Electroanalytical methods

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Electrochemical methods

In electrochemical methods of instrumental analysis, one measures voltage (potential) and/or current signals. A variety of electrochemical methods have been developed, out of which we are going to discuss the following ones only:

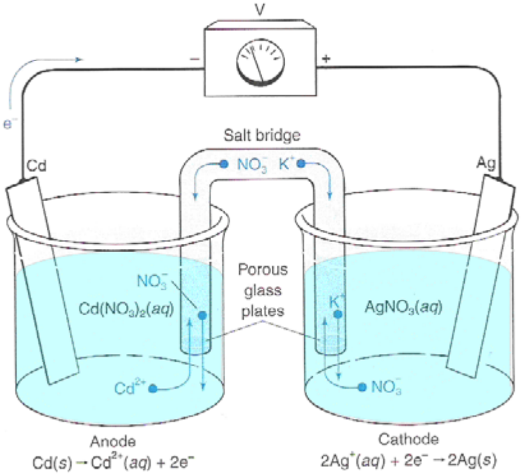
- potentiometry
- conductometry
- coulombmetry
- electrogravimetry
- voltammetry (polarography/amperometry/stripping v.)

The discussion of electrochemical methods assumes the knowledge of redox reactions, the Nernst equation, galvanic cells and electrodes… so first we are going to review these notions briefly.

Electrodes

Electrodes are interfaces between metallic and electrolyte conductors of electricity. Electrical conduction in metals means the transportation of electrons, whereas cations and anions are the mobile charge carriers in electrolytes. Thus, any instrumental setup, which measures current and/or voltage signals, neccessarily will have an interface between metallic conductors (wires) and electrolytes.

Electrochemical (galvanic) cells



$$Cd(s)\ |\ Cd(NO_3)_2(aq)\ \|\ AgNO_3(aq)\ |\ Ag(s)$$

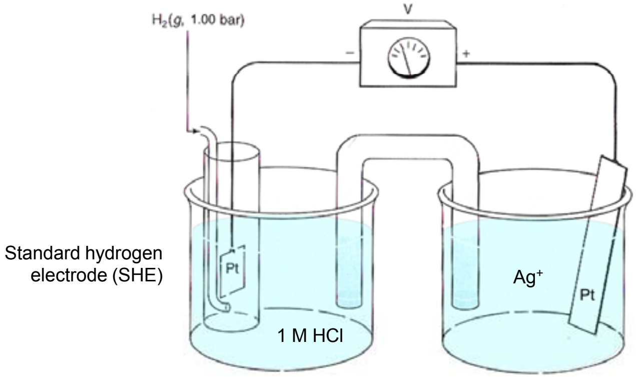
Nernst equation, electromotive force

$$Nernst\ equation:\ E = E_0 + \frac{R \cdot T}{n \cdot F} \cdot \ln \frac{A_{oxidized}}{A_{reduced}} = E_0 - \frac{R \cdot T}{n \cdot F} \cdot \ln \frac{A_{reduced}}{A_{oxidized}}$$

$$At\ 298K\ and\ in\ dilute\ solutions:\ E = E_0 + \frac{0.0591}{n} \cdot \lg \frac{c_{oxidized}}{c_{reduced}}$$

$$U = EMF = E_{cathode} - E_{anode}$$

How can a galvanic cell be used for analysis?



$$U = E_{cathode} - E_{anode} = \left(E_{0,Ag^+} + \frac{0.0591}{1} \cdot \lg c_{Ag^+} \right) - 0$$

$$\lg c_{Ag^+} = \frac{U - E_{0,Ag^+}}{0.0591} \rightarrow c_{Ag^+} = 10^{\left(\frac{U - 0.799}{0.0591}\right)}$$

Potentiometry

Reference electrodes

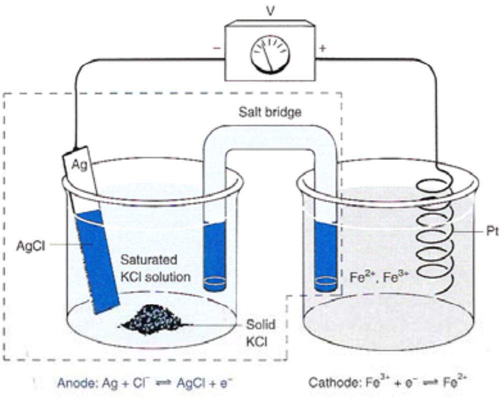
Most common types of ***reference electrodes***:

- standard hydrogen electrode (SHE)
- Ag/AgCl electrode
- Hg_2Cl_2 (calomel) electrode

The latter two types are more frequently used in analytical chemistry, because they have a more practical construction.

Ag/AgCl reference electrode

Equations governing the potential



e.g. a cell assembled to determine the $[Fe^{3+}]/[Fe^{2+}]$

$$Ag^+ + e^- \leftrightarrow Ag_{(s)}$$

$$E = E_{0,Ag^+} + \frac{0.0591}{1} \cdot \lg c_{Ag^+}$$

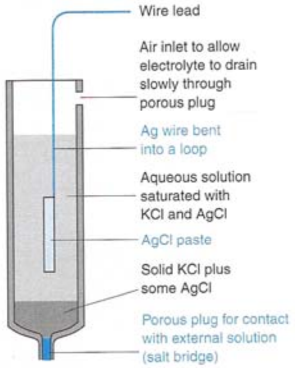
$$L_{AgCl} = c_{Ag^+} \cdot c_{Cl^-}$$

$$E = E_{0,Ag^+} + 0.0591 \cdot \lg \frac{L_{AgCl}}{c_{Cl^-}}$$

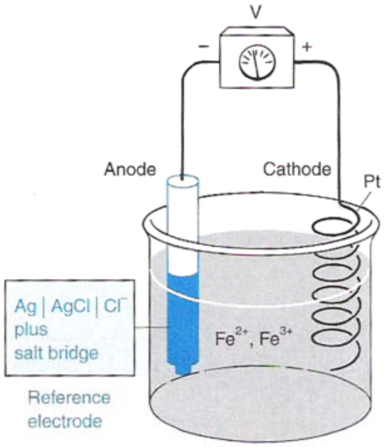
$$E = E_0' - 0.0591 \cdot \lg c_{Cl^-}$$

Ag/AgCl reference electrode

A practical construction



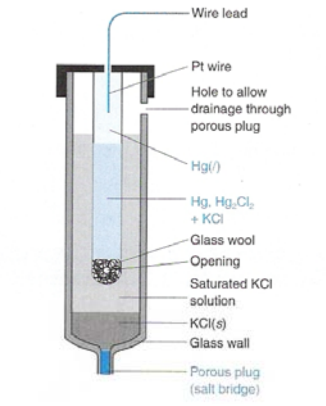
a compact Ag/AgCl reference electrode



a more practical cell assembly for the determination of $[Fe^{3+}]/[Fe^{2+}]$, with a compact reference electrode

Calomel reference electrode

Equations governing the potential



compact Hg_2Cl_2 reference electrode

$$Hg_2^{2+} + 2e^- \leftrightarrow 2Hg_{(s)}$$

$$E = E_{0,Ag^+} + \frac{0.0591}{2} \cdot \lg c_{Hg_2^{2+}}$$

$$L_{Hg_2Cl_2} = c_{Hg_2^{2+}} \cdot c_{Cl^-}^2$$

$$E = E_{0,Hg_2^{2+}} + \frac{0.0591}{2} \cdot \lg \frac{L_{Hg_2Cl_2}}{c_{Cl^-}^2}$$

$$E = E_0' - 0.0591 \cdot \lg c_{Cl^-}$$

Calomel electrodes prepared with	Potential	Temperature coefficient
0.1 M KCl	+0.3335 V	-0.06 mV/°C
1.0 M KCl	+0.2810 V	-0.24 mV/°C
saturated KCl	+0.2420 V	-0.65 mV/°C

Indicator electrodes

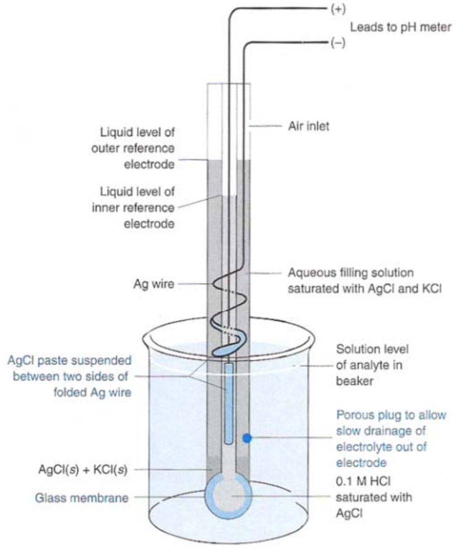
Indicator electrodes are electrodes, whose potential indicates the quantity (concentration) of an analyte species, that is the potential is a function of the analyte concentration. There are three main groups of indicator electrodes:

- metal electrodes
- ion-selective electrodes
- compound (composite) electrodes

Metal electrodes are large surface inert metals (Pt, Ag, Au, etc.) which do not participate in direct chemical reactions. These electrodes simply provide surface for the electrochemical reactions, and transmit electrons to or from species in solution.

In ***ion-selective electrodes***, the selective binding of one type of ion to a membrane generates an electric potential.

