Monograph

Introduction to Polarography and Voltammetry

Univ.-Prof. Dr. Günter Henze

Metrohm

Introduction to Polarography and Voltammetry

Univ.-Prof. Dr. Günter Henze

Printed in Switzerland by Metrohm Ltd., CH-9101 Herisau
8.108.5087 – 2003 – 08

Table of Contents

1. Terminology

Polarography and ***voltammetry*** are the names of analytical methods based on current-potential measurements in electrochemical cells. The analytical signal is the current – normally a faradaic current – which flows through the cell during the reaction of the analyte at the working electrode with a small surface. The analyte may be a cation, an anion or a molecule.

The founder of this method, Jaroslav Heyrovský, introduced the dropping mercury electrode as the working electrode. The electrode consists of a thick-walled glass capillary from which the mercury drops into the sample solution under the pressure of a column of mercury. In his paper *Electrolysis with the dropping mercury cathode* (1922) he called the recorded current-potential curves polarograms and introduced the term ***polarography***.

The term ***voltammetry*** results from ***volt-am****(père)*-***metry*** and should not be confused with voltametry – written with one *m* – which is described by IUPAC (International Union of Pure and Applied Chemistry) as being a *controlled-current potentiometric titration*.

The terms polarography and voltammetry are frequently used in the reverse sense or are used inaccurately. According to the IUPAC rules, the term ***polarography*** should always be used when the current-potential curve is recorded by using a liquid working electrode whose surface can be renewed periodically or continuously (e.g. by drops). This includes the classical dropping mercury drop electrode (DME) and the subsequently developed static mercury drop electrode (SMDE – see Section 6).

Voltammetry includes all methods in which the current-potential measurements are made at stationary and fixed working electrodes (irrespective of their material composition). These include the hanging mercury drop electrode (HMDE), the thin mercury film electrode (TMFE), glassy carbon electrodes (GCE) and carbon paste electrodes (CPE). Working electrodes made of noble metals (e.g. gold or platinum) are used less frequently.

Various methods are assigned to the terms polarography and voltammetry; these differ in the measuring technique and the type of electric potential used to excite the determination process.

2. Direct current methods

In the simplest case the polarography measuring principle is based on the registration of the current that flows through the DME as working electrode during a linear (direct) voltage alteration (classical ***direct current polarography***, DCP). The counter electrode is normally an electrode of the second kind, e.g. a calomel or silver chloride electrode which, in contrast to the relationship in modern measuring setups (three-electrode technique, see Section 6), is at the same time the reference electrode.

On closer observation the current flowing through the working electrode is made up of two components, the ***faradaic current i_F***, which is based on the reduction or oxidation of the analyte, and the ***capacitive current i_C***, which is caused by the charging and discharging of the electrochemical double layer on the surface of the working electrode. For most polarographic determinations the faradaic current provides the measuring signal (useful signal) and the capacitive current the unwanted interference components (interference signal). This relationship is shown in Fig. 1.

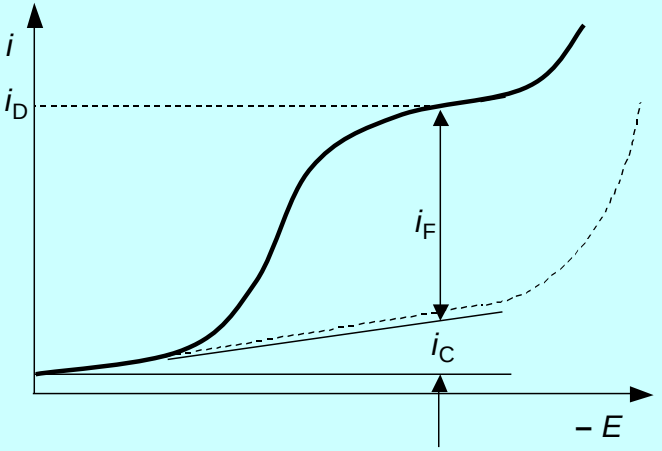


Fig. 1: Relationship between the faradaic current i_F and capacitive current i_c in a direct current polarogram; i_D is the diffusion current.

Under practical conditions the potential-dependent capacitive current can grow up to 10^{-7} A and is then within the range of the faradaic diffusion current i_D of an analyte solution with 10^{-5} mol/L. If i_C has the same value as i_F ($i_F/i_C = 1$), then the useful signal can no longer be separated from the interference signal; i.e. the detection limit for direct current polarographic determinations is limited by the relationship between the useful signal and interference signal (also known as the signal-noise ratio).

The diffusion current i_D is the maximum value for i_F which is obtained when all the analyte particles transported to the surface of the mercury drop by diffusion have been converted, i.e. reduced or oxidized (charge-transfer reaction). The relationship between the diffusion current and the analyte concentration is described by the ***Ilkovič equation***.

Ilkovič equation

$$i_D = 0{,}607 \cdot n \cdot D^{1/2} \cdot m^{2/3} \cdot t_d^{1/6} \cdot c_a \qquad \text{(Eq. 1)}$$

i_D	Diffusion current
n	Number of electrons exchanged in the charge-transfer reaction
D	Diffusion coefficient of the analyte
m	Mercury flow rate
t_d	Dropping time of the mercury drop
c_a	Concentration of the analyte

Polarographic determinations with a higher sensitivity are only possible if the ratio i_F/i_C can be improved by other measuring techniques (by increasing i_F or reducing i_C). Considerations concerning the (partial) elimination of the capacitive current led to ***sampled DC polarography***[1] and to the ***pulse methods***. Attempts to increase the faradaic current resulted in ***stripping voltammetry***, in which the analyte is accumulated electrolytically at a stationary working electrode before its voltammetric determination. In addition, the performance of both polarographic and voltammetric methods has been improved by the introduction of digital instruments and the use of a static mercury drop electrode (SMDE) instead of the dropping mercury electrode (DME) – (see Instrumentation, Section 6).

In digital instruments the direct current polarograms are no longer recorded with a linear potential alteration, but by using a staircase ramp as the excitation signal. In the measuring technique shown in Fig. 2 the current in the measuring time t_m is always measured at the end of a potential step (the potential ramp is synchronized with the drop life at the SMDE), i.e. at a constant potential (part b) and at an electrode surface area that remains constant (part a); this reduces the contribution of the capacitive current to the measuring signal to a minimum.

[1] When the current is *sampled* at the end of a drop life, then i_C is at its smallest in comparison to i_F, as during the dropping time the diffusion current increases with $t^{1/6}$, whereas the capacitive current decreases with $t^{-1/3}$.

This method is known as ***sampled DC polarography***; in comparison to classical DC polarography it produces smooth (oscillation-free) polarograms (part c) and, because of the reduction of the capacitive current contribution to the measuring signal, is more sensitive by about one order of magnitude.

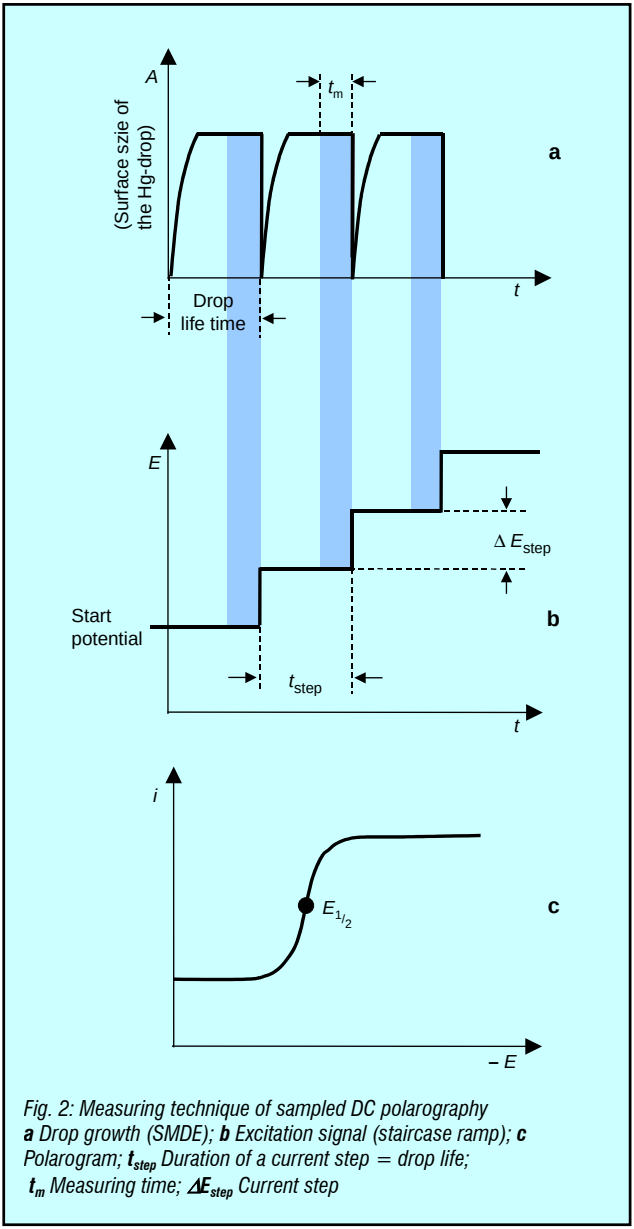


Fig. 2: Measuring technique of sampled DC polarography
***a** Drop growth (SMDE); **b** Excitation signal (staircase ramp); **c** Polarogram; t_{step} Duration of a current step = drop life; t_m Measuring time; ΔE_{step} Current step*

3. Pulse methods

The pulse methods include ***square-wave polarography***, ***normal pulse polarography*** and ***differential pulse polarography.***

A general feature of these methods is that the electrode processes are excited in different ways with periodically changing square wave potentials at a constant or increasing amplitude ΔE_A. In this way it appears that during the pulse time the faradaic current i_F decreases with $t^{-½}$ and the capacitive current i_C with e^{-kt} (see Eq. 2).[2] As a result, in a measurement toward the end of the pulse time t_P it is chiefly the faradaic contribution which is recorded, as at this time the capacitive current has almost completely vanished (see Fig. 3).

Reduction of the capacitive current during the pulse time

$$i_C = \frac{\Delta E_A}{R} \cdot e^{-\frac{t}{R \cdot C_D}} \qquad \text{(Eq. 2)}$$

i_C	Capacitive current
ΔE_A	Pulse amplitude
R	Discharge resistance
t	Time after pulse application
C_D	Double layer capacity of working electrode

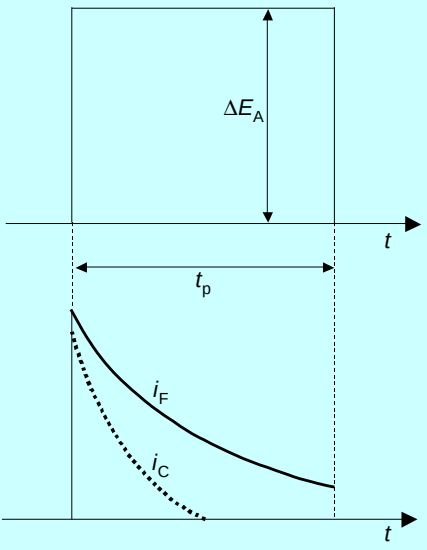


Fig. 3: Principle of the pulse methods

The methods developed with square wave potential pulses differ in the frequency and height (amplitude) of the applied pulses as well as in the formation principle of the measured value. All methods can be carried out polarographically with the static mercury drop electrode or voltammetrically with stationary mercury electrodes or with solid-state electrodes.

[2] Eq. 2 corresponds to the equation for a capacitor with discharge resistance R and double layer capacity C_D

The ***square wave polarography*** (SWP) introduced by Barker and Jenkins 1952 is based on the fact that a linearly increasing direct potential has a square wave alternating potential of a constant size (square wave potential amplitude ΔE_A up to 50 mV) and frequency (usually 125 Hz) superimposed on it. In digital instruments a staircase-shaped potential increase is applied instead of the linearly increasing basic potential. Each potential step (ramp) has superimposed either one potential pulse or several (up to 250) square potential cycles (oscillation frequency f) with defined and constant pulse amplitudes. In addition, modern instruments are equipped with a static mercury drop electrode, which ensures that the measurements are not only made at a constant potential, but also with a constant electrode surface area.

