
ANALYTICAL CHEMISTRY

Analytical chemistry

- **ανάλυσις** = analysis
- Material \Rightarrow decomposition \Rightarrow A, B, C \Rightarrow identification
- Science : **Analytical Chemistry**(ACH)
- Methodology: **Chemical Analysis**
- Analytical chemistry is the science of creation and evaluation of analytical signals carrying information about the chemical composition of the sample
- Analytical Chemistry
 - **qualitative** \Rightarrow EVIDENCE (WHAT?)
 - **quantitative** \Rightarrow DETERMINATION? (HOW MUCH)

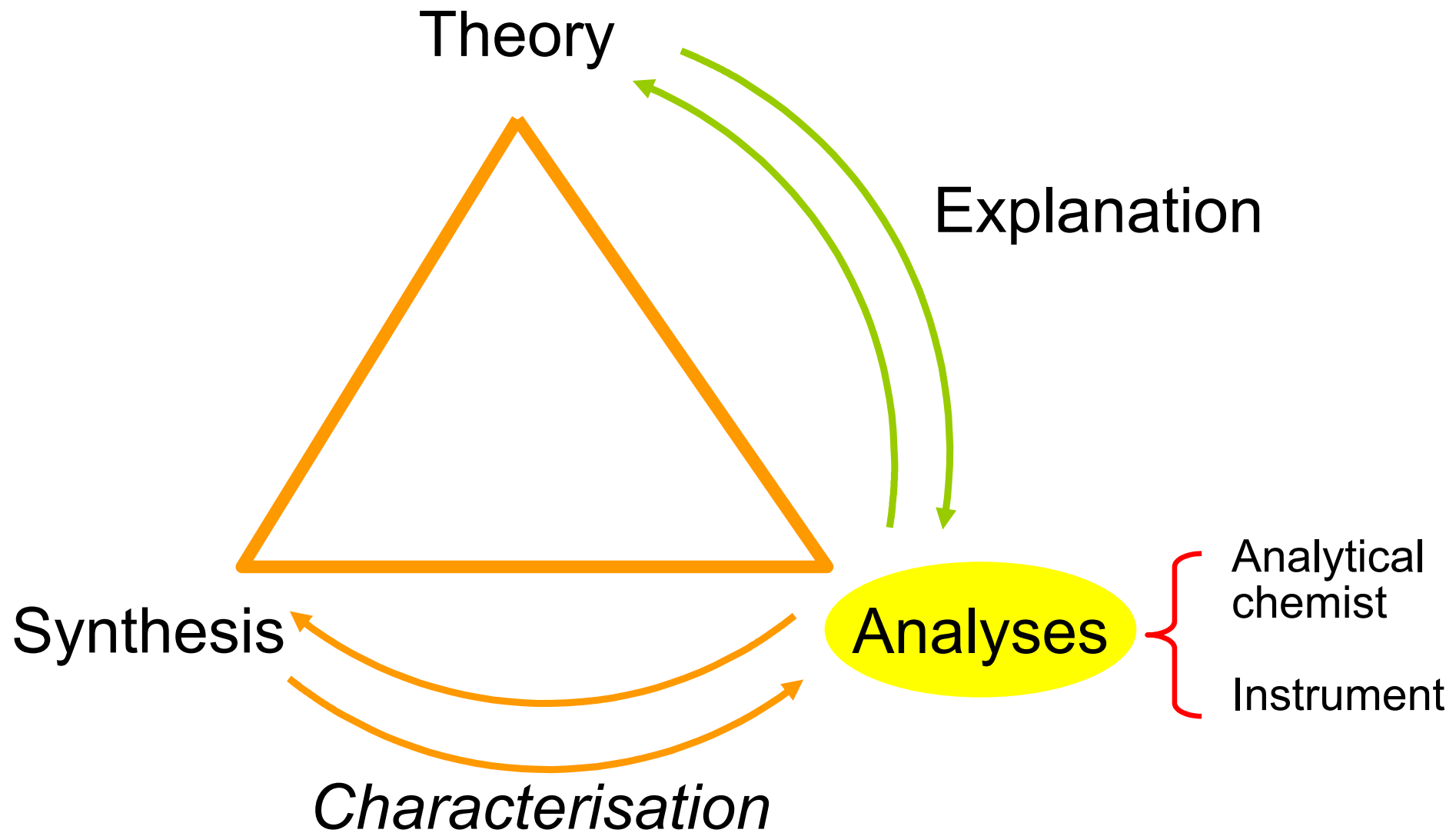
History of Analytical Chemistry

- Egypt, China, India, Greece (Demokritos, Platon, Aristoteles, (5.-4. st. BC), Middle Ages– alchemists
- analysis
 - „dry“ - reaction in solid phase (heating of solids – metallurgy)
 - „wet“ – in solution
- fundamentals
 - R. Boyle 17. century
 - J. Dalton 18.-19. century
 - A. L. Lavoisier 18. century
 - Fresenius (19. st.): separation and identification of cations using hydrogen sulphide
 - Instrumental methods: spectral analysis, Bunsen a Kirchhoff (19.cent.)
 - J. Heyrovský: polarography, Nobel Prize 1959

Methodology of analytical chemistry

- **Analytical approach in Science and Humanities**
 - Partition of problem into particular simpler parts, solution of these partial tasks and combining of individual information for understanding of the whole
 - Decomposition of material into chemical species \Rightarrow molecules, atoms, ions
 - X
 - Analysis by physical methods— study of matter in solid state, without decomposition, dissolution
- **Computer Based Analytical Chemistry (COBAC)**
- ACH is a scientific discipline that develops and applies methods, instruments and strategies to gather information on the composition and nature of matter in space and time

Chemistry



Classification of analytical methods according to principle

- Chemical methods (chemical reactions)
 - Gravimetry
 - Volumetry (titrimetry)

- Physico-chemical methods
 - Spectroscopic (radiations, particles - electrons, ions)
 - Separation (separation of components in time and space between two phases)
 - Electrochemical (electrode processes)

- Biochemical methods (enzymes, microorganisms)

Classification of analytical methods according to object of analysis

- Material (examples)
 - water, geological, metallurgical, ceramics, building, environmental, pharmaceutical, foodstuff, clinical
- Determined component type - analyte (examples):
 - Elemental analysis of samples with inorganic and organic matrix
 - Analysis of organic compounds
 - Determination of radioactive isotopes
- Analyte content
 - Total analysis (main constituents, $\Sigma=100\%$)
 - trace($\mu\text{g/g}$) and ultratrace(ng/g , pg/g) analysis
- Sample size (g, mg, μg , ng, μl , nl)

Elemental analysis

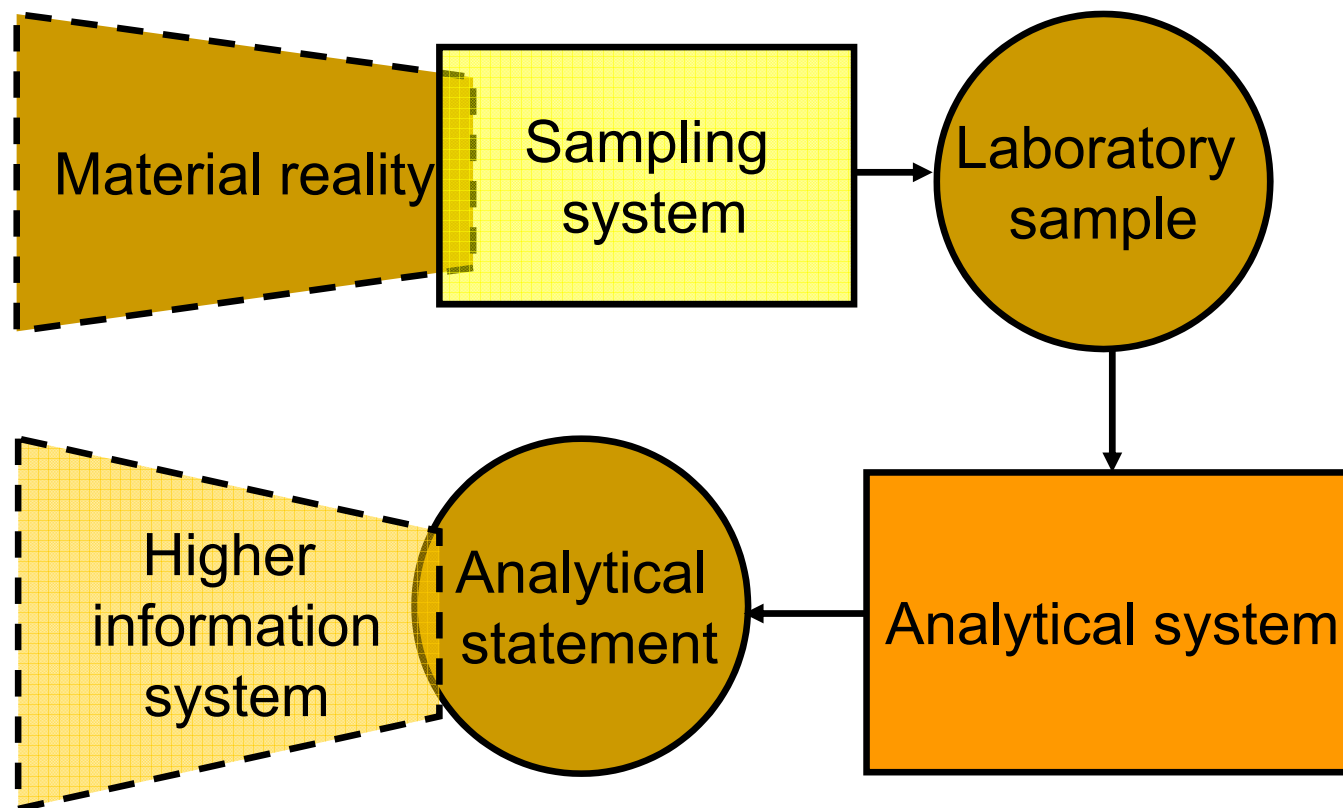
- Elemental analysis enables:
 - verification of the presence of the element (qualitative analysis)
 - determination of elemental concentration/content (quantitative analysis)
 - identification of structure, in which the element is present (structural analysis)
 - identification of compound, in which the element is bound (speciation)
- **WHOWHO analysis**
 - **what** (qualitative)
 - **how much** (quantitative)
 - **where** (structure)
 - **how bound** (speciation)
- The aim is to find structure vs properties relation

General procedure for analysis

- Sampling
 - Representative sample
 - Homogeneous sample
- Sample transfer to a form suitable for analysis
 - Decomposition, dissolution, pressing of powdered samples
 - Separation of components (from matrix, separation of individual analytes), concentration of constituents
- Analytical signal measurement
 - mass, volume, flow of electromagnetic radiation or ions, electrochemical potential, current, charge, conductivity
- Data evaluation
 - Mean value, standard deviation, error, uncertainties, validation
- Conclusions, analytical report

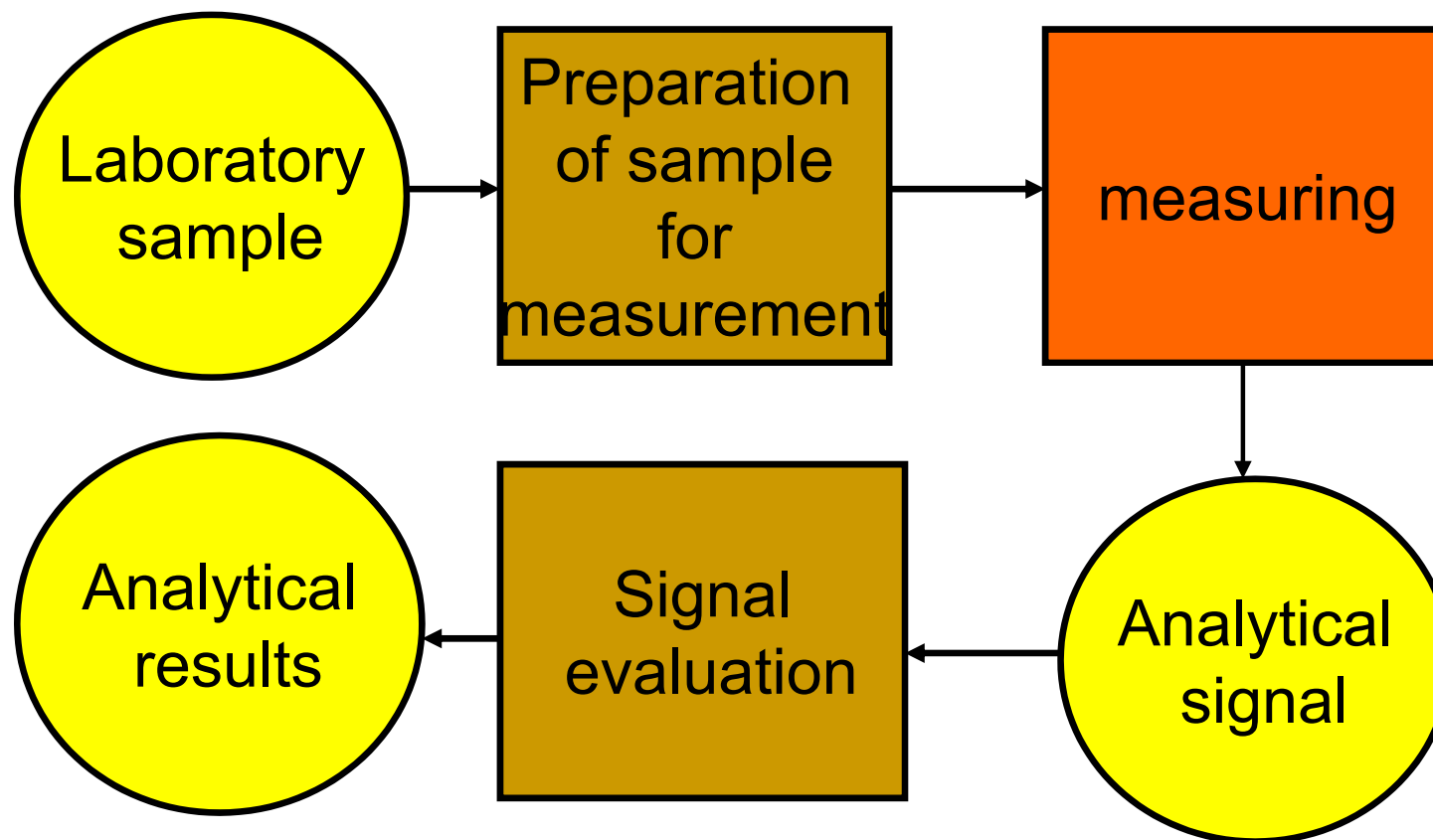
Analytical system

- Analytical system is a subsystem of higher information system
- Sampling system and analytical system



