Lecture 10. Analytical Chemistry

Basic concepts

What is Analytical Chemistry ?

It deals with:

- separation

- identification

- determination of components in a sample.

It includes coverage of chemical equilibrium and statistical treatment of data.

It encompasses any type of tests that provide information relating to the chemical composition of a sample.

- Analytical chemistry is divided into two areas of analysis:

- Qualitative – recognizes the particles which are present in a sample.

- Quantitative – identifies how much of particles is present in a sample.

- The substance to be analyzed within a sample is known as an **analyte**, whereas the substances which may cause incorrect or inaccurate results are known as **chemical interferents**.

Qualitative analysis

- Qualitative analysis is used to separate an analyte from interferents existing in a sample and to detect the previous one.

➢ It gives negative, positive, or yes/no types of data.

➢ It informs whether or not the analyte is present in a sample.

Examples of qualitative analysis

Analysis of an inorganic sample

The classical procedure for systematic analysis of an inorganic sample consists of several parts:

➢ preliminary tests (heating, solubility in water, appearance of moisture)

➢ more complicated tests e.g.

✓ introducing the sample into a flame and noting the colour produced;

➢ determination of anionic or cationic constituents of solute dissolved in water

Flame test

Solutions of ions, when mixed with concentrated HCl and heated on a nickel/chromium wire in a flame, cause the flame to change to a colour characteristic of the element.
Visible colours occur with the following ions:

Sodium	Bright yellow (intense, persistent)
Potassium	Pale violet (slight, fleeting)
Calcium	Brick red (medium, fleeting)
Strontium	Crimson (medium)
Barium	Light green (slight)
Lead	Pale bluish (slight, fleeting)
Copper	Green or blue (medium, persistent)

Flame test as qualitative analysis of cations

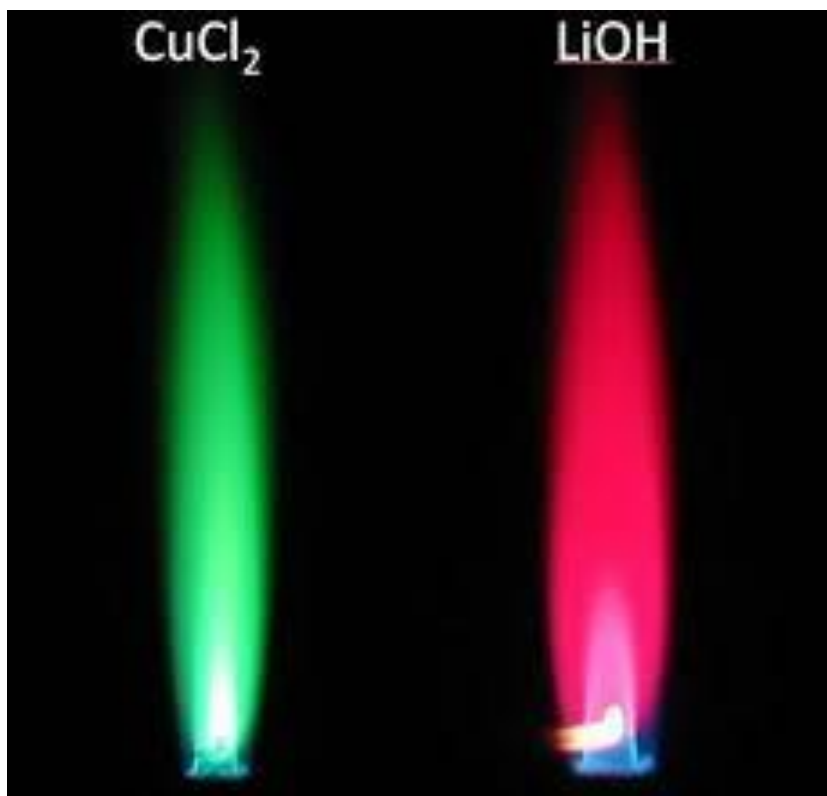A   B   C

Barium Potassium Sodium Calcium Zinc

CuCl$_2$ LiOH

Physical appearance of inorganic salts

|	Salt	Colour
1	MnO, MnO_2, FeO, CuO, Co_3O_4, Ni_2O_3; sulphides of Ag^+, Cu^+, Cu^{2+}, Fe^{2+}, Co^{2+}, Pb^{2+}, Hg^{2+}	Black
2	Hydrated Cu^{2+} salts	Blue
3	HgO, HgI_2, Pb_3O_4	Red
4	Cr^{3+}, Ni^{2+}, hydrated Fe^{2+} salts	green
5	Hydrated Mn^{2+} salts	Light Pink
6	K_2O, $K_2Cr_2O_7$, Sb_2S_3, ferricyanides	Orange
7	Hydrated Co^{2+} salts	Reddish Pink
8	Chromates, $AgBr$, As_2S_3, AgI, PbI_2, CdS	Yellow
9	CdO, Fe_2O_3, PbO_2, $CuCrO_4$	Dark brown

Determination of cation or anion

The procedure is based on treating the solution with a succession of reagents which are specified to a certain group of constituents.

The groups are then treated successively with reagents that divide a large group into subgroups or separate the constituents singly.

Portions of the material are dissolved separately, and different procedures are used for each to detect the cationic and anionic constituents.
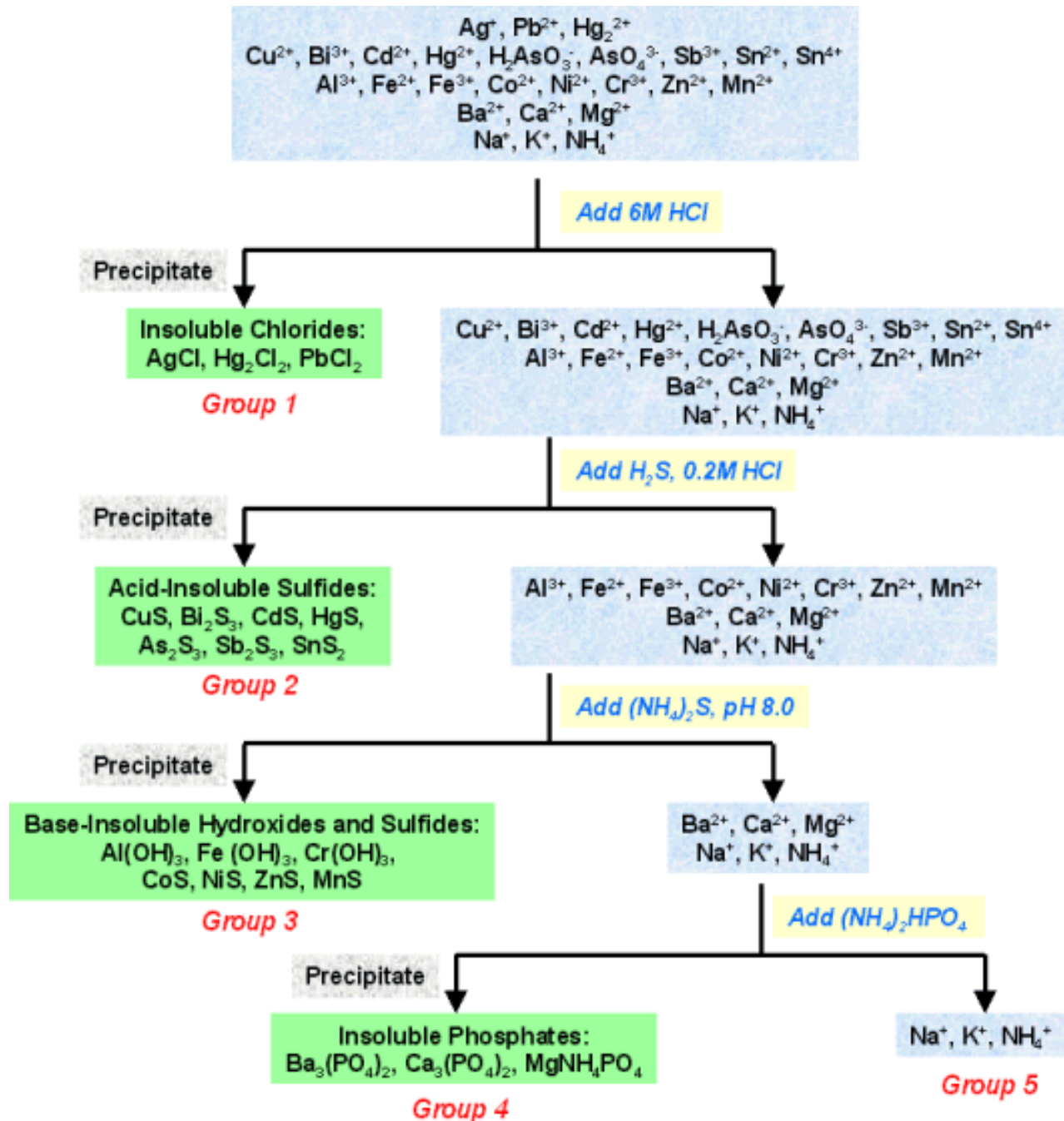
Analysis of organic compounds

The organic nature of a compound is generally indicated by its behaviour on being heated in the air. Solids usually melt, then burn with either a smoky or non-smoky flame, in some instances leaving a black residue of carbon.

The following elements are usually present in these compounds: carbon, hydrogen, oxygen, nitrogen, sulfur, occasionally, phosphorus, halogens, and some metals. Specific tests are available for each of the individual elements.

Quantitative analysis

- It determines number of moles or mass of particular substance in a sample.

- Quantitative data are inherently normally expressed in a numerical format:

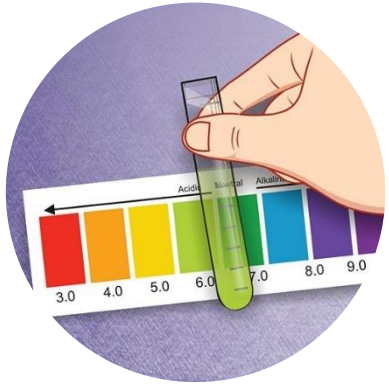➢ the sign (negative or positive)

➢ the magnitude.

Both give the meaningful information.
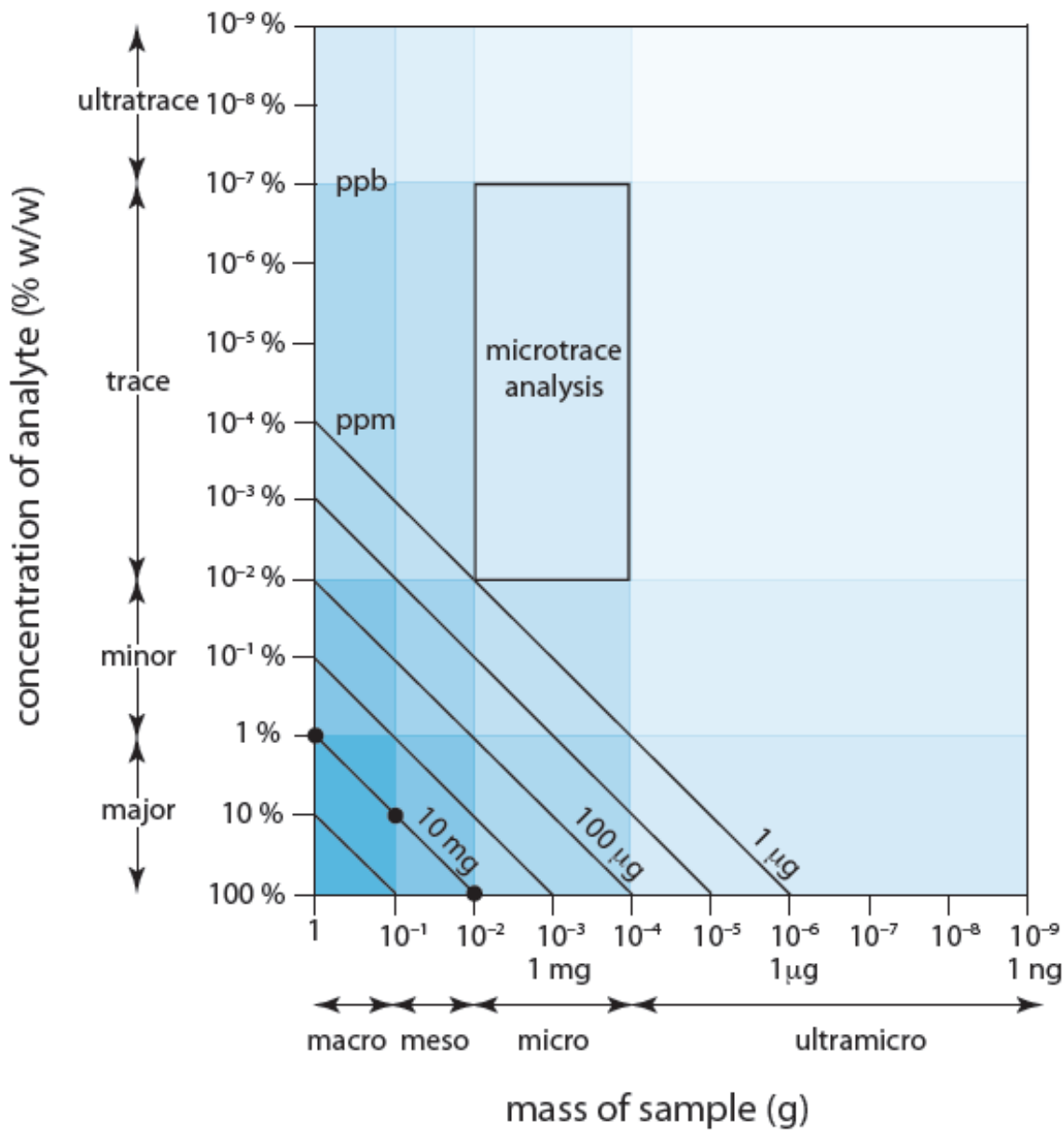
Scale of operations for analytical methods

Examples of quantitative analysis

Methods used in quantitative analysis involve:

- ■ classical methods

- ✓ gravimetric,

- ✓ volumetric,

- Instrumental methods

➤ Electroanalytical (potentiometry, conductometry)

➤ Spectroscopic (UV-VIS, IR, AAS, FES)

➤ Mass spectrometry

➤ Methods involving radioactivity measurement

➤ Methods which involve both separation and quantitative analysis (chromatography, electrophoresis)

➤ Other

Classical methods of quantitative analysis

Gravimetric analysis (gravimetry) is the quantitative

isolation of a substance by precipitation and weighing of the

precipitate.

