Pierpaolo Protti

AMEL
ELECTROCHEMISTRY

Introduction to Modern Voltammetric and Polarographic Analisys Techniques

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Qualitative and quantitative analysis in Voltammetry

Voltammetry is an analytical technique based on the measure of the current flowing through an electrode dipped in a solution containing electro-active compounds, while a potential scanning is imposed upon it.

This electrode, is called **working electrode** and could be made with several materials. Usually, it has a very little surface in order to assume quickly and accurately the potential imposed by the electrical circuit. The electrode can be solid (gold, platinum or glassy carbon) or formed by a drop of mercury hanging from a tip of a capillary. If the electrode is formed by a drop of mercury rhythmically dropping from a capillary, the analytical technique is called **Polarography.**

Voltammetry is a versatile technique for research purposes, it allow to search into several aspects of the electrochemical reactions, namely those reactions in which electrons exchanges are involved between reagents and products. For those reactions it is possible to investigate on the laws governing the dependence of the current by the potential imposed on an electrode dipped into the reaction environment. Generally those laws are very complicated, just like the redox reactions and the environment in which they take place are.

The use of the voltammetric techniques is the basis of the comprehension of the laws concerning several electrochemical phenomena and has a great importance in several thecnological fields, like:

- Research of corrosion proof materials (corrosion is a consequence of a series of electro – chemical reactions)
- Research of new electrodic processes for chemical industries (in fact, for example, million of tons of aluminium, chlorine, soda are produced by means of electrochemical reactions)
- Production of new type of batteries that can store rapidly a great quantities of energy.

One of the most important application of Voltammetry is the quantitative analysis of trace of metals (or, anyway, of those reducible or oxidizable chemicals) at μg/L levels or less.

This introduction deals with the quali – quantitative aspects of the voltammetric analysis of trace of heavy metals and of organic substances in solution.

1. DISCHARGE PROCESS AT A CONSTANT POTENTIAL ELECTRODE

For a complete comprehension of the mechanism on which the voltammetric technique is based on, we can consider a simple model:

we can suppose that a working electrode is dipped in a solution containing an electro-active compound, A_{ox}, that can be reducible (or is able to gain an electron at the electrode) accordingly to the following reaction:

$$A_{ox} + ne \longrightarrow A_{red}$$

(i.e.: $Pb^{2+} + 2e \longrightarrow Pb$*)*

and that a reducible (meaning a lower or more negative) potential is imposed to the electrode respect to the reduction potential of the compound A_{ox}.
*In this way the conditions for the **discharge** of A_{ox} to the surface of the electrode are fulfilled.*
Finally, we can suppose to measure the electric current flowing through the electrode, while A_{ox} is discharging itself.

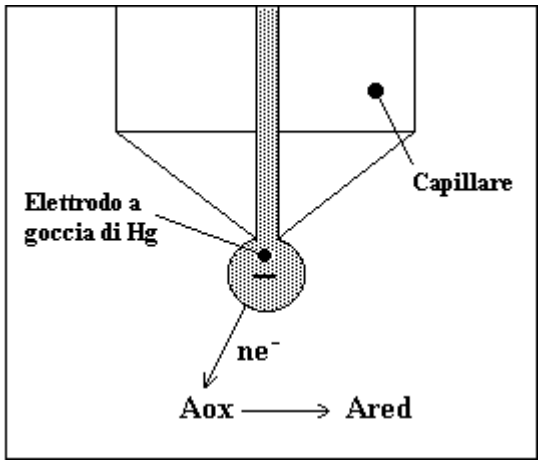


Fig. 1 – Discharging process of A_{ox} on a mercury drop electrode.
The electrode has a negative charge and the correct potential that allows the flowing of electrons toward A_{ox} (i.e. Pb^{2+}). In this way A_{ox} reduces itself and give raise to A_{red} (i.e. Pb^{2+}).

In order that the discharge (and than the flowing of the current through the electrode) can occur, is necessary that A_{ox} can reach the electrode starting from the bulk solution and also that A_{ox} can accept the electrons from the electrode. The process than proceeds under the influence of two kinetic factors:

- the speed (v_d) of the chemical compound that reach the electrode from the bulk solution
- the speed (v_e) of the electronic exchange between the electrode and the solution.

In analytical Voltammetry is necessary to use redox processes or, at least, to realise operating conditions, for which the second speed is higher than the first (**$v_e >> v_d$),** or, that is the same, that the discharge of A_{ox} on the electrode is practically *instantaneous.* In this way the discharging current can depend only on v_d and than on the modality with which A_{ox} reaches the electrode.

1.1 – The motion of the particles in a solution

The processes allowing the motion of a chemical compound in solution are, principally three:

- convection
- migration
- diffusion

The **convection,** is realised when, independently by the discharge process, a solution is stirred or when in the solution is present a temperature or a density gradient. In this case the molecules of the solvent and the analyte move themselves with a more or less troublesome motion, but that become more laminar in the vicinity of the electrode surface. The layer of solution closer to the electrode surface is practically stationary.

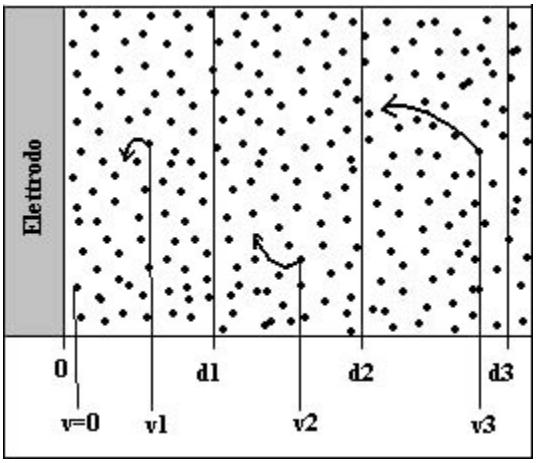


Fig 2 – Convection in a stirred solution.
Particles move themselves more or less untidily depending on the imposed stirring.
Closely to the electrode, the motion becomes more attenuated and laminar. In the layer closer to the electrode surface the particles have a null speed.
For simplicity only one particle for each layer has been pointed out.
d = distance from the electrode(d3>d2>d1)
v = particle speed (v3>v2>v1)

The **migration** is the moving due to the *attraction force* of the electric field generated by the electrode toward every ion having opposite charge and also due to the contemporary *repulsion force* of every ion having the same charge of the electrode.

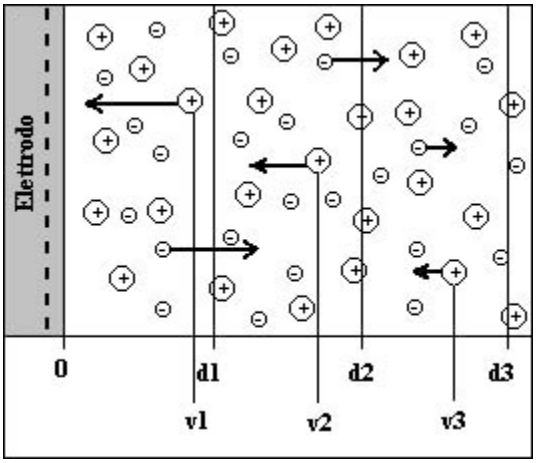


Fig. 3 – Migration in a quiet solution.
The negative electrode attracts positive charged particles and repels the negative charged ones with a force that diminishing exponentially while the distance is increased.
For simplicity only one positive particle (and one negative) for each layer has been pointed out
d = distance from the electrode (d3>d2>d1)
v = particle speed (v1>v2>v3)

The **diffusion** is the spontaneous movement of those chemical compounds subjected to a concentration gradient that means a situation in which a zone of the solution is poorer than another. With the process of diffusion the system tries to destabilise its homogeneity.

During the discharging process the solution closer to the electrode becomes ever more *poor* in A_{ox} in respect to the bulk solution. The growing concentration gradient recalls other electro-active compound, A_{ox}, from bulk solution toward the electrode.

The diffusion speed is directly proportional to the concentration gradient and than to the concentration of the electro-active compound in the solution.

Among the three described phenomena only diffusion can be related to the concentration of the electro-active compound, called also *depolarizer*. This is way in a voltammetric analysis is necessary to take adequate steps in order to secure that an electro-active compound can move itself prevalently by diffusion during a discharge process.

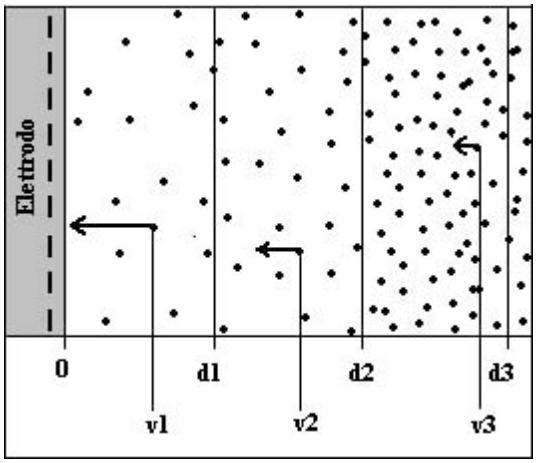


Fig 4 – Diffusion in a quiet solution.
While the particle of A_{ox} are discharging, the layers of the solution closer to the electrode become ever more poorer of this compound.
This causes a motion of particles coming from the farther layers with a speed proportional to the created concentration gradient.
For simplicity only one particle for each layer has been pointed out.
d = distance from the electrode(d3>d2>d1)
v = particle speed (v1>v2>v3)

Particularly, to avoid the convection, a constant temperature (usually ambient temperature) has to be maintained in a quiet solution (not stirred). When an Hydrodynamic Voltammetry is performed (see 3.6) the solution is stirred reproducibly, avoiding troublesome and realising a laminar flow closer to the electrode surface.

1.2 – The supporting electrolyte

Limitation of migration is achieved by screening the electrode using a **supporting electrolyte**, meaning a solution which ions do not discharge themselves at the electrode in the experimental conditions. This electrolyte is added at high concentration to the sample and could be a simple salt, or acid, or base or also a buffer solution or a chelating reagent. The supporting electrolyte surrounds the electrode with ions having the same charge of the depolarising agent, reducing in this way the electrostatic attraction toward the latter.

Relating to the behaviour of the depolarizer, the choice of the supporting electrolyte has to be made on the basis of the following characteristics:

- be chemically not reactive
- do not interfere with diffusion and with the electrons exchange on the electrode surface
- have a different discharge potential (at least 100 – 200 mV)
- have an high ionic conductivity and guarantee a low electrical resistance

1.3 – Faradic current and capacitive current

The electric current flowing through the working electrode has two components:

- the first, **the faradic current,** follows the Faraday laws and is due to the discharge of the electro active compound (A_{ox}),
- The second, **the capacitive current**, is produced by the growth of a double electric layer on the interface between the electrode and the solution. This double layer (see fig. 5) is due to the high concentration of the supporting electrolyte in the solution and acts as a condenser with high capacity. The total current flowing through the electrode is finally due to the sum of the charging current (capacitive current) of this condenser and the faradic current.

The capacitive current acts as a non specific background interference of the faradic current, and sometimes can be higher than the latter, when the depolarizer is present at low concentration in solution. In this cases the measure of the faradic

current is difficult and some electronic adjustment has to be used. That's why Polarography (and Voltammetry) is growth, as analytical technique, only after the progress in the electronic field: so we can now affirm that the development of this technique is strictly linked to the tentative to electronically overcome problems due to capacitive current.

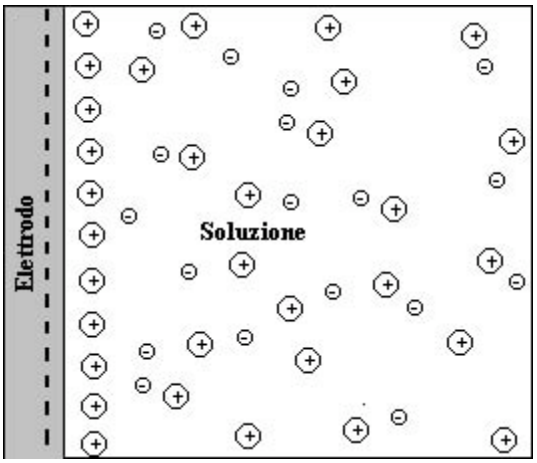
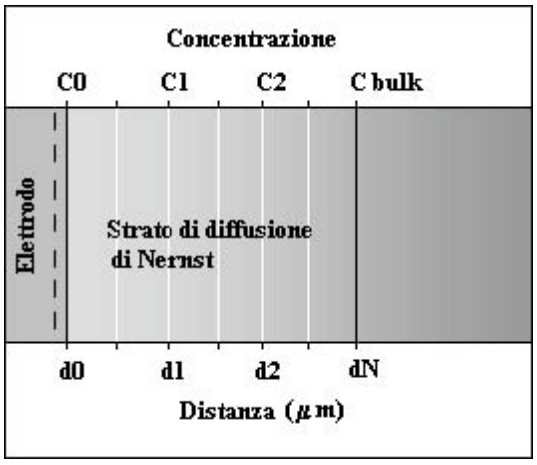


Fig. 5 – Simplified double electric layer.
When a negative potential is applied to the electrode and in the solution the concentration of positive ions is high, a double electric layer take place onto the surface of the electrode. This works just like a condenser.

