Modern Methods in Heterogeneous Catalysis Research

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Chemical (Elemental) Analysis

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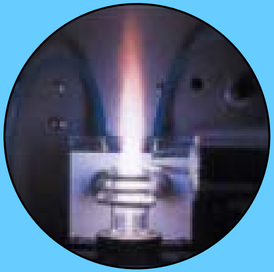
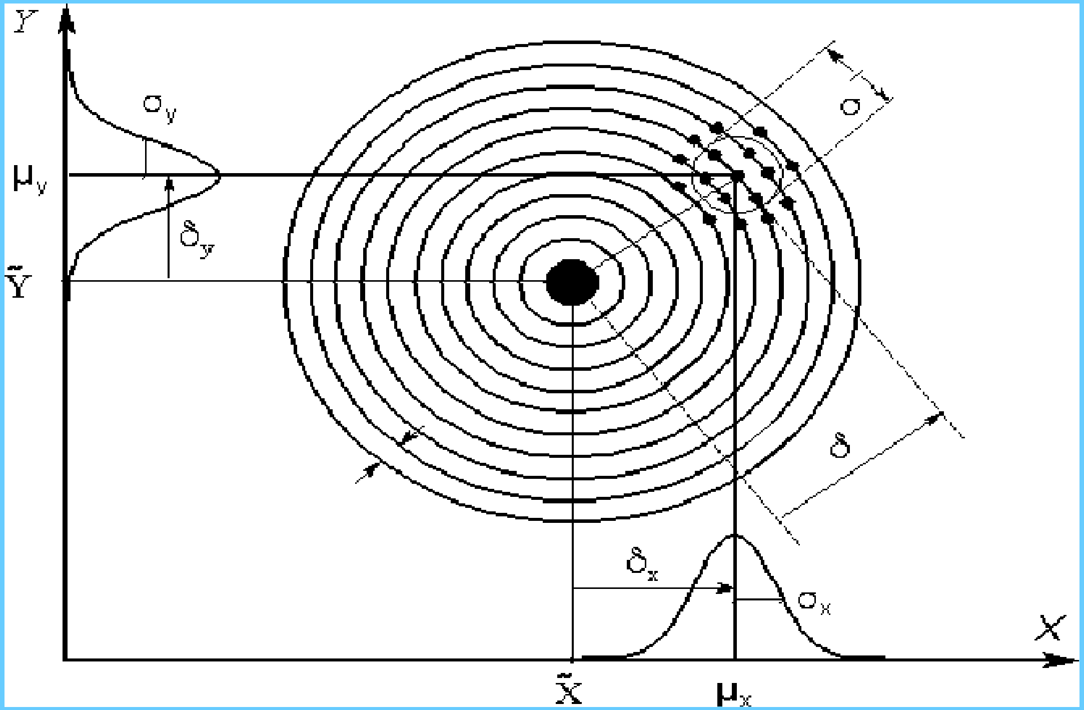




Outline

1. Introduction

1.1 Concentration Ranges

1.2 Accuracy and Precision

1.3 Decision Limit, Detection Limit, Quantification Limit

2. Methods for Quantitative Elemental Analysis

2.1 Chemical Methods

- 2.1.1 Volumetric Methods
- 2.1.2 Gravimetric Methods

Outline

2.2 Spectroscopic Methods

- 2.2.1 Atomic Emission Spectroscopy
- 2.2.2 Atomic Absorption Spectroscopy
- 2.2.3 Inductively Coupled Plasma Mass Spectrometry
- 2.2.4 X-Ray Fluorescence Spectroscopy
- 2.2.5 Scanning Electron Microscopy – Energy Dispersive X-Ray Fluorescence Spectroscopy (SEM-EDX)