Procedure of gravimetric analysis:

➢Weigh the sample to be analyzed

➢Dissolve the sample in a suitable solvent, e g, water

➢Add an excess of the precipitating reagent to precipitate the analyte

➢Filter the mixture to separate the precipitate from the solution

➢Wash the precipitate to remove any impurities

➢Dry the precipitate by heating to remove water

➢Cool the precipitate in a desiccator to prevent the precipitate absorbing moisture from the air

➢Weigh the cooled precipitate

➢Repeat the drying and weighing process until a constant mass for the precipitate is achieved

Gravimetric analysis yields more accurate data about the composition of a sample than volumetric analysis does. However, the first one takes more time to perform in the laboratory. Volumetric analysis in the other side doesn't take that much time and the results that we obtain are in the most cases satisfactory.

Examples of gravimetric calculations

Calculate the mass of analyte in the sample.

General calculation of the percent by mass of analyte in a sample:

- Write the balanced chemical equation for the precipitation reaction. E.g.

$$aA + bB \rightarrow cC$$

- Calculate the moles of precipitate (n= $\frac{mass}{molecular\ mass}$)

- Calculate moles of analyte from the balanced chemical equation using the mole ratio of analyte : precipitate (e.g. ratio $\frac{a\ mole}{c\ mole} = \frac{mole\ of\ used\ analyte}{mole\ of\ obtained\ precipitate}$)

- Calculate mass of analyte: (mass = moles x molecular mass)

Calculation – working example

When an sample of impure potassium chloride (0.4500g) was dissolved in water and treated with an excess of silver nitrate. 0.8402 g of dry silver chloride precipitate was obtained. Calculate the percentage KCl in the original sample.

$KCl_{(aq)} + AgNO_{3(aq)} \rightarrow AgCl_{(S)} + KNO_{3(aq)}$
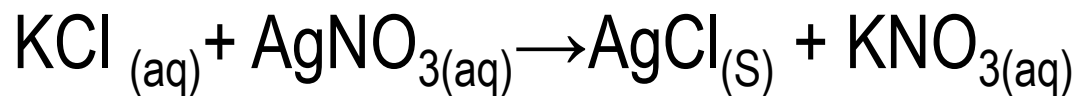
Molecular mass of AgCl = 142.5 g/mol

Molecular mass of KCl = 74.5 g/mol

Number of moles of AgCl = $\dfrac{0.8402\ g}{142.5\frac{g}{mol}}$ = 5.9 x 10^{-3} moles

Ratio between KCl and AgCl from balanced reaction is 1:1

So the same number of moles of KCl reacted =

5.9 x 10^{-3} moles

Mass of KCl = 74.5 g/mol x 5.9 x 10^{-3} moles = 0.4396 g

% of KCl = $\dfrac{(0.4396\ g)}{(0.4500\ g)} \cdot 100\% = 97.7\%$

Quiz

If 20.0 mL of 0.600 M $BaCl_2$ reacts with 25.0 mL of 0.500 M H_2SO_4, the expected mass of $BaSO_4$ produced is ...

Sources of Error:

Reason of error	result comparing with real status
Incomplete precipitation	too low percentage of analyte
Incomplete drying of sample	too high percentage of analyte
Contamination of precipitate with other ions	too high percentage of analyte

There are two main areas of application for gravimetric methods:

1. Analysis of standards to be used for the testing and calibration of instrumental techniques.

2. Analysis requiring high accuracy, although the time consuming nature of gravimetry limits this application to small numbers of determinations.

Quiz

In a particular gravimetric analysis, the precipitate of barium sulfate was balanced before it was completely dried. The likely impact of this error on the calculated result is ...

1. a higher result than the correct value.

2. minimal, because the calculation assumes a hydrated sample is produced.

3. minimal, because the mass of water is likely to be very low.

4. a lower result than the correct value.

Volumetry (volumentric analys)

Volumetric analysis (volumetry) can be simply a titration based on:

➤ a neutralization reactions between acid and base

➤ a precipitation reaction in which insoluble precipitate is

   formed (argentometry)

➤ complexation – reaction between metal ions and standard

   solution in which complex compounds are formed (titrant

    e.g.EDTA- ethylene diamine tetra acetic acid).

➤redox- reaction between oxidizing agent and reducing agent.

Volumetric analysis is linked with instrumental determination of

equivalent point.

Rules of thumbs for successful volumetric analysis

- The titrant should either be a standard or be standardized.

- The reaction should proceed to a stable and well defined equivalence point.

- The equivalence point must be able to be detected.

- The titrant's and sample's volume or mass must be accurately known.

- The reaction must proceed by a definite chemistry.

- The reaction should be nearly complete at the equivalence point.

     In other words, chemical equilibrium favours products.

- The reaction rate should be fast enough to be practical.

Application of volumetric analysis

Volumetry analyses:

1. wastewater e.g. measure ammonia levels in combination with other reactants to quantify other chemicals present.
2. food products - help determine their nutritional implications.e.g. acidity of the orange juice

 3. improve wine production by measuring its acidity

4. pharmaceutical industry to ensure quality control or to make the process more efficient.

- 25 cm^3 of sodium hydroxide is neutralized exactly by 35 cm^3 of 0.1 M hydrochloric acid. What is the molarity of sodium hydroxide?

Quiz .
It's true or false.

➢ Standards is the reagent solution of known conc. which is used to completely react with the target analyte

✓ In volumetric analysis the volume of a reagent of known conc. needed to completely react with the target analyte is measured.

Instrumental analysis

- **Instrumental methods** involve analytical measurements of some sample properties (conductivity, electrode potential, light absorption or emission, mass-to-charge ratio, fluorescence etc.). These measurements are made using instrumentation (equipment).

Stimulus — Energy source

System under study
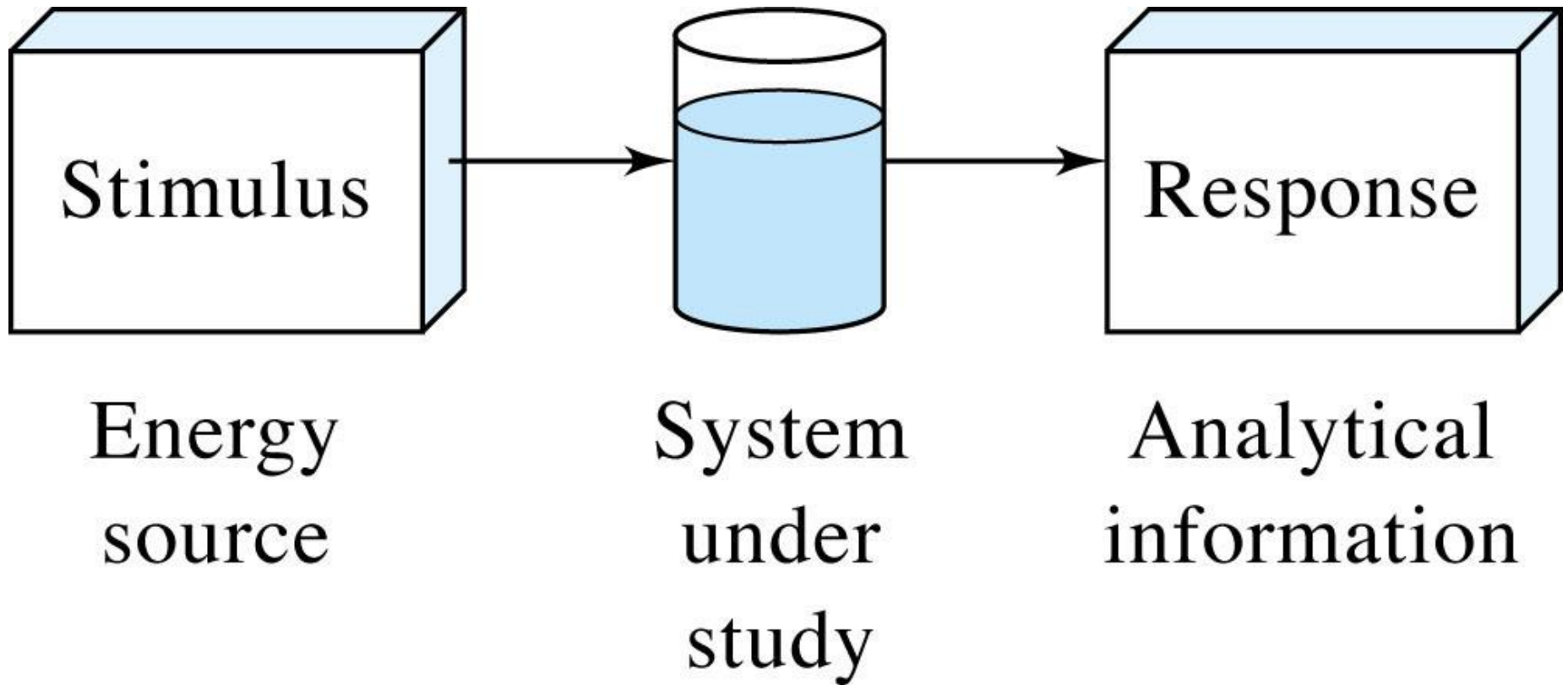
Response — Analytical information

Block diagram of an instrumental measurement

Applications of Instrumental Methods

1. Bioanalytical: biological molecules and/or biological matrices (e.g., proteins, amino acids, blood, urine)

2. Environmental: pesticides, pollution, air, water, soil

3. Material science: polymers, characterization of new materials

4. Forensic science (application of science to the law): body fluids, DNA, gun shot residue, hair, fibers, elemental analysis, drugs, alcohols, poisoning, fingerprints, etc.

Statistical treatment of data

Calibration of Instrumental Methods

■ All types of analytical methods require calibration for quantitation.

■ Calibration is a process that relates the measured analytical signal to the concentration of an analyte.

■ The **three** most common calibration methods are:

• Calibration curve

• Standard addition method
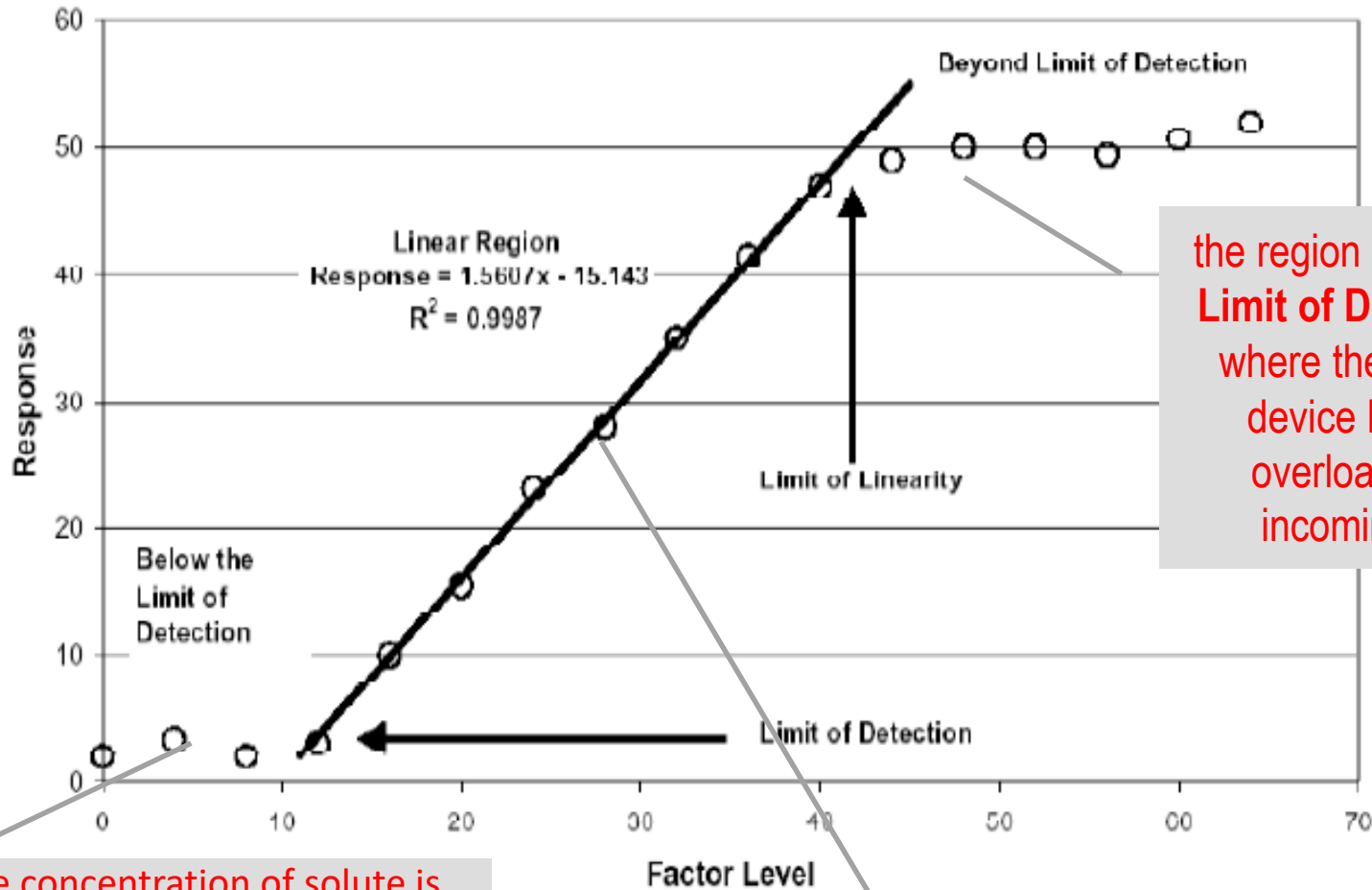
• Internal standard method

Calibration curve

- It is a general method for determining the concentration of unknown sample by its comparing the to a set of standard samples of known concentration.