Analytical system

- Scheme of analytical process



Analytical signal

- Analytical chemistry is the science of creation and evaluation of the analytical signal (AS), carrying information about the chemical composition of the sample
- AS has two aspects - dimensions:
 - Position (wavelength of radiation, half-wave potential), corresponding to quality (WHAT?)
 - Magnitude, intensity (radiant flux, limiting diffusion current, corresponding to quantity (HOW MUCH?))
- Analytical signal intensity is generally a function of concentration of determined analyte c_A , concentration of other components c_{z_i} , and a number of variables p_j (instrumental parameters, reagents)

$$S = S(c_A, c_{z_i}, p_j)$$

Generating of analytical signal in optical atomic emission spectrometry (OES) and mass spectrometry (MS)

Solid sample

Gaseous sample

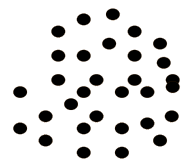
MS

Solid particles

molecules

atoms

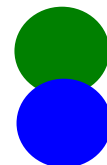
ions



desolvation



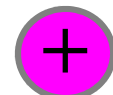
vaporization



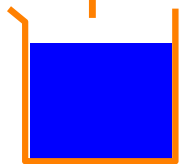
dissociation



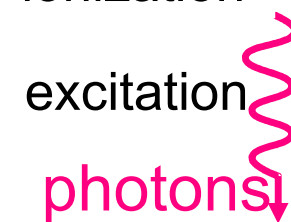
ionization



nebulizations



solution



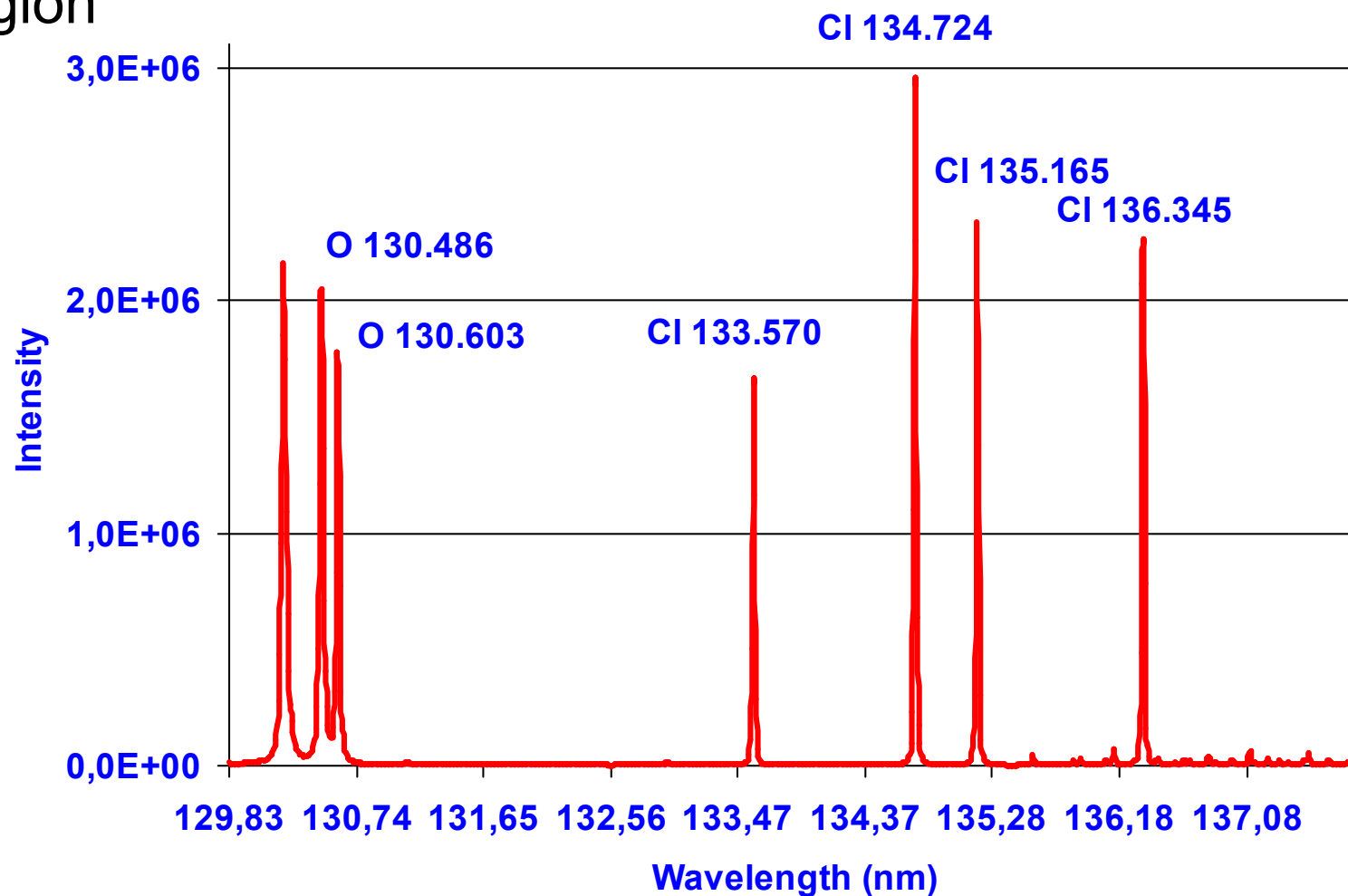
excitation

photons

OES

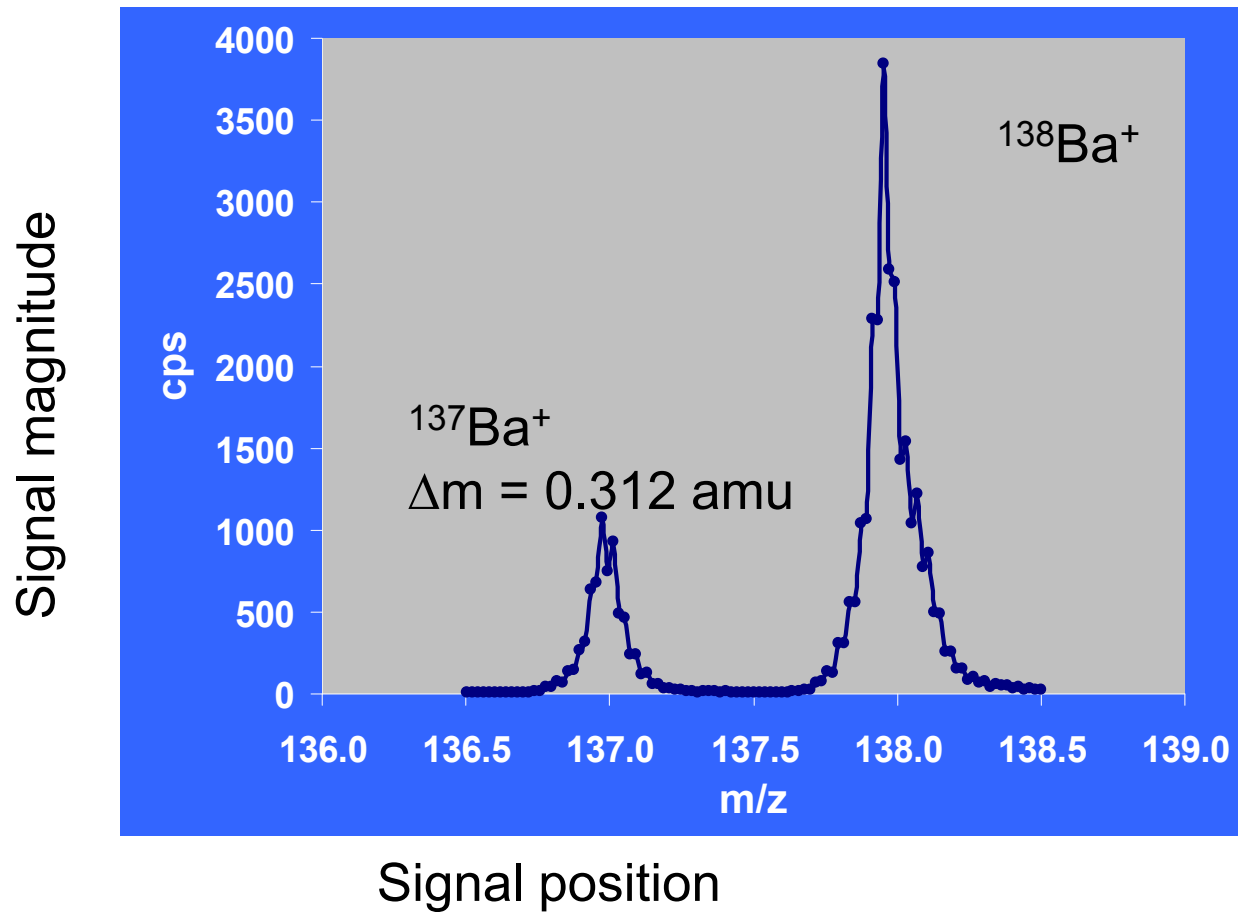
Atomic (optical) emission spectrometry in inductively coupled plasma ICP-AES, ICP-OES