Glass (pH) indicator electrode
Internal construction



The specialty is the composition of the thin (ca. 100 μm) glass membrane at the tip of the electrode (alumino-silicate containing Na, Ca and lanthanide ions). Its potential will depend on the c_{H^+} of the solution it is brought in contact with:

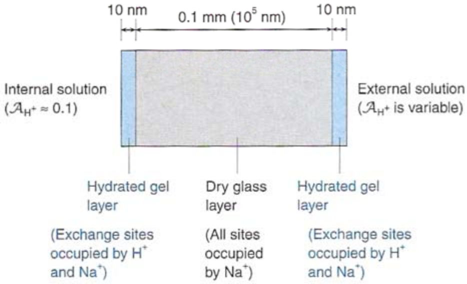
$$E = E_0 + 0.0591 \cdot \lg c_{H^+}$$

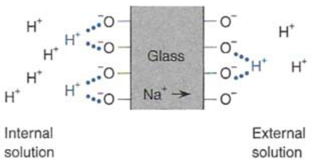
$$E = E_0 - 0.0591 \cdot pH$$

Glass (pH) indicator electrodes
Functioning

Glass membrane selectively binds H⁺

$$\underbrace{\mathrm{Ag}(s)\,|\,\mathrm{AgCl}(s)\,|\,\mathrm{Cl}^-(aq)}_{\text{Outer reference electrode}}\;||\;\underbrace{\mathrm{H}^+(aq,\text{ outside})}_{\text{H}^+\text{ outside glass electrode (analyte solution)}}\,\vdots\,\underbrace{\mathrm{H}^+(aq,\text{ inside})}_{\text{H}^+\text{ inside glass electrode}},\;\underbrace{\mathrm{Cl}^-(aq)\,|\,\mathrm{AgCl}(s)\,|\,\mathrm{Ag}(s)}_{\text{Inner reference electrode}}$$





Glass (pH) indicator electrodes

Alkaline and acid errors

In reality, the glass electrode is not fully selective towards H^+ ions. It also responses to the concentration of alkaline elements (inherently present in glass):

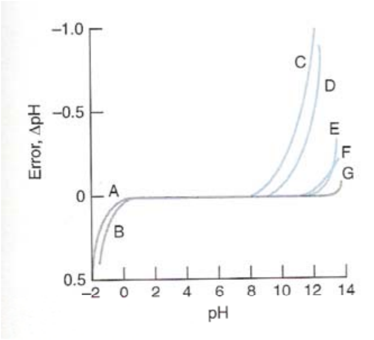
$$E = E_0 + 0.0591 \cdot \lg\left(c_{H^+} + k_1 \cdot c_{Na^+} + k_2 \cdot c_{K^+} + etc.\right)$$

where k constants are the ***selectivity coefficients***. For good glass electrodes, these coefficients are 0.001 or less. When the $c_H{}^+$ is low, and say $c_{Na}{}^+$ is high, then the measured pH is lower than the real one. This is called the ***alkaline error***.

In strong acids, when $c_H{}^+$ is very high, then the measured pH is higher than the actual one. It is so probably because the glass surface is saturated and can not take on more H^+. This error is called the ***acid error.***

Glass (pH) indicator electrodes

Practicalities

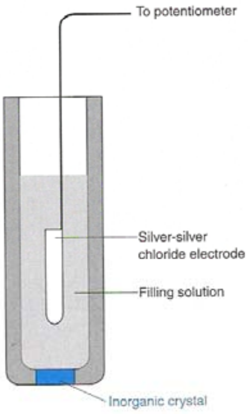


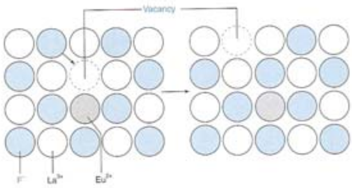
Acid and alkaline errors of some glass electrodes. A: Corning 015, H_2SO_4. B: Corning 015, HCl. C: Corning 015, 1 M Na^+. D: Beckman-GP, 1 M Na^+. E: L & N Black Dot, 1 M Na^+. F: Beckman Type E, 1 M Na^+. G: Ross electrode.

Glass electrodes are very fragile, need to be recalibrated frequently (every 2 hours), should not be left to dry out and show strong tendency to age. Due to the alkaline and acid errors as well as other effects, pH measurements by glass electrodes are accurate only to ca. ±0.02 pH units.

Solid-state membrane indicator electrodes
Internal construction

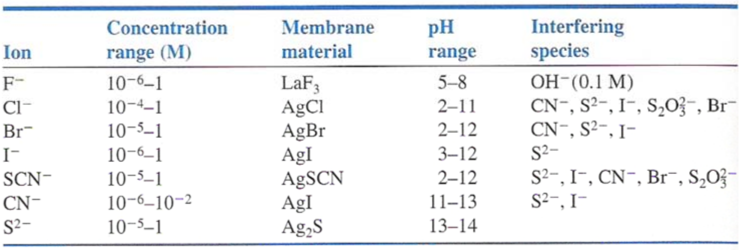
Solid-state membrane electrodes are based on inorganic crystals. For example, the common F^- selective electrode contains LaF_3 crystals. All crystals adsorb their own ions best, but this can be further facilitated by doping the LaF_3 with EuF_2, thereby creating vacancies. Adsorption will then cause a build-up of a potential on the membrane.





Solid-state membrane indicator electrodes
Interferences

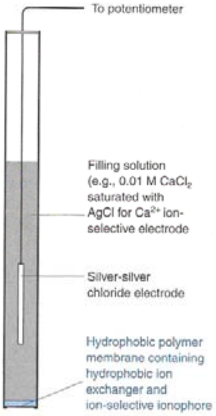
Other compositions are also used (e.g. see below). Analogous to glass electrodes, solid-state membrane electrodes also have interferences – such ions, which have high affinity to bond with the metal in the crystal lattice also generate response.



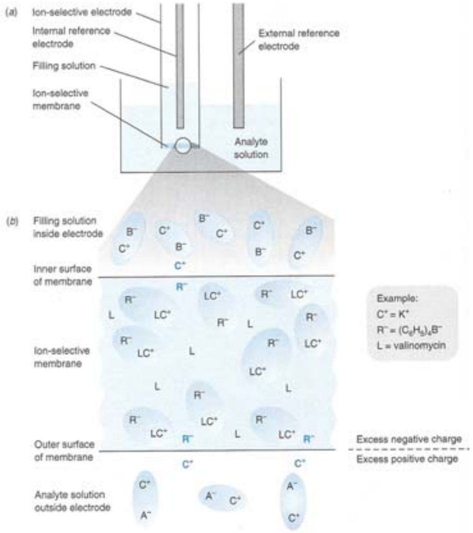
Ion	Concentration range (M)	Membrane material	pH range	Interfering species
F^-	10^{-6}–1	LaF_3	5–8	OH^- (0.1 M)
Cl^-	10^{-4}–1	AgCl	2–11	CN^-, S^{2-}, I^-, $S_2O_3^{2-}$, Br^-
Br^-	10^{-5}–1	AgBr	2–12	CN^-, S^{2-}, I^-
I^-	10^{-6}–1	AgI	3–12	S^{2-}
SCN^-	10^{-5}–1	AgSCN	2–12	S^{2-}, I^-, CN^-, Br^-, $S_2O_3^{2-}$
CN^-	10^{-6}–10^{-2}	AgI	11–13	S^{2-}, I^-
S^{2-}	10^{-5}–1	Ag_2S	13–14	

Liquid-based membrane indicator electrodes
Internal construction

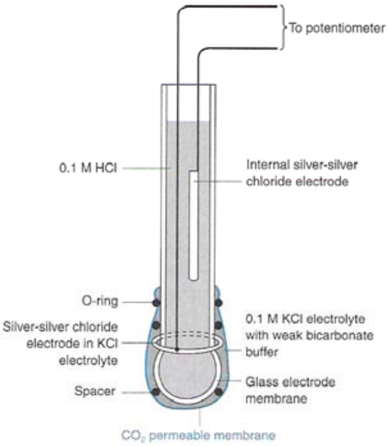
Ion-selective electrodes can also be built using liquids. In this case, the ion-selective membrane is a hydrophobic organic polymer impregnated with a viscous organic solution containing an ion-exchanger type compound (for charge neutrality) and a neutral ligand that selectively binds the analyte ion. The analyte ion moves out from the membrane until a build-up of a positive excess charge causes the transport to stop. This leads to a potential across the membrane, which can be calibrated to signal the analyte concentration.



Liquid-based membrane indicator electrode
Functioning - a closer look



Compound indicator electrodes
Functioning - a closer look



Compound (composite) ion-selective electrodes can also be constructed around e.g. a glass electrode. For example, gases like CO_2, NH_3, SO_2, H_2S, etc. can be analyzed via their pH-changing effect on an internal electrolyte by diffusing through a gas-permeable membrane.

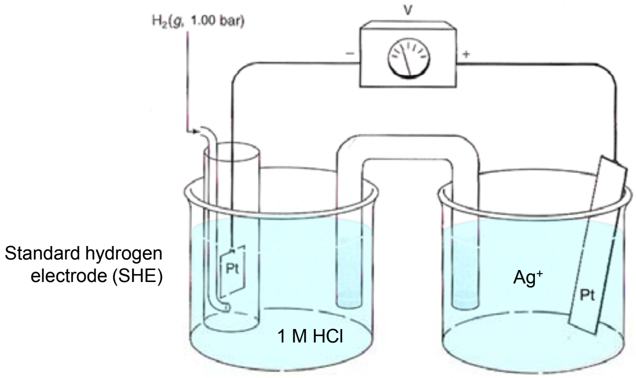
Enzyme electrodes are another class of compound electrodes.