3 Specification of an Analytical Result

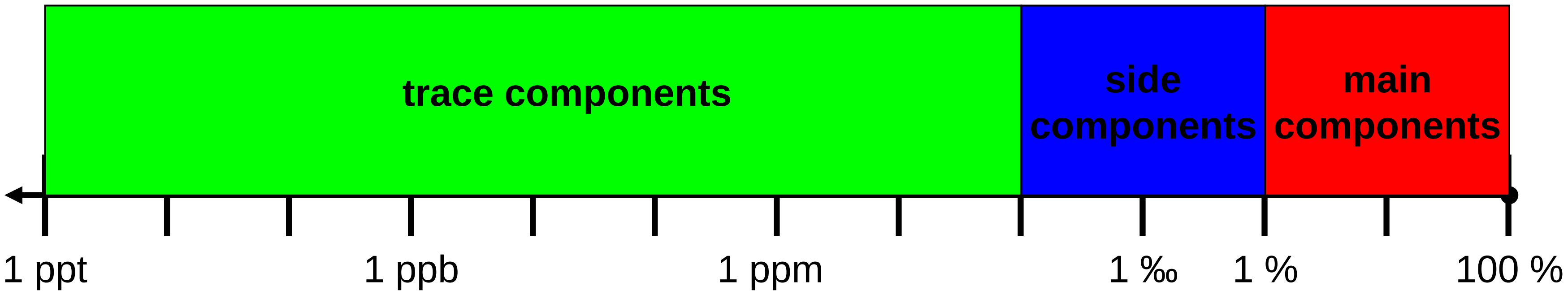
4 Summary

5 Literature

1. Introduction

1.1 Concentration Ranges

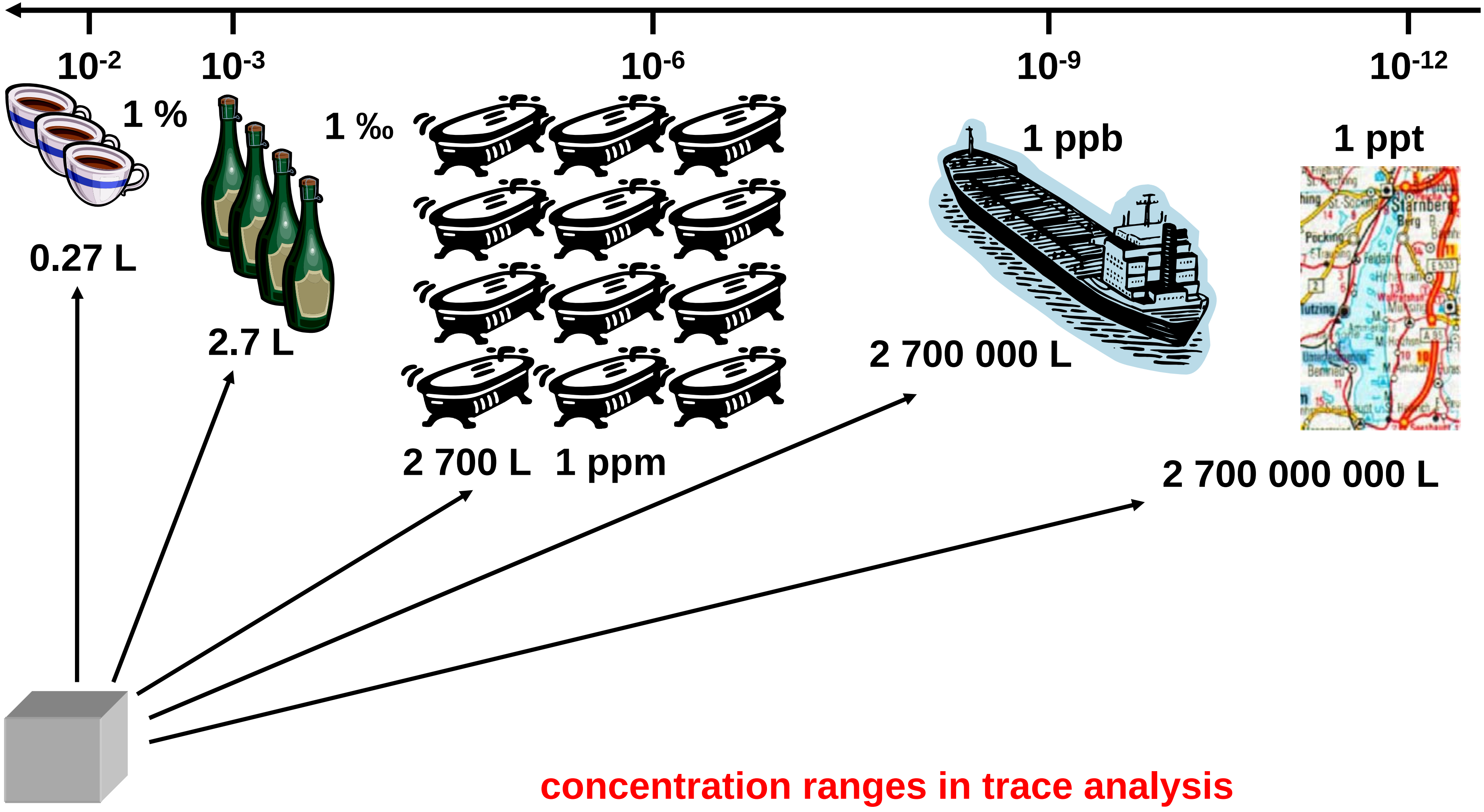
concentration ranges in elemental analysis



