**Summary Analytical Chemistry**

**Analyte:** The species in the sample about which analytical information is sought.

**Analytical Chemistry:** Chemical discipline which uses scientific methods to find information about an analyte.

**Blank Solution:** A solution containing the solvent and all of the reagents in an analysis, but none of the sample.

**Calibration:** To check or adjust the graduation of a quantitative measuring instrument:
- A process whereby volumes contained by graduated glassware is verified; i.e. auxiliary devices (volumetric flasks, pipettes, burettes, etc.).
- To check or adjust the graduation of a quantitative measuring instrument, instrumentation (balance, chromatographer, spectrometers, etc.).
- The process whereby the analytical signal is caused to bear a known relation to the amount of analyte in the sample, analytical methods.

**C. Curve:** Spectrometry - In order to use absorbance for analytical purposes, it is necessary to prepare a calibration curve by measuring the absorbance of a series of standard analyte solutions having known concentrations of a certain compound.

- Deviations of a linear calibration curve: The ideal graph starts from the origin (0) and proceeds with a linear slope towards a maximum; a, proportionality constant
  \[ S_i = a \cdot c_i + b \]
  b, blank value resulting in an offset
  k, non-linearity coefficient

**Concentration Units:** The following equations are commonly used when operating with liquid mixtures.

- **β - Mass Concentration:** The mass of solute per liter of solution:
  \[ \beta_{(s)} = \frac{m_{(s)}}{V_{(Sln)}} \] [g/L]

- **w - Mass Percent Composition** (weight percentage): The percent by mass of one solvent over the total mass of solvent and solution: e.g.: 30% NaCl in 70% water
  \[ w_{(A)} = \frac{100 \cdot m_{(A)}}{m_{(A)} + m_{(B)} + etc.} \] [%]

- **n - Molar Amount:** The amount of an element per molar mass:
  \[ n_{(x)} = \frac{m_{(x)}}{M_{(x)}} \] [mol]

- **c - Molar Concentration** (M - molarity): The number of moles of solute in 1L of solution (c increases w/ temp.):
  \[ c_{(x)} = \frac{n_{(x)}}{V_{(Sln)}} \] [mol/L]

**Matrix:** The medium that contains the analyte; those substances that are present during the analytical work but that are not of interest and therefore not determined.

**SNR** (signal to noise ratio): SNR is a much better figure of merit than noise alone for describing the quality of an analytical method or the performance of an instrument. For a DC signal, the magnitude of the noise is defined as the standard deviation \( s \) of the measured signal strength, whereas the signal is given by the mean \( \bar{x} \) of the measurement. Thus, \( \text{SNR} = \frac{\text{mean}}{\text{standard deviation}} (\bar{x}/s) \).

**Statistics:** Methods based on observation of systems in equilibrium.

**Error:** The difference between an experimental measurement and its accepted value; the smaller the error the better the reproducibility of a result.
- **Random E. (or Intermediate E.):** Errors that affect the precision of a measurement; usually those sort of errors that are non-predictable and statistically based.
- **Systematic E. (or determinate E.):** Errors that affect the accuracy of results; usually user-related errors which are made during the analytical process.

**µ - Mean** (or \( \bar{x} \)): Synonymous with arithmetic mean, average; a way of reporting what is considered the most representative value for a set of replicate measurements.

\[ \mu = \frac{\sum x_i}{N} \]
x<sub>i</sub>, individual result
N, total number of measurements

**Spread:** The difference in range of a set of replicate measurements between the highest and the lowest result; base of a Gaussian peak defined as: \( w = 4 \cdot \sigma \)

**σ - Standard deviation:** Defines the bounds about the mean \( \mu \) (\( \bar{x} \)) within which approximately 67% of the data in a Gaussian distribution can be expected.

\[ \sigma = \sqrt{\frac{\sum(x_i - \mu)^2}{N}} \]
x<sub>i</sub>, individual result
\( \mu \), mean (or \( \bar{x} \))
N, total number of measurements

**σ<sub>m</sub> - Standard error of the mean:** The standard deviation divided by the square root of the number of measurements in the set.

\[ \sigma_m = \frac{\sigma}{\sqrt{N}} \]
\( \sigma \), standard deviation
N, total number of measurements
Validation: Verification, substantiation of suitable steps that an analytical method does perform the way it should; this includes:

Correctness (accuracy and precision): A qualitative property outlining the wrong from the correct (true); i.e. the correlation of the measured values and the mean - can be falsified by the presence of systematic and random errors.

- Accuracy: The closeness of a result to its true or accepted value; a measure of the agreement between an analytical result and the accepted value for the quantity measured; this agreement is measured in terms of errors (systematic and accidental errors); a result can be accurate (mean) even though the individual values deviate enormously (low precision).

- Precision (reproducibility): The closeness of data to other data that have been obtained in exactly the same way; a result can be precise but poor in accuracy when the mean value is shifted towards the absolute value with a certain bias.

Limit of Detection (LOD, D = Nachweigrenze): The lowest concentration which can still be detected but not quantified.

Limit of Quantification (LOQ, D = Bestimmungsgrenze): The lowest concentration at which quantitative measurements can be made; SNR better than 6.

Robustness (reliability): ???????????????????

Selectivity: The tendency for a reagent or instrumental methods to respond similarly with several species; any one species thus represents a potential interference in the analysis of any of the others of the group; the property of an analytical method to detect the analyte despite a massive interference with the of other components (matrix); it can be:

- substance specific: detects a certain substance only;
- selective: detects a series of chemical substances;

Methods in applied Analytical Chemistry:

Gravimetric Method: An experimental procedure that involves the measurement of mass; i.e. a quantitative method that is based upon determination of mass of a pure compound to which the analyte is chemically related. Most often used with ionic compounds and involves the formation, isolation, and mass determination of a precipitate.

Hydration: A process in which an ion or a molecule is surrounded by water molecules arranged in a specific manner; e.g.: water - H2O molecules attach to a central ion (ion-dipole interaction).

Hydrated Anion: Hydrogen bonds form between the H of water and the central anion; e.g.: SO4^2-.

Hydrated Cation: Ion-dipole forces between the O of water and the central ion; e.g.: Be^2+.

Solubility: The maximum amount of solute that can be dissolved in a given quantity of a specific solvent at a specific temperature (for gases: at a specific pressure); the concentration of a saturated solution of a substance; e.g.: how much of a salt can be dissolved in a solvent.

\[ K_{sp} = \text{Product} \]

For solutions with low ionic concentrations:

\[ K_{sp} = a_{\text{anion}} \cdot a_{\text{cation}} \]

Precipitate: The solid formed in a precipitation reaction; i.e. an insoluble solid (phase change) that separated from the solution.

- P. methods of analysis: Gravimetric and titrimetric methods involving the formation (or less frequently), the disappearance of a precipitate.