Potentiometry

Potentiometry involves the measurement of the cell potential, thus it measures the potential difference between a reference and an indicator electrode. There are two basic kinds of potentiometry:

- direct potentiometry
- indirect potentiometry (potentiometric titration or calibration)

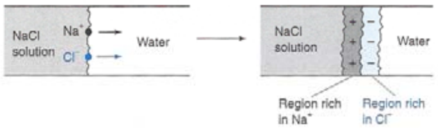
Direct potentiometry
Application of the Nernst equation



$$U = E_{cathode} - E_{anode} = \left(E_{0,Ag^+} + \frac{0.0591}{1} \cdot \lg c_{Ag^+} \right) - 0$$

$$\lg c_{Ag^+} = \frac{U - E_{0,Ag^+}}{0.0591} \quad \rightarrow \quad c_{Ag^+} = 10^{\left(\frac{U-0.799}{0.0591}\right)}$$

Direct potentiometry
Junction (diffusion) potential



The standard potential of a reference electrode is only correct if there is no liquid junction potential formed at the porous plug between the filling solution and the sample solution. At this junction, a potential difference will develop as a result of the tendency of the smaller and faster ions to move across the boundary more quickly than those of lower mobility. These potentials are difficult to reproduce, tend to be unstable, and are seldom known with any accuracy; so steps must be taken to minimise them, especially in direct potentiometry.

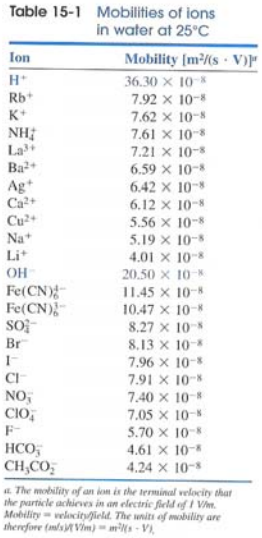


Table 15-1 Mobilities of ions in water at 25°C

Ion	Mobility [m^2/(s · V)][a]
H^+	36.30×10^{-8}
Rb^+	7.92×10^{-8}
K^+	7.62×10^{-8}
NH_4^+	7.61×10^{-8}
La^{3+}	7.21×10^{-8}
Ba^{2+}	6.59×10^{-8}
Ag^+	6.42×10^{-8}
Ca^{2+}	6.12×10^{-8}
Cu^{2+}	5.56×10^{-8}
Na^+	5.19×10^{-8}
Li^+	4.01×10^{-8}
OH^-	20.50×10^{-8}
$Fe(CN)_6^{4-}$	11.45×10^{-8}
$Fe(CN)_6^{3-}$	10.47×10^{-8}
SO_4^{2-}	8.27×10^{-8}
Br^-	8.13×10^{-8}
I^-	7.96×10^{-8}
Cl^-	7.91×10^{-8}
NO_3^-	7.40×10^{-8}
ClO_4^-	7.05×10^{-8}
F^-	5.70×10^{-8}
HCO_3^-	4.61×10^{-8}
$CH_3CO_2^-$	4.24×10^{-8}

[a] *The mobility of an ion is the terminal velocity that the particle achieves in an electric field of 1 V/m. Mobility = velocity/field. The units of mobility are therefore (m/s)/(V/m) = m^2/(s · V).*

Direct potentiometry

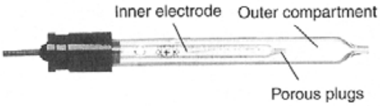
Junction (diffusion) potential – steps to prevent it

- Only use reference electrodes that have an internal filing solution that is equi-transferrent; the mobility of its ions is very similar (e.g. K^+, Cl^-/NO_3^-)
- Use of a highly concentrated internal filling solution (saturated or a 4 M KCl) ensures that the current flowing through the electrode is mainly conducted by the equi-transferrent ions.
- The construction provides a constant hydrostatic head for the internal filling solution, so there is a slow outward flow, which inhibits the backdiffusion of ions into the porous plug (an alternative is to use gel fillings).

However, the outward flow of this concentrated internal electrolyte may contaminate the sample solution and may interfere with the operation of the ion-selective (indicator) electrode. For example, problems can arise if low levels of K^+, Cl^- or Ag^+ ions are to be measured.

Direct potentiometry

Double junction reference electrodes



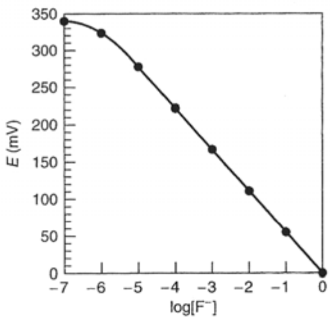
In the double junction reference electrodes, this problem is solved by introducing a second electrolyte filling and porous plug. The outer filling solution serves is chosen so that it does not contaminate the test solution with any ions which would effect the analysis. Examples:

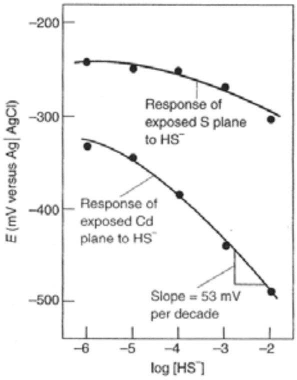
KNO_3: for Br^-, Cd^{2+}, Cl^-, Cu^{2+}, CN^-, I^-, Pb^{2+}, Hg^{2+}, Ag^+, S^{2-}, SCN^-
NaCl: for K^+
Ammonium sulphate: for NO_3^-
Magnesium sulphate: for NH_4^+

One disadvantage is that they introduce an extra interface between two electrolytes and thus give the opportunity for an extra liquid junction potential to develop…

Direct potentiometry

Performance

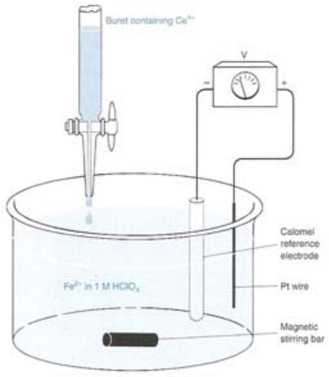




Potentiometric titration (indirect potentiometry)

By using appropriate indicator electrodes, many titration reactions can be followed by potentiometric end-point detection (instead of an indicator dye). For instance:

- acid/base titrations:
  glass electrode
- redox titrations:
  metallic (Pt) electrode
- precipitation titrations:
  ion-selective electrodes



Conductometry

Conductometry

The concept – part 1.

If two Pt electrodes are immersed into an electrolyte solution and connected to a source of electricity, the current (*I*) is determined by both the applied voltage (*U*) and electrical resistance of the solution. The ***conductance*** (*G*) of a solution is the reciprocal of the resistance (that may be calculated from Ohm's Law).

$$G = \frac{1}{R} = \frac{I}{U}$$

G is measured in Siemens (Ω^{-1}). If all this sounds to you as electrolysis, then you are right. That is why one needs to apply alternating voltage (of some kHz frequency) to measure conductivity – this way the each half cycle practically recreates what was transformed by the former one thus more or less preserving the composition of the solution.

Conductometry

The concept – part 2.

Conductance depends on the geometry of the electrodes (distance, surface area, etc.) and the quality and quantity of the ions in the electrolyte. This is expressed in the following formula:

$$G = \Theta \cdot \sum z_i c_i \lambda_i$$

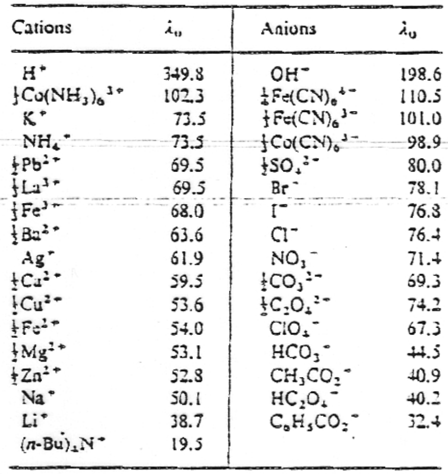
where Θ is the ***cell constant*** (representing all geometry conditions) and λ denotes the ***equivalent ionic conductance***. z_i is the charge and c_i of the ions. λ gives quantitative information concerning the relative contribution of the ions to the conductivity. Tables usually give λ_0 measured in very diluted (almost zero concentration) solution and for one unit charge.