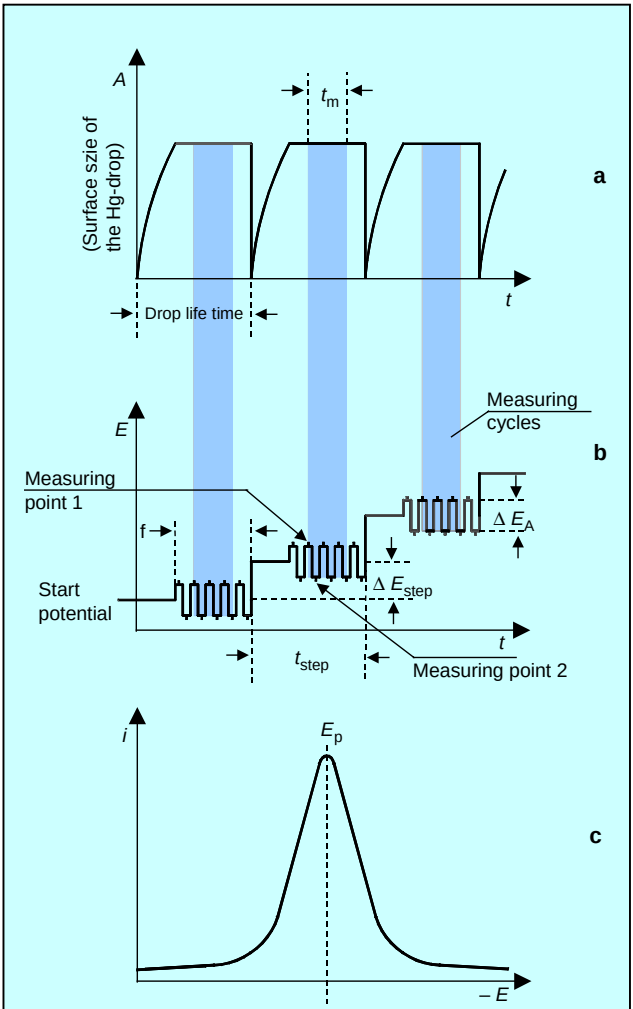


Fig. 4: Measuring technique of square wave polarography
***a** Drop growth (SMDE); **b** Excitation signal; **c** Polarogram;* ΔE_{step} *Potential step for staircase ramp (up to 2-12 mV);* t_{step} *Duration of a potential step (0.5-10 s);* ΔE_A *Square wave potential amplitude (~ 25 mV);* t_m *Measuring time; **f** Oscillation frequency (approx. 125 Hz for t = 40 ms)*

In the measuring technique shown in Fig. 4 two current values are measured at each oscillation: i_+ at the positive pulse end (measuring point 1) and i_- at the negative pulse end (measuring point 2). When the difference between the two current values $i_+ - i_-$ determined for a potential ramp is plotted against the particular potential then a peak-shaped polarogram is obtained with the peak potential E_P and the peak current i_P (see Eq. 3) For reversible processes E_P corresponds to the direct current polarographic half-wave potential $E_{½}$.

The height and half-width $b_{½}$ of a peak ($b_{½}$ is at $i = i_P/2$) depend on the electron exchange n of the charge-transfer reaction and the height of the superimposed square wave pulses (for a small ΔE_A then $b_{½} = 90/n$ mV).

Peak current in a square wave polarogram

$$i_P = k \cdot n^2 \cdot D^{1/2} \cdot \Delta E_A \cdot c_a \qquad \text{(Eq. 3)}$$

i_P	Peak current
k	Constant
n	No. of exchanged electrons in the charge-transfer reaction
D	Diffusion coefficient of the analyte
ΔE_A	Pulse amplitude
c_a	Concentration of the analyte

With ΔE_A = const. the peak current i_P increases as the square of the number n of the exchanged electrons and also when, at a given electron exchange n, the square wave potential amplitude is increased. The larger the value of n, the narrower the peaks. However, this relationship only applies to reversible processes. This is why the sensitivity of square wave polarographic determinations is at its greatest when the charge-transfer reaction (with a large n) takes place reversibly, and when the measurements are carried out with a large pulse amplitude. Under such conditions the detection limit is approx. 10^{-8} mol/L.

The method of working known as ***square wave voltammetry*** (SWV) according to Osteryoung is characterized by the fact that the whole measuring procedure takes place at a single mercury drop with rapid potential sweeps. The duration of a potential step is identical with the length of the square wave pulse and is 5-10 ms; i.e. to each potential step only one square wave potential cycle with a relatively large amplitude of ΔE_A = 50 mV is added; this is shown in Fig. 5.

The difference in the measured values obtained in points 1 and 2 (at very short measuring times) is plotted against the potential and, as in the case of square wave polarography, results in a bell-shaped current-potential curve.

The pulse times in the ms-range (frequencies up to 250 Hz) allow speeds for the potential sweeps of up to 1000 mV·s^{-1}, whereas only a single mercury drop is required for each individual measuring procedure. Under these conditions interfering signals from irreversible reactions (e.g. the signal produced by oxygen reduction) can be eliminated and rapid measurement in flowing media can be carried out on a single mercury drop (flow-through voltammetry).

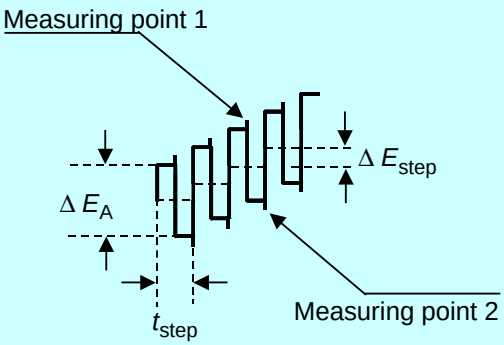


Fig. 5: Measuring technique of square wave voltammetry acc. to Osteryoung t_{step} *Duration of a potential step or a square wave pulse (10 ms);* ΔE_A *Square wave potential amplitude (20 mV);* ΔE_{step} *Potential step of the staircase ramp (4 mV)*

In ***normal pulse polarography*** (NPP) the potential is not altered by a continuously increasing potential ramp, but by square wave potential pulses with increasing height (pulse amplitude ΔE_A), overlaid on a constant initial potential. The superimposing of the pulse is synchronized with the drop formation, with each drop having a single potential pulse with a pulse time of about 50 ms applied to it. The amplitude increases from one drop to the next by a constant amount and achieves a maximum of 1000 mV. The current is measured at the end of the *drop life* about 10 to 15 ms before the expiration of the pulse time t_P. As potential alteration at each drop is relatively large and the pulse time very short, a large concentration gradient is produced and, as a result, a large faradaic current. In contrast, the capacitive current remains small, as the measurement is made with the surface of the mercury drop remaining constant and i_C has practically vanished at the time that the measurement is made. The measured current is recorded or stored until the next measurement (on the following drop). If the individual current values are plotted against the potential alteration of the pulse then step-shaped current-potential curves are obtained. The curves are peak-shaped if the current of each preceding pulse is subtracted from the stored measured value of the following one. The sensitivity that can be achieved is approx. 10^{-7} mol/L; the resolution is given as ~100 mV. Fig. 6A shows the excitation signal and current-potential curve for NPP.

The most efficient pulse method is ***differential pulse polarography*** (DPP). In digital instruments the excitation signal consists of a staircase-shaped increasing direct potential (potential step ΔE_{step}), to which small square wave pulses with a constant potential (pulse amplitude ΔE_A) are applied in periodic succession. The superimposition is synchronized with the drop time and takes place when the electrode surface no longer changes. Fig. 6B shows the DPP measuring technique and the polarographic curves.

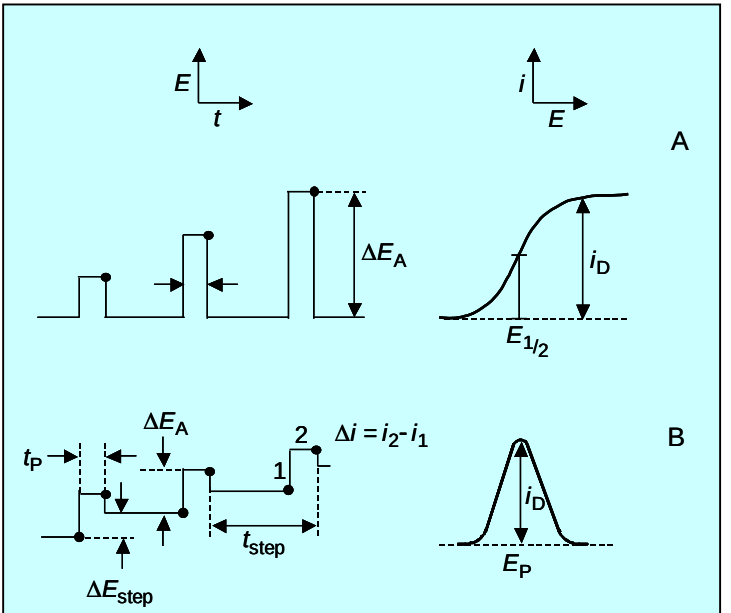


Fig. 6: Excitation signals and current-potential curves for normal pulse polarography (A) and differential pulse polarography (B).

The current is measured twice at each mercury drop, before each pulse and at the end of the pulse time t_P. The difference between the measurements (Δi) is plotted against the direct potential and produces peak-shaped polarograms, as Δi is largest for potential alterations in the region of the half-wave potential. The formation of this difference also leads to a further reduction of the capacitive current contribution and therefore to an increase in sensitivity, even when compared with determinations by normal pulse polarography.

According to Eq. 4, for reversible electrode processes the peak height i_P in the DP polarograms is proportional to the analyte concentration c_a and is determined by the amplitude ΔE_A of the square wave pulses as well as by the pulse time t_P, among other factors.

Peak current in a differential pulse polarogram

$$i_P = \frac{n^2F^2}{4RT} A \cdot c_a \cdot \Delta E_A \sqrt{\frac{D}{\pi t_P}} \qquad \text{(Eq. 4)}$$

i_P	Peak current
n	No. of exchanged electrons in charge-transfer reaction
F	Faraday constant
R	Gas constant
T	Absolute temperature
A	Electrode surface area
c_a	Concentration of the analyte
ΔE_A	Pulse amplitude
D	Diffusion coefficient of the analyte
t_P	Pulse duration

The detection limit for determinations by differential pulse polarography is similar to that for square wave polarography at about 10^{-7}-10^{-8} mol/L; however, the decrease in sensitivity resulting from irreversibility is lower.

4. Alternating current methods

In the ***alternating current polarography*** (ACP) introduced by Breyer in 1952 a linear or staircase-shaped direct potential ($E_{=}$) is modulated by a sinusodial voltage ($E_{\sim}$) with a small amplitude (ΔE_A = 5-20 mV). This produces an alternating current $i_{\sim}$, whose size is determined by the direct potential $E_{=}$ currently applied and which is greatest at the half-wave potential. As shown in Fig. 7, by plotting the selectively measured alternating current against the direct potential a peak-shaped alternating current polarogram is obtained.

For reversible processes and with a small alternating voltage amplitude $E_P = E_{½}$. In addition, according to Eq. 5, under these conditions the peak current is proportional to the concentration and depends on the frequency f of the superimposed AC voltage.

Peak current in an alternating current polarogram

$$i_{P\sim} = c_a \cdot n^2 \cdot F^2 \cdot A \cdot (2\pi \cdot f \cdot D)^{1/2} \cdot \frac{\Delta E_{A\sim}}{4RT} \qquad \text{(Eq. 5)}$$

$i_{P\sim}$	Peak current
c_a	Concentration of the analyte
n	No. of exchanged electrons in the charge-transfer reaction
F	Faraday constant
A	Electrode surface area
f	AC voltage frequency
D	Diffusion coefficient of the analyte
$\Delta E_{A\sim}$	Amplitude of the superimposed AC voltage
R	Gas constant
T	Absolute temperature

The dependency of the AC polarographic peak currents on the kinetics of the charge-transfer reaction is so marked that the signals of strongly irreversible processes can be suppressed.

For reversible processes the half-width of the peak after $b_{½}$ = 90/n (mV) depends on the electron exchange; therefore the larger n is, the narrower is $b_{½}$. This statement only applies to reversible processes, as slow processes broaden the peak.

Because of the high capacitive current contribution, which is mainly caused by the periodic charging and discharging of the double layer, alternating current polarographic determinations are limited to a sensitivity of about 10^{-5} mol/L. For reversible redox processes the sensitivity can be improved to about $5 \cdot 10^{-7}$ mol/L, if the alternating current is measured at a particular phase shift with reference to the excitation signal in order to separate the faradaic and capacitive current (***AC1 polarography***).

The measurement of the harmonics of the alternating current resulting from the non-linearity of the faradaic resistance, e.g. the 2nd harmonic, with the aid of phase-selective rectification (***AC2 polarography***) again reduces the capacitive current contribution. In this way not only a further increase in sensitivity is achieved, but also the selectivity of the determinations is improved.

The polarographic instruments from Metrohm Ltd. are equipped with a selectable phase angle and allow both peak-shaped AC1 and sine-shaped AC2 polarograms to be recorded.

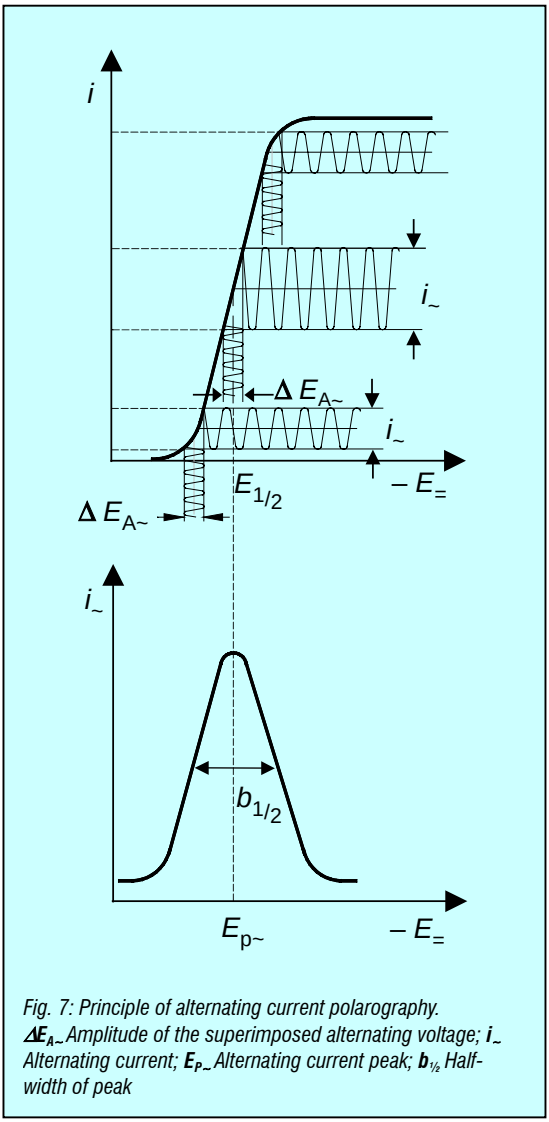


Fig. 7: Principle of alternating current polarography. ***ΔE*** $_{A\sim}$ *Amplitude of the superimposed alternating voltage;* ***i*** $_{\sim}$ *Alternating current;* ***E*** $_{P\sim}$ *Alternating current peak;* ***b*** $_{½}$ *Half-width of peak*

5. Stripping methods

Stripping voltammetry methods are the most efficient electrochemical techniques for trace analysis and species analysis. The unusually high sensitivity and selectivity are based on the fact that the analyte is accumulated before it is determined (composite method) and that both accumulation and determination are electrochemical processes whose 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. This means that stripping methods are among the most sensitive instrumental analysis methods of all; they are also superior to other trace analysis techniques as regards the correctness of the measured values obtained. As both accumulation and the determination take place at the same electrode without needing to change vessels this means that the occurrence of systematic errors by contamination or evaporation can be kept at a very low level.

