Modern Methods in Heterogeneous Catalysis Research

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Chemical (Elemental) Analysis

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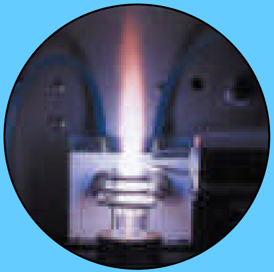

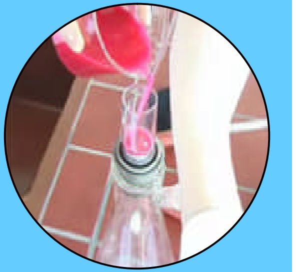

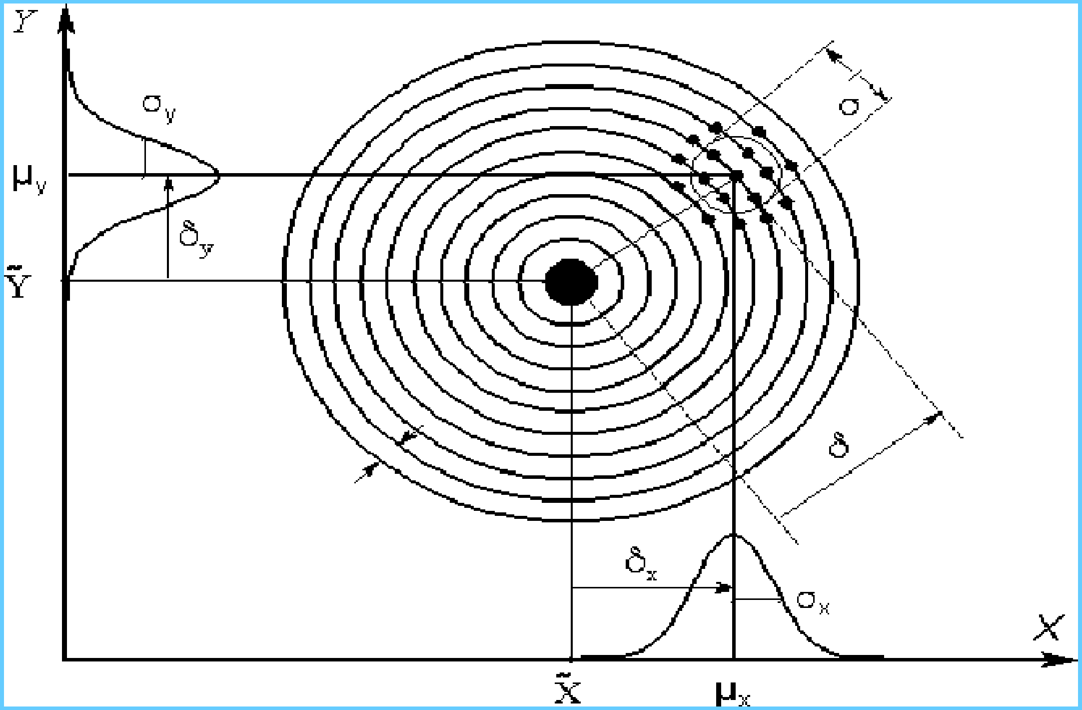

Outline

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1.2 Accuracy and Precision

1.3 Decision Limit, Detection Limit, Determination Limit

2. Methods for Quantitative Elemental Analysis

2.1 Chemical Methods

- 2.1.1 Volumetric Methods
- 2.1.2 Gravimetric Methods

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- 2.2.1 Potentiometry
- 2.2.2 Polarography

Outline

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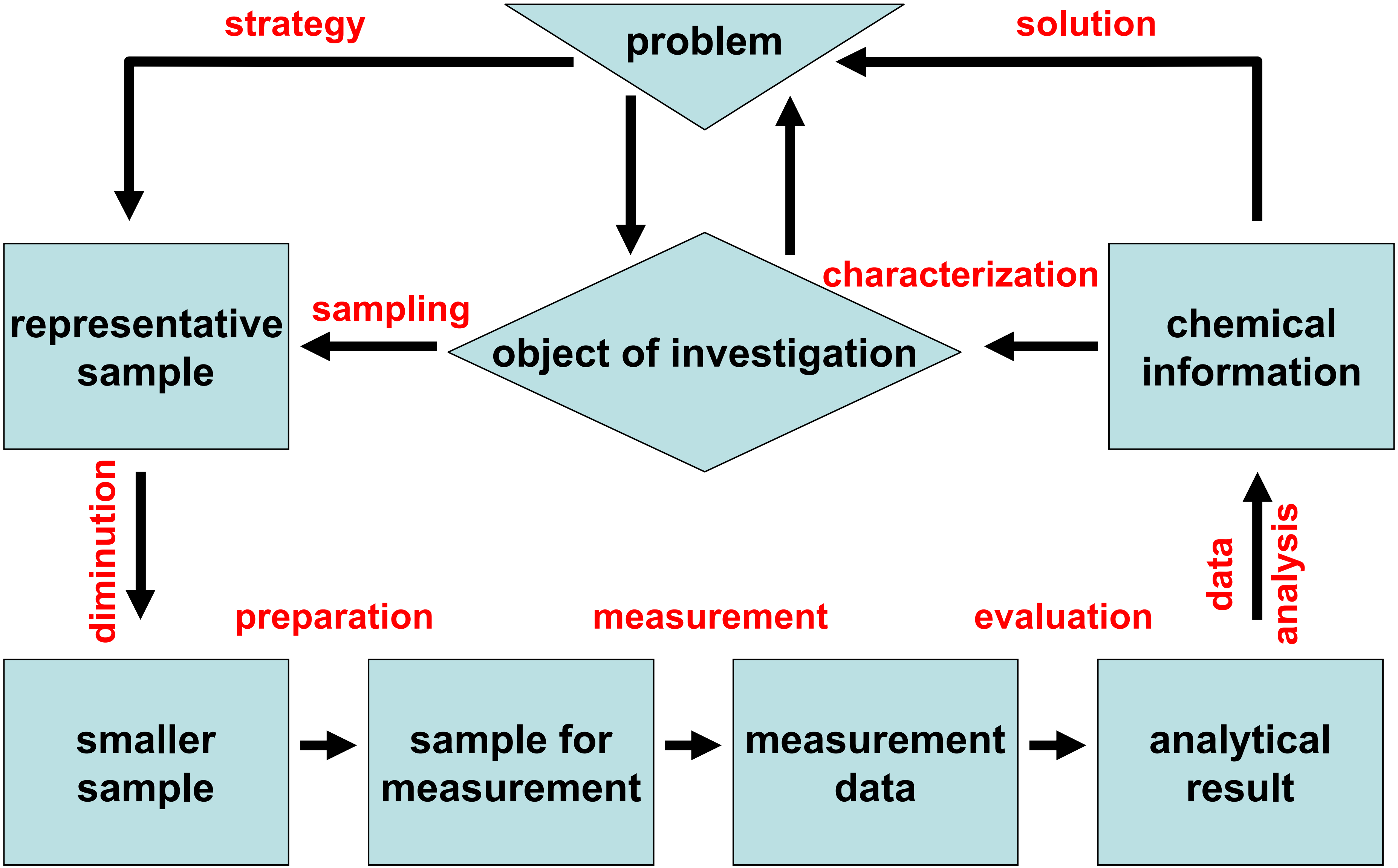
The Analytical Process



strategy

problem

solution

characterization

sampling

representative sample

object of investigation

chemical information

diminution

data analysis

preparation

measurement

evaluation

smaller sample

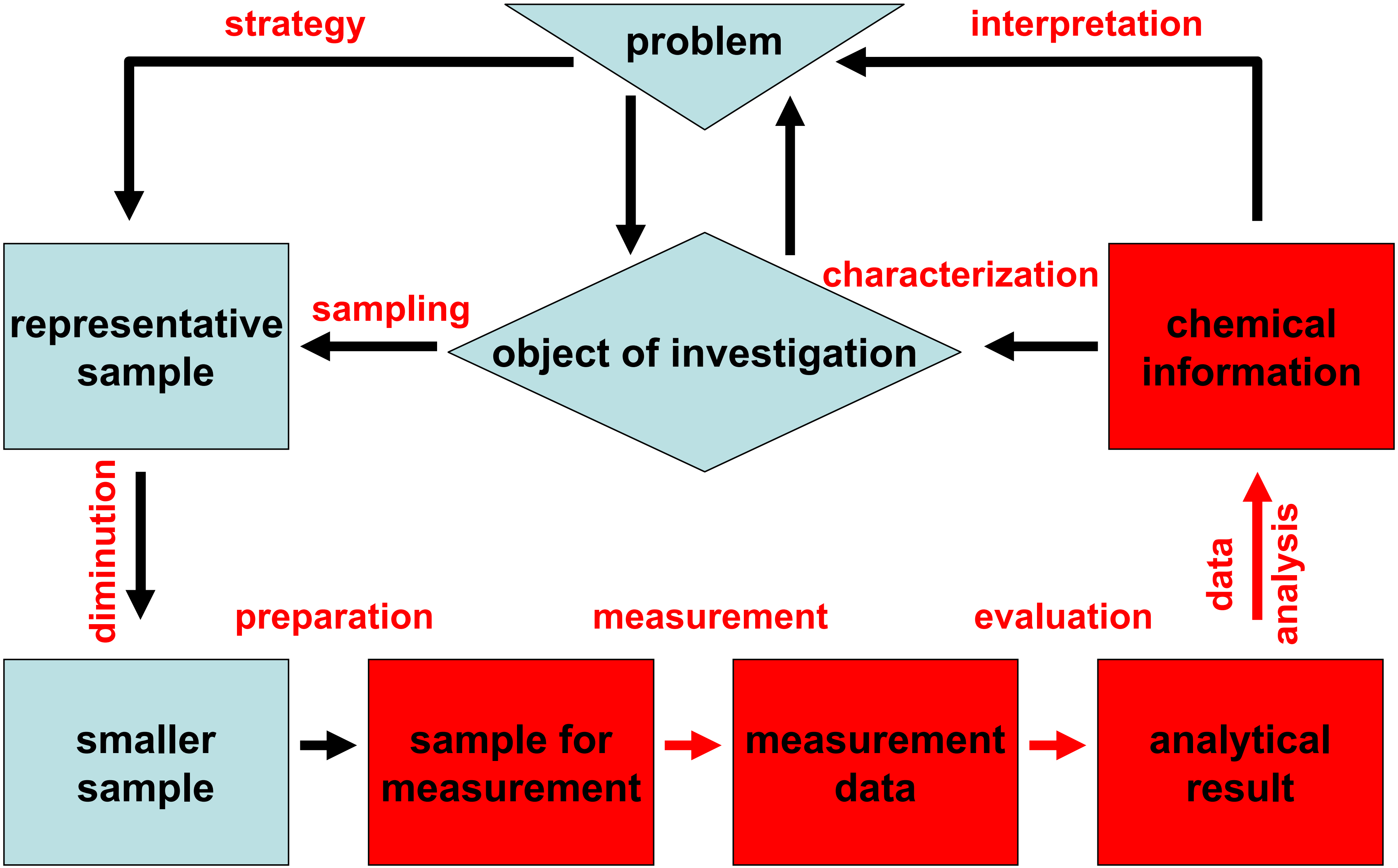
sample for measurement

measurement data

analytical result

Backup Slide

The Analytical Process



strategy

problem

interpretation

characterization

sampling

representative sample

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measurement

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smaller sample

sample for measurement

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Backup Slide

Analytical Problems in Science, Industry, Law…

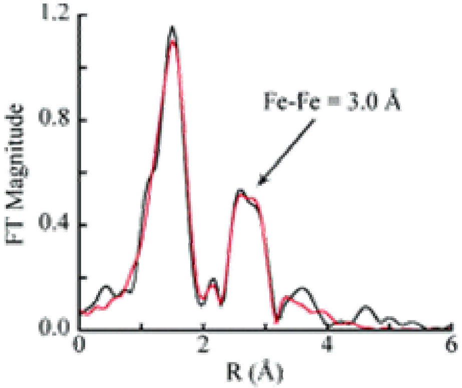
Science

example: Determination by X-ray Absorption Spectroscopy of the Fe-Fe Separation in the Oxidized Form of the Hydroxylase of Methane Monooxygenase Alone and in the Presence of MMOD

Rudd D. J., Sazinsky M. H., Merkx M., et al. *Inorg. Chem.* **2004**, 43 (15), 4579-4589, 2004

Motivation

fundamental interest
future developments



Industry

example: manufacturer of iron - Shall I by this iron ore or not ?

Motivation

money

precision (e.g.)

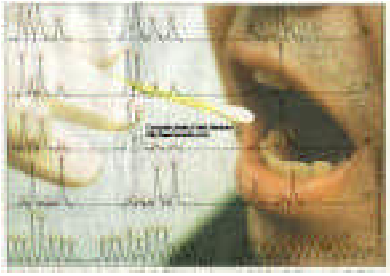
53 ⌖ 5wt% vs. 53 ⌖ 1wt%

accuracy (e.g.)

53 ⌖ 1wt% vs. 51 ⌖ 1wt%

Law

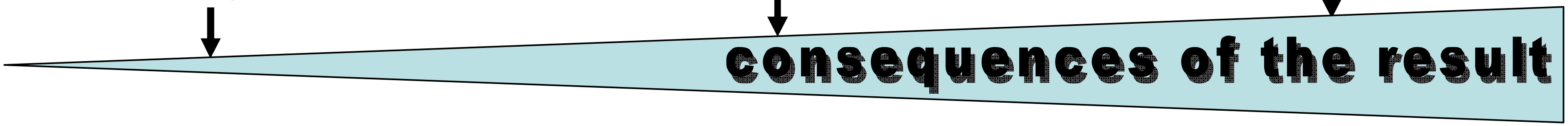
example: Is the accused guilty or not guilty ?



Motivation

human fate

murder conviction
genetic fingerprint fits – lifelong prison
genetic fingerprint does not fit - acquittal

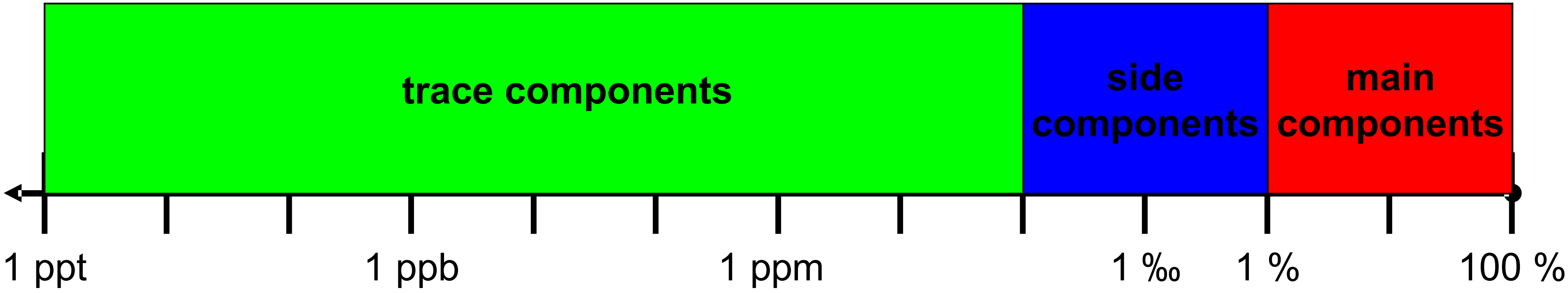


consequences of the result

1. Introduction

1.1 Concentration Ranges

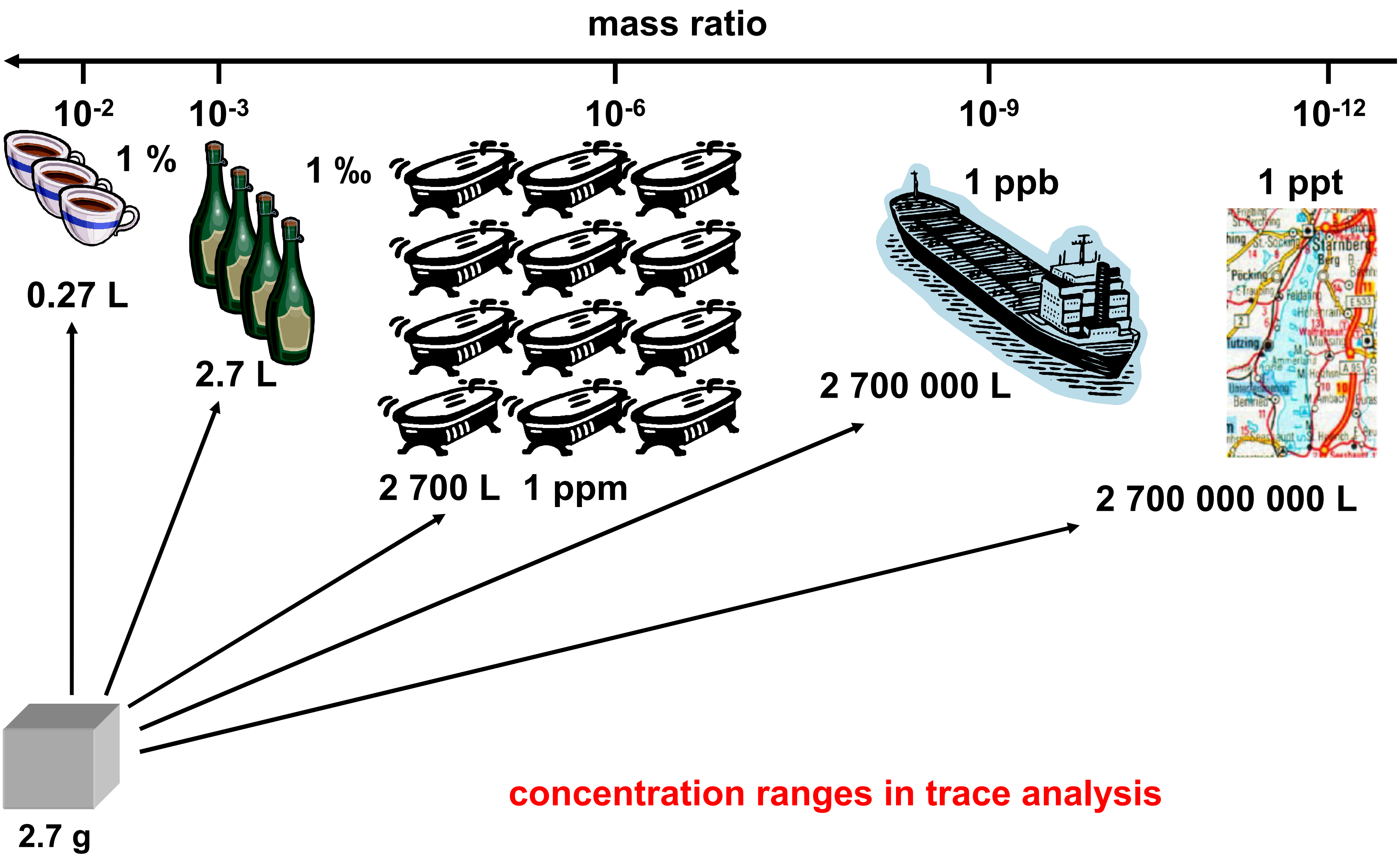
concentration ranges in elemental analysis



ppt (w/w)	ppp (w/w)	ppm (w/w)	‰ (w/w)	% (w/w)
10^{-12} g/g	10^{-9} g/g	10^{-6} g/g	10^{-3} g/g	10^{-2} g/g
pg/g	ng/g	µg/g	mg/g	0.01 g/g
ng/kg	µg/kg	mg/kg	g/kg	10 mg/kg

1. Introduction

1.1 Concentration Ranges



mass ratio

10^{-2} 1 % 0.27 L

10^{-3} 1 ‰ 2.7 L

10^{-6} 1 ppm 2 700 L

10^{-9} 1 ppb 2 700 000 L

10^{-12} 1 ppt 2 700 000 000 L

2.7 g

concentration ranges in trace analysis

1. Introduction

1.2 Accuracy and Precision

accuracy:

- can be defined as the consistency between the mean of an analytic result and the value held as the true value
- has to be verified before each analysis by means of standards
- describing quantities:

$$error_{\bar{x}} = \pm\left|\bar{x} - \hat{x}'\right|$$

$$relative\ error_{\bar{x}} = \frac{\pm\left|\bar{x} - \hat{x}'\right|}{\hat{x}'} \times 100$$

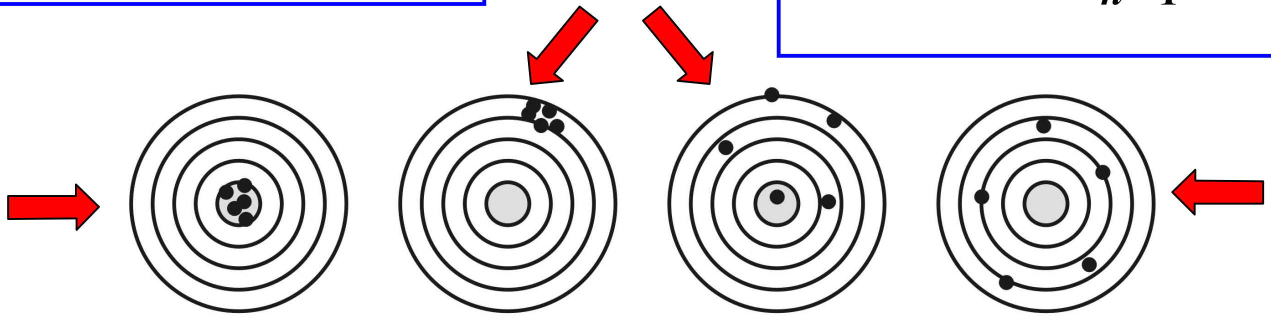
precision (uncertainty):