Specific conductance is also sometimes used:

$$\kappa = \frac{G}{\Theta}$$

Conductometry

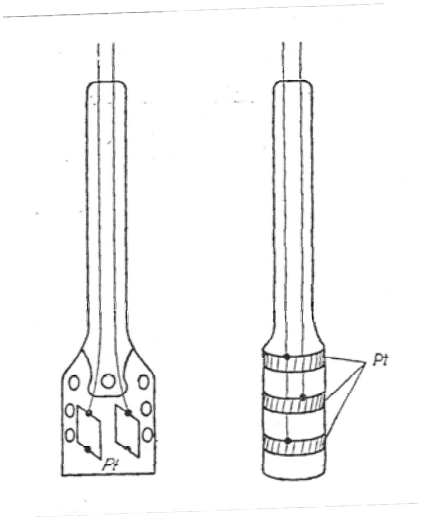
Equivalent ionic conductances (λ_0)



Cations	λ_0	Anions	λ_0
H^+	349.8	OH^-	198.6
$\frac{1}{3}Co(NH_3)_6^{3+}$	102.3	$\frac{1}{4}Fe(CN)_6^{4-}$	110.5
K^+	73.5	$\frac{1}{3}Fe(CN)_6^{3-}$	101.0
NH_4^+	73.5	$\frac{1}{3}Co(CN)_6^{3-}$	98.9
$\frac{1}{2}Pb^{2+}$	69.5	$\frac{1}{2}SO_4^{2-}$	80.0
$\frac{1}{3}La^{3+}$	69.5	Br^-	78.1
$\frac{1}{3}Fe^{3+}$	68.0	I^-	76.8
$\frac{1}{2}Ba^{2+}$	63.6	Cl^-	76.4
Ag^+	61.9	NO_3^-	71.4
$\frac{1}{2}Ca^{2+}$	59.5	$\frac{1}{2}CO_3^{2-}$	69.3
$\frac{1}{2}Cu^{2+}$	53.6	$\frac{1}{2}C_2O_4^{2-}$	74.2
$\frac{1}{2}Fe^{2+}$	54.0	ClO_4^-	67.3
$\frac{1}{2}Mg^{2+}$	53.1	HCO_3^-	44.5
$\frac{1}{2}Zn^{2+}$	52.8	$CH_3CO_2^-$	40.9
Na^+	50.1	$HC_2O_4^-$	40.2
Li^+	38.7	$C_6H_5CO_2^-$	32.4
$(n\text{-}Bu)_4N^+$	19.5		

Conductometry

Bell and ring type electrodes



Conductometry

But it is not selective... What is it good for then?

Conductivity measurements are obviously not selective. Therefore they are not very useful in direct analytical applications. But ***conductometry can be used to characterize the total electrolyte content of solutions or***, more importantly, to follow the course of a titration ***as an end-point detection method*** in simple systems. For such measurements, it is not neccessary to know the cell constant or calibrate the instrument; we are only interested in the characteristic changes in conductance around the end-point.

Acid-base and precipitation titrations can be followed by conductometric end-point detection, as in these instances the mobility and/or the concentration of the conducting ions changes at the end-point. In contrast to this, redox or complexometric titrations can not be followed by conductometric end-point detection.

Conductometric acid-base titration

Case of HCl and NaOH (strong acid – strong base)

At the start of titration:

$$\underset{\text{high }\lambda}{H^+} + \underset{\text{medium }\lambda}{Cl^-}$$

conductance is high

During titration, before the end-point:

$$\underbrace{H^+ + Cl^-}_{\text{originally present}} + \underbrace{Na^+ + OH^-}_{\text{added}} \rightarrow \underset{\text{no conductance}}{H_2O} + \underset{\substack{\text{medium }\lambda\\ \text{(NaCl dissociates fully)}}}{Na^+ + Cl^-}$$

in the reaction we loose high λ H^+ and gain only medium λ Na^+ (Cl^- "intact"), so the net change: conductance is decreasing fast

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Conductometric acid-base titration

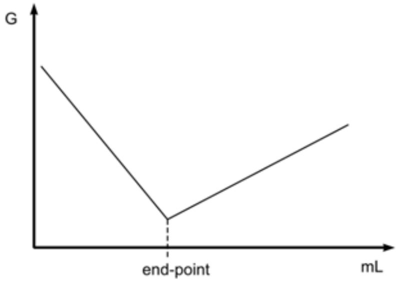
Case of HCl and NaOH (strong acid – strong base)

At the end-point:

Na^+ and Cl^- ions are present only (medium λ), plus water which is not conducting, so conductance is minimal

During titration, after the end-point:

no further chemical reaction, all added ions, but especially high λ OH^- cause that the conductance is increasing fast



Conductometric acid-base titration
Case of CH_3COOH and NH_4OH (weak acid – weak base)

At the start of titration:

$$CH_3COOH \leftrightarrow \underset{\text{medium } \lambda}{\underset{\uparrow}{CH_3COO^-}} + \underset{\text{high } \lambda}{\underset{\uparrow}{H^+}}$$

acid is weak, so dissociation is poor, therefore there are only small amounts of the above ions present: <u>conductance is low</u>

During titration, before end-point:

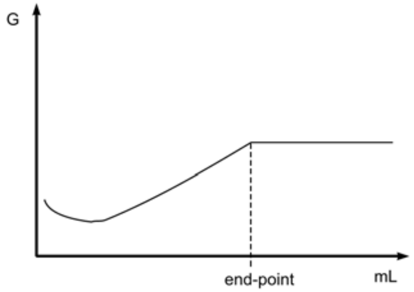
$$\underbrace{CH_3COOH}_{\text{originally present}} + \underbrace{NH_4OH}_{\text{added}} \rightarrow \underset{\text{no conductance}}{\underset{\uparrow}{H_2O}} + \underset{\text{medium } \lambda}{\underset{\nwarrow \quad \nearrow}{CH_3COO^- + NH_4^+}}$$

the reaction releases medium λ ion acetate and NH_4^+,
we also loose the little H^+ that originated from the dissociation of acetic acid, but the net change: <u>conductance is increasing</u>

Conductometric acid-base titration
Case of CH_3COOH and NH_4OH (weak acid – weak base)

At and after the end-point:

there is no further chemical reaction, and the added NH_4OH, which is a weak base (dissociates poorly) contributes to the conductance with almost nothing, so the <u>conductance does not change</u>



Conductometric precipitation titration

Case of $AgNO_3$ and LiCl

At the start of titration:

$$\underset{\text{high }\lambda}{\overset{\uparrow}{}Ag^+} + \underset{\text{high }\lambda}{NO_3^-}$$

conductance is high (above average)

During titration, before the end-point:

$$\underbrace{Ag^+ + NO_3^-}_{\text{originally present}} + \underbrace{Li^+ + Cl^-}_{\text{added}} \rightarrow \underset{\text{highly insoluble precipitate}}{\underline{AgCl}} + \underset{\text{medium }\lambda}{Li^+} + NO_3^-$$

in the reaction we loose relatively high λ Ag^+ and gain only medium λ Li^+ (NO_3^- "intact"), so the net change: conductance is decreasing

---

Conductometric precipitation titration

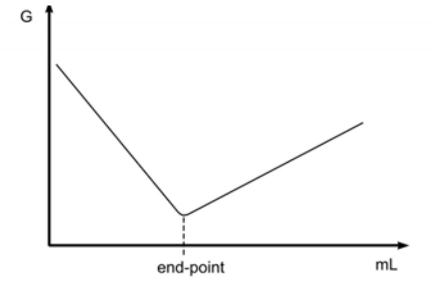
Case of $AgNO_3$ and LiCl

At the end-point:

Only the precipitate is present, which maintains a very low equilibrium concentration of Ag^+ and Cl^- ions, therefore the conductance is minimal

After the end-point:

no further chemical reaction, all added ions increase conductance



Electrogravimetry

Electrogravimetry
Fundamentals of electrolysis

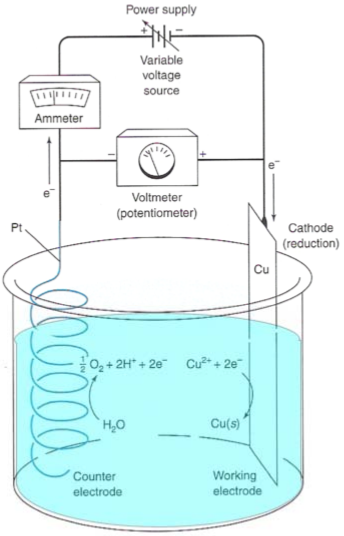
Suppose we dip Cu and Pt electrodes into a solution of Cu^{2+} and force electric current through the cell to deposit copper metal at the cathode.

Cathode: $Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$

Anode: $H_2O \rightleftharpoons \frac{1}{2}O_2(g) + 2H^+ + 2e^-$

Net reaction: $H_2O + Cu^{2+} \rightleftharpoons Cu(s) + \frac{1}{2}O_2(g) + 2H^+$

The electrode, where the reaction of interest occurs is called the ***working electrode***.



Electrogravimetry
Fundamentals of electrolysis

If a current I flows for a time t, the charge passing through the circuit is

$$Q = I \cdot t$$

and the number of moles of electrons is

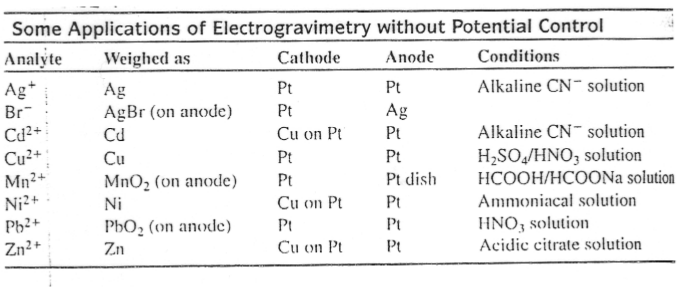
$$moles \;\; of \;\; electrons = \frac{I \cdot t}{F}$$

where F is the ***Faraday constant*** (ca. 96485 C/mol). If a reaction requires *n* electrons per molecule, the quantity reacting is

$$moles \;\; reacted = \frac{I \cdot t}{n \cdot F}$$

Electrogravimetry
The concept

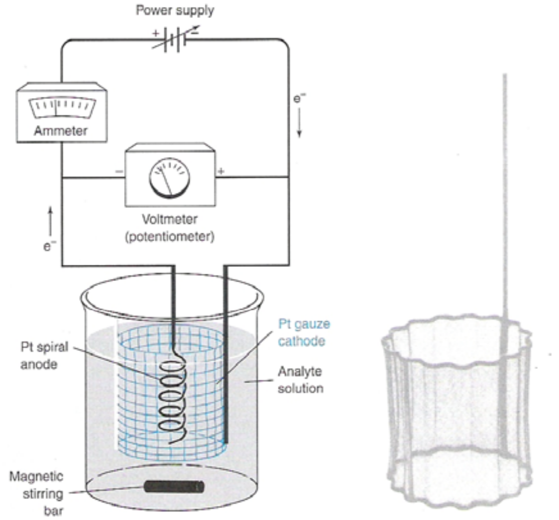
The concept of electrogravimetry is simple: a controlled electrolysis is performed, when the analyte from the sample solution is deposited onto the working electrode (either the cathode or anode) in some chemical form. The working electrode is weighed before and after the electrolysis, thus the amount and concentration of the analyte can be calculated in the solution. (Note: potential control may be needed…)