The term *stripping* stands for the fact that during the determination the accumulated product is removed from the working electrode. This process can be followed voltammetrically or chronopotentiometrically[3], this is expressed by the terms ***stripping voltammetry*** 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 and 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 removal of the accumulated analyte species from the working electrode – the real determination step – is based on an oxidation or reduction process. In the classical case where the analyte is accumulated at the mercury drop or mercury film electrode as an amalgam the determination is the reverse process to accumulation, which is where the name *inverse voltammetry* originated from.

Mechanism for anodic stripping voltammetry

$$Me^{n+} + n\,e^- + (Hg) \underset{\text{Determination (anodic)}}{\overset{\text{Deposition (cathodic)}}{\rightleftharpoons}} Me°(Hg)$$

[3] Chronopotentiometry, see Section 5.4

In order to differentiate this method from other methods in which the determination does not take place by oxidation, but by reduction of the accumulated product, the term *anodic stripping voltammetry* (ASV) is used. In the other cases the method is known as cathodic stripping voltammetry (CSV). With adsorptive accumulation of the analyte the method is known as adsorptive stripping voltammetry (AdSV).

5.1 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 steps in an ASV determination are shown in Fig. 8.

Section **a** is the accumulation time, in which the analyte is deposited at the working electrode at a constant potential and with the sample solution being stirred continuously. 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).

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** in Fig. 8 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 measuring signal is the peak current i_P, which in Section **d** changes into the anodic current for the dissolution of the electrode mercury.

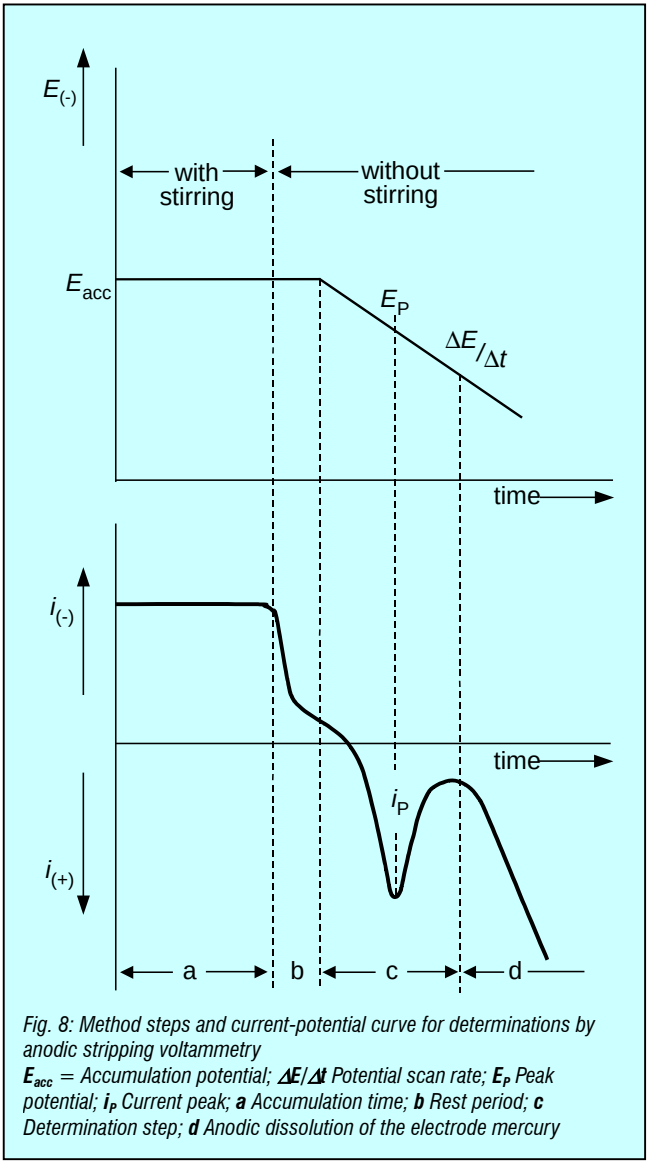


Fig. 8: Method steps and current-potential curve for determinations by anodic stripping voltammetry
E_{acc} *= Accumulation potential;* ***$\Delta E/\Delta t$*** *Potential scan rate;* ***E_P*** *Peak potential;* ***i_P*** *Current peak;* ***a*** *Accumulation time;* ***b*** *Rest period;* ***c*** *Determination step;* ***d*** *Anodic dissolution of the electrode mercury*

According to Eq. 6, the ***accumulation***, i.e. the amount of metal cathodically deposited or the concentration of the metal in the amalgam, depends on the electrolysis current, the accumulation duration and the volume of the mercury drop or mercury film.

Amount of cathodically accumulated metal in the amalgam

$$c_{Me^{\circ}(Hg)} = \frac{i_{acc} \cdot t_{acc}}{V_{Hg} \cdot n \cdot F} \qquad \text{(Eq. 6)}$$

$c_{Me^{\circ}(Hg)}$	Concentration of the metal (accumulated analyte) in the amalgam
i_{acc}	Electrolysis current during accumulation
t_{acc}	Accumulation time
n	Electron transfer during reduction of the analyte
F	Faraday constant
V_{Hg}	Volume of the hanging mercury drop

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

or the mercury film

$$V_{Hg} = A_F \cdot \vartheta$$

r	Radius of the mercury drop
A_F	Surface area of the mercury film
ϑ	Thickness of the mercury film

The electrolysis current i_{acc} is determined by the transport of the analyte and the potential at which accumulation takes place. For high accumulation rates the solution should be stirred and the accumulation potential should be in the diffusion current range. The direct current polarograms or the half-wave or peak potentials can be used as guidelines for this. As a rule of thumb it can be said that the accumulation potential should be about 200-400 mV more negative than the polarographic half-wave potential.

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. 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.

The accumulation time depends on the concentration of the analyte in the sample solution and must be chosen in a way that the measuring signal remains linear throughout as large a concentration range as possible. Deposition is never fully complete; at voltammetric working electrodes this could in any case only be achieved with very small samples volumes (< 0.1 mL) and long electrolysis times. Under normal working conditions with 5 to 20 mL sample solution and about 1 min accumulation at a mercury drop with a surface area of a few mm^2 only a few tenths of a percent are deposited.

In ASV the ***determination*** is based on the anodic dissolution of the accumulated analyte. This process is followed voltammetrically and produces a current peak which, when the HMDE is used, is proportional to the potential scan rate and the radius of the mercury drop r^2 (Eq. 7) .

Peak current in an anodic stripping voltammogram using a HMDE

$$i_p = k \cdot n^{3/2} \cdot D_{Me^\circ(Hg)}^{1/2} \cdot c_{Me^\circ(Hg)} \cdot \nu^{1/2} \cdot r^2 \cdot t_{acc} \qquad \text{(Eq. 7)}$$

i_P	Peak current
k	Constant
n	Electron transfer during oxidation of the analyte
$D_{Me^\circ(Hg)}^{1/2}$	Diffusion coefficient of the metal deposited in the amalgam
$c_{Me^\circ(Hg)}$	Concentration of the metal (accumulated analyte) in the amalgam
ν	Scan rate
r	Radius of mercury drop
t_{acc}	Accumulation time

Eq. 8 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.

Peak current in an anodic stripping voltammogram using the TMFE

$$i_p = k \cdot n^2 \cdot A_F \cdot \nu \cdot t_{acc} \cdot c_{Me^{\circ}(Hg)} \qquad \text{(Eq. 8)}$$

i_P	Peak current
k	Constant
n	Electron transfer during the oxidation of the analyte
A_F	Surface area of mercury film
ν	Scan rate
t_{acc}	Accumulation time
$c_{Me^{\circ}(Hg)}$	Concentration of metal (accumulated analyte) in the amalgam

In both cases the peak current depends on the accumulation time t_{acc} and is therefore also proportional to the concentration of the analyte $c_{Me^{\circ}(Hg)}$ in the amalgam and indirectly proportional to the concentration of the analyte in the sample solution.

In general, in ASV determinations with mercury film electrodes higher sensitivities are to be expected than with mercury drop electrodes. In addition the peaks are narrower, so that neighboring peaks are separated better. The reason for this is the different geometric structures of the two electrodes. As the film electrode normally has a larger surface area, the mass transfer is larger at the film than at the drop for the same accumulation rate.

A decisive factor for the sensitivity of voltammetric determinations is not only the size of the electrode surface, but also the attempt by the deposited metal to distribute itself uniformly in the mercury. This means that higher metal concentrations occur at the surface of the film than at the drop surface.

Measurements with mercury film electrodes produce higher signal currents and narrower peak shapes, but also have relatively high background currents. Similarly good results (with lower background currents) can also be achieved with the drop electrode, if the voltammogram is recorded at a slow scan rate and with very small drops (e.g. with the multi-mode electrode from Metrohm Ltd., see Fig. 19). 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 mercury drop electrode is used more frequently in practice than the mercury film electrode.

The current-potential curve can be recorded for every voltammetric method. The working method can be recognized from the acronym of the scan mode (*scan wave modulation*) that stands in front of the abbreviation of the voltammetric method. For example, DCASV stands for the recording of an anodic stripping voltammogram by direct current voltammetry and DPASV shows the use of differential pulse voltammetry.

In analytical practice anodic stripping voltammograms after amalgam accumulation are chiefly recorded in the DP or SW mode (DPASV or SWASV). Under the same conditions this method is also generally more sensitive than the DC voltammetry version (DCASV). Alternating current voltammetry (ACASV) can be very useful in many cases for limiting the interference from irreversible reactions.

The stripping voltammetry peak potentials are, like the polarographic half-wave potentials, characteristic quantities that are influenced neither by the type of accumulation nor the accumulation rate. The peak potential i_P is only dependent on the scan rate if a TMFE is used as the working electrode. In this case the potential position also depends on the film thickness, so that the difference to the half-wave potential may be even larger than in determinations with the HMDE.

In the case of reversible processes i_P is 28.5/n mV more positive than the half-wave potential $E_{½}$ and for cathodic processes more negative by the same amount. Fig. 9 explains the relationship between the half-wave and peak potentials using the determination of lead in the presence of cadmium and zinc as an example. It can also be seen that the selectivity of ASV determinations can be controlled via the accumulation potential.

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 less noble 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.

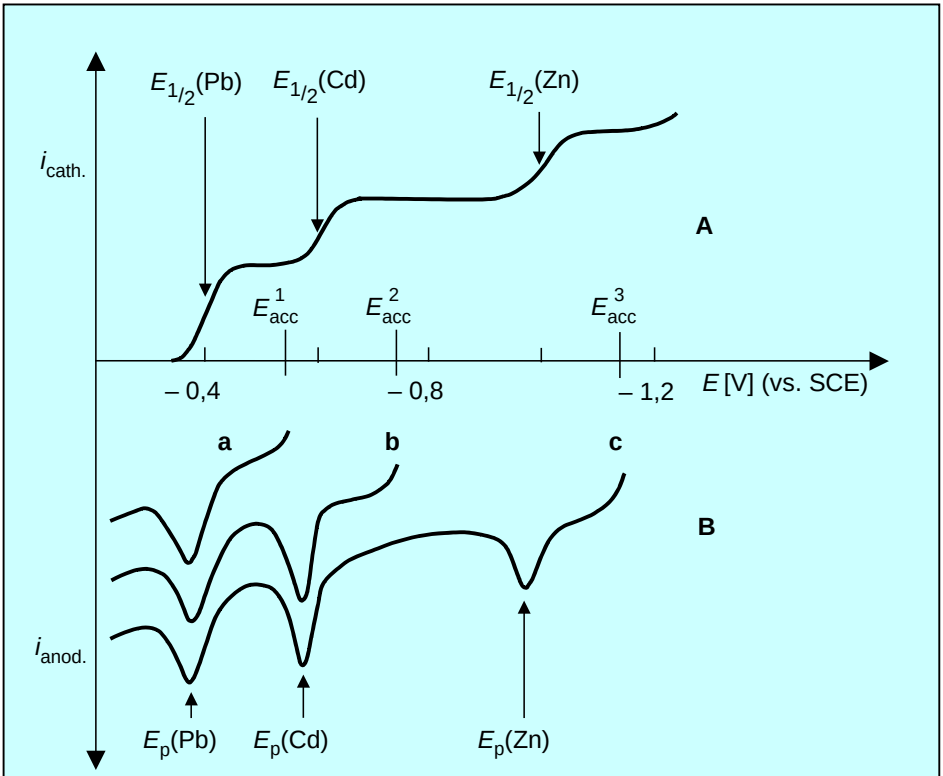


Fig. 9: Principle of selective and simultaneous ASV determination of lead, cadmium and zinc
***A** DC polarogram of Pb, Cd and Zn (each 10^{-3} mol/L) in 0.1 mol/L KCl; **B** Stripping voltammogram of Pb, Cd and Zn (each 10^{-5} mol/L) in 0.1 mol/L KCl after accumulation at different potentials; **a** E^1_{acc} for lead; **b** E^2_{acc} for lead and cadmium; **c** E^3_{acc} for lead, cadmium and zinc*

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 (also for the reduction of the complex compound) and give separate peaks in the stripping voltammogram. If only the non-complexed sample component is to be determined then the electrolysis is carried out at a (less negative) potential at which the complexed components are not reduced.