- It is also a plot of how the instrumental response (analytical signal) changes with the concentration of the analyte.
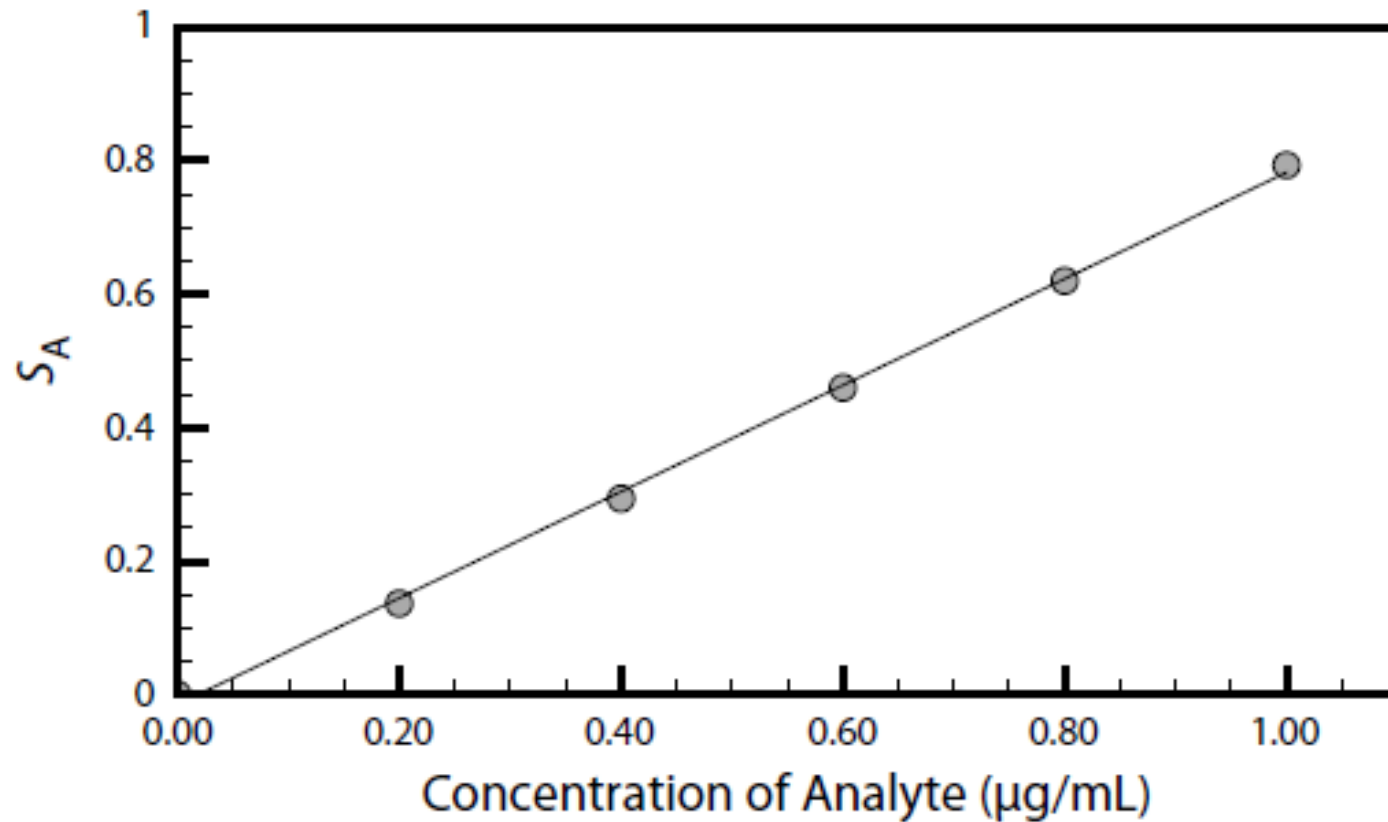
Example of a calibration curve. The filled circles (•) are the individual results for the standard samples and the line is the best fit to the data determined by a linear regression analysis.

Figure 1: Calibration Curve

Figure 1: Calibration Curve

Beyond Limit of Detection

Linear Region
Response = 1.5607x - 15.143
$R^2 = 0.9987$

Below the Limit of Detection

Limit of Linearity

Limit of Detection

Response

Factor Level

the region **beyond the Limit of Detection,** or where the detection device becomes overloaded with incoming data.

The concentration of solute is not intense enough to produce a signal greater than background noise of the instrument

The Linear Region where the response is proportional to the concentration. As it increases, response increases.

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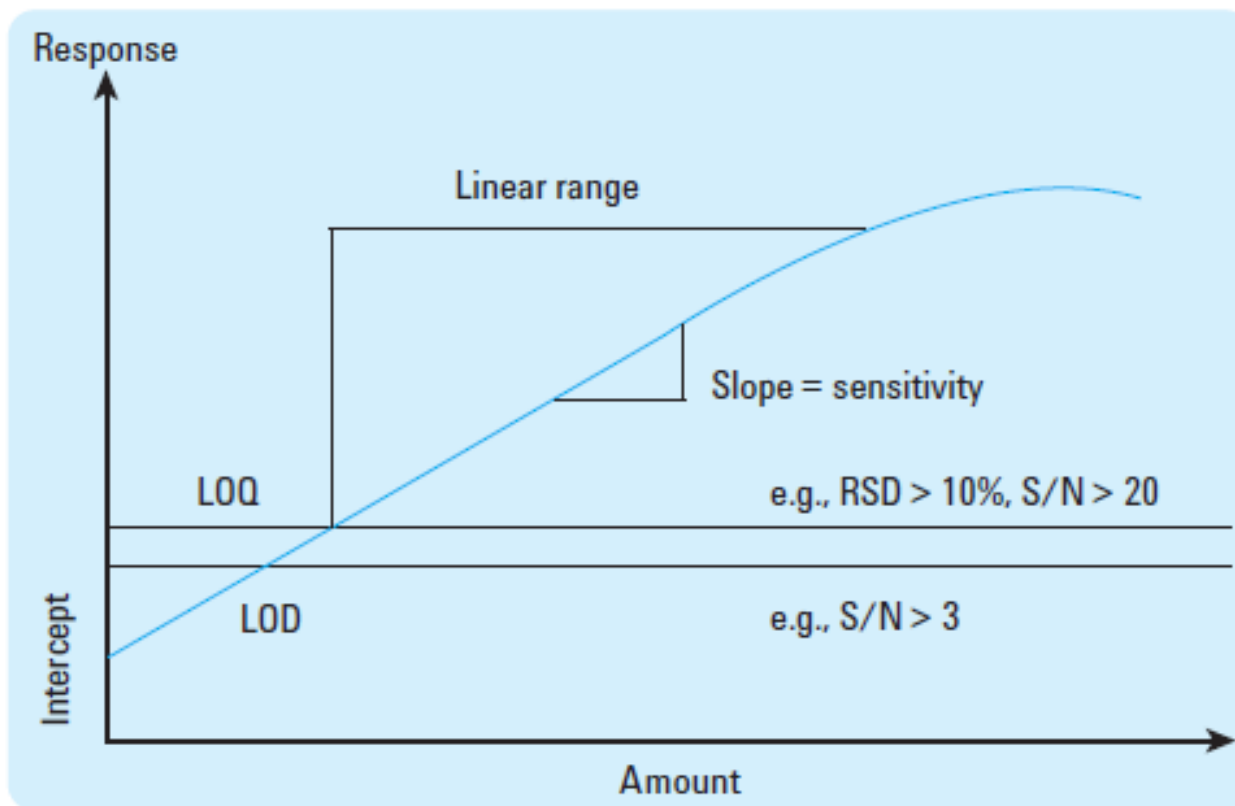
Figure 6
Definition for linearity and range.

- **Detection Limit (Limit of detection, LOD):** The minimum concentration of an analyte that can be detected with a specific method at a known confidence level.

  LOD is determined by S/N, where, S/N = Signal-to-noise ratio = (magnitude of the signal)/(magnitude of the noise)

- Noise is unwanted baseline fluctuations in the absence of analyte signal (standard deviation of the background)

- The detection limit (LOD)is given by,

$$C_m = (S_m - S_{bl})/m,$$

where, C_m = minimum concentration,

S_m = minimum distinguishable analytical signal (i.e., S/N = 2 or S/N = 3),

S_{bl} = mean blank signal

m = sensitivity (i.e., slope of calibration curve)

- The amount of analyte necessary to yield a net signal equal to 2 or 3x the standard deviation of the background.

■ **Dynamic range** starts from the lowest concentration at which quantitative measurements can be made (limit of quantitation, or LOQ) and finishes at the highest concentration at which the calibration curve starts to depart from linearity (limit of linearity, or LOL).

The **lower limit of quantitative** (LOQ) **measurements** is generally taken to be equal to ten times the standard deviation of repetitive measurements on a blank (10 S_{bl}).
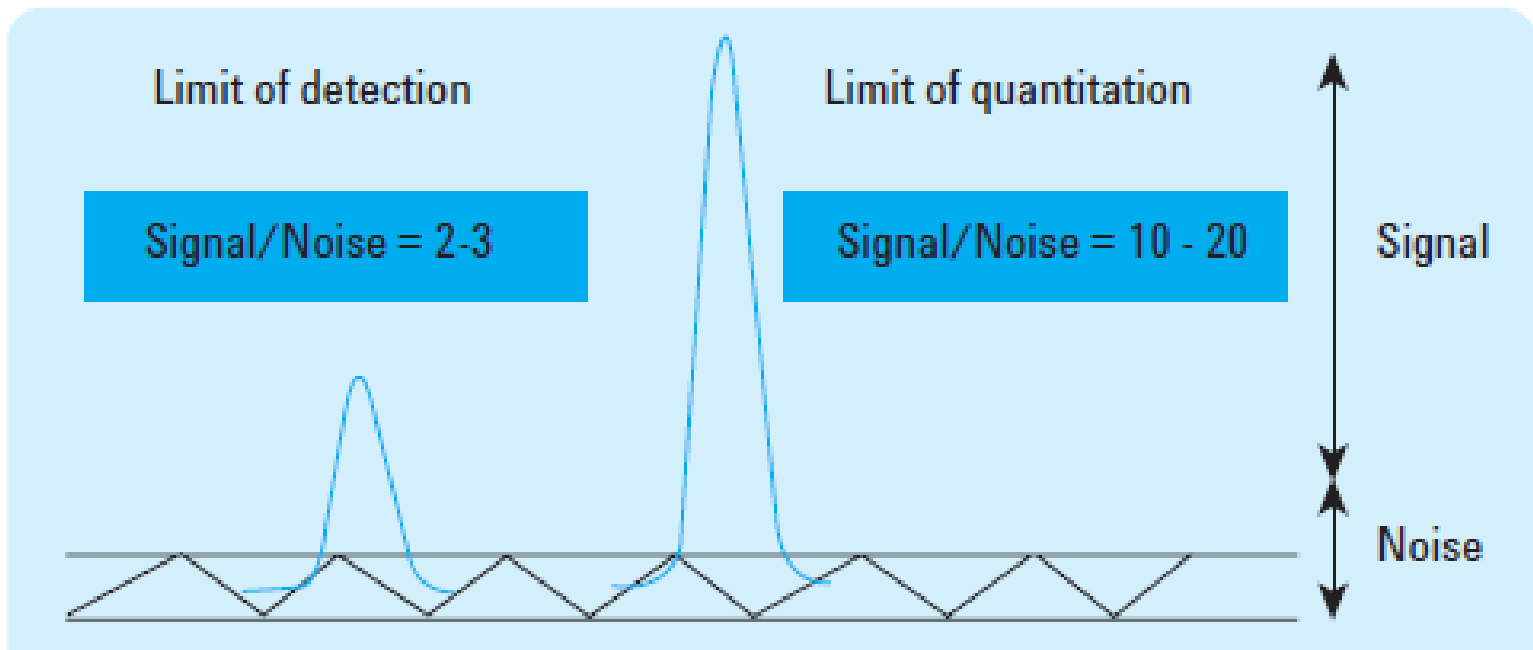
Limit of detection and limit of quantitation via signal-to-noise.

Standard addition method

- The standard is added directly to the solution of analyzed sample.

- This method is used in situations where sample matrix also contributes to the analytical signal. Such situation is known as the matrix effect. It makes impossible to compare the analytical signal between sample and standard using the traditional calibration curve approach.

Internal standard method

- The method of internal standards is used to improve the precision of quantitative analysis. An internal standard is a known concentration of a substance that is present in every sample that is analyzed. Internal standards can be used with either the calibration curve or standard addition methods, although the former is probably more common.

https://facultystaff.richmond.edu/~cstevens/301/is_general.html

- The purpose of the internal standard is to behave similarly to the analyte but to provide a signal that can be distinguished from that of the analyte. Thus any factor that affects the analyte signal will also affect the signal of the internal standard to the same degree. Therefore the ratio of the two signals will exhibit less variability than the analyte signal.

- Internal standards are often used in chromatography, mass spectroscopy and atomic emission spectroscopy. They can also be used to correct for variability due to analyte loss in sample storage and treatment.