Some Applications of Electrogravimetry without Potential Control

Analyte	Weighed as	Cathode	Anode	Conditions
Ag^+	Ag	Pt	Pt	Alkaline CN^- solution
Br^-	AgBr (on anode)	Pt	Ag	
Cd^{2+}	Cd	Cu on Pt	Pt	Alkaline CN^- solution
Cu^{2+}	Cu	Pt	Pt	H_2SO_4/HNO_3 solution
Mn^{2+}	MnO_2 (on anode)	Pt	Pt dish	HCOOH/HCOONa solution
Ni^{2+}	Ni	Cu on Pt	Pt	Ammoniacal solution
Pb^{2+}	PbO_2 (on anode)	Pt	Pt	HNO_3 solution
Zn^{2+}	Zn	Cu on Pt	Pt	Acidic citrate solution

Electrogravimetry
The apparatus



Electrogravimetry
Methods of detecting the end of deposition

Method No. 1.: If the analyte is a colored ion (e.g. Cu^{2+}, Co^{2+}), you can detect the disappearence of this color from the sample solution.

Method No 2.: Expose, by e.g. raising the beaker, a fresh part of the surface of the Pt gauze to the solution during the electrolysis and check, if deposit has formed on this part after some time.

Method No 3.: You remove a droplet of the solution and spot test it for the analyte ion.

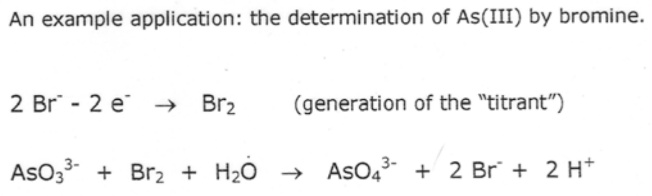
Method No 4.: Use of more somplicated instrumental setup that allow monitoring the concentration of some substance or physical quantity (e.g. three-electrode potentiostatic setup)

Coulometry

Coulometry

The concept

Coulometry is based on counting the electrons needed to complete a redox reaction (in other words, it is a „titration using electrons”). Most commonly, the electrolysis is carried out at a ***constant current*** (as opposed to ***constant potential***) and ***indirectly***. Indirect mode means that on one of the electrodes, which is called generator electrode, the titrant is generated *in-situ*. This also allows the use of exotic titrants, which are impractical in other titrations because they are volatile or reactive (e.g. Br_2, Cl_2). In any case, ***100% current efficiency*** is a must.



An example application: the determination of As(III) by bromine.

$2\,Br^- - 2\,e^- \rightarrow Br_2$ (generation of the "titrant")

$AsO_3^{3-} + Br_2 + H_2O \rightarrow AsO_4^{3-} + 2\,Br^- + 2\,H^+$

Coulometry

End-point detection

The completeness of the reaction (end-point) needs to be detected; this can be done by applying some indicator electrodes. In the given example, both Br_2 and Br^- will only be present together from the end-point on; this situation can be detected in two ways.

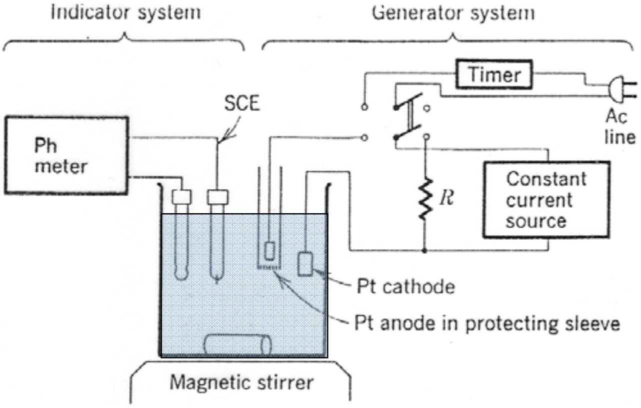
Method 1.: An indicator electrode pair consisting of a Pt (redox) electrode and a reference electrode can be used to monitor the redox potential in the system. The end-point can be detected by a sharp increase of the potential or checked against the Nernstian theoretical end-point potential.

Method 2.: An amperometric electrode pair consisting of two Pt electrodes can be used to detect the sharp increase of current between these electrodes at a small (ca. 0.25 V) voltage.

Coulometry

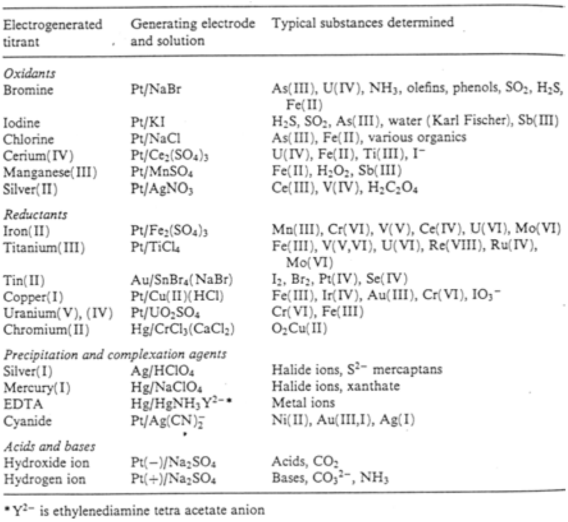
The apparatus

If needed, the ***counter electrode*** can be placed in a sintered protecting glass sleeve (such as below), so the evolving gases can bubble out without interfering with the coulometric titration.



Coulometry

Applications



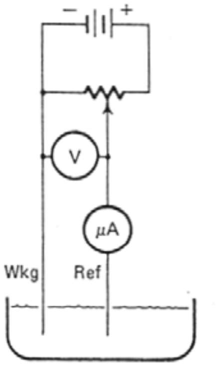
Electrogenerated titrant	Generating electrode and solution	Typical substances determined
Oxidants		
Bromine	Pt/NaBr	As(III), U(IV), NH_3, olefins, phenols, SO_2, H_2S, Fe(II)
Iodine	Pt/KI	H_2S, SO_2, As(III), water (Karl Fischer), Sb(III)
Chlorine	Pt/NaCl	As(III), Fe(II), various organics
Cerium(IV)	Pt/$Ce_2(SO_4)_3$	U(IV), Fe(II), Ti(III), I^-
Manganese(III)	Pt/$MnSO_4$	Fe(II), H_2O_2, Sb(III)
Silver(II)	Pt/$AgNO_3$	Ce(III), V(IV), $H_2C_2O_4$
Reductants		
Iron(II)	Pt/$Fe_2(SO_4)_3$	Mn(III), Cr(VI), V(V), Ce(IV), U(VI), Mo(VI)
Titanium(III)	Pt/$TiCl_4$	Fe(III), V(V,VI), U(VI), Re(VIII), Ru(IV), Mo(VI)
Tin(II)	Au/$SnBr_4$(NaBr)	I_2, Br_2, Pt(IV), Se(IV)
Copper(I)	Pt/Cu(II)(HCl)	Fe(III), Ir(IV), Au(III), Cr(VI), IO_3^-
Uranium(V), (IV)	Pt/UO_2SO_4	Cr(VI), Fe(III)
Chromium(II)	Hg/$CrCl_3$($CaCl_2$)	O_2Cu(II)
Precipitation and complexation agents		
Silver(I)	Ag/$HClO_4$	Halide ions, S^{2-} mercaptans
Mercury(I)	Hg/$NaClO_4$	Halide ions, xanthate
EDTA	Hg/$HgNH_3Y^{2-}$*	Metal ions
Cyanide	Pt/$Ag(CN)_2^-$	Ni(II), Au(III,I), Ag(I)
Acids and bases		
Hydroxide ion	Pt(−)/Na_2SO_4	Acids, CO_2
Hydrogen ion	Pt(+)/Na_2SO_4	Bases, CO_3^{2-}, NH_3

* Y^{2-} is ethylenediamine tetra acetate anion

Voltammetry

Voltammetry

Concept and basic setup

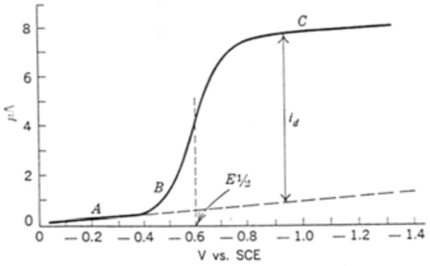


In voltammetry, we apply a controlled (may be fixed, but typically scanned) voltage across two electrodes immersing into the sample solution and measure the resulting current that flows through the sample. Because we use conditions ensure that ensure that the current stays low (μA range), hence we actually perform „microelectrolysis” of the sample components.