A different procedure that can be used for the separation of electrochemically similar analytes is the so-called ***solution exchange*** or ***medium exchange***. The principle is that after the accumulation step the base solution is exchanged for a solution with a complexing agent so

that the complexes are first formed during the dissolution process. In this way it is possible to separate the peaks of two analytes from each other if only one of the analytes forms a complex when the solutions are exchanged, or if the complex formation constants of the two analytes are different. Fig. 10 shows the potential positions for the peaks of thallium, lead and tin in base solutions with various complexing agents.

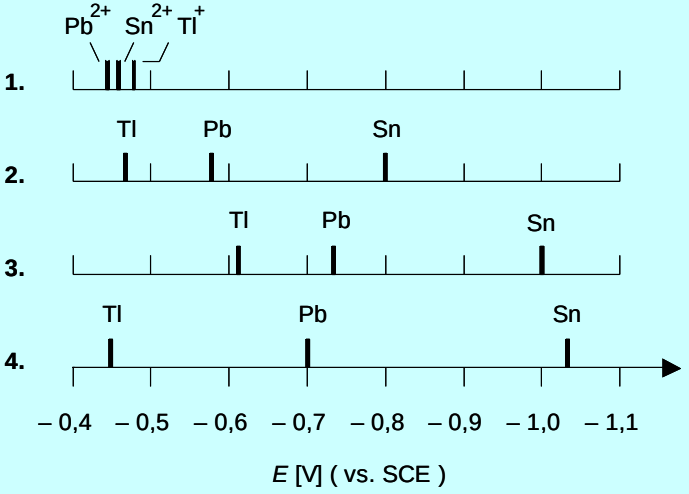


Fig. 10: Separating the stripping voltammetric peaks of lead, tin and thallium after solution exchange. Base solution
1. *1 mol/L HCl;* ***2.*** *1 mol/L HCl + 2 mol/L ethylenediamine;* ***3.*** *1 mol/L HCl + 2 mol/L NaOH + 0.2 mol/L EDTA;* ***4.*** *1 mol/L HCl + 2 mol/L NaOH + 0.2 mol/L sodium potassium tartrate.*

Hydrochloric acid is quite suitable for use as the base solution for the mutual accumulation of lead, tin and thallium, but not for the formation of separate peaks in the anodic stripping voltammogram. The relationships change when the hydrochloric acid is replaced after electrolysis by a base solution containing a complexing agent, e.g. by a solution containing ethylenediamine, EDTA or tartrate. Lead and tin, but not thallium, form relatively stable complexes with these compounds that are reduced at more negative potentials than the non-complexed cations. In all cases the peaks are then so far apart that lead, tin and thallium can be determined together. In other cases neighboring peaks can easily be separated by altering the pH of the base solution.

Various techniques have been developed for exchanging the base solution. In the simplest case the measuring vessel is replaced after accumulation by another containing the degassed exchange solution. This procedure is not only complicated, but can also lead to incorrect results. Exchanging the solutions in voltammetric flow-through cells is less susceptible to interference and easier to handle.

Anodic stripping voltammetry with mercury working electrodes (HMDE, TMFE) is primarily used for the trace analysis of lead, copper, cadmium, antimony, tin, zinc, bismuth, indium, manganese and thallium.

ASV is particularly important for the trace analysis of zinc, cadmium, lead and copper in aqueous samples. However, the analysis of surface water (river and lake water), industrial and communal wastewater, landfill leachate as well as beverages and biological fluids (e.g. urine) will only produce correct results when the existing organic sample constituents have first been destroyed by UV-photolysis or microwave treatment. The working procedure (irradiation duration and the use of H_2O_2 as an oxidizing agent) differs and depends on the TOC content. Sample preparation is not necessary for drinking water and seawater.

UV-photolysis is not only used for the destruction of organic substances, but is also important for the differentiation of *labile* (kinetically unstable) and *inert* (kinetically stable) heavy metal complexes in natural waters. These type of analyses form a part of ***speciation analysis***, which can be carried out particularly efficiently by voltammetric methods. In accordance with the speciation flowchart (working instructions) the total content of a metal in a polluted water sample can be correctly determined only after a UV-photolysis has first been carried out.

An example of this is standard method DIN 38406 part 16 from the German Institute for Standardization (*DIN - Deutsches Institut für Normung*) for the determination of the total concentration of zinc, cadmium, lead, copper, thallium, nickel and cobalt in drinking, ground, surface waters and precipitation by stripping voltammetry after UV digestion (Fig. 11).

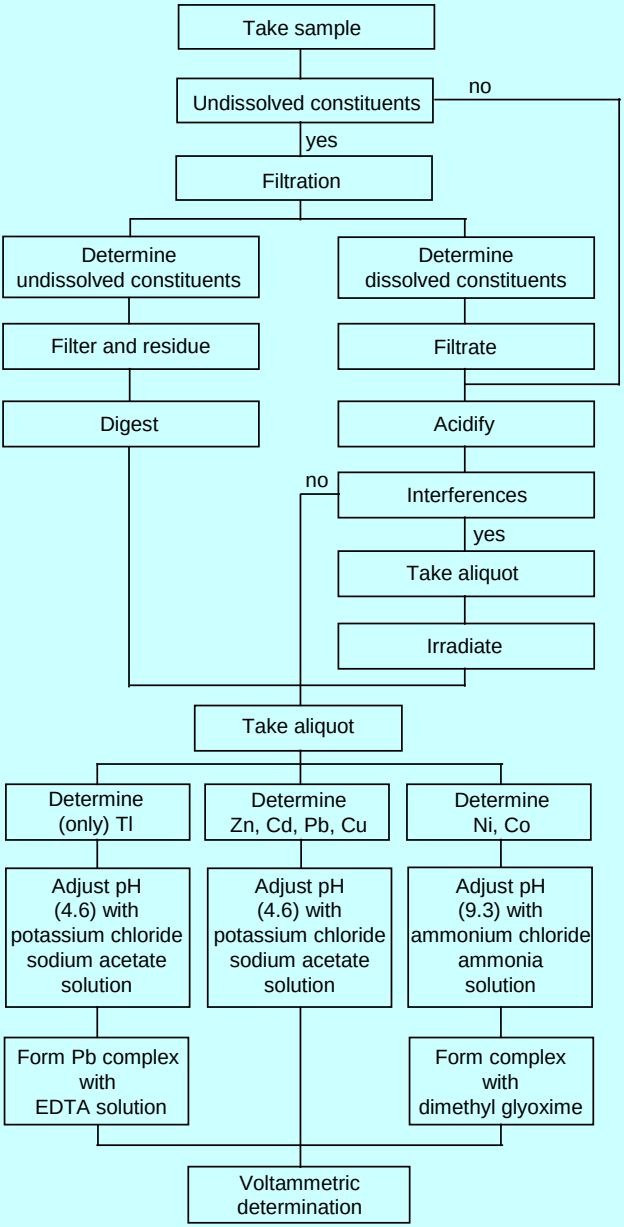


Fig. 11: Working steps for the determination of zinc, cadmium, lead, copper, thallium, cobalt and nickel in drinking, ground and surface waters and precipitation according to DIN 38406 part 16

Chemical digestions are necessary for the ASV determinations of traces of metals in strongly polluted water (e.g. in wastewater). Oxidizing wet-chemical digestions in a flask fitted with a reflux condenser and absorption vessel or in a Digesdahl digestion apparatus are most frequently carried out (digestion as per DIN 38414 part 2 (1983) and part 7 (1982)). The same applies for the digestion of sewage sludge, soils and sediments.

As well as the elements mentioned above, gallium, indium, germanium, tin, antimony and bismuth can all be accumulated at mercury electrodes and analyzed by anodic stripping voltammetry. The determination of silver and gold, which are also easily soluble in mercury, is not possible because the metals are nobler than mercury, so that in the stripping process only the electrode mercury is dissolved and not the analyte. This is why these and other noble metals can only be accumulated and determined at inert electrodes made of noble metals or carbon. Finally, it is also possible to determine mercury by ASV, by accumulating it as an amalgam at a gold electrode, e.g. at a rotating gold disk electrode (see Section 6) and dissolving it again in the anodic stripping scan.

Gold electrodes are also used for the ASV determination of arsenic(V) and arsenic(III). Both oxidation states are reduced to elemental arsenic by nascent hydrogen, which is produced from the hydrochloric acid base solution at –1.2 V at the gold electrode. This elemental arsenic is accumulated at the electrode surface and is anodically dissolved for the determination.

5.2 Cathodic stripping voltammetry

The ***cathodic stripping voltammetry*** (CSV) method is used for the determination of inorganic and organic anions and not only differs from anodic stripping voltammetry in the determination procedure, but also in the accumulation process.

For accumulation the analyte is deposited anodically as a sparingly soluble mercury(I) salt or cathodically as an intermetallic compound at the electrode surface. The simplest and most frequent process is accumulation as the mercury(I) salt Hg_2A_2. The Hg_2^{2+} ions come from the electrode mercury, which is oxidized at even slightly negative potentials, depending on the base solution, the solubility product K_L of the compound produced and the concentration of the analyte in sample solution. In many cases the potential range for the accumulation of the anions lies between -0.2 V and +0.4 V (against Ag/AgCl/ 3 mol/L KCl).

During the determination the Hg_2^{2+} of the accumulated Hg_2A_2 is cathodically reduced, so that the mechanism can be described as follows:

Mechanism of cathodic stripping voltammetry

Deposition: $2\ Hg \rightleftharpoons 2\ Hg_2^{2+} + 2\ e^-$

$2\ Hg_2^{2+} + 2\ A^- \rightleftharpoons Hg_2A_2$

Determination: $Hg_2A_2 + 2\ e^- \rightleftharpoons 2\ Hg + 2\ A^-$

Halides, pseudohalides, oxometallates and organic anions can be determined in the trace range with this (indirect) working procedure. As in each case the determination process is based on the reduction of the Hg_2^{2+} ions of the sparingly soluble compound deposited on the electrode surface during accumulation, the peaks have similar potentials.

Organic substances can also be determined by cathodic stripping voltammetry in a similar way to inorganic anions; among the substances that react with the Hg_2^{2+} ions are thiols, mercaptans, cysteine, glutathione, thiourea, thioamine, barbituric acid, uracil derivatives.

In addition, cathodic stripping voltammetry is also used for the determination of several elements that are sparingly soluble in mercury, but can be accumulated together with an added solution partner on the electrode surface as an intermetallic compound. These elements are arsenic, selenium and tellurium; the solution partner for this *co-electrolysis* is a copper(II) salt.

After accumulation with copper (Me_2^{n+}) the particular analyte Me_1^{n+} can be removed from the intermetallic compound by oxidation or reduction. In an anodic dissolution the stripping scan produces several peaks, which then have to be assigned to the oxidation of the analyte, the copper and the electrode mercury. In contrast, cathodic stripping voltammograms only have a single peak, which corresponds in detail to the conversion to As^{3-}, Se^{2-} and Te^{2-}.

The processes can be described by the following reaction equations:

Accumulation of the analyte by co-electrolysis with subsequent CSV or ASV determination

$Me_1^{n+} + Me_1^{n+} + 2\ n\ e^- + (Hg) \longrightarrow Me_1{}^{\circ}Me_2{}^{\circ}(Hg)$

CSV: $\longrightarrow Me_1^{n-} + Me_2{}^{\circ}(Hg) - n\ e^-$

ASV: $\longrightarrow Me_1^{n+} + Me_2^{n+} + (Hg_2)^{2+} + (2n + 2)\ e^-$

For the determination of arsenic by cathodic stripping voltammetry or other voltammetric and polarographic methods the analyte must always be present at the oxidation state +3; In all the base solutions used up to now arsenic(V) cannot be reduced electrochemically. In real water samples the small arsenic content is predominantly present in oxidation state +5 (as a result of oxidation by oxygen), so that reduction to As(III) must be carried out before each voltammetric determination (with hydrazine or sodium sulfite). In practice this method is less suitable than the ASV determination of arsenic at the gold electrode (see Section 5.1).

More efficient and particularly valuable for routine analysis is CSV (after co-electrolysis with copper) for the individual and simultaneous trace analysis of selenium and tellurium.

5.3 Adsorptive stripping voltammetry

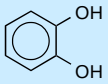
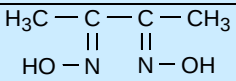
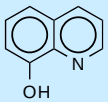
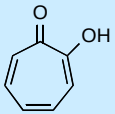
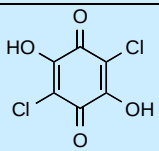
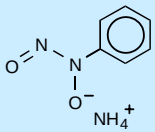
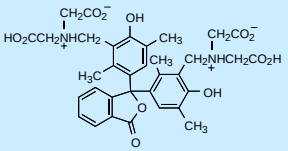
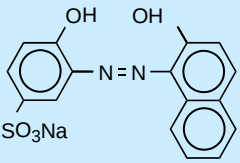
The combination of accumulation and voltammetric determination is known as ***adsorptive stripping voltammetry*** (AdSV), if the analyte can be accumulated in a suitable form by adsorption on the electrode surface and then voltammetrically determined by oxidation or reduction.