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 g/kg

1. Introduction

1.1 Concentration Ranges



mass ratio

10^{-2} 1 % 0.27 L

10^{-3} 1 ‰ 2.7 L

10^{-6} 2 700 L 1 ppm

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

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

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

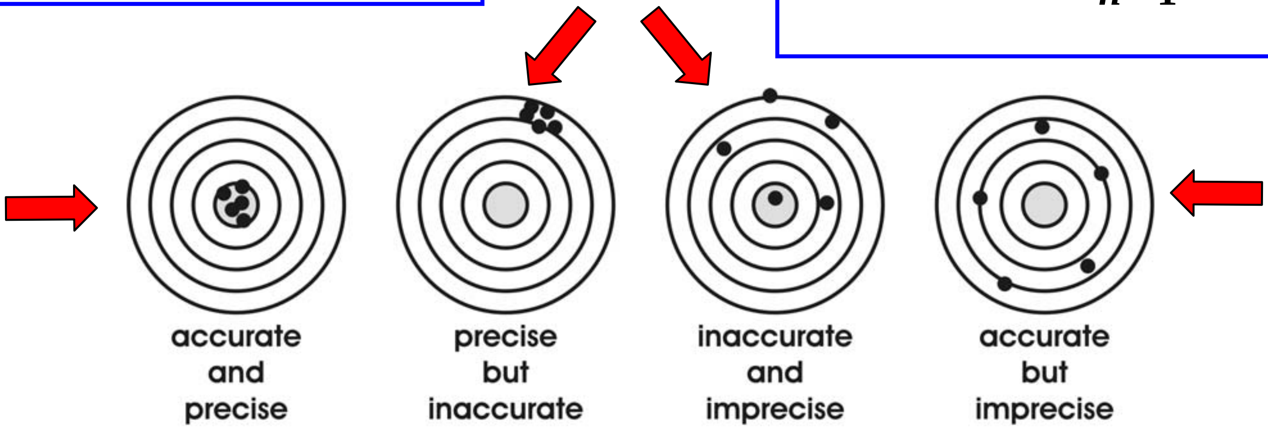
precision (uncertainty):

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

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

Gaussian distributed errors!