- describes in a positive (negative) manner the influence of random errors on an analytic result
- describing quantities:

$$s = \sqrt{\frac{\sum_i \left(x_i - \bar{x}\right)^2}{n - 1}}$$

Gaussian distributed errors!

$$v = s^2 = \frac{\sum_i \left(x_i - \bar{x}\right)^2}{n - 1}$$



wrong results

main and side component analysis

trace and ultra trace analysis

accurate and precise

precise but inaccurate

inaccurate and imprecise

accurate but imprecise

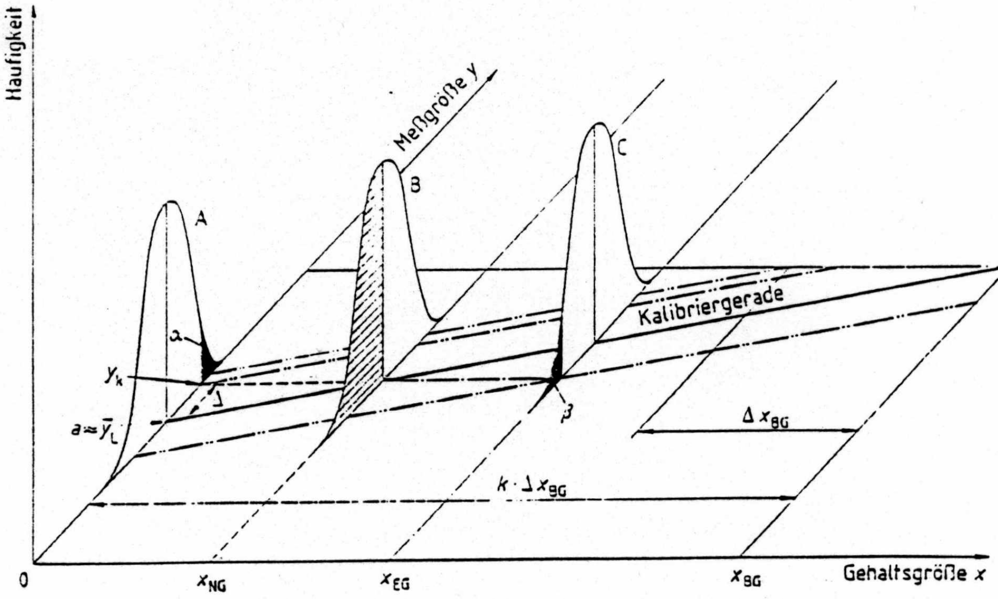
1. Introduction

1.3 Decision Limit, Detection Limit, Determination Limit

- the lower the concentration of an analyte, the more difficult becomes its qualitative detection and its quantification
- stochastic errors become more and more pronounced
- the decision limit and the detection limit are lower limits characterizing the performance of a method to discriminate a true value from a blank value
- the determination limit guaranties the quality of a quantitative result (user specific)

$$y_k = \bar{y}_B + \frac{t_{f,\alpha} \cdot s_B}{\sqrt{n}} \quad \Rightarrow \quad \mathrm{y_k} = \bar{y}_B + \mathrm{bx_{NG}} \quad \Rightarrow \quad x_{NG} = \frac{t_{f,\alpha} \cdot s_B}{b \cdot \sqrt{n}}$$

for $\alpha = \beta$ $\quad x_{EG} = 2 \cdot x_{NG}$



y_k	Kritischer Wert der Meßgröße
a	Ordinatenabschnitt der Kalibrierfunktion
$\bar{y}_L$	Leerwert
Δ	Breite des einseitigen Prognoseintervalls $\Delta = \Delta a$ (Kalibriergeradenmethode) $\Delta = \Delta \bar{y}_L$ (Leerwertmethode)
Δx_{BG}	Halbe Breite des zweiseitigen Prognoseintervalls der Bestimmungsgrenze
$1/k$	Relative Ergebnisunsicherheit zur Charakterisierung der Bestimmungsgrenze
x_{NG}	Nachweisgrenze
x_{EG}	Erfassungsgrenze
x_{BG}	Bestimmungsgrenze
A	Verteilung der Meßwerte der Leerprobe
B	Verteilung der Meßwerte einer Probe mit dem Gehalt der Nachweisgrenze
C	Verteilung der Meßwerte einer Probe mit dem Gehalt der Erfassungsgrenze

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2. Methods for Quantitative Elemental Analysis

2.1 Chemical Methods

- volumetric methods
- gravimetric methods

2.2 Electroanalytical Methods

- potentiometry
- polarography

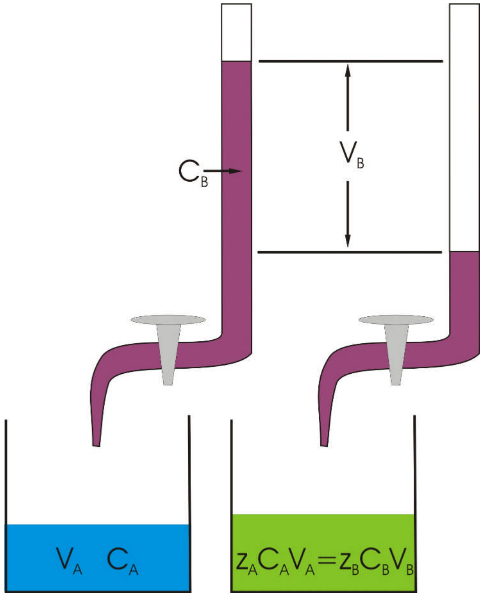
2.3 Spectroscopic Methods

- atomic emission
- atomic absorption
- inductively coupled plasma mass spectrometry
- X-ray fluorescence
- electron probe X-ray microanalysis

2.1 Chemical Methods

2.1.1 Volumetric Methods - Principle

principle of volumetric methods



$A + B \rightarrow C + D$

- fast, complete and stoichiometric well defined reaction
- the extend of the reaction can be monitored (e.g. pH, electric potential)
- the point of equivalence can be detected precisely (e.g. sudden color change, steep pH or potential change)

evaluation of the result

$$p = V_B \cdot k \cdot N \cdot \frac{100}{m_e} \quad \text{in } \%$$

p = percentage of the analyte in the sample

V_B = volume in ml dropped in from the burette

k = stoichiometric factor (mg analyte/ml)

N = correction factor for the theoretical value k

e = weighted sample (in mg)

$$\frac{\sigma_P}{p} = \sqrt{\left(\frac{\sigma_{m_e}}{m_e}\right)^2 + \left(\frac{\sigma_{V_B}}{V_B}\right)^2 + \left(\frac{\sigma_N}{N}\right)^2}$$

inserting typical values

$$0.1\% < \frac{\sigma_P}{p} < 1\%$$

advantage: high precision!!!

2.1 Chemical Methods

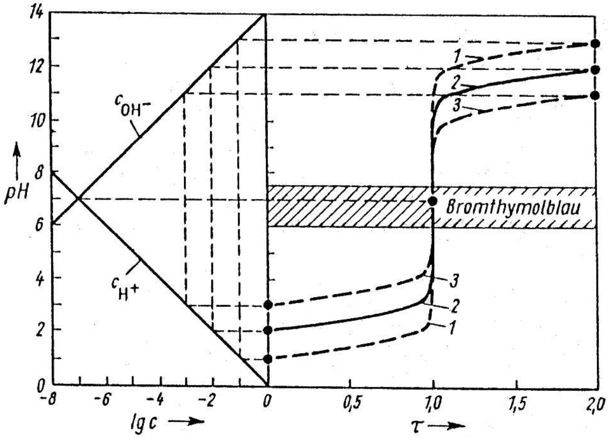
2.1.1 Volumetric Methods – Acid Base Titration

acid – base reaction: $H_nA + nBOH \rightleftharpoons A^{n-} + nB^+ + nH_2O \; (z_A=n,\ z_B=1)$

titration curve:

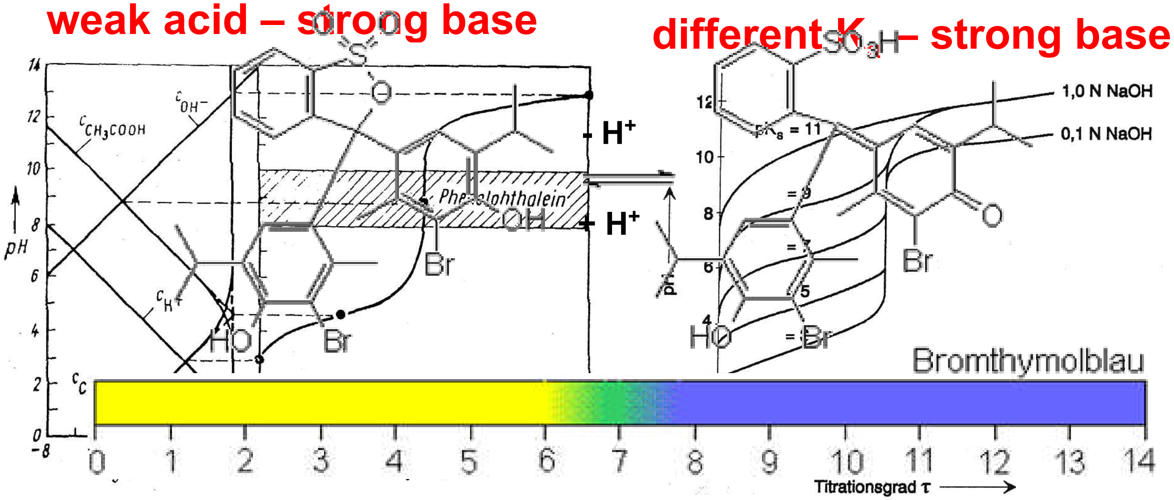
$$t = \frac{z_B \cdot C_B \cdot V_B}{z_A \cdot C_A \cdot V_A} = \frac{K_a}{10^{-pH} + K_a} + \frac{V_S + V}{C_S \cdot V_S} \cdot \left(\frac{K_w}{10^{-pH}} - 10^{-pH} \right) \qquad K_w = [H^+][OH^-]$$

strong acid – strong base



weak acid – strong base

different K_a – strong base



$$pH = pK_{a,Ind} \pm 1$$

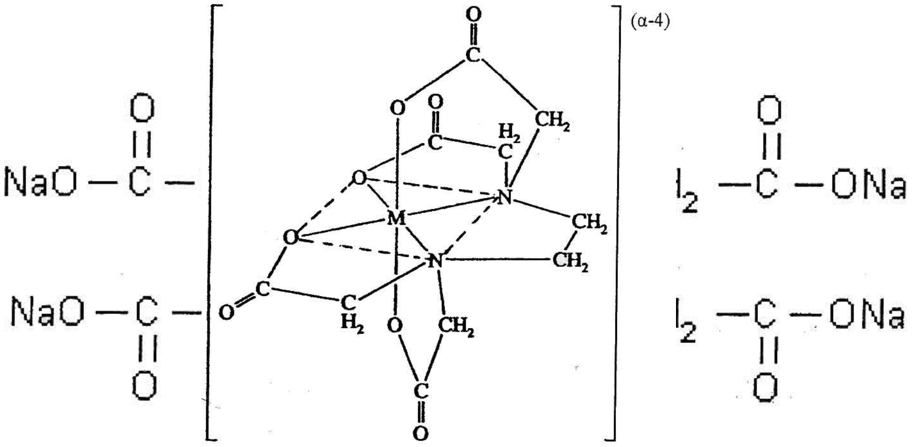
- **choice of the indicator depends on K_a**
- **very weak acids (bases) can be titrated in non-aqueous solvents as liquid ammonia or 100% acetic acid**

2.3 Chemical Methods

2.1.1 Volumetric Methods - Complexometry

complex formation: $nL + M^{m+} \rightleftharpoons ML_n^{m+}$

most used ligand - EDTA



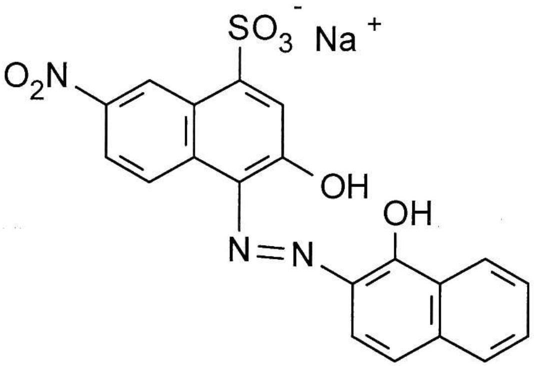
M-EDTA chelate

$H_{4-n}Y^{n-} + M^{m+} \rightleftharpoons [MY]^{(m-4)} + (4-n)H^+ \; (z_A=1, z_B=1)$

$$[M^{m+}] = \frac{[MY^{(m-4)}]}{K_f \times [EDTA]_{total} \times a_{Y^{4-}}}$$

complex formation only with Y^{4-}
$\Rightarrow$ buffer required

indication: $HI^{2-} + M^{m+} \rightleftharpoons MI^{(m-3)} + H^+$
e.g. Eriochromschwarz T



applicable for the determination of:

Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} at pH 8-11

Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+}, Pb^{2+}, VO^{2+} at pH 4-7

Bi^{3+}, Co^{3+}, Cr^{3+}, Fe^{3+}, Ga^{3+}, In^{3+}, Sc^{3+}, Ti^{3+}, V^{3+}, Th^{4+} at pH 1-4

2.1 Chemical Methods

2.1.1 Volumetric Methods – Redox Titration

redox reaction: $n_BOx_B + n_ARed_A \rightleftharpoons n_BRed_B + n_AOx_A \quad (z_A=n_B,\ z_B=n_A)$

examples: $MnO_4^- + 5Fe^{2+} + 8H^+ \rightleftharpoons Mn^{2+} + 5Fe^{3+} + 4H_2O$

$Ce^{4+} + Fe^{2+} \rightleftharpoons Ce^{3+} + Fe^{3+}$

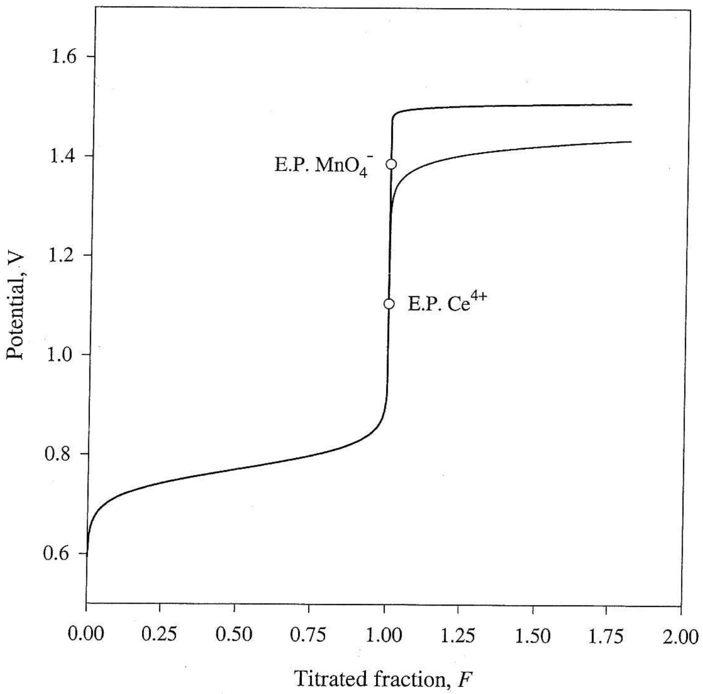
$$t = \frac{z_A \cdot C_A \cdot V_A}{z_B \cdot C_B \cdot V_B}$$

$$0 < t < 1 \quad U = U_A = U_A^{\ominus} + \frac{RT}{n_B F} \cdot \ln \frac{t}{1 - t}$$

$$t = 1 \quad U_{eq} = \frac{n_A U_B^{\ominus} + n_B U_A^{\ominus}}{n_A + n_B}$$

$$t > 1 \quad U = U_B = U_B^{\ominus} + \frac{RT}{n_A F} \cdot \ln(t - 1)$$

titration curve



indication: self indication (violet $MnO_4^- \rightarrow$ colorless Mn^{2+})
redox indicator ($In_{Red} \rightleftharpoons In_{Ox} + ne^-$)
potentiometric endpoint detection

2.1 Chemical Methods

2.1.2 Gravimetric Methods

precipitation reaction: $\nu_+ M^{z+}(aq) + \nu_- A^{z-}(aq) \leftrightarrow M_{\nu_+} A_{\nu_-}(s)$

- **precipitation of the ion to be determined by a suitable precipitating agent**
- **filtering and washing of the precipitate**
- **transformation into a compound of well defined stoichiometry (drying/calcination) → weighing**

examples

$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4$ ($K_L = [Ba^{2+}] \cdot [SO_4^{2-}] = 1 \cdot 10^{-10}$ mol²/l²) as $BaSO_4$

$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3$ ($K_L = [Fe^{3+}] \cdot [OH^-]^3 = 1 \cdot 10^{-38}$ mol⁴/l⁴) as Fe_2O_3

$$[M^{z+}] = \sqrt[\nu_+ + \nu_-]{K_L \left(\frac{\nu_+}{\nu_-}\right)^{\nu_-}} \qquad [A^{z-}] = \sqrt[\nu_+ + \nu_-]{K_L \left(\frac{\nu_-}{\nu_+}\right)^{\nu_+}}$$

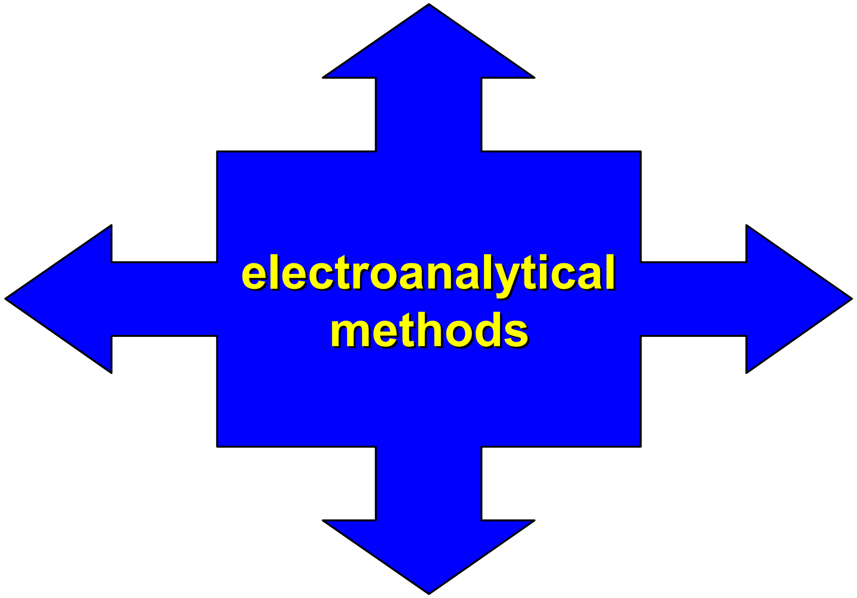
- **for analytical purposes:** $\alpha_p = 1 - \frac{[M^{z+}] \cdot V}{[M^{z+}]_o \cdot V_0} \geq 0.997$

- **advantage**

  ⇒ **one of the most precise analytical methods**

$$\frac{\sigma_m}{m} = \sqrt{\left(\frac{\sigma_{m_e}}{m_e}\right)^2 + \left(\frac{\sigma_{m_a}}{m_a}\right)^2} \qquad 0.01\% < \frac{\sigma_m}{m} < 0.1\%$$

2.2 Electroanalytical Methods



electrode reaction, $I_{Faraday}=0$ (potentiometry)

- ion-selective electrodes

electrode reaction, DC,
$I_{Faraday}{}^{1}0$ (voltametry)

- coulometry

electroanalytical methods

no electrode
reaction, AC, high
frequency

- conductometry

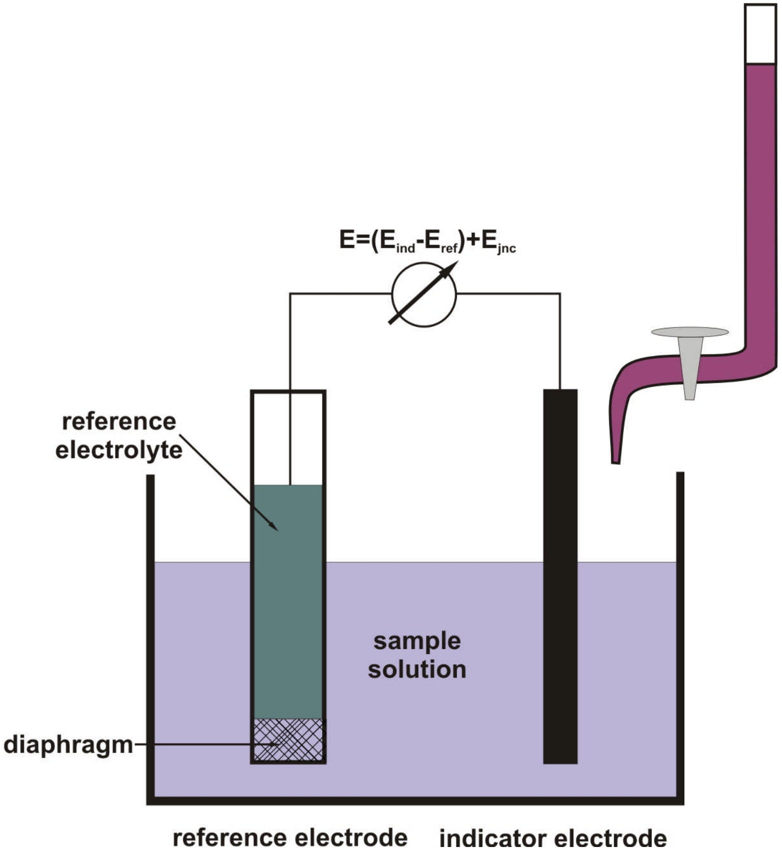
electrode reaction, AC,
$I_{Faraday}{}^{1}0$