1.3 –The diffusion layer

Near the electrode surface, during the discharge, a thin layer of solution, called *diffusion layer*, is formed, either the solution is stirred or not. This layer has a thickness of about 10-100 μm if the solution is stirred, or about 500 μm if the solution is quiescent and the motion of the particles in it is due only to the diffusion.
For this reason the quantity of analyte that reaches the electrode is directly proportional to its concentration in the solution and the intensity of the discharging (faradic) current gets to a limit value due to the velocity with which the electro active compound reaches the diffusion layer starting from bulk solution.

Fig. 6 –Diffusion layer.
When the discharging process of the electro active substance is stationary, a thin layer of solution close to the electrode is itself created. A concentration gradient is thus established in this layer ($C_{bulk}>C_2>C_1>C_0$) that attracts the particles from bulk solution.
If the solution is quiet, the diffusion layer is about 500 μm thick (but it becomes higher during the time), if, vice and versa, the solution is stirred, the layer is thinner (about 10 – 100 μm).



2. THE DISCHARGING PROCESS – II- THE POTENTIAL SCANNING

Let's improve the preceding model:

we can suppose now, instead of keeping constant the electrode potential, to vary the latter during the time, to make, in other words, a ***scanning*** *of the potential in increasing or decreasing way.*

If we consider the kinetics aspects, when an electro active compound is submitted to a potential scanning, three possibilities could take place:

1. The exchange of electrons between the working electrode and the solution is faster than the potential variation and hence than the velocity of the diffusion ($v_s > v_d$). In this way the potential of the working electrode corresponds, in every moment, to the one expected on the basis of Nernst law. The electron exchange is than due to a rapid (or reversible) redox couple, or, anyway the overpotential is absent and the discharging process is due only to the diffusion.
2. The velocity of the electron transfer is lower than the diffusion velocity ($v_s < v_d$). The redox system, in this case, is called slow or irreversible, or is characterised by high overpotential phenomenon: its potential is, in fact, "in late" respect on the one expected on the basis of Nernst law.
3. Both the velocity are similar. The redox couple has intermediate characteristics and the discharging process is ruled by both the diffusion and the velocity of the electron transfer

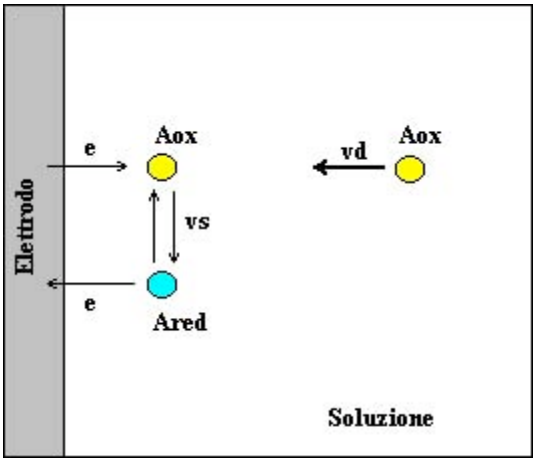


Fig. 7 – Discharging process during the potential scanning.
The phenomenon is ruled by two factors:
- the velocity of electron transfer (v_s) from electrode and redox system
- the diffusion velocity (v_d) of the motion of electro active compound toward the electrode surface.

2.1 – The discharge of Pb^{2+} at the electrode during a linear scanning of potential

For simplicity let's consider to make a rapid and linear potential scanning with a rapid (meaning reversible and without overpotential) redox system, that is ruled by the Nernst law. Let's also consider that during the discharge no adsorption process on the electrode or chemical collateral reactions take place and finally that the thickness of diffusion layer remains constant.

A real case is described in fig. 8 which represent a graph obtained when the variation of the electric current flowing though a stationary dropping mercury electrode is plotted while a rapid and reducing potential scanning is applied to a aqueous solution of Pb^{2+} and 0.1 M KCl as supporting electrolyte.

The operative condition are set in order that the reaction:

$Pb^{2+} + 2e \qquad Pb(Hg) \longrightarrow$

Follows the Nernst law:

$$E = E^0 + \frac{0.1984 \cdot T}{2} \log \frac{[Pb^{2+}]}{[Pb(Hg)]}$$

Where potential are expressed in mV, E^0 is the standard potential of the couple Pb^{2+}/Pb, that is –365 mV (referred to SSC), T is the temperature in K; $[Pb^{2+}]$ is the concentration of ionic lead in the solution and [Pb(Hg)] is the concentration of metallic lead in mercury amalgam.

If we consider the graph potential/current plotted during the scanning, we could note four characteristic regions (fig 8):

Starting background current (part A in fig 8). The potential is not sufficient to cause the discharge of Pb^{2+}, the measured background current is due to several causes, like the resistance of the cell, the discharge of residual oxygen, the capacitive current and the electronic noise of the electric circuit.

Ascending part of the peak (part B in fig 8*).* Close to the discharge potential, the curve rear up: the Pb^{2+} ions discharge themselves to the electrode at velocity every time faster; the diffusion layer become every time poorer and a spontaneous flow of other Pb^{2+} ions is established from bulk solution. The velocity of the motion of Pb^{2+} ions toward the diffusion layer is proportional to the concentration in the bulk. Contemporaneously the discharge of Pb^{2+} ions causes the appearance and the progressive enhancement of metallic Pb on the surface of the mercury (with which it form an amalgam).

Descending part of the peak (part C in fig 8). The concentration of Pb^{2+} into the layer of solution close to the electrode is practically equal to zero because the diffusion layer become dramatically impoverished of Pb^{2+}. The current decrease because the potential scanning velocity is so high that the electro active compound is not able to reach early the electrode. At these values of potential, all Pb^{2+} ions arriving to the electrode are reduced immediately and their concentration in the diffusion layer is very low. Current trends than to diminish (*part D of the curve).*

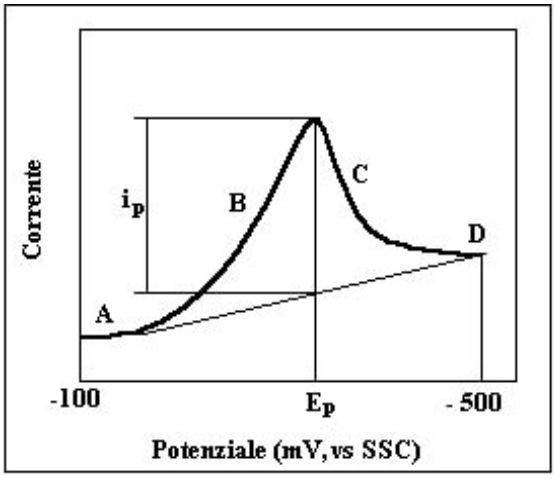


Fig 8 – Voltammogram inherent the discharge of Pb^{2+} (in 0.1 M KCl) on a drop mercury electrode which is subject to a slow linear potential scanning (between –100 and –400 mV).
Following conventional rules, cathodic current is positive and the potentials decreases from left to right on the abscissa axis.
E_p = peak potential
I_p = peak current height
Voltammograms peak – shaped are obtained also using differential scanning techniques (see 3.4 and 3.5).

Total or partial reversibility and/or the presence/absence of overpotential phenomena of the redox system subject to the voltammetric scanning bias on the shape and the quality of the potential/current graph: low reversible systems (or systems characterised by an high overpotential) give rise to more or less distorted

peaks, but completely irreversible systems (or systems characterised by a very high overpotential) cannot give rise to a significant peak.

2.2 – Peak potential

The higher point of a peak correspond to the point in which the half quantity of Pb^{2+} ions that reach the electrode discharge themselves, then the ratio $Pb^{2+}/Pb(Hg)$ at the electrode/solution interface become equal to 1. It can be demonstrated that the measured potential is not so far from the redox potential of the redox couple (obviously, in the supporting electrolyte solution…). The potential peak is than the analytical parameter that allows to make a *qualitative* characterisation a redox couple in a solution..

2.3 - Peak current height - Peak height (h_{peak})

The peak current height is proportional to the concentration of the electro active compound in the solution:

$i_p = K \cdot [Pb^{2+}]$

and than correspond to the analytical parameter useful for a *quantitative analysis.*

3. VOLTAMMETRIC TECHNIQUES

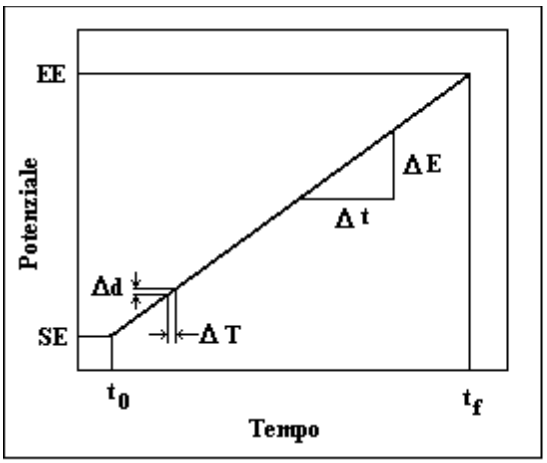
Let's now consider the most common voltammetric techniques

3.1 - Rapid scan Voltammetry – Linear Sweep Voltammetry, LSV

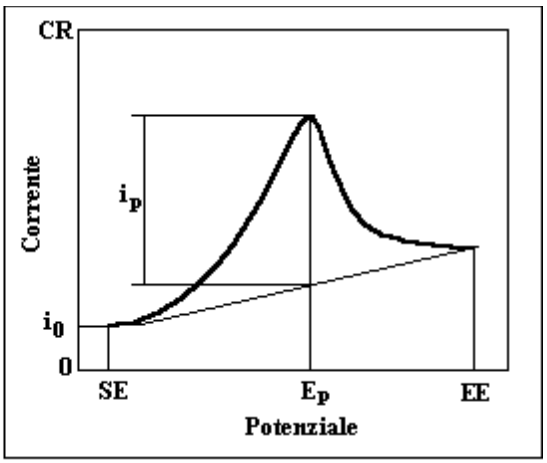
Rapid scan Voltammetry is the simplest technique. At the working electrode is applied a rapid potential scanning that varies linearly (20 – 100 mV/s). The scanning starts before the discharging potential and stops afterwards,

The phenomena involved during the potential scanning have been yet described (see 2.1). Capacitive current increases when the velocity of scanning is increased and cannot be electronically compensated. Thus the performance of this technique are strongly restricted.

Detection limits range at mg/l levels.



a



b

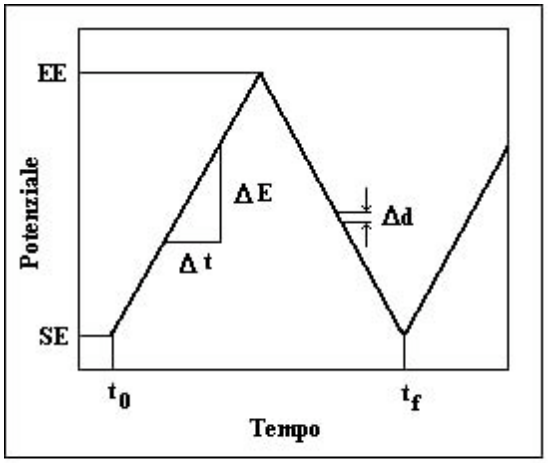
Start Potential.....(mV)	-800
End Potential.....(mV)	-200
Current Range.....(nA/µA/mA)	±20.48 µA
Scan Speed.....[mV/s]	5.0
Delta-E between Data.....(mV)	10
Number of Cycles.....	1
Delay Before Sweep.....(s)	5
Purge and Stir Time.....(s)	0
Stirring Speed.....(r.p.m.)	300
Drop Size.....(a.u.)	20

c

Fig 9 – Linear sweep Voltammetry
a- Anodic scanning of the potential; b- Plot of voltammogram; c- Typical parameters of an anodic scanning.
SE = Start potential; EE= End potential; t_0 e t_f = starting and final time tempo of the scanning, i_0= Current at the beginning of the scanning; i_p = Peak current; E_p= Peak potential; Δd (Delta E between data; ΔT = sampling time; CR Current range; Scan speed) = ΔE/Δt.