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



wrong results

main and side component analysis

trace and ultra trace analysis

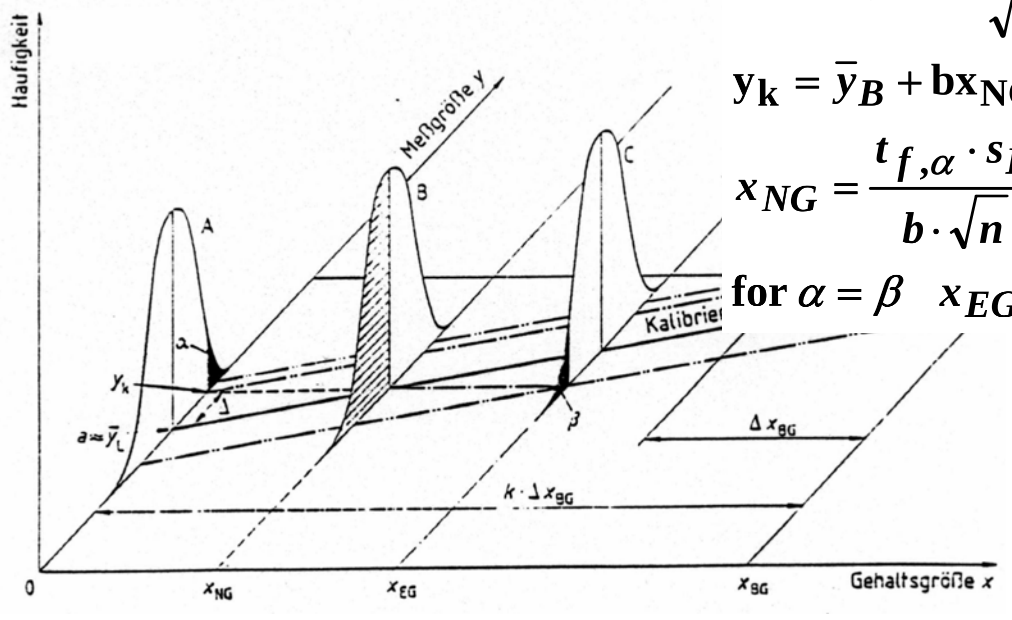
1. Introduction

1.3 Decision Limit, Detection Limit, Quantification Limit

What is the lowest concentration of an analyte that I can detect ?

- 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

- at Decision Limit, risk of false positive (α) small, typically 5% but risk of false negative 50%
- at Detection limit, risk of false positive (α) and risk of false negative (β) both small, typically 5%



$$y_k = \bar{y}_B + \frac{t_{f,\alpha} \cdot s_B}{\sqrt{n}}$$

$$y_k = \bar{y}_B + b x_{NG}$$

$$x_{NG} = \frac{t_{f,\alpha} \cdot s_B}{b \cdot \sqrt{n}}$$

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

1. Introduction

1.3 Decision Limit, Detection Limit, Quantification Limit

What is the lowest concentration of an analyte that I can quantify ?

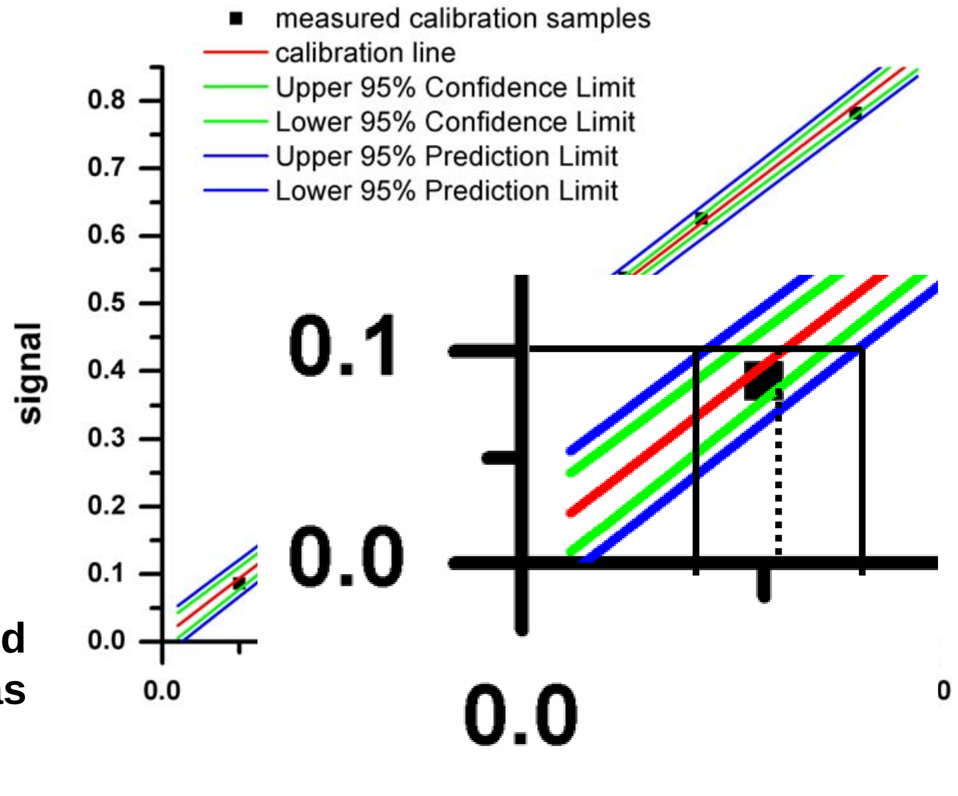
- this depends on how precise you want the quantification to be
- you need to specify the relative precision for the result
- very often k is chosen to be 3 (33.3% relative precision)