- Atomic (line) emission spectrum of chlorine and oxygen in UV region

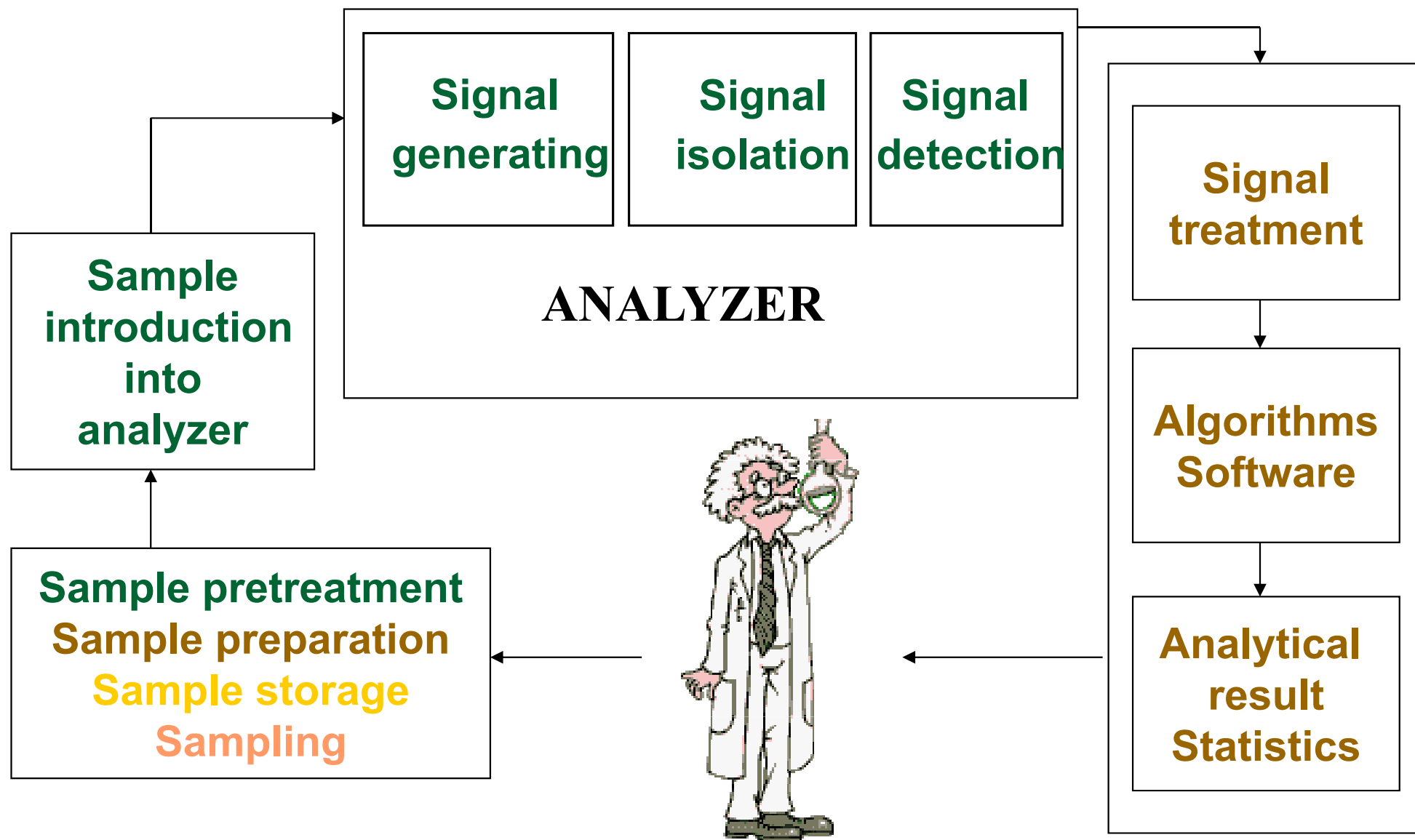


Mass spectrometry ICP-TOF-MS

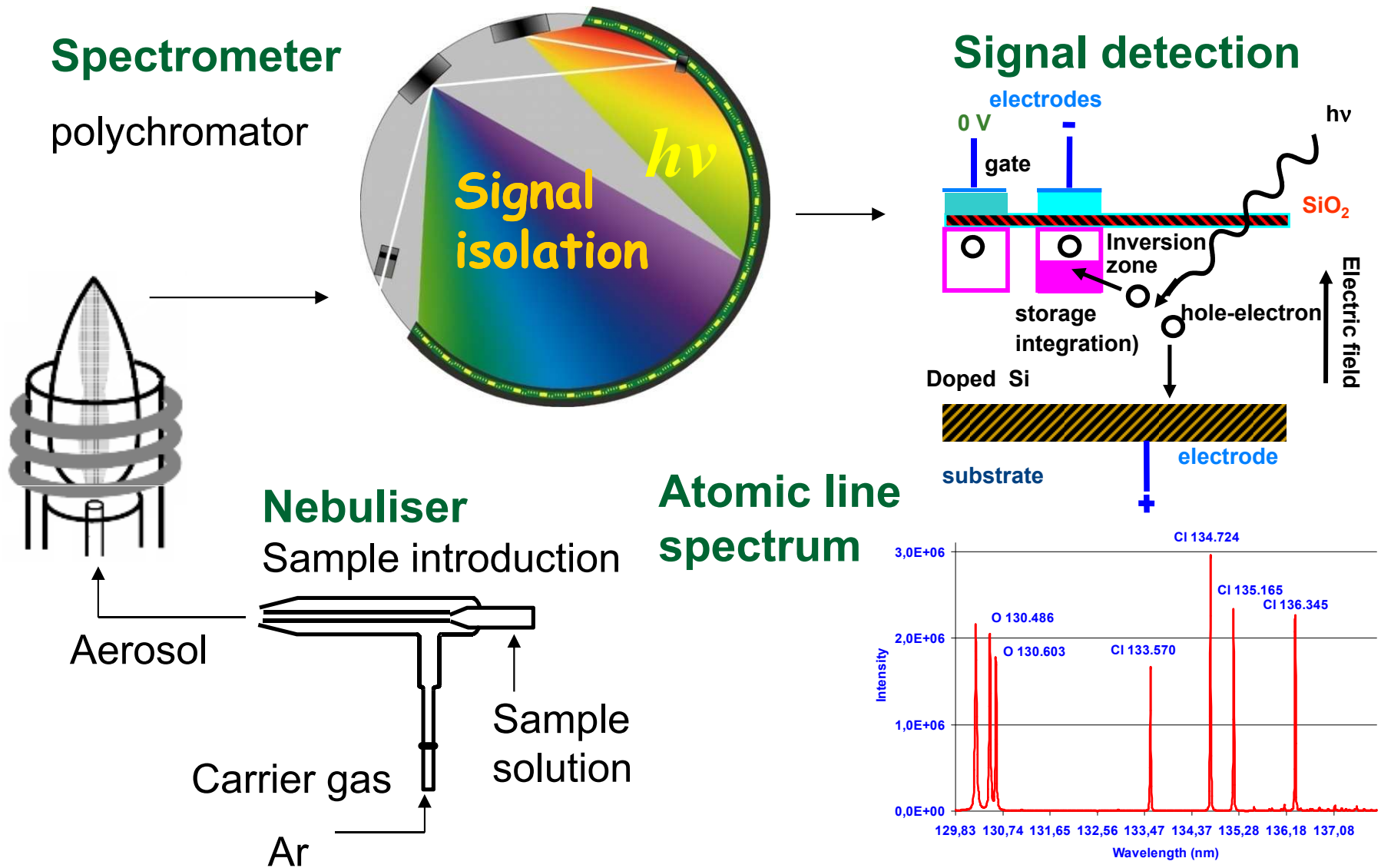
- Resolution m/z : $^{137}\text{Ba}^+$ a $^{138}\text{Ba}^+$
- Mass spectrum



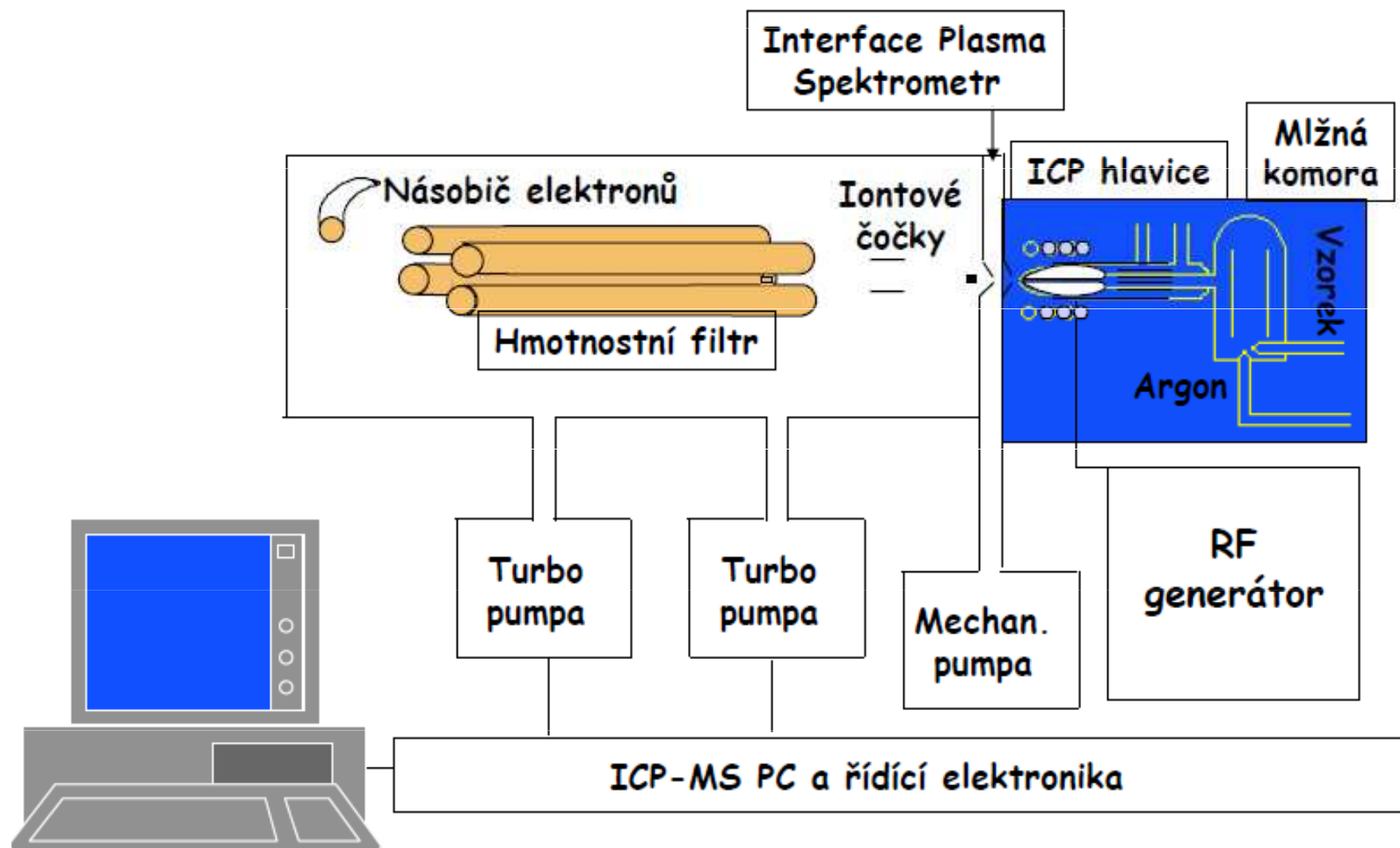
Analytical process scheme



Inductively coupled plasma



Mass (inorganic) spectrometry in inductively coupled plasma source ICP-MS



Analytical method

- Sampling and sample storage, preservation of representative material
- Processing of the part of the sample for quantitative analysis
- Determination
- Calculation of results

DEFINITION (ISO 3534)

- ❑ **random error** = component of measurement error, which changes in the course of repeated measurements in an unpredictable way
- ❑ **systematic error, bias** = component of measurement error, which does not change in the course of repeated measurements or changes in a predictable way

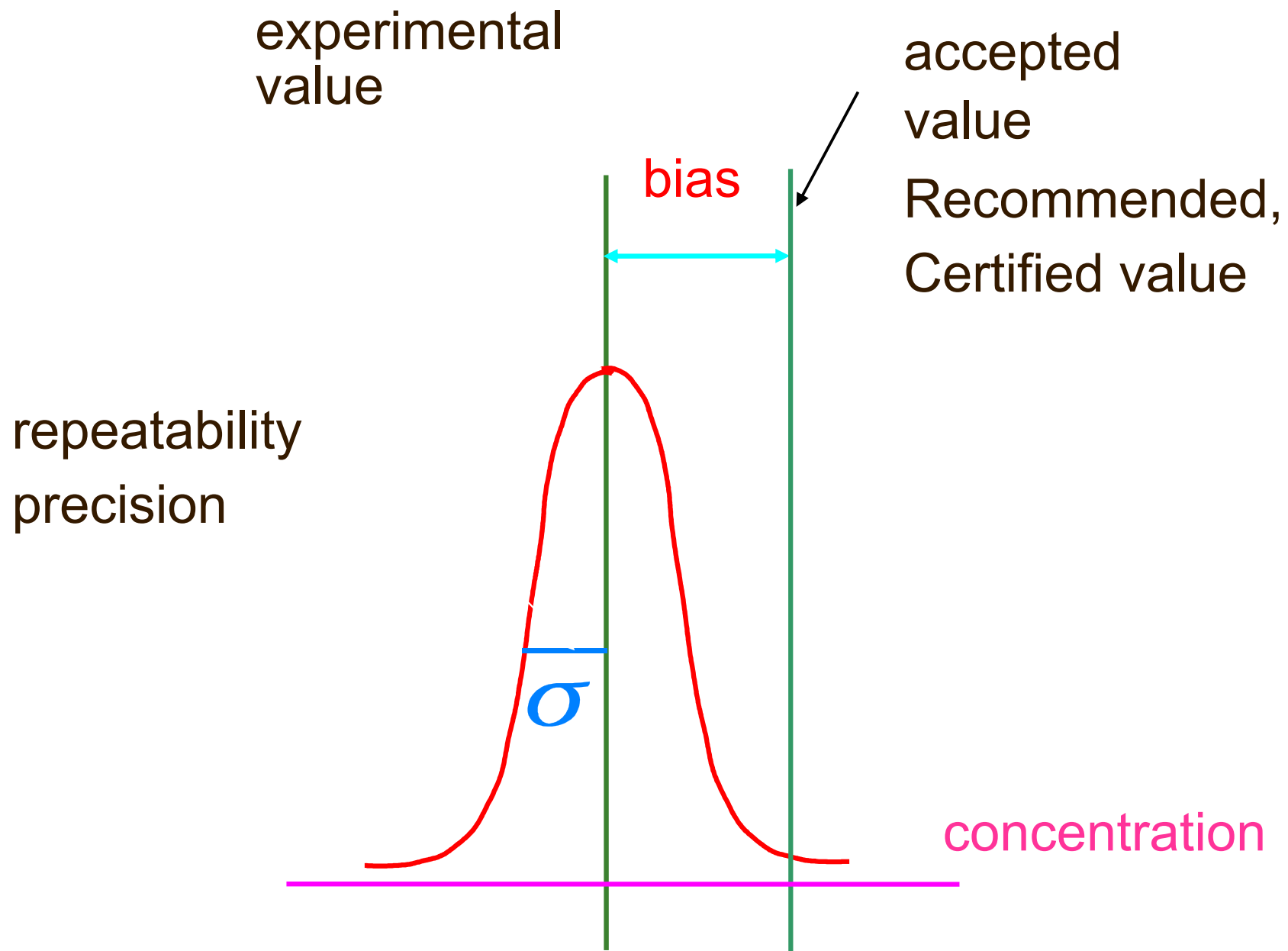
Analytická metoda

DEFINICE (ISO 3534)

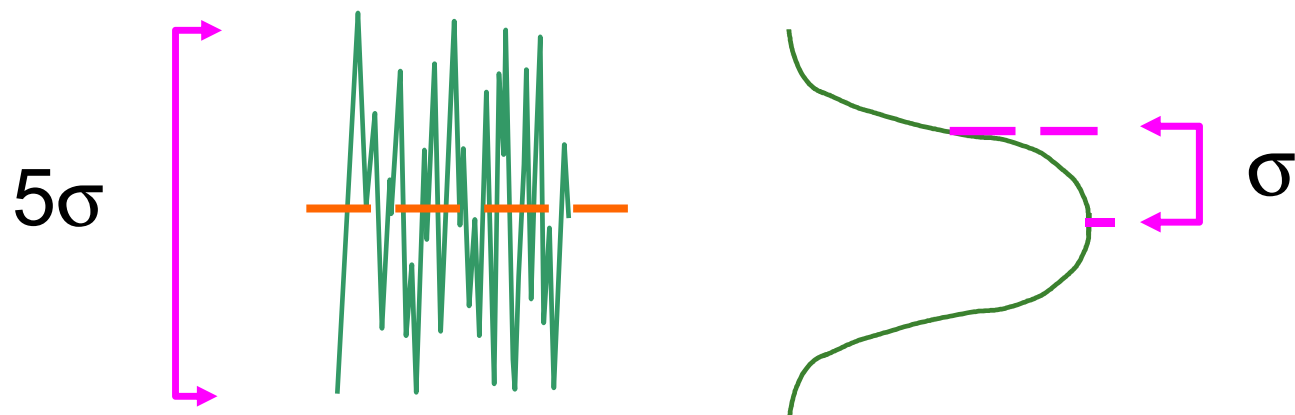
- **precision** = tightness of agreement between the results obtained with the repeated use of the same experimental procedure under defined conditions (random error)
 - Repeatability
 - Reproducibility
- **trueness** = tightness of agreement between the „true (actual) value“ and the mean value of measured results (systematic error, bias)
- **accuracy** = method is accurate if it is satisfied at the same time precision and trueness of the results

Repeatability

- **Repeatability** represents random fluctuations of the measured values of the analytical signal (or results) around the mean value within one experiment (a series of replicates)
- Cause of fluctuations is noise: in case of emission spectrometry – example:
 - ❑ shot noise (photons)
 - ❑ flicker noise (sample introduction noise)
 - ❑ detector noise
- Repeatability is usually expressed as standard deviation (SD) or relative standard deviation (RSD)



Standard deviation and fluctuation peak - peak



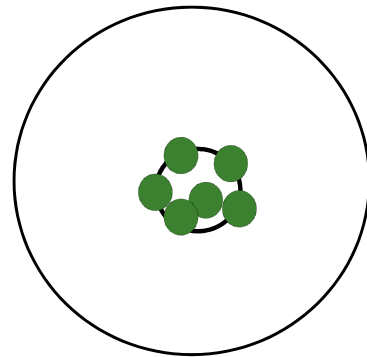
5σ includes 99% of the population

For mean value 100 and standard deviation 1 are
fluctuations between 97.5 and 102.5

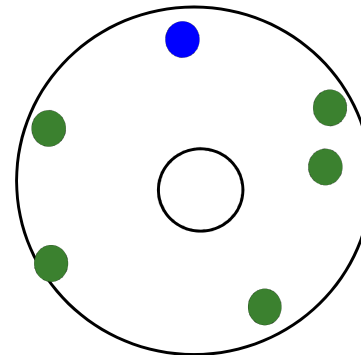
Reproducibility

- Principle as in the case of repeatability, in addition, one other parameter changes
- Reproducibility may be:
 - Between laboratories
 - Between operators in one laboratory
 - Between analyzers
 - In different days
 - etc...