Describing method properties

Selectivity is a measure of a method's freedom from interferences. A selectivity coefficient, $K_{A,I}$ *presents t*he selectivity of a method for the interferent relative to the analyte.

$$K_{A,I} = \frac{k_I}{k_A}$$

which may be positive or negative depending on the sign of k_I and k_A. *The selectivity coefficient is greater than +1 when the method is more selective for the interferent than for the analyte.*

No analytical method is totally free from interference from other species, and steps need to be taken to minimize the effects of these interferences.

The **specificity** of the test answers the question how the method responds to the presence of a particular analyte. So if a method is totally specific then it will respond only to the analyte of interest and in this case no chemical interferents will interfere with the analyte.

e.g. method is based on the reaction of various ions with chloride ion. Silver ions are settled out when reacted with chloride ion, whereas sodium forms soluble salt. Thus for the mixture of Na and Ag ion adding Cl ion will be specific for the identification of Ag ion.

- The **sensitivity** of a test (method) describes how close or similar in magnitude two readings may be, and still be distinguished from each other.

- e.g. if the sensitivity of Pb^{2+} determination in some method is 1 ppm - it means that we can distinguish 200 and 201 ppm, but 200.5 and 200.6 ppm is hard to distinguish.

Measurement Limitations (Uncertainty Analysis)

Measurements of chemical data have limitations. These limitations are either inherent to the analytical equipment performing the measurement or to the operator using the equipment.

The **precision describes the reproducibility of the data.** **It is a measure of** how carefully the result is determined without reference to any true value (precision is related to uncertainty, e.g., Δx)

Three terms are used to describe the precision of a set of replicate data: **standard deviation, variance, and coefficient of variation.**

Standard deviation of the sample, s, describes the spread of data around the mean value for a set of replicate measurement.

$$S = \frac{\sqrt{\sum_{i=1}^{N}(X_i - X_{mean})^2}}{N - 1}$$

- Variance – is an alternate measure, it is also sometimes used as a measure of the reproducibility or precision of technique.

- The variance = s^2

- Coefficient of Variation ,C_v;

C_v = s/ mean value

TABLE 1-5 Figures of Merit for Precision of Analytical Methods

Terms	Definition*
Absolute standard deviation, s	$s = \sqrt{\dfrac{\sum_{i=1}^{N}(x_i - \bar{x})^2}{N-1}}$
Relative standard deviation (RSD)	$RSD = \dfrac{s}{\bar{x}}$
Standard error of the mean, s_m	$s_m = s/\sqrt{N}$
Coefficient of variation (CV)	$CV = \dfrac{s}{\bar{x}} \times 100\%$
Variance	s^2

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- **Accuracy**: How close the measurement approaches the real value.

- We can express accuracy as an absolute error, e

  - e = obtained result - expected result

  - or as a percentage relative error, %er

$$\%e_r = \frac{\text{obtained result} - \text{expected result}}{\text{expected result}} \times 100$$

Quiz

- Calculate accuracy of the analysis (express it as the relative error in terms of part per cent). The analysis gives 115 ppm Fe and the true value is, in fact, 110 ppm Fe content.

- A) 15%; b)10%; c) 4.5%; d) 3.0%; e) 2.5%

Question to be answered

1. What is the difference between qualitative and quantitative analysis?

2. Consider the method in which the mixture of Cu^{2+}; Pb^{2+} and Ag^+ cations are determined by reaction with Cl^- (the result of this reaction is precipitate, but only silver chloride is water insoluble). This method is specific with respect to………ions, whereas it is not specific toward ……..

Calculations

- Replicate measurements for the lead content of a water sample taken from a river gave the following data.1) 19.4; 2) 20.6; 3) 18.7; 4) 19.2; 5) 21.6; 6) 18.9; 7) 19.9.

- Calculate the standard deviation of the data of Pb content in ppm

- Mean result is 19.76 ppm

$$s = \frac{\sqrt{(19.4 - 19.76)^2 + (20.6 - 19.76)^2 + (18.7 - 19.76)^2 + (19.2 - 19.76)^2 - \cdots \ldots}}{6}$$

$$S = 1.07 \; ppm$$

Signals which are employed in instrumental methods of analysis are present in table below

Signal	Instrumental Methods
Emission of radiation	Emission spectroscopy (X-ray, UV, visible, electron); fluorescence,
Absorption of radiation	Spectrophotometry and photometry (X-ray, UV, visible, IR)
Scattering of radiation	Turbidimetry; nephelometry;
Refraction of radiation	Refractometry;
Rotation of radiation	Polarimetry; optical rotary dispersion; circular dichroism
Electrical potential	Potentiometry;
Electrical charge	Coulometry
Electrical current	Polarography; amperometry
Mass-to-charge ratio	Mass spectrometry
Rate of reaction	Kinetic methods
Thermal properties	Thermal conductivity and enthalpy
Radioactivity	Activation and isotope dilution methods

Review of some instrumental methods

Electroanalytical methods

- They are a class of techniques in which the analyte amount is determined by measuring the potential (V) and/or current (A) in an electrochemical cell containing the analyte.

The main categories are:

- potentiometry (the difference in electrode potentials is measured),

- coulometry (the cell's current is measured over time),

- voltammetry (the cell's current is measured while actively altering the cell's potential).

- conductometry

Potentiometry

Method is based on the determination of the potential differences between two half cells

Electrical lead

Inner tube containing a paste of Hg, Hg_2Cl_2, and saturated KCl

Saturated KCl

Small hole

Fritted disk (or a porous fiber)

Ground glass sleeve

Saturated Calomel Electrode (SCE)
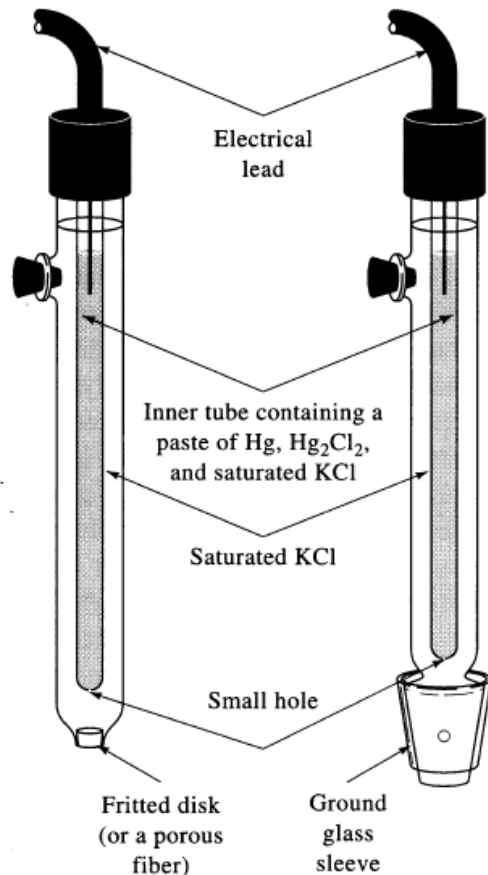
Two half cells:
1. External reference electrode (ERE) – the potential of this electrode is constant with respect to that of the sample
2. The ion selective electrode (ISE)- „working electrode" is composed of an internal reference electrode (IRE) bathed in a reference solution of the analysed analyte. The IRE is separated from the sample solution by membrane, selectively permeable to the analyte being studied.

Measuring Concentration using electrodes:

Working (indicator electrode) electrode is used with reference electrode to measure potential of unknown solution

$$E_{cell} = E_{ISE} - E_{ERE}$$

• potential of ISE is proportional to measured ion activity

$$E = 2.303 \; \frac{RT}{zF} \log \frac{a_{i \; sol}}{a_{i \; ref}}$$

Electrodes can be

- specific (one ion)
- selective (several ions)
- simple
- complicated

Electrode kind

Electrodes of the first kind. It responds directly to changing activity of electrode ion e.g. Cu I Cu^{2+}.

The equilibrium potential of this electrode is a function of the concentration (more correctly of activity) of the cation of the electrode metal in the solution.

In general, electrodes of first kind:

➢ simple

➢ not very selective

➢ some metals easily oxidized (deaerated solutions)

➢ some metals (Zn, Cd) dissolve in acidic solutions

Electrode kind

Electrodes of the second kind - respond to changes in ion activity through formation of complex.

Ag │ AgCl │ Ag$^+$ or Ag │ AgCl │ Cl$^-$
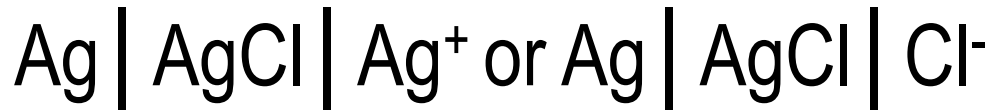
The potential of the metal is controlled by the concentration of its cation in the solution, but this, in turn, is controlled by the anion concentration in the solution through the solubility product of the slightly soluble metal salt.

Example: Silver works as halide indicator electrode if coated with silver halide.
Silver wire in KCl (sat'd) forms AgCl layer on surface

$$AgCl(s) + e^- \leftrightarrow Ag(s) + Cl^- \quad E^0 = +0.222 \text{ V}$$
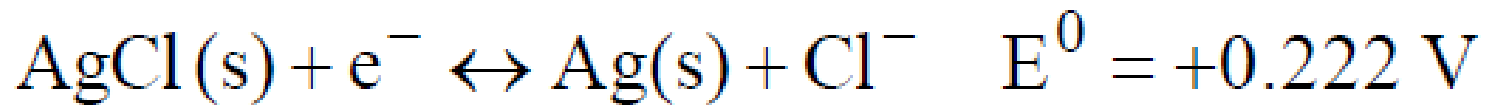
$$E_{ind} = +0.222 - \frac{0.0592}{n} \log a_{Cl^-}$$

$$= +0.222 + 0.0592pCl$$

Electrode kind

Electrodes of the third kind - respond to changes of different ion than metal electrode.

The assembly consists of a metal in contact with two slightly soluble salts (one containing the cation of the solid metal, the other the cation to be determined, with both salts having a common anion) immersed in a solution containing a salt of the second metal (e.g., zinc metal--zinc oxalate--calcium oxalate--calcium salt solution).

$$Zn \mid ZnC_2O_4 \mid CaC_2O_4 \mid Ca^{2+}$$

More complicated electrodes

Membrane (Ion Selective) Electrodes:

Membrane:

• solids with low solubility

• semi-solids and polymers.

Some electrical conductivity - often by

doping.

Selectivity - part of membrane binds/reacts

with analyte.

Types of membrane electrodes

- Non-crystalline membranes:

✓ Glass - silicate glasses for H^+, Na^+

✓ Liquid - liquid ion exchanger for Ca^{2+}

✓ Immobilized liquid - liquid/PVC matrix for Ca^{2+} and NO_3^-

- Crystalline membranes:

➢ Single crystal - LaF_3 for F^-

➢ Polycrystalline or mixed crystal - AgS for S^{2-} and Ag^+

The glass pH electrode

$$\overbrace{\text{SCE}}^{\text{Ref 1}}||\overbrace{\text{H}_3\text{O}^+(a=a_1)|\text{Membrane}|\underbrace{\text{H}_3\text{O}^+(a=a_2),\text{Cl}^-(a=1\,\text{M}),\text{AgCl(sat'd)}|\text{Ag}}_{\text{Ref 2}}}^{\text{Analyte} \qquad\qquad \text{Glass Electrode}}$$
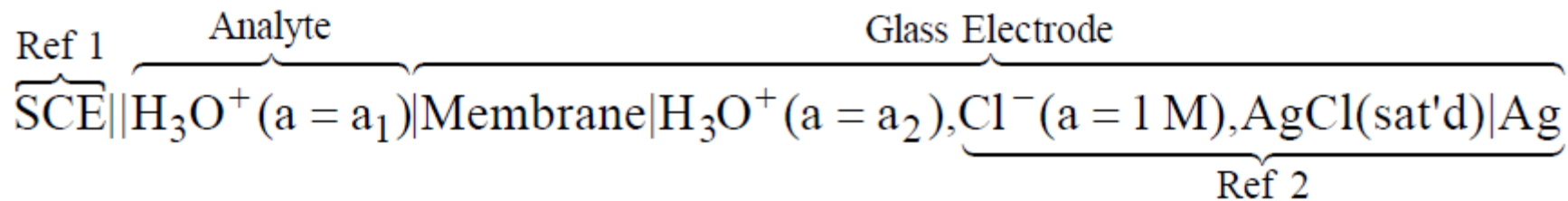
$$E_{(pH)} = E_{(constant)} + \left(\frac{2.3 \cdot RT}{n\,F}\right) \cdot \log[H^+]$$