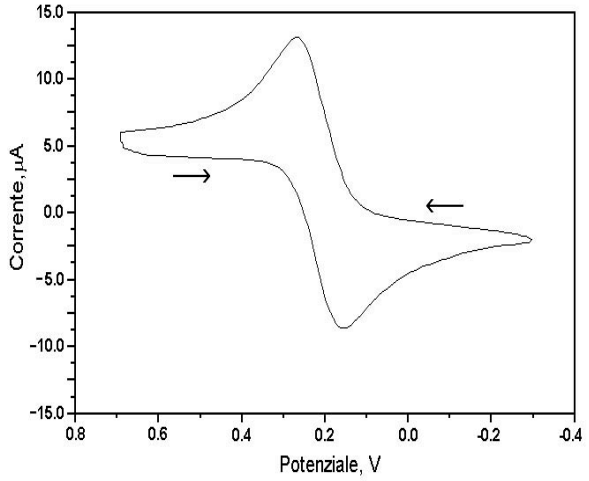
3.2 – Cyclic Voltammetry, CV

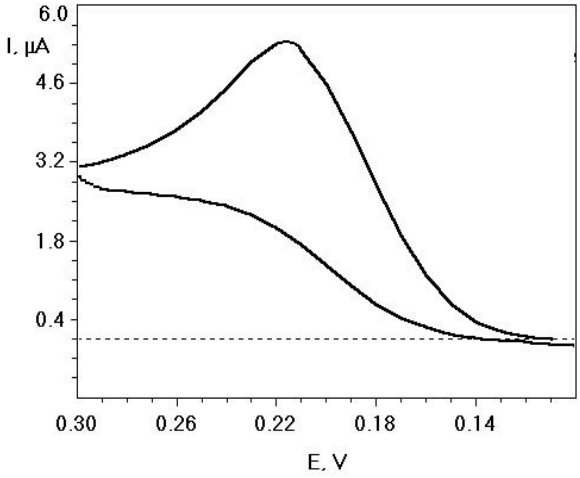
Cyclic Voltammetry is a technique devote to the theoretical study of the behaviour of redox couples. Cyclic Voltammetry is a particular LSV that perform a triangular shaped scanning at the working electrode. In this way a redox couple in solution is exposed before to an oxidation and afterwards to a reduction (or vice and versa).



Start Potential	(mV)	-500
End Potential	(mV)	500
Current Range	(nA/µA/mA)	±1.024 µA
Scan Speed	(mV/s)	200.0
Delta-E between Data	(mV)	5
Number of Cycles		10
Delay Before Sweep	(s)	1
Purge and Stir Time	(s)	0
Stirring Speed	(r.p.m.)	300
Drop Size	(a.u.)	60

b





c **d**

Fig. 10 –Cyclic voltammetry

a- Potential scanning starting from an anodic sense; b- Typical parameters of a cyclic scanning;

c- Cyclic voltammogram of a reversible redox system: $5 \cdot 10^{-3}$ M $K_3Fe(CN)_6$ solution in 1M KNO_3. Pt electrode.

In the cathodic (bottom) range takes place the reaction: $Fe(CN)_6^{3-} + e \longrightarrow Fe(CN)_6^{4-}$

In the anodic (top) range takes place the reaction: $Fe(CN)_6^{4-} \longrightarrow Fe(CN)_6^{3-} + e$

d- Cyclic voltammogram of 10^{-3} M L-ascorbic acid solution in 0.1 M $NaClO_4$. Dropping mercury electrode. The system is strongly irreversible the cathodic peak (bottom) is completely absent.

The cyclic scanning has to be ruled on the basis of few simply basic rules:

- a scanning starts in the cathodic sense has to be stopped at a potential lower than 100 mV (at least) respect on the peak potential;
- a scanning starts in the anodic sense has to be stopped at a potential higher than 100 mV (at least) respect on the peak potential;
- alternatively, a pause of 1 minute can be set between the go and back scanning.

The plot of a cyclic voltammetry consist on a close curve: reversible redox couples show both as cathodic and anodic peak, while irreversible redox systems show only one peak.
The following relations can be useful to establish the standard potential of a reversible redox couple and the number of electrons involved in the discharge process:

$$E^0 \cong E_{1/2} \cong \frac{E_{pa} + E_{pc}}{2}$$

and

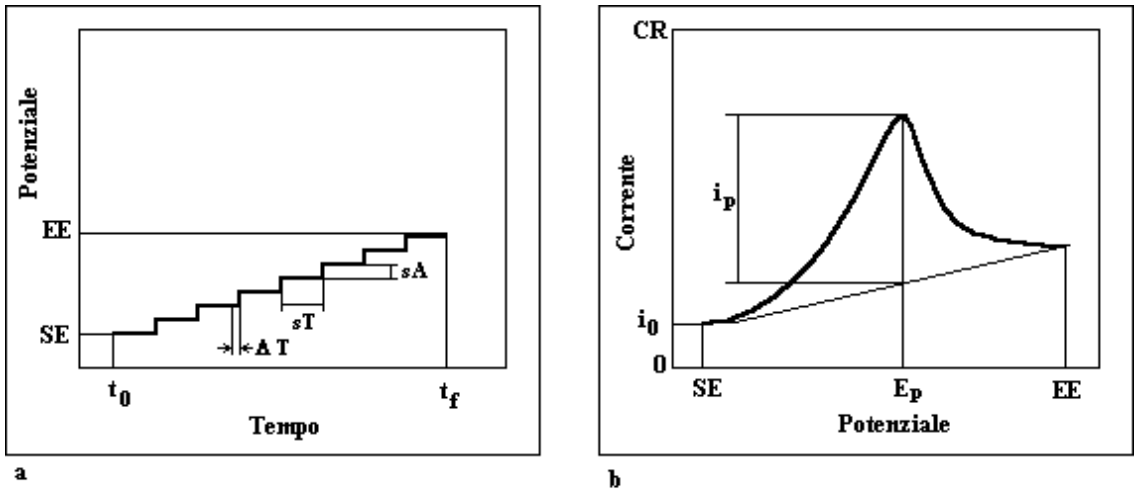
$$(E_{pa} - E_{pc}) \cong \frac{0.1984 \cdot T}{n}$$

where E_{pa}= anodic peak potential , in mV e E_{pc}= cathodic peak potential.

Generally this technique is not used for quantitative analysis because its poor sensitivity

3.3 - Staircase Voltammetry, STCV

A different variant of the LSV technique consist in a regular potential step scanning. The current is sampled just before the subsequent step. Thus the signal is less influenced by the capacitive current.



Start Potential	(mV)	-800
End Potential	(mV)	-200
Current Range	(nA/µA/mA)	±20.48 µA
Step Amplitude	(mV)	10
Step Time	(ms)	50
Sampling Time	(ms)	8
Delay Before Sweep	(s)	5
Purge and Stir Time	(s)	0
Stirring Speed	(r.p.m.)	300
Drop Size	(a.u.)	20

c

Fig 11 – Staircase voltammetry
a- Anodic scanning of the potential; b- Plot of voltammogram; c- Typical parameters of an anodic scanning.
SE = Start potential; EE= End potential; t_0 e t_f = starting and final time tempo of the scanning, i_0= Current at the beginning of the scanning; i_p = Peak current; E_p= Peak potential; ΔT = sampling time; CR Current range; sA (step Amplitude of potential); sT step Time.

3.4 - Differential Pulse Voltammetry, DPV

If a series of periodical constant pulse of potential is superimposed to a linear scanning, a consistent enhancement of the signal is achieved. Moreover, if the difference between the current just before and at the end of the pulse is measured, a reading less influenced by the capacitive current can be performed. In this way this differential reading of the current generates a peak shaped voltammogram.

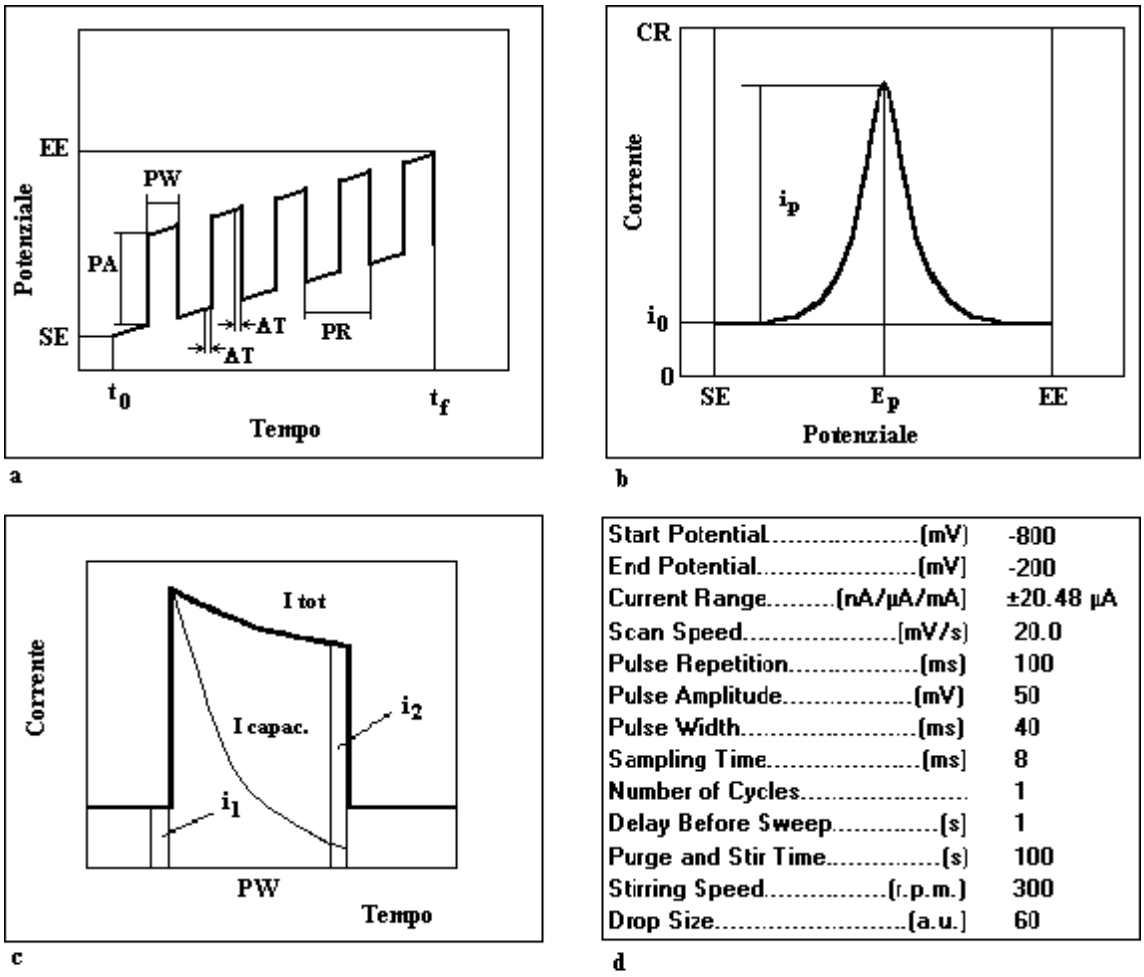


Fig. 12 – Differential Pulse Voltammetry
a- Anodic scanning of the potential; b- Plot of voltammogram; c- Progress of the current during a pulse; d- Typical parameters of an anodic scanning.
SE = Start potential; EE= End potential; t_0 e t_f = starting and final time tempo of the scanning, i_0= Current at the beginning of the scanning; i_p = Peak current; E_p= Peak potential; ΔT = sampling time; CR = Current range; PA = Potential Pulse Amplitude; PW = Pulse Time; PR = Pulse Repetition Time; i1= Current before the pulse; i2= Current at the end of the pulse; I_{tot}= Total current; $I_{capac=}$ capacitive current. Note how capacitive current reaches the maximum at the beginning of the pulse and how after decreases rapidly. Practically, at the end of the pulse only the faradic current is sampled.

Seeing fig. 12 b and c, the currents measured during each pulse i_1 and $i_{2,}$, before the peak are practically equal to zero and their difference is equal to zero too (a part from the residual current…). But when the potential, step by step, get closer to the discharge potential, the currents raise up (i_2 more than i_1) and their difference increases reaching a maximum. After, the currents fall down and the difference becomes near zero again.

The technique is very sensitive and detection limits range near 10 – 100 µg/l.

3.5 - Square Wave Voltammetry, SWV

This technique represents a further development of the preceding one. A rapid step scanning of potential is applied to the electrode and, moreover on each step is superimposed an high frequency square wave (20 – 100 Hz). The current is sampled two times at the end of the two half waves. If the amplitude of the wave is very little and the redox system is reversible, during the first half wave the electro active compound can be reduced (or oxidised), while, in the second half wave, at the contrary, it can be oxidised (or reduced). The two current are then summed up and so, the sensitivity is increased.