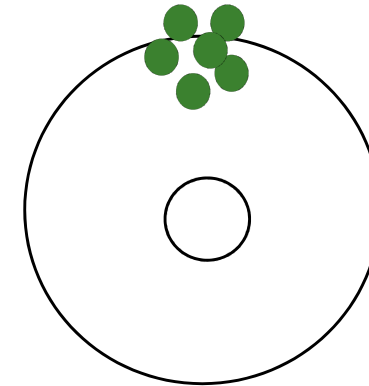
Repeatability x Trueness



good



poor



good

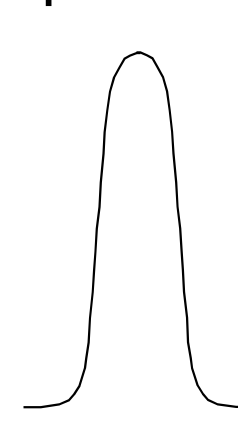
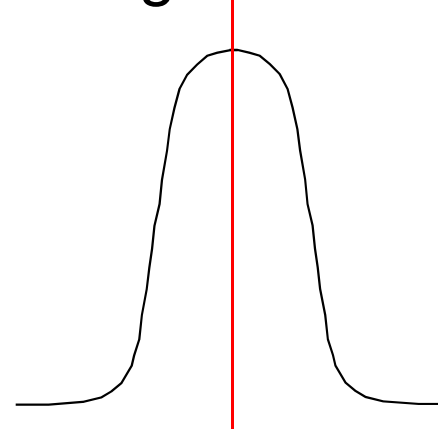
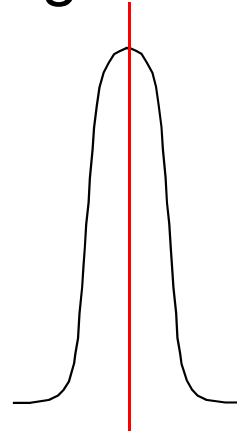
repeatability

trueness

good

good

poor



Parameters of data sets

- **Arithmetic mean** = mean value of Gaussian = normal distribution, n values
$$\bar{X} = \sum_{i=1}^n \frac{X_i}{n}$$

- **Sample standard deviation** = dispersion parameter of the sample set, for $n > 7$
$$s = \sqrt{\frac{1}{n-1} \left[\sum_{i=1}^n (X_i - \bar{X})^2 \right]}$$

- **median** = mean value insensitive to outliers

- For odd n the median of a set of values arranged by size $X_1, \dots, X_{(n+1)/2}, \dots, X_n$ is equal to the middle value of the series:

$$\tilde{X} = X_{(n+1)/2}$$

- For even n the median is equal to arithmetic mean of the central pair

$$\tilde{X} = \frac{1}{2}(X_{n/2} + X_{n/2+1})$$

Parameters of data sets - Span

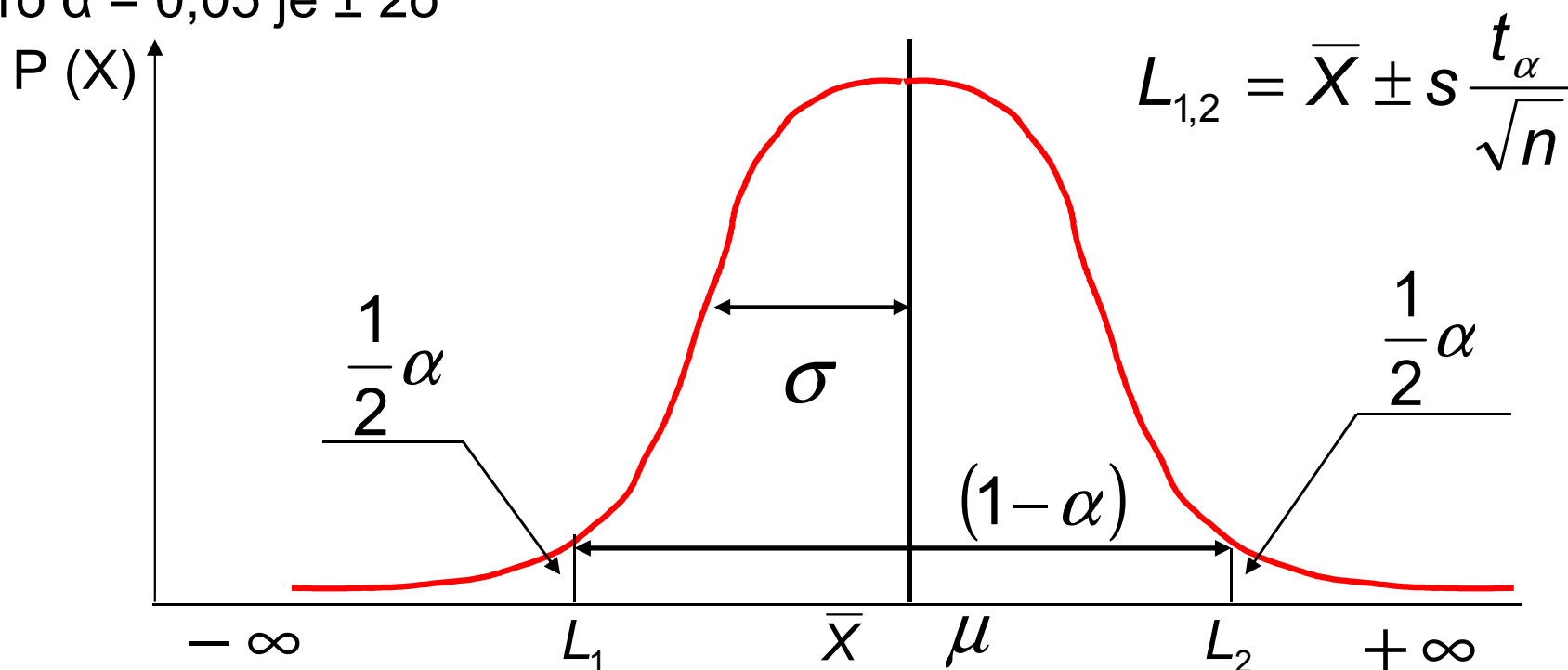
- Standard deviation s_R of data set for $n \leq 7$ is calculated from the span of values:

$$s_R = k_n \cdot R$$

$$R = X_{\max} - X_{\min}$$

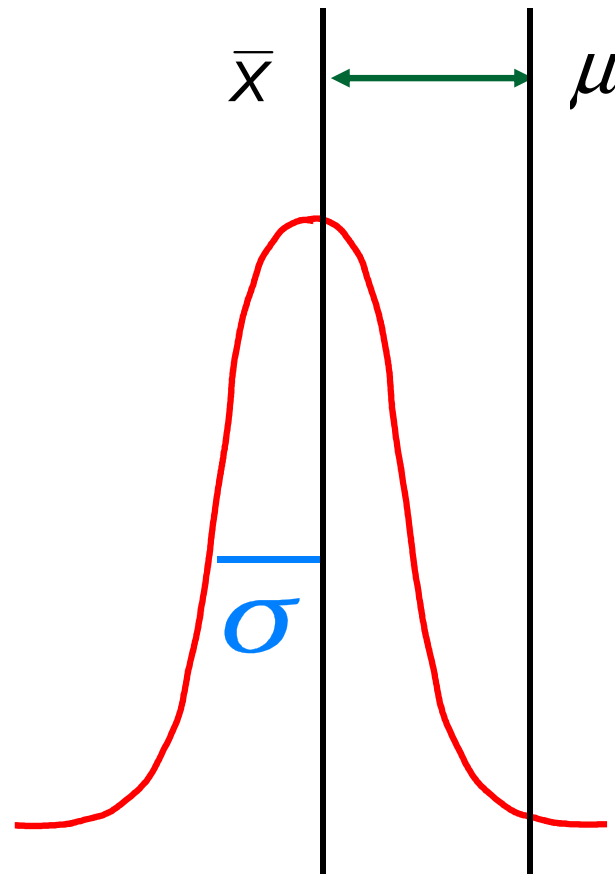
Level of significance and confidence interval of mean

- A level of significance indicates the probability that the true parameter value does not lie within the $100(1 - \alpha)\%$ interval
- Confidence interval $L_{1,2}$ of the mean \bar{X} on the level of significance α is an interval, in which the true value μ lies with probability $(1 - \alpha)$
- pro $\alpha = 0,05$ je $\pm 2\sigma$



Trueness

- Standard deviation **s** is estimate of σ



Statistical testing

- Comparison of results of analyses
- **null hypothesis**: the assumption that between the compared values is no other difference than that which can be explained by the presence of random errors
- null hypothesis H_0 is rejected if the actual difference exceeds a critical value that corresponds to the pre-selected significance level α
- risk that we reject the correct null hypothesis is called the **error of the 1st kind** and is given by the significance level α
 - $P_1 = 1 - \alpha$ is the probability that we accept the correct null hypothesis

Test of Trueness

- Student test (Gosset), trueness:

$$t = \frac{|\bar{X} - \mu|}{s / \sqrt{n}} \quad \text{if} \quad t \geq t_{krit}(v, \alpha) \quad n > 7$$

- for the number of degrees of freedom $v = n-1$ and the chosen significance level α , e.g. $\alpha = 0.05$ for $P = 95\%$, then the difference is statistically significant

Test of Trueness using span

- Lord test

$$n \leq 7$$

$$u_n = \frac{|\bar{X} - \mu|}{R}$$

$$u_n \geq n_{krit}(n, \alpha) \rightarrow \text{statistically significant difference}$$

Correspondence of results

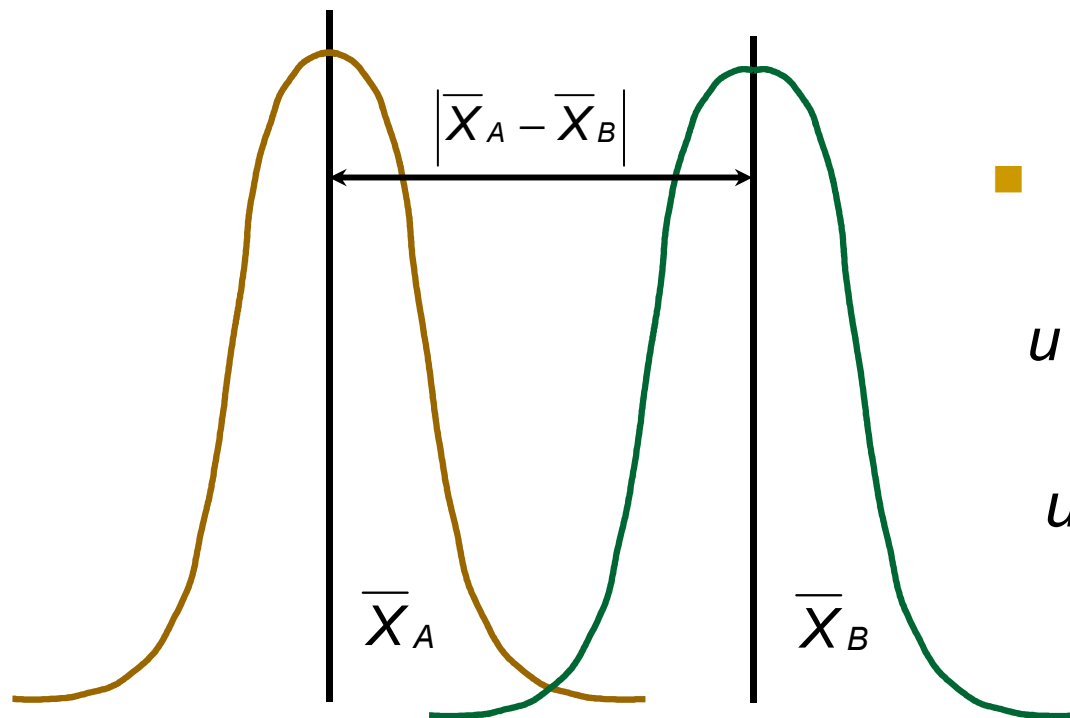
■ Moore test of outliers

$$U = \frac{|\bar{X}_A - \bar{X}_B|}{R_A + R_B}$$

$$U \geq U_{\alpha, \text{krit}}$$

$$n_A, n_B \leq 7$$

$$n_A \neq n_B, n_A \leq n_B$$



■ Lord test of outliers

$$u = \frac{|\bar{X}_A - \bar{X}_B|}{R_A + R_B} \quad n \leq 7$$

$$u \geq u_{\alpha, \text{krit}}$$

$$n = n_A = n_B$$

rozdíl statisticky významný

Correspondence of results

- test of averages (**Student test**)

$$\bar{X}_A, \bar{X}_B \quad n_A, n_B \quad \nu = n_A + n_B - 2 \quad n_A, n_B \geq 7$$
$$S_A \approx S_B$$

- If the value t is greater than the critical value t_{krit} , the difference in averages is statistically significant:

$$t = \frac{|\bar{X}_A - \bar{X}_B|}{S} \cdot \sqrt{\frac{n_A \cdot n_B}{n_A + n_B}} \quad t \geq t_{krit}(\alpha, \nu)$$

$$S^2 = \frac{\sum_i (x_{iA} - \bar{X}_A)^2 + \sum_i (x_{iB} - \bar{X}_B)^2}{n_A + n_B - 2}$$

Correspondence of results

- test of averages (Studentův test)

$$n = n_A = n_B$$

$$t = \frac{|\bar{X}_A - \bar{X}_B|}{\sqrt{(S_A^2 + S_B^2)}} \cdot \sqrt{(n-1)} \quad t \geq t_{krit}(\alpha, \nu)$$

- If t is greater than the critical value, then the difference is statistically significant

Exclusion of outliers

- T-test; Grubbs test for $n > 7$

$$X_1 \leq X_2 \leq \dots \leq X_n$$

$$T_1 = \frac{\bar{X} - X_1}{S_n} \quad T_n = \frac{X_n - \bar{X}}{S_n}$$

$$\bar{X} = \sum_{i=1}^n \frac{X_i}{n}$$

$$S_n = \sqrt{\frac{1}{n} \left[\sum_{i=1}^n (X_i - \bar{X})^2 \right]}$$

$$T_1, T_n \geq T_{krit}(\alpha, n) \Rightarrow \text{extreme values are outliers}$$

Exclusion of outliers

- Q-test; Dean-Dixon test for $n \leq 7$

$$X_1 \leq X_2 \leq \dots \leq X_n$$

$$Q_1 = \frac{X_2 - X_1}{R} \quad Q_n = \frac{X_n - X_{n-1}}{R} \quad 3 \leq n \leq 7$$

if

$$Q_1, Q_n \geq Q_{krit}(\alpha, \nu)$$

Then are Q_1 a Q_n outliers

Types of analytical methods

- ISO Guide 32 proposal classifies methods of chemical analysis according to calibration procedure:
 - **Absolute methods** (calculable methods) – result can be calculated on the basis of relations resulting from chemical and physical laws, using measured values (titrimetry, gravimetry, coulometry)
 - **Relative methods** – analyzed sample is compared with a set of calibration samples with known contents using the detection system, which has a linear response to the concentration of fixed components
 - differences between calibration and analyzed samples do not affect the signal in comparison with the magnitude of uncertainty
 - samples before measurement can be adjusted (adjustment of the matrix of calibration samples to the matrix of analyzed samples, elimination of interferences)