- AC polarography

2.2 Electroanalytical Methods

2.2.1 potentiometry, potentiometric titration

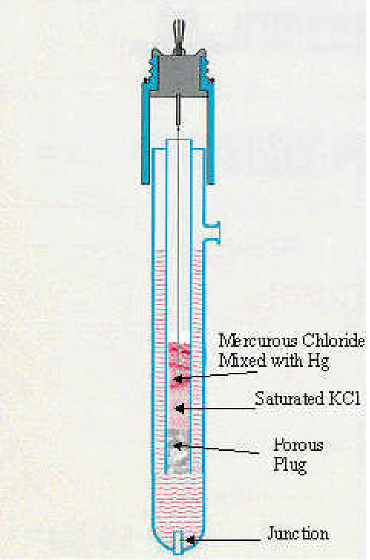
- **principle Þ measurement of the cell potential (potential between two electrodes at zero current)**
- **relation of the cell potential and the analyte concentration**



typical reference electrode
calomel electrode

$$Hg_2Cl_2(s) + 2e^- ✞ 2Hg(l) + 2Cl^-$$

$$E = E^{0'} - \frac{0.05916V}{2}\log[Cl^-]^2$$

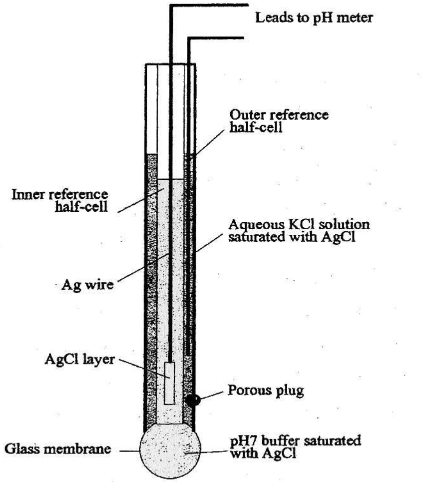


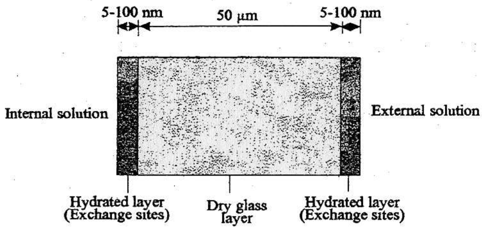
- **electrolyte = saturated KCl solution (3.8mol/l at 25°C) Þ [Cl$^-$] = constant Þ ref. pot. E = const.**

2.2 Electroanalytical Methods

2.2.1 Potentiometry, Potentiometric Titration

pH measurement with the glass electrode

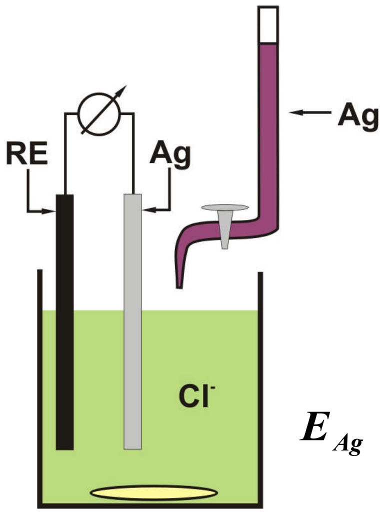




$Ag/AgCl/KCl_{sat}/H^+_{in}/H^+_{out}/KCl_{sat}/AgCl/Ag$

$$E = \Delta\varphi_{As} + \Delta\varphi_{Diff} + \frac{RT}{F}\ln 10 \cdot (pH_{in} - pH_{out})$$

Cl⁻ determination with a silver electrode

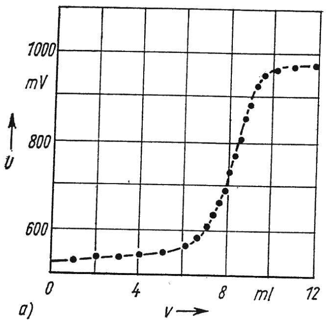


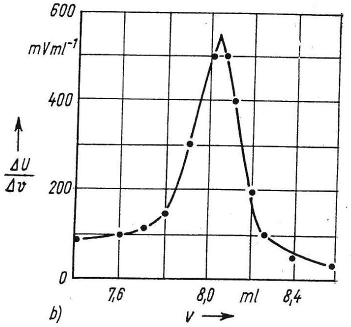
$Ag^+ + Cl^- \rightleftharpoons AgCl_{(s)}$

$K_L = 1.8 \cdot 10^{-10} mol^2/l^2$

$$E_{Ag} = E^0_{Ag/Ag^+} - \frac{2.303RT}{1 \cdot F}\log\frac{1}{a_{Ag^+}}$$

$$E_{Ag} = E^0_{Ag/Ag^+} + 0.059\log K_L - 0.059\log[Cl^-]$$





2.2 Electroanalytical Methods

2.2.2 Polarography

- measurement of current – voltage curves (voltametry) gives information of the chemical composition and the concentration of the analytes in the sample (working range $1 \times 10^{-6} < c_A < 1 \times 10^{-3}$ mol/l)
- polarography was invented in 1922 by Jaroslav Heyrovsky (Nobelprice 1959)
- a polarographic cell contains:

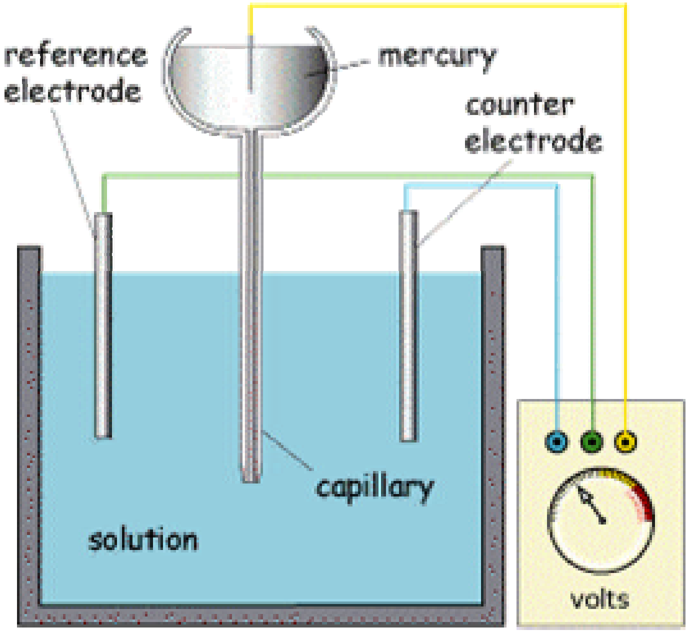
  a polarizable working electrode
  (dropping mercury electrode)

  a non-polarizable counter electrode
  (e.g. Pt wire)

  a reference electrode
  (e.g. calomel electrode)

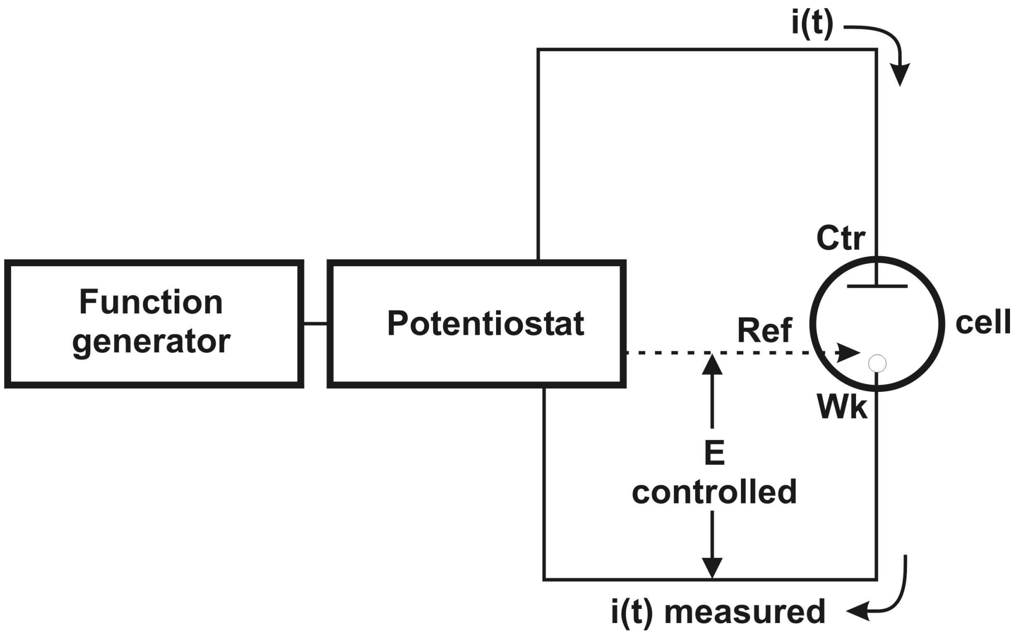
  a supporting electrolyte
  (e.g. Li^+ Cl^- in H_2O)

electrode arrangement for polarographic measurements



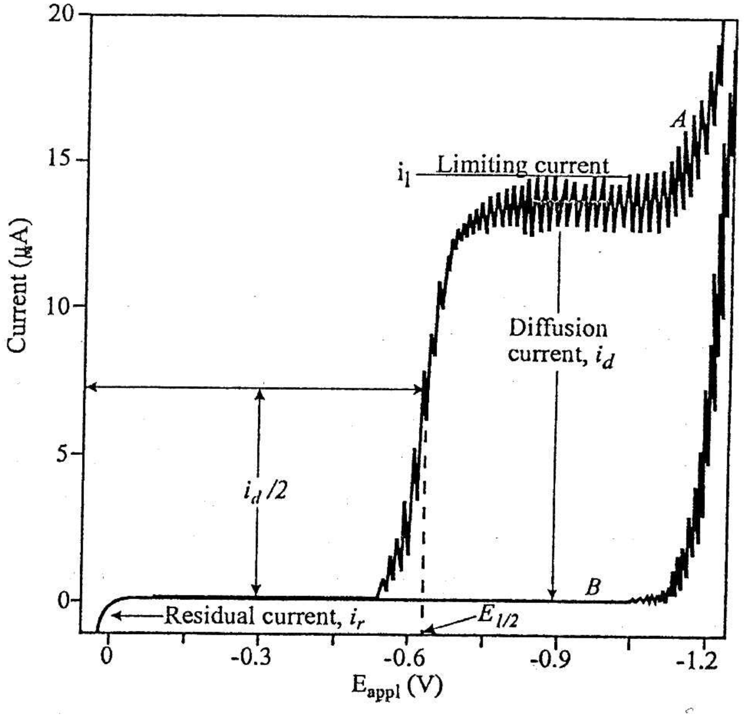
2.2 Electroanalytical Methods

2.2.2 Polarography



- half step potential ($E_{1/2}$) charcteristic for the analyte
- hight of the step ($i_d/2$) proportional to the concentration of the analyte
- working potential range $-2.2V < E_{appl} < 0.3V$
- applicable to reducible or oxidizable metal ions or organic compounds

example: Cd determination

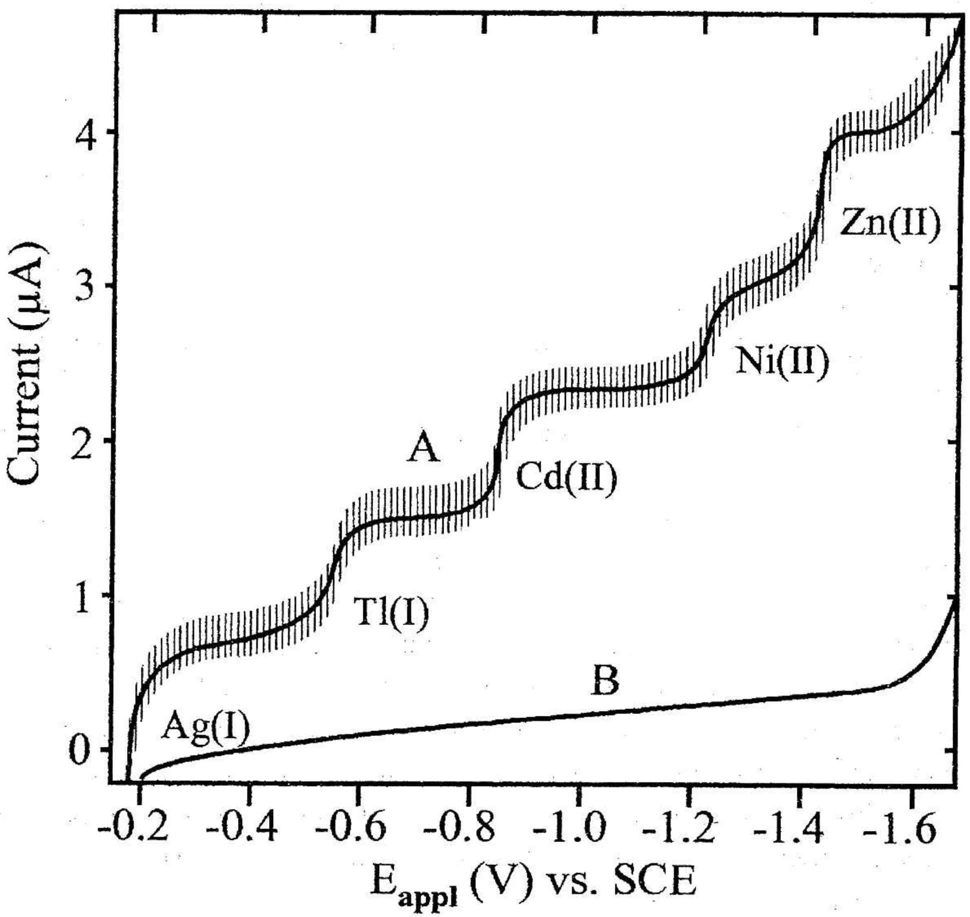


A: 5×10^{-4} mol Cd^{2+} in 1 mol/l HCl as supporting electrolyte

B: pure supporting electrolyte

2.2.2 Polarography

polarographic oligo-element determination



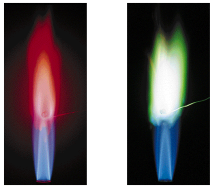
A: 1×10^{-4} mol/l Ag^+, Tl^+, Cd^{2+}, Ni^{2+}, Zn^{2+} in 1 mol/l NH_3 and 1 mol/l NH_4Cl supporting electrolyte

B: pure supporting electrolyte

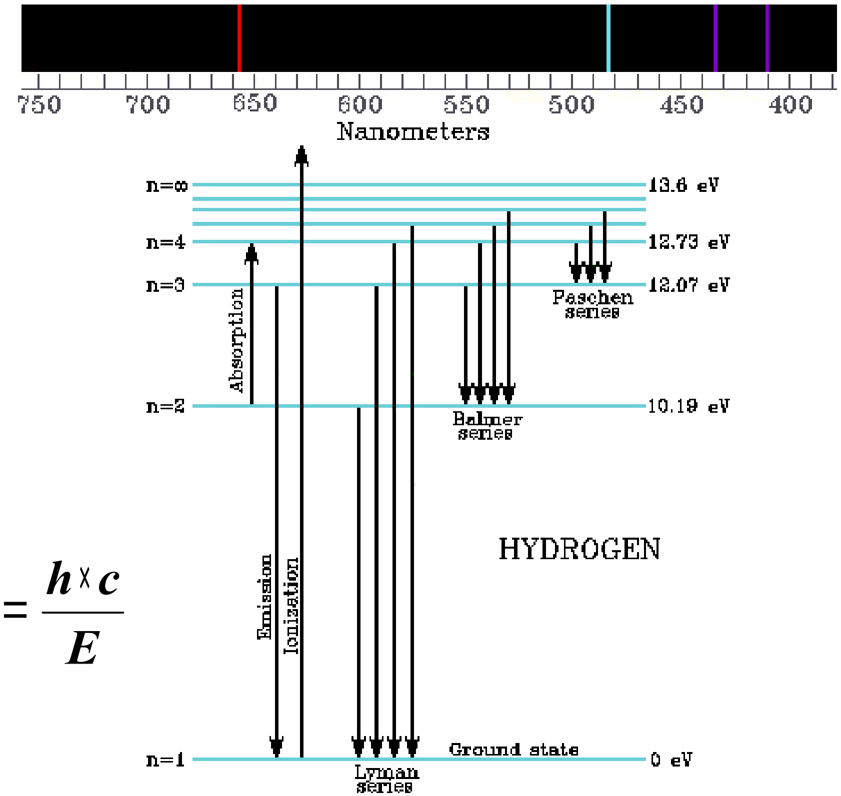
2.3 Spectroscopic Methods

2.3.1 Atomic Emission Spectroscopy

- history: one of the oldest methods for elemental analysis (flame emission - Bunsen, Kirchhoff 1860)
- principle: recording of line spectra emitted by excited atoms or ions during radiative de-excitation (valence electrons)



optical transitions and emission spectrum of H



$$\lambda = \frac{h\cdot c}{E}$$

intensity of an emission line

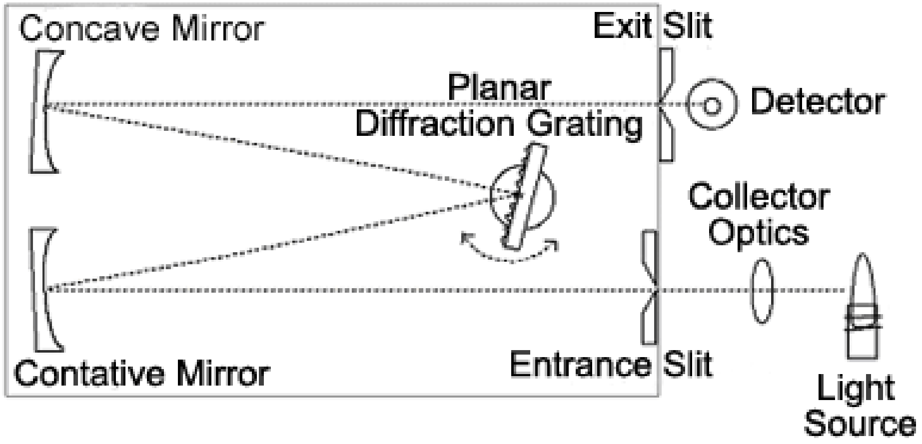
$$I = \Phi\left(\frac{h\cdot c\cdot g_m\cdot A\cdot N}{4\pi\cdot\lambda\cdot Z}\right)\cdot\exp\left(\frac{-E_m}{kT}\right)$$

- intensity of a spectral line ~N, i.e. ~C
- population of excited states requires high temperatures (typical 2000 K-7000 K)
- relative method, calibration required

2.3 Spectroscopic Methods

2.3.1 Atomic Emission Spectroscopy

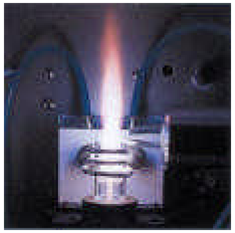
instrumentation



radiation sources (classification)

inductively coupled plasma (ICP)
flame

liquid samples



spark
arc
glow discharge
laser

solid samples

analytical performance

- multielement method (with arc 60-70 elements)
- presiscion: £ 1% RSD for spark, flame and plasma; arc 5-10% RSD
- decision limits: 0.1-1 ppm with arc, 1-10ppm with spark, 1ppb-10ppm with flame, 10ppt-5ppb for ICP

application:

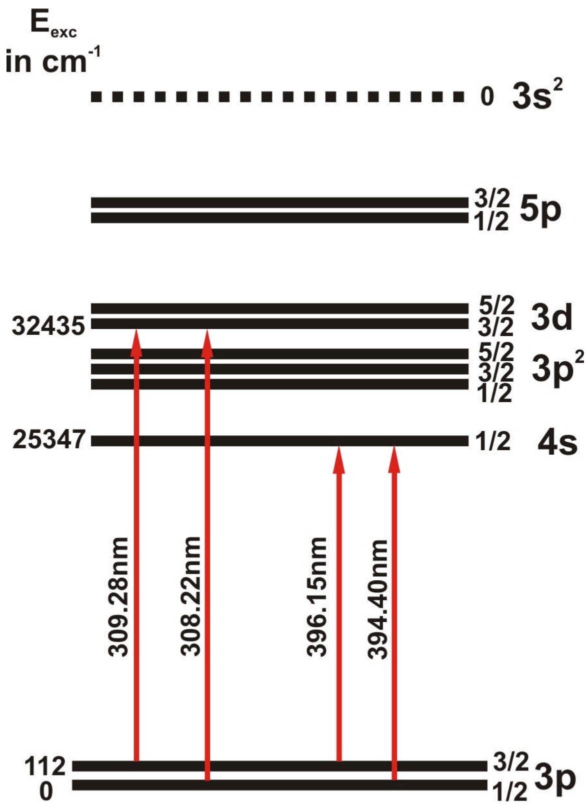
- flame AES – low cost system for alkali and earth alkaline metals
- ICP AES – suited for any sample that can be brought into solution
- arc AES – with photographic plate for qualitative overview analysis
- spark AES – unsurpassable for metal analysis (steel, alloys)
- laser ablation – for direct analysis of solids (transient signals)