Enzymatic electrodes

anode-oxidation   Cathode-reduction
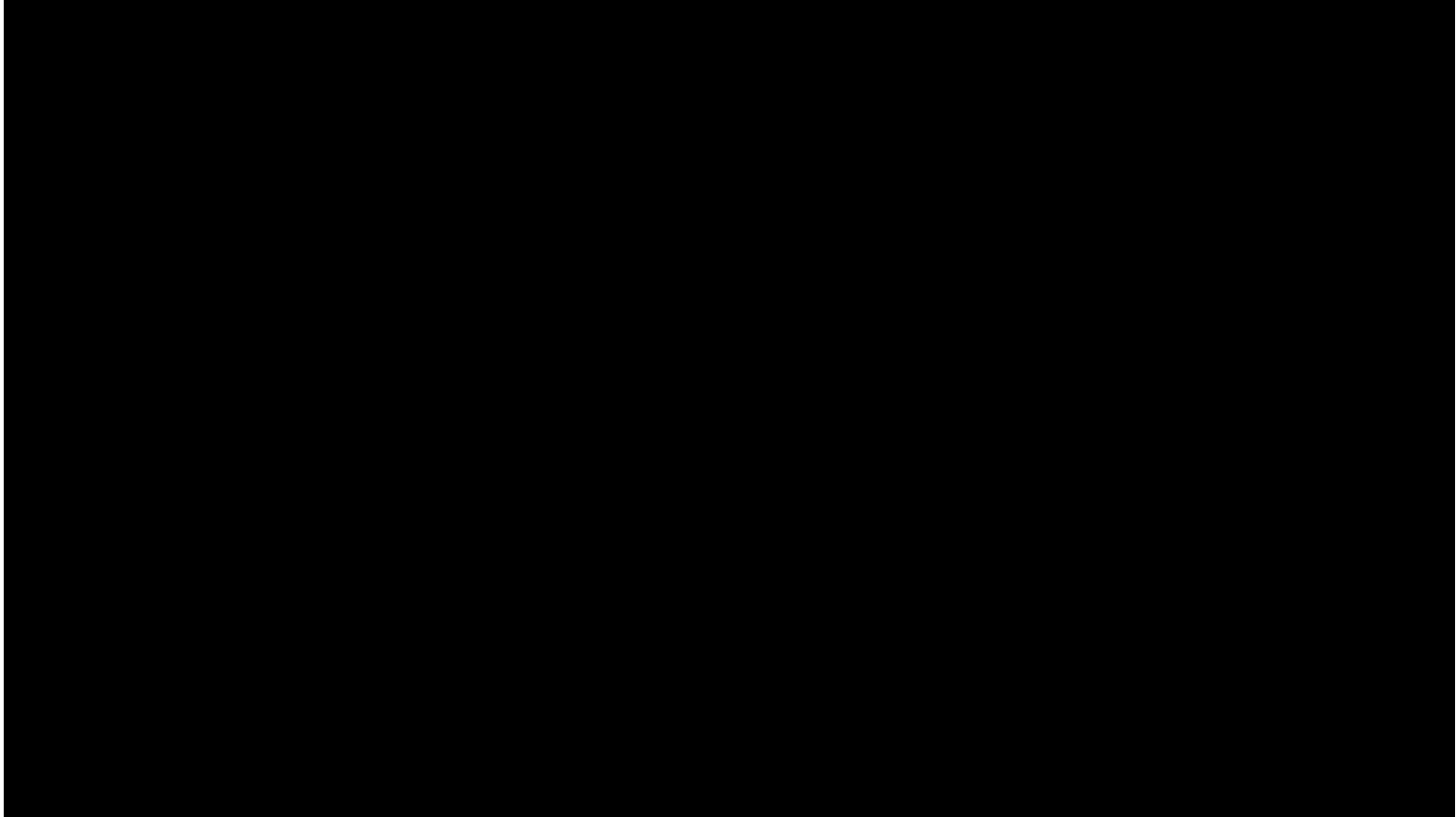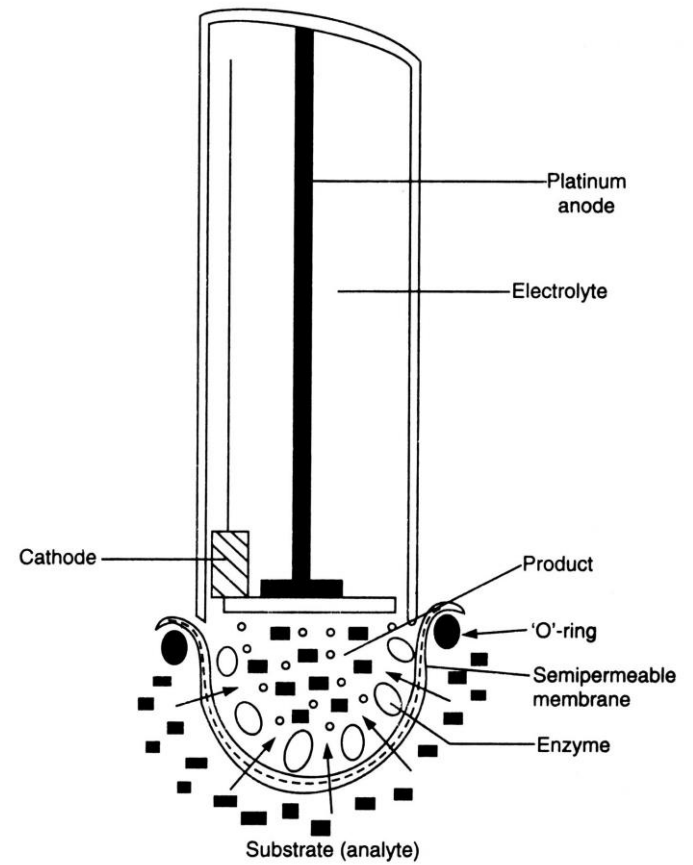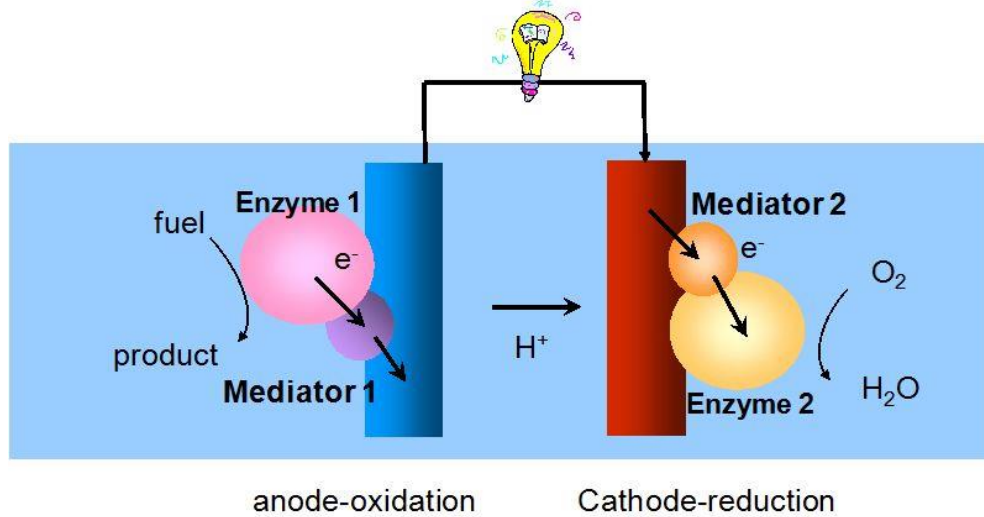
Crystalline Membrane Electrodes

Crystalline Membrane Electrodes:

• Usually ionic compound

• Single crystal

• Crushed powder, melted and formed

• Sometimes doped (Li^+) to increase conductivity

• Operation similar to glass membrane
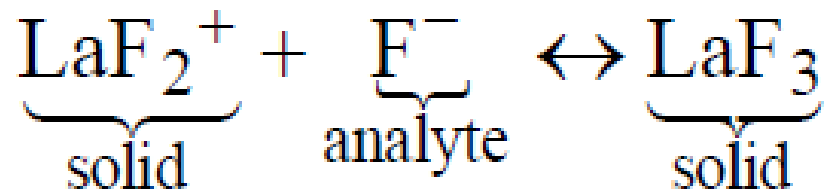
$$\underbrace{LaF_2^+}_{solid} + \underbrace{F^-}_{analyte} \leftrightarrow \underbrace{LaF_3}_{solid}$$

$$E_{ind} = L + 0.0592 \log \frac{1}{a_{F^-}}$$
$$= L - 0.0592 \log a_{F^-}$$
$$= L + 0.0592 \, pF$$

Solid state crystalline membrane electrode
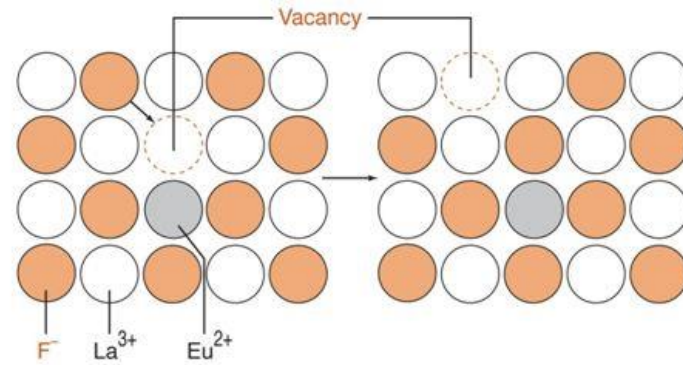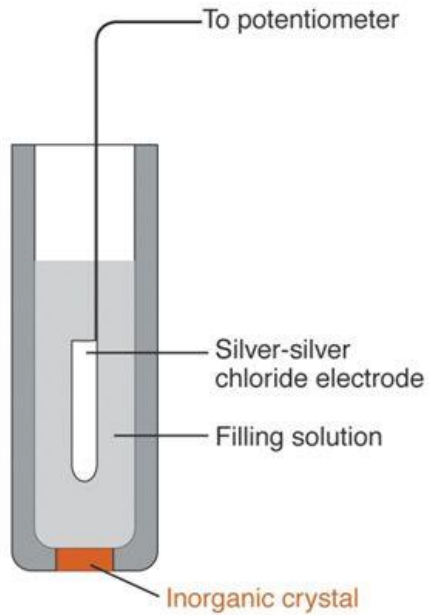
Migration of F^- through LaF_3 doped with EuF_2.

Potentiometric measurements are often used in routine analyses because they are simple to achieve. The LOD of the electrodes is in the range of 10^{-5}–10^{-6} M. However, the observed detection limit is governed by the presence of interfering ions or impurities.

Some routine applications of the method are:

- in agriculture, the analysis of nitrates in soil samples

- in foodstuffs, the analysis of ions such as NO_3^-; F^-; Br^-; Ca^{2+}, etc. in drinks, milk, meat, or fruit juices

- in industry, the analyses of Cl^- in paper paste, CN^- in electrolysis baths, Cl^- and F^- in galvanic processes

- in clinical chemistry, the analysis of certain ions in serum and other biological fluids.

pH

Vol
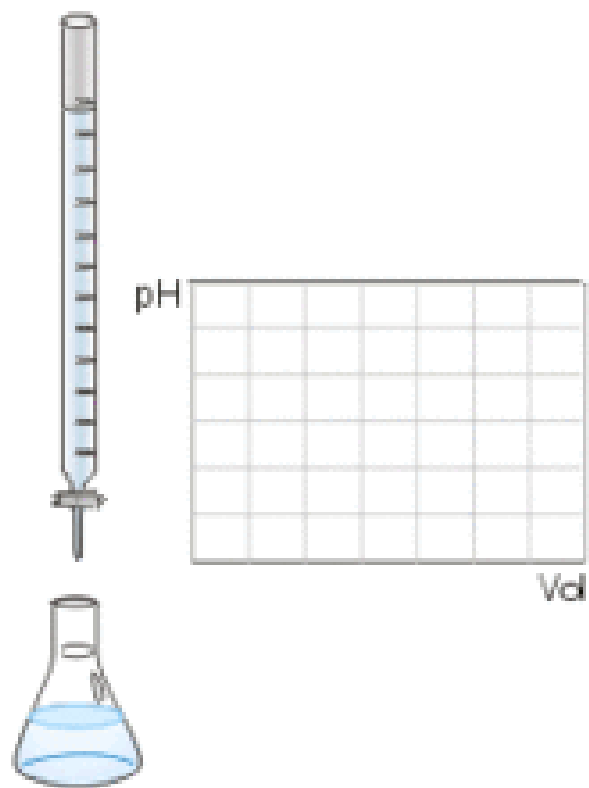
Quiz

- Describe the kind of electrode among the presented above half cells:

1) $Cu \mid Cu^{2+}$;

2) $Ag \mid Ag^+$

3) $Hg \mid Hg_2Cl_2 \mid Hg^+$

4) $Ag \mid AgCl \mid Ag^+$

5) $Zn \mid ZnC_2O_4 \mid CaC_2O_4 \mid Ca^{2+}$
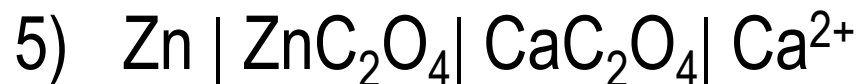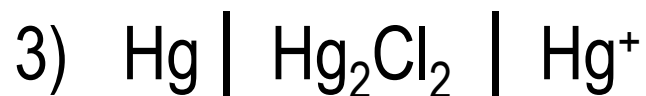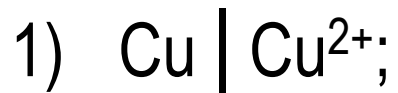
Voltammetric methods

- They determine components in the solution that can be electrochemically oxidized or reduced.

- In these methods the potential is applied to the sample via a conductive electrode (working electrode) which is immersed in the sample solution.

- The potential, which serves as the driving force, is scanned over a region of interest. If at a particular potential a component of the solution is oxidized or reduced, then a current will flow at the working electrode.