- P. from homogenous solutions: The chemical generation of a precipitating agent within the solution that contains the analyte; i.e. homogenous precipitation: e.g. supersaturated urea solution

\[(\text{NH}_2\text{H})_2\text{CO} + 3\text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{NH}_4^+ + 2\text{OH}^- \]

- P. reaction with increased pH: Any change of pH containing a metal ion will form an insoluble precipitate once the pH rises (increased OH^- activity); the extent of precipitation depends upon the solubility product of the metal precipitate (KSP) and the temperature (see table below); e.g.

\[ \text{Me}^{2+} + 2\text{OH}^- \rightarrow \text{Me(OH)}_2 \]

Amphoteric Hydroxide: An Me^{2+}(OH)^2 that exhibits both acidic and basic properties; this results in a stable precipitation window which should be buffered; i.e. below and above this window the hydroxide is aqeous: [Al(H_2O)_6]^{3+}

acid: [Al(H_2O)_6]^{3+} + 3\text{OH}^- \rightarrow \text{Al(H}_2\text{O})_3\text{OH}_3(s) + 3\text{H}_2\text{O} 

base: Al(H_2O)_3OH_3(s) + \text{OH}^- \rightarrow [\text{Al(H}_2\text{O})_2\text{OH}_4^+] + \text{H}_2\text{O} 

**Electroanalytical Method**: A group of quantitative analytical methods that are based upon the electrical properties of a solution of the analyte when it is made part of an electrochemical cell. Electrochemical methods are used to (1) determine the activity of ions; i.e. ion-sensitive electrodes, and (2) for the determination of the equivalence point in titrimetric analysis.

- **Electrochemical Cell** (Voltaic Cell): A system consisting of two electrodes in contact with an electrolyte.
  - **Galvanic** C. An electrochemical cell used to produce electricity by means of a spontaneous redox reaction (see anorganic chemistry - ecs)
  - **Electric** C.: An electrochemical cell in which an electric current is used to cause chemical change; Here anode (+), cathode (-) to start a reaction by imposing an external force during electrolysis. e.g.: Zn electrode (anode) + Cu electrode (cathode) produces an electric current if emerged in an electrolyte; resulting in two half reactions:

\[ \text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^- \quad 2e^- + \text{Cu}^{2+}(aq) \rightarrow \text{Cu}(s) \]

overall reaction: \[ \text{Zn}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s) \]

**Electroanalytical Methods working w/o a current:**

- **Potentiometry**: That branch of electrochemistry concerned with the relation between potential and analyte concentration; used for the detection of ions (H\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), Ag\(^{+}\), Pb\(^{2+}\), Cd\(^{2+}\), Cu\(^{2+}\), alkaline species, etc.), halogens (Cl\(^-\), and CN\(^-\), SCN\(^-\), S\(^2-\), NO\(_3^-\)), neutral molecules (NH\(_3\), NO\(_x\), SO\(_2\), CO\(_2\),...all indirectly) and organic molecules (e.g. NH\(_2\)-CO-NH\(_2\), glucose, etc.)

- **Electrode**: A conductor at the surface of which electron transfer to or from the surrounding solution takes place. Generally, if two different metal dip into an ionic solution, the metal with the higher E\(^0\) becomes reduced (Me\(_{\text{red}}\)) while oxidizing the metal with the lower E\(^0\) (Me\(_{\text{aq}}\)).

- **Electrode of the 1\(^{\text{st}}\) kind** (reference electrode): A pure metal electrode whose potential is proportional to the logarithm of the analyte concentration (activity) of a cation that is derived from that metal:

\[ \text{Me}^{n+}(aq) + n \cdot e^- \leftrightarrow \text{Me}(s) \]

**Electrode of the 2\(^{\text{nd}}\) kind**: A metallic electrode (e.g. Ag) whose response is proportional to the logarithm (activity) of an anion (Cl\(^-\)) that either forms a sparingly soluble species or complexes with a cation that is derived from the electrode metal:

\[ \text{AgCl}(s) \leftrightarrow \text{Ag}(s) + \text{Cl^-(aq)} \]

- **Membrane Electrode**: An indicator electrode whose response is due to ion-exchange processes on each side of a thin membrane; e.g. glass to measure pH, pCa, pNO\(_3^-\), etc. A glass electrode is based on the mobility of either an anion or cation (solid state ionic conductor); once dipped into an electrolyte, these ions leaving/reentering the membrane surface result in a boundary potential (in the case of pH, dependant upon the hydrogen ion activity).

- **Alkaline Error**: In basic solutions, glass electrodes respond to the concentration of both H\(^+\) ions and alkali metal ions. The extent of the error depends upon the concentration of the base, charge and type of metallic acid metal ion (the measured pH values are lower than the true values, generally at low base concentration and high level of alkali metal ions present in the solution).

- **RedOx Electrode** (Inert electrode): An electrode made of an inert metal (Au, Pt, Pd, C) whose potential is proportional to the logarithm of the ionic concentration (activity) of the analyte; e.g.:

\[ \text{Fe}^{3+} + e^- \leftrightarrow \text{Fe}^{2+} ; \quad \text{E}_{\text{red}}, \text{ electrode potential of Me } \quad [\text{V}] \]

\[ \text{E}_{\text{ind}} = \text{E}_{\text{Me(n+)}} + \frac{0.0592}{n} \cdot \ln \left( \frac{a_{\text{Me(n+)}}}{a_{\text{Me}}(s)} \right) \quad [\text{V}] \]

\[ n, \text{ number of electrons involved} \quad [\text{mol/L}] \]

\[ \text{E}^0_{\text{Me(n+)}} \text{, standard electrode pot.} \quad [\text{V}] \]

\[ a_{\text{Me(n+)}} \text{, activity of Me-ion} \quad [\text{mol/L}] \]

\[ E_{\text{ind}} = E_{\text{Me(n+)}} + 0.0592 \cdot \log \left( \frac{a_{\text{Me(n+)}}}{a_{\text{Me}}(s)} \right) \]

\[ n, \text{number of electrons involved} \quad [-] \]

- **Standard Electrode Potential**: Is defined as the electrode potential when all reactants and product of a half-reaction are at unit activity (see table below):

\[ \text{Me}^{n+}(aq) + n \cdot e^- \leftrightarrow \text{Me}(s) \]

\[ \text{E}_{\text{ind}} = \text{E}_{\text{Me(n+)}} + 0.0592 \cdot \ln(a_{\text{Me(n+)}}) \quad [\text{V}] \]

\[ n, \text{number of electrons involved} \quad [\text{mol/L}] \]
Electroanalytical Methods involving a current:

**Conductometry**: Determination of the specific resistance of 1cm³ (=1mL) of an ionic solution; to avoid polarizing effects usually executed with alternating current in the kHz/MHz-range. It can provide a quick estimate about the contamination level of a water body. d, distance of electrodes [m]

\[ \chi = \frac{d}{R \cdot A} \quad [S/m] \]

R, Resistance [Ω]

A, area of electrode [m²]

Conductometric detector: A detector for charges species, used in ion chromatography.

Conductometric Titration: Change of ionic concentration during titration - i.e. conductivity is minimum (max. specific resistance) at the equivalence point.