2.3 Spectroscopic Methods

2.3.2 Atomic Absorption Spectroscopy

- **principle: measurement of the absorption of light by free atoms in their electronic ground state**

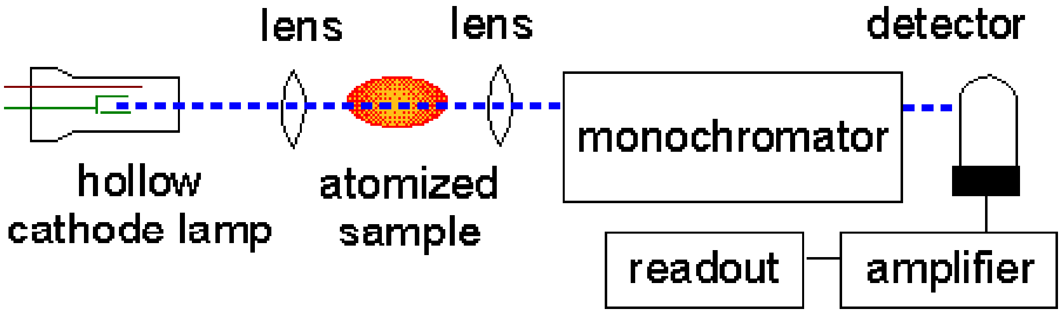
ground and excited states of Al and optical transitions used for AAS



linear relation between absorbance and concentration

$$A_{abs} = \log\left(\frac{I_0}{I}\right) = 0.434 \cdot A \cdot \frac{g_m}{g_0} \cdot \frac{\lambda^4}{8\pi c} \cdot \frac{1}{\Delta\lambda_{eff}} \cdot n_0 \cdot l$$

AAS instrumentation



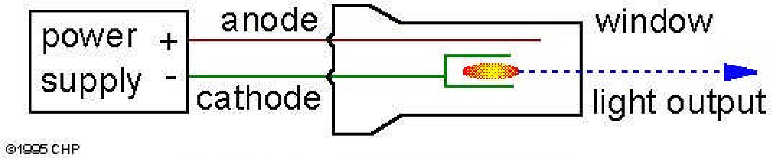
2.3 Spectroscopic Methods

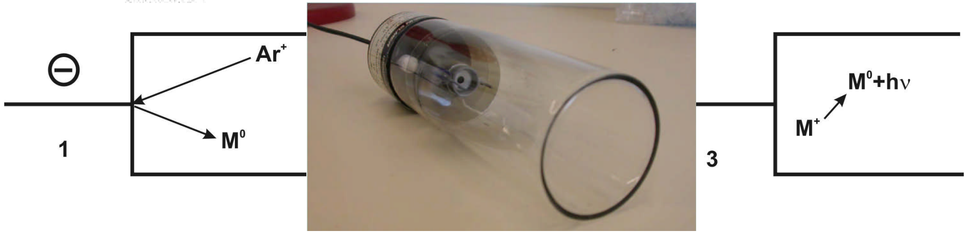
2.3.2 Atomic Absorption Spectroscopy

radiation source

- atomic absorption lines are very small (Dl£0.005nm) Þ narrow excitation lines required
- hollow cathode lamp filled with Ar (~5 Torr) Þ discharge in cathode cup
- cup-shaped cathode made from the element to be determined Þ emission of sharp de-excitation lines

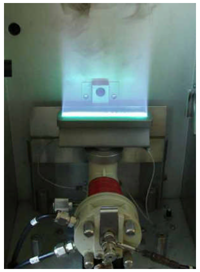
working principle of hollow cathode lamps





source of free atoms

flame



- pneumatic nebulization of the liquid sample into the flame or hydrid generation (e.g. for As, Bi, Ge)
- air/C_2H_2 for nonrefractory elements (e.g. Ca, Cr, Fe)
- N_2O/C_2H_2 for refractory elements (e.g. Al, Si, Ta)

graphite furnace

- electrically heated graphite tube (T_{max}=3000°C, under Ar)
- T vs. t program Þ drying, ashing, atomization, cleaning
- transient signals
- liquid and solid samples

2.3 Spectroscopic Methods

2.3.2 Atomic Absorption Spectroscopy

interferences in atomic absorption spectroscopy

- flame and furnace AAS are sensitive to matrix interferences Þ i.e. matrix constituents (anything but the analyte) influence the analyte signal
- there are two types of interferences Þ chemical and spectral interferences

chemical interferences

- limited temperature of the flame does not ensure full dissociation and atomization of thermally stable compounds (e.g. Ca phosphates) Þ hotter N_2O flame (La buffer)
- large amounts of easily ionized elements (alkali metals) modifies the equilibrium between atoms and ions Þ adding excess of Cs
- loss of volatile analyte species during the ashing process in GF-AAS (e.g. $ZnCl_2$) Þ adding of matrix modifiers

NH_4NO_3 + NaCl ® NH_4Cl + $NaNO_3$

spectral interferences

- two spectral lines overlap within the band pass of the dispersive element (e.g. $\mathrm{D l}_d$ » 0.1nm, Cd 228.802nm and As 228.812nm) Þ select another line
- nonspecific absorptions from solid or liquid particles in the atomizer (e.g. light scatterring by liquid or solid NaCl particles)
- emission of molecular bands by molecules and radicals present in the atomizer
  (metal halides from 200 - 400nm)
- background correction necessary

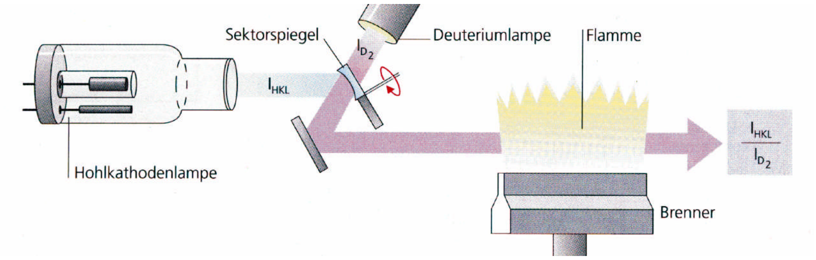
2.3 Spectroscopic Methods

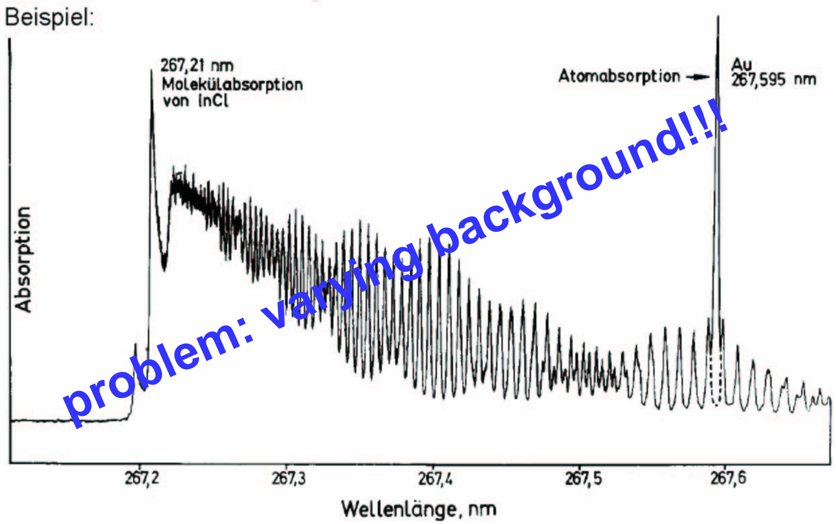
2.3.2 Atomic Absorption Spectroscopy

deuterium background correction

- deuterium lamp emits a continuous spectrum in the range 200-380nm
- alternating measurement of deuterium and hollow cathode lamp absorption

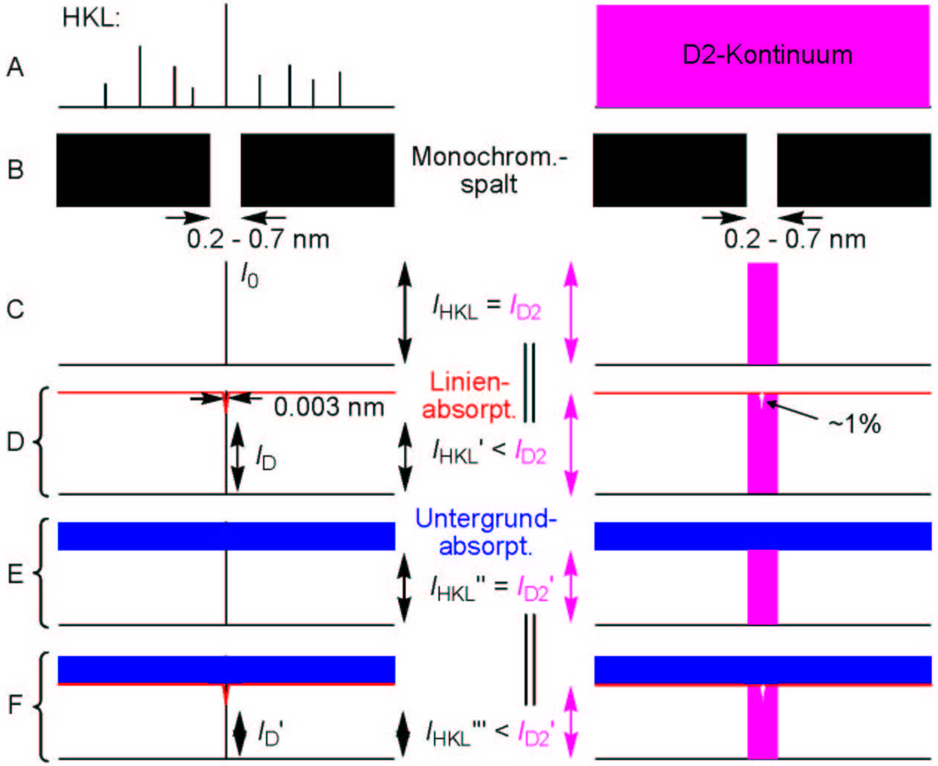
setup sketch





problem: varying background!!!

working principle



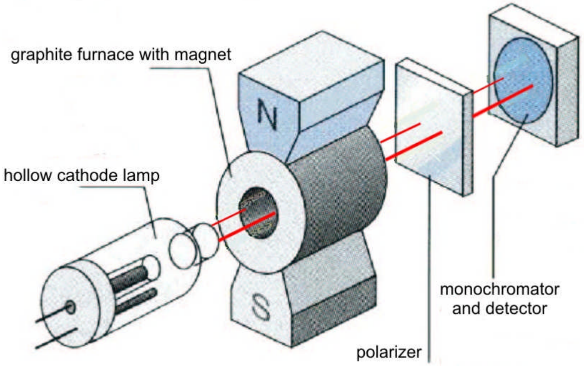
2.3 Spectroscopic Methods

2.3.2 Atomic Absorption Spectroscopy

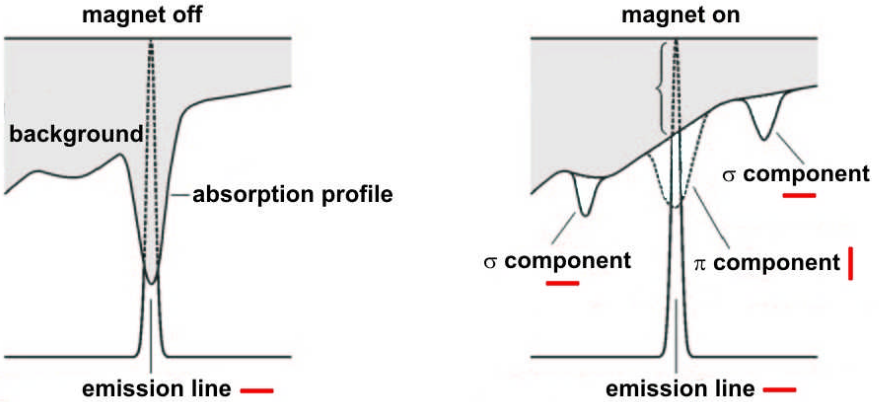
Zeeman background correction

- Zeeman effect: splitting of atomic energy levels in a magnetic field
- applied in AAS for correction of strong varying backgrounds

setup sketch

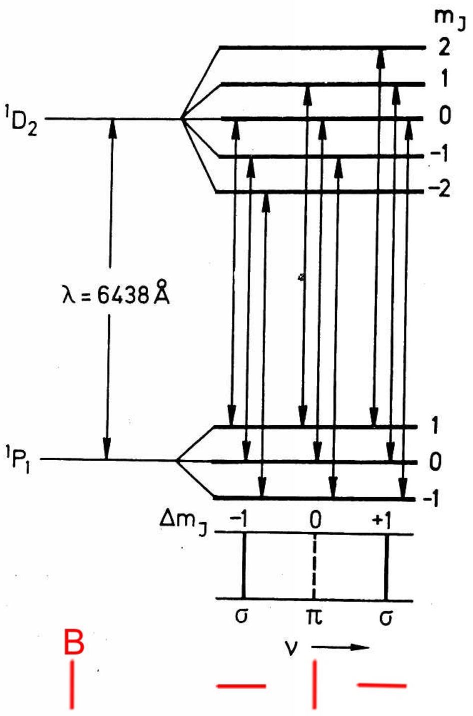


working principle



normal Zeeman effect (S=0)

(e.g. Cd atoms)



2.3 Spectroscopic Methods

2.3.2 Atomic Absorption Spectroscopy

analytical performance

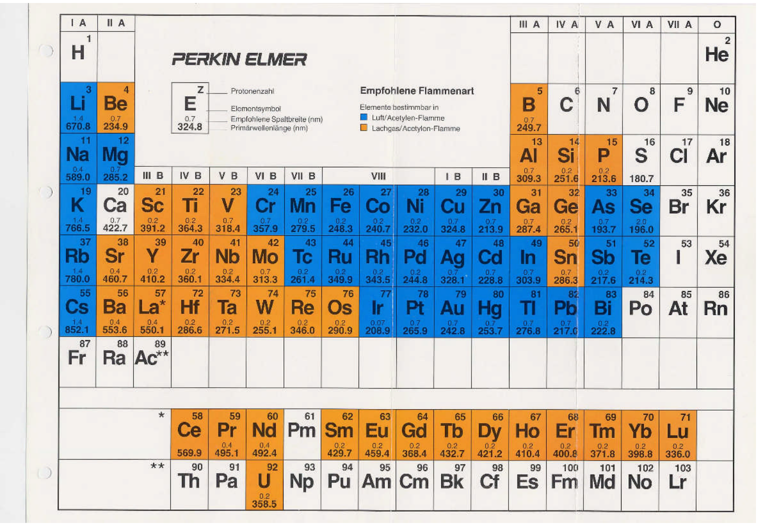
- ➢ AAS is most popular among the instrumental methods for elemental analysis

flame-AAS:

- 👍 relatively good limits decision limits (ng/ml)
- 👍 working range mg/l (liner range)
- 👍 easy to use, stable, comparably cheap
- 👍 few and well known spectral interferences
- 👎 single element method (up to 6 in parallel)
- 👎 high sample consumption

graphite furnace – AAS:

- 👍 superior decision limits (pg/ml) (trace and ultra-trace analysis)
- 👍 very low sample consumption
- 👍 analysis of solids and liquids
- 👍 analyte matrix separation possible
- 👎 demanding operation



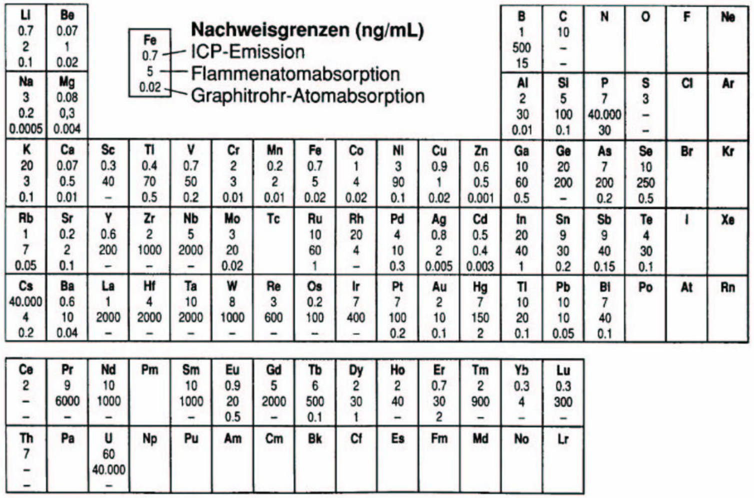
PERKIN ELMER

Z — Protonenzahl
E — Elementsymbol
0.7 — Empfohlene Spaltbreite (nm)
324.8 — Primärwellenlänge (nm)

Empfohlene Flammenart

Elemente bestimmbar in
🟦 Luft/Acetylen-Flamme
🟧 Lachgas/Acetylen-Flamme

I A	II A	III B	IV B	V B	VI B	VII B	VIII			I B	II B	III A	IV A	V A	VI A	VII A	O
1 H																	2 He
3 Li 🟦 1.4 670.8	4 Be 🟧 0.7 234.9											5 B 🟧 0.7 249.7	6 C	7 N	8 O	9 F	10 Ne
11 Na 🟦 0.4 589.0	12 Mg 🟦 0.7 285.2											13 Al 🟧 0.7 309.3	14 Si 🟧 0.2 251.6	15 P 🟧 0.2 213.6	16 S 180.7	17 Cl	18 Ar
19 K 🟦 1.4 766.5	20 Ca 0.7 422.7	21 Sc 🟧 0.2 391.2	22 Ti 🟧 0.2 364.3	23 V 🟧 0.7 318.4	24 Cr 🟦 0.7 357.9	25 Mn 🟦 0.2 279.5	26 Fe 🟦 0.2 248.3	27 Co 🟦 0.2 240.7	28 Ni 🟦 0.2 232.0	29 Cu 🟦 0.7 324.8	30 Zn 🟦 0.7 213.9	31 Ga 🟧 0.7 287.4	32 Ge 🟧 0.2 265.1	33 As 🟦 0.7 193.7	34 Se 🟦 2.0 196.0	35 Br	36 Kr
37 Rb 🟦 1.4 780.0	38 Sr 🟧 0.4 460.7	39 Y 🟧 0.2 410.2	40 Zr 🟧 0.2 360.1	41 Nb 🟧 0.2 334.4	42 Mo 🟧 0.7 313.3	43 Tc 🟦 0.2 261.4	44 Ru 🟦 0.2 349.9	45 Rh 🟦 0.2 343.5	46 Pd 🟦 0.2 244.8	47 Ag 🟦 0.7 328.1	48 Cd 🟦 0.7 228.8	49 In 🟦 0.7 303.9	50 Sn 🟧 0.7 286.3	51 Sb 🟦 0.2 217.6	52 Te 🟦 0.2 214.3	53 I	54 Xe
55 Cs 🟦 1.4 852.1	56 Ba 🟧 0.4 553.6	57 La* 🟧 0.4 550.1	72 Hf 🟧 0.2 286.6	73 Ta 🟧 0.2 271.5	74 W 🟧 0.2 255.1	75 Re 🟧 0.2 346.0	76 Os 🟧 0.2 290.9	77 Ir 🟦 0.07 208.9	78 Pt 🟦 0.7 265.9	79 Au 🟦 0.7 242.8	80 Hg 🟦 0.7 253.7	81 Tl 🟦 0.7 276.8	82 Pb 🟦 0.7 217.0	83 Bi 🟦 0.2 222.8	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac**															
		*	58 Ce 🟧 569.9	59 Pr 🟧 0.4 495.1	60 Nd 🟧 0.4 492.4	61 Pm	62 Sm 🟧 0.2 429.7	63 Eu 🟧 0.2 459.4	64 Gd 🟧 0.2 368.4	65 Tb 🟧 0.2 432.7	66 Dy 🟧 0.2 421.2	67 Ho 🟧 0.2 410.4	68 Er 🟧 0.2 400.8	69 Tm 🟧 0.2 371.8	70 Yb 🟧 0.2 398.8	71 Lu 🟧 0.2 336.0	
		**	90 Th	91 Pa	92 U 🟧 0.2 358.5	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	



Nachweisgrenzen (ng/mL)

Fe
0.7 — ICP-Emission
5 — Flammenatomabsorption
0.02 — Graphitrohr-Atomabsorption