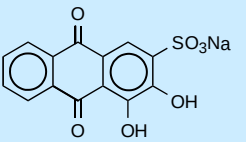
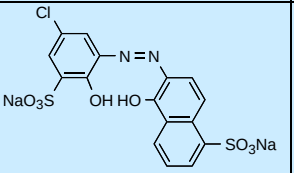
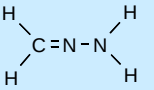
Adsorptive accumulation is a valuable addition to electrolysis, because it makes stripping voltammetry interesting even for those elements that cannot be accumulated or determined owing to irreversible electrode reactions or lack of amalgam formation at mercury electrodes. Among others, these include aluminum, iron, cobalt, nickel, titanium, chromium, molybdenum, tungsten, antimony, vanadium, uranium and the platinum metals. In addition, AdSV is also suitable for the trace analysis of numerous organic compounds.

Whereas organic substances with surface-active properties are adsorbed directly at the electrode surface, traces of elements must first be converted into sparingly soluble and adsorbable complexes. The subsequent determination procedure is based either on the reduction of the central atom, catalytic hydrogen generation or the reduction of ligands of the complex compound.

A summary of frequently-used complexing agents for the determination of trace elements in aqueous, biological and pharmaceutical sample is given in Table 1.

Table 1: Complexing agents for the determination of elements by adsorptive stripping voltammetry

Complexing agent	Structural formula	Elements	CAS number
Reduction of the central atom			
1,2-Dihydroxybenzene (catechol, pyrocatechol, 1,2-benzenediol)		U, Cu, Fe, V, Ge, Sb, Sn, As	120-80-9
2,3-Butandione dioxime (dimethylglyoxime, diacetyldioxime)		Co, Ni, Pd	95-45-4
8-Hydroxyquinoline (8-quinolinol, oxine)		Mo, Cu, Cd, Pb, U	148-24-3
2-Hydroxy-2,4,6-cycloheptatrienone (tropolone)		Mo, Sn	533-75-5
2,5-Dichloro-3,6-dihydroxy-1,4-benzoquinone (chloranilic acid)		U, Mo, Sn, V, Sb	87-88-7
N-Nitroso-N-phenylhydroxylamine (cupferron)		U, Mo, Tl	135-20-6
Reduction of ligands			
o-Cresol phthalexone (OCP, o-cresolphthalein complexone)		Ce, La, Pr	2411-89-4
Solochrome violet RS (SVRS, acid alizarin violet N, mordant violet 5, acid chrome violet K)		Al, Fe, Ga, Ti, Y, Zr, V, Tl, Mg; alkali + alkaline earth metals	2092-55-9

1,2-Dihydroxyanthraquinone-3-sulfonic acid (DASA, alizarin red S)		Al	130-22-3
6-(5-Chloro-2-hydroxy-3-sulfophenylazo)-5-hydroxy-1-naphthalene sulfonic acid disodium salt (MB9, mordant blue 9)		Th, U	3624-68-8
Catalytic hydrogen generation			
Formazone (formed in solution from formaldehyde and hydrazine)		Pt	

In principle, adsorptive stripping voltammetry is even more efficient than anodic stripping voltammetry; the determination limits are in the upper to medium ng/L range. The higher sensitivity of the method is based on the fact that the adsorbed compound remains on the electrode surface, whereas in ASV the deposited metal diffuses into the mercury film or mercury drop. As a result, after adsorptive accumulation the local accumulation factor, i.e. the analyte concentration available for the stripping process at the electrode surface, is larger than that after electrolysis and amalgam formation.

In detail the adsorptive stripping voltammetric methods differ in the complex formation process and in the accumulation mechanism.

1. In the simplest case the analyte M^{n+} forms the adsorbable complex with the ligand L in the solution, this is then adsorbed on the surface of the working electrode.

Complex formation in the solution

$$M^{n+} + n\,L_{(dissolved)} \rightleftharpoons ML_n^{n+}{}_{(dissolved)}$$

$$ML_n^{n+}{}_{(dissolved)} \rightleftharpoons ML_n^{n+}{}_{(adsorbed)}$$

2. In other cases the complexing agent is adsorbed on the electrode, so that complex formation takes place on the electrode surface.

Complex formation after adsorption of the complexing agent

$$n\,L_{(dissolved)} \rightleftharpoons n\,L_{(adsorbed)}$$

$$M^{n+} + n\,L_{(adsorbed)} \rightleftharpoons ML_n^{n+}{}_{(adsorbed)}$$

3. If M^{n+} does not form a surface-active compound with the complexing agent, the analyte will be electrochemically reduced or oxidized and transformed into a suitable oxidation state for complex formation. The process takes place either in the solution or on the electrode surface.

Complex formation after electrochemical conversion of the analyte

$$M^{n+} \pm m\,e^- \rightleftharpoons M^{(n\pm m)+}$$

$$M^{(n\pm m)+} + (n\pm m)\,L_{(dissolved\ or\ adsorbed)} \rightleftharpoons M^{(n\pm m)+}L_{(n\pm m)\ (adsorbed)}$$

According to Eq. 9, the amount of adsorbed compound Γ, which after an accumulation time t_{acc} covers the electrode surface A, determines the sensitivity of the measuring signal.

Peak current in an adsorptive stripping voltammogram

$$i_p = k \cdot A \cdot \Gamma = k \cdot A \cdot c_a \cdot \left[\frac{D}{r} \cdot t_{acc} + 2 \sqrt{\frac{D}{\pi} \cdot t_{acc}^{1/2}} \right] \qquad \text{(Eq. 9)}$$

i_P	Peak current
k	Constant $k = \frac{n^2 \cdot F^2 \cdot \nu}{4 \cdot R \cdot T}$
A	Electrode surface area
Γ	Amount of adsorbed compound
c_a	Concentration of the analyte
D	Diffusion coefficient of the analyte
r	Radius of the mercury drop
t_{acc}	Accumulation time
n	Electron exchange
F	Faraday constant
ν	Scan rate
R	Gas constant
T	Absolute temperature

Until the electrode surface becomes saturated (Γ_{max} after $t_{acc(max)}^{1/2}$) the peak current increases linearly with t_{acc} and reaches a maximum, this is given in Eq. 10.

Maximum peak current in an adsorptive stripping voltammogram

$$i_{p(max)} = k \cdot A \cdot \Gamma_{max} \qquad \text{(Eq. 10)}$$

Eq. 11 is valid up to this point, with the limitation that the linear dependency only applies to the low to medium μg/L range and that the accumulation times are shorter than $t_{acc(max)}^{1/2}$.

Dependency of the peak current on the accumulation time

$$i_p \sim c_a \cdot t_{acc}^{1/2} \qquad \text{(Eq. 11)}$$

In practice any variations from linearity at higher analyte concentrations or after too long accumulation times (*overloading* the working electrode) are regulated by the experimental conditions. Either the accumulation time is shortened or the generally practiced stirring during accumulation is not carried out; as a final measure the sample solution can also be diluted.

An important field of application for adsorptive stripping voltammetry is the determination of trace elements in aquatic environmental samples. Some methods are listed in Table 2. In all cases the determination limits are in the middle to lower ng/L range. This means that, together with much more complicated techniques such as mass spectrometry and neutron activation analysis (which require a much greater expenditure on apparatus), adsorptive stripping voltammetry is one of the most sensitive methods encountered in instrumental analysis.

Table 2 : AdSV determination of heavy metal traces in surface water

Analyte	Ligand	Base solution	Sample preparation	Determination limit (ng/L)[4]
Platinum	Formazone	Formaldehyde + hydrazine + 0.5 mol/L H_2SO_4	UV digestion	0.01
Uranium	1,2-Dihydroxy-benzene	Acetate buffer, pH 4.7	Separation by ion exchange	240
Uranium	1,2-Dihydroxy-benzene	HEPES + 0.5 mol/L NaOH, pH 6.8	UV digestion (exceptions: sea-water, drinking/ground water)	70
Uranium	Oxine	0.01 mol/L PIPES + 0.5 mol/L NaOH, pH 6.7	UV digestion (exceptions: sea-water, drinking/ground water)	700
Uranium	Chloranilic acid	HCl, pH 2.5	Direct determination without digestion	24
Titanium	Mandelic acid	$KClO_3$ + NH_3, pH 3.2	UV digestion	0.05
Tin	Tropolone	HCl, pH 2.8	UV digestion	5
Tin	Chloranilic acid	Acetate buffer, pH 4.3	UV digestion	25
Aluminum	DASA	BES, pH 7.1	UV digestion (exceptions: sea-water, drinking/ground water)	30
Molybdenum	Chloranilic acid	HCl, pH 2.7	UV digestion (exceptions: sea-water, drinking/ground water)	20
Gallium	Solochrome violet RS	Acetate buffer, pH 4.8	UV digestion (exceptions: sea-water, drinking/ground water)	80
Thorium	Mordant blue 9	Acetate buffer, pH 6.5	UV digestion	100
Vanadium	1,2-Dihydroxy-benzene	PIPES, pH 6.9	UV digestion	5
Antimony(III)	Chloranilic acid	HCl, pH 1	UV digestion or microwave digestion	210
Nickel	Dimethylglyoxime	NH_3/NH_4Cl, pH 9.2	UV digestion	1
Cobalt	Dimethylglyoxime	NH_3/NH_4Cl, pH 9.2	UV digestion	1
Zinc	Pyrrolidine dithiocarbamate	BES, pH 7.3	UV digestion	0.5

HEPES *4-(2-Hydroxy-ethyl)-piperazine-1-ethane-sulfonic acid, CAS 7365-45-9*
PIPES *Piperazine-1,4-bis(2-ethane-sulfonic acid), CAS 5625-37-6*
DASA *1,2-Dihydroxyanthraquinone-3-sulfonic acid, alizarin red S, CAS 130-22-3*
BES *N,N-bis-(2-hydroxyethyl)-2-amino-ethane-sulfonic acid, CAS 10191-18-1*

[4] The detection limits given in Table 2 are to be regarded as approximate values, these are determined by the working conditions, particularly by the accumulation time.

The very high sensitivity of the platinum determination is immediately obvious, this can be explained by the catalytic reduction of the hydrogen overvoltage after adsorption of a compound of platinum(II) with formazone. The determination limit is given as 10 pg/L. This method is used for the determination of traces of platinum in seawater, body fluids and tissues and allows investigations into the ultimate destination of the platinum released into the environment from automobile catalytic converters.

Surface-active compounds, with a few exceptions, interfere with the adsorption of the metal complexes on the electrode surface. The extent of the interference depends on the electrode processes, i.e. from the mutual adsorption behavior of the metal complexes and organic compounds. Whereas in all samples the determination of platinum and titanium, which is based on catalytic effects, could only be carried out without interference after UV digestion, other elements could be analyzed by AdSV in very slightly polluted water samples without any sample preparation. This is the case when the metal complex is adsorbed in a different potential range from the surface-active substances in the sample solution. An interesting example of the unimpeded adsorption of metal complexes is the determination of uranium(VI) with chloranilic acid (2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone). With this complexing agent traces of uranium can be determined without sample preparation even in strongly polluted river water, this can be seen in the stripping voltammogram in Fig. 12, curve **b**. The attempt to determine the uranium content of the same sample with dihydroxybenzene as the complexing agent produced, as a result of non-specific adsorption processes (mixed adsorption or adsorption displacement), curve **a** shown alongside.

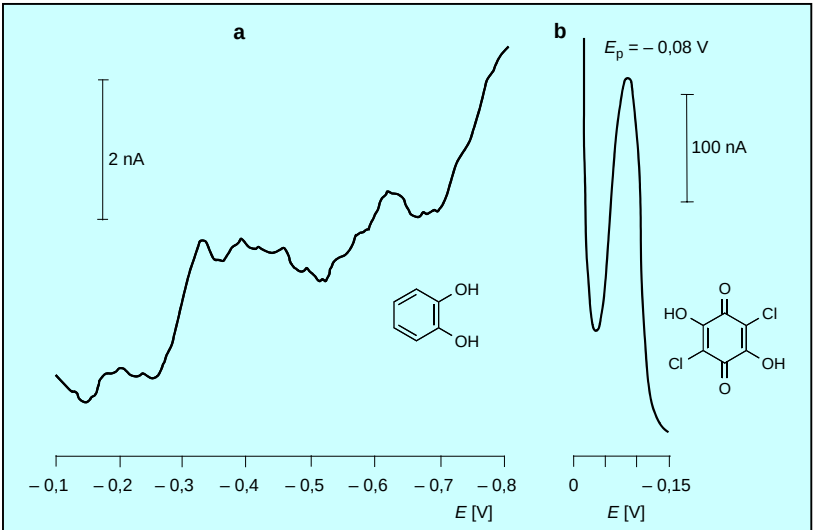


Fig. 12: Determination of uranium in River Elbe water (sample from 1990)
***a** with dihydroxybenzene ($1 \cdot 10^{-4}$ mol/L, pH 4.5) and **b** with chloranilic acid ($2.5 \cdot 10^{-4}$ mol/L, pH 2.7) as complexing agent and after accumulation at $E_{acc} = +100$ mV*

This uranium determination is a good example of how the stripping voltammetry method can easily be automated with equipment available today. The automation principle is the auto-batch technique or the flow-through technique. In the *batch method* the base solution and the sample solution are transferred batch by batch to the measuring vessel and analyzed under stationary conditions. A measuring setup designed for this purpose is shown in Fig. 13.