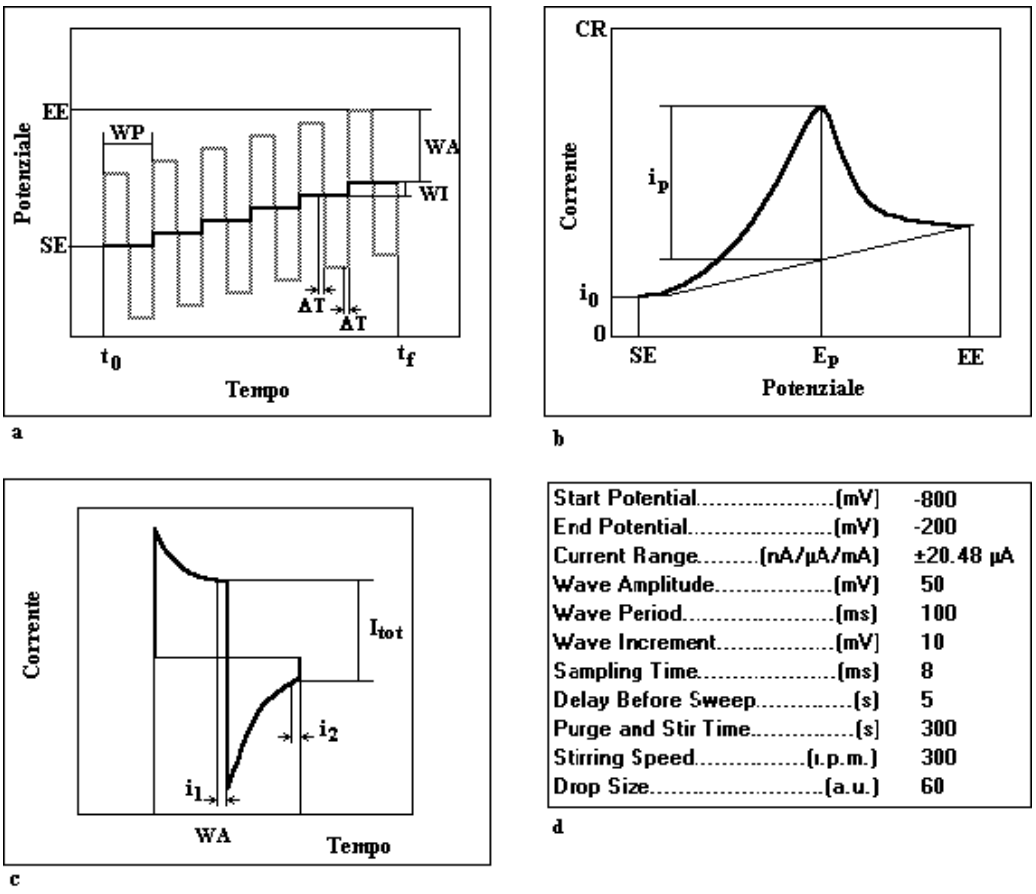


Fig 13 – Square wave voltammetry
a- Anodic scanning of the potential; b- Plot of voltammogram; c- Progress of the current during a square pulse, while a depolarizer is discharging itself; d- Typical parameters of an anodic scanning. SE = Start potential; EE= End potential; t_0 e t_f = starting and final time of the scanning, i_0= Current at the beginning of the scanning; i_p = Peak current; E_p= Peak potential; ΔT = sampling time; CR = Current range; WA = Wave Amplitude; WP = Wave Period; WI = Wave Increment; i1= measured current during the positive part of the pulse; i2= current during the negative part of the pulse; I_{tot}= total current. Note in c that the measured total current represent the algebraic sum of the anodic and cathodic current.

The sensitivity of this technique can be increased by enhancing the amplitude of the square wave or the frequency. The limits of the enhancing is strictly related to the kinetics aspects of the redox system: it has not to be slower than the velocity of the scanning of potential. The interference due to capacitive current are lowered to minimum because the current is sampled just at the end of the half waves, when the current of the double electrical layer is the least.

Detection limits range from 5 – 50 µg/l.

3.6 – Hydrodynamic Voltammetry

Rotating Disk Voltammetry, RDV - Rotating Ring-Disk Voltammetry, RRDV

In the hydrodynamic techniques the scanning of the potential takes place while the solution is in motion toward the electrode. In this way the solution closed to the Nernst (practically quiet) layer is continuously renewed.

The motion is actuated in 3 different ways:

- the electrode is stationary and the solution is stirred. This technique has low reproducibility and is practically not used.
- the solid electrode rotates around the own axis, the solution is than stirred. The electrode is a disk or a disk coupled with a ring.
- The solution flows into a tubular electrode at constant velocity. This system is used as voltammetric detector in HPLC.

The obtained voltammogram is a wave. In fact (see fig. 15 b) the plot potential /current is characterised by an initial residual current (A) that grows up just in correspondence (B) of the discharging potential ($E_{1/2}$, half wave potential). Successively the current increases, but slowly until a stationary level is reached. At this values of potential the ions reaching the electrode discharge themselves immediately, thus the concentration of the analyte in the diffusion layer is practically null. The continuos flowing of ions onto the diffusion layer, due to the stirring, maintains a constant current (C)

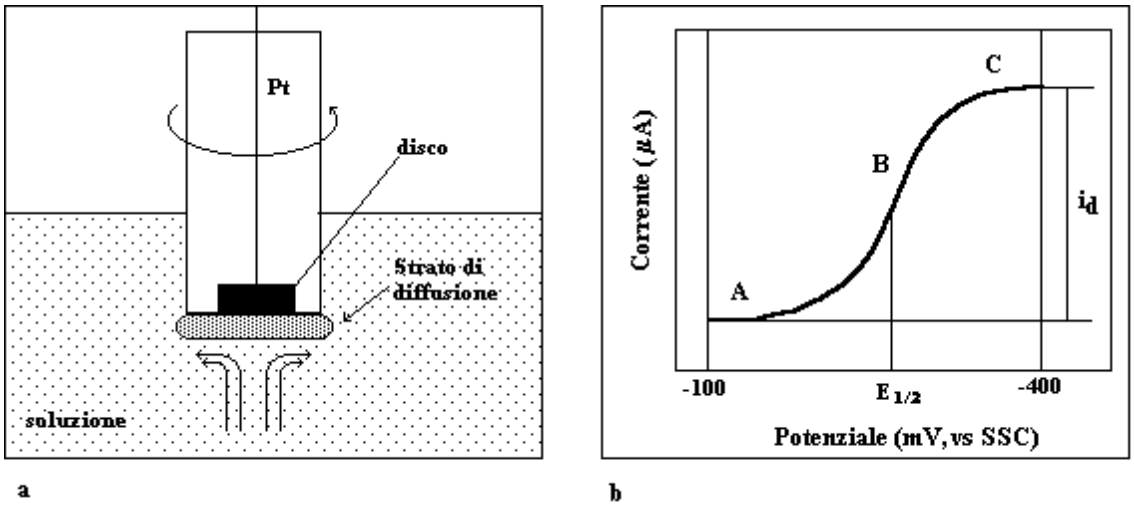


Fig. 15 – Hydrodynamic voltammetry
a- Rotating electrode; b- typical hydrodynamic voltammogram wave shaped.

3.7 - Stripping Voltammetry, SV

Anodic Stripping Voltammetry, ASV – Cathodic Stripping Voltammetry, CSV

Some metals forms an amalgam with the working electrode and some anions forms insoluble salts with it. The stripping voltammetry is based upon these properties.

The technique follows two main steps:

- A pre-concentration of the analyte onto the electrode
- The successive stripping of the cumulate compound onto the electrode toward the solution.

The stripping takes place during a scanning with the usual techniques (linear or differential pulsed or square wave scanning).

The usual working electrode is a dropping (or a film) mercury and the most common technique is the anodic stripping, meaning that a negative potential is applied to the electrode and the cations are discharged as metallic atoms into the mercury (amalgam). Successively the metal atoms are oxidised again, during an anodic scanning of potential. During the scanning of the potential, the current is measured and plotted, so the resulting voltammogram is a peak shaped graphic. The position and the heght of this peak are related, respectively, to the type and to the concentration of the analyte.

The analysis of anions on mercury takes place following a inverse way: first mercury oxidise itself and forms a insoluble salt with the anion and after, by applying a cathodic scanning, mercury reduce itself and the anion come back in solution.

Exemple:

$2Hg + 2Cl^- \longrightarrow Hg_2Cl_2 + 2e$ pre-concentration

$Hg_2Cl_2 + 2e \longrightarrow 2Hg + 2Cl^-$ reducing (cathodic) scanning

This technique allows to considerably enhance the sensitivity because during the pre-concentration step a great quantity of analyte in a small volume of electrode (the mercury drop) and the measured stripping currents are greater than the ones obtained using a non accumulative voltammetric techniques.
In this way detection limits below μg/l are achieved.

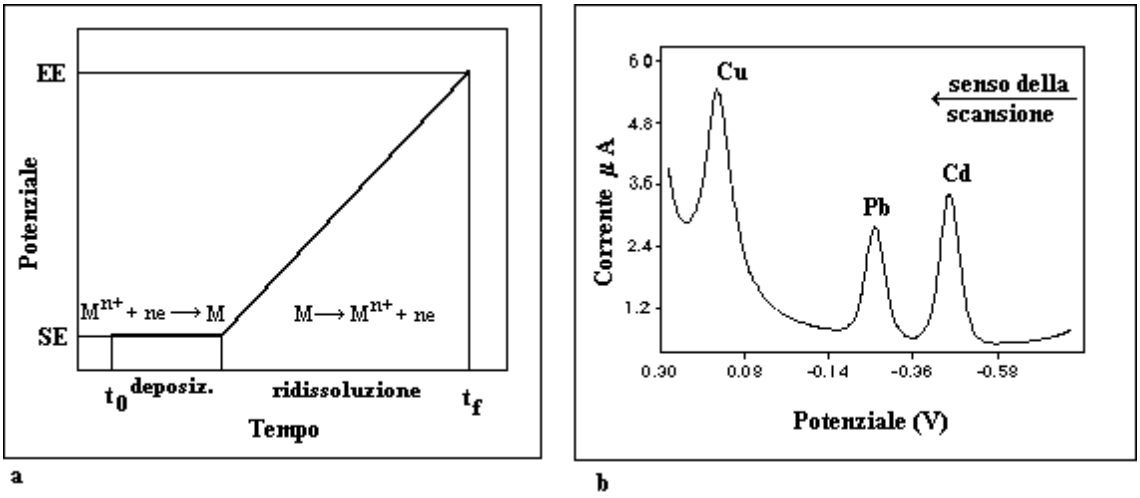


Fig. 16 – Anodic stripping voltammetry in a solution containing Pb^{2+}, Cd^{2+} e Cu^{2+}.
a- Potential scanning ; b- Voltammogram.
The scanning in the figure is linear but could be also a differential pulse or square wave ones.
Deposition potential = Starting potential (SE) = -800 mV; End potential (EE) = +300 mV; deposition time = 60 sec. For the other parameters see the relatives techniques (LSV, DPV or SWV).

3.8 - Adsorbtive Voltammetry, AdV - Adsorbtive Stripping Voltammetry, AdSV

Some metallic complex and some organic substances are adsorbed onto the surface of the electrode at specific potential. This phenomenon can be useful exploited when metals do not form amalgam onto the mercury, but form complex that can be adsorbed onto the latter and analysed with a direct scanning or a stripping technique. The detection limits are below the μg/l, while the linear range is often short.

3.9 - Adsorbtive Stripping Tensammetry, AdST

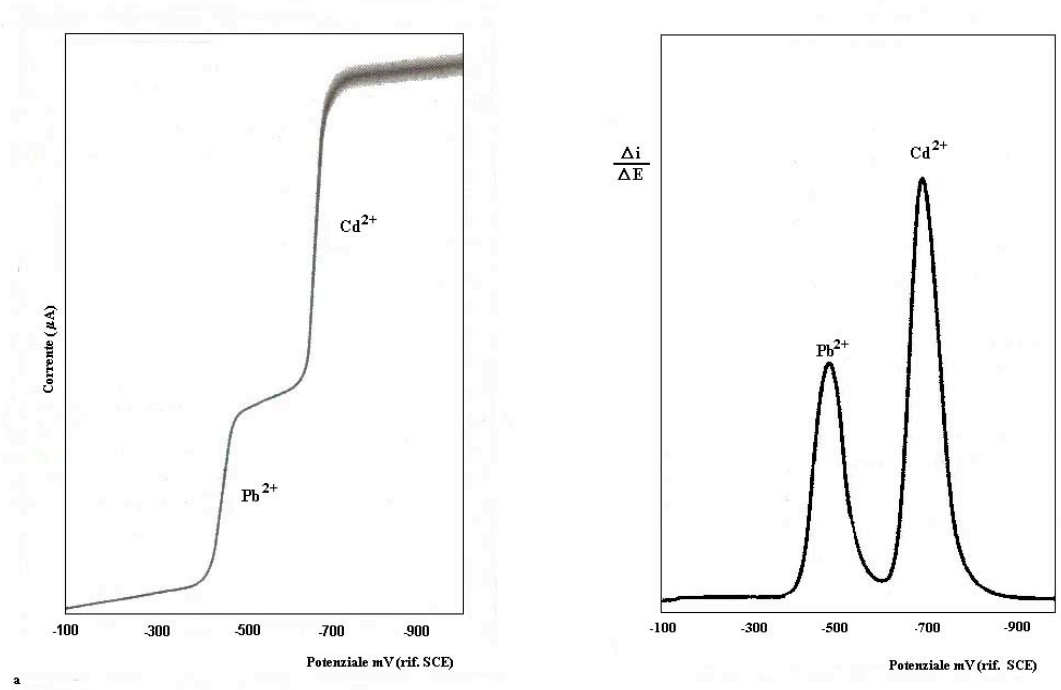
Some organic substances, like surfactants, are not electrically active, but show an electrical activity at the solution/electrode interface, while a pulsed or a rapid linear scanning is applied to the electrode. In correspondence of the desorbtion/adsorbtion potential a tensammetric peak is obtained. The analyte can be so analysed at mg/l levels.

3.10 – Polarographic techniques

Classical Polarography, developed by Heyrowsky, is now an obsolete technique. In the following pages are reported only few techniques that are already used.