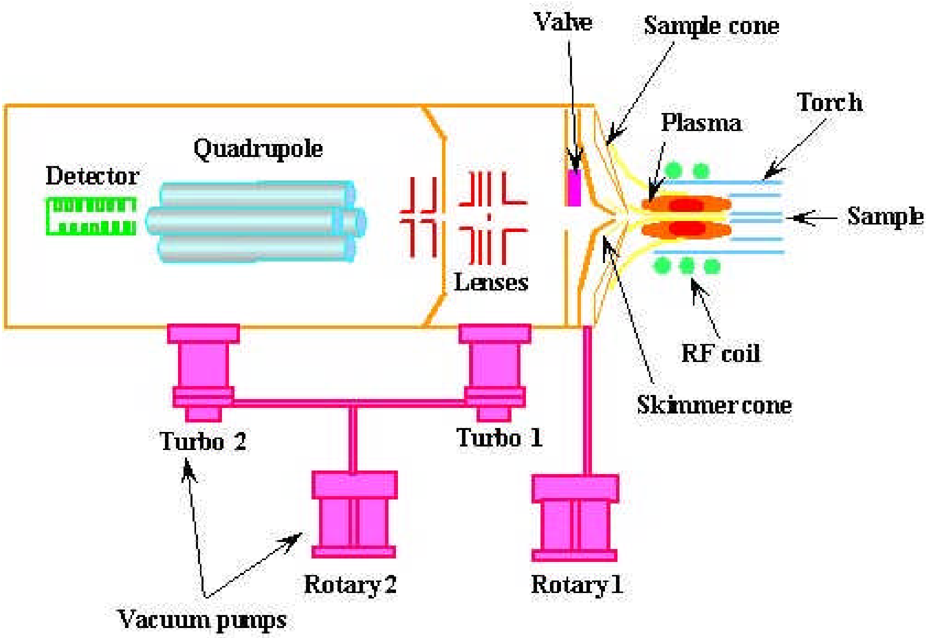
Li 0.7 2 0.1	Be 0.07 1 0.02											B 1 500 15	C 10 – –	N	O	F	Ne
Na 3 0.2 0.0005	Mg 0.08 0,3 0.004											Al 2 30 0.01	Si 5 100 0.1	P 7 40.000 30	S 3 – –	Cl	Ar
K 20 3 0.1	Ca 0.07 0.5 0.01	Sc 0.3 40 –	Ti 0.4 70 0.5	V 0.7 50 0.2	Cr 2 3 0.01	Mn 0.2 2 0.01	Fe 0.7 5 0.02	Co 1 4 0.02	Ni 3 90 0.1	Cu 0.9 1 0.02	Zn 0.6 0.5 0.001	Ga 10 60 0.5	Ge 20 200 –	As 7 200 0.2	Se 10 250 0.5	Br	Kr
Rb 1 7 0.05	Sr 0.2 2 0.1	Y 0.6 200 –	Zr 2 1000 –	Nb 5 2000 –	Mo 3 20 0.02	Tc	Ru 10 60 1	Rh 20 4 –	Pd 4 10 0.3	Ag 0.8 2 0.005	Cd 0.5 0.4 0.003	In 20 40 1	Sn 9 30 0.2	Sb 9 40 0.15	Te 4 30 0.1	I	Xe
Cs 40.000 4 0.2	Ba 0.6 10 0.04	La 1 2000 –	Hf 4 2000 –	Ta 10 2000 –	W 8 1000 –	Re 3 600 –	Os 0.2 100 –	Ir 7 400 –	Pt 7 100 0.2	Au 2 10 0.1	Hg 7 150 2	Tl 10 20 0.1	Pb 10 10 0.05	Bi 7 40 0.1	Po	At	Rn
Ce 2 – –	Pr 9 6000 –	Nd 10 1000 –	Pm	Sm 10 1000 –	Eu 0.9 20 0.5	Gd 5 2000 –	Tb 6 500 0.1	Dy 2 30 1	Ho 2 40 –	Er 0.7 30 2	Tm 2 900 –	Yb 0.3 4 –	Lu 0.3 300 –				
Th 7 – –	Pa	U 60 40.000 –	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr				

2.3 Spectroscopic Methods

2.3.3 Inductively Coupled Plasma Mass Spectrometry

- a mass spectrometer separates a stream of gaseous ions into ions with different mass to charge ratio m/z (mass range in inorganic mass spectrometry from 1 – 300 u)
- in combination with an ion source (ICP, spark, glow discharge, laser ablation) as analytical method for elemental analysis
- most popular combination Þ **I**nductively **C**oupled **P**lasma + quadrupol **M**ass **S**pectrometer = **ICP - MS**

setup scheme



sample introduction

- pneumatic nebulizer
  (liquid samples)
- electro thermal vaporization (graphite furnace)
  liquid and solid samples
- laser ablation
  solid samples

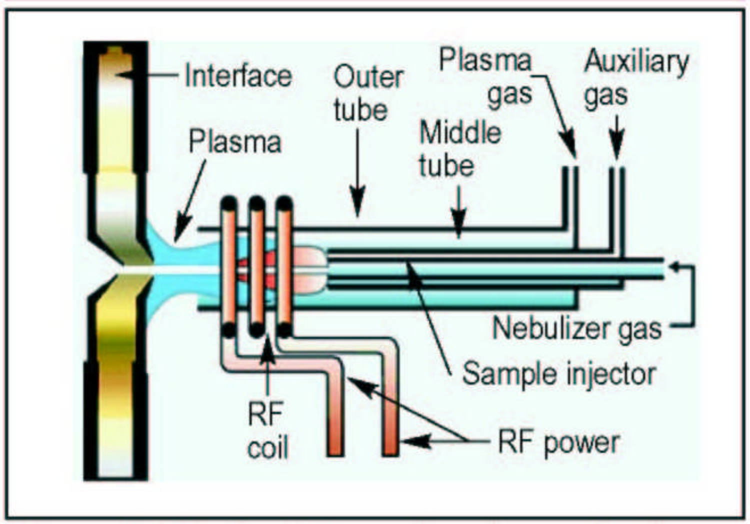
2.3 Spectroscopic Methods

2.3.3 Inductively Coupled Plasma Mass Spectrometry

ICP as ion source

- plasma generation by inductively heating of a gas (e.g. argon) using a high frequency field

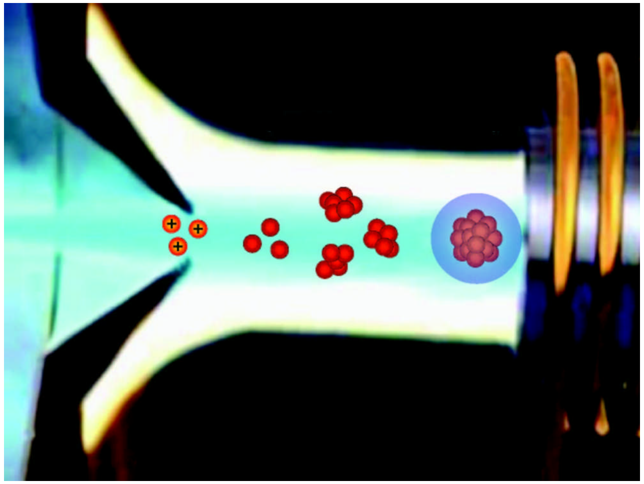
ICP assembly



- ICP works under atmospheric pressure, MS under high vacuum Þ differentially pumped interface required
- typical RF frequencies 27 or 40 MHz
- power consumption 1 – 5 kW

2.3 Spectroscopic Methods

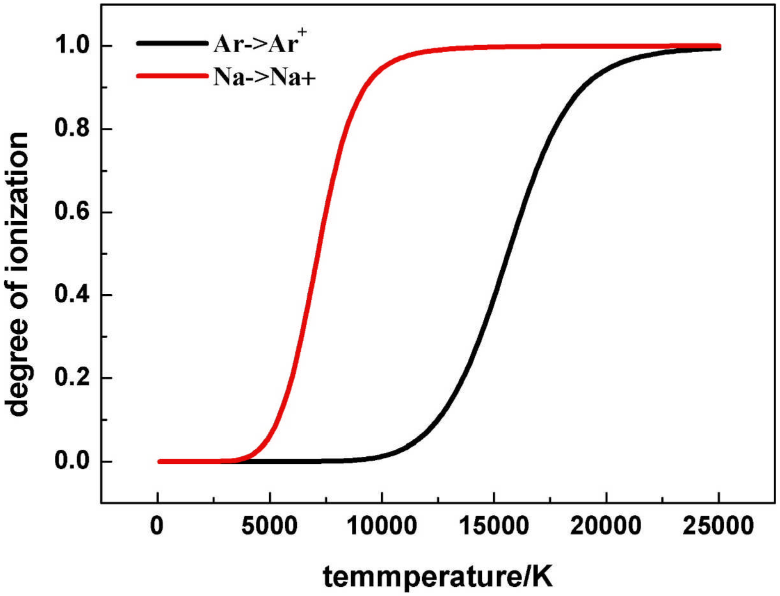
2.3.3 Inductively Coupled Plasma Mass Spectrometry



- sample droplets + carrier gas (inner tube connected to nebulizer) punch a channel through the toroidal plasma
- sample transformations in the plasma:
  desolvation → vaporization → atomization → ionization
- ionization behavior depends on the temperature ⇒ Saha equation (law of mass action for ionization equilibria)

$$\frac{\alpha_i(1+\alpha_e)}{\alpha_{i+1}\alpha_e} = pK_p^{(i+1)}(T) \qquad K_p^{(i+1)}(T) = \frac{g_i}{g_e g_{i+1}}\,\frac{\lambda_e^3}{T}\exp\left(\frac{I_{i+1}}{T}\right)$$

- example: $Ar^0\ (^1S_0) \rightarrow Ar^+\ (^2P_{3/2})$ $I_+=15.76$ eV, 1 bar
  $Na^0\ (^2S_{1/2}) \rightarrow Na^+\ (^1S_0)$ $I_+=5.14$ eV



2.3 Spectroscopic Methods

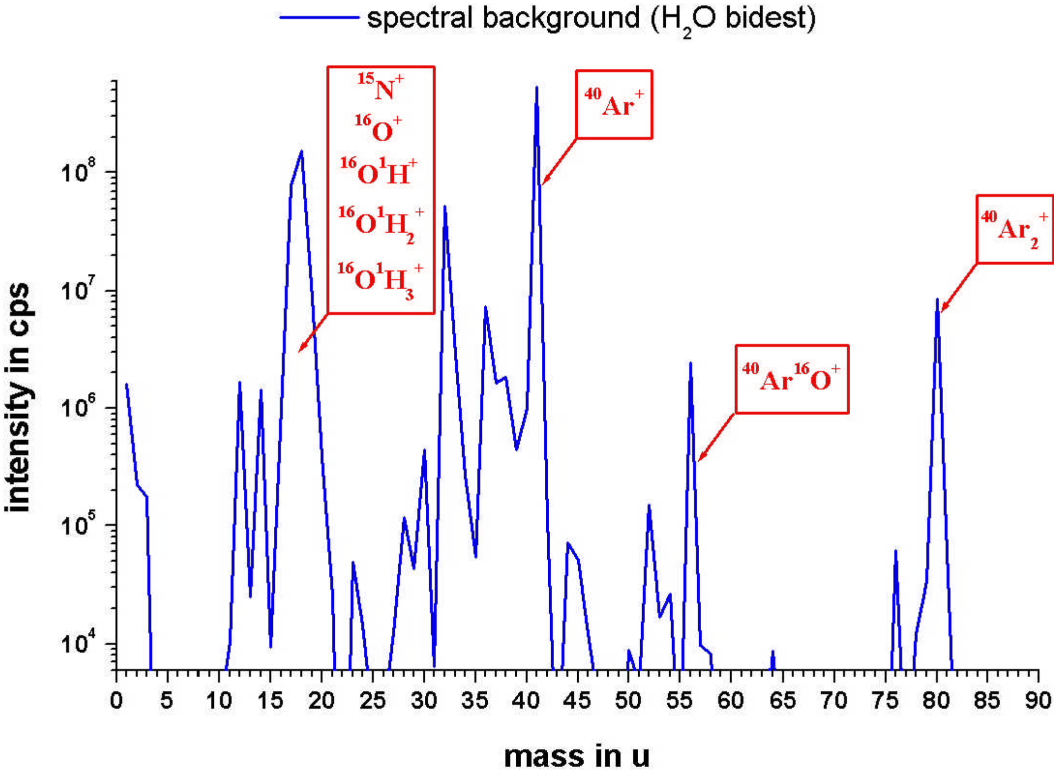
2.3.3 Inductively Coupled Plasma Mass Spectrometry

- **determination of elements Z < 80 u by ICP - MS suffers from spectral interferences caused by the plasma gas, solvent, sample matrix etc.**

types of spectral interferences

- **isobaric overlaps**
- **oxide-, hydroxide species**
- **doubly charged ions**

interference	analyte
$^{40}Ar^+$	$^{40}Ca^+$
$^{40}Ar^{16}O^+$	$^{56}Fe^+$
$^{138}Ba^{2+}$	$^{69}Ga^+$



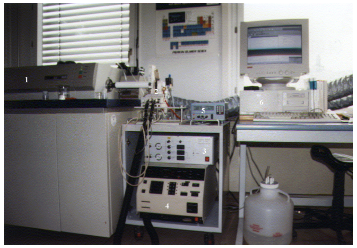
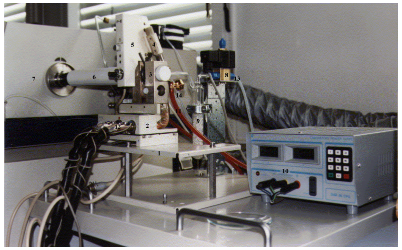
- **spectral interferences cause a high background Þ higher decision limit for disturbed analytes (e.g. x_d(Fe)»10 µg/l, x_d(Ag)»0.03 µg/l)**

2.3 Spectroscopic Methods

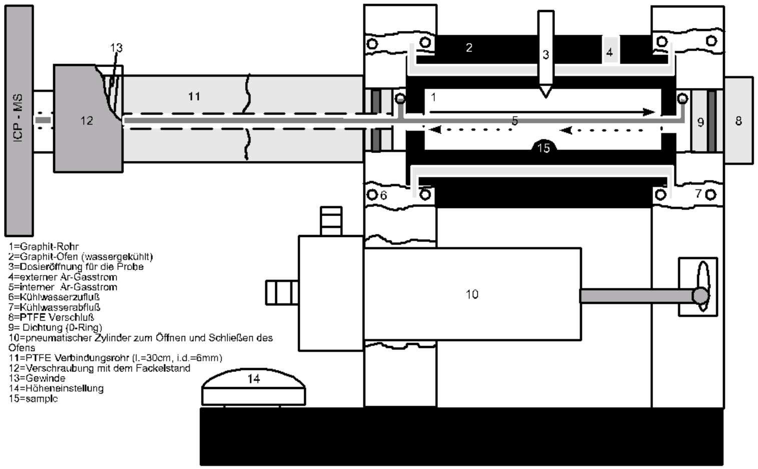
2.3.3 ETV – ICP – MS

- **analyte – matrix separation by coupling of an ElectroThermal Vaporization to the ICP-MS ® ETV-ICP-MS**

setup picture

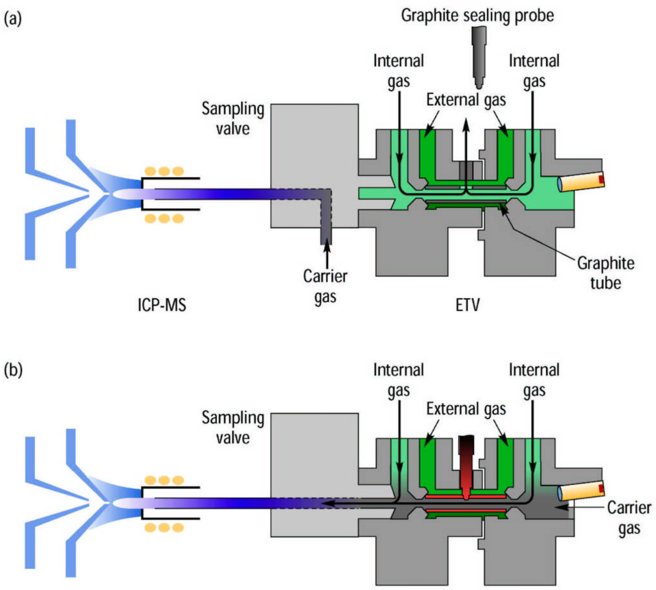



scheme of the ETV unit



1=Graphit-Rohr
2=Graphit-Ofen (wassergekühlt)
3=Dosieröffnung für die Probe
4=externer Ar-Gasstrom
5=interner Ar-Gasstrom
6=Kühlwasserzufluß
7=Kühlwasserabfluß
8=PTFE Verschluß
9= Dichtung (O-Ring)
10=pneumatischer Zylinder zum Öffnen und Schließen des Ofens
11=PTFE Verbindungsrohr (l.=30cm, i.d.=6mm)
12=Verschraubung mit dem Fackelstand
13=Gewinde
14=Höheneinstellung
15=sample

operation principle



- **quenching of the sample vapor by mixing it with cold carrier gas**

$$d_k = 4\sigma \cdot \frac{V_m}{k \cdot T \cdot \ln S} \qquad S = \frac{p}{p_{eq}(T)}$$

- **sample transport as condensed particles if the condensation nuclei exceed the critical diameter**

2.3 Spectroscopic Methods

2.3.3 ETV – ICP – MS

- **one touchstone in ICP-MS analytics is the determination of light elements in saline solutions, e.g. seawater)**
- **example: Zn determination in sea water**

relevant spectral interferences

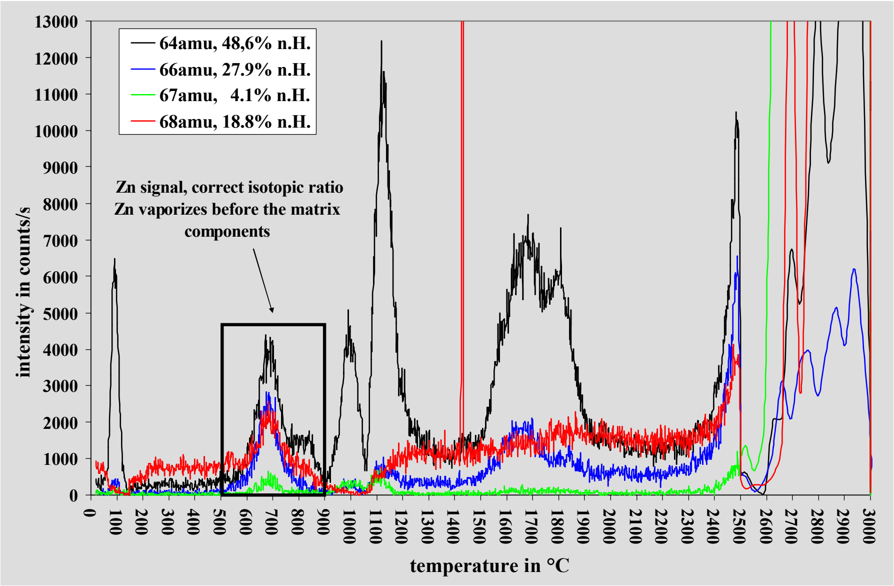
ion	64 u	66 u	67 u	68 u	concentration in seawater
Zn^{2+}	48.6% n.a.	27.9% n.a.	4.1% n.a.	18.8% n.a.	~1 ng/ml
Cl^-			$^{35}Cl^{16}O^{16}O^+$	$^{35}Cl^{16}O^{17}O^+$	ca. 16 mg/l
SO_4^{2-}	$^{32}S^{16}O^{16}O^+$ $^{32}S^{32}S^+$	$^{34}S^{16}O^{16}O^+$ $^{32}S^{34}S^+$ $^{33}S^{33}S^+$ $^{32}S^{17}O^{17}O^+$ $^{32}S^{16}O^{18}O^+$ $^{33}S^{16}O^{17}O^+$	$^{33}S^{34}S^+$ $^{32}S^{17}O^{18}O^+$ $^{33}S^{16}O^{18}O^+$ $^{33}S^{17}O^{17}O^+$ $^{34}S^{16}O^{17}O^+$	$^{36}S^{16}O^{16}O^+$ $^{32}S^{36}S^+$ $^{34}S^{17}O^{17}O^+$ $^{34}S^{16}O^{18}O^+$ $^{34}S^{34}S^+$ $^{33}S^{17}O^{18}O^+$ $^{32}S^{18}O^{18}O^+$	ca. 2 mg/l
Mg^{2+}	$^{24}Mg^{40}Ar^+$ $^{26}Mg^{38}Ar^+$	$^{26}Mg^{40}Ar^+$			ca. 1 mg/ml

2.3 Spectroscopic Methods

2.3.3 ETV – ICP – MS

- **analyte – matrix separation by ETV**
- **sample matrix can be vaporized prior the analyte or in reversed fashion**
- **application of modifiers (ETV as thermochemical reactor, cp. atomic absorption spectroscopy)**

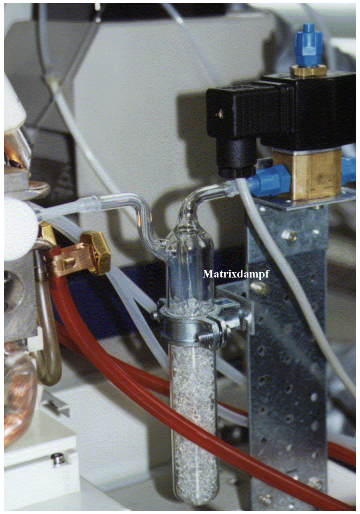
application to the Zn in seawater problem



Zn signal, correct isotopic ratio
Zn vaporizes before the matrix
components

- **resulting temperature – time program**

step	T / °C	ramp time / s	hold time / s	function
1	150	10	60	drying
2	150	0	30	baseline
3	800	1	59	Zn vaporization (prob. as $ZnCl_2$ BP=732°C)
4	2500	5	5	cleaning