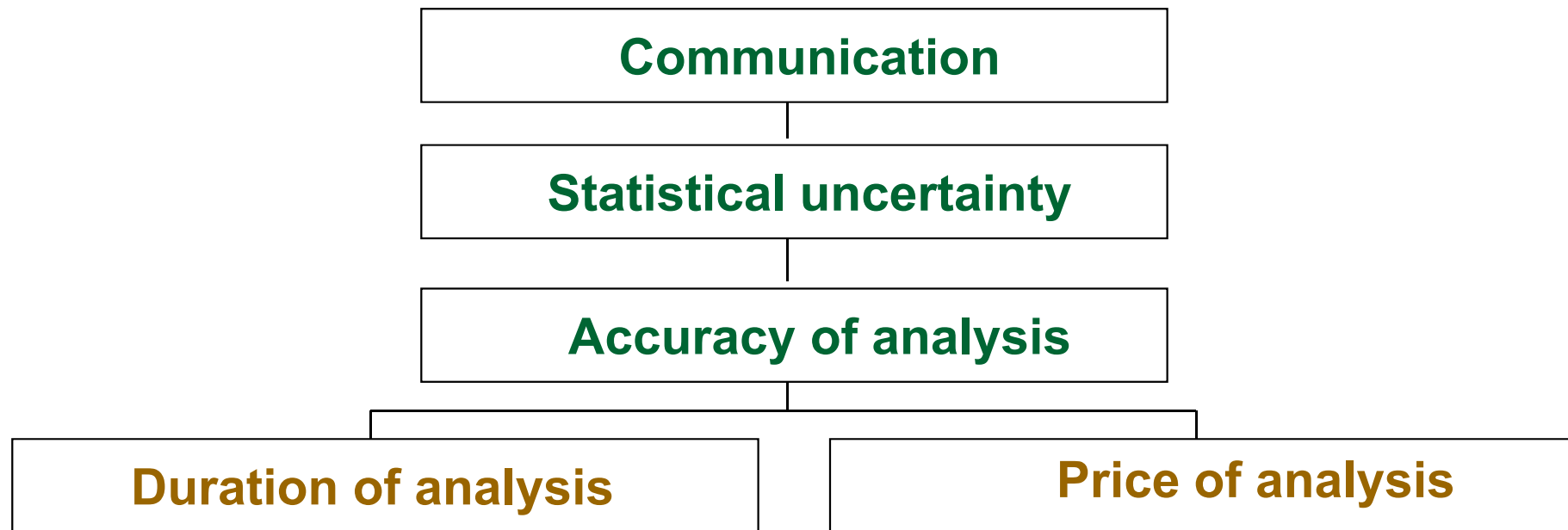
Types of analytical methods

- **Comparative methods** - analyzed sample is compared with a set of calibration samples with known contents using the detection system, which responds not only to the fixed component, but also to change the composition of the matrix
 - calibration of such a method requires use of certified reference materials (CRM)
 - it is a quick method to control technological processes (wave-dispersive X-ray fluorescence spectrometry in the production of steel, alloys, oxide powder, ceramic materials, etc.)

Analytical chemist

- 80% in industrial laboratories, the analytical chemist is a solver of problems and issues
- good theoretical knowledge of the methods used and the ability to develop experimental techniques and to select relevant, the optimal method
- development of specialized analytical procedures for analysis of routine and unique, unusual samples, communication with experts from other disciplines to obtain information about analyzed materials, the ability to choose a compromise between the cost analysis and its accuracy

Industrial analytical laboratory environment

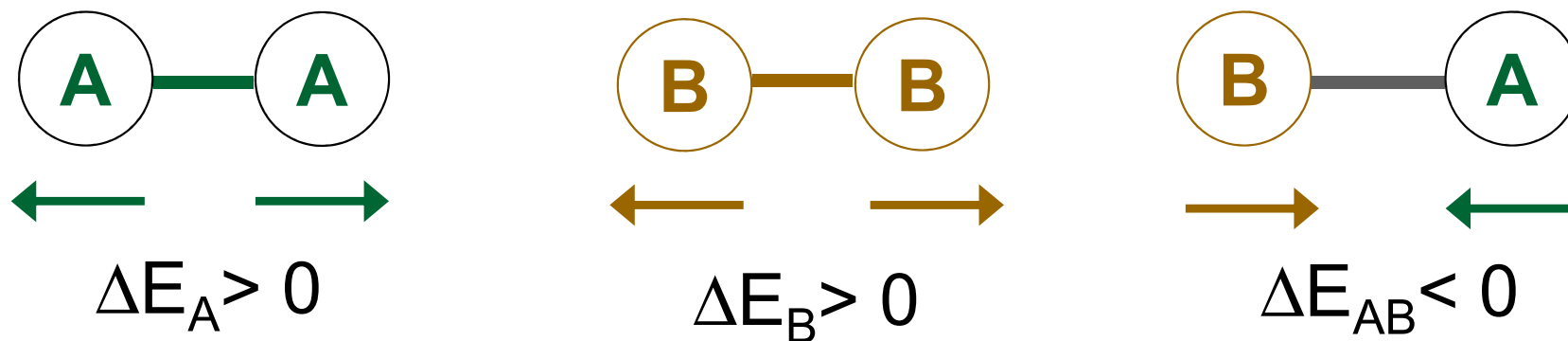


Method of analytical problem solving

- knowledge of chemistry of the problem
- knowledge of sampling and sample processing
- use of suitable separation methods
- use of proper calibration and standards
- selection of the best methods for measuring the analytical signal

Theoretical Foundations of Analytical Chemistry

- Dissolving of substances and solutions
 - solution: solid, liquid, gaseous
 - Analytical chemistry– liquid solvents
 - dissolution = overcoming of intermolecular forces between particles
 - Dissolution of A = dispersion of A in a solvent B



$$\Delta E_A + \Delta E_B + \Delta E_{AB} < 0 \Rightarrow \Delta E_{AB} > \Delta E_A + \Delta E_B$$

Nature of intermolecular forces and dissolution

Substance to be dissolved	solvent	Nature of intermolecular forces	solubility
electrolyte	polar	similar	⊕
electrolyte	nonpolar	different	⊖
nonelectrolyte	polar	different	⊖
nonelectrolyte	nonpolar	similar	⊕

Dissolution

- Relative permittivity $\approx \epsilon_R$ dielectric constant
dipole moment D
- **Nonpolar solvents**
 - van der Waals forces
 - **Solid nonelectrolytes:**
 - Solubility is given (to 10^{-3} mol/l) $\Delta H_t =$ latent heat of melting \approx increasing of distances between particles, dispersion
 - **Liquids:** miscibility according to ϵ_R
 - **Gases- nonpolar molecules:** O_2 , N_2 , H_2 , CH_4 better soluble in n-pentane and n-hexane than in water

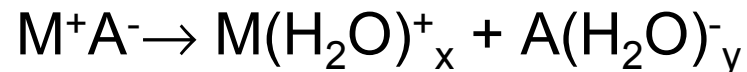
Dissolution

■ Polar solvents

- Electrostatic forces
- H₂O: D = 1,84; ε_R = 80

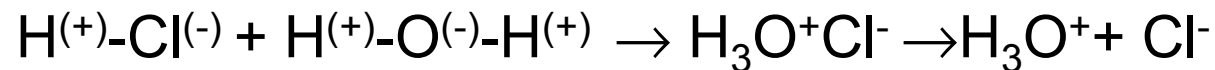
■ shielding of attractive forces between ions in solution

- Ionic compounds : dissociation



- Degree of dissociation α, conductivity, strong electrolytes, conc. × activity

- Polar compounds: ionization+ dissociation:



Solubility of electrolytes in water

- Solid electrolyte
 - Ions in crystal lattice
 - Polar molecules
- Energy necessary for disruption of chemical bond
 - Gain by hydration of ions \Rightarrow solubility $\approx \Delta E$ (bond strength, hydration)
- **Bond strength in ionic compounds**
 - Lattice energy $U = f(z, r, k)$, $z =$ charge, $r =$ ion radius, $k =$ coordination number
- $U = \text{const} \times z^2/r_0$ for similar ions, $r_0 = r_K + r_A$
 r_K, r_A - crystallographic values \Rightarrow influence of particular ions
 $(dU/dr) = \text{const} \times (z^2/r_0^2) = \text{const} \times (z/r_0)^2$ square of ionic potential, changes in series of similar compounds
- **Hydration energy of ions E_H** – is proportional to:
 - bond strength between ion and water molecule (dipole) $\approx z^2/r$
 - number of coordinated water molecules
- Ions bound molecules of H_2O the stronger, the greater is z and smaller r
- Change of $E_H \approx \text{const} \times (z^2/r^2) \approx z/r$

Solubility of electrolytes in water

- Ionic potential z/r decreases (z decreases, r increases) $\Rightarrow U$, E_H decrease, hydration energy decreases slower, because at higher r number of coordinated water molecules increases (compensation of the decrease)
- Solubility of ionic compounds depends on balance $E_H + U$
 - **ionization** (dissociation) = endothermic process, $U > 0$
 - **hydration** = exothermic process, $E_H < 0$
- Compound dissolve:
 - well, if $E_H + U < 0$, ($U < |E_H|$)
 - with difficulty, if $E_H + U > 0$, ($U > |E_H|$)
- Solubility of fluorides of alkali metals increases $\text{LiF} \Rightarrow \text{CsF}$, because U decreases from $\text{Li} \rightarrow \text{Cs}$ steeper than E_H (decrease of E_H is hindered by growth of coordinated molecules H_2O (Li^+ 4 H_2O , Cs^+ 8 H_2O))

Solubility of electrolytes in water

- Solubility of salts of **small** ion (Li^+ , Na^+ , F^-) **increases with** decrease of z/r of counterion:
 - $\text{LiF} < \text{LiCl} = \text{LiBr} < \text{LiI}$
 - $\text{NaF} < \text{NaCl} < \text{NaBr} < \text{NaI}$
 - $\text{LiF} < \text{NaF} < \text{KF} < \text{CsF}$
- Solubility of salts of **big** ion (Cs^+ , I^-) **diminishes** with decrease of z/r of counterion
 - $\text{CsF} > \text{CsCl} > \text{CsBr} > \text{CsI}$
 - $\text{LiI} > \text{NaI} > \text{KI} > \text{RbI} > \text{CsI}$
- Solubility of salts of **medium-size** ion (K^+ , Rb^+ , Cl^- , Br^-) at first with decrease of z/r **diminishes** and then slightly **increases** or remains **constant**:
 - $\text{KF} > \text{KCl} > \text{KBr} > \text{KI}$
 - $\text{RbF} > \text{RbCl} > \text{RbBr} < \text{RbI}$
 - $\text{LiCl} > \text{NaCl} > \text{KCl} < \text{RbCl} < \text{CsCl}$
- $\text{OH}^- = \text{small ion} \Rightarrow \text{Mg}(\text{OH})_2 < \text{Ca}(\text{OH})_2 < \text{Sr}(\text{OH})_2 < \text{Ba}(\text{OH})_2$
- Ionic potential: **3,08** **2,02** **1,77** **1,48**
- Big ions: PO_4^{3-} , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, SiF_6^{2-} , CrO_4^{2-} , IO_3^- , NO_3^- : \Rightarrow
 - $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$ (in this sense decreases z/r of cations)

Solubility of electrolytes in water

- Effect of electron shell – example Pb^{2+} a Tl^+ :

Pb^{2+}	2	8	18	32	2	PbS	PbCrO_4	PbI_2	PbCl_2
Tl^+	2	8	18	32	2	Tl_2S	Tl_2CrO_4	TlI_2	TlCl

- Similarity of Rb^+ s Tl^+

Little soluble salts

- Soluble hydroxides RbOH , TlOH and carbonates Rb_2CO_3 , Tl_2CO_3
 - Little soluble $\text{Rb}_2[\text{PtCl}_6]$, $\text{Tl}_2[\text{PtCl}_6]$
- exception: F^- : $\text{CaF}_2 < \text{SrF}_2 < \text{MgF}_2 < \text{BaF}_2$ (small ion)
- exception: CO_3^{2-} : $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Ba}^{2+} > \text{Sr}^{2+}$ (big ion)
- exception: $\text{C}_2\text{O}_4^{2-}$: $\text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+} > \text{Mg}^{2+}$ (big ion)
- Effect of z/r on solubility of salts of cations of transition elements is limited
 - Prevails influence of unoccupied d-orbitals (ligand field, stabilization energy)

Solubility of electrolytes in water

- Electrolytes with polar covalent bond
- Strength is higher then corresponds to ionic attraction
- The smaller the difference of electronegativities the stronger the bond and lower solubility
- **example:** according to z/r the AgCl solubility should be comparable with that of KCl, generally of halogenides, but AgF only is well soluble

Theoretical fundamentals of analytical chemistry

- Analytical reactions:
 - Sample treatment (decomposition)
 - Separation and preconcentration of analytes in solution
 - determination
- Evaluation of chemical reaction:
 - Thermodynamic criterion
 - Kinetic criterion
 - Chemical thermodynamics – change of energy
 - Chemical kinetics – reaction path, mechanism, reaction rate
- Analytical reaction occurs (in solutions)
 - At constant pressure
 - At constant temperature
- Change of energy content = change of Gibbs energy
- kinetics:
 - Ion reactions
 - Radical reactions

Requirements for analytical reactions

1. **Fast reactions** - během promíchání (titrace)
2. **Unambiguous reactions** - without byproducts
3. **Completeness of conversion** – equilibrium \rightarrow products

Chemical equilibrium

Collision theory of chemical reactions



$N_A N_B$ – number of particles in a given volume

Number of collisions AB is given by combinatorial number:

$$(N_A + N_B)!/[2!(N_A + N_B - 2)!] - N_A!/[2!(N_A - 2)!] - N_B!/[2!(N_B - 2)!] = N_A \cdot N_B$$

Similarly for $aA + bB \Leftrightarrow A_a B_b$ the number of possible groupings reads =

$$= (N_A)^a \cdot (N_B)^b / a! \cdot b!$$

Instant reaction rate

$$v = k[A]^a \cdot [B]^b$$

Requirements for analytical reactions



$$v = k[A]^a \cdot [B]^b \quad v' = k'[C]^c \cdot [D]^d \quad K = k/k'$$

- Thermodynamic equilibrium constant

$$K_a = \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}$$

- Standard thermodynamic quantities ΔG° , ΔH° , ΔS°
- $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = -RT \ln K_a$ $T, p = \text{const.}$
- $\Delta = \text{final} - \text{initial state}$, $R = 8,314 \text{ J K}^{-1}\text{mol}^{-1}$
- $\Delta G^\circ = 5,708 \cdot 10^3 \log K_a$, $\Delta G^\circ \approx \text{J mol}^{-1}$
- Molar concentration of substance $c_A = n_A/V$
 n_A – number of moles, V – volume