3.10.1 - Rapid DC Polarography

The mercury drops fall down, rhythmically, from the capillary with a imposed rhythm, while a linear scanning is imposed to the electrode. The obtained polarogram is a wave characterised by strong oscillations due to the rhythmic falling of the drop (that means a rhythmic interruption of the electrical circuit).



a **b**

Fig. 17 - Rapid DC polarography.
a- Rapid DC polarogram of Cd^{2+} e Pb^{2+} (50 mg/l each) in 0.1 M KCl solution.
b- Polarogram of the same solution plotted as first derivative.

3.10.2 - Sampled (or Test) DC Polarography - Staircase Polarography

The interference of capacitive current in the previous technique is strong. Capacitive current reach its maximum in the first moments of life of the drop and goes to the minimum just before the drop fall down.

In this technique, the potential is increased (or decreased) at the beginning by a step and maintained constant during the life of each drop. The current is measured in the last moment of life of the drop. A stepped wave polarogram, with a smaller noise, is thus obtained.

3.10.3 - Normal Pulse Polarography, NPP - Differential Pulse Polarography, DPP

Pulsed techniques allow to reduce the capacitive current. In the *Normal Pulse Polarography* a potential pulse is imposed to the drop during its last moment of life. The pulse height is linearly increased during the time. In the *Differential Pulse Polarography* the potential pulse is constant but is over imposed to a linear scanning of the potential (see DPV).

The polarogram is a wave in NPP and a peak in DPP and the height of both are related to the concentration of the analyte.

DPP was been, for a long time, the most used technique and it has allowed to develop the first procedures and is the basis for the further developments of the analytical voltammetric techniques.

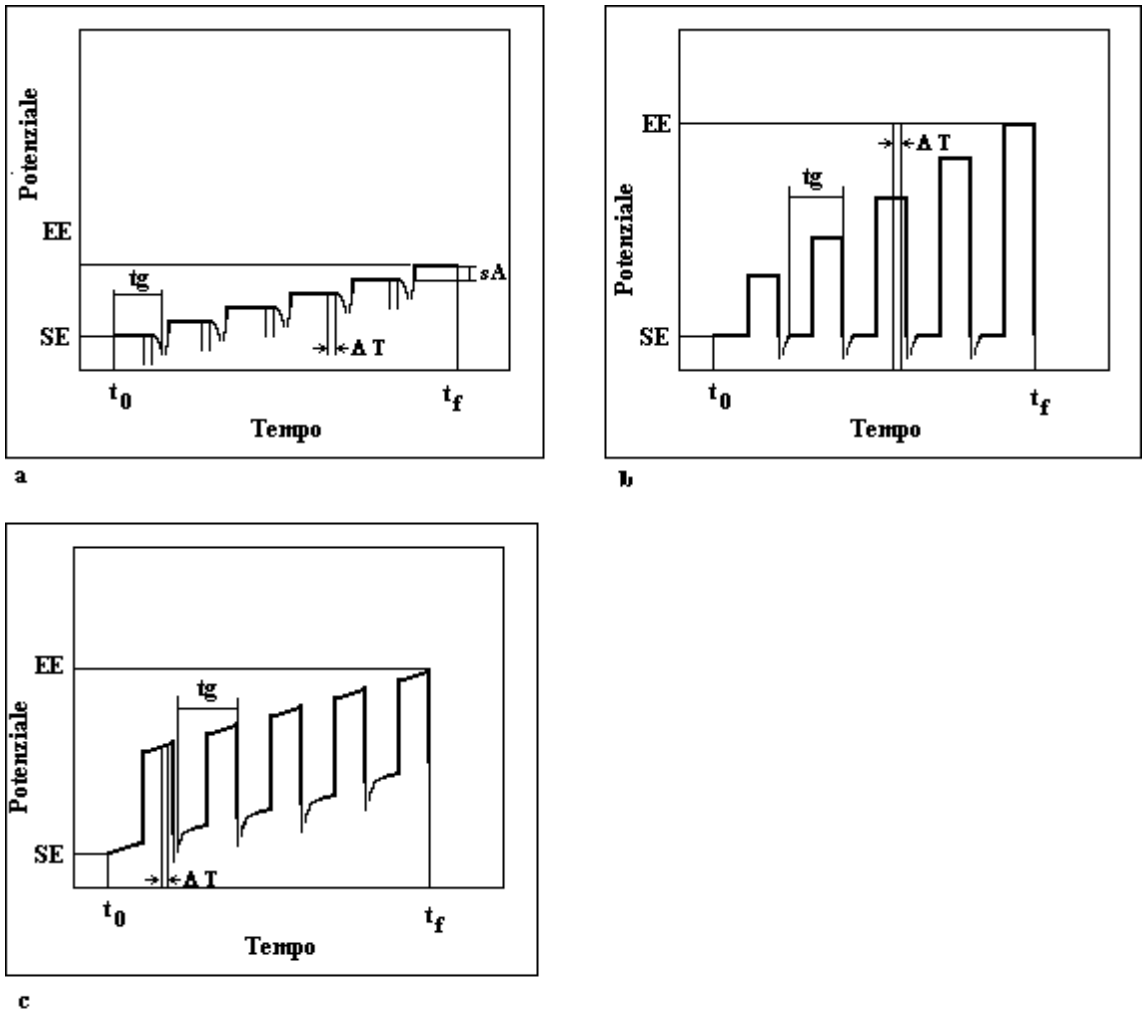


Fig. 18 - Potential scanning during : a- Staircase Polarography, b- NPP c- DPP
SE = Start potential; EE= End potential; ; t_0 e t_f = starting and final time of the scanning ; ΔT = Sampling Time; tg = dropping time; sA: height of potential step.

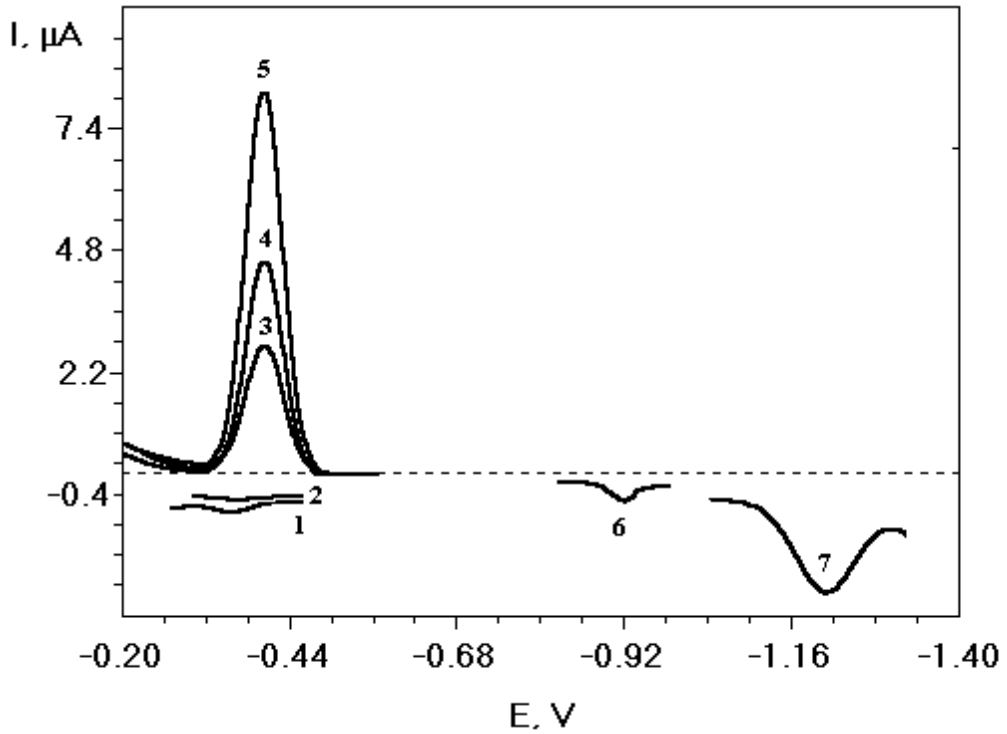


Fig 19 – Sensitivity of polarographic and voltammetric techniques.

1- 100 µg/l of Pb^{2+} with DPV (e in SWV). Sensitivity: 1.7 nA· l /µg
2- 100 µg/l of Pb^{2+} with DPP. Sensitivity: 0.8 nA· l /µg
3- 100 µg/l of Pb^{2+} with DPS con 30 sec. of deposition. Sensitivity: 26.3 nA· l /µg
4- 100 µg/l of Pb^{2+} with DPS con 60 sec. of deposition. Sensitivity: 45.3 nA· l /µg
5- 100 µg/l of Pb^{2+} with DPS con 120 sec. of deposition. Sensitivity: 82.6 nA· l /µg
6- 15 µg/l of Ni^{2+} with AdDPV. Sensitivity: 24.3 nA· l /µg
7- 0.6 µg/l of Cr (VI) with AdDPS. Sensitivity: 2700 nA· l /µg

4. THE INSTRUMENT

The main parts of a polarographic analyser are:
The polarographic cell
The potentiostat
A PC with the application software

The polarographic cell is a glass or teflon vessel in which are inserted a tube for the bubbling of nitrogen and three electrodes:

The working electrode – A capillary connected with a mercury container or a solid electrode

The reference electrode – A simply Ag/AgCl, saturated KCl electrode.

The auxiliary electrode – A platinum wire inserted on a teflon rod.

The stirring of the sample solution is allowed by a magnetic stirrer and a magnetic rod.

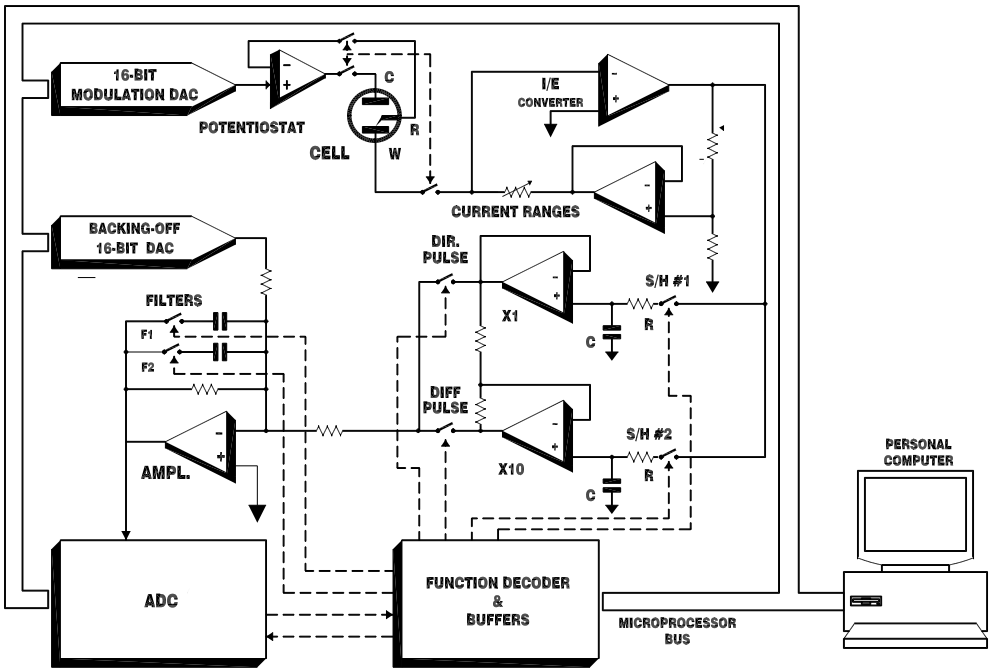


Fig. 19 – Main parts of a potentiostatic polarographic analyser.
The PC send to the function decoder and buffer the scanning parameters and the data handling instructions. The instructions for the scanning are then send to the DAC (digital to analogical converter) and, finally to the polarographic cell (C= counter electrode, R= reference electrode, W= working electrode). The output signals of current and potential are amplified and converted in digit form and send to the PC. Here the software handles the data.
Current Range appropriate current range selection circuit.
Dir Pulse e Diff. Pulse = circuits for the recording of the signals before and after a differential pulse.
Backing off = circuit for the compensation of the background current.

The potentiostat allow to impose the desired potential scanning between working and reference electrodes while the current flowing in the circuit is recorded between working and auxiliary electrodes.

The PC is interfaced to measuring system and the software has the following functions:

- send to the potentiostatic analyser the scanning parameters
- check if the execution of the scanning is correct or not
- handle the output data (current and potential).

4.1 – Working electrode

The operating range of a potential scanning depends on:

- kind of solvent
- chemical structure of the electrode
- surface characteristics of the electrode
- supporting solution
- sensitivity of the instrument

In water solution this range restricted in the cathodic side by the hydrogen discharge:

$$2H^+ + 2\,e \rightleftharpoons H_2$$

While, in the anodic side by the oxidation of water:

$$O_2 + 4H^+ + 4\,e \rightleftharpoons 2H_2O$$

or by the discharge of the constituent material of the electrode i. e.

$$Hg^{2+} + 2e \rightleftharpoons Hg$$

The potentials of the two discharging processes above described, can shift considerably depending on the overpotential phenomena due to chemical structure of the electrode.

Let's now consider the most important materials for electrodes.

4.2 – Mercury electrode

Mercury is the best metal for cathodic scanning because of the large overpotential that the hydrogen discharge undergo on this element. The density of the discharge of the hydrogen on mercury is 10^9 time less than the platinum and gold ones. On mercury the hydrogen discharge occur at -1 V (Vs SSC, in acidic solution) or at – 2 V (Vs SSC, in alkaline solution), instead of a theoretical potential of –0.2 V (Vs SSC).