Voltammetry

Voltammetric waves

When the voltage exceeds the redox potential of a certain sample species, then oxidation or reduction of it will occur. During this process, the current will linearly increase with the further scanned voltage. If the voltage is increased further, the current will then become more or less constant, then another species starts reacting, etc.



The result is a series of steplike „voltammetric waves”. The position of steps on the voltage axis (***$E_{1/2}$***) is characteristic to the quality of the chemical species in reaction, and the height of the jump on the current scale (***i_d***) relates to the quantity (concentration) of the reacting species.

Voltammetry

Diffusion current

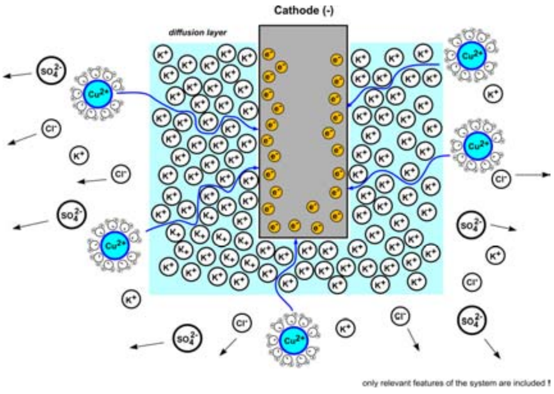
It is a crucial in voltammetry that we perform the measurements under conditions that ensures that ***the current is limited by the diffusion of the analyte species*** only. We do this, as then the current will be conveniently proportional to the analyte concentration. This is so, because the diffusion rate is known to be proportional to the concentration according to Fick's law:

$$\frac{dN}{dt} = -D \cdot \frac{dc}{dx}$$

One has to understand that the overall reduction/oxidation rate of reaction at the electrode is limited by the slowest of all the subprocesses involved. These typically include transportation the solvated ion to the electrode surface, the desolvation of the ion, then the redox reaction, etc. The slowest of these processes will limit the overall rate of reaction. If we would not limit the current, then it could not be used for quantitation, as it would be in the control of experimental conditions that are not related to analyte concentration.

Voltammetry

Background electrolyte



It is a key that we create conditions that will make diffusion the slowest of all processes involved in the redox reaction of the analyte. This we can achieve simply by performing the measurement in an appropriate ***background electrolyte***. This electrolyte should provide cations and anions that are inert to redox reactions at the voltage applied (e.g. K^+, Na^+, ClO_3^-, ClO_4^-, SO_4^{2-} etc.) Also, this electrolyte should have a much larger concentration (say 0.1 M KCl) than the analyte.

Voltammetry

Electrode types

Generally speaking, the electrodes that we know from potentiometry can be used in voltammetry as working or reference electrodes, but two things must be considered.

First, at the surface of the working electrode, actual electrolysis will commence and we would dislike to see the solvent (water, mainly) to take part in this by

$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^-$ oxidation, at positive potential

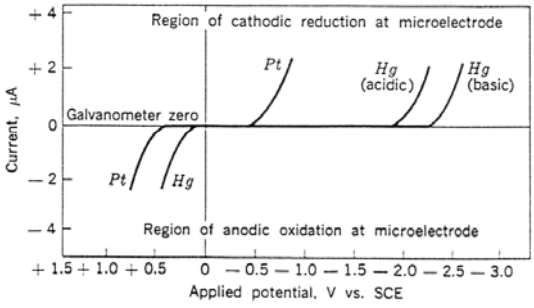
$2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^-$ reduction, at negative potential

As it depends on the quality of the metal electrodes that at which potential these reactions will occur, this condition limits the applicable voltage (potential) range at the working electrode and also determines that which metal is useful as working electrode in the analyte redox reaction.

Voltammetry

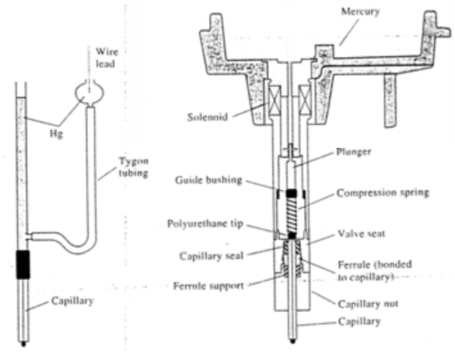
Electrode types

Platinum and mercury are the most useful working electrodes in voltammetry, but other electrodes such as glassy carbon are also used.



Voltammetry
Electrode types

As mercury is a liquid metal, it is not easy to imagine how it can be used as an electrode. It is actually used in the form of a ***dropping mercury electrode (DME)***. Basically, it is mercury dropping out of a capillary in a controlled manner. The added benefit of this design is that it ensures the renewal of the electrode surface with each drop falling down.



Voltammetry
Polarography and amperometry

The second thing to consider is that we need to control and measure very small currents (μA range) accurately. This requires a very stable reference electrode; a good approach is to use a „***mercury pond***” electrode (contaminations have less influence on the potential).

A simple classification of voltammetric methods is based on the electrode type. A certain group of voltammetric methods, that use dropping mercury electrode (DME) as working electrode is called ***polarography.*** There is ***stripping voltammetry*** that uses a Hg film electrode. All other types of voltammetry basically fall into the category of ***amperometry*** (working electrode is not Hg).

Voltammetry

Stripping voltammetry

Polarography

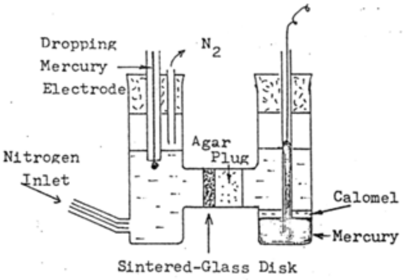
Amperometry

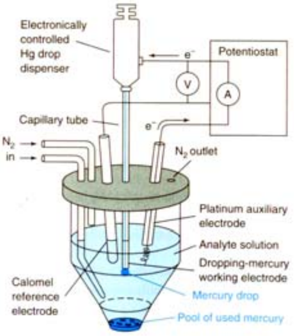
Polarography

Polarography

The setup

This, once so popular, voltammetric method is now rarely used because of the inconvenience of handling mercury and because other methods can provide better analytical performance. This method uses DME as the „working electrode”. The reference electrode is usually calomel or a Hg „pond”. Nitrogen flushing of the solution is needed to keep away oxygen that could interfere with the redox reactions in the solution.

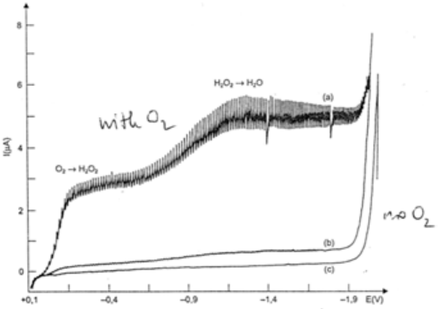


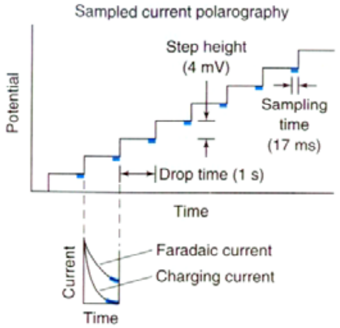


Polarography

The polarogram

A typical polarogram of distilled water is shown on the left, which also illustrates why inert gas bubbling is needed (to eliminate dissolved oxygen content). It also shows the „oscillations” in the current typical of DME. This nuissanse can be avoided with modern data acquisition electronics, by sampling the current only for a short period of time (*sampled current polarography*, on the right).





Polarography

The Ilkovič equation

In polarography, diffusion current is a function of a number factors described by the Ilkovič equation:

$$i_d = 706 \cdot n \cdot c \cdot D^{1/2} \cdot m^{2/3} \cdot t^{1/6}$$

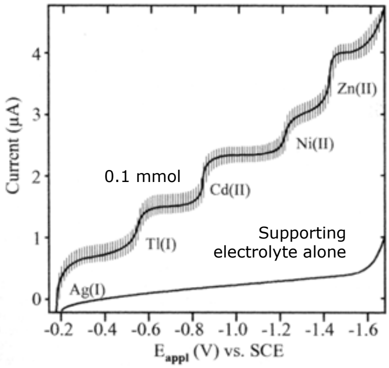
here the current is meant in µA, *706* is the product of several constants, *n* is the number of electrons involved in the reaction, *c* is the concentration of the electro-active substance (mmol/l), *D* is Fick’s diffusion coefficient of the substance, *t* is the time elapsing between two drops and *m* is the dropping speed (g/s).

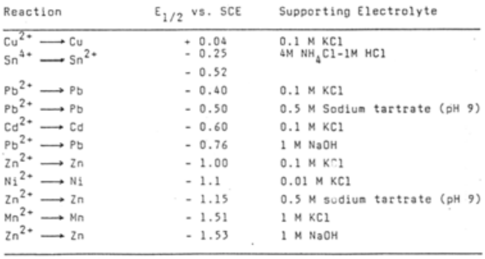
This equation just states the simple fact that i_d is proportional to the concentration - provided that everything else is fixed (like the hydrostatic head, glass capillary diameter, temperature, etc.).

Polarography

Applications – metal ions

The determination of metal ions by polarography in aqueous solutions can be easily imagined. i_d values measured for standard solutions provide a calibration curve that can be then used to determine the concentration of the analyte in the unknown solution.