- The potential ($E_{1/2}$) at which reduction or oxidation of analyte occurs is characteristic of the component (qualitative analysis). Whereas the amount of current produced is proportional to the concentration of that component in the solution (quantitative analysis).
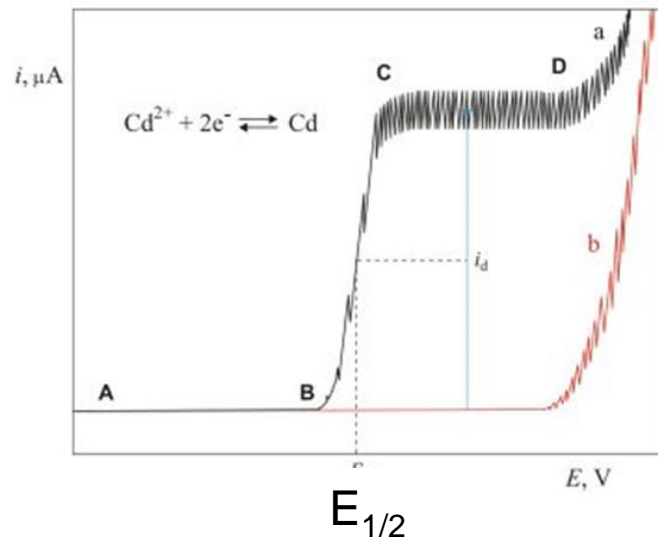
The polarogram of Cd determination
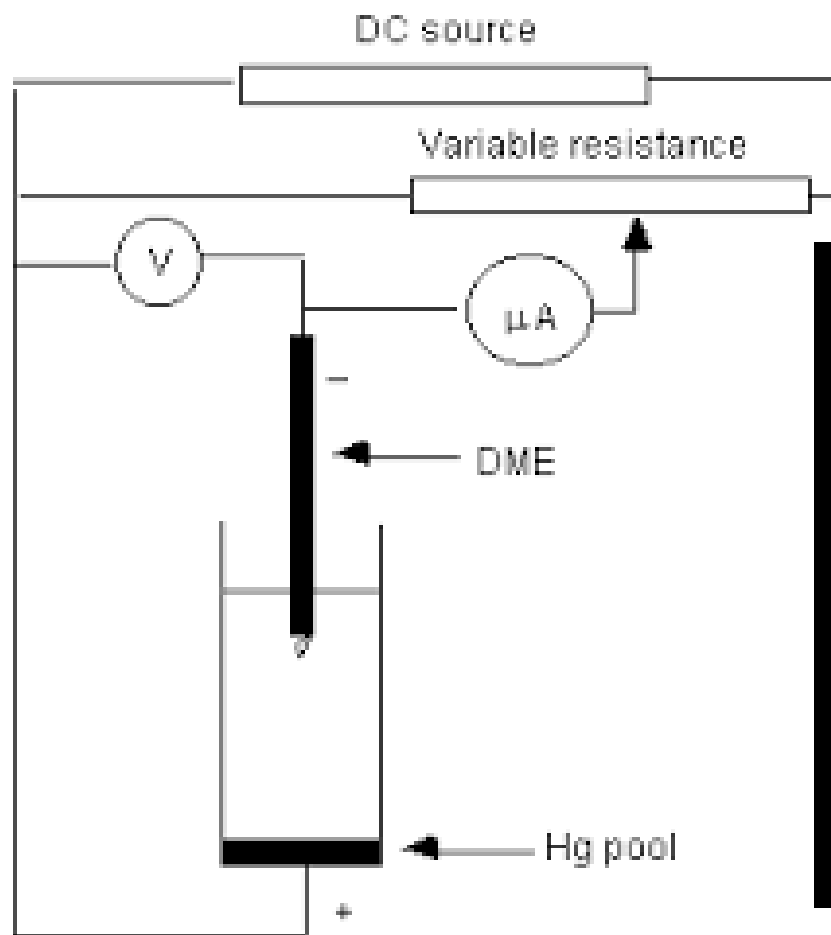
Mercury-drop electrode.

- Voltammetric methods rank among the most sensitive analytical techniques available. They are routinely used for the determination of electroactive inorganic elements and organic substances in nanogram and even picogram amounts; often the analysis takes place in seconds.

Conductometry
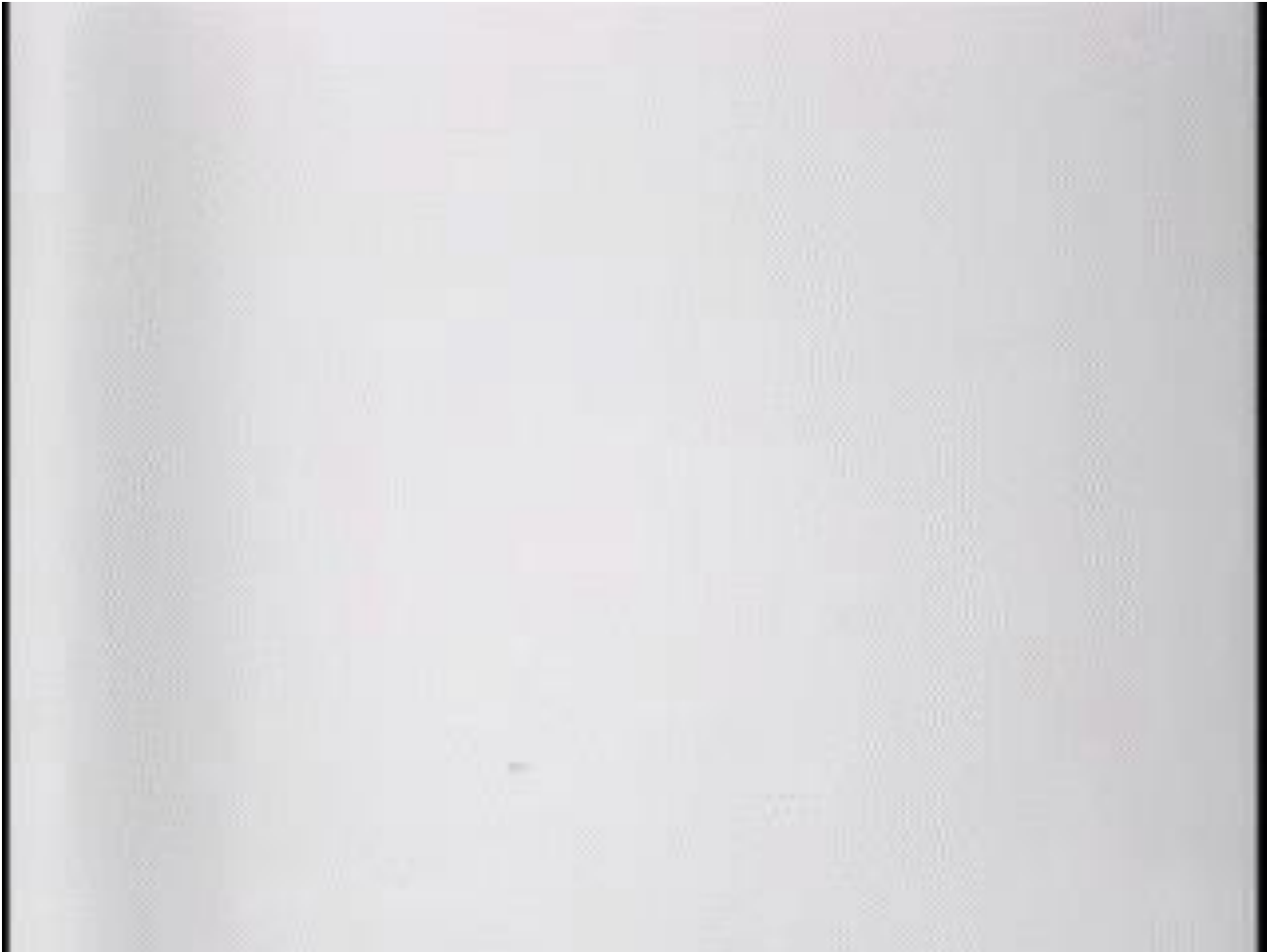
Solutions that contain ionic species conduct electricity.
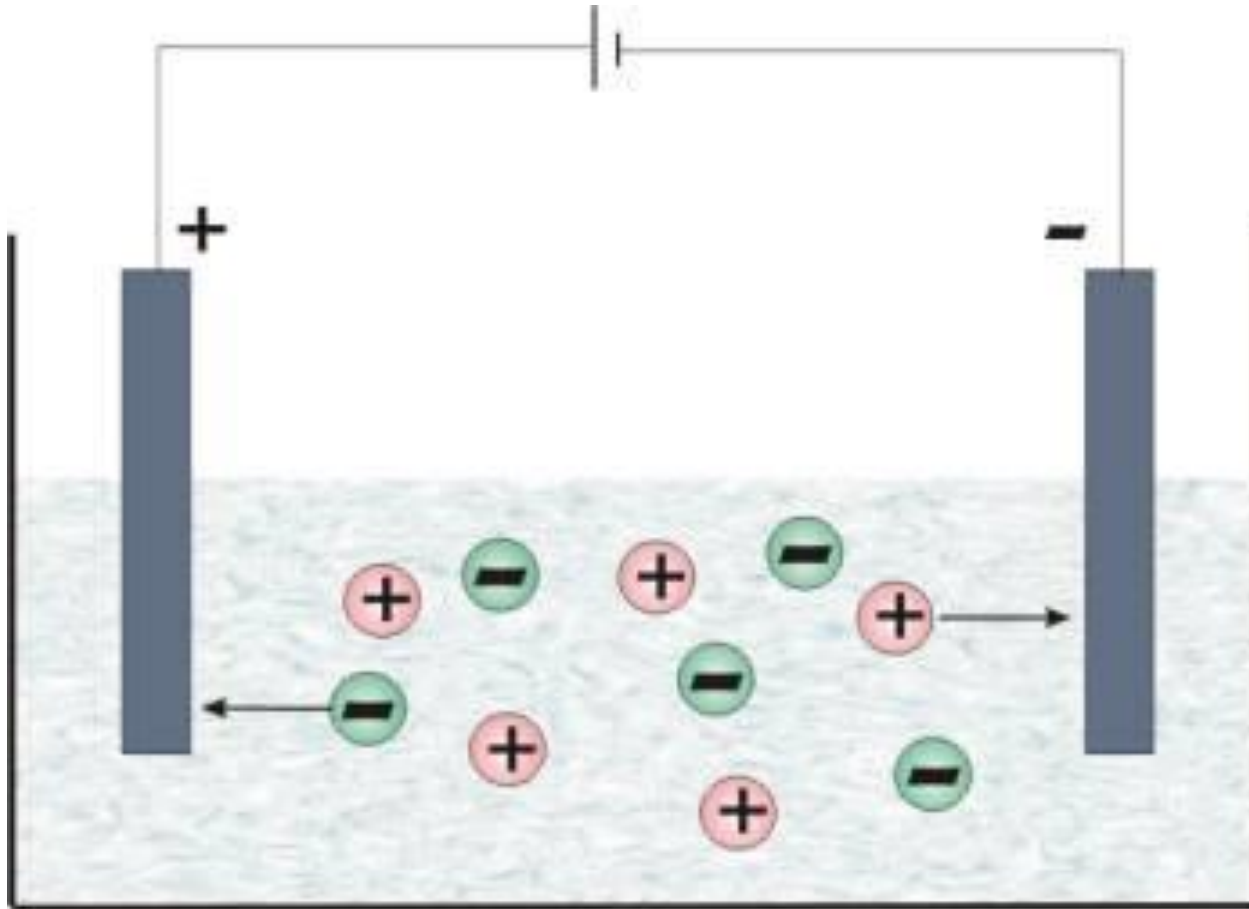
Conductivity in water is affected by the presence of inorganic dissolved solids which consist of:

- anions (Cl^-, NO_3^-, SO_4^{2-}, and PO_4^{3-})
- cations (Na^+, Mg^{2+}, Ca^{2+}, Fe^{3+}, and Al^{3+}).

Organic compounds like oil, phenol, alcohol, and sugar do not conduct electrical current very well and therefore have a low conductivity when in water.

Conductance can be defined as the reciprocal of resistance which means that the conductance of an electrolytic solution is simply the reciprocal of its electrical resistance.

Usually, conductance is given the symbol G and given the units of ohm^{-1} or, in SI units, the siemens (S).

The ability of a solute to conduct electricity is called molar conductance (Λ) which is defined in the equation:

$$\Lambda = \frac{\kappa}{c}$$

K = kappa; conductivity

C = concentration in M

- ✓ Specific conductivity it is a conductivity offered by a substance of 1cm length and 1sq.cm surface area.

- ✓ Equivalent conductivity it is a conductivity offered by a solution containing equivalent weight of solute in it.

- ✓ An equivalent ionic conductance of an ion is defined as its molar conductance divided by the charge on the ion (positive or negative).