**Coulometry**: Use of a coulometer permits measurement of the quantity of charge. The charge is a direct indicator of the energy consumed during quantitative electrolysis (100% of the analytes converted).

\[ q = \frac{M \cdot z \cdot F}{M} \quad [g] \]

z, number of electrons swapped [-]

M, molar mass of analyte [g/mol]

F, Faraday constant 96493 [C/mol]

Electronic coulometers evaluate the integral of the current/time curve;

Chemical coulometers are based on the extent of reaction in an auxiliary cell.

**Electrogravimetry**: A branch of gravimetric analysis that involves measuring the mass of species deposited on an electrode of an electrochemical cell.

**Voltammetry**: A collective term for a large group of instrumental techniques that are based on the current resulting from the application of a continuously varying voltage to small electrodes. It is based on the RedOx-properties of the analyte in solution, which includes not only ions but also neutral molecules (hormones, etc.); sensitivity as low as 1pg!

- **Amperometry**: An externally applied constant DC voltage will force a current through the solution containing the analyte; the change of current while changing the concentration of the analyte

Amperometric Detector: In Chromatography

Amperometric Titration: A method based on the application of a constant potential to a working electrode and measurement of the resulting current; a linear segment curve is obtained.

**CE (Capillary-Electrophoresis)**: CE is a process in which charged species (ions or colloidal particles) are separated based upon differential migration rates in an electrical field. Migration is strongly dependent upon pH, ion strength of buffer, charge and particle size of analyte, strength of externally applied electric field, and temperature.

**Electro-Osmotic Flow (EOF)**: EOF occurs in which the solvent moves from the vessel containing the positive electrode (anode) to the one containing the negative (cathode). The fixed negative charges on the capillary surface arise from dissociation of functional groups making up the fused-silica surface. The mobile positive ions that ring the interior surface of the tubing are attracted to the negative electrode carrying solvent molecules with them. A unique feature of EOF is that the flow profile is nearly flat.

**Reversed EOF**: Reversion of EOF to the anode can be achieved by introducing a large quantity of negatively charged ions (anions) which redirect the flow direction to positive electrode (anode).

- **Polarography**: It is based on the diffusion controlled migration of an analyte to the surface of a dropping mercury electrode; i.e. electrolytic process at the Hg-electrode yields the composition of the separated species involved according to the voltage, current and concentration of the analyte. Used for the detection of environmentally relevant species like Pb, Cd, Tl, As (sensitivity: <10ng).

- **Potentiometric Titration**: A titrimetric method involving measurement of the potential between two electrodes (a reference electrode and an indicator electrode) as a function of titrant volume.
Chromatography: A term for methods of separation based upon the partition of analyte species between a stationary phase and a mobile phase. Chromatographic separation is based on the various migration rates of the individual species of the analyte.

- **Adsorption-C.**: A separation technique in which the stationary phase is a finely divided solid; partition is accomplished by altering the composition of the mobile phase.
- **Verteilungs-C.**: Distribution of analyte according to its solubility properties in a two phase mixture.
- **Band Broadening**: The tendency of analytes to spread as they pass through a chromatographic column; caused by various diffusion and mass transfer processes:
  - **Eddy Diffusion**: Diffusion of solutes that contributes to broadening of chromatographic bands, the result of differences in the pathways for solutes as they traverse the column.
  - **Flow Profile**: A gradient (parabolic shape) of relative velocity exists in which the fluid layers closest to the stationary phase have the lowest (zero) while those in the center the maximum relative velocity.
  - **Longitudinal Diffusion Term**: The ratio of longitudinal diffusion to the velocity of the mobile phase; low velocities of the mobile phase result in backwards directed diffusion of separated species
  - **Stationary Phase Mass Transfer**: A measure of the ability of analyte molecules to traverse the stationary phase; analyte molecules trapped in the pores of the stationary phase can only continue species separation by backwards diffusion out of the pore.

Chromatogram: A plot of some function of solute concentration versus elution time or elution volume.

**Chromatographic Band**: The distribution (ideally Gaussian) of eluted species about a central value; the result of variations in the time that the analyte species resides in the mobile phase.

**Eluent**: A solvent used to carry the components of a mixture through a stationary phase.

**Elution**: A process in which solutes are washed through a stationary phase by the movement of a mobile phase.

**Phase**: In chromatography, a distinct state of matter, or solubility properties.

- **Mobile P.**: The phase that moves over or through the stationary phase, carrying the analyte with it.
- **Stationary P.**: The phase that is fixed in place either in a column or on a planar surface.

**Retention Time**: The time between injection of a sample and the appearance of a solute peak at the detector of a chromatographic column.

**Theoretical Plate**: Equilibria between the analyte and the stationary phase; the longer the chromatographic system, the more plates can be resolved - the better the separation of the species of the analyte.

\[
N = 16 \cdot \left(\frac{t_{re}}{w}\right)^2 \quad [-]
\]

\[
t_{re}, \text{ retention time} \quad [s]
\]

\[
w, \text{ peak-width at the base} \quad [s]
\]

**Chromatographic methods**:

**Thin Layer Chromatography** (TLC): Separation is performed on a glass plate that is coated with a thin and adherent layer of finely divided particles (stationary phase). The mobile phase is somewhat similar to the analyte in that sense that the probe can be moderately dissolved in it.

- **Retention Factor** \( R_f = \text{distance of analyte from start-position} / \text{distance of upper limit of mobile phase} \)
- **Elutropic Series**: Established to evaluate the polarity of solvents (after Snyder); he classified strong polar and weak (weakly polar or nonpolar) solvents. The basis of this polarity scale is solubility measurements in dioxane, nitromethane and ethanol.

**High Performance Liquid Chromatography** (HPLC): A type of chromatography that employs a liquid mobile phase and a very finely divided stationary phase. In order to obtain satisfactory flow rates, the liquid must be pressurized (up to 400bar). The smaller the particle size of the stationary phase the better the performance of separation. Detectors in HPLC are mostly UV-Spectrometers or Photometric Array detectors.

**Gas-Chromatography** (GC): Methods that make use of a gaseous mobile phase (e.g. H₂, N₂ or He, low viscosity) and a liquid (GLC) or a solid (GSC) stationary phase. Only those substances with a high vapor pressure can be scanned by GC.

- **GLC**: In GLC, the mobile phase is a gas and the stationary phase is a liquid that is retained on the surface on an inert solid by adsorption or chemical bonding.
- **GSC**: In GSC, the mobile phase is a gas and the stationary phase is a solid that retained the analytes by physical adsorption.
Spectroscopy: A general term to describe analytical methods based on absorbance, chemi-luminescence, emission, or fluorescence; i.e. an optical method mainly based on the interaction between electromagnetic radiation and matter.

- **Absorbance**: The logarithm of the ratio between the initial power of a beam radiation and its power after it has traversed an absorbing medium; usually given as absorbance units [au].
  \[ A = \log \frac{I_0}{I} \text{ [au]} \]
  where \( I_0 \) is the initial intensity and \( I \) is the intensity after passing through the absorbing medium.

- **Amplitude**: The vector quantity of a wave that provides a measure of the electrical or magnetic field strength at a maximum in the wave.