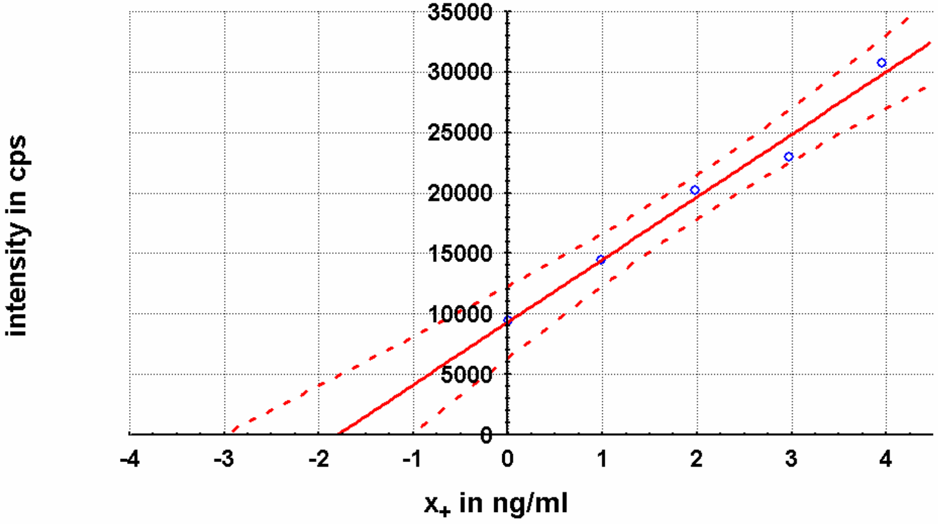
2.3 Spectroscopic Methods

2.3.3 ETV – ICP – MS

- if matrix matched calibration samples are not available Þ standard addition
- principle of the standard addition method:
  - measurement of the analysis sample
  - stepwise addition of analyte ($x_+ = x_A \ldots 4x_A$)
  - evaluation of x_A by extrapolation of the calibration function to the intercept point with the x-axis ($y = f(x_+) = 0$ Þ x_A)

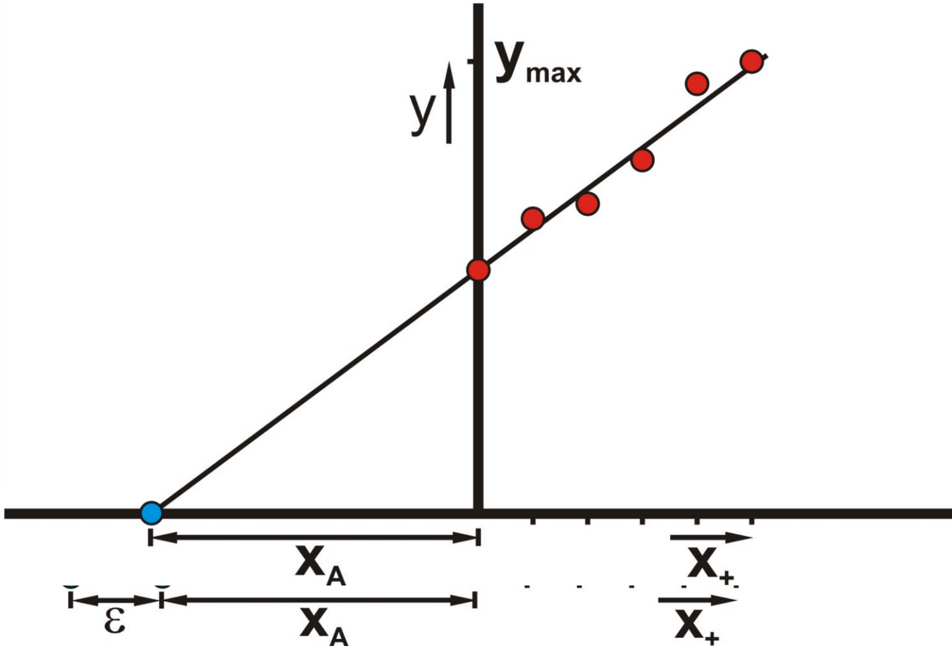
Zn in seawater by ETV-ICP-MS

standard addition



result: 1 ng/ml < C_{Zn} < 3 ng/ml

certified value: 1.24 ng/ml



2.3 Spectroscopic Methods

2.3.3 Inductively Coupled Plasma Mass Spectrometry

analytical performance of ICP-MS

- multi-element method (more than 20 analytes in parallel)
- good performance in precision (a few percent), accuracy, number of determinable elements, decision limit (depending on the instrument 0.01-100 ng/l) and sample throughput
- linear dynamic range Þ 3-5 orders of magnitude
- difficult for elements with m/z < 80 u (spectral interferences)
- mostly applied for liquid sample, ETV and laser vaporization enable direct analysis of solid samples
- supplies information about the isotopic ratio of an element
    - isotop dilution analysis for ultra-trace analysis (sub ppt range)
    - age determination of biological and geological samples
- relatively young analysis method (1980) Þ high innovative potential

Backup Slide

Specifity and Selectivity of Analytical Methods

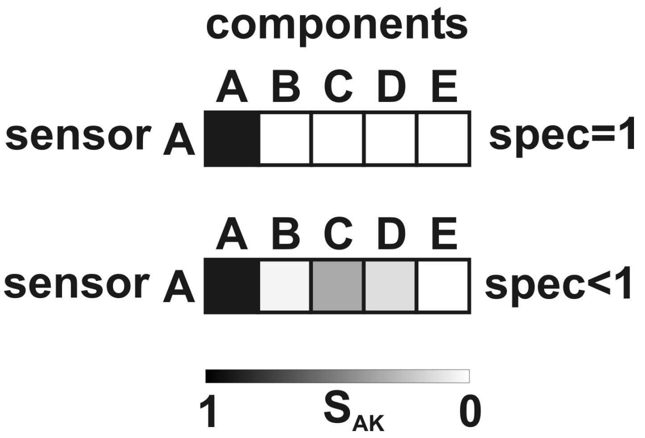
specificity…

- …describes the ability of a method to detect *1* particular analyte on *1* sensor undisturbed from all other components present in the sample
- …refers to a single component analysis
- …is based upon the concept of partial sensitivities $S_{IJ} = \frac{¶y_I}{¶x_J}$

vector of partial sensitivities

$$\underline{s}_A = \left(S_{AA} S_{AB} \ldots S_{AZ}\right)$$

$$spec\left(A / B,\ldots,Z\right) = \frac{S_{AA} \cdot x_A}{\overset{Z}{\underset{K=A}{å}} S_{AK} \cdot x_K}$$



components

	A	B	C	D	E	
sensor A	■	□	□	□	□	spec=1
sensor A	■	▨	▨	▨	□	spec<1

1 S_{AK} 0

0 £ spec(A/B,…,Z) £ 1

for practical work spec(A/B,…,Z)>0.9 sufficient

Backup Slide

Specifity and Selectivity of Analytical Methods

selectivity…

- …describes the ability of a method to determine *n* analytes on *n* sensors undisturbed and independent from each other and from other components present in the sample
- …refers to a multi-component analysis
- …is based upon the concept of partial sensitivities $S_{IJ} = \frac{\partial y_I}{\partial x}$

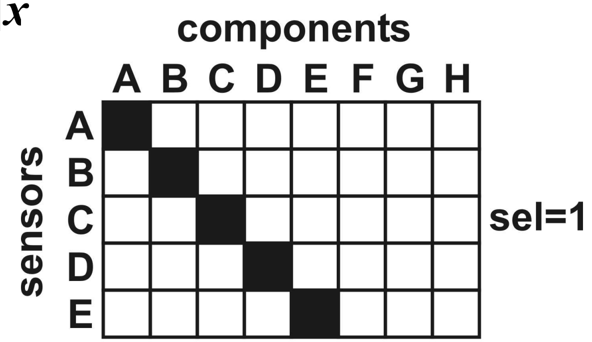
matrix of partial sensitivities

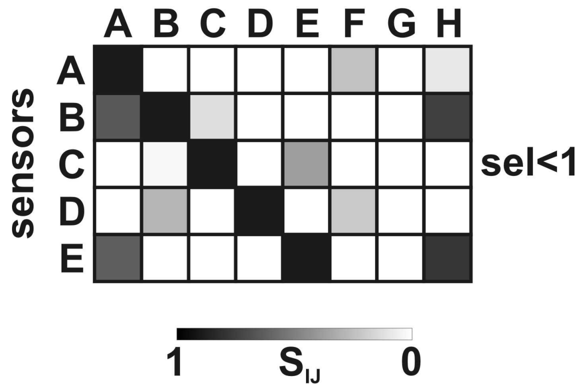
$$\underline{S} = \begin{pmatrix} S_{AA} & S_{AB} & \cdots & S_{AN} & S_{AN+1} & \cdots & S_{AZ} \\ S_{BA} & S_{BB} & \cdots & S_{BN} & S_{BN+1} & \cdots & S_{BZ} \\ \vdots & \vdots & \ddots & \vdots & \vdots & \cdots & \vdots \\ S_{NA} & S_{NB} & \cdots & S_{NN} & S_{NN+1} & \cdots & S_{NZ} \end{pmatrix}$$

$$sel(A,B,\ldots,N/N+1,\ldots,Z) = \frac{\sum_{I=A}^{N} S_{II}\cdot x_I}{\sum_{J=A}^{N}\sum_{I=A}^{Z} S_{IJ}\cdot x_I}$$

$$0 \le \mathrm{sel}(A,B,\ldots,N/N+1,\ldots,Z) \le 1$$

for practical work sel(A,B,…,N/N+1,…,Z) >0.9 sufficient





Backup Slide

Specifity and Selectivity of Analytical Methods

- application of the selectivity/specificity concept to compare PN-ICP-MS and ETV-ICP-MS for the determination of Zn in seawater

specificity matrix for the sensors (masses) 64,66,67,68 u

$$S = \begin{pmatrix} \frac{\Delta I_{64amu}}{\Delta C_{Zn^{2+}}} & \frac{\Delta I_{66amu}}{\Delta C_{Zn^{2+}}} & \frac{\Delta I_{67amu}}{\Delta C_{Zn^{2+}}} & \frac{\Delta I_{68amu}}{\Delta C_{Zn^{2+}}} \\ \frac{\Delta I_{64amu}}{\Delta C_{Cl^-}} & \frac{\Delta I_{66amu}}{\Delta C_{Cl^-}} & \frac{\Delta I_{67amu}}{\Delta C_{Cl^-}} & \frac{\Delta I_{68amu}}{\Delta C_{Cl^-}} \\ \frac{\Delta I_{64amu}}{\Delta C_{SO_4^{2-}}} & \frac{\Delta I_{66amu}}{\Delta C_{SO_4^{2-}}} & \frac{\Delta I_{67amu}}{\Delta C_{SO_4^{2-}}} & \frac{\Delta I_{68amu}}{\Delta C_{SO_4^{2-}}} \\ \frac{\Delta I_{64amu}}{\Delta C_{Mg^{2+}}} & \frac{\Delta I_{66amu}}{\Delta C_{Mg^{2+}}} & \frac{\Delta I_{67amu}}{\Delta C_{Mg^{2+}}} & \frac{\Delta I_{68amu}}{\Delta C_{Mg^{2+}}} \end{pmatrix}$$

test samples to determine S

sample	$[Zn^{2+}]$ in ng/ml	$[Cl^-]$ in mg/ml	$[SO_4^{2-}]$ in mg/ml	$[Mg^{2+}]$ in mg/ml
1	**50**	**10**	**1**	**0.5**
2	**100**	**10**	**1**	**0.5**
3	**50**	**20**	**1**	**0.5**
4	**50**	**10**	**5**	**0.5**
5	**50**	**10**	**1**	**1.5**

Backup Slide

Specifity and Selectivity of Analytical Methods

- **experimental specificity matrices after t-test (comparison of two mean values)**

$$S_{PN} = \left(\begin{array}{lcccc} & 64amu & 66amu & 67amu & 68amu \\ Zn^{2+} & 616 & 378 & 63.9 & 265 \\ Cl^{-} & 1.22 \cdot 10^{-3} & -3.48 \cdot 10^{-4} & 0 & 0 \\ SO_4^{2-} & 18.6 \cdot 10^{-3} & 0 & 0 & 0 \\ Mg^{2+} & 28.5 \cdot 10^{-3} & 14.3 \cdot 10^{-3} & 2.52 \cdot 10^{-3} & 8.97 \cdot 10^{-3} \end{array} \right) \quad S_{ETV} = \left(\begin{array}{lcccc} & 64amu & 66amu & 67amu & 68amu \\ Zn^{2+} & 5669 & 3557 & 524 & 2438 \\ Cl^{-} & -10.2 \cdot 10^{-3} & -5.67 \cdot 10^{-3} & -1.01 \cdot 10^{-3} & -4.13 \cdot 10^{-3} \\ SO_4^{2-} & 0 & -23.0 \cdot 10^{-3} & 0 & -17.3 \cdot 10^{-3} \\ Mg^{2+} & 0 & -40.4 \cdot 10^{-3} & 0 & -33.4 \cdot 10^{-3} \end{array} \right)$$

- **ETV-ICP-MS about 10 times more sensitive than PN-ICP-MS**

- **positive partial sensitivities in S_{PN} reflect spectral interferences (e.g. interference of $^{24}Mg^{40}Ar^{+}$ and $^{26}Mg^{38}Ar^{+}$ on $^{64}Zn^{+}$)**

- **negative partial sensitivities in S_{ETV} reflect non-spectral interferences**

- **influence of Cl^{-} : $Zn^{2+} + 2Cl^{-} \rightarrow ZnCl_{2(s)} \rightarrow ZnCl_{2(g)}$**
  (the less Cl^{-} in solution the less Zn^{2+} vaporizes as $ZnCl_2$) ⇒ non-spectral interference due to sample transport mechanism

- **influence of SO_4^{2-} on the drying step: $Zn^{2+} + SO_4^{2-} \rightarrow ZnSO_{4(s)}$**
  above 770°C $ZnSO_{4(s)} \rightarrow ZnO$ (mp = 1974°C) + $SO_2 + ½ O_2$
  ⇒ as the vaporization step is done at 800°C SO_4^{2-} ions cause a loss of Zn^{2+}

Backup Slide

Specifity and Selectivity of Analytical Methods

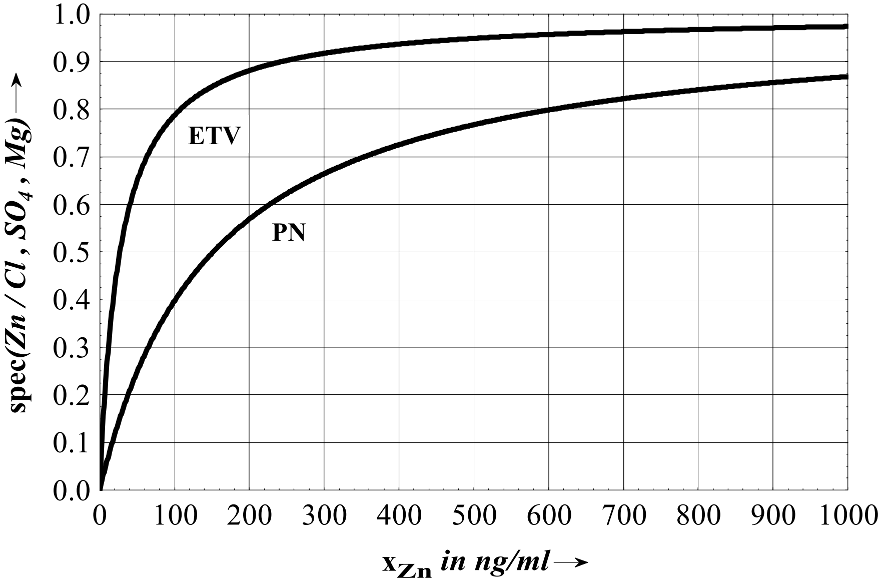
- specificities for a typical seawater sample

ion	C in ng/ml	$S_{prakt.}$ 64amu PN	$S_{prakt.}$ 66amu PN	$S_{prakt.}$ 67amu PN	$S_{prakt.}$ 68amu PN	$S_{prakt.}$ 64amu ETV	$S_{prakt.}$ 66amu ETV	$S_{prakt.}$ 67amu ETV	$S_{prakt.}$ 68amu ETV
Zn^{2+}	75	0.33	0.59	0.66	0.69	0.74	0.59	0.72	0.57
Cl^-	15×10^6								
SO_4^{2-}	2.5×10^6								
Mg^{2+}	1.0×10^6								

no external calibration (i.e. standards) possible for ng/ml concentrations

$$spec_{PN,64amu}(Zn^{2+} / Cl^-, SO_4^{2-}, Mg^{2+}) = \frac{616 \times x_{Zn^{2+}}}{616 \times x_{Zn^{2+}} + 93300}$$

$$spec_{ETV,64amu}(Zn^{2+} / Cl^-, SO_4^{2-}, Mg^{2+}) = \frac{5669 \times x_{Zn^{2+}}}{5669 \times x_{Zn^{2+}} + 153000}$$

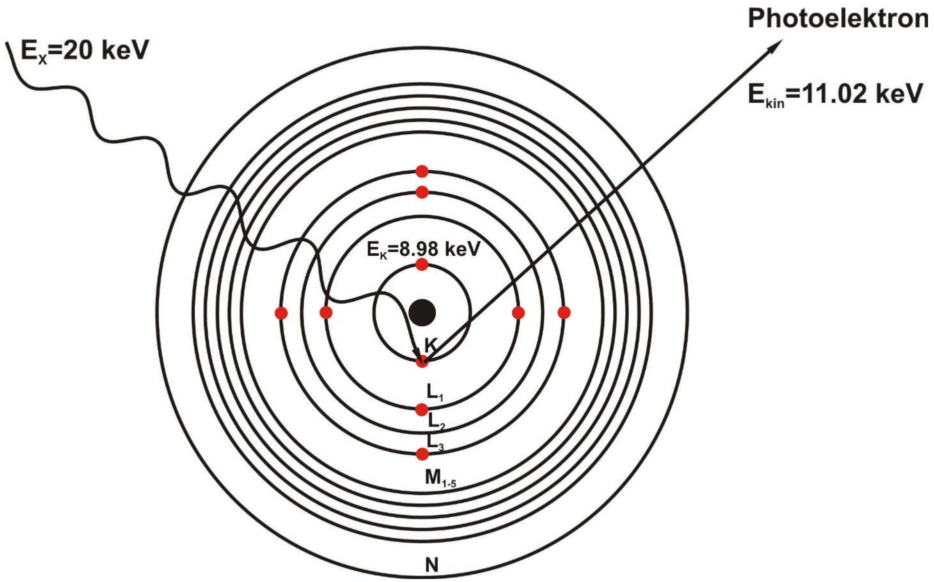


2.3 Spectroscopic Methods

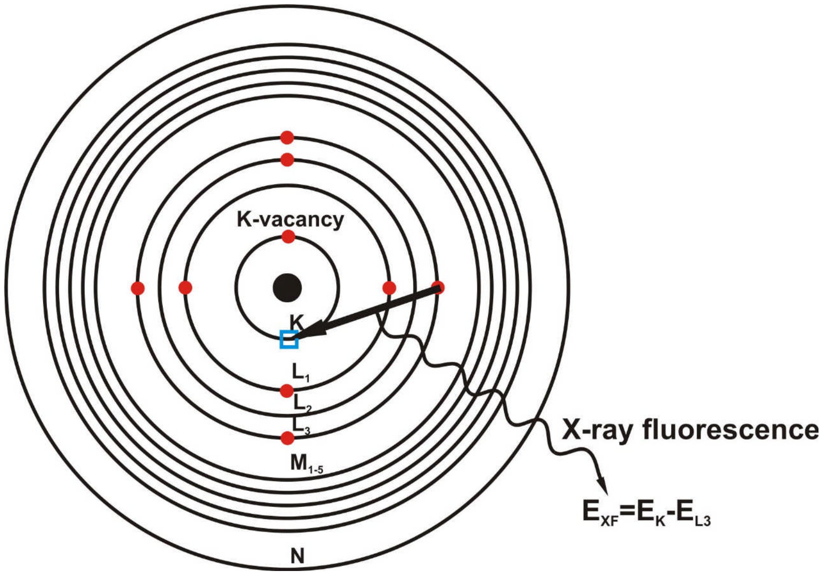
2.3.4 X-Ray Fluorescence Spectroscopy

- **instrumental analytical technique for the elemental analysis of solids and liquids**
- **wide concentration ranges (ppm - %), minimal sample preparation**
- **principle: detection of element specific X – rays (characteristic X-rays) emitted from a sample under X-ray excitation (X-ray fluorescence)**

interaction of X-rays with matter



emission of a core level electron (here from copper) by absorption of a X-ray photon



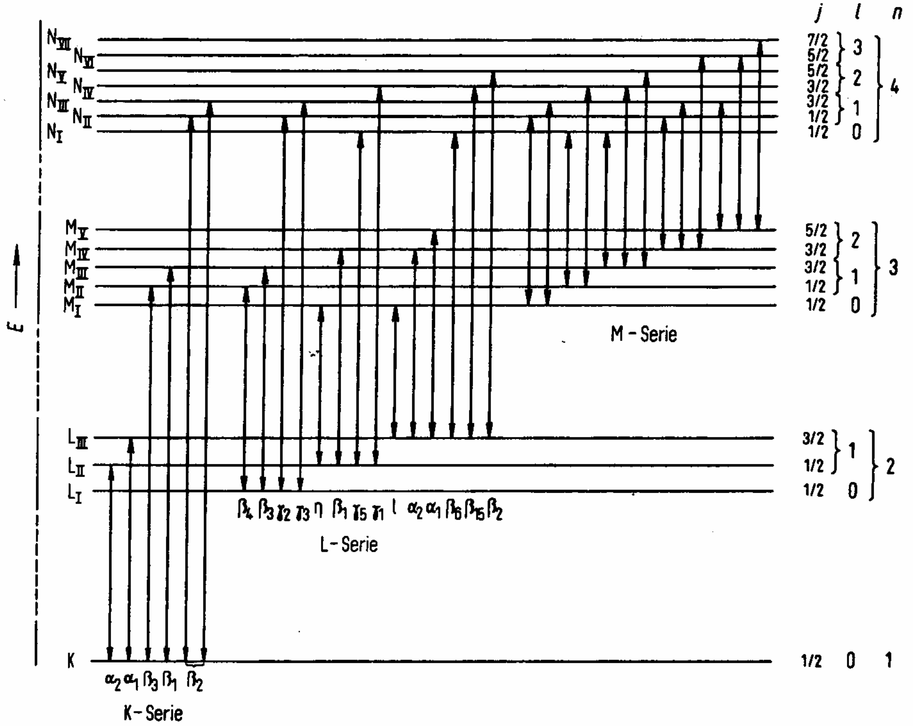
energetic relaxation by X-ray fluorescence