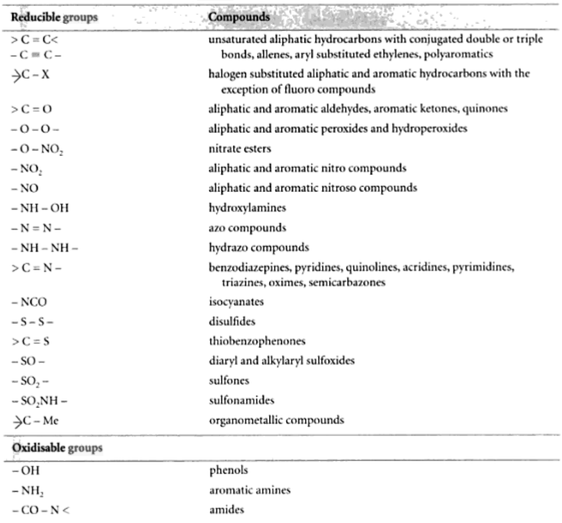


Reaction	$E_{1/2}$ vs. SCE	Supporting Electrolyte
$Cu^{2+} \longrightarrow Cu$	+ 0.04	0.1 M KCl
$Sn^{4+} \longrightarrow Sn^{2+}$	- 0.25	4M NH_4Cl-1M HCl
	- 0.52	
$Pb^{2+} \longrightarrow Pb$	- 0.40	0.1 M KCl
$Pb^{2+} \longrightarrow Pb$	- 0.50	0.5 M Sodium tartrate (pH 9)
$Cd^{2+} \longrightarrow Cd$	- 0.60	0.1 M KCl
$Pb^{2+} \longrightarrow Pb$	- 0.76	1 M NaOH
$Zn^{2+} \longrightarrow Zn$	- 1.00	0.1 M KCl
$Ni^{2+} \longrightarrow Ni$	- 1.1	0.01 M KCl
$Zn^{2+} \longrightarrow Zn$	- 1.15	0.5 M sodium tartrate (pH 9)
$Mn^{2+} \longrightarrow Mn$	- 1.51	1 M KCl
$Zn^{2+} \longrightarrow Zn$	- 1.53	1 M NaOH

Polarography

Applications – organic functional groups

Electroactive functional groups for the voltammetric determination of organic compounds.



Reducible groups	**Compounds**
$>C=C<$ $-C \equiv C-$	unsaturated aliphatic hydrocarbons with conjugated double or triple bonds, allenes, aryl substituted ethylenes, polyaromatics
$>\!\!-C-X$	halogen substituted aliphatic and aromatic hydrocarbons with the exception of fluoro compounds
$>C=O$	aliphatic and aromatic aldehydes, aromatic ketones, quinones
$-O-O-$	aliphatic and aromatic peroxides and hydroperoxides
$-O-NO_2$	nitrate esters
$-NO_2$	aliphatic and aromatic nitro compounds
$-NO$	aliphatic and aromatic nitroso compounds
$-NH-OH$	hydroxylamines
$-N=N-$	azo compounds
$-NH-NH-$	hydrazo compounds
$>C=N-$	benzodiazepines, pyridines, quinolines, acridines, pyrimidines, triazines, oximes, semicarbazones
$-NCO$	isocyanates
$-S-S-$	disulfides
$>C=S$	thiobenzophenones
$-SO-$	diaryl and alkylaryl sulfoxides
$-SO_2-$	sulfones
$-SO_2NH-$	sulfonamides
$>\!\!-C-Me$	organometallic compounds
Oxidisable groups	
$-OH$	phenols
$-NH_2$	aromatic amines
$-CO-N<$	amides

With organic compounds, the only difficulty is to find a solvent for the sample compound which is also able to dissolve the supporting electrolyte. Examples for such solvents include: *ketones, alcohols, acetonitrile, ethylendiamine*, etc.

As supporting electrolytes, quaternary ammonium salts (e.g. tetrabutylammonium iodide) can be used.

Stripping voltammetry

Stripping voltammetry

The concept

Stripping voltammetry, is composed of three related techniques: anodic, cathodic, and adsorptive stripping voltammetry. We will only discuss anodic stripping voltammetry (ASV). The setup is very similar to polarography, except that the working electrode here is a Hg film.

Anodic stripping voltammetry consists of two steps*. The first step* is basically a preconcentration step, a controlled potential electrolysis, in which the analyte ion is reduced and deposited on the working electrode, in the form of amalgam.

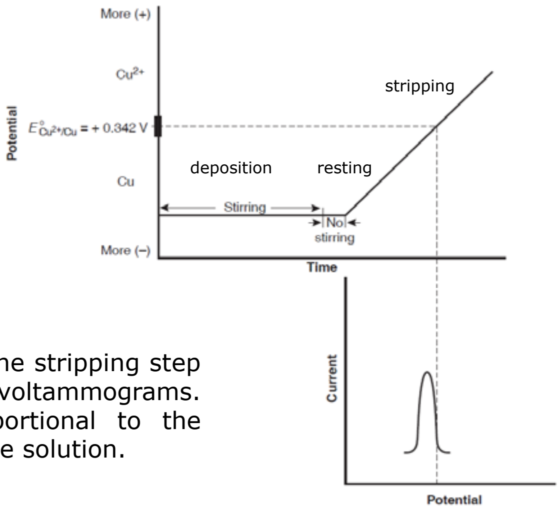
$$\mathrm{Cu}^{2+}(aq) + 2e^{-} \longleftrightarrow Cu(Hg)$$

Comment: Actually, the very first step is a preparatory step, in which the preparation of the fresh Hg film on a clean working electrode (usually) glassy carbon is done, by depositing it from a Hg^{2+} solution.

Stripping voltammetry
The signal

In the second step, the potential is scanned toward more positive potentials. When the potential of the working electrode is sufficiently positive, the analyte is *stripped* from the electrode

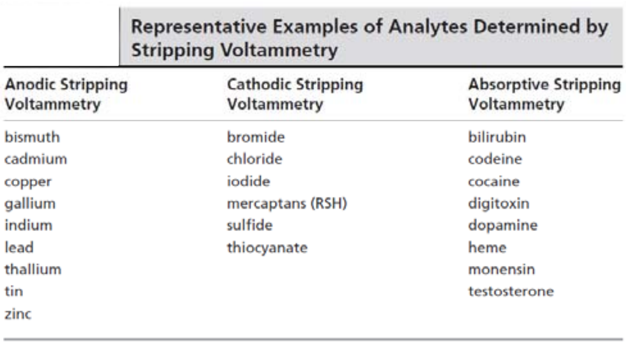
$\mathrm{Cu(Hg)} \longleftrightarrow \mathrm{Cu}^{2+}(aq) + 2e^-$



Current monitoring during the stripping step gives rise to peak-shaped voltammograms. The peak current is proportional to the analyte's concentration in the solution.

Stripping voltammetry
Applications

Anodic stripping voltammetry has very low detection limits (due to the preconcentration step, which can provide enrichment factors of 100-1000), but is also very sensitive to experimental conditions, which must be carefully controlled. Key variables include the area of the mercury film, the deposition time, the rest time, the rate of stirring, and the scan rate during the stripping step.



Representative Examples of Analytes Determined by Stripping Voltammetry

Anodic Stripping Voltammetry	Cathodic Stripping Voltammetry	Absorptive Stripping Voltammetry
bismuth	bromide	bilirubin
cadmium	chloride	codeine
copper	iodide	cocaine
gallium	mercaptans (RSH)	digitoxin
indium	sulfide	dopamine
lead	thiocyanate	heme
thallium		monensin
tin		testosterone
zinc		

Amperometry/biamperometry

Amperometry

The concept

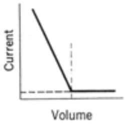
Amperometry typically uses is a fixed voltage (potential difference) in the typical voltammetric arrangement (background electolyte, etc.), built with a non-mercury working electrode (mostly Pt). The concept is still that we measure the current through the electrodes and it will be proportional with the concentration of the analyte (assuming there is no interference). Because the potential at the working electrode is fixed, this method measures one selected component only.

This concept can be used either as an *end-point indication method in titrations* or as a standalone, *specialized measurement system*.

Amperometry

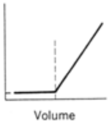
Titrimetric applications

Amperometric titration Most of the applications are based on complexometric or precipitation reactions. Examples (precipitation):



Sample: Pb^{2+} (and KNO_3)
Titrant: oxalate solution
Voltage: -1.0 V (DME against SCE)

Titration of a reducible species by a nonreducible species (only the analyte is electro-active). Pb-oxalate precipitates.



Sample: oxalate (and KNO_3)
Titrant: $Pb2^{+}$
Voltage: -1.0 V (DME against SCE)

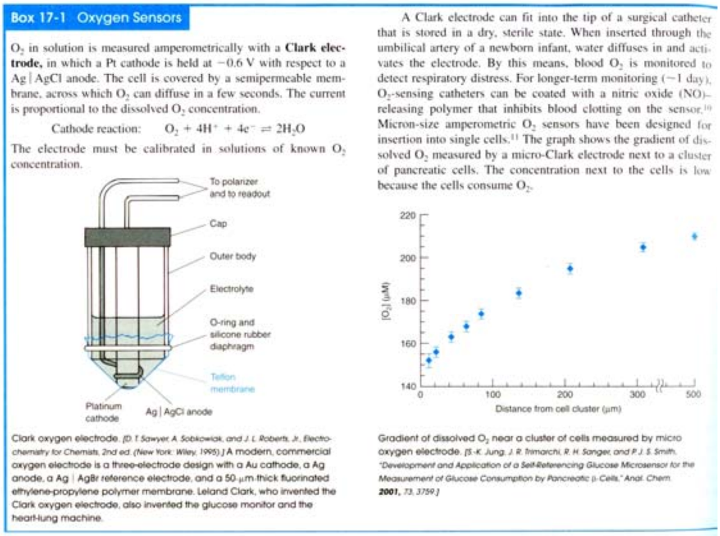
Pb^{2+} can't accumulate (cause an increase in current) as long as oxalate is present the sample. Pb-oxalate precipitates.