Requirements for analytical reactions

- Activity $a_A = [A] y_A$ [A] – equilibrium concentration
- y_A – activity coefficient, expresses differences in behaviour:
 - solvation, electrostatic effects between ions
- Concentration \times thermodynamic constant

$$K_a = \frac{[C]^c [D]^d}{[A]^a [B]^b} \cdot \frac{y_C^c y_D^d}{y_A^a y_B^b} = K \cdot \frac{y_C^c y_D^d}{y_A^a y_B^b}$$

- Activity coefficients, theory **Debye-Hückel**:
 - Molal activity coefficients γ
 - Molar activity coefficients y
 - Molar fraction, activity coefficients f

Requirements for analytical reactions

■ Strong electrolytes

□ Debye-Hückel:

$$-\log \gamma = 0.5115 \cdot z_i^2 \sqrt{I} / [1 + \sqrt{I}] \quad 25^\circ\text{C}, z_i - \text{ion charge},$$
$$I = \frac{1}{2} \sum c_i z_i^2 \text{ ionic strength}$$

valid for $c < 10^{-3} \text{ mol/l}$

limit D-H relation: $-\log y_i = 0.5115 z_i^2 \sqrt{I}$

■ Weak electrolytes (in the absence of strong electrolytes)

□ Activity = molar concentration, valid for molecules without charge up to $c < 0,1 \text{ mol/l}$ (non-dissociated weak electrolytes)

■ Nonelectrolytes (in presence of strong electrolytes)

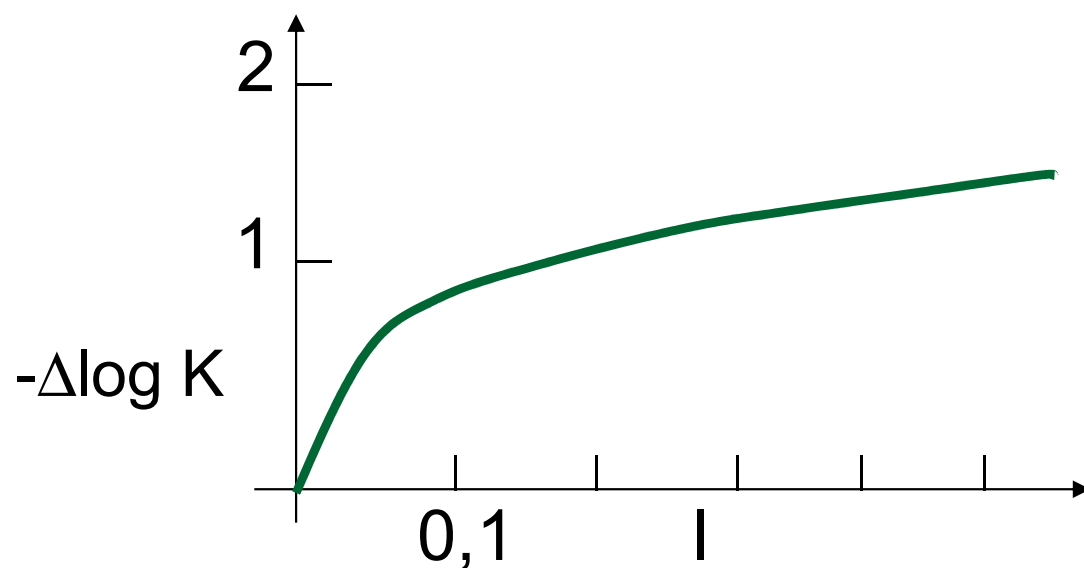
□ For concentrations $c_0 < 0,5 \text{ mol/l}$ and $I < 5 \text{ je}$

$$\log y_0 = k \cdot I$$

□ Activity of nonelectrolytes increases in presence of ions \Rightarrow their solubility decreases (salting out of solutions)

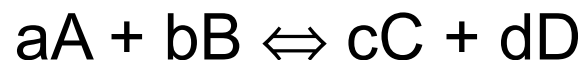
Thermodynamic and concentration equilibrium constants

- $K_a = \lim (\log K) \text{ for } I \rightarrow 0$
- $\log K = \log (K_a) + \Delta \log K$
- $\Delta \log K = \log K - \log (K_a) = \Delta z_i^2 (\sqrt{I}) / [1 + \sqrt{I}] - 0,3I$
- $\Delta z_i^2 =$ algebraic sum of charges, Δz_i^2 of products > 0 , Δz_i^2 of reactants < 0



K depends most steeply at ionic strength $I < 0,1$

Completeness of reaction from equilibrium constant



c_A, c_B initial concentrations of reactants, conversion to 99,90 %
at equilibrium $[A] = [B] = 0,001c_A$, $[C] = [D] = 0,999c_A$

$$K = \frac{0,999^2}{0,001^2} = 9,98 \cdot 10^5 = 10^6$$

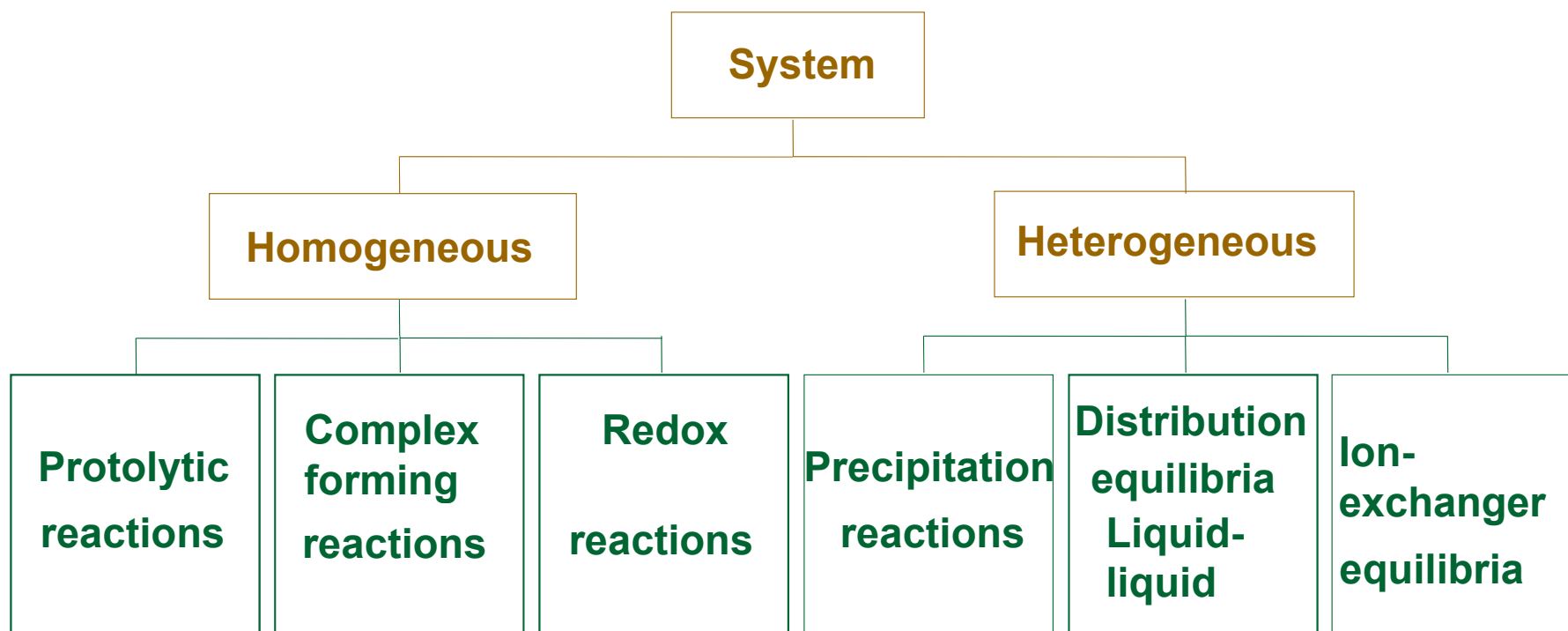
je-li $K = 10^6 \Rightarrow 99,9\%$
conversion to products
 $K = x^2/(1-x)^2$

- posun rovnováhy nadbytkem činidla
(fotometrie, gravimetrie, extrakce) \times rušení, vedlejší reakce

Effect of reaction kinetics

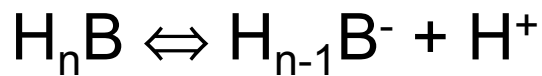
- Halftime of reaction < 10 s, titration, redox processes at $n_1 \neq n_2$ are slow
- Exploitation in kinetic methods – determination of concentrations from time dependences
- Increase in the reaction rate: heating, transfer to reaction complex using catalyst

Types of chemical equilibria



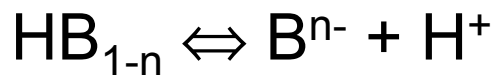
Protolytic equilibria

polyprotic acid H_nB



consecutive equilibria

Stepwise = consecutive



overall equilibrium



$$K_{a1} = \frac{[H^+][H_{n-1}B^-]}{[H_nB]}$$



stepwise dissociation
constant

$$K_{H_n} = \frac{[H_nB]}{[H^+][H_{n-1}B^-]}$$



stepwise protonization
constant

$$K_{a2} = \frac{[H^+][H_{n-2}B^{2-}]}{[H_{n-1}B^-]}$$



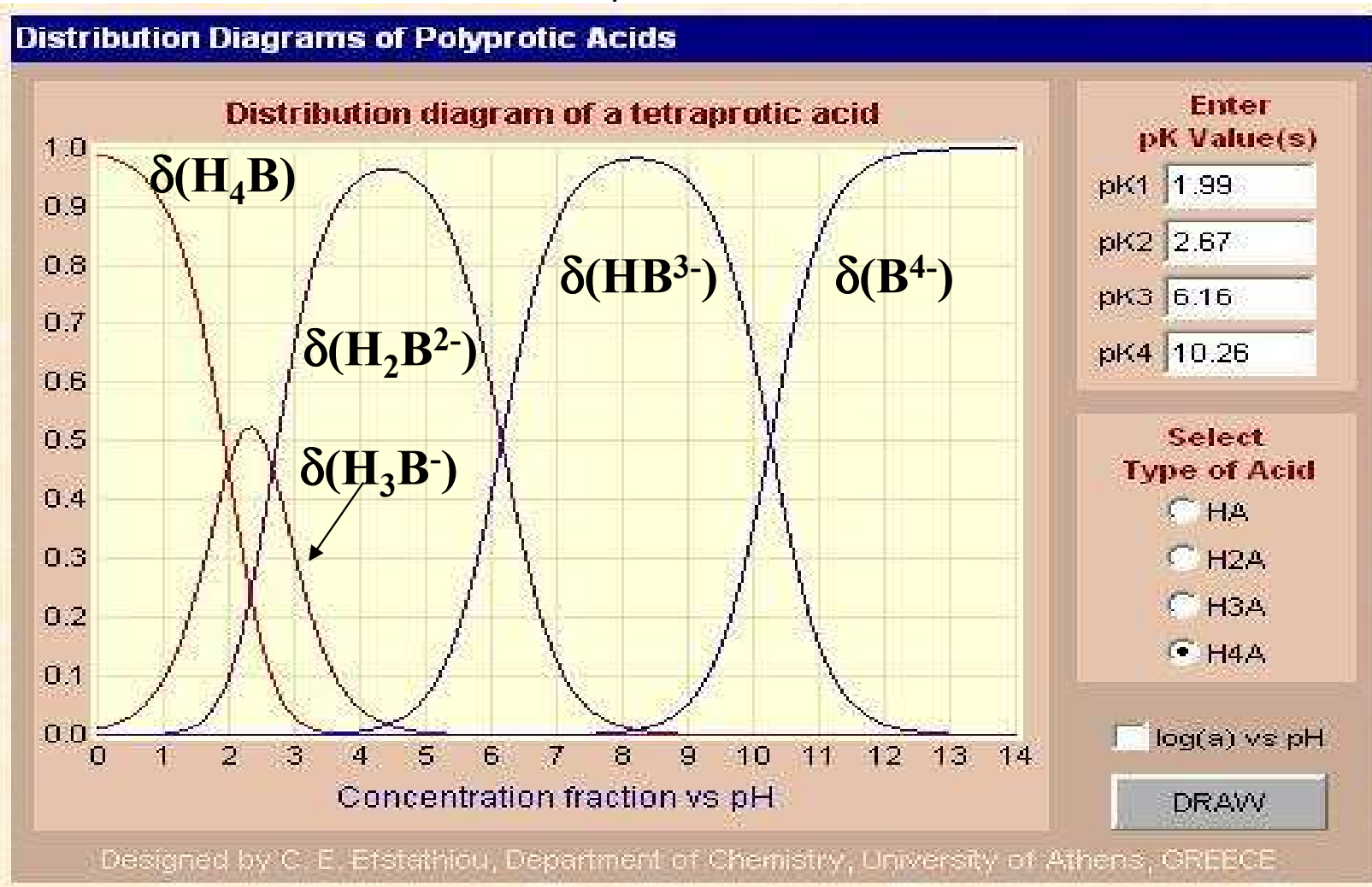
overall constant

$$\beta_{H_n} = \frac{[H^+]^n [B^{n-}]}{[H_nB]} = K_{a1} K_{a2} \dots K_{an}$$



Protolytic equilibria

- Distribution diagram of H_4B acid



Protolytic equilibria

- 2 conjugated acid-base pairs
- Acid-base equilibrium of amphiprotic solvent= autoprotolysis
 - $2 \text{SH} \rightleftharpoons \text{SH}_2^+ + \text{S}^-$ $K_{\text{SH}} = \frac{[\text{SH}_2^+][\text{S}^-]}{[\text{SH}]^2}$
- Protolytic equilibrium of acid
 - $\text{HB} + \text{SH} \rightleftharpoons \text{SH}_2^+ + \text{B}^-$ $\longrightarrow K_{\text{HB}} = \frac{[\text{SH}_2^+][\text{B}^-]}{[\text{HB}][\text{SH}]}$
 - $[\text{SH}] \gg [\text{HB}], [\text{B}^-], [\text{SH}_2^+]$
- Dissociation constant of base
 - $\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ $\longrightarrow K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}$
- Acidic dissociation constant of base
 - $\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$ $\longrightarrow K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]}$
- $K_a K_b = K_w = [\text{H}^+][\text{OH}^-]$ - ion product of water (self-ionization)