2.3 Spectroscopic Methods

2.3.4 X-Ray Fluorescence Spectroscopy

- **transitions are governed by quantum mechanical selection rules (Dn>1, Dl=⌖1, Dj=0,⌖1)**
- **K – lines originate from vacancies in the K – shell, L – lines from vacancies in the L – shell …**
- **denotation of lines:**
  i) IUPAC notation – Fe KL_3
  ii) Siegbahn notation – Fe a1
- **line intensities depend on:**
  i) the energetic difference of the levels (the higher the energetic difference the lower the transition probability)
  ii) the degeneracy of the levels
  iii) the fluorescence yield
- **K – lines best suited for analysis of elements Z < 45 (Rh) (mostly K-$L_{3,2}$)**
- **L – lines for analysis of elements Z > 45 (mostly L_3-$M_{5,4}$)**

atomic energy levels and allowed transitions

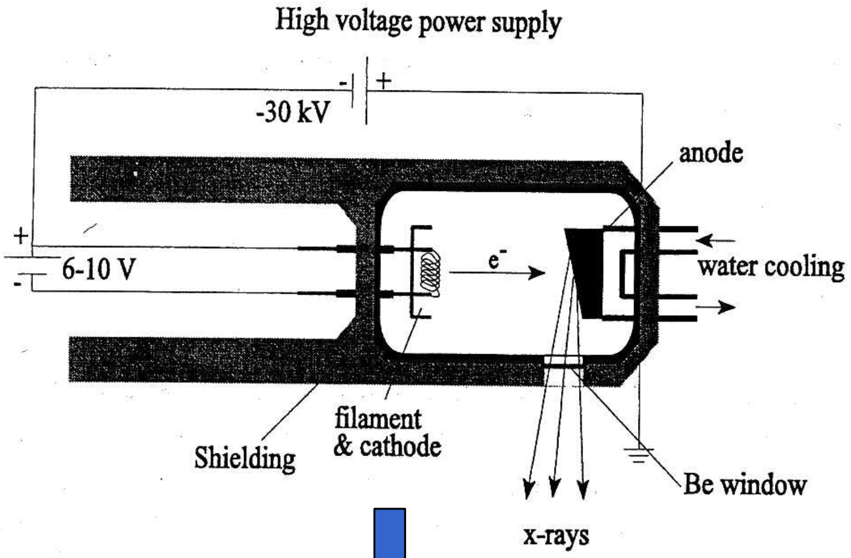


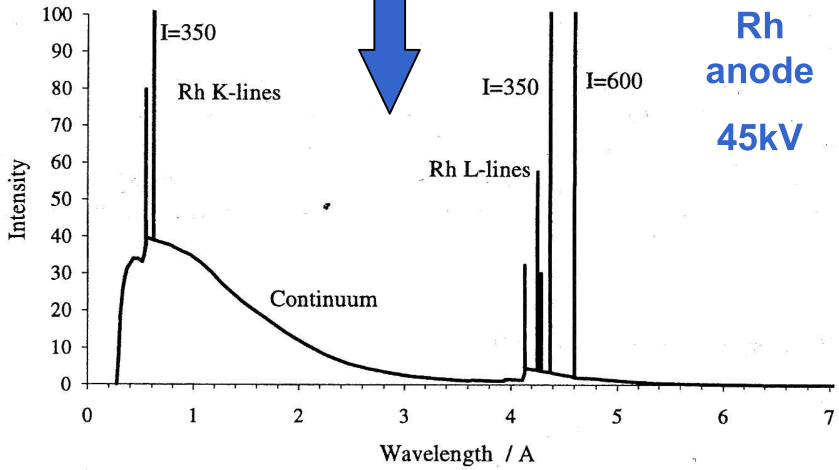
2.3 Spectroscopic Methods

2.3.4 X-Ray Fluorescence Spectroscopy

instrumentation – X-ray source

- **generation of X-rays by collision of high energetic electrons with a pure metal target (Rh, Mo, Cr, Ag, W)**
- **continuous X-rays by decelerating collisions with the target atoms (Bremsstrahlung)**
- **characteristic X-rays by refilling of core level vacancies in the target atoms created by the impinging electrons**
- **the short wavelength limit of the source depends on the accelerating voltage, the long wavelength tail depends on the Be-window thickness**
- **only ~1% of the electric power is converted to X-rays, rest is heat Þ effective water or air cooling required**
- **quantitative work Þ stable filament heating and accelerating voltage required**





Rh anode

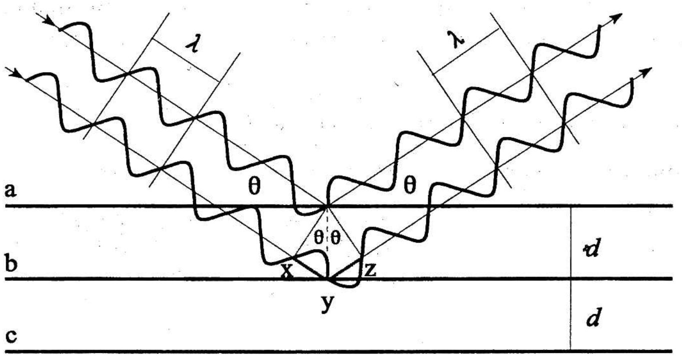
45kV

2.3 Spectroscopic Methods

2.3.4 X-Ray Fluorescence Spectroscopy

instrumentation – wavelength dispersive instruments

- irradiated sample emits polychromatic X-rays

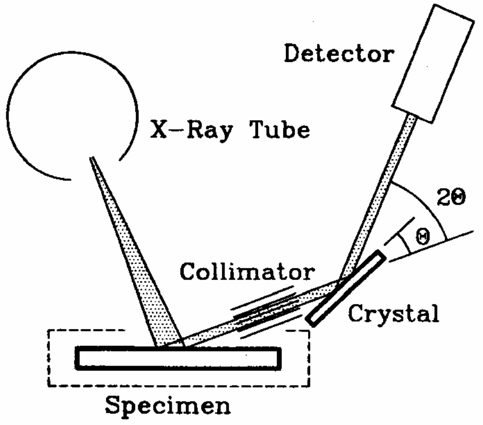


- crystal as dispersive element
- wavelength selection according to Bragg's law

$$n \cdot \lambda = 2 \cdot d \cdot \sin\theta$$

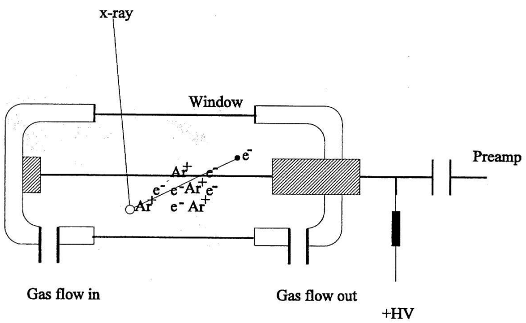
- wavelength scan by varying $\theta \Rightarrow$ rotation of the crystal with respect to the incoming beam

geometric arrangement

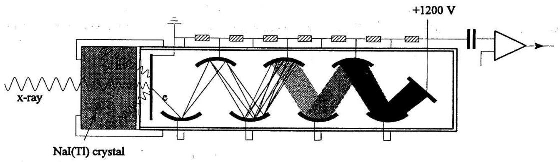


detector

flow proportional counter for low energetic X-rays



scintillation counter for high energetic X-rays

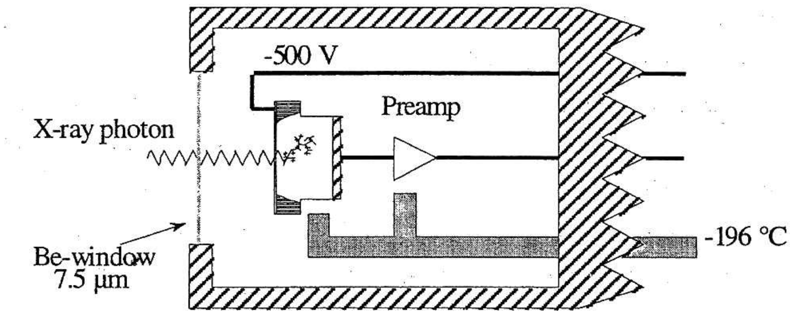


2.3 Spectroscopic Methods

2.3.4 X-Ray Fluorescence Spectroscopy

instrumentation – energy dispersive instruments

- energy dispersion and X-ray photon counting in one step
- detector Þ semiconductor crystal (Si(Li), hyperpure Ge) at liquid nitrogen temperature (-196°C)



- incoming X-ray photons create electron hole pairs Þ current Þ voltage pulse
- the number of electron – hole pairs is proportional to the energy
- best suited for energies > 2 keV

example

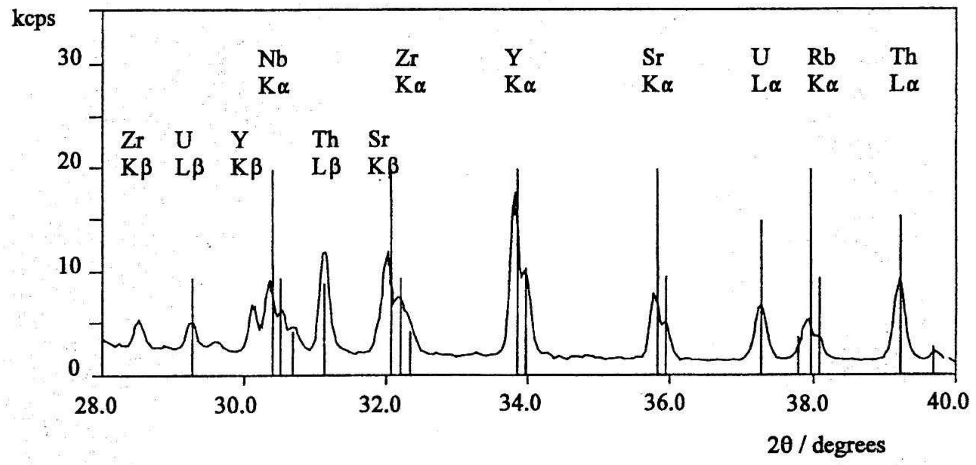
- an Fe K-L3,2 X-ray photon (E=6.400keV) hits a Si detector
- energy to create 1 electron – hole pair = 3.85eV Þ creation of 1662 ehp's
- the preamplifier converts this current in voltage pulse of e.g. 32mV
- a connected ADC translates the amplified pulse height into a digital number, e.g. 320 Þ channel 320 in a memory is increased by 1
- common memories employ 1024 or 2048 channels (0-20 keV and 0 – 40 keV respectively) Þ resolution ~20 eV

2.3 Spectroscopic Methods

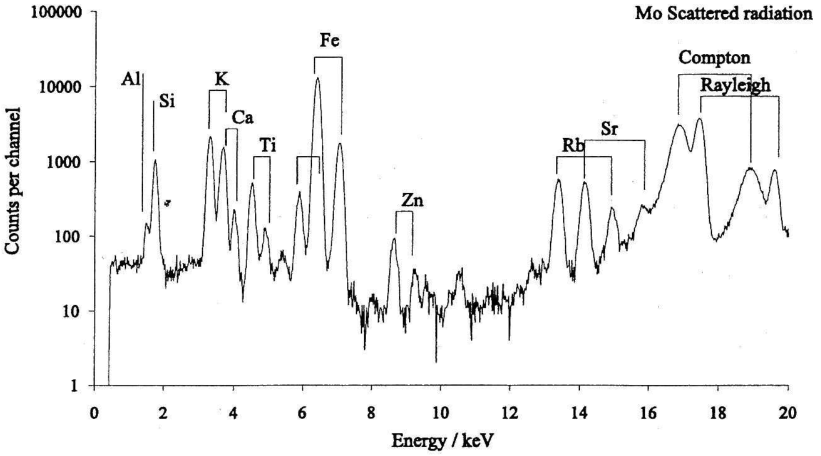
2.3.4 X-Ray Fluorescence Spectroscopy

- application of XRF: qualitative and quantitative analysis of elements with Z ³ 9 (F)
  Þ multi-element method
- relatively simple sample preparation
  (bulk solids, pressed powder pellets, fused discs, liquids)
- information depth in the µm range Þ homogeneous and smoothed surface required
- qualitative analysis by recording the entire fluorescence spectrum Þ software assisted element identification by assigning the element specific K,L,M – lines

qualitative analysis by XRF



WD-XRF



ED-XRF

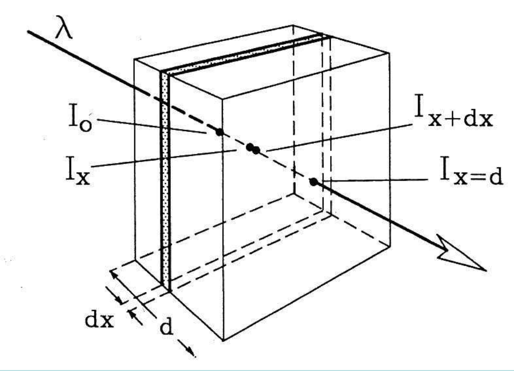
2.3 Spectroscopic Methods

2.3.4 X-Ray Fluorescence Spectroscopy

- quantitative analysis requires relation between line intensity and element concentration
- 2 step process: i) determination of the net peak intensity (background subtraction)
  ii) conversion of the net peak intensity to concentration

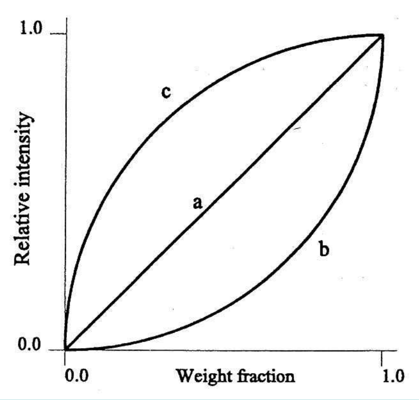
quantitative analysis complicated by

x-ray attenuation



$$I_x = I_0 \cdot \exp(-\mu \cdot \rho \cdot x)$$

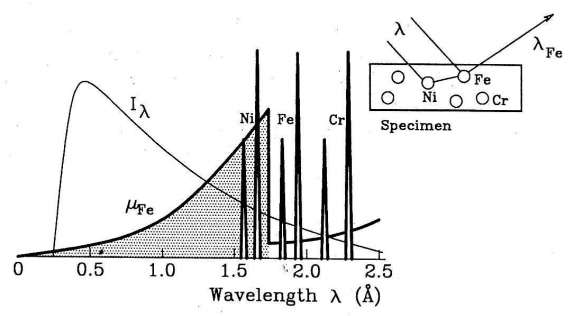
$$\mu_{sample} = \sum_i C_i \mu_i$$



a) no matrix effect
b) attenuation
c) enhancement

fundamental parameters approach (implemented in software)

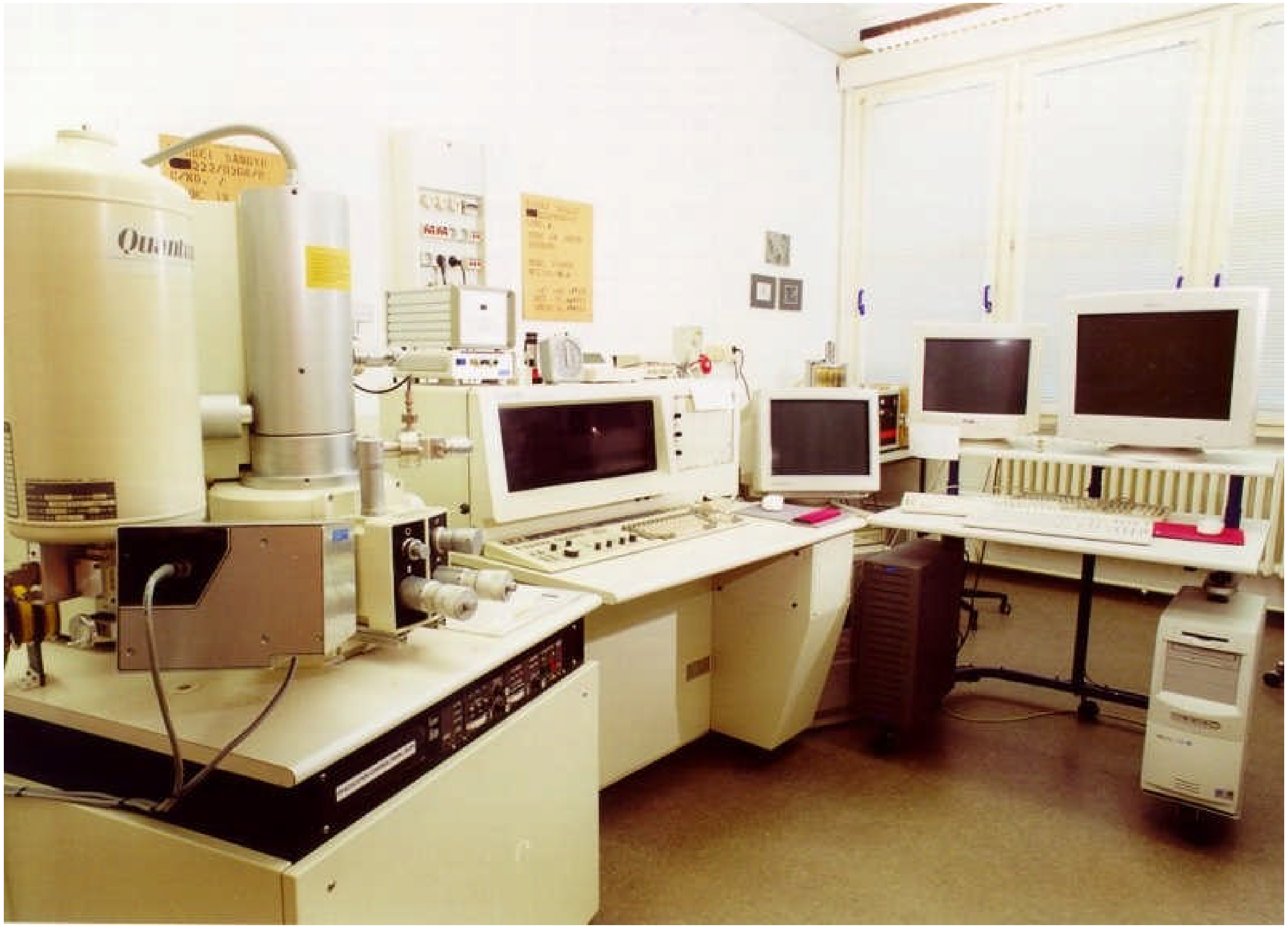
x-ray enhancement



- excitation of the Fe - K lines by the two Ni – K lines
- observed Fe – K line intensity = sum of primary and secondary fluorescence
- Cr – K line intensity = sum of primary, secondary and tertiary fluorescence

2.3.5 Electron Probe X-ray Microanalysis (EPXMA)

EPXMA at the Fritz-Haber-Institute
(Inorganic Chemistry Department, Building L)

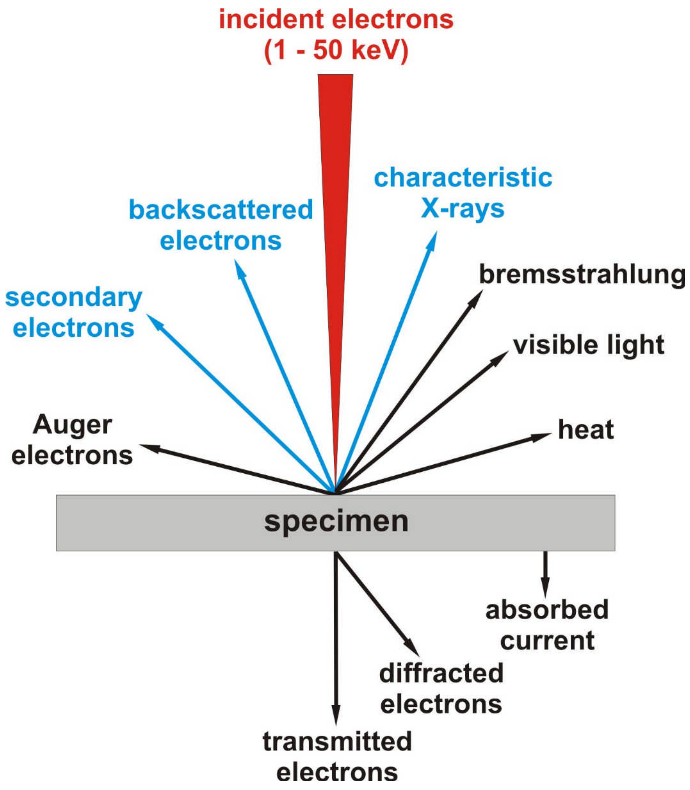


2.3 Spectroscopic Methods

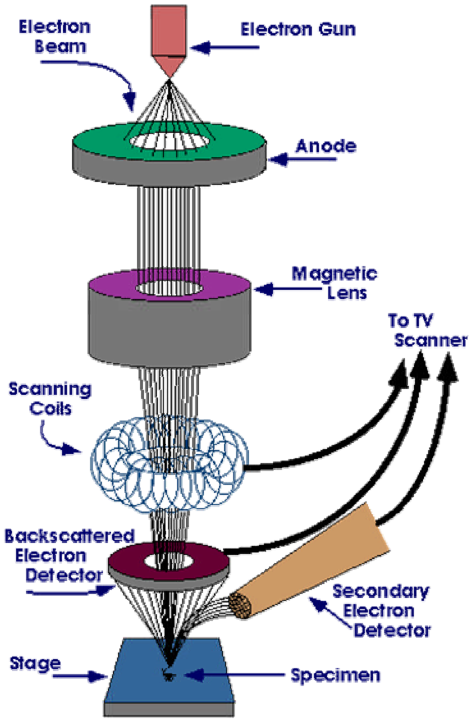
2.3.5 Electron Probe X-ray Microanalysis (EPXMA)