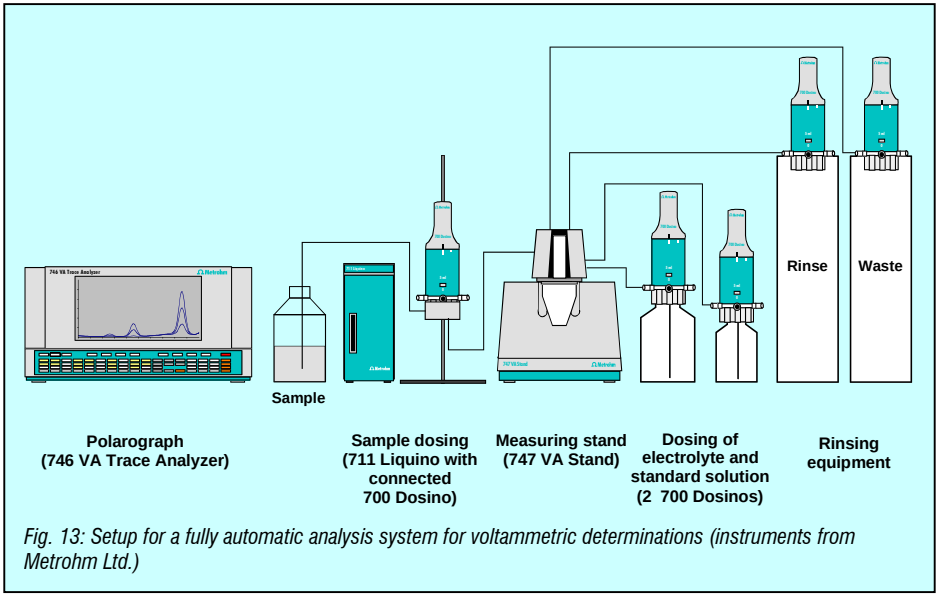


Fig. 13: Setup for a fully automatic analysis system for voltammetric determinations (instruments from Metrohm Ltd.)

This automatic analysis system consists of a VA Trace Analyzer, a VA Stand with measuring cell and electrode, one Dosino each for the base solution and the standard solution and an additional Dosino for adding the sample solution; this is controlled by a Liquino. A further two Dosinos are used for aspirating off the solutions and for cleaning the measuring cell. The VA Trace Analyzer controls the voltammetric analysis and all the components of the analysis system, records the measuring data and evaluates it automatically (instruments from Metrohm Ltd.).

Normally the current peaks in the AdSV voltammograms are based on the reduction of the central atom of the complex compound. In other cases the signal in the stripping voltammogram is produced by the reduction of a ligand (see Table 1). In this way it is possible to determine elements which cannot be reduced electrochemically (or are very difficult to reduce) in aqueous solution. Among these is aluminum, whose determination by trace analysis is anyway quite problematic. With 1,2-dihydroxyanthraquinone-3-sulfonic acid (alizarin red S) it has been possible to find a suitable complexing agent that can be used for the analysis of traces of aluminum down to 1 μg/L.

Adsorptive stripping voltammetry is an efficient method for the trace analysis of elements and can also be used for the determination of surface-active organic molecules with electro-

chemically active functional groups. The determination limits in the ultra-trace range are down to $\sim 10^{-10}$ mol/L and below.

Among the compounds which can be adsorptively accumulated and determined by oxidation or reduction by stripping voltammetry are dyes, benzodiazepines, tetracyclines, indoles and various crop protection agents.

Just as for anodic stripping voltammetry, differential pulse voltammetry (DPAdSV) is also the most important scan mode for AdSV determinations. However, in ASV the potential scan rate is limited by the diffusion speed with which the accumulated metal can diffuse from the interior of the mercury drop to its surface. In contrast, after adsorptive accumulation the analyte is already at the electrode surface, so that the signal current is not dependent on diffusion processes but is only determined by the scan rate. The more reversible that the electrode process is, the more the signal current increases as the scan rate increases. Square-wave voltammetry (SWAdSV) is advantageous for such processes, in particular the rapid SWV as per Osteryoung, which permits very rapid sweeps.

5.4 Stripping chronopotentiometry

As in stripping voltammetry, the electrolytic accumulation of the analyte at a working electrode produces a higher sensitivity also in chronopotentiometric determinations.

Chronopotentiometry is, as *galvanostatic voltammetry,* a voltammetry variant. The only difference is that, instead of time-controlled potential alteration, a constant current density j (A/cm^2) is applied to a stationary working electrode and not the current, but the change in electrode potential is measured as a function of time (voltammetry at a constant current). The chronopotentiometric curve is shown in Fig. 14.

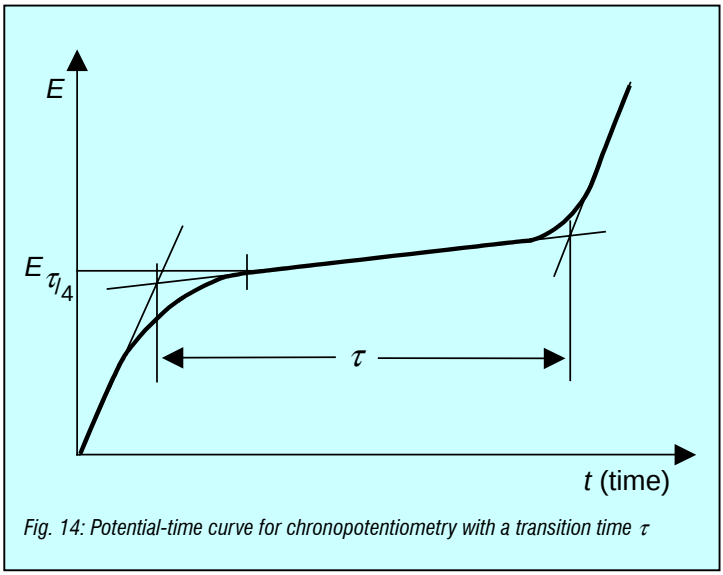


Fig. 14: Potential-time curve for chronopotentiometry with a transition time τ

The two time sectors in which the potential increases relatively quickly are characteristic for the potential-time curve. From an analytical point of view it is the time between them (known as the ***transition time*** τ) that is important; at a constant current density j (current intensity i per electrode surface area A in the units A/cm^2) it is proportional to the concentration of the analyte.

The determination limits of chronopotentiometry are in the range 10^{-4} to 10^{-5} mol/L. This means that for trace analysis the method is only important when used in combination with electrolytic accumulation of the analyte as stripping chronopotentiometry.

The ***stripping chronopotentiometry*** (SCP) method has several different versions. In every case the measuring signal is the transition time τ (Fig. 15).

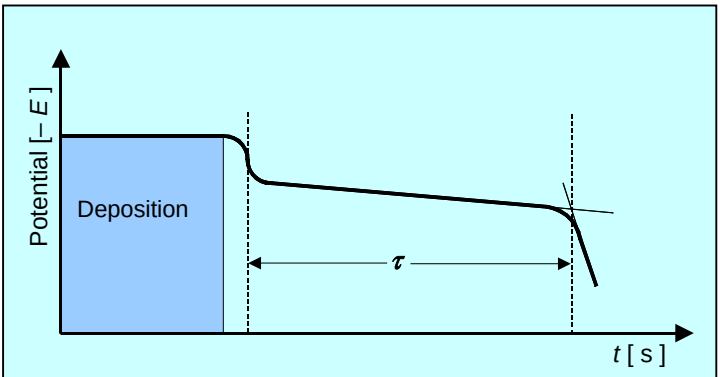


Fig. 15: A stripping chronopotentiogram

Accumulation takes place at a constant potential and for a controlled time at a mercury, glassy carbon or platinum electrode in a stirred sample solution. Mercury films are normally used for deposition of metals, these are applied to a graphite support by the *in situ* or *pre-coating* method.

The dissolution of the accumulated analyte takes place by either chemical or electrochemical oxidation. In electrochemical (anodic) dissolution the current is kept constant and the alteration of the potential as a function of time is followed at the working electrode. So-called anodic stripping chronopotentiometry (ASCP) provides an *inverse* potential-time curve, from which the transition time τ – in the same way as the peak current i_P in a current-potential curve – is used for determining the concentration.

These two curves are compared in Fig. 16. They show that, for reversible processes, $E_{\tau/4}$ in the stripping chronopotentiogram and E_P in the stripping voltammogram coincide.

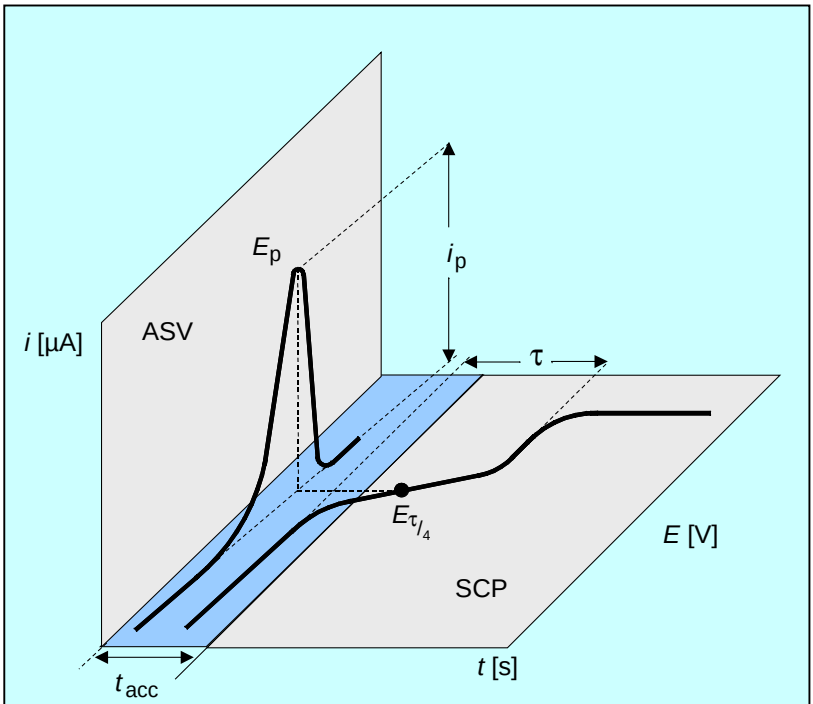


Fig. 16: Comparison between the curves obtained by anodic stripping voltammetry (ASV) and stripping chronopotentiometry (SCP)

The transition times obtained by the anodic dissolution of the metal from the mercury drop or mercury film electrode are different and correspond approximately to the following relationships:

Dependency of the transition time

using an HMDE

$$\tau_{HMDE} = n \cdot F \cdot c_{Me^{\circ}(Hg)} \cdot \frac{r}{3j} \qquad \text{(Eq. 12)}$$

and using a TMFE

$$\tau_{TMFE} = n \cdot F \cdot c_{Me^{\circ}(Hg)} \cdot \frac{d}{j} \qquad \text{(Eq. 13)}$$

τ	Transition time
n	Electron exchange
F	Faraday constant
$c_{Me^{\circ}(Hg)}$	Concentration of the metal (accumulated analyte) in the amalgam after accumulation
r	Radius of mercury drop
j	Current density
d	Thickness of mercury film

Anodic stripping chronopotentiometry is, like anodic stripping voltammetry, suitable for simultaneous determinations if the potential-time curves or the transition times for the analytes present lie in separate potential ranges (> 50 mV). The ratio τ_1/τ_2 for the dissolution of two metals depends on the amalgam concentrations $c_{1\ amalg}$ and $c_{2\ amalg}$ and on the electron exchange n_1 and n_2 of the particular electrode reaction.

Relationship between the transition times in the dissolution of two metals

$$\frac{\tau_1}{\tau_2} = \frac{n_1 \cdot c_{1\,amalg}}{n_2 \cdot c_{2\,amalg}} \qquad \text{(Eq. 14)}$$

τ	Transition time
n	Electron exchange
c_{amalg}	Concentration of the metal in the amalgam after accumulation

The electrolysis time and the current intensity with which the electrolysis product is anodically dissolved are decisive for the sensitivity of the determination. Long accumulation times and small current densities lead to sensitive signals with determination limits in the lower and medium μg/L range. In order to achieve high sensitivities the sample solutions must not contain any effective oxidizing agents such as oxygen or Hg^{2+} ions. This is why the solutions must be degassed and, for determinations with the mercury film electrode, the coating must be made in a separate working step (*ex situ* coating). Neither of these conditions is necessary when anodic dissolution is replaced by chemical oxidation. The method is then known as ***potentiometric stripping analysis*** (PSA). The oxidizing agents are usually Hg^{2+} ions or the oxygen dissolved in the sample.

In PSA determinations the analyte is usually accumulated cathodically as a metal at a constant potential on an *ex situ* or *in situ* formed mercury film and, after interrupting the current circuit, dissolved by chemical oxidation. If several metals are deposited then the dissolution occurs in the order of their electrochemical potentials. In a similar way anodically separated deposits, e.g. manganese(IV) oxide, can be dissolved and determined by chemical reduction with hydroquinone. In all cases potential-time curves are produced with transition times that depend on the concentration of the accumulated analyte, either on the concentration of the metal in the amalgam or on the amount of the deposited precipitate on the electrode surface.

The evaluation is easier if, instead of E, the derivative dE/dt is plotted as a function of t; this measuring principle is known as ***derivative potentiometric stripping analysis*** (deriv. PSA) and obtains the transition time from the distance between two maximum values. Further developments have led to ***differential potentiometric stripping analysis*** (dif. PSA), which in analytical practice is the most important of all the chronopotentiometric techniques. The calculation of the curves obtained with dt/dE against E and processing of the measured values (peak heights or peak areas) is most easily carried out with a computer-controlled measuring setup.

Fig. 17 shows the normal potential-time curve for the determination of zinc, cadmium and lead compared with the differential curve calculated from it.