$$\frac{\Delta x_{QL}}{x_{QL}} = \frac{1}{k}$$

$$\Delta x = t_{\alpha/2,n-2}\,\frac{s_{cal}}{b_1}\sqrt{\frac{1}{m}+\frac{1}{n}+\frac{(\bar{x}_s-\bar{x}_{cal})^2}{\sum_i (x_{i,cal}-\bar{x}_{cal})^2}}$$

$$x_{QL} = k\cdot t_{\alpha/2,n-2}\,\frac{s_{cal}}{b_1}\sqrt{\frac{1}{m}+\frac{1}{n}+\frac{(x_{QL}-\bar{x}_{cal})^2}{\sum_i (x_{i,cal}-\bar{x}_{cal})^2}}$$

- the quantification limit x_{QL} is calculated recursively, e.g. with the decision limit x_{NG} as starting point



2.1 Chemical Methods

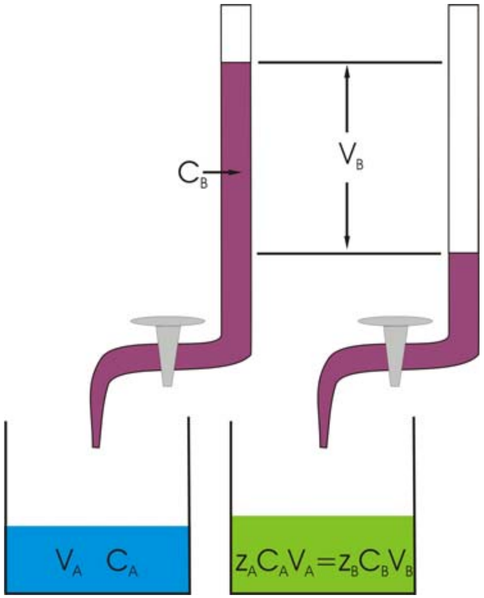
2.1.1 volumetric methods

2.1.2 gravimetric methods

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

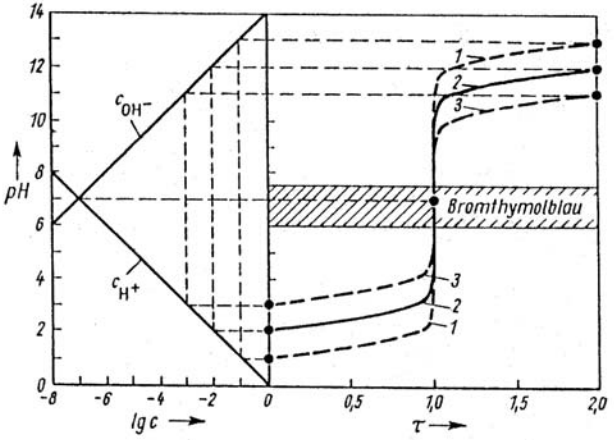
2.1.1 Volumetric Methods – Acid Base Titration

