,000 for more sophisticated instruments. In general, less expensive instrumentation is limited to linear potential scans, and the more expensive instruments allow for more complex potential-excitation signals using potential pulses.
- Except for stripping voltammetry, which uses long deposition times, voltammetric analyses are relatively rapid.

Application

- **Clinical Samples:** voltammetry and stripping voltammetry have been used to determine the concentration of trace metals in a variety of matrices, including blood, urine, and tissue samples. The determination of lead in blood is of considerable interest due to concerns about lead poisoning.

- Besides environmental and clinical samples, voltammetry and stripping voltammetry have been used for the analysis of trace metals in other samples, including food, steels and other alloys, gasoline, gunpowder residues, and pharmaceuticals.
- Voltammetry is also an important tool for the quantitative analysis of organics, particularly in the pharmaceutical industry, in which it is used to determine the concentration of drugs and vitamins in formulations.

- Analysis of available copper, zinc and manganese contents in soil and vegetable samples.

- Determination of food contaminants -toxic metals, pesticide, fertilizers and veterinary drugs residuals , trace essential elements, food additive dyes and other organic compounds of biological significance.