Complex (forming) equilibria

■ Complex:

- Coordination compound– association equilibrium:

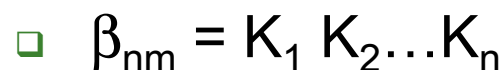


■ Cumulative (overall) stability (formation)

Constant β_{nm}

$$\beta_{nm} = \frac{[M_m L_n]}{[M]^m [L]^n}$$

■ Consecutive stability constants K:



$$K_1 = \frac{[ML]}{[M][L]} \quad K_2 = \frac{[ML_2]}{[ML][L]}$$

■ Bjerrum formation function \bar{n} :

- Average number of particles of ligand L bound to the central ion M at the overall composition of the complex forming system

Complex (forming) equilibria

- Bjerrum formation function

$$\bar{n} = \frac{c_L - [L]}{c_M} = \frac{\sum_{k=1}^n k\beta_k [L]^k}{1 + \sum_{k=1}^n \beta_k [L]^k}$$

- c_M and c_L – total (analytical) concentrations of metal (ion) and ligand [L]

$$c_L - [L] = [ML] + 2 [ML_2] + \dots + n [ML_n] = \\ \beta_1[M][L] + 2 \beta_2[M][L]^2 + \dots + n \beta_n [M][L]^n =$$

$$= \sum_{k=1}^n [M]k\beta_k [L]^k = [M]\sum_{k=1}^n k\beta_k [L]^k$$

Complex (forming) equilibria

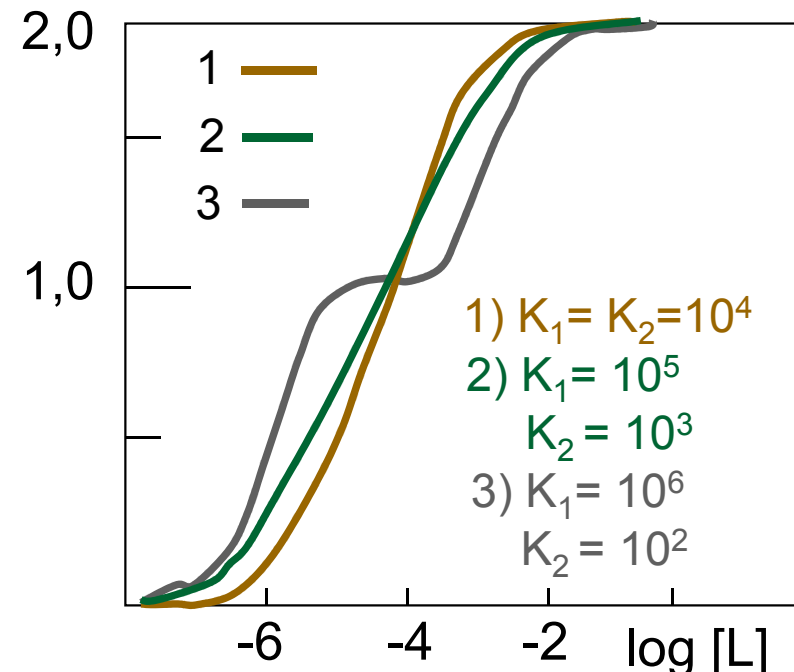
$$c_M = [M] + [ML] + \dots + [ML_n] = [M] + [M] \beta_1 [L] + \dots + [M] \beta_n [L]^n =$$

$$= [M] \{1 + \beta_1 [L] + \dots + \beta_n [L]^n\} =$$

$$= [M] \left\{ 1 + \sum_{k=1}^n \beta_k [L]^k \right\}, \text{ [M] in the nominator and denominator reduces}$$

\Rightarrow relation for \bar{n}

Formation f. $\bar{n} = f \{ \log [L] \}$



Complex (forming) equilibria

- **Distribution coefficient** indicates the relative share of individual complexes

$$\delta_k = [ML_k]/c_M \quad \delta_k = \frac{\beta_k [L]^k}{1 + \sum_{k=1}^n \beta_k [L]^k} = \frac{\beta_k [L]^k}{\alpha_{M(L)}}$$

$$\bar{n} = \delta_1 + 2\delta_2 + \dots k\delta_k + \dots n\delta_n \quad \alpha_{M(L)} = \text{side reaction coefficient}$$

- **Conditional stability constant** conditioned concentration (asterisk)

$$\beta_{ML}^* = \frac{[ML^*]}{[M^*][L^*]}$$

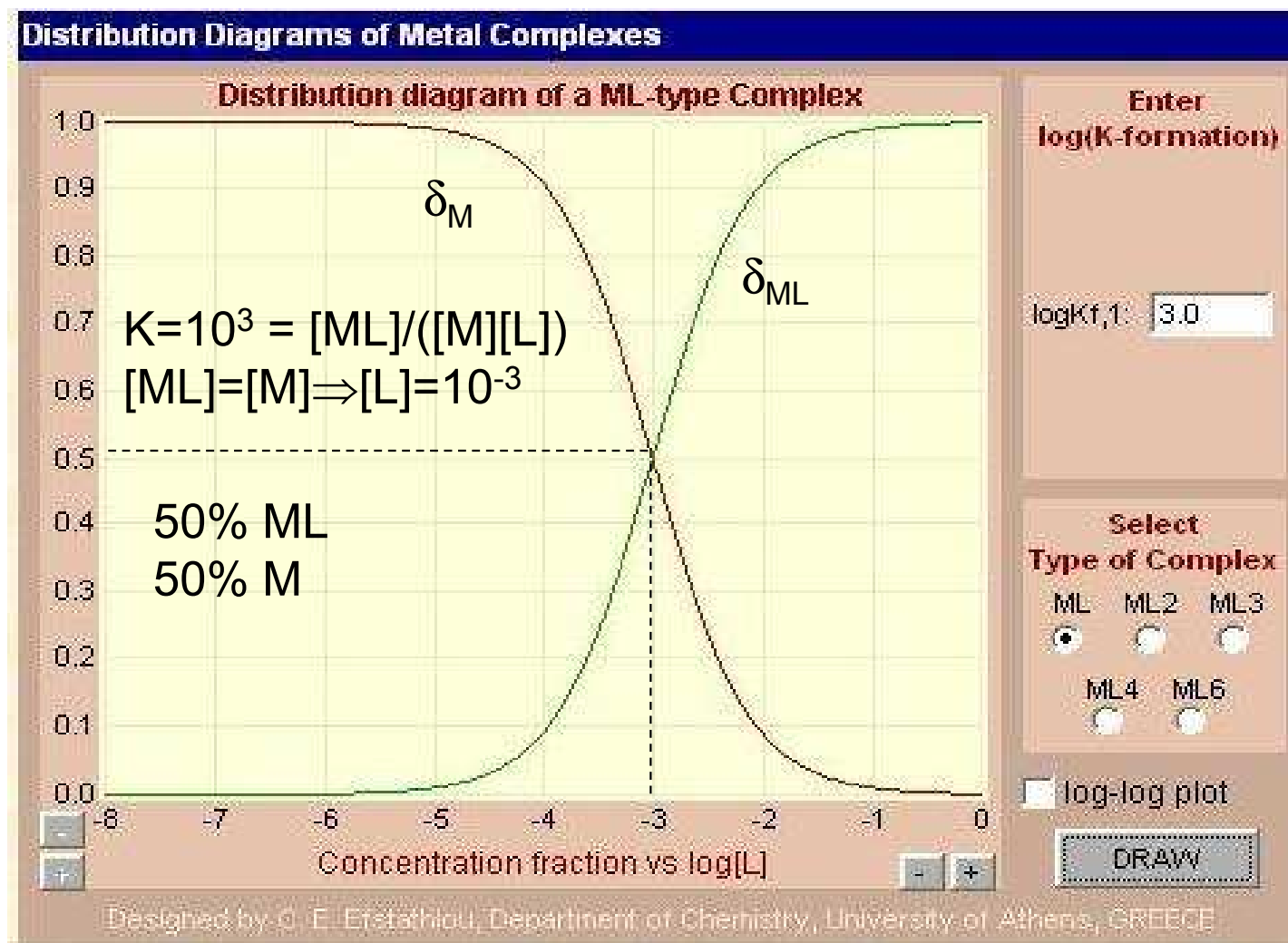
$$\begin{aligned} [ML^*] &= [ML] + [MHL] + \dots = \alpha_{ML} [ML] \\ [M^*] &= c_M - [ML^*] = [M] + [MOH] + \dots = \alpha_M [M] \\ [L^*] &= c_L - [ML^*] = [L] + [HL] + \dots = \alpha_L [L] \end{aligned}$$