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

titration curve:

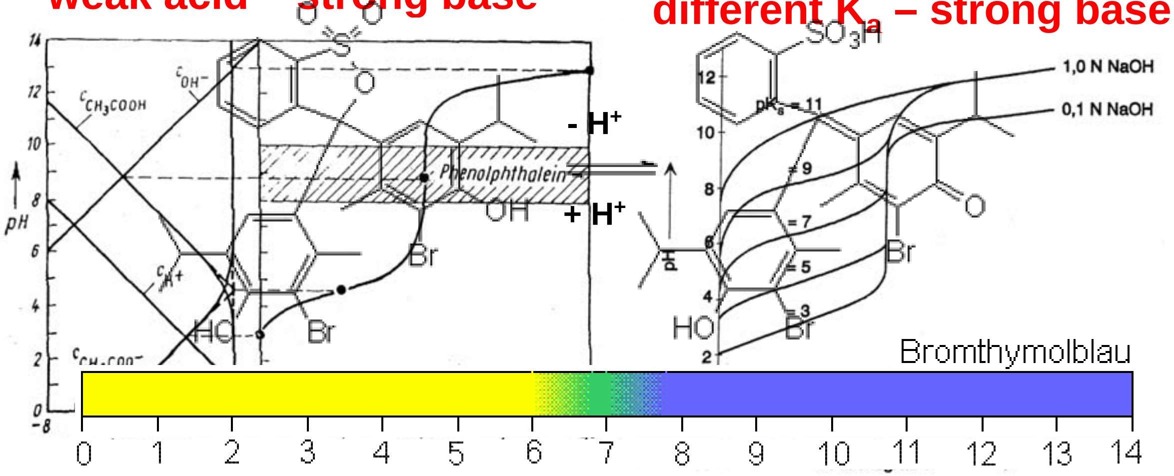
$$\tau = \frac{z_B \cdot C_B \cdot V_B}{z_A \cdot C_A \cdot V_A} = \frac{K_a}{10^{-pH} + K_a} + \frac{V_S + V}{C_S \cdot V_S} \cdot \left(\frac{K_w}{10^{-pH}} - 10^{-pH} \right) \quad K_w = [H^+][OH^-]$$

strong acid – strong base



weak acid – strong base

different K_a – strong base



- ➢ **choice of the indicator depends on K_a**

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

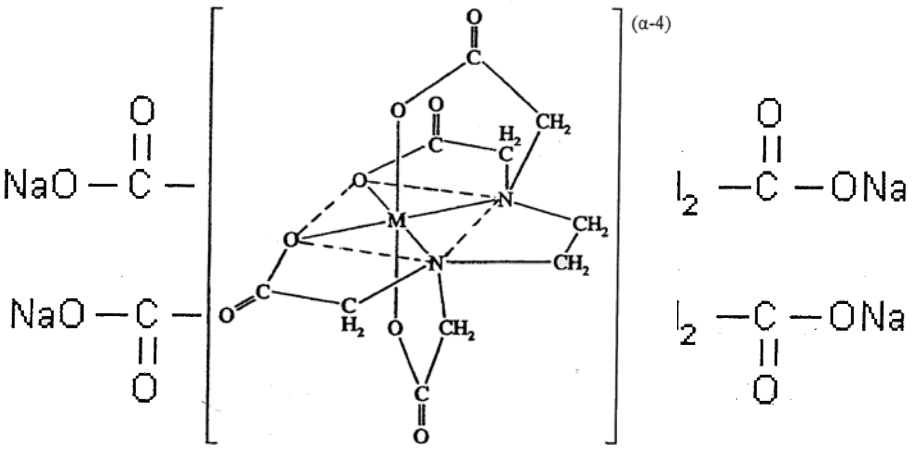
- ➢ **very weak acids (bases) can be titrated in non-aqueous solvents as liquid ammonia or 100% acetic acid**
- ➢ **application of acid base titration: determination of nitrogen (NH_3, NO_3^-, NO_2^-…), sulfur (e.g. as H_2SO_3, H_2SO_4), phosphorous, boron (as boric acid), carbon (e.g. in carbonates, CO_2)**