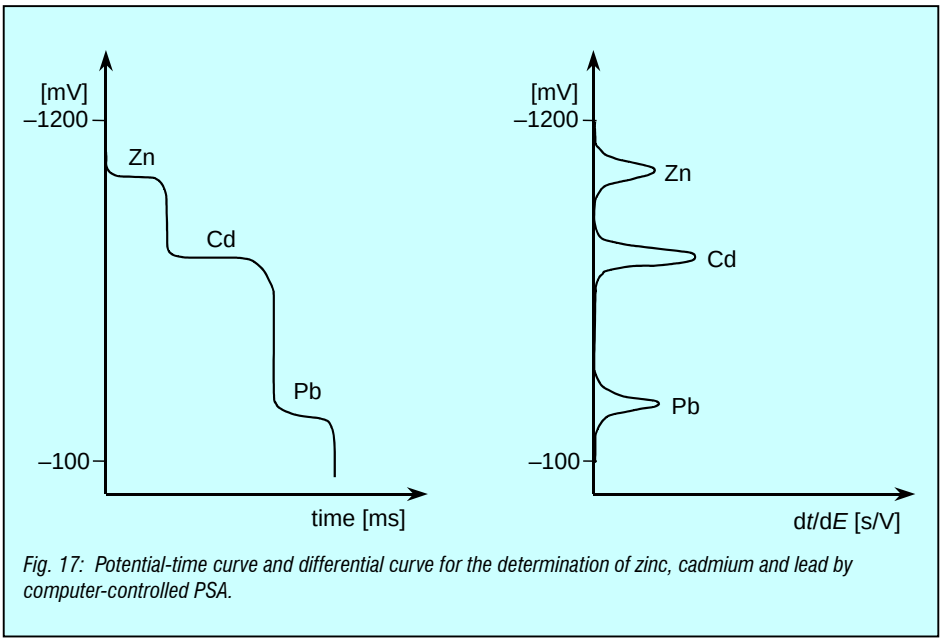


Fig. 17: Potential-time curve and differential curve for the determination of zinc, cadmium and lead by computer-controlled PSA.

As the interference from organic contaminants in the trace analysis of elements by stripping chronopotentiometry is less then in stripping voltammetric determinations, UV or microwave treatment of aqueous samples is not always necessary. It is often sufficient if the strongly polluted water samples are diluted before analysis. Degassing is also unnecessary, as the dissolved oxygen is required for the oxidation of the accumulated analyte.

Cadmium and lead are most frequently analyzed by PSA at the mercury film electrode, in some cases copper and zinc. The determinations are made in natural water and wastewater samples, in urine and blood, in milk and honey as well as in beer and wine. All the methods are based on oxidative processes, whereas the determination of selenium in biological samples (blood samples, powdered milk) takes place reductively. In addition to various elements, PSA can also be used for the analysis of organic compounds, including insulin and other peptides or proteins. These are adsorbed on a carbon paste electrode and determined by using their oxidizable groups.

6. Instrumentation

The setup for the determinations consists of a ***measuring stand***, an ***interface*** with its own ***microprocessor*** and a digital ***computer***.

The measuring stand contains the potentiostat with analog electronics, a current measuring amplifier, a digital-analog (DAC) and analog-digital converter (ADC) as well as controls for the gas valves and stirrer. Other components are the measuring cell with three electrodes and a stirrer. The potentiostat controls the potential for the direct potential ramp (potentiostat for ± 4 V), for the superimposed modulation potential (square wave, normal and differential pulse polarography/voltammetry) and for the sine-shaped alternating current voltage (AC polarography/voltammetry).

As well as the working and reference electrodes, the measuring cell also includes the counter electrode, which is also known as the auxiliary electrode. The ***three-electrode technique*** is used for compensation of the ohmic potential drop in the sample solution and is a further development of the classical two-electrode technique. The addition of the counter electrode means that the flow of current between the reference and working electrode is to a large extent suppressed. As a result the current flows between the working electrode and the counter electrode, so that the reference electrode only acts as a reference point for defining the potential at the working electrode.

The ***reference electrodes*** normally used in practice are electrodes of the second kind, the most important of which today is the silver/silver chloride electrode besides the formerly preferred calomel electrode.

The computer used can either be an integrated instrument with keyboard and monitor (VA Trace Analyzer from Metrohm Ltd.) or a normal commercially available personal computer, as with the VA Computrace from Metrohm Ltd.. On the user interface of the computer the measuring parameters for the polarographic or voltammetric experiment are selected (measuring mode, potential range, degassing and stirring times, standard addition) and transferred to the control and evaluation software. The measuring sequences are put together from the entries and transferred to the interface, which then carries out the measurement and transmits the recorded data to the computer. The computer software evaluates the data it has received, calculates the results which then appear on the screen and can be printed out.

A block diagram of a computer-controlled polarograph is shown in Fig. 18. The block diagram of of the VA Computrace differs only in that the VA Trace Analyzer is replaced by a PC.

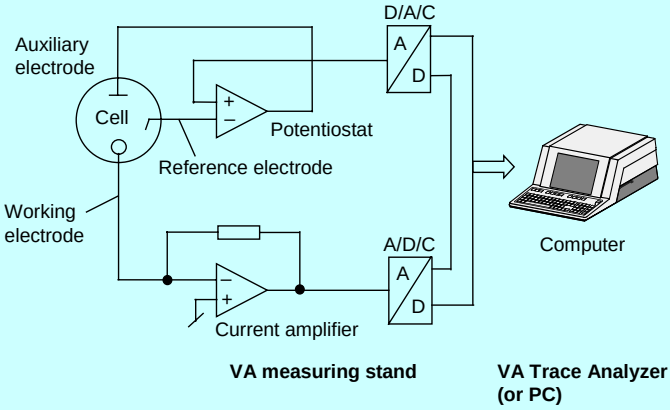


Fig. 18: Block diagram of a polarograph for various voltammetric and polarographic measuring techniques (Metrohm Ltd.)

The most important types of ***working electrodes*** are the valve-controlled mercury electrodes. These consist of relatively narrow capillaries connected to the mercury reservoirs. The mercury flow is controlled by a valve. This is briefly opened (20-200 ms) for drop formation and then immediately closed again in order to obtain very rapidly an individual Hg drop with a constant surface area or, after repetition, a series of mercury drops (***static mercury drop electrode***, SMDE).

The SMDE is used for all polarographic and voltammetric measuring processes and, in comparison to the DME where the electrode surface area increases as the drop grows, has the advantage that the current during the measuring time is always recorded at a constant electrode surface area (to obtain a higher sensitivity).

The distinctive features of the SMDE are its double function as stationary and as dropping electrode and the possibility of synchronizing drop formation with the measuring procedure. The construction of an electrode that can be used either as an SMDE, HMDE or DME is shown in Fig. 19: the ***Multi-Mode Electrode*** (MME) from Metrohm Ltd..

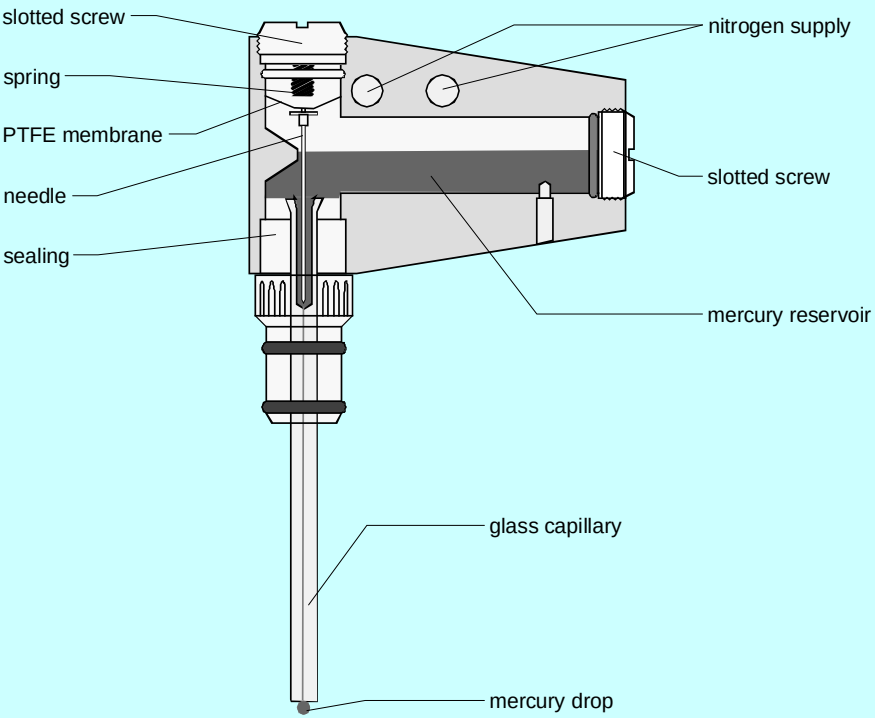


Fig. 19: Schematic diagram of the Multi-Mode Electrode from Metrohm Ltd..

In the Multi-Mode Electrode the mercury is controlled pneumatically via a needle valve; the inner diameter of the capillary is about 50 μm. Small mercury drops with a surface area of 0.1 to 0.6 mm^2 are generated (can be set in 9 steps), with which in ASV determinations similarly narrow peaks can be obtained to those produced by mercury film electrodes.

(Thin) Mercury film electrodes (TMFE) are chiefly used for stripping voltammetry and potentiometric stripping analysis. The best support for the mercury film has proved to be glassy carbon or iridium. Platinum is less suitable as it is gradually dissolved by the mercury.

Mercury deposition takes place electrolytically, either in a separate working step before the determination method or together with the analyte during accumulation electrolysis (*in situ* coated TMFE).

Of the ***solid state electrodes*** the rotating gold electrode (*rotating disc electrode*, RDE) is used for the ASV determination of mercury (Metrohm Application Bulletin 96) and arsenic (Metrohm Application Bulletin 226).

For the ***Ultra-Trace graphite electrode*** with its graphite skeleton methods have been developed for the simultaneous determination of cadmium and lead by ASV (Metrohm Application Bulletin 241), zinc, cadmium, lead and copper by ASV (Metrohm Application Bulletin 254) as for as for the determination of chromium (Metrohm Application Bulletin 243) and tungsten (Metrohm Application Bulletin 242) by AdSV.

7. Sample preparation

Polarographic and voltammetric determinations can only be made on solutions in which the analyte is present in a *measurable* form. Interfering components must be separated from the sample solutions and solid samples must be dissolved (see the Metrohm monograph *Sample preparation techniques in voltammetric trace analysis*).

The preparation of aqueous samples, i.e. the destruction of organic constituents by ***UV photolysis,*** has already been mentioned (see Section 5.1). Oxidizing digestions with acids (***wet-chemistry digestion, microwave digestion***) are suitable for dissolving solid samples; these can be carried out in a Kjeldahl flask or in commercially available instruments (e.g. in a Digesdahl digestion apparatus). The disadvantages of wet-chemistry digestions are the relatively large amount of reagents required – this can lead to high blank values – and the risk of volatilization of elemental compounds, mainly mercury, arsenic and selenium compounds. This means that ***digestions under pressure*** (wet-chemistry digestions in sealed containers) offer more advantages; these can be carried out either at high temperatures with the high-pressure asher HPA-S or in a microwave oven (both from Anton Paar).

For polarographic and voltammetric investigations aqueous solutions are chiefly used and other polar solvents only rarely. The so-called base solution contains an inert electrolyte, which as ***supporting electrolyte*** carries out the following tasks during the determination process:

- The supporting electrolyte increases the conductivity in the measuring cell and reduces the ohmic voltage drop that occurs when the current flows.
- Migration currents, i.e. currents that are based on the migration of analyte ions in an electric field, are reduced so that the analyte is only transported to the working electrode by diffusion.
- By using acids, bases or buffers as the supporting electrolyte the sample solutions can be adjusted to a suitable pH value for the particular electrode reaction.
- The supporting electrolyte can convert sample constituents into complex compounds with different electrochemical behaviors. Complex formation leads to the masking of sample constituents or – depending on the stability of the complexes formed – to a displacement of the half-wave and peak potentials. This removes interferences and improves the resolution of neighboring current signals (see Fig. 10).

Frequently used supporting electrolytes are

- Chlorides, nitrates, sulfates of Li, Na and K.
- Perchlorates of Li and Na.
- Salts of tetraalkylammonium bases with the general formula $NR_4^+X^-$ (R = methyl, ethyl, butyl and X^- = Cl^-, Br^-, J^-, ClO_4^-), e.g. TMA (tetramethylammonium), TEA (tetraethylammonium) or TBA (tetrabutylammonium salts).
- Acids (HCl, H_2SO_4).
- Bases (LiOH, NaOH, $NR_4^+OH^-$).
- Buffer solutions.

Simple ligands are used for complex formation, e.g. CN^-, OH^-, F^-, Cl^-, NH_3, oxalate, EDTA, citrate or tartrate.

Examples of the positions of half-wave potentials of selected elements in frequently used supporting electrolytes are shown in Fig. 20.