$$\beta_{ML}^* = \beta_{ML} \frac{\alpha_{ML}}{\alpha_M - \alpha_L}$$

α_{ML} = side reaction coefficient

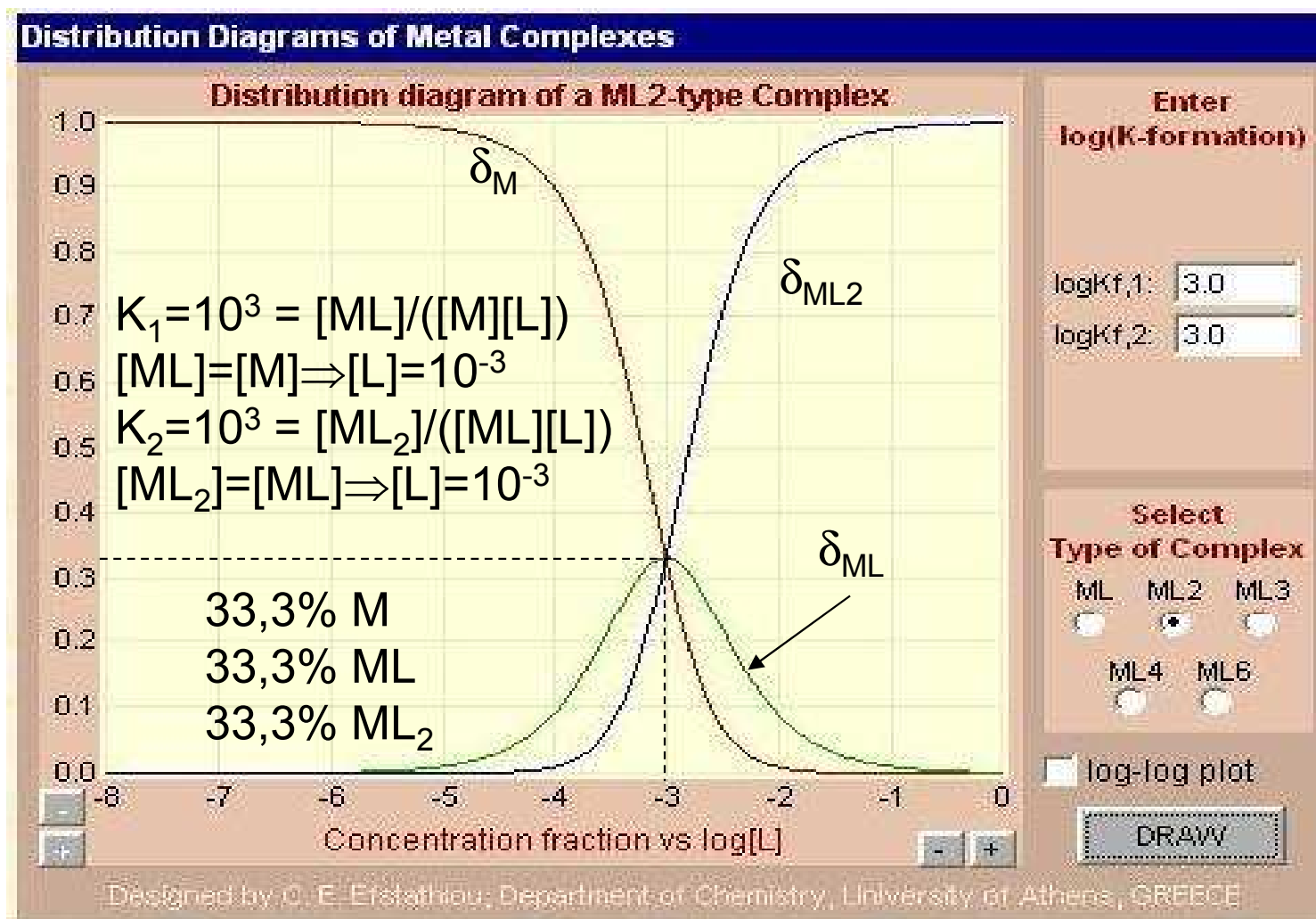
Complex (forming) equilibria

- distribution diagram of complex ML (1:1), $\log K = 3,0$



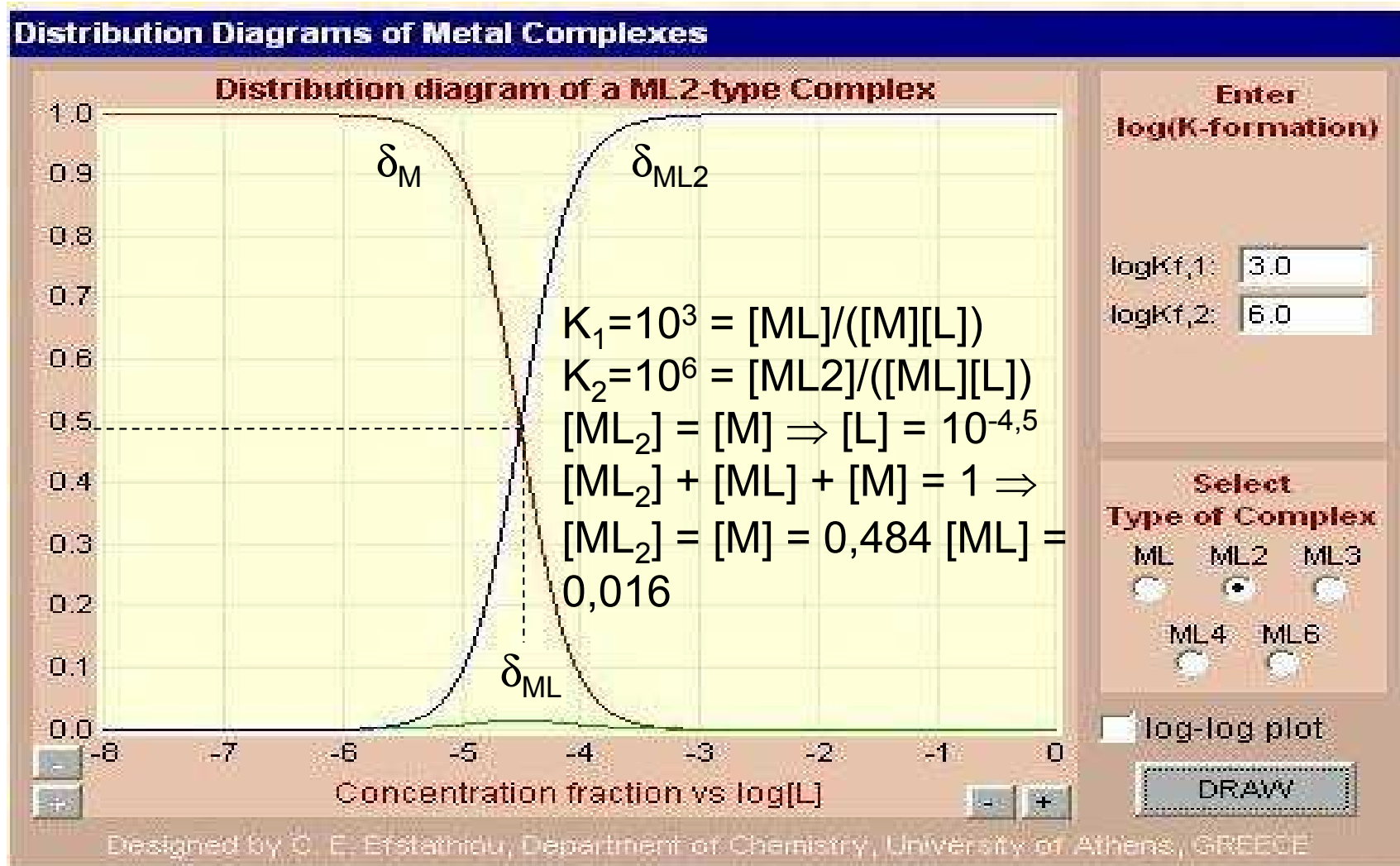
Complex (forming) equilibria

- distribution diagram of complexes ML a ML_2 , $\log K_1 = \log K_2 = 3,0$

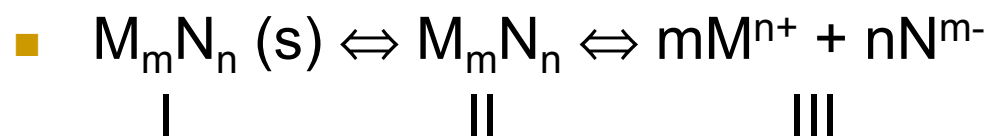


Complex (forming) equilibria

- distribution diagram of complexes ML and ML₂, log K₁= 3 log K₂= 6,0



Solubility equilibria



■ Strong electrolytes:

- In polar solvent I + III
- In non-polar solvent I + II

■ Weak electrolytes: in polar solvent I + II + III

■ Chemical potential

Gibbs energy

Partial molar free enthalpy

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_{j \neq i}}$$

■ Isothermal-isobaric process

- $G = U + pV - TS = H - TS$
- $\mu_i = \mu_{i0} + RT \ln a_i$ $\mu_i - \mu_{i0} = RT \ln a_i$

is work associated with the transfer of 1 mole of solute from the state of unit activity to activity a_i

Solubility equilibria

- Equilibrium between solid phase and saturated solution $\Delta G = 0$

- $\mu_I = \mu_{III} = m\mu_M^0 + mRT \cdot \ln a_M + n\mu_N^0 + nRT \cdot \ln a_N$

- Activities are constant and unit in solid phase

- $\mu_I^0 = \mu_{III}^0 + RT \cdot \ln a_M^m \cdot a_N^n$

- **Solubility product constant** $(K_s)_a = a_M^m \cdot a_N^n$, const. at const. T

- $a_M = [M^{n+}] \cdot y_M$ $a_N = [N^{m-}] \cdot y_N$

$$K_s = [M^{n+}]^m [N^{m-}]^n = (K_s)_a / (y_M \cdot y_N)$$

⇒ for a certain value of ionic strength

- **Conditional solubility product** $K_s^* = K_s \cdot (\alpha_{M(L)})^m (\alpha_{N(H)})^n$

- **Electrolyte solubility:** c [mol/l]

- Stoichiometry of precipitate:

$$n(M_m N_n) : nM : nN = 1 : m : n \Rightarrow [M^{n+}] = m \cdot c, [N^{m-}] = n \cdot c$$

$$\Rightarrow c = \sqrt[m+n]{\frac{K_s}{m^m \cdot n^n}}$$

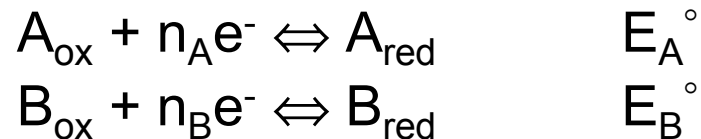
Redox equilibria

- **Redox processes** – electric work is exerted \times protolytic and complex forming equilibria
- **Electric work** is associated with transfer of $n = n_A n_B$ electrons from reduced form of substance B onto oxidized form of substance A:

$$-\Delta G = n_A n_B F E^\circ$$

where n_A , n_B are amounts of substances, F is Faraday constant (96 484 C mol⁻¹) and E° is standard cell voltage

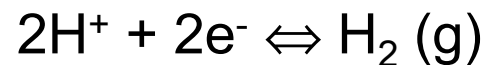
- **Redox pairs** = partial reactions:



- **Nernst-Peters equation:**

$$E_A = E_A^\circ + [RT/(n_A F)] \ln(a_{A_{\text{ox}}}/a_{A_{\text{red}}})$$

standard H-electrode, $p = 101,32$ kPa, $a_{\text{H}^+} = 1$, $c = 1,18$ mol/l HCl, Pt black, H₂ gaseous



Redox equilibria

- $E^0_{\text{H}^+/\text{H}_2} = 0$; $E_A^0 > 0$; A_{ox} is stronger oxidant than H^+
 $E_A^0 < 0$; A_{red} is stronger reductant than H_2
- $-\Delta G^0 = RT \ln (K_a) \Rightarrow \log (K_a) = -\Delta G^0 / (2,303RT) =$
 $= n_A \cdot n_B \cdot F \cdot E^0 / (2,303 RT)$; $E^0 = E_A^0 - E_B^0$:
„total conversion“ (99,9 %) at $n_A = n_B$ is at $K_a = 10^6$
- $T = 25 \text{ }^\circ\text{C}$

Sampling and sample preparation for analysis

- composition of the analyzed sample must correspond to the composition of the examined substances
 - Sampling of solids ČSN 650611, liquids ČSN 650512
- Sampling involves two operations
 - gross sample collection from analyzed substance
 - **gross sample** – sample portion taken from analyzed substance; from solid material – it is processed by mechanical mixing, quartering, splitting, grinding, sieving and gradual sample reduction
 - analytical sample collection from gross sample
 - **analytický vzorek** – must have identical composition with analyzed material

Transferring the sample into a solution

A) Dissolution in

- 1) water
- 2) acids
- 3) hydroxides

„Wet“ decomposition:

- ❑ HCl, HNO₃, H₂SO₄, HClO₄, HF
- ❑ Beakers, dishes, pressurized autoclaves: glass, quartz, porcelain, PTFE
- ❑ heating: gas burner, hotplate, microwave oven

B) Fusion

- 1) acid
- 2) alkaline

„Dry“ decomposition:

- ❑ Sodium carbonate, potassium carbonate, borax, disulphate, hydroxides– conversion to salts dissoluble in acids and in H₂O
- ❑ Crucibles Pt, Ni, Fe, glassy graphite
- ❑ Burner, muffle furnace

Transferring the sample into a solution

- **Dissolution**
- spontaneous process in which particles are released from the range of forces, which bind them in solid phase by the effect of solvation forces that stabilize the particles in solution

- **Solvent**
 - ❑ Liquid capable of dissolving gases, liquids or solids, without chemically reacting with them
 - ❑ Most important - water

Transferring the sample into a solution

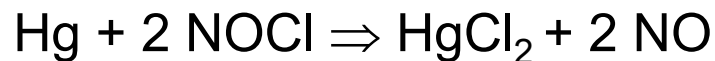
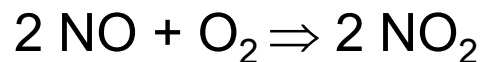
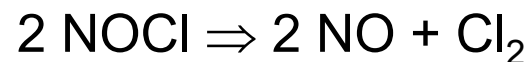
- Decomposition in acids
 - **HCl**, diluted 1+1 (6 mol/l), without the effect of oxidation
 - dissolves:
 - 1) Metal with negative reduction potential
 - 2) Alloys Fe s Cr, Co, Ni, Ti
 - 3) Salts of weak acids
 - 4) Carbonate ores
 - 5) Oxidic ores (Zn, Mn, Fe)
 - 6) Hydrolytic products (BiOCl)
 - does not dissolve:
 - 1) Bauxite, corindum
 - 2) spinels $M^{II}O \cdot M^{III}_2O_3$

Transferring the sample into a solution

- **HNO₃**, diluted 1+1 (cca 4,6 mol/l, 30%), conc. too, oxidation effects, nitrates - soluble
- dissolves:
 - 1) Most of metals with exception of Au and platinum group metals
 - 2) alloys: Bi, Cd, Cu, Pb, Fe-Mn, Fe-P
 - 3) ores: Cu, Mo, Co, Ni
- $M^{II} + 2 NO_3^- + 8 H^+ \Leftrightarrow 3 M^{2+} + 2 NO + 4 H_2O$
- As, Sb transferred into solution (H₃AsO₃)
- Sn – precipitates stannic acid:
$$Sn + 4 NO_3^- + 4 H^+ + (x-2) H_2O \Leftrightarrow SnO_2 \cdot x H_2O + 4 NO_2^-$$
- Concentrated HNO₃
 - Passivation Al, Cr, Fe
 - Oxidation of organic compounds

Transferring the sample into a solution

- **HCl + HNO₃** (3+1) aqua regia
 - dissolves:
 - 1) PGM and Au
 - 2) Ores and some silicates
 - 3) phosphides, arsenides, antimonides, sulphides ⇒ acids: phosphoric, arsenic, chloroantimonic
 - Active component Cl₂ a NOCl



Transferring the sample into a solution

□ HF conc.

- Decomposes all silicates:



- Rocks, ores (Nb, Ta, W), glasses, ceramics, alloys
- Used in mixture with H_2SO_4 or HClO_4 (increased boiling point), H_2SO_4 binds water and prevents thus hydrolysis, perchloric acid exhibits oxidative effects

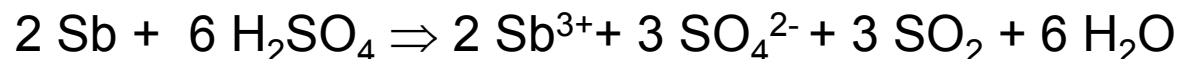
□ H_2SO_4

- Diluted behaves as HCl:

- alone – limited use, sulphates less soluble than chlorides

- Concentrated

- Oxidative effects, diss. Sb:



- phosphides, arsenides \Rightarrow phosphoric and arsenic acids
- Kjeldalization – mineralization of organic nitrogen containing substances

Transferring the sample into a solution

- **HClO₄** conc. (72%) exhibits oxidative effects at elevated temperature
 - dissolves:
 - 1) steels(Cr, Si, V, P)
 - 2) carbides
 - 3) In mixture with HF for decomposition of silicates
 - advantage: soluble salts
 - disadvantage: explosive with organic compounds

- **H₃PO₄**
 - 1) alloys
 - 2) ferrovanadium, ferrosilicium, ferrochromium, ferroboron

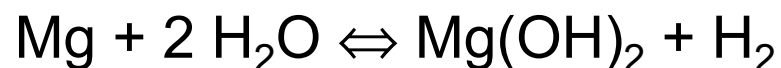
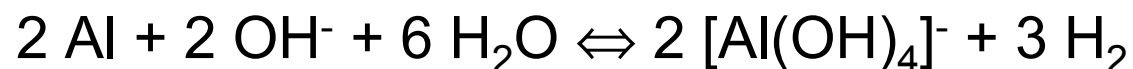
Transferring the sample into a solution

- Decomposition in hydroxides

- **NaOH, KOH (35%)**

- dissolves:

- 1) Light alloys (Al, Zn, Si, Mg), resulting aluminates, zincates, silicates:



Transferring the sample into a solution

■ Fusion

- process, where high-temperature heated material changes from solid to liquid
 - Resulting products are dissoluble in water or dissolved acids
 - According to fusion agent: **alkaline and acidic fusion**
 - **Alkaline fusion**: transfer of acidic components (silicates, sulphates) in a solution by melting, flux is anhydrous sodium carbonate or a mixture of sodium carbonate and potassium
 - **Acidic fusion**: conversion of base-forming oxides to soluble salts (metal oxides, etc.). Transfer into solution by fusion with potassium sulphate, or sodium tetraborate.

■ Fusion agents

- Reagents used for decomposition by fusion
- Alkaline fusion: sodium carbonate, alkaline hydroxide, mixture of sodium carbonate and sulphur; for acidic fusion: potassium disulphate, boron oxid, boric acid, sodium tetraborate

Převádění vzorku do roztoku

■ Alkaline fusion

- decomposed: quartz, glass, porcelain, enamels, cement, aluminosilicates

□ Na_2CO_3

- 1) Aluminosilicates are converted into soluble alkaline aluminates and silicates
- 2) Other oxides are converted to carbonates or depolymerize and in HCl are converted into soluble chlorides

□ NaOH , KOH

fusion in crucibles Ag, Ni or Fe

- decomposed: ores W, Sn, Cr, Ti, Sb, Zr, corindum, bauxit, partially silicates

□ $\text{Li}_2\text{B}_4\text{O}_7$, LiBO_2

- 1) Formation of borate glasses soluble in diluted acids –Si retained in solution

Převádění vzorku do roztoku

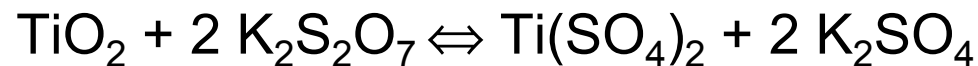
■ Sintration

- Reaction in solid phase at increased temperature but below the melting point of sinteration reagent (Na_2O_2)
- Pt crucibles, sintered material soluble in water

Převádění vzorku do roztoku

- Acidic fusion

- **KHSO₄, K₂S₂O₇**



- decomposed: aluminates, spinels, ores Cu, Sb, Ni, Ti
- Leaching of sulphates Zr a Ti at cold by addition of H₂SO₄
- Active constituent is SO₃