Factors affecting conductivity

- Temperature
- Ion size
- Number of ions (concentration)
- Ion charge
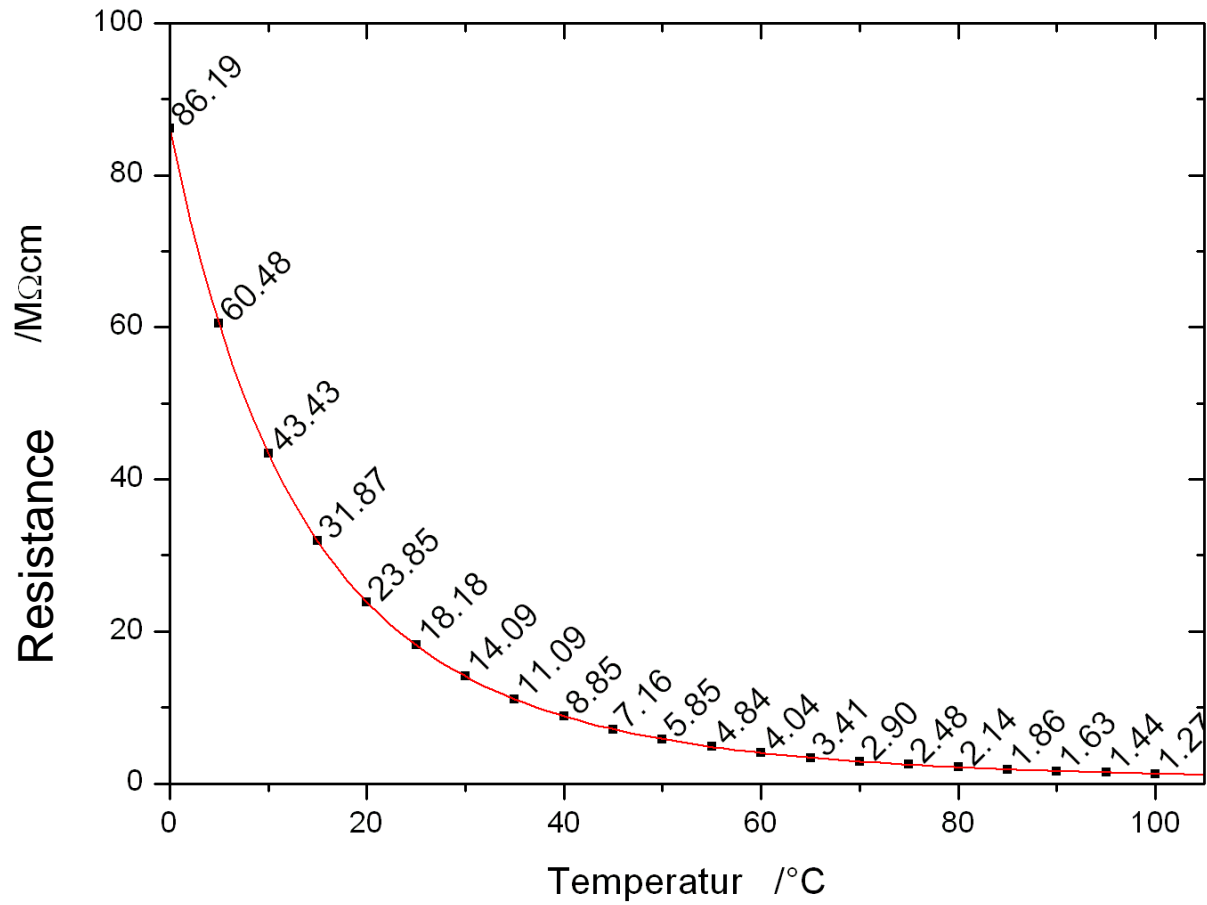
Fig. Resistance of solution vs. temperature

Molar conductance (Λ_m) of various ions at infinite dilution at 25°C

ions	molar conductance
K^+	73.52
Na^+	50.11
Li^+	38.69
H^+	349.82
Ag^+	61.92
Cl^-	76.34
Br^-	78.40
OH^-	198.00
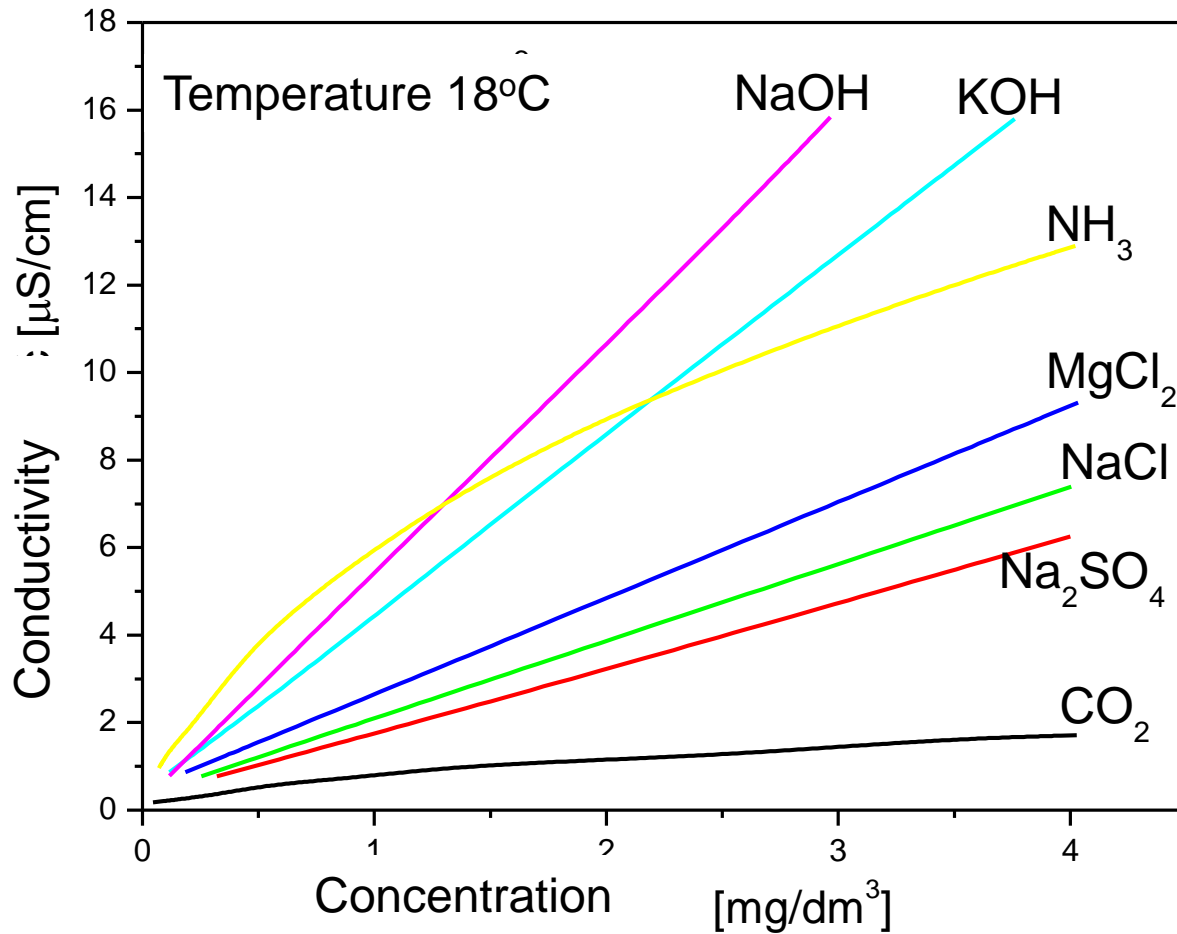
Fig. Relationships concentration of electrolytes vs. conductivity
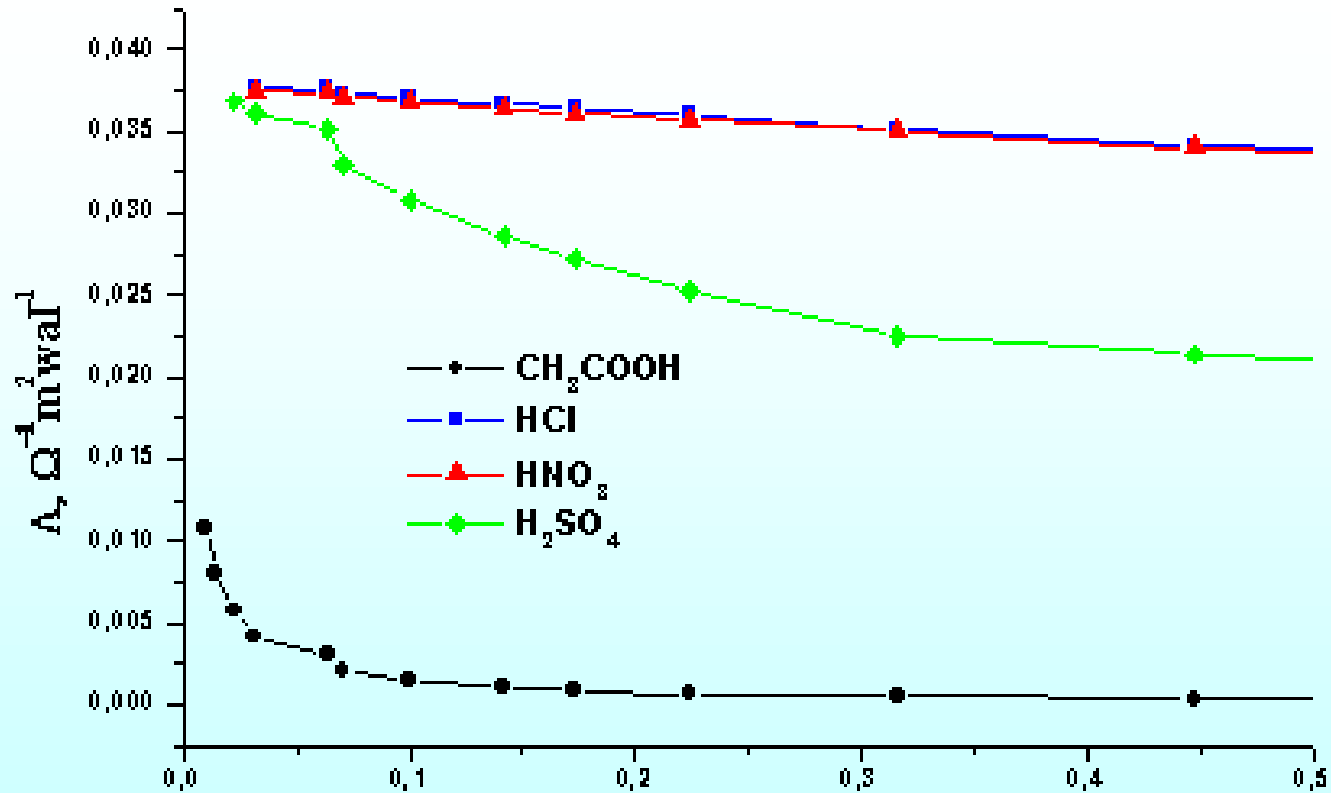
Fig. Electrolyte equivalent conductivity vs. concentration of electrolyte (presented as the square root of concentration).

Tab. 1. Molar conductivity vs concentration relationships for chosen electrolytes.

	Molar conductivity of some solution Λ [cm$^2\cdot$S/mol] 25°C		
C [mol/dm^3]	HCl	NaCl	KCl
0.0005	422.53	124.44	147.74
0.001	421.15	123.68	146.68
0.005	415.59	120.59	143.48
0.01	411.80	118.45	141.09
0.05	398.89	111.01	133.30
0.1	391.13	106.69	128.52
0.5	360.7	93.70	117.41
1	332.2	85.88	112.05
5	167.4	49.5	-
10	70.7	-	-

The molar conductivity (Λ_m) of a strong electrolyte varies with molar concentration in accord with the empirical law discovered by Friedrich Kohlrausch in 1876:

$$\Lambda_m = \Lambda_m^o - K\sqrt{c}$$

Λ_m^0 - the limiting molar conductivity, is the molar conductivity in the limit of such low concentration that the ions no longer interact with one another. The constant K takes into account the effect of these interactions when the concentration is nonzero

When the ions are so far apart that their interactions
can be ignored, we can suspect that the molar conductivity
is due to the independent migration of cations in one direction and
of anions in the opposite direction, and write

$$\Lambda_m^o = \lambda_+ + \lambda_-$$

Tab. 2. Limiting ions conductivity

Cation	$\lambda^{*o}\,[\,S\cdot cm^2\,]$	Anion	$\lambda^{o}\,[\,S\cdot cm^2\,]$
H^+	349.82	OH^-	197.60
Li^+	38.70	Cl^-	76.34
Na^+	50.10	Br^-	77.70
K^+	73.50	J^-	76.85
Ag^+	61.90	NO_3^-	71.46
Mg^{2+}	106.12	$C_2O_4^{2-}$	40.90
Ca^{2+}	122.00	SO_4^{2-}	159.60
Ba^{2+}	130.00	CO_3^{2-}	166.60

Calculations

- Determine the limiting molar conductivity of $CaCl_2$ if the limiting ion conductivity of Ca^{2+} ($\lambda^0 = 122.50$ S cm^2) and Cl^{-1} ($\lambda^0 = 76.32$ S cm^2).

Λ^0 of $CaCl_2 = \lambda^0_{Ca} + 2\,\lambda^0_{Cl} = [122.50 + 2\,(76.32)]$ S cm^2

$= 275.14$ S cm^2

Determination of solute properties

- Degree of dissociation

$$\alpha = \frac{\Lambda}{\Lambda_0}$$

$$\alpha = \frac{(molar\ conductance\ at\ a\ given\ concentration)}{(molar\ conductance\ at\ an\ infinite\ dilution)}$$

For acids and bases the concentrations can be calculated when the value(s) of the acid dissociation constant(s) is(are) known.

$$K_a = \frac{c \cdot \alpha^2}{1-\alpha}$$

For a monoprotic acid, HA, dissociation constant K_a is linked with molar conductivities by:

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^0} + \frac{\Lambda_m c}{K_a (\Lambda_m^0)^2}$$

- Limiting molar conductivity of some weak organic acid water solution is equal to 402,0 S cm ^{2} mol $^{-1}$. 0.1 M solution of the same acid has molar conductivity equal to 15,1 S cm^2 mol $^{-1}$. Calculate:
- a) dissociation degree of this acid
- b) dissociation constant K of this acid

Conductivity can be also used for the determination of:

➢ Solubility of sparingly soluble salts
➢ Ionic product of water
➢ Basicity of organic acids
➢ Salinity of sea water (oceanographic work)
➢ Chemical equilibrium in ionic reactions
➢ Conductometric titration

Applications

Conductivity measurements are used extensively in many industries to monitor quality in:

➢ public water supplies,
➢ in hospitals,
➢ in boiler water
➢ industries which depend on water quality such as brewing.
➢ Conductivity detectors are commonly used with ion chromatography

Checking purity of water

Table of Aqueous Conductivities

Solution	µS/cm	mS/cm	ppm
Totally pure water	0.055		
Typical DI water	0.1		
Distilled water	0.5		
RO water	50-100		25-50
Domestic "tap" water	500-800	0.5-0.8	250-400
Potable water (max)	1055	1.055	528
Sea water	56,000	56	28,000
Brackish water	100,000	100	50,000