- **2D elemental analysis by combination of Scanning Electron Microscopy and X-Ray Fluorescence Analysis**

electron sample interaction


incident electrons
(1 - 50 keV)
characteristic
X-rays
backscattered
electrons
bremsstrahlung
secondary
electrons
visible light
Auger
electrons
heat
specimen
absorbed
current
diffracted
electrons
transmitted
electrons

SEM instrumentation

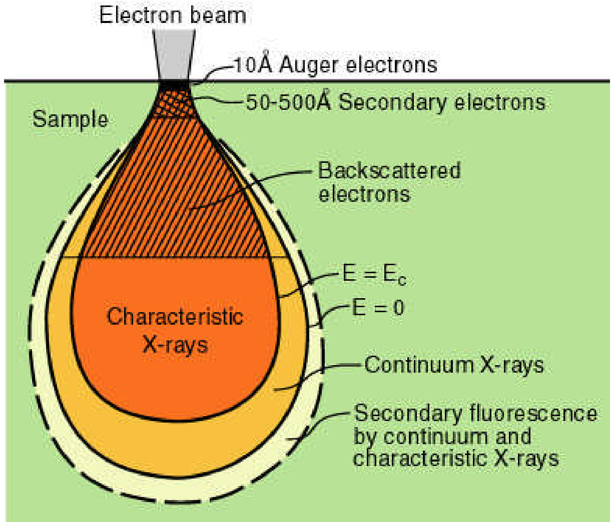


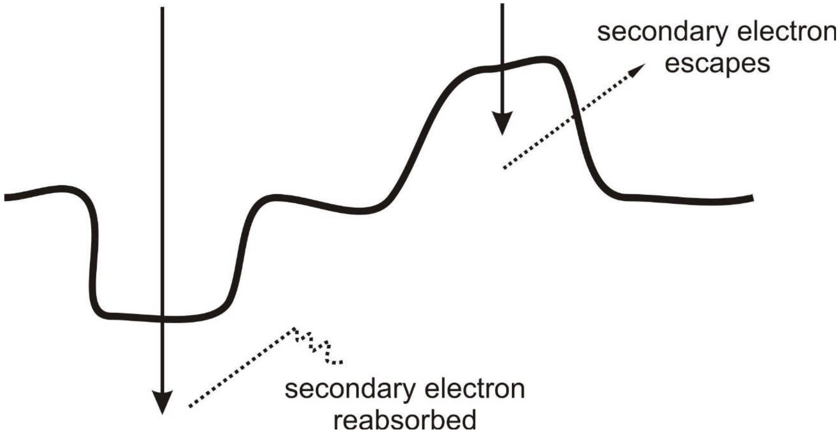
- **topographic sample image by synchronizing the TV – scanner with the scanning coils**
- **X-ray detection by a solid – state detector (Si single crystal) as in XRF (not shown above)**

2.3 Spectroscopic Methods

2.3.5 Electron Probe X-ray Microanalysis (EPXMA)

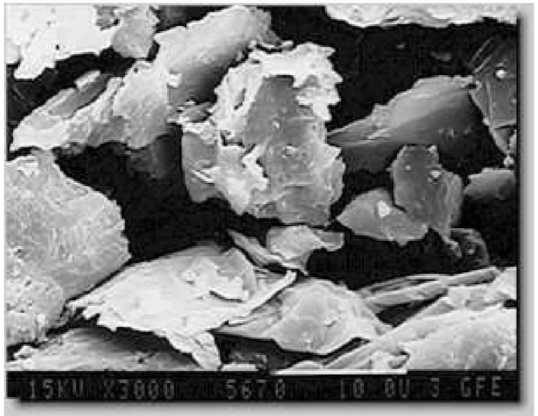
information depths, spatial resolution





- in most cases, the SEM image is created using secondary electrons
- secondary electrons are of low energy (<50eV), surface sensitive and supply an topographic image of the sample surface
- spatial resolution < 0.1 ① possible

secondary electron image

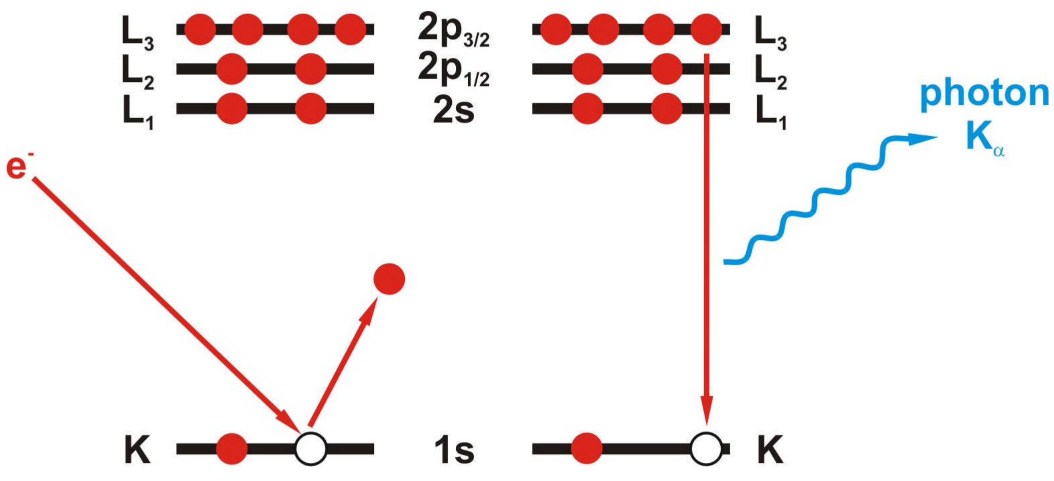


synthetic graphite (25keV, ´3000)

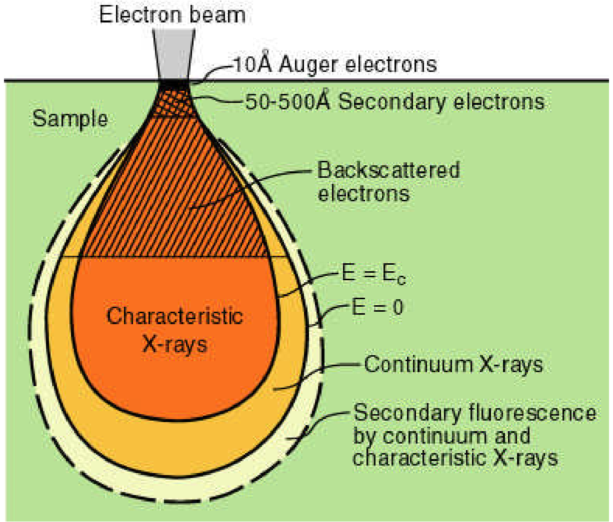
2.3 Spectroscopic Methods

2.3.5 Electron Probe X-ray Microanalysis (EPXMA)

X – ray generation



information depths, spatial resolution



- X-ray generation process similar to XRF
- X-ray spatial resolution much lower than by secondary electrons

2.3 Spectroscopic Methods

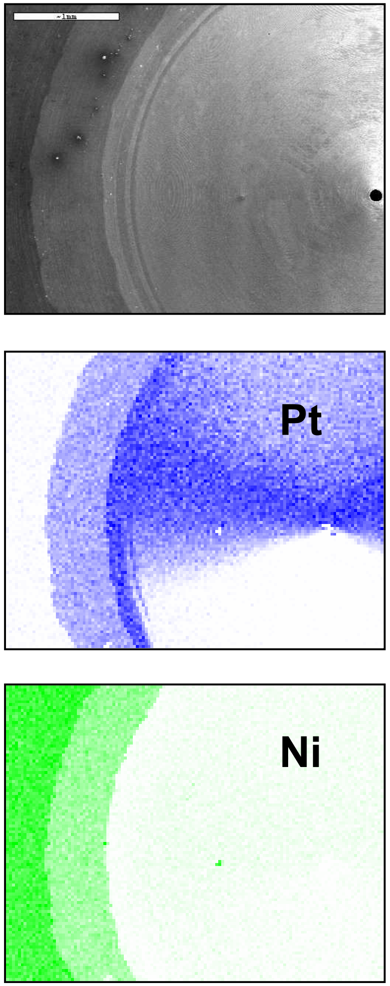
2.3.5 Electron Probe X-ray Microanalysis (EPXMA)

analytical performance

- qualitative elemental analysis from Z > 11 by identification of the characteristic KLM peaks (software assisted)
- detection limit ~1%
- minimal sample preparation and sample damage
- quantitative analysis can be performed from element concentrations of 1 – 100% with a relative precision of 1-5%
- similar to XAF, relating net peak intensity with element concentration requires either sophisticated mathematical models (e.g. ZAF correction) or suitable calibration samples

example

(pinhole for molecular beam setup)



3. Specification of an Analytical Result

- any quantitative analysis relies on a relationship between the measurement value y and the analyte concentration x ⇒ $y = f(x)$
- if $y = f(x)$ is known, x can be calculated by $x = f^{-1}(y)$
- the mathematical form of $f(x)$ and $f^{-1}(y)$ depends on the analytical method

analytical methods			
absolute methods	relative methods		
	definite methods	reference methods	
		direct RM	indirect RM
$y = b \cdot x$			$Y = f(x)$
$b = F$	$b = k \cdot F$	$B = y_r/x_r$	$Y = a+bx$

gravimetry

$$m_{A_qB_p} = \underbrace{\boxed{\frac{M_{A_qB_p}}{q \cdot M_A}}}_{\downarrow\ B} \cdot m_A$$

photometry

$$A_\lambda = \overbrace{\boxed{\varepsilon_\lambda \cdot d}}^{B\ \uparrow} \cdot c_A$$

XPS

$$\frac{I_A}{I_R} = \frac{F_X S(E_k)\sigma(E_k)\lambda(E_k)\cos\theta \cdot n_A}{F_X S(E_k)\sigma(E_k)\lambda(E_k)\cos\theta \cdot n_R} = \frac{n_A}{n_R}$$

$$I_A = \boxed{\frac{I_R}{n_R}} \cdot n_A \longrightarrow B$$

ICP-MS, AES, AAS

3. Specification of an Analytical Result

- if the accuracy of the method is assured (e.g. by certified reference materials), the analytical result can be specified as follows

$$x = \bar{x} \pm \Delta\bar{x}$$

$$\bar{x} = \text{mean of } n_p \text{ parallel determinations}$$

$$\Delta\bar{x} = \text{prediction interval of } \bar{x}$$

- verbal: with a probability of P is the concentration x of the analyte A in the concentration range $\bar{x} \pm \Delta\bar{x}$
- results from measurements with absolute, definite and direct reference methods can be evaluated using n_p parallel determinations (entire sample preparation process) and the uncertainties of all values in B using the rules of error propagation $\Rightarrow$ $x = B^{-1} \cdot y$
- specification of results from measurements with an indirect reference method (experimental calibration) requires to evaluate both the uncertainty of the analysis and of the calibration

3. Specification of an Analytical Result

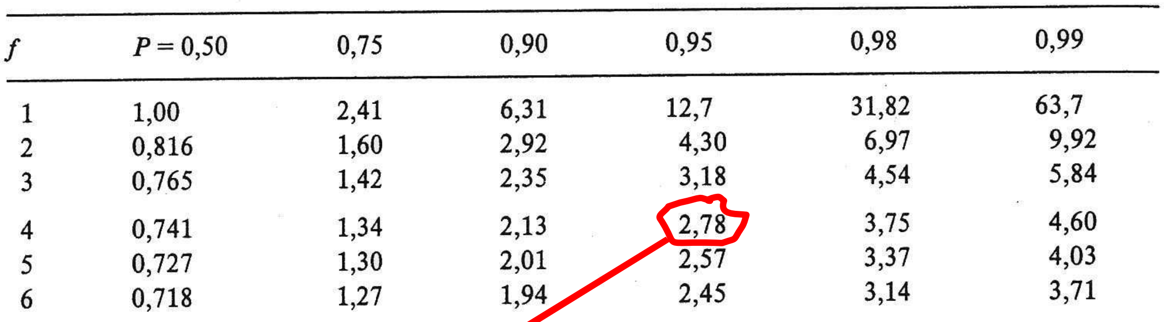
example 1: gravimetric determination of Fe_2O_3 in an iron ore

- **results of n_p=5 parallel determinations 38,71% 38,99% 38,62% 38,74% 38,73%**

$$\text{mean}: \quad \bar{x} = \frac{1}{n_p}\sum_i x_i = 38.76\% \qquad \text{standard deviation}: \quad s = \sqrt{\frac{\sum_i (x_i - \bar{x})^2}{n_p - 1}} = 0.1381\%$$

$$\text{degrees of freedom}: \quad f = n_p - 1 = 4 \qquad \text{confidence level}: \quad P = 95\%$$

t-table



f	P = 0,50	0,75	0,90	0,95	0,98	0,99
1	1,00	2,41	6,31	12,7	31,82	63,7
2	0,816	1,60	2,92	4,30	6,97	9,92
3	0,765	1,42	2,35	3,18	4,54	5,84
4	0,741	1,34	2,13	2,78	3,75	4,60
5	0,727	1,30	2,01	2,57	3,37	4,03
6	0,718	1,27	1,94	2,45	3,14	3,71

$$\text{result}: \quad \bar{x} \pm \Delta\bar{x} = \bar{x} \pm \frac{s \cdot t(0.95,4)}{\sqrt{n_p}} = 38.76\% \pm \frac{0.1381\% \cdot 2.78}{\sqrt{5}} = 38.76\% \pm 0.17\%$$

3. Specification of an Analytical Result

example 2: Zn determination by AAS

- calibration: m samples (x_i, y_i) ⇒ f = m-2
- x_i taken as error free
- least squares fit

x_i/ppm	2	4	6	8	10
y_i ($E=\log(I_0/I)$)	0.266	0.598	0.856	1.222	1.467

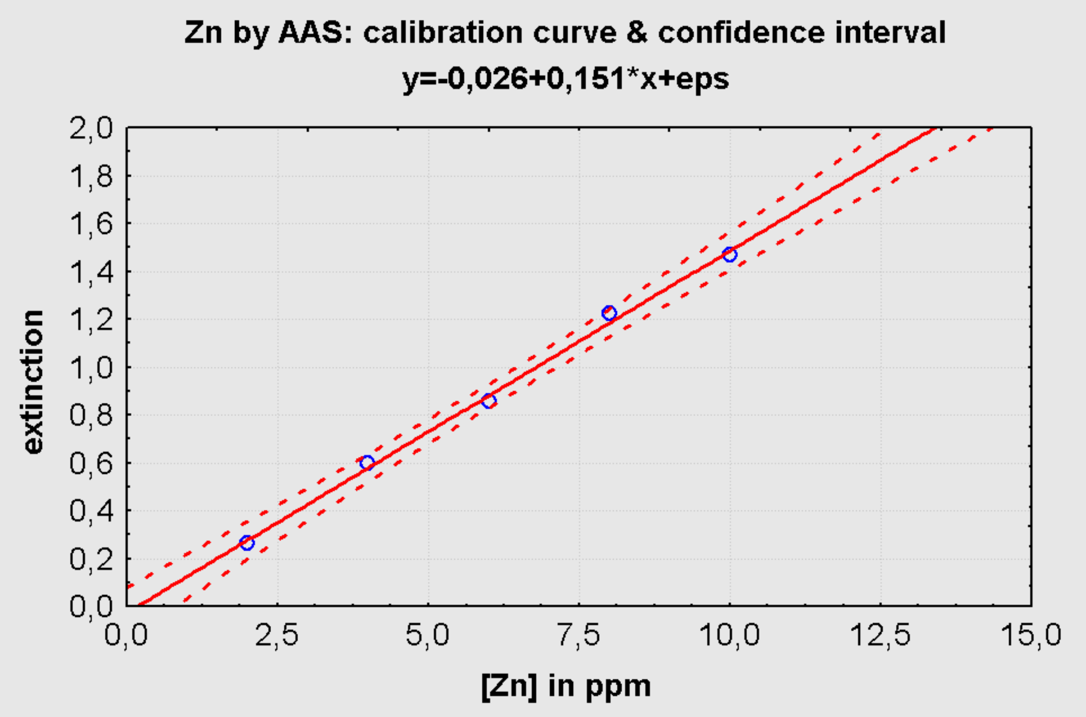
$$y = \hat{a} + b\hat{x}$$

$$\hat{b} = \frac{\sum_i (x_i - \bar{x})(y_i - \bar{y})}{\sum_i (x_i - \bar{x})^2}$$

$$\hat{a} = \frac{\sum_i y_i - b \sum_i x_i}{m}$$

$$s_0^2 = \frac{\sum_i (y_i - \hat{y}_i)^2}{m - 2}$$

$$\Delta\hat{y}_k = t(P, f)\sqrt{s_0^2 \left[\frac{1}{m} + \frac{(x_k - \bar{x})^2}{\sum_i (x_i - \bar{x})^2}\right]}$$



Zn by AAS: calibration curve & confidence interval

y=-0,026+0,151*x+eps

3. Specification of an Analytical Result

example 2: Zn determination by AAS

- analysis: n_p measurement samples (e.g. n_p=3 parallel determinations)

n_p	1	2	3
y_i ($E=\log(I_0/I)$)	1.064	0.930	0.942

$$\bar{y} = 0.979$$

- calculation of $$\bar{x} = \frac{\bar{y} - \hat{a}}{\hat{b}} = \frac{0.979 - (-0.026)}{0.151} = 6.656\,ppm$$

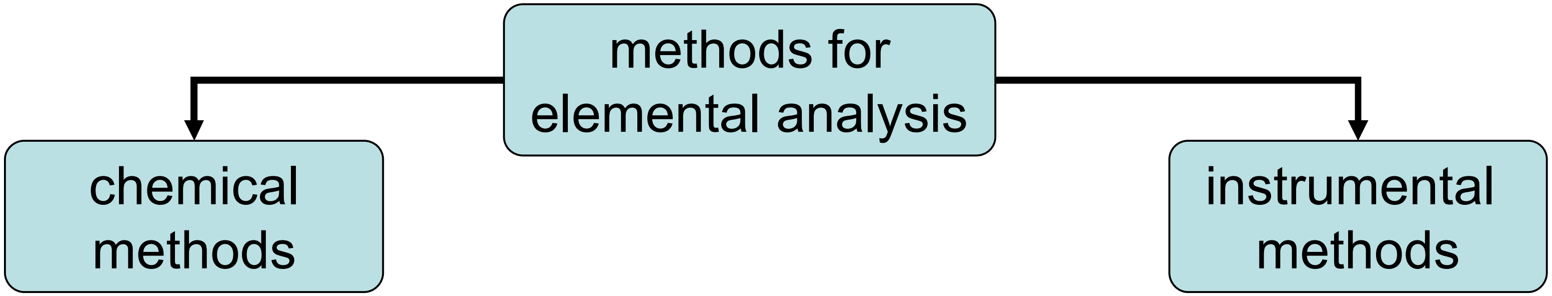
- calculation of $$\Delta\bar{x} = t(P,f) \cdot \frac{s_0}{\hat{b}} \cdot \sqrt{\frac{1}{m} + \frac{1}{n_p} + \frac{(\bar{x} - \bar{\bar{x}})^2}{\sum_i (x_i - \bar{\bar{x}})^2}}$$

$$\Delta\bar{x} = 3.18 \cdot \frac{0.0314\,ppm}{0.151} \cdot \sqrt{\frac{1}{5} + \frac{1}{3} + \frac{(6.656 - 6)^2\,ppm^2}{40\,ppm^2}} = 0.488\,ppm$$

$$\bar{x} \pm \Delta\bar{x} = 6.656 \pm 0.488\,ppm$$

4. Summary

- a wide variety of methods are available to determine quantitatively the elemental composition of inorganic samples



methods for elemental analysis

chemical methods

instrumental methods

chemical methods

advantages

cheap, direct, easy to understand, precise

disadvantages

cumbersome, restricted to main components, danger of systematic errors, liquid samples only

instrumental methods

advantages

cover concentrations from 100% to sub ppt, solid and liquid samples, multi-element character

disadvantages

expensive, “black box” character, operation requires expertise

- the choice of the right method depends on numerous parameters (liquid or solid sample, available amount of sample, which and how many elements, expected concentrations, accuracy and precision, decision limit…)

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