- **Electronic Transition**: Involves the transfer of an electron from one electronic orbital to another. An atom lacks EV + ER; EV, interatomic vibrational energy; ER, molecular rotational energy.

- **Frequency**: The number of oscillations that occur in one second in [Hz].

- **Monochromator**: A device for resolving polychromatic radiation into its component wavelengths.

- **T - Period**: The time in [s] for the passage of successive maxima or minima to pass a point in space.

- **Photon**: Is a particle of electromagnetic radiation having zero mass and the energy \( E = \nu \cdot h \) [J⋅m] in which \( \nu \), frequency [1/s] = [Hz] and \( h \), Planck's constant 6.63⋅10^{-34} [J⋅s].

- **Spectrum**: The splitting of white light into its distinct components. Continuous S.: It is made up of many closely spaced lines that are difficult to resolve. Line S.: The line widths in a typical atomic spectrum are about 1 pm; the wavelengths of atomic lines are unique for each element and are often used for qualitative analysis.

- **Absorption S.**: A continuous spectrum, like that of white light, interrupted by dark lines or bands that result from the absorption of certain frequencies of light by a substance through which the radiant energy passes; a plot of absorbance as a function of wavelength (e.g. Fraunhofer lines).

- **Emission S.**: The distribution of wavelengths in the light from a luminous source; every element has its particular distinguishable pattern of electron energy level (responsible for chemical properties) and therefore emits its own characteristic collection of spectral lines that are observed when species in exited states relax by giving off their excess energy as electromagnetic radiation (E = νh).

- **Transmittance**: The fraction of incident electromagnetic radiation that is transmitted by a sample as stated by the Lambert-Beer's Law:
  \[ T = \frac{I}{I_0} \text{ [-]} \]
  where \( I_0 \) is the initial intensity of the radiation and \( I \) is the intensity after passing through the absorbing medium.

- **Wavenumber**: The reciprocal of the wavelength in [1/cm].

- **Wavelength**: The distance between successive maxima or minima of a wave in [m].

Spectroscopic methods: A spectroscopy is an optical instrument that separates light into its constituent frequencies in the form of spectral lines.

**Absorption spectroscopy** (AS): In principle based on the absorption of radiation by inducing vibration in electrons of atoms, using heat as the stimulating source, a light source identical to the expected sample (e.g. Na-pressure lamp), and a photometer as a detector.

Processes occuring during atomization (increasing temperature from left to right)

<table>
<thead>
<tr>
<th>nebulization</th>
<th>desolvation</th>
<th>volatilization</th>
<th>dissociation</th>
<th>ionization</th>
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<tr>
<td>solution of analyte</td>
<td>spray</td>
<td>solid/gas aerosol</td>
<td>exited molecules</td>
<td>atoms</td>
</tr>
<tr>
<td>addition of gas and oxidants (dry)</td>
<td></td>
<td>(melting, gaseous)</td>
<td>exited molecules</td>
<td></td>
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AS works at room temperature and works with a limited set of emitted lines according to the energy levels allowed for a particular element. An energy level diagram of an outer electron of a particular atom is based on the quantum numbers:

- **Quantum Number**: The quantum numbers of quantum mechanics which describe the distribution of electrons, labels the state of the electron and specifies the value of a property in atoms.
  1. \( n \) - Principal QN (shell number): The average distance of the electron from the nucleus in a particular orbital; can have integral values of 1, 2, 3, and so forth (higher values = greater average energy e.g.): \( 1 = 1^{\text{st}} \) period, \( 7 = 7^{\text{th}} \) period;
  2. \( l \) - Angular Momentum QN.(shubshell of one shell): Its value reflects the orbital shape; correlates with \( n \); (\( l = n-1 \)); which reveals 0 for the s-, 1 for the p-, 2 for the d-; 3 for the f-, 4 for the g- 5 for the h-orbital.
  3. \( m_l \) - Magnetic QN: It describes the orientation of the orbit in space and depends upon \( l \); \( m_l = 2/-1 \) e.g.: \( m_l = 1 \) a sphere; \( m_l = 3 \) gives \(-1/0/+1 \) (x,y,z-orientation); \( m_l = 5 \) gives \(-2/-1/0/1/2 \) etc.
  4. \( m_s \) - Electron Spin QN: According to the electromagnetic theory, spinning electrons posses a magnetic orientation; \( m_s = n \) \( m_s \) can either be \(-1/2 \) or \(+1/2 \); with \( m_s = 3 \) giving 3 magnetic spins: \(-1/2 \) or \(+1/2 \) or \(-1/2 \).
Atomic Absorption S (AAS) A highly selective method based on the absorption of radiation emitted by a primary radiation source by the atom in the ground state. A flame atomizer (for elements with low ionization energy, i.e. alkali and alkaline earth metals), or a graphite furnace (elements requiring higher ionization energies, i.e. transition metals, lanthanides, actinides, metalloids, nonmetals, etc.) generate the atomic vapor of the sample; i.e. nebulization converts it into a mist of finely divided droplets by a jet of a compressed gas which carries the sample into a heated region where atomization takes place. Thus an atomic absorption spectrum typically consists predominantly of resonance lines which are the result of transition from the ground state to upper levels.

Continuous Atomization: The sample is fed into the flame atomizer continuously at a constant rate yielding a signal that is constant with time.

Discrete Atomization: A measured quantity of sample is introduced as a plug of liquid or solid into the electrothermal atomizer. AAS provides a signal that rises to a maximum and then decreases to zero.

Infrared S. (IRS): Vibrational absorption of IR-frequencies result in an IR-spectrum, which shows closely spaced absorption peaks resulting from transitions among the various vibrational and rotational quantum levels of functional groups contained in the sample molecule. IRS is not useful in determining quantitative measurements but provide a powerful tool for qualitative analysis (except for a few homonuclear molecules such as O₂, N₂, Cl₂) since most molecular species absorb IR radiation.

Stretching Vibration (also valence vibration): It involves a continuous change in the interatomic distance along the axis of the bond between the atoms.

Bending Vibration (deformative vibration): Are characterized by a change in the angle between two bonds and are of four types: scissoring, rocking, twisting, wagging.

UV-VIS-Spectroscopy (UltraViolet and VISible S.): A spectrometer that detects radiation associated with electronic transitions in atoms and molecules in the electromagnetic spectrum between 180-780nm.

Colorimeter: Quantitative Determination of a dissolved Substance according to the hue yielded in the visible spectrum. In colorimetry, the human eye functions as the detector.

Spectro-photometer: A spectrometer designed for the measurement of absorbance. It uses a monochromator to analyze the absorbance of a distinct wavelength.

Emission spectroscopy: The collection of spectral lines that are observed when species in excited states relax by giving off their excess energy as electromagnetic radiation.

Atomic Emission S. (AES): A method that makes use emission characteristics of the analyte.

At room temperature, essentially all of the atoms of a sample of matter are in the ground state. Excitation of an outer electron to higher orbitals can be brought about by the heat of a flame or an electric arc or spark. The lifetime of an excited atom is brief and its return to the ground state is accomplished by the emission of a photon of radiation. Emission spectra contain far more information (i.e. peaks) than AAS, which requires a high resolving power of the monochromator.