In the anodic side the operating limit is restricted by the discharge of mercury itself:

$$Hg_2^{2+} + 2\,e \rightleftharpoons 2Hg$$

$$Hg^{2+} + 2\,e \rightleftharpoons Hg$$

Practically, it is impossible use the mercury electrode above 0.3 V (Vs. SSC).

Another advantage on the use of mercury as electrode is due to the opportunity of eliminate a drop of this element at the end of the scanning. In this way the surface of the electrode can be renewed before each analysis.

On the other hand, mercury is a toxic metal, rather volatile. Anyway the modern instruments are perfectly sealed and the volume of the mercury container is very small.

The latest version of this electrode, the Static Mercury Dropping Electrode, SMDE is a capillary (0.15 – 0.2 mm ID) connected to the mercury container. A valve, operated by a PC, adjust the dimension of the drop, while a platinum wire ensure the electrical connection with the electrical circuit.

The older DME (Dropping Mercury Electrode), in which the mercury flowed down simply by gravity or the HMDE (Hanging Mercury Dropping Electrode), in which a piston developed the drop are not in use. The SMDE (Long Lasting Sessile Dropping Mercury Electrode) is still used when then scanning has to be prolonged at values smaller than –1.4 V. At these potentials the drop on the SMDE inclines to fall down for electrostatic phenomena.

4.3 – Gold, Platinum and Glassy Carbon electrodes

These electrodes are used chiefly for anodic scanning. The limit of this range is due to the water oxidation at more than 1 V in acidic solution (Vs SSC). The disadvantage represented by these electrodes is the progressive poisoning of their surfaces. Anyway a cleaning reverse scanning is mandatory between an analysis and the following one.

The electrode is a 1-4 mm disk of material inserted on a teflon rod. The rotating electrode is made of a disk or/and a ring inserted on a reproducible rotating device; the operator can select the rotating speed.

Elettrodo	Solvente	Elettrolita di supporto	Potenziale (V, rif. a SSC) +4 +3 +2 +1 0 -1 -2 -3
Hg	acqua	H_2SO_4 1 M	
		KCl 1M	
		NaOH 1 M	
		Et_4NOH 0,1 M	
C	acqua	$HClO_4$ 1 M	
		KCl 1M	
Pt	acqua	H_2SO_4 1 M	
		tampone pH 7	
		NaOH 1 M	
	acetonitrile	$TBABF_4$ 0,1 M	
	benzonitrile	$TBABF_4$ 0,1 M	
	PC	TEAP 0,1 M	
	tetraidrofurano	TBAP 0,1 M	
	dimetilformammide	TBAP 0,1 M	
	cloruro di metilene	TBAP 0,1 M	

Fig. 20 – Operating range of mercury, gold, platinum and glassy carbon electrodes in water solution and in other solvents.

5. APPLICATIONS

Every oxidizable or reducible substance that can be dissolved in an appropriate solvent can be analysed by Voltammetry, using appropriate conditions (supporting electrolyte, kind of electrode, scanning technique and scanning parameters) for its discharge. The main application field of the voltammetric techniques is the trace analysis of heavy metal in several different matrix like water, food, soil, air, industrial product, pharmaceutical, biology and so on.

In table 1 are reported the detectable elements with voltammetric techniques.

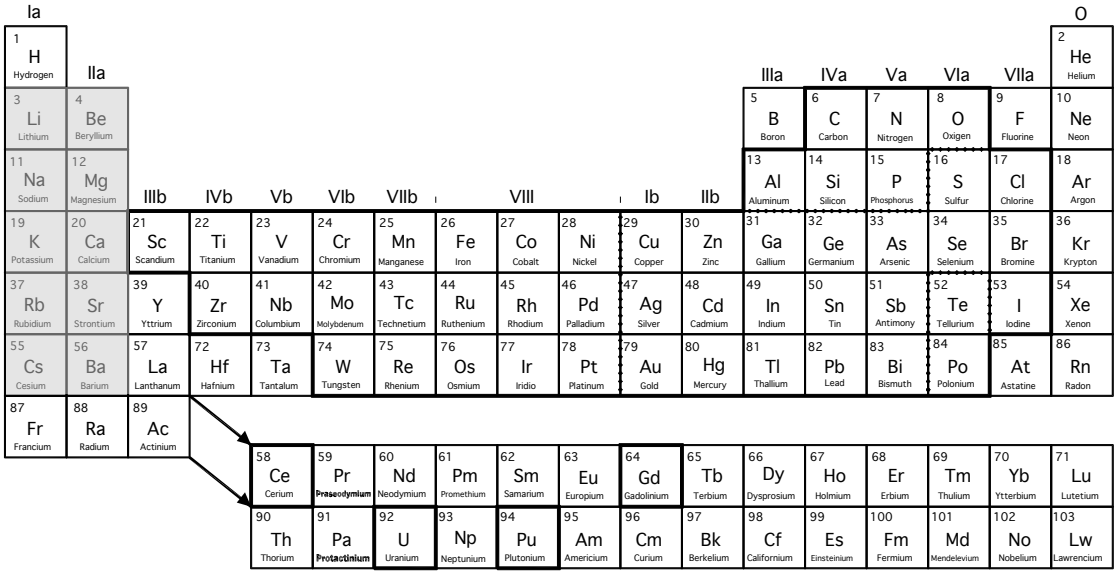


Table 1 – Detectable elements with Voltammetry

Polarography and Voltammetry
Elements of first and second group are detectable only if present alone in the solution.
Stripping Voltammetry

Naturally, also anion (see table 2) and organic compound (table 3) are detectable with voltammetric techniques.

Cl^-, ClO^-, ClO_2^-, ClO_3^-, Cl_2, Br^-, I^-, IO_3^-, I_2
S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, SCN^-, $S_2O_8^{2-}$
NO_2^-, NO_3^-
PO_4^{3-}
SiO_3^{2-}
CN^-
BO_3^{3-}

Tab. 2 - Inorganic anions detectable with voltammetric techniques.

Double bond	Triple bound
Aromatics	Alcohols, phenols and ethers
Aldehydes and Ketons	Quinones and quinhydrones
Coniugated carboxylic acids	Aromatic carboxylic acids
Sulphides and disulphides	Sulphonic salts
Thiocyanates	Sulphonates
Chlorides, Bromides and Iodides	Etherocycles
Organomellics	Peroxides
Imines e oximes	Nitriles
Nitro e nitroso compounds	Diazo compounds
Amines	

Table 3 – Main functional organic groups detectable with voltammetric techniques.

6. COMPARING VOLTAMMETRY WITH ATOMIC ABSORPTION SPECTROPHOTOMETRY AND INDUCTIVELY COUPLED PLASMA SPECTROMETRY

Detection limits and reproducibility of the voltammetric techniques are comparable with those of Graphite Furnace Atomic Absorption Spectrophotometry and Inductively Coupled Plasma Spectrometry.

Voltammetry is a electrochemical technique, otherwise the others are optical techniques.

Optical techniques allow to analyse only metals (and also sulphur and phosphorous), in solution, while voltammetric techniques allow to analyse also oxidizable or reducible anions and organic compounds.

Optical techniques allow to analyse total metals, while voltammetric techniques allow to analyse also metals at different oxidation numbers (i. e. Cr (III) and Cr(VI), Fe(II) and Fe(III), As(III) and As(V)).

The spare parts and the costs of a single analysis using optical techniques are very high, while the Voltammetry is cheaper.

GFAAS needs an accurate adjusting of the analytical method when the sample matrix is rich in compounds. GFAAS needs therefore very expert analysts and also a great number of lamps (virtually one for each detectable element). For a better reproducibility of GFAAS an automatic sampler and injection system is strictly necessary. Furthermore GFAAS needs a frequent replacement of graphite tubes and a lot of waste of inert gas (argon).

ICP and ICP-MS suffer for a great waste of argon and for necessity to use very diluted solutions. ICP-MS needs very expert analysts, principally for the mass spectrometry. Furthermore the injection system of a ICP is very easily getting dirty or broken and also is very expensive.

Voltammetric techniques need analysts specialised in electrochemistry and don not allow to analyse metals of first and second group (Na, K, Li, Ca, Mg, Ba, Sr …). Furthermore it's not possible to use automatic sampler. The most replaceable part is the capillary, but, anyway the spare parts of a Voltammeter are cheaper than the optical techniques ones. Solutions to be analysed must have a pH lower than 10 and higher than 1 to save the functionality of the capillary. At the moment of the analysis a supporting solution has to be added to the sample to adjust the reaction environment and also the discharging condition of the analyte. The times for an analysis is higher in Voltammetry, but the technique is not destructive and the sample can be analysed for several time and different analytes. Mercury is a toxic pollutant and must be recovered in a proper way.

Sensitivity for some elements like Pb, Cd and Se is greater in Voltammetry than in Optical techniques. And some element. like i.e. Ni, can be analysed in sea water only using Voltammetry.

The correct analytical method for Voltammetric analysis is the standard addition method (single or multiple); this allows to compensate the matrix effect of the sample (see par. 8).

Finally, a voltammetric system for metal trace analysis is recommended for medium little laboratories with low number of samples with a large variety of elements or other compounds) to process, or is mandatory for large laboratories when an alternative (to the optical techniques) methods has to be used for sensitivity or matrix problems or when a validation of the method is request.

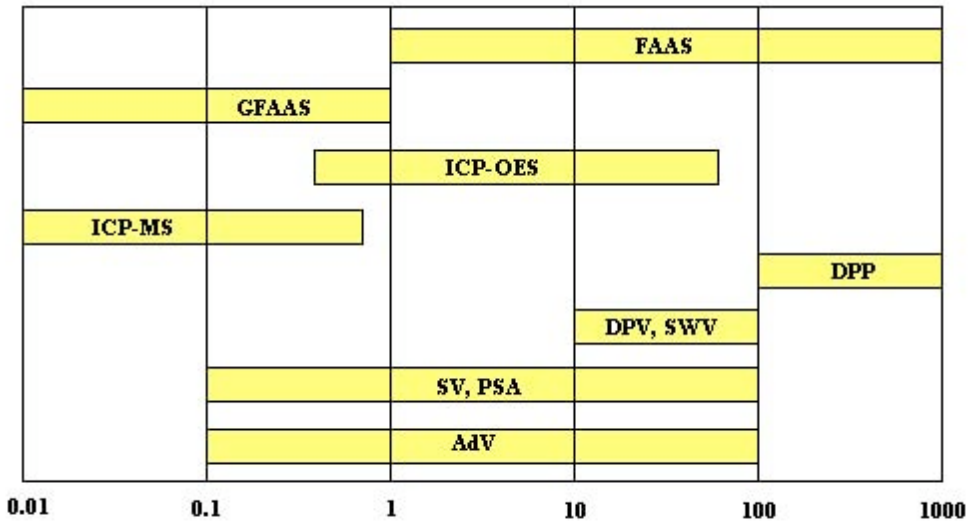


Fig 21 – Detection limits (μg/L) of the principal techniques for trace analysis.
FAAS: Flame Atomic Absorption Spectrophotometry
GFAAS: Graphite Furnace Atomic Absorption Spectrophotometry
ICP-OES: Optical Emission Inductively Coupled Plasma Spectrometry
ICP-MS: Inductively Coupled Plasma Spectrometry interfaced with Mass Spectrometry
DPP: Differential Pulse Polarography
DPV: Differential Pulse Voltammetry
SWV: Square Wave Voltammetry
SV: Stripping Voltammetry
PSA: Potentiometric stripping
AdV: Adsorptive Voltammetry.

7. QUALITATIVE ANALYSIS

Voltammetry is not dedicated to the quantitative analysis. In fact the peak potential or the half wave potential can vary depending on the sample matrix, the type of supporting electrolyte and on the presence of chelating reagents. When necessary the presence/absence of an analyte is proved by the enrichment technique, namely, by adding an aliquot of standard solution.

8. QUANTITATIVE ANALYSIS

The peak (or wave) height is proportional to the concentration of the analyte, as it is shown in table 4.

Quantitative analysis is than performed considering the peak (or wave) height and using the (single or multiple) standard addition method. This is in fact the best method for lowering the matrix interference. When the sample matrix is very simple or reproducible the calibration curve methods could be used.

8.1 – Standard addition method

The unknown concentration of a sample can be established with usual quantitative methods if only some kind of interference don't take place

- During the titration, for example, the titrant has to react exclusively with the analyte. If one or more substances that could react with the analyte are present in the sample matrix, this interference has to be removed or, at least, neutralised.
- If an analyst prepare a calibration curve using standard solution in distilled water, some difficulties could be encountered if the sample to be analysed has a complex matrix (meaning a matrix rich of general chemical compounds). In fact, these substances can vary significantly some physical characteristics of the solution, (like viscosity, or refraction index and so on), or they can vary the not specific background instrumental signal or the analyte signal, or, finally, they could increase or decrease the analytical signal, reacting with the analyte or with the specifying reagent added to the solution in order to give rise to the instrumental signal. Also in this case, attempts have to be made to remove or neutralise the effect of the interfering substances, or instead, to prepare standard solutions in a matrix similar to the sample one.