Quiz

Conductivity is defined as

- **A)** the ability of a substance to repel electric current.
- **B)** the ability of a substance to conduct electric current, which is the same as resistivity.
- **C)** the ability of a substance to conduct electric current, which is the reciprocal of resistivity.
- **D)** the ability of a substance to conduct variable resistance.
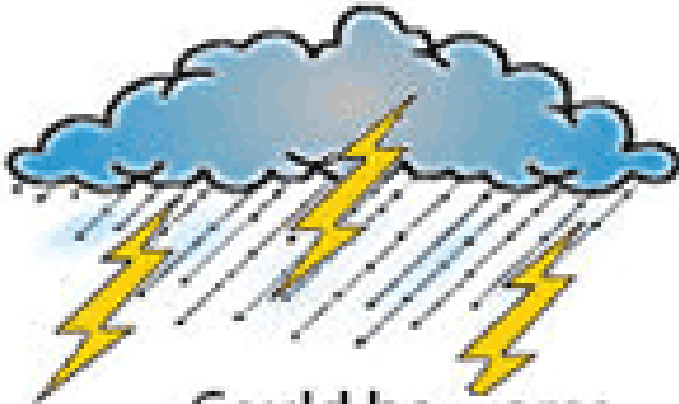
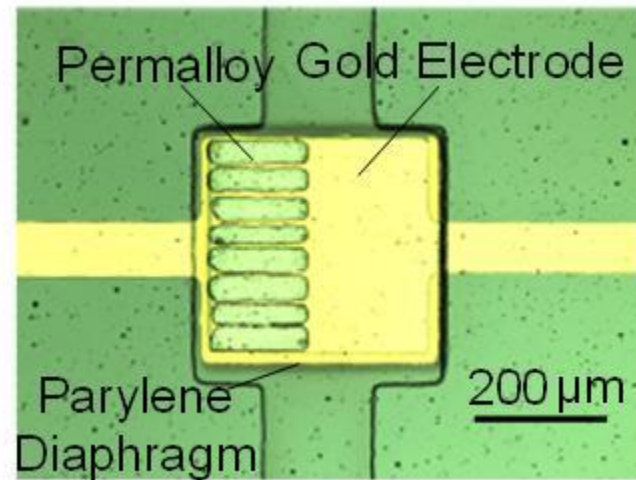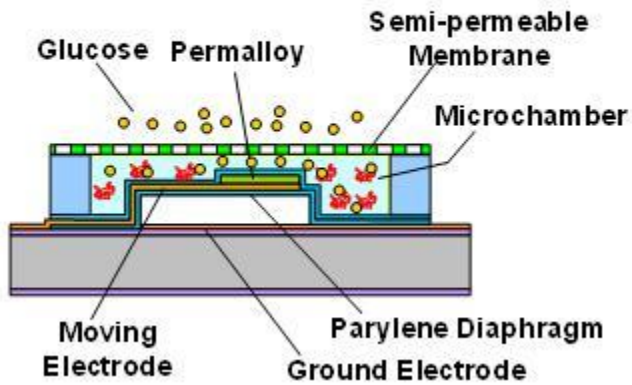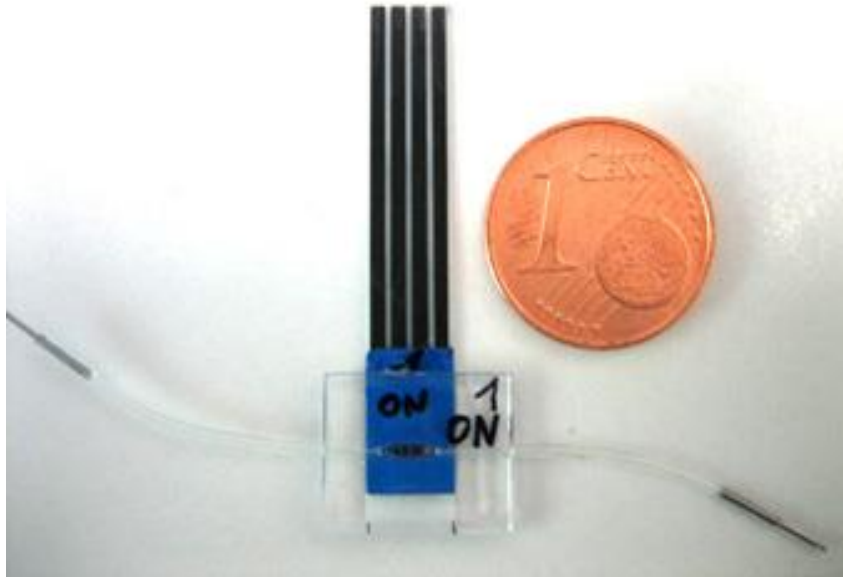Could be worse.
At least I'm bathing
in distilled water!

http://ga.water.usgs.gov/edu/electrical-conductivity.html

Biosensors

http://www.intechopen.com/books/biosensors-emerging-materials-and-applications/development-of-potentiometric-urea-biosensor-based-on-canavalia-ensiformis-urease
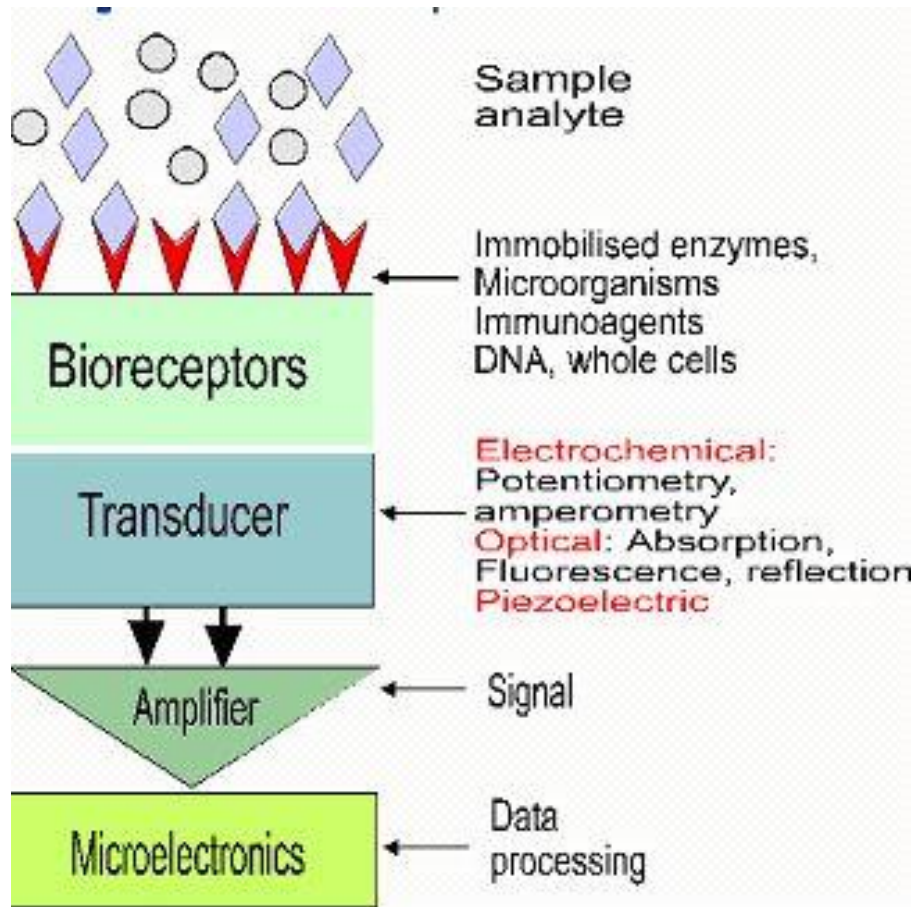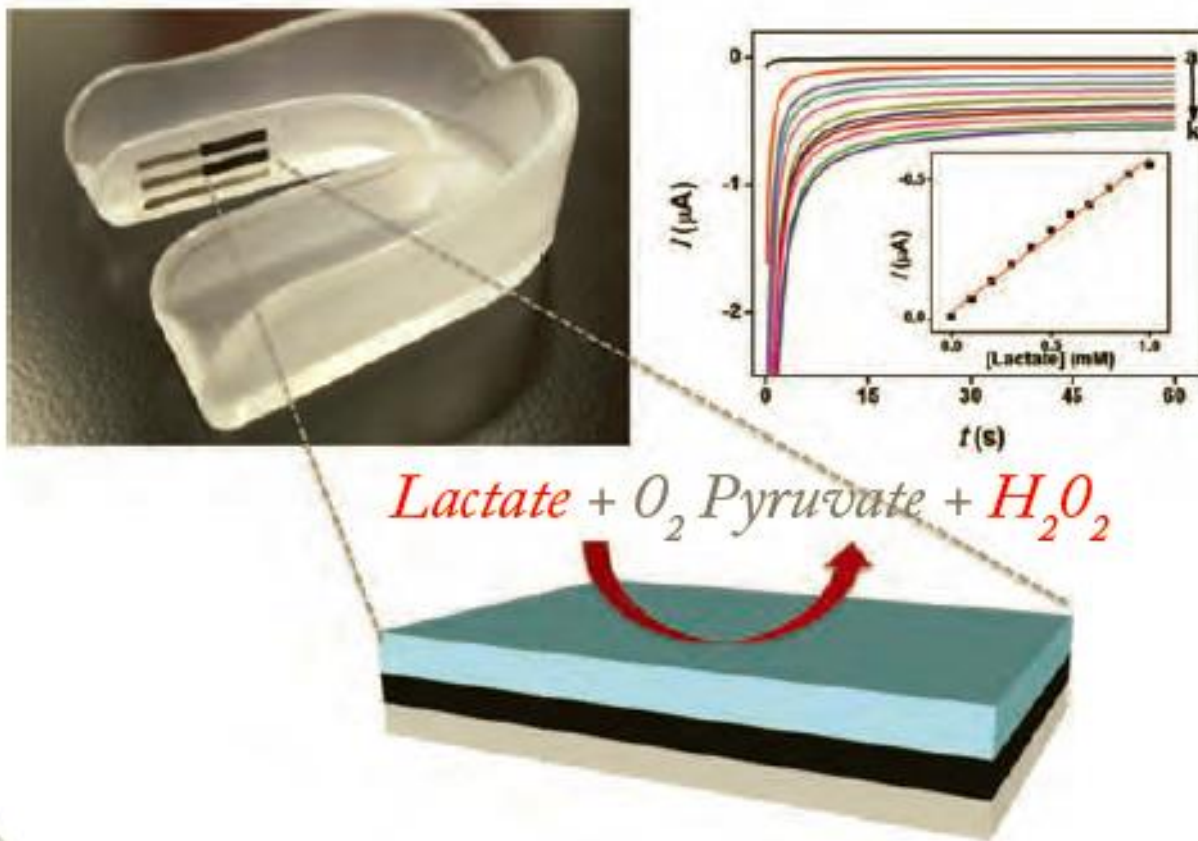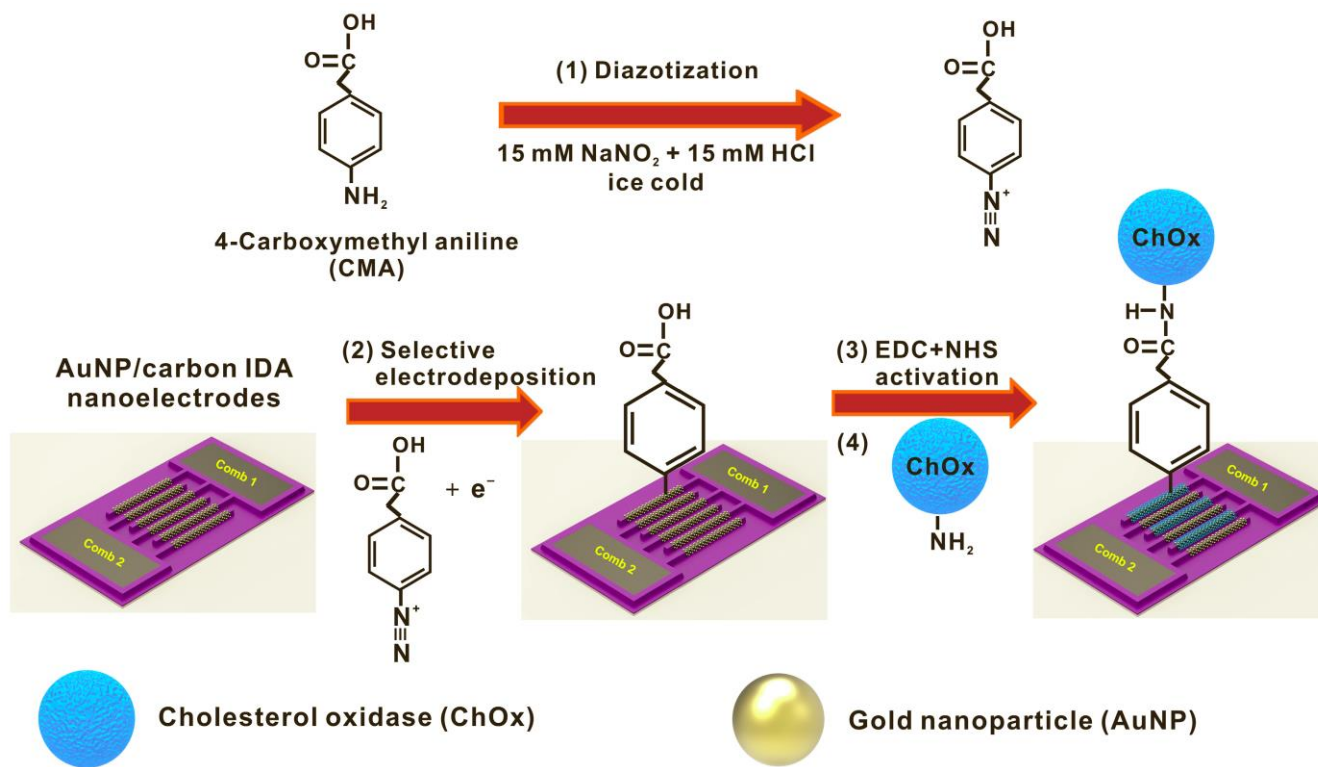
Glucose sensors

Fig. Continuous monitoring of metabolites in saliva using mouthguard provides instant information about health, fitness and stress of the wearer.

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