Atomic Fluorescence S. (AFS): A method that makes use fluorescence characteristics of the analyte.

Fluorometry: A method for quantitative fluorescence measurements of fluorescing molecules. Fluorescence radiation is propagated from the sample in all directions, but is most conveniently observed at right angles to the excitation beam. The emitted radiation passes through a second monochromator to reach the photometer; fluorometric methods are 10 to 1000 times more sensitive than absorption methods.

Self absorption: The exciting radiation increases in amplitude as it propagates through the sample.

Quenching: The attenuation of fluorescence by some other species (often an anion) in a solution.

Photometer: An instrument for the measurement of absorbance; it incorporates a filter for wavelength selection and a photoelectric detector.

X-Ray Spectroscopy: A method used to analyze atoms using x-rays.

Mass Spectroscopy (MS): MS is based on the generation of gaseous ions from analyte molecules, the subsequent separation of these ions according to their mass-to-charge (m/z) ratio, and the detection of these ions. Ionization of the sample is brought about bombarding it with electrons, ions, molecules, or photons. The (usually) positive ions are accelerated into the mass analyzer and deviated perpendicularly towards the detector (via a strong electromagnetic or electrostatic field). The mass-to-charge ratio of the ion is proportional externally applied external field.

The resulting mass spectrum is a plot of the (relative) abundance of the ions produced as a function of the m/z ratio.
Analytical Chemistry

Titrmetric Method: It is based upon determination of the quantity of a reagent of known strength (tirant) that is required to react completely with the analyte. The reagent may be a standard solution of a chemical (or an electric current of known magnitude); the gradual addition of a solution of accurately known concentration to another solution of unknown concentration until the chemical reaction between the two solutions is complete (shift to the right of the EQ).

• Buffer: A mixture of a weak acid/base and its conjugate base/acid that resists changes in pH of a solution.

• Equivalence Point (stoichiometric point): The stage in a titration when exactly the right volume of solution needed to complete n, molar amount [mol] the reaction has been added; $n(An)_{An} = n(Ti)_{Ti}$

• Equivalence Concentration: Molar concentration of equivalent $z^*$ [mol/L]; a fictive unit which facilitates the handling of standard solutions, and analytic results of titrations; *Neutralization*: Equivalent in terms of protons (H$^+$): HCl, 1/2H$_2$SO$_4$, 1/3H$_3$PO$_4$, 1/2Ba(OH)$_2$

• *Redox*-Equivalent in terms of electrons (e$^-$): Fe$^{2+}$, Fe$^{3+}$, 1/5KMnO$_4$ (5e$^-$), 1/6KBrO$_3$ (6e$^-$)

• *Ion*-Equivalent: Na$^+$, 1/2Mg$^{2+}$, 1/3Al$^{3+}$

• Indicator: A weak organic acid or base that changes color when it shifts from acid to its base form; i.e. acid-base neutralization (acid-base indicator) or from its oxidized to its reduced form (redox indicator); see also table below:

\[
\text{HInd(aq) + H}_2\text{O(l)} \leftrightarrow \text{H}_3\text{O}^+(aq) + \text{Ind}^-(aq)\]

where $c(H_3O^+)$ is the H$^+$ concentration (pH) of the anylate.

\[
K_{(Ind)} / c(H_3O^+) = c(\text{HInd}) / c(\text{Ind^-}) \ [\text{mol/l}]
\]

- if $c(\text{HInd}) / c(\text{Ind^-}) > 1$, color of acid (Hind) predominates
- if $c(\text{HInd}) / c(\text{Ind^-}) < 1$, color of conjugate base (Ind$^-$) predominates

Preconditions are: 1) HIn and In$^-$ have to be water soluble, 2) HIn and In$^-$ have to separate colors, 3) Indicator concentration $c(HIn)$ has to be low, 4) $c(H_3O^+)$ of indicator should measure only pH of solution.

• Standard Solution: A solution in which the concentration of a solute is known with high reliability:

Primary S. (Urtitter): This is an ultrapure compound that serves as the reference material for a titrimetric method of analysis, with the following features: high purity, stability towards air, should correspond to the stoichiometric formula, reasonable large molar mass (reduces weighing errors), stable (as substance and as solution)

Secondary S. (Reference solution): This is a compound whose purity has been established by chemical analysis and serves as the reference material for a titrimetric method of analysis.

• Titration Curve: The sigmoidal profile of pH vs. $\tau$ (level of titration) of the anlylate over the volume of titrant added. The titrimetric process can be observed in the following manner:

Colorimetric T.: Traditional method using a chemical indicator for the detection of the EP;

Conductometric T.: Conductivity measurement during titration; conductivity is minimum at the EP;

Coulometric T.: A variety of coulometric analysis that involves measurement of the time needed for a constant current to complete a chemical reaction.

Photometric T.: Absorbence of the reaction is detected by the photometer (similarly as in colorimetry);

Potentiometric T.: A titrimetric method involving measurement of the potential b/w two electrodes (a *reference* and an *indicator* electrode) as a function of titrant volume;

Voltammetric T.: based on current detection resulting from the application of continuously varying voltage to small electrodes;

• Titration Points: Several characteristic points characterize a titration:

End Point: The point in a titration when a physical change that is associated with the condition of chemical equivalence occurs.

Equivalence Point: The point in a titration at which the amount of standard titrant (Ti) added is equivalent to the amount of analyte (An) in the sample.

\[
c_{An}V_{An} = c_{Ti}V_{Ti}
\]

$V$, volume of probes [L]
$c$, molar concentration [mol/L]
Titrimetric Applications:

**Complex Formation**: A complex reaction of at least one polydentate ligand (tooth-like projections) that forms a ring of atoms encapsulating the central atom (see table below).

**EDTA**: Ethylene-Diamine-Tetra-Acetic Acid is a hexadentate ligand considered to be the most important and widely used reagents in titrimetry. In very acidic medium $H_4Y$ predominates, in extremely basic medium $Y^4\text{-}$ predominates:

\[
H_4Y \leftrightarrow (1E^{-2}) \leftrightarrow H_3Y^- \leftrightarrow (1E^{-2.7}) \leftrightarrow H_2Y^{2-} \leftrightarrow (1E^{-6.7}) \leftrightarrow HY^{3-} \leftrightarrow (1E^{-10.3}) \leftrightarrow Y^{4-}
\]

**Me$^{n+}$ + $Y^{4-}$ \[\leftrightarrow\] Me$Y^{(n-4)+}$

\[
K_{MeY} = \frac{[MeY^{(n-4)+}]}{[Me^{n+}][Y^{4-}]}
\]

*Instable MeY* require a high concentration of $Y^{4-}$ under basic conditions;
*Stable MeY* can be done with a low concentration of $Y^{4-}$ under acidic conditions.