Anyway, whatever the analytical method is used, the interference affects are to be removed, avoiding analytical errors. The best method to avoid some matrix interference is the *multiple standard addition method* or, simpler, the *single standard addition method.* These methods, unfortunately, cannot allow to compensate the not specific interference that raise the background signal. The only valid strategy to compensate this kind of interference is to measure the signal as difference between the analytical signal and a background of a blank solution, or, at least, to zero the signal with an appropriate blank solution.

Essential condition for the use of the standard addition in Voltammetry is to make the scanning related to each addition using the same parameters. In table 4 are reported the equations correlating the concentration to the peak (or wave) height for the most important voltammetric techniques. As can be seen, several are the parameters to be considered in order to keep constant the proportionality between concentration and peak (or wave) height among different scanning.

Another important condition is to work in the linear range of the relation between concentration and peak (or wave) height. This range, in some case is very narrow.

Tab. 4 – Equations relating the voltammetric peak (or wave) height to the concentration, in the main voltammetric techniques. Mercury electrode.

LSV – Randles Sevcik Equation	$i_p = 2.69 \cdot 10^5 \cdot n^{2/3} \cdot A \cdot D^{1/2} \cdot v^{1/2} \cdot C$
SWV	$i_p = k' \cdot \frac{n^2 \cdot F^2}{R \cdot T} \cdot \Delta E \cdot C$
DPP	$i_p = \frac{n^2 \cdot F^2 \cdot A}{4 \cdot R \cdot T} \cdot \left(\frac{D}{\pi \cdot t_g} \right)^{1/2} \cdot \Delta E \cdot C$
Hydrodynamic Voltammetry – stirred solution	$i_l = \frac{n \cdot F \cdot A \cdot D}{\delta} \cdot C$
Hydrodynamic Voltammetry – rotating disk electrode – Sevcik equation	$i_l = 0.620 \cdot n \cdot F \cdot A \cdot D^{2/3} \cdot \nu^{-1/6} \cdot \varpi^{1/2} \cdot C$
LSSV	$i_p = 2.72 \cdot 10^5 \cdot n^{2/3} \cdot A \cdot D^{1/2} \cdot v^{1/2} \cdot t_d \cdot C$
DPSV	$i_p = k'' \cdot n^2 \cdot r \cdot \Delta E \cdot U^{1/2} \cdot t_d \cdot C$

Where:
k' e k'' = constants
C = analyte concentration
n = electron number in the redox reaction
F = Faraday constant
R = thermodynamic gas constant
T = temperature (K)
A = area of the electrode surface
D = diffusion coefficient of the analyte
v = scanning speed
ν = cinematic viscosity of the liquid (solvent)
ω = angular speed of the disk
U = stirring speed of the solution
ΔE = pulse height of a square wave
t_d = deposition time
t_g = dropping time
r = radius of the mercury drop
δ = thickness of the Nernst layer

8.2 – Multiple standard addition method in Voltammetry

Prepare an aliquot of sample and add another aliquot of supporting electrolyte. Register the voltammogram and after add several aliquots of standard solution registering each time the voltammogram. At the end handle the data.

> **Example.** Analysis of copper in wine: add to 10 ml of wine, 1 ml of supporting electrolyte (HCl 2 M + $H_2C_20_4$ 1 M). Register the voltammogram. After, add 200 μL of standard copper solution 10 mg/L and register the voltammogram. Repeat the procedure for 2 – 4 times.

Data handling

Calculate the *added analyte concentration* (*Ca*) after each addition*:*

$$Ca = \frac{Vst \cdot Cst}{Vx} \quad (1)$$

where • *Vst* e *Cst* are, respectively the volume (in mL) and the concentration of the standard solution • *Vx* is the sample volume.

Calculate also the diluting factor *(d)* after each addition*:*

$$d = \frac{Vtot}{Vx} = \frac{Vx + Vst + Vr}{Vx} \quad (2)$$

where • *Vx* is the sample volume • *Vst* is the volume of standard solution added each time • *Vr* is the volume of the solvent add (if one) + of the supporting electrolyte.

Multiply each peak height for the relative diluting factor, obtaining in this way a *corrected height*.

At the end report on a graph the *added concentration* and the *corrected height*. The negative intercept on the abscissa, of the graph will return the sample concentration.

This procedure allow to compensate the dilution of the sample solution after each addition of a volume of standard solution, multiplying the peak height for the diluting factor and can be used only in the linear range of the relationship between concentration and peak height.

Demonstration of the principle

Let's consider the linear relationship between concentration and peak height:

$$h = K \cdot C \quad (3)$$

where • *h* is the peak height • *C* is the analyte concentration • *K = constant.*

After each addition the peak height increase in consequence of the increasing in total analyte concentration, *C*. The latter varies as follows:

$$C = \frac{Vx \cdot Cx}{Vtot} + \frac{Vst \cdot Cst}{Vtot}$$

:

where •*Vtot* is the total volume after each addition, equal to: *Vx* + *Vst* + *Vr* • *Cx* is the unknown concentration.

The relationship peak height/concentration (3) becomes than:

$$h = K \cdot \left(\frac{Cx \cdot Vx}{Vtot} + \frac{Cst \cdot Vst}{Vtot} \right)$$

And multiplying both the members for *Vtot/Vx*:

$$h \cdot \frac{Vtot}{Vx} = K \cdot \left(Cx + Cst \cdot \frac{Vst}{Vx} \right)$$

Than on the basis of the (1) and of the (2):

$$h \cdot d = K \cdot Cx + K \cdot Ca$$

By setting $h = 0$, the equation becomes::

$$0 = Cx + C'a$$

or:

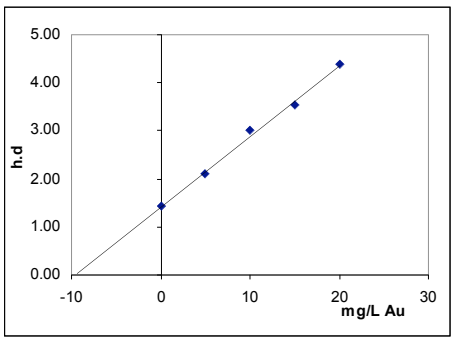
$$Cx = -C'a$$

where $-C'a$ is the negative abscissa intercept and correspond to the unknown concentration, *Cx*.

Example: Analysis of Au in a gold plating bath by DPV (cathodic scanning).

Sample volume (Vx): 10 mL
Supporting electrolyte volume (Vr): 2 mL
Concentration of Au (III) standard solution (Cst): 1000 mg/L
Table of the addition and the peak height *(Ep* ≅ 600 mV):

add. Vol. µL	add. Conc. mg/l	p. height. µA	Dilution f.	Correct ht.
0	0	1.18	1.200	1.42
50	5	1.74	1.205	2.10
100	10	2.48	1.210	3.00
150	15	3.01	1.215	3.55
200	20	3.59	1.22	4.38



Equation of the straight line:
y = 1,416 + 0,150 · x
where: $y = h \cdot d$ and $x = Ca$ *(mg/L)*
Abscissa intercept: - 9,4 mg/L
Than the analyte concentration is:
Cx = 9,4 mg/L

8.3 – Single standard addition method

The single standard addition is used as survey method because is less accurate than the previous one.

Prepare an aliquot of sample (*Vx*) and add another aliquot of supporting electrolyte (*Vr*). Register the voltammogram and measure the peak height (*hx*), after add a single aliquot *(Va)* of standard solution, register a new voltammogram and measure the peak height (*ha)*.

The concentration (*C*) of the analyte in the solution, before the addition is:

$$C = \frac{Cx \cdot Vx}{Vx + Vr}$$

where • *Cx* is the concentration of the analyte in the sample

While, after the addition of the standard solution the new concentration *(Ca)* becomes*:*

$$Ca = \frac{Cx \cdot Vx}{Vx + Va + Vr} + \frac{Cst \cdot Va}{Vx + Va + Vr}$$

where • *Cst* is the concentration of standard solution

Since the relationship between conc. and peak height is proportional we can write :

$$\frac{C}{hx} = \frac{Ca}{ha}$$

and than, making the appropriate substitutions, the preceding equation becomes:

$$\frac{Cx \cdot Vx}{hx \cdot (Vx + Vr)} = \frac{Cx \cdot Vx + Cst \cdot Va}{(Vx + Va + Vr) \cdot ha}$$

From which we obtain:

$$Cx = \frac{Cst \cdot hx}{ha + (ha - hx) \cdot \dfrac{Vx + Vr}{Va}} \cdot \left(1 + \frac{Vr}{Vx}\right)$$

If the volume of the standard addition is negligible as regards to the total volume, the equation becomes simpler:

$$Cx = \frac{Cst \cdot hx}{(ha - hx)} \cdot \frac{Va}{Vx}$$

Example: Analysis of Au in a gold plating bath by DPV (cathodic scanning).
Sample volume (Vx): 10 mL
Supporting electrolyte volume (Vr): 2 mL
Concentration of Au (III) standard solution (Cst): 1000 mg/L
Addition volume, (Va): 50 μL
Sample peak height (hx): 1,18 μA
Peak height after the addition (ha): 1,74 μA

Au Concentration in the sample:

$$Au(mg/L) = \frac{1000\,(mg/L) \cdot 1{,}18}{1{,}74 + (1{,}74 - 1{,}18) \cdot \dfrac{10 + 2}{0{,}05}} \cdot \left(1 + \frac{2}{10}\right) = 10{,}4\,(mg/L)$$

Or, using the simplified equation

$$Au(mg/L) = \frac{1000\,(mg/L) \cdot 1{,}18 \cdot 0{,}05}{(1{,}74 - 1{,}18) \cdot 10} = 10{,}5\,(mg/L)$$

9. STEPS IN A VOLTAMMETRIC ANALYSIS

Sample treatment

For a voltammetric analysis the sample has to be a solution. If the sample is solid, it has to be dissolved in a proper way. Liquids with complex matrix and low soluble solids are to be digested or extracted. Rarely, it is not necessary to digest complex matrices, i.e. the analysis of ascorbic acid in fruit juice can be performed without any treatment.

At the end of any treatment the obtained solution has to have the following characteristics:

- No suspended solids. If present they have to be eliminated by filtering or centrifuging. The separate solid can be analysed separately.
- No colloids. Colloids compete with electrochemical processes, sometime stopping them or keeping them not reproducible. Often a simple oxidising treatment with UV lamp is sufficient to overcome this interference.
- No surfactants, because they also can stop the electrochemical processes or decreasing the sensitivity of the method. Also in this case a simple oxidising treatment with UV lamp is sufficient to overcome this interference.
- pH between 1 and 10 (also 12 in NaOH is not present) and atmosphere neither too much oxidising nor too much reducing, otherwise the mercury electrode can react or give raise to a very noisy signal. This latter phenomena effect also solids electrode. Digested solutions have to be accurately neutralised or buffered. It is necessary also to boil the digested solution until the nitrous or hydrogen peroxide not react or other vapours are removed from solution.
- If the analysis is performed in a solvent different from water, when possible, an electrolyte has to be added increasing the electrical conductivity of the solution

Addition of the supporting electrolyte

Every analysis has to be performed using a typical supporting electrolyte. The characteristics of this solution is described in the manual or reported in literature.

Bubbling of the solution with nitrogen

Oxygen is always present in solution and give rise to 2 voltammetric peaks; the first at 0 V and the other one at 1 V. This gas has to be eliminated from the solution before the analysis, by a prolonged bubbling of nitrogen. Lower is the analyte concentration to be found, greater has to be the bubbling time.

Pause (delay)

Solution has to be leave quiescent stopping after the bubbling.

Electrode cleaning

- Mercury electrode: some drops are discharged
- Solid electrode: an inverse scanning has to be performed

Scanning and registration of the sample voltammogram

Addition of standard solution of analyte

Scanning and registration of the voltammogram after the addition (the process is repeated 2-8times)

Measure of the all peak (or wave) heights

Drawing the graph

Reading of the unknown concentration

10. TRACE ANALYSIS OF METALS

10.1 – Cleaning procedure for glassware and working area

Trace analysis need sophisticated and very sensitive instruments. Results cannot reach the same reproducibility as for high concentration analysis. In fact, typical percentages of standard deviation of results in trace analysis are in the range of 15-20%.

Moreover, lead, zinc, iron and sodium are environmental pollutants. These metals are very widespread and it is very difficult to find any material completely lacking in these metals. Distilled and deionized water, acids and chemicals normally used for the preparation of solutions or for the sample treatment are anyway polluted with these metals. A also in the air powder is polluted and some time some particle of pollutants can fall down in sample or standard solutions, before or during the analysis.

For these reasons is mandatory to adopt strict cleaning procedure, especially for the analysis of lead, zinc, iron and sodium. The best strategy to avoid errors consist in:

- the cleaning of the glassware for the analysis,
- the analysis of the blank solutions
- the control of the analytical data.

Finally, the analysis of mercury has to be performed with dedicated glassware to avoid any pollution. (don't use the same glassware used for the analysis with mercury drop or film electrode). Stock gold electrode and cells far from mercury and accurately clean Pt and reference electrodes, magnetic rod and the top of the cell. Obviously analyse Pt using a glassy carbon reference electrode (instead a Pt one…)

10.2 – Glassware cleaning

Stock the glassware (volumetric flasks, pipette and bottles) dedicated to the preparation of standard solutions far from the one for the sample treatments.