Sample: Pb^{2+} (and KNO_3)
Titrant: dichromate solution
Voltage: -1.0 V (DME against SCE)

Both the analyte and the titrant ions are reducible at the DME. Pb-chromate precipitates.

Amperometry

The Clark oxygen sensor



Box 17-1 Oxygen Sensors

O_2 in solution is measured amperometrically with a **Clark electrode,** in which a Pt cathode is held at −0.6 V with respect to a Ag | AgCl anode. The cell is covered by a semipermeable membrane, across which O_2 can diffuse in a few seconds. The current is proportional to the dissolved O_2 concentration.

$$\text{Cathode reaction:} \quad O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$$

The electrode must be calibrated in solutions of known O_2 concentration.

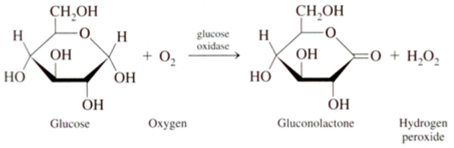
Clark oxygen electrode. *[D. T. Sawyer, A. Sobkowiak, and J. L. Roberts, Jr., Electrochemistry for Chemists, 2nd ed. (New York: Wiley, 1995).]* A modern, commercial oxygen electrode is a three-electrode design with a Au cathode, a Ag anode, a Ag | AgBr reference electrode, and a 50-μm-thick fluorinated ethylene-propylene polymer membrane. Leland Clark, who invented the Clark oxygen electrode, also invented the glucose monitor and the heart-lung machine.

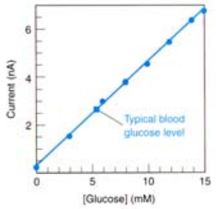
A Clark electrode can fit into the tip of a surgical catheter that is stored in a dry, sterile state. When inserted through the umbilical artery of a newborn infant, water diffuses in and activates the electrode. By this means, blood O_2 is monitored to detect respiratory distress. For longer-term monitoring (~1 day), O_2-sensing catheters can be coated with a nitric oxide (NO)-releasing polymer that inhibits blood clotting on the sensor.[10] Micron-size amperometric O_2 sensors have been designed for insertion into single cells.[11] The graph shows the gradient of dissolved O_2 measured by a micro-Clark electrode next to a cluster of pancreatic cells. The concentration next to the cells is low because the cells consume O_2.

Gradient of dissolved O_2 near a cluster of cells measured by micro oxygen electrode. *[S.-K. Jung, J. R. Trimarchi, R. H. Sanger, and P. J. S. Smith, "Development and Application of a Self-Referencing Glucose Microsensor for the Measurement of Glucose Consumption by Pancreatic β-Cells," Anal. Chem.* ***2001,*** *73, 3759.]*

Amperometry
The glucose biosensor

The first generation of the glucose biosensor (measuring the blood glucose concentration) simply used two electrodes: one Ag/AgCl reference and one carbon working electrode covered with the glucose oxidase enzyme. At +0.6V potential of the working electrode, the following reactions commenced:





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

Thus, the currect generated was proportional to $[H_2O_2]$ and then to [glucose].

Problems with this glucose amperometric sensor construction included:

a) blood oxygen concentration influenced the results
b) at +0.6V potential, other components potentially also present (ascorbic acid, acetaminophen, etc.) also oxidize, so they contribute to the current signal

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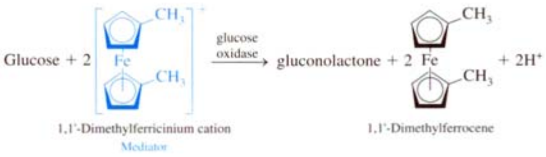
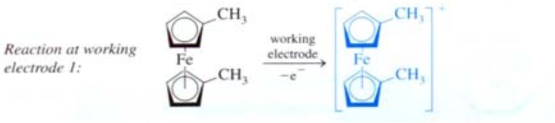
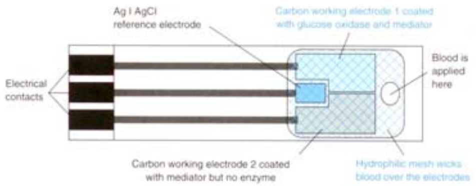
Amperometry
The glucose biosensor

Reaction in the presence of enzyme +mediator:



At the working electrode 1 (regeneration of the mediator):





The first problem was solved by adding a mediator (dimethyl-ferrocene) also to the working electrode. Hence, the presence of oxygen is not needed anymore, thus it can not influence the results.

Solution to the other problem came in the form of adding a second working electrode coated only with the mediator but no enzyme. This second working electrode, measuring on the same droplet of blood, hence can provide a background signal coming from all other compounds oxidazible at this potential.

Amperometry

Examples of other amperometric biosensors

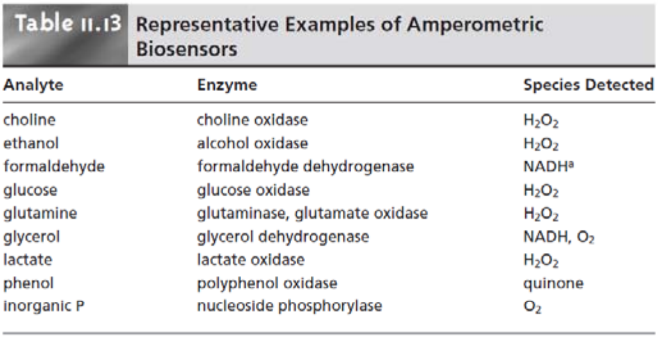


Table 11.13 Representative Examples of Amperometric Biosensors

Analyte	Enzyme	Species Detected
choline	choline oxidase	H_2O_2
ethanol	alcohol oxidase	H_2O_2
formaldehyde	formaldehyde dehydrogenase	NADH[a]
glucose	glucose oxidase	H_2O_2
glutamine	glutaminase, glutamate oxidase	H_2O_2
glycerol	glycerol dehydrogenase	NADH, O_2
lactate	lactate oxidase	H_2O_2
phenol	polyphenol oxidase	quinone
inorganic P	nucleoside phosphorylase	O_2

Biamperometry

The concept

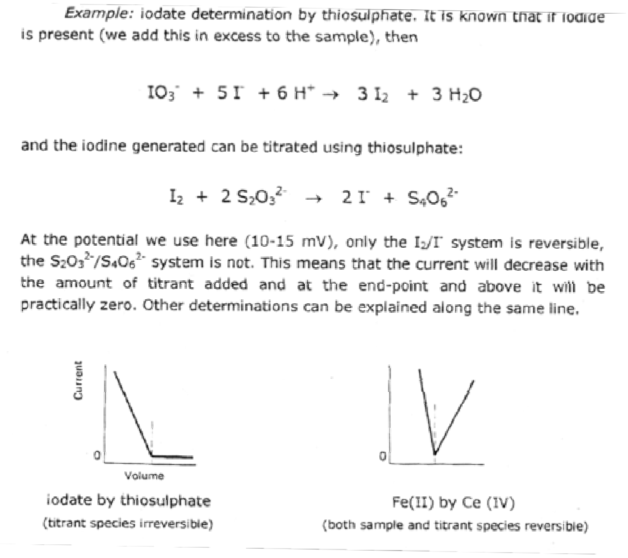
Biamperometry also uses a fixed, small voltage in the typical voltammetric arrangement (background electolyte, etc.), built with a non-mercury working electrode (mostly Pt). The difference is that biamperometry uses a Pt electrode in place of the reference electrode.

If now a reversible redox system is present in the sample solution (e.g. both Fe(II) and Fe(III)) then a small current will flow through the solution because on one electrode the reversible system will proceed towards oxidation while it reduction takes place on the other (cathode: Fe(III) → Fe (II), anode: Fe(II) → Fe(III)).

Imagine that we titrate (consume) a component in the reversible redox system (either Fe(II) or Fe(III) in the above example). Then the current measurable will be zero in the end-point of the titration, because then there will only be half of the redox system present and it can not support the current (***dead-stop titration***). Thus, biamperometry presents an elegant way of end-point detection for titrations.

Biamperometry

An application



Example: iodate determination by thiosulphate. It is known that if iodide is present (we add this in excess to the sample), then

$$IO_3^- + 5\,I^- + 6\,H^+ \rightarrow 3\,I_2 + 3\,H_2O$$

and the iodine generated can be titrated using thiosulphate:

$$I_2 + 2\,S_2O_3^{2-} \rightarrow 2\,I^- + S_4O_6^{2-}$$

At the potential we use here (10-15 mV), only the I_2/I^- system is reversible, the $S_2O_3^{2-}/S_4O_6^{2-}$ system is not. This means that the current will decrease with the amount of titrant added and at the end-point and above it will be practically zero. Other determinations can be explained along the same line.

iodate by thiosulphate

(titrant species irreversible)

Fe(II) by Ce (IV)

(both sample and titrant species reversible)