- **Chelate**: Is a complex formed when a cation is bonded by two or more donor groups contained in a single ligand.
- **Chelation**: The reaction between a metal ion and a chelating reagent.
- **Coordination Number**: The number of covalent bonds a cation tends to form with electron-donor species.
- **Ligand**: An ion or molecule that form a covalent bond with a cation or a neutral metal atom by donating a pair of electrons, which are then shared by the two.
- **Me-Specific Indicator**: *Eriochrome Black T* (EBT): Me-ion indicator used in titrations of several common cations; it behaves like a weak acid (between pH 6.3 and pH 11.5):

\[
H_2EBT^- \overset{\text{red}}{\leftrightarrow} \overset{\text{pH 6.3}}{\leftrightarrow} \overset{\text{HI}^- + H^+ \overset{\text{blue}}{\leftrightarrow} \overset{\text{pH 11.5}}{\leftrightarrow} H_2O + H^+ \overset{\text{orange}}{\leftrightarrow} \overset{\text{pH 11.5}}{\leftrightarrow} \overset{\text{IH}^- \overset{\text{red}}{\leftrightarrow} \overset{\text{pH 6.3}}{\leftrightarrow} H_2O}
\]

**Neutralization T.**: A titration involving the neutralization reaction of an acid with a base (and vice versa) T. involving a strong acid and base: Equivalence point oscillates around pH 7 (steep rise at EP).
T. i.a. weak acid and strong base: Equivalence point oscillates around levels pH 7 - 14,
T. i.a. weak base and strong acid: Equivalence point oscillates around levels pH 1 - 7.
T. i.a. a weak acid and base: Equivalence point oscillates around pH 7, with a flat EP, hard to determine.

**Redox T.**: A Redox-reaction is a process in which there is either a transfer of electrons or a change in the oxidation numbers of the substances taking part in the reaction. Oxidation and reduction takes place simultaneously, because an electron that is lost by one atom is accepted by another. Oxidation-reduction reactions are important means of energy transfer in living systems. e.g.: Ca(s) + $\frac{1}{2}$O2(g) \[\rightarrow\] CaO(s);
A Redox T. imploys.................

- **Half Cell Reaction**: Oxidation and reduction reactions at the electrodes.
- **Nernst Equation**: The EQ expressing the cell potential in terms of the concentrations of the reagents taking part in the cell reaction; the more positive $E^\circ$ of one of the reaction partners involved, the stronger the shift to the reduced form of that partner (i.e. in example below, to the right):

\[
E_{\text{Red/Ox}} = E^\circ + \log(c_{\text{Ox}}/c_{\text{Red}}) + 0.059/z \ [V]
\]

\[
e.g.: \ 2Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+} \ [c_{\text{Ox/Red}}-\text{concentration} \ [\text{mol/L}]
\]

\[
Fe^{3+} + e^- \rightarrow Fe^{2+} \ (E^\circ = +0.77V) \quad z, \text{number of swapped } e^-
\]

\[
Sn^{4+} + 2e^- \rightarrow Sn^{2+} \ (E^\circ = +0.13V)
\]

**Oxidation**: 1) Combination with oxygen. 2) A reaction in which an atom, ion, or molecule loses an electron; e.g.: Ca(s) \[\rightarrow\] Ca$^{2+}$(s) + 2e$^-$ (represents the Ca in CaO).

- **O. Agent**: A substance that can accept electrons from another substance or increase the oxidation number in another substance (being oxidized); where the substance itself is reduced; e.g.: O$_2$, O$_3$, MnO$_4^-$, Fe$^{3+}$

N$_{\text{ox}}$ - O. Number: The effective charge on an atom in a compound, calculated according to a set of rules. An increase in ON corresponds to oxidation, and a decrease to reduction.

**Reduction**: (L. reductio, bringing back) 1) The removal of oxygen form (bringing back a metal from its oxide) or the addition of hydrogen to a compound. 2) A reaction in which an atom, an ion, or a molecule gains an electron; reduction takes place simultaneously with oxidation; e.g.: $\frac{1}{2}$O$_2$(g) + 2e$^-$ \[\rightarrow\] O$^2-$ (represents the O in CaO).

- **R. Agent**: A substance that can donate electrons to another substance or decrease the oxidation numbers in another substance (being reduced), where the substance itself is oxidized; e.g.: H$_2$; H$_2$S; SO$_3^{2-}$

**Redox Couple**: Consists of the oxidized and reduced species taking part in the half reaction; e.g.: Red (Zn) / Ox (Zn$^{2+}$).
Steps in quantitative analysis

Start

Problem (what and how)

Definition of problem
(analyze logically, gain extra information, and select a method)

Sampling strategy
(obtain a representative sample, prepare a lab-sample, and define replicate samples)

Sample processing
(dissolve the samples and eliminate interference)

Measurement
(measure property of the analyte)

Evaluation
(calculate results)

Quality control/assurance
(verify credibility and reliability of results)

Result (final data)

No

Problem solved?

Yes

End

- Qualitative Analysis (what is searched for)
- Quantitative Analysis (how much is there)
- Interaction (how it’s done, synergies, distribution, reciprocal interference)
- Time required (how much time)

Internal feedback loop

External feedback loop

Solubility Product and theoretical pH values for precipitation of Me-hydroxides

<table>
<thead>
<tr>
<th>Precipitate</th>
<th>$K_{sp}$ ($pK_{sp}$)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgOH</td>
<td>$1 \cdot 10^{7.7}$ (7.7)</td>
</tr>
<tr>
<td>Ca(OH)$_2$</td>
<td>$1 \cdot 10^{10.5}$ (10.9)</td>
</tr>
<tr>
<td>Mg(OH)$_2$</td>
<td>$1 \cdot 10^{13.5}$ (13.5)</td>
</tr>
<tr>
<td>Fe(OH)$_2$</td>
<td>$1 \cdot 10^{13.8}$ (13.8)</td>
</tr>
<tr>
<td>Ni(OH)$_2$</td>
<td>$1 \cdot 10^{13.9}$ (13.9)</td>
</tr>
<tr>
<td>Cd(OH)$_2$</td>
<td>$1 \cdot 10^{14.2}$ (14.2)</td>
</tr>
<tr>
<td>Mn(OH)$_2$</td>
<td>$1 \cdot 10^{15.8}$ (15.6)</td>
</tr>
<tr>
<td>Pb(OH)$_2$</td>
<td>$1 \cdot 10^{15.7}$ (15.7)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Precipitate</th>
<th>$K_{sp}$ ($pK_{sp}$)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(OH)$_2$</td>
<td>$1 \cdot 10^{16.8}$ (16.8)</td>
</tr>
<tr>
<td>Be(OH)$_2$</td>
<td>$1 \cdot 10^{18.6}$ (18.6)</td>
</tr>
<tr>
<td>Cu(OH)$_2$</td>
<td>$1 \cdot 10^{19.6}$ (19.8)</td>
</tr>
<tr>
<td>Sn(OH)$_2$</td>
<td>$1 \cdot 10^{25.4}$ (25.3)</td>
</tr>
<tr>
<td>Ni(OH)$_2$</td>
<td>almost insoluble</td>
</tr>
<tr>
<td>Cd(OH)$_2$</td>
<td>Cr(OH)$_3$</td>
</tr>
<tr>
<td>Mn(OH)$_2$</td>
<td>Al(OH)$_3$</td>
</tr>
<tr>
<td>Pb(OH)$_2$</td>
<td>Fe(OH)$_3$</td>
</tr>
<tr>
<td>Co(OH)$_2$</td>
<td>Sn(OH)$_3$</td>
</tr>
</tbody>
</table>