Clean the glassware with copious distilled water, then with 1-2% HNO_3 and finally, again with copious distilled water.

Dip the cells in 1-5% HNO_3 at the end of the analysis till a new analytical session. Don't use the same cell for the following analysis.

Accurately clean the instrument and the working area (pay attention to the powder falling down from old fume hood….)

Copiously wash the electrodes and the top of the cell at the end of the analysis.

Preferably start with low concentration sample analysis and continue with high concentration ones.

11. MAINTENANCE AND CLEANING

11.1 - Mercury drop electrode

- **At the end of each analysis**, wash the capillary with distilled water; take care to avoid to aim the water flow directly on the tip of the capillary. Clean while the mercury valve (function n. 6 of the supporting block: Start to open mercury valve). Pay attention to avoid the water flows into the capillary and to avoid the scattering of mercury drops on the working area.
- **At the end of a working day**, accurately wash the capillary, dry it and leave the capillary with a drop dropping from the tip (use function n. 6 of the supporting block: Start to open mercury valve) in a clean and dry cell**.** Check that there are not salt deposits nearby the tip of the capillary.
- **During long periods of inactivity** it is better to make a scanning with an indifferent supporting electrolyte (i.e. 0.1 M KCl) every week (or two) avoiding the stagnation of mercury in the capillary.
- **If the capillary is obstructed** , or if the current don't flow in the circuit, or if the noise of the signal is very high, try to set it free applying the vacuum pump at the end of the capillary. When the maximum of the vacuum is reached, open the mercury valve (use function n. 6 of the supporting block: Start to open mercury valve). Aspirate some mercury drop and disconnect the tube of the vacuum pump (remember: don't close the water tap before disconnecting the tube). If the problem cannot to be solved, change the capillary.
- **Stock the exhausted mercury** in a strictly closed polythene bottles, under a water layer. Don't leave the bottle open !
- **Mercury waste** can occur during the maintenance procedure or during the replacement of the capillary. Due to the mercury toxicity and vapour pressure the scattered drops must be recovered using a vacuum pump and the working area must be cleaned using proper devices (cleaning kits are available).

11.2 - Gold, platinum and glassy carbon electrodes

Main sources of surface pollution for solid electrodes are fat (or hydrophobic compounds), arising typically from the fingers of the operator. Clean solid electrodes carefully rubbing the active surface with soft paper imbibed with acetone or thin abrasive paste (i.e. 0.3 μ alumina powder in distilled water). Rinse finally with distilled water and check that the electrode surface is mirrored using a lens.

Deep incrusted electrodes in 2 M HNO_3 and rinse with distilled water.

After the cleaning and, anyway, every time a new electrode is used, make a cathodic cleaning at a potential which can discharge any metallic impurity. It's better to make the cathodic cleaning also before each potential scanning, during an analysis.

Store clean and dry electrodes at the air, without any further particular care.

Quality of the electrode surface can be controlled analysing a blank or a reference solution.

11.3 - Auxiliary platinum electrode

The auxiliary platinum electrode has to be cleaned and stored just like the other solid electrodes. The cathodic cleaning is no necessary.

11.4 - Reference electrode

Reference electrode contains a concentrated solution of a salt (normally KCl) which ions have the same mobility to diminish the junction. Those solution is, of

course, saturated of AgCl. During analysis is mandatory to check that the ions of the sample don't interfere with the ones present in the internal reference electrode solution. It could happen in the following situations:

analysis of traces of silver

analysis of chloride

analysis of sulphide, bromide and iodide that can react with Ag developing insoluble salts and obstructing the diaphragm and, at the end, increasing the junction potential.

These problems can be overcome using a double junction reference electrode, containing a KNO_3 solution as a final junction.

Moreover the level of the internal solution of the reference electrode has to be higher than the level of the external sample solution in the cell assuring a very low flow of solution from the inner toward the outer (and not vice and versa). In this way the pollution of the internal solution of the reference electrode is reduced and the potential readings are more reproducible.

When a diaphragm is obstructed (that means that the peak position fluctuate among different scanning) it is better to change completely the glassy body of the electrode.

After periods of inactivity the electrode cover itself by a white layer of KCl. Simply wash the electrode with distilled water and if necessary add more 3 M KCl internal solution.

11.5 - Cells

Clean glass and Teflon cells using distilled water or acid solution.

Dip the cells in 5 – 10% HNO_3 for 2 –3 days before the trace analyse of metals.

12. PREPARING FILM ELECTRODES

12.1 - Mercury film on glassy carbon electrode

- Dip the clean glassy carbon electrode in a 800 mg/l in 1.3 M HC1 Hg^{2+} solution, or in a 1000 mg/l Hg^{2+} solution for AA Spectrophotometry
- Bring the electrode potential at -1100 mV for 2 minutes
- Rinse with distilled water.
- Never leave the electrode to dry
- Don't touch the Hg film for any reason film
- Check if the surface of the film is uniform, grey and opaque before the use. If not, clean the electrode using soft paper, rinse with water and depose another film.
- Store the Hg film electrode in distilled water until next analysis. Before starting a new series of analysis, check the electrode performances (see KCl test).
- After the first time it is necessary to run a series of scanning before the electrode rise to a complete settlement.

Maintenance and cleaning of mercury film electrode on glassy carbon

Store the mercury film electrode dipped in distilled water. When in use, leave it on air only for short periods.

When the film is clearly scratched or striped, clean it with soft paper, rinse with distilled water and depose e new film.

12.2 - Gold film electrode on glassy carbon

- Dip the clean glassy carbon electrode in a Au^{3+} solution (1000 mg/l in 1 M HC1)
- Bring the electrode potential at -400 mV for 2 minutes i.
- Rinse with distilled water.
- Never leave the electrode to dry
- Don't touch the Au film for any reason film
- Check if the surface of the film is uniform, gilded before the use. If not, clean the electrode using soft paper, rinse with water and depose another film.
- Store the Au film electrode in distilled water until next analysis. Before starting a new series of analysis, check the electrode performances.

Maintenance e cleaning of gold film electrode

Store the gold film electrode dipped in distilled water. When in use, leave it on air only for short periods.

When the film is clearly scratched or striped, clean it with very thin abrasive paste on soft paper, rinse with distilled water and depose e new film.

13. REAGENTS FOR TRACE ANALYSIS

Use only reagents for trace analysis grade. If this is not possible analyse blank solution before sample analysis.

13.1 – Preparing standard solutions

Buy directly the concentrated standard solution of metals (1 g/l of the analyte). The solution for AAS are generally suitable.

Prepare standard solutions anions or organic compounds starting from a pure, analytical grade substance. Dry the substance in a oven at 110°C eliminating the humidity if this procedure do not compromise the stability of the compound.

Prepare diluted standard solutions starting from the concentrated ones. Add 1-2% HNO_3 unless it is differently specified.

Throw away the standard solutions less than 100 mg/l at the end of an analytical session.

13.2 – Preparing supporting electrolytes

Prepare supporting electrolytes using pure, analytical grade reagents. It's better to check the presence of the analyte in the blank, before starting the analysis.

The most common supporting electrolyte and buffer are the following:

0.1 M EDTA solution
Dissolve 37.2 g of EDTA-Na_2 in 1 l of distilled water, in a volumetric flask.

0.1 or 1 M HCl solution
Dilute 8.2 (or 82) ml of 37% HCl in 1 l of distilled water, in a volumetric flask.

0.1 or 1 M KCl solution
Dissolve 7.5 (o 75) g of KCl in 1 l of distilled water, in a volumetric flask.

0.1 M KCNS solution
Dissolve 9.72 g of KCNS in 1 l of distilled water, in a volumetric flask.

0.1 o 1 M KNO_3 solution
Dissolve 10 (o 100) g of KNO_3 in 1 l of distilled water, in a volumetric flask.

0.1 M LiCl / LiOH solution
Dissolve 2.4 g of LiOH and 4.3 g of LiCl in 1 l of distilled water, in a volumetric flask.

1 M NaF solution
Dissolve 42 g of NaF in 1 l of distilled water, in a volumetric flask. Heat if necessary.

0.1 M acetate buffer solution at pH 4.5 (CH_3COONa / CH_3COOH)
Dissolve 8.2 g of anhydrous CH_3COONa (or 13.6 g of $CH_3COONa{\cdot}3H_2O$) in 800 ml of distilled water. Add 5.75 ml of glacial CH_3COOH. Check the pH. Bring to mark volume in a 1 l volumetric flask with distilled water.

0.1 M ammonia buffer solution at pH 9.4 (NH_4Cl / NH_3)
Dissolve 5.4 g of NH_4Cl in 900 ml of water. Add 6.9 ml of 26% NH_3. Check the pH. Bring to mark in a 1 l volumetric flask with distilled water.

0.1 M borate buffer solution at pH 9.5 (NaH_2BO_3 / H_3BO_3)
Dissolve 5.1 g of H_3BO_3 in 900 ml of water. Add 2 g of NaOH. Check the pH. Bring to mark in a 1 l volumetric flask with distilled water.
Britton Robinson buffer solution at various pH
Common solution
Mix:
- 100 ml of 0.04 M H_3BO_3 (2.04 g / 100 ml) aqueous solution.
- 100 ml of 0.04 M CH_3COOH (2.3 ml of glacial CH_3COOH / 100 ml) aqueous solution.
- 100 ml of 0.04 M H_3PO_4 (2.8 ml of 85% H_3PO_4 / 100 ml) aqueous solution.

Solutions at desired pH:
Bring the preceding solution at the desired pH Using a 0.2 M NaOH solution.

0.2 M ammonia citrate buffer solution at pH 3 (ammonia citrate / citric acid)
Dissolve 42.5 g of mono hydrate citric acid in 800 ml of water. Add 26% NH_3 until pH 3. Bring to mark in a 1 l volumetric flask with distilled water.

0.2 M sodium citrate buffer solution at pH 3 (sodium citrate / citric acid)
Dissolve 42.5 g of mono hydrate sodium citrate in 800 ml of water. Add 20% NaOH until pH 3. Bring to mark in a 1 l volumetric flask with distilled water.

0.2 M phosphate buffer solution at pH 6.8
Dissolve 24 g of $NaH_2PO_4{\cdot}H_2O$ in 800 ml of water. Add 85% H_3PO_4 until pH 6.8. Bring to mark in a 1 l volumetric flask with distilled water.

0.2 M ammonia tartrate buffer solution at pH 9 (ammonia tartrate / tartaric acid)
Dissolve 300 g of tartaric acid in 800 ml of water. Add 26% NH_3 until pH 9. Bring to mark in a 1 l volumetric flask with distilled water.

0.2 M sodium tartrate buffer solution at pH 9 (sodium tartrate / tartaric acid)
Dissolve 300 g of tartaric acid in 800 ml of water. Add 20% NaOH until pH 9. Bring to mark in a 1 l volumetric flask with distilled water.

0.3 M TEA / 0.1 M KOH buffer solution
Dissolve 45 g of TEA (triethanolamine) and 5.6 g of KOH in 1 l of distilled water, in a volumetric flask.

0.3 M TEA / 0.1 M NaOH buffer solution
Dissolve 45 g of TEA (triethanolamine) and 8 g of NaOH in 1 l of distilled water, in a volumetric flask.

14. CHECKING THE POLAROGRAPH PERFORMANCES

14.1 - 0.1 M KCl test

The following test allows to check if the instrument (particularly the capillary) works correctly and maintains the his performances for a long the time.

Activate this procedure immediately, just before the instrument reach your laboratory, collecting in this way an "historical" data series as reference.

Reagents
- 10 mg/l Cadmium standard solution. Prepare a fresh solution before each analysis, starting from a 1000 mg/l standard solution.
- 0.1 M KCl checking solution. Dissolve 15 g of KCl in 2 litres of 1% HNO_3 (20 ml of 65% HNO_3 in 2 l of distilled water), in a volumetric flask, add 100 µl of Cd standard solution (1 g/l). Store this solution in a polythene bottle. Use the same solid KCl, stored in a polythene bottle, if prolonged check are needed.

Procedure
Every time an analytical series start (it means each day, or week…) pour 10 ml of checking solution in the cell. Bubble nitrogen for 5 minutes. Analyse Cadmium using single (quicker) or multiple (longer) standard addition (100 µl of 10 mg/1 Cd each addition).
Prepare a control chart after 10 – 15 analysis,.

Results control
- The peak position has to be constant, into a specific confidential range. Use statistics and control chart for this purpose.
  If the peak position significantly varies check the conditions of the reference electrode
- During the time, the results of the analysis have to agree to each other, into a confidential range. Use statistics and control chart for this purpose.
  If the results do not agree to each other verify the following:
  - *quality of the solutions (KCl and Cd standard solutions)*
  - *the conditions of the capillary*
  - *the cleaning procedure for the glassware, the instrument and the operator*

  Warning ! Strong smokers have the finger dirty of high level of Cadmium. If necessary, change the analyte of the checking procedure (avoid anyway lead, iron and zinc because they are environmental pollutant anyway !)