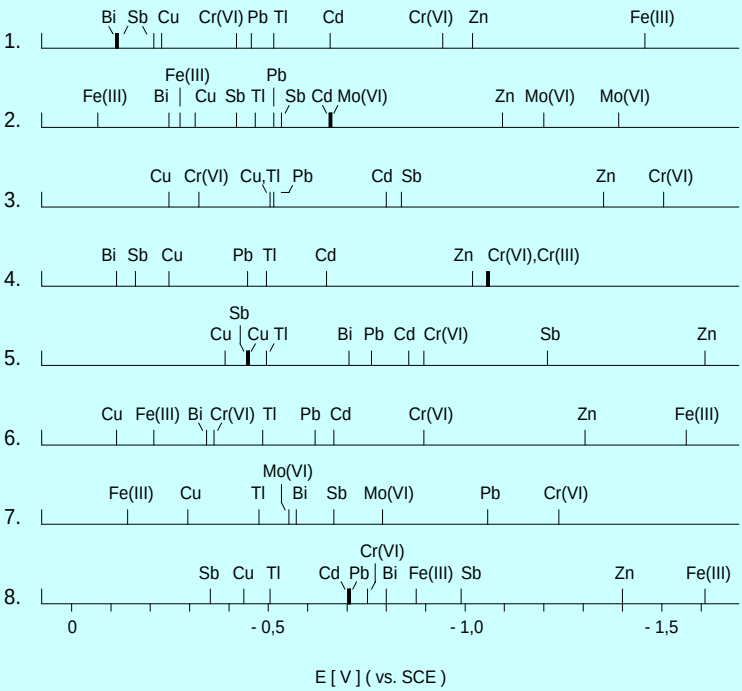


Fig. 20: Direct current polarographic half-wave potentials of selected elements for various supporting electrolytes:
***1.** 1 mol/L KCl; **2.** 2 mol/L CH_3COOH + 2 mol/L CH_3COONH_4; **3.** 1 mol/L NH_3 + 1 mol/L NH_4Cl; **4.** 1 mol/L HCl; **5.** 1 mol/L NaOH; **6.** 0.5 mol/L Na-tartrate; **7.** 0.1 mol/L Na_2-EDTA; **8.** 1 mol/L Na-citrate + 0.1 mol/L NaOH (measured against the saturated calomel electrode)*

Supporting electrolytes not only influence the position of the current signals, but also the useable potential (working) range for the determination. In the cathodic direction the range is limited by the reduction of the cations of the supporting electrolyte; the H^+ reduction from acidic solution depends on the material of the working electrode and has the largest overvoltage at mercury. In the anodic direction the working range is defined by the oxidation of the water or the anions of the supporting electrolyte, on the other hand it is also limited by the oxidation of the electrode mercury.

Normal supporting electrolyte concentrations lie between 0.1 and 1 mol/L. A high salt content, which could result from the digestion process or a previous separation process, alters the viscosity of the supporting electrolyte and the size of the current signal.

Before each polarographic or voltammetric determination the supporting electrolyte must be freed from dissolved oxygen by *degassing*. Oxygen is contained in aqueous solutions at up to 10^{-3} mol/L and is reduced at the working electrode in two stages. The processes are pH-dependent and take place according to the following equations:

Interference by oxygen

1. Reduction of oxygen in acidic solution

$$O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O_2$$

$$H_2O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O$$

2. Reduction of oxygen in alkaline solution

$$O_2 + 2\,H_2O + 2\,e^- \rightarrow H_2O_2 + 2\,OH^-$$

$$H_2O_2 + 2\,e^- \rightarrow 2\,OH^-$$

The reduction current of the oxygen increases the background current and influences the sensitivity of polarographic or voltammetric determinations. In order to prevent this the oxygen is removed by passing a stream of pure nitrogen or argon though the supporting electrolyte for 5-10 min. Argon is often preferred as it is heavier than nitrogen and protects the polarographic cell better against atmospheric oxygen. In alkaline solutions the oxygen can also be removed reductively by the addition of Na_2SO_3. The reaction takes place slowly and frequently remains incomplete.

8. Table

Half-wave potentials of important inorganic ions in various electrolyte solutions at the mercury electrode [calculated against the silver-silver chloride electrode with c(KCl) = 3 mol/L]

Substance	Symbol	Electrolyte solution													
		c(acetic acid) = 2 mol/L + c(NH_4-acetate) = 2 mol/L	c(NH_3) = 1 mol/L + c(NH_4Cl) = 1 mol/L	c(KCl) = 1 mol/L	c(HCl) = 1 mol/L	c(NaOH) = 1 mol/L	c(KNO_3) = 0.1 mol/L	c(KSCN) = 1 mol/L	c(Na_2EDTA) = 0.1 mol/L	c(Na_2-tartrate) = 0.5 mol/L	c(Na_3-citrate) = 0.1 mol/L + c(NaOH) = 0.1 mol/L	c($(NH_4)_2$-oxalate) = 0.1 mol/L, pH = 2 with c(H2SO4) = 1 mol/L	c($(NH_4)_2$-oxalate) = 0.1 mol/L, pH = 4 with c(H2SO4) = 1 mol/L	c($(NH_4)_2$-oxalate) = 0.1 mol/L, pH = 6 with c(NH3) = 2 mol/L	c($(NH_4)_2$-oxalate) = 0.1 mol/L, pH = 8 with c(NH3) = 2 mol/L
Aluminum(III)	Al^{3+}	NR	NR	-1.59 i	NR	NR	NR	NR	NR	NR	NR				
Antimony(III)	Sb^{3+}	-0.39	-0.81 w	-0.07	-0.12 w	-0.42	-0.19 w	-0.58 w	-0.64 w	NR	-0.33	-0.33 w	-0.46 w	-0.41 w	-0.76 w
		-0.50 w		-0.15 w		-1.18		-0.70			-0.95 w			-0.57 w	
Arsenic(III)	As^{3+}	-0.95	-1.62 i	-0.07 i	-0.38 w	-0.25	-0.11 w	NR	-1.23 w	NR	-0.22 w	NR	-1.56 w	-1.70 i	-1.58 i
					-0.62										
Bismuth(III)	Bi^{3+}	-0.21 w	NR	-0.06 w	-0.07 w	-0.68	-1.17 i↓	NR	-0.54w	-0.31 wcw	-0.77 w	-0.13 w	-0.21 w	-0.22 w	-0.26 w↓
Cadmium(II)	Cd^{2+}	-0.63 w	-0.77 w	-0.62 w	-0.61 w	-0.82 i	-0.55 w	-0.62 w	NR cw	-0.64	-0.68 i	-0.56 w	-0.61 w	-0.62 w	-0.62 w
Chromium(III)	Cr^{3+}	-1.20 i	-1.34 w↓	-1.03	-1.00 w	NR↓	-0.87	-1.01 w	-1.20 w	-1.58 i	NR	NR	NR	-1.73 i	NR
							-1.01								
Chromium(VI)	Cr^{6+}	NR	-0.28 w	-0.38	-1.03 i	-0.85 w	-0.32	-0.41	-1.20 w	-0.33	-0.73 w	NR	NR	-0.02 w	-1.14 w
			-1.45 w	-0.88 w			-1.10	-1.00 w		-0.86					-1.72 i
			-1.68							-1.71					
Cobalt(II)	Co^{2+}	NR	-1.26	-1.38	NR	NR↓	-1.27w	-1.11	NR	-1.53	NR	NR	NR	NR	-1.52 i
							-1.54								

Substance	Symbol	Electrolyte solution												
		c(acetic acid) = 2 mol/L + c(NH_4-acetate) = 2 mol/L	c(NH_3) = 1 mol/L + c(NH_4Cl) = 1 mol/L	c(KCl) = 1 mol/L	c(HCl) = 1 mol/L	c(NaOH) = 1 mol/L	c(KNO_3) = 0.1 mol/L	c(KSCN) = 1 mol/L	c(Na_2EDTA) = 0.1 mol/L	c(Na_2-tartrate) = 0.5 mol/L	c(Na_3-citrate) = 0.1 mol/L + c(NaOH) = 0.1 mol/L	c($(NH_4)_2$-oxalate) = 0.1 mol/L, pH = 2 with c(H2SO4) = 1 mol/L	c($(NH_4)_2$-oxalate) = 0.1 mol/L, pH = 4 with c(H2SO4) = 1 mol/L	c($(NH_4)_2$-oxalate) = 0.1 mol/L, pH = 6 with c(NH3) = 2 mol/L	c($(NH_4)_2$-oxalate) = 0.1 mol/L, pH = 8 with c(NH3) = 2 mol/L
Copper(II)	Cu^{2+}	-0.25 w	-0.20 w	-0.18	-0.20	-0.35	NR	-0.64	-0.26 w	-0.08 w	-0.41 w	-0.05 w	-0.15 w	-0.18 w	-0.18 w
			-0.46 w			-0.43									
Germanium(IV)	Ge^{4+}	-1.34 i	-1.41	NR	NR	NR	-1.26 iow	i cw	NR	NR	NR	NR	NR	-1.38 w	-1.38 w
Indium(III)	In^{3+}	-0.67 w	-1.08	-0.57	-0.57	-1.12 w	-0.90 i	-0.59 w	NR	NR	-1.17	-0.61 w	-0.67 w	-0.68 w	-0.70 w
													-0.84 w	-0.87 w	-1.18
Iron(II)	Fe^{2+}	NR	-1.44 w	-1.57 iow	i ow	-1.55 i ↓	-1.31	-1.59 w	-0.09 w	-1.51 i	-0.83 w	-0.02 w	-0.17	-0.18 w	-0.18 w
							-1.56 iow				-1.57 w				-1.61 i
Iron(III)	Fe^{3+}	-0.02	NR ↓	-1.42 i	NR	NR ↓	-1.29 i	-1.56 w	-0.11 w	-0.19	-0.85 w	-0.18 w	-0.17 w	-0.19 w	-0.19 w
		-0.24								-1.53 w	-1.59 w				
Lead(II)	Pb^{2+}	-0.47 w	-0.47 w	-0.41 w	-0.41 w	-0.73 ↓	-0.36 w	-0.39 w	-1.03 w	-0.59	-0.69 w	-0.40 w	-0.45 w	-0.56 w	-0.57 w
Manganese(II)	Mn^{2+}	NR	-1.59 w	-1.55 w	NR	-1.68 i ↓	-1.46 i	-1.56 i	NR	-1.52 w	NR	NR	NR	-1.61 i	-1.60 i
Molybdenum(VI)	Mo^{6+}	-0.63 w	NR	NR	-0.08 i	NR	NR	NR	-0.52	NR	NR	-0.02	-0.17 w	NR	NR
		-1.15							-0.75 w			-0.11	-0.29		
		-1.30										-0.33 w	-0.59		
											-0.74 w				

Substance	Symbol	Electrolyte solution														
		c(acetic acid) = 2 mol/L + c(NH_4-acetate) = 2 mol/L	c(NH_3) = 1 mol/L + c(NH_4Cl) = 1 mol/L	c(KCl) = 1 mol/L	c(HCl) = 1 mol/L	c(NaOH) = 1 mol/L	c(KNO_3) = 0.1 mol/L	c(KSCN) = 1 mol/L	c(Na_2EDTA) = 0.1 mol/L	c(Na_2-tartrate) = 0.5 mol/L	c(Na_3-citrate) = 0.1 mol/L + c(NaOH) = 0.1 mol/L	c($(NH_4)_2$-oxalate) = 0.1 mol/L, pH = 2 with c(H2SO4) = 1 mol/L	c($(NH_4)_2$-oxalate) = 0.1 mol/L, pH = 4 with c(H2SO4) = 1 mol/L	c($(NH_4)_2$-oxalate) = 0.1 mol/L, pH = 6 with c(NH_3) = 2 mol/L	c($(NH_4)_2$-oxalate) = 0.1 mol/L, pH = 8 with c(NH_3) = 2 mol/L
Nickel(II)	Ni^{2+}	-1.09 w	-1.07 w	-1.03	NR	NR↓	-1.00 w	-0.66 w	NR	NR	NR	NR	NR	NR	-1.32
Selenium(IV)	Se^{4+}	-0.70 w	-1.54 w	NR	-0.06	NR	NR	NR	-0.67 w	-1.21	NR	-0.03	-0.68 w	-1.35	-1.35
		-1.19			-0.47				-1.20 w			-0.60 w	-1.11		
Thallium(I)	Tl^{+}	-0.44 w	-0.46 w	-0.47	-0.46 w	-0.45	-0.43 w	-0.50 w	-0.44 w	-0.45 w	-0.47 w	-0.44	-0.44	-0.44	-0.44
Tin(II)	Sn^{2+}	-0.13 w	-0.72	-0.43 w	-0.45 w	-0.83	-0.35 w	-0.45 w	-0.13	-0.54	-0.83 w	-0.12 w	-0.15 w	-0.26 w	-0.51 i
		-0.63 w				-1.15 w		-1.59 w		-0.83	-1.08 w	-0.51 w	-0.62 w	-0.62 w	-0.64 i
										-1.06					
Tin(IV)	Sn^{4+}	NR	NR	NR↓	-0.45	NR↓	NR	-1.57	-1.16 i	NR	NR	-0.51 w	NR	NR	NR
Tungsten(VI)	W^{6+}	-0.26 i	NR	NR	-1.01 irrev	NR	NR	NR	-1.26 i	NR	NR				
Vanadium(V)	V^{5+}	i crw	-1.12	-1.10 irrev	-1.11 i	-0.40 i	-1.03 i	-0.50 w	-1.23	-0.33 i	-0.76	NR	NR	-0.90	-0.19 w
			-1.29 i								-1.11 w			-1.30 w	-0.88
															-1.29 w
Zinc(II)	Zn^{2+}	-1.05	-1.32 w	-0.99 w	-0.99 i	-1.58	-0.97	-1.01 w	NR	-1.27 w	-1.38 w	NR	NR	-1.38	-1.29

W	Very well defined wave or peak
i	Poor or non-evaluable wave (e.g. in rising part of supporting electrolyte curve)
cw	Catalytic hydrogen wave (in some cases can be used for quantitative analysis)
↓	Precipitate formation, observe solubility product!
NR	No wave or peak

9. Literature

Günter Henze
Polarographie und Voltammetrie – Grundlagen und analytische Praxis
Springer-Verlag, Berlin Heidelberg New York, 2001
ISBN 3 540 41394 4

F. G. Thomas, G. Henze
Introduction to Voltammetric Analysis – Theory and Practice
CSIRO Publishing, Collingwood VIC, Australia, 2001
ISBN 0 643 06593 8

www.metrohm.com

8.108.5087EN – 2003-08

Metrohm