(*) a pH of 7.7 is required to produce a precipitate of AgOH
### Some common acid-base indicators:

<table>
<thead>
<tr>
<th>Indicator</th>
<th>color in acid</th>
<th>color in base</th>
<th>pH range*</th>
<th>Ready to use solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal violet</td>
<td>Yellow</td>
<td>Blue</td>
<td>0.3 - 1.8</td>
<td></td>
</tr>
<tr>
<td>Erythrosin B</td>
<td>Colorless-red</td>
<td>Red-colorless</td>
<td>1.2 - 2.7</td>
<td></td>
</tr>
<tr>
<td>Thymol blue</td>
<td>Red</td>
<td>Yellow</td>
<td>2.2 - 3.6</td>
<td>0.04% in 20% EtOH</td>
</tr>
<tr>
<td>2,4-Dinitrophenol</td>
<td>Colorless</td>
<td>Yellow</td>
<td>2.8 - 4.0</td>
<td></td>
</tr>
<tr>
<td>Bromophenol blue</td>
<td>Yellow</td>
<td>Bluish purple</td>
<td>3.0 - 4.6</td>
<td></td>
</tr>
<tr>
<td>Methyl orange</td>
<td>Orange</td>
<td>Yellow</td>
<td>3.1 - 4.4</td>
<td>0.04% in H₂O</td>
</tr>
<tr>
<td>Brom cresol green</td>
<td>Yellow</td>
<td>Blue</td>
<td>3.8 - 5.4</td>
<td>0.1% in 20% EtOH</td>
</tr>
<tr>
<td>Methyl red</td>
<td>Red</td>
<td>Yellow</td>
<td>4.2 - 6.3</td>
<td>0.1% in EtOH</td>
</tr>
<tr>
<td>Chlorophenol blue</td>
<td>Yellow</td>
<td>Red</td>
<td>4.8 - 6.4</td>
<td></td>
</tr>
<tr>
<td>Eriochrome Black T</td>
<td>Red</td>
<td>Blue</td>
<td>4.9 - 6.4</td>
<td></td>
</tr>
<tr>
<td>Lackmus</td>
<td>Red</td>
<td>Blue</td>
<td>5.0 - 8.0</td>
<td>0.2% in EtOH</td>
</tr>
<tr>
<td>Brom cresol purple</td>
<td>Yellow</td>
<td>Purple</td>
<td>5.2 - 6.8</td>
<td>0.1% in 20% EtOH</td>
</tr>
<tr>
<td>Alizarin</td>
<td>Yellow</td>
<td>Red</td>
<td>5.7 - 7.3</td>
<td></td>
</tr>
<tr>
<td>Bromothymol blue</td>
<td>Yellow</td>
<td>Blue</td>
<td>6.0 - 7.6</td>
<td>0.1% in 20% EtOH</td>
</tr>
<tr>
<td>Phenol red</td>
<td>Yellow</td>
<td>Red</td>
<td>6.8 - 8.3</td>
<td></td>
</tr>
<tr>
<td>Neutral red</td>
<td>Red</td>
<td>Yellow</td>
<td>6.8 - 8.0</td>
<td>0.1% in 70% EtOH</td>
</tr>
<tr>
<td>m-Nitrophenol</td>
<td>Colorless</td>
<td>Yellow</td>
<td>6.8 - 8.6</td>
<td></td>
</tr>
<tr>
<td>Cresol red</td>
<td>Yellow</td>
<td>Red</td>
<td>7.2 - 8.8</td>
<td></td>
</tr>
<tr>
<td>o-Cresolphthalein</td>
<td>Colorless</td>
<td>Red</td>
<td>8.2 - 9.7</td>
<td></td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>Colorless</td>
<td>Reddish pink</td>
<td>8.3 - 9.9</td>
<td>0.1% in EtOH</td>
</tr>
<tr>
<td>Thymolphthalein</td>
<td>Colorless</td>
<td>Blue</td>
<td>9.3 - 10.5</td>
<td>0.05-0.1% in 50% EtOH</td>
</tr>
<tr>
<td>Alizarin Yellow GG</td>
<td>Orange</td>
<td>Red</td>
<td>10.1-12.1</td>
<td></td>
</tr>
<tr>
<td>Epsilon blue</td>
<td>Orange</td>
<td>Purple</td>
<td>12.0-13.0</td>
<td>0.1% in H₂O</td>
</tr>
</tbody>
</table>

(*) pH range is defined as the range over which the indicator changes from acid color to the base color.

### Formation Constant for EDTA Complexes

<table>
<thead>
<tr>
<th>Cation</th>
<th>K_{MeY}</th>
<th>pK_{MeY}*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag⁺</td>
<td>2.1 E⁻⁷</td>
<td>7.32</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>4.9 E⁻³</td>
<td>8.69</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>5.8 E⁻⁷</td>
<td>7.76</td>
</tr>
<tr>
<td>Sr⁺</td>
<td>4.3 E⁻³</td>
<td>8.63</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>5.0 E⁻¹⁰</td>
<td>10.70</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>6.2 E⁻³</td>
<td>13.79</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>2.1 E⁻¹⁴</td>
<td>14.33</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>1.3 E⁻⁶</td>
<td>16.13</td>
</tr>
<tr>
<td>Co³⁺</td>
<td>2.0 E⁻¹⁶</td>
<td>16.31</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cation</th>
<th>K_{MeY}</th>
<th>pK_{MeY}*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd²⁺</td>
<td>2.9 E⁻¹⁶</td>
<td>16.46</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>3.2 E⁻¹⁶</td>
<td>16.50</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>1.1 E⁻¹⁶</td>
<td>18.04</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>4.2 E⁻¹⁸</td>
<td>18.62</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>6.3 E⁻¹⁸</td>
<td>18.80</td>
</tr>
<tr>
<td>Hg²⁺</td>
<td>6.3 E⁻²¹</td>
<td>21.80</td>
</tr>
<tr>
<td>Th⁴⁺</td>
<td>1.6 E⁻²¹</td>
<td>23.20</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>1.3 E⁻²³</td>
<td>25.10</td>
</tr>
<tr>
<td>V³⁺</td>
<td>7.9 E⁻²³</td>
<td>25.90</td>
</tr>
</tbody>
</table>

(*) pK_{MeY} = -log c[Me^{n⁺}]
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Standard reduction potentials at 25°C ECS

<table>
<thead>
<tr>
<th>Red</th>
<th>oxidizing agent</th>
<th>reducing agent</th>
<th>Ox</th>
<th>E° [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>weak</td>
<td>F₂(g) + 2e⁻ → 2F(aq)</td>
<td>strong</td>
<td>+2.87</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O₂(g) + 2H⁺(aq) + 2e → O₂(g) + H₂O(l)</td>
<td></td>
<td>+2.07</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Co³⁺(aq) + e⁻ → Co²⁺(aq)</td>
<td></td>
<td>+1.82</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2H₂O₂(aq) + 2H⁺(aq) + 2e → 2H₂O</td>
<td></td>
<td>+1.77</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PbO₂(s) + 4H⁺(aq) + SO₄²⁻(aq) + 2e → PbSO₄(s) + 2H₂O(l)</td>
<td></td>
<td>+1.70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ce⁴⁺(aq) + e⁻ → Ce³⁺(aq)</td>
<td></td>
<td>+1.61</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MnO₂⁺(aq) + 8H⁺(aq) + 5e⁻ → Mn²⁺(aq) + 4H₂O(l)</td>
<td></td>
<td>+1.51</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Au³⁺(aq) + 3e⁻ → Au(s)</td>
<td></td>
<td>+1.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cl₂(g) + 2e⁻ → 2Cl⁻(aq)</td>
<td></td>
<td>+1.36</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CrO₂⁻(s) + 14H⁺(aq) + 6e⁻ → 2Cr³⁺(aq) + 7H₂O(l)</td>
<td></td>
<td>+1.33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MnO₂(s) + 4H⁺(aq) + 2e⁻ → Mn²⁺(aq) + 2H₂O(l)</td>
<td></td>
<td>+1.23</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O₂(g) + 4H⁺(aq) + 4e⁻ → 2H₂O(l)</td>
<td></td>
<td>+1.23</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Br₂(l) + 2e⁻ → 2Br⁻(aq)</td>
<td></td>
<td>+1.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NO₃⁻(aq) + 4H⁺(aq) + 3e⁻ → NO(g) + 2H₂O(l)</td>
<td></td>
<td>+0.96</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2Hg²⁺(aq) + 2e⁻ → 2Hg(l)</td>
<td></td>
<td>+0.92</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hg₂Cl₂(s) + 2e⁻ → 2Hg(l) + 2Cl⁻(aq)</td>
<td></td>
<td>+0.85</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ag⁺(aq) + e⁻ → Ag(s)</td>
<td></td>
<td>+0.80</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe³⁺(aq) + e⁻ → Fe²⁺(aq)</td>
<td></td>
<td>+0.77</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O₂(g) + 2H⁺(aq) + 2e⁻ → H₂O₂(aq)</td>
<td></td>
<td>+0.68</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MnO₂⁺(aq) + 2H₂O + 3e⁻ → MnO₂(s) + 4OH⁻(aq)</td>
<td></td>
<td>+0.59</td>
<td></td>
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<tr>
<td></td>
<td>I₂(s) + 2e⁻ → 2I⁻(aq)</td>
<td></td>
<td>+0.53</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O₂(g) + 2H₂O + 4e⁻ → 4OH⁻(aq)</td>
<td></td>
<td>+0.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cu²⁺(aq) + 2e⁻ → Cu(s)</td>
<td></td>
<td>+0.34</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hg₂Cl₂(s) + 2e⁻ → 2Hg(l) + 2Cl⁻(aq)</td>
<td></td>
<td>+0.27</td>
<td></td>
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<tr>
<td></td>
<td>AgCl(s) + e⁻ → Ag(s) + Cl⁻(aq)</td>
<td></td>
<td>+0.22</td>
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<tr>
<td></td>
<td>SO₄²⁻(aq) + 4H⁺ + 2e⁻ → SO₂(g) + 2H₂O(g)</td>
<td></td>
<td>+0.20</td>
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<tr>
<td></td>
<td>Cu²⁺(aq) + e⁻ → Cu⁺(aq)</td>
<td></td>
<td>+0.15</td>
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</tr>
<tr>
<td></td>
<td>Sn⁺⁺(aq) + 2e⁻ → Sn⁺⁺(aq)</td>
<td></td>
<td>+0.13</td>
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</tr>
<tr>
<td></td>
<td>2H⁺(aq) + 2e⁻ → H₂(g)</td>
<td></td>
<td>0.00</td>
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<tr>
<td></td>
<td>Pb²⁺(aq) + 2e⁻ → Pb(s)</td>
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<td>-0.13</td>
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</tr>
<tr>
<td></td>
<td>Sn⁺⁺(aq) + 2e⁻ → Sn(s)</td>
<td></td>
<td>-0.14</td>
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<td></td>
<td>AgI(s) + e⁻ → Ag⁺(aq) + I⁻(aq)</td>
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<td>-0.15</td>
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<tr>
<td></td>
<td>Ni²⁺(aq) + 2e⁻ → Ni(s)</td>
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<td>-0.25</td>
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</tr>
<tr>
<td></td>
<td>Co²⁺(aq) + 2e⁻ → Co(s)</td>
<td></td>
<td>-0.28</td>
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<tr>
<td></td>
<td>PbSO₄(s) + 2e⁻ → 2Pb(s) + SO₄²⁻(aq)</td>
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<tr>
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<td>Cd²⁺(aq) + 2e⁻ → Cd(s)</td>
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<tr>
<td></td>
<td>Fe⁺⁺(aq) + 2e⁻ → Fe(s)</td>
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<td>-0.44</td>
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<td>Cr⁺⁺(aq) + 3e⁻ → Cr(s)</td>
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<td>-0.74</td>
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<tr>
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<td>Zn⁺⁺(aq) + 2e⁻ → Zn(s)</td>
<td></td>
<td>-0.76</td>
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<tr>
<td></td>
<td>2H₂O(l) + 2e⁻ → 2H₂(g) + 2OH⁻(aq)</td>
<td></td>
<td>-0.83</td>
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<tr>
<td></td>
<td>Mn²⁺(aq) + 2e⁻ → Mn(s)</td>
<td></td>
<td>-1.18</td>
<td></td>
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<tr>
<td></td>
<td>Al³⁺(aq) + 3e⁻ → Al(s)</td>
<td></td>
<td>-1.66</td>
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<tr>
<td></td>
<td>Be⁺⁺(aq) + 2e⁻ → Be(s)</td>
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<td>-1.85</td>
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<td>Mg⁺⁺(aq) + 2e⁻ → Mg(s)</td>
<td></td>
<td>-2.37</td>
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<tr>
<td></td>
<td>Na⁺(aq) + e⁻ → Na(s)</td>
<td></td>
<td>-2.71</td>
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<tr>
<td></td>
<td>Ca⁺⁺(aq) + 2e⁻ → Ca(s)</td>
<td></td>
<td>-2.87</td>
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<tr>
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<td>Sr²⁺(aq) + 2e⁻ → Sr(s)</td>
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<td>-2.89</td>
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<tr>
<td></td>
<td>Ba²⁺(aq) + 2e⁻ → Ba(s)</td>
<td></td>
<td>-2.90</td>
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<tr>
<td></td>
<td>K⁺(aq) + e⁻ → K(s)</td>
<td></td>
<td>-2.93</td>
<td></td>
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<tr>
<td>strong</td>
<td>Li⁺(aq) + e⁻ → Li(s)</td>
<td>weak</td>
<td>-3.05</td>
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