2.3 Chemical Methods

2.1.1 Volumetric Methods - Complexometry

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

most used ligand - EDTA



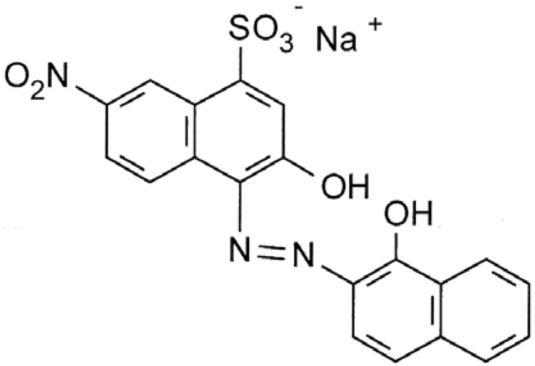
M-EDTA chelate

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

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

complex formation only with Y^{4-}
⇒ buffer required

indication: $HI^{2-} + M^{m+} \rightleftharpoons MI^{(m-3)} + H^+$
e.g. Eriochrom Black 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+}, Hg^{2+}, Sn^{2+} at pH 1-4

2.1 Chemical Methods

2.1.1 Volumetric Methods – Redox Titration

redox reaction: $n_BOx_B + n_ARed_A$ ✞ $n_BRed_B + n_AOx_A$ $(z_A{=}n_B,\ z_B{=}n_A)$

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

$Ce^{4+} + Fe^{2+}$ ✞ $Ce^{3+} + Fe^{3+}$

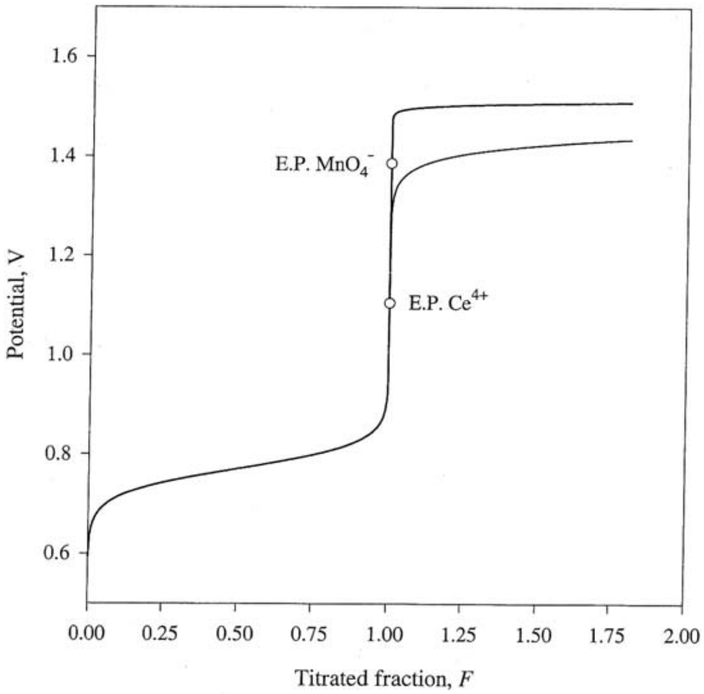
$$\tau = \frac{z_A \cdot C_A \cdot V_A}{z_B \cdot C_B \cdot V_B}$$

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

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

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

titration curve



indication: self indication (violet MnO_4^- → colorless Mn^{2+})
redox indicator (In_{Red} ☞ $In_{Ox} + ne^-$)
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

$Ba^{2+} + SO_4^{2-}$ ☞ $BaSO_4$ $(K_L=[Ba^{2+}]\cdot[SO_4^{2-}]=1\cdot10^{-10}\,mol^2/l^2)$ as $BaSO_4$

$Fe^{3+} + 3OH^-$ ☞ $Fe(OH)_3$ $(K_L=[Fe^{3+}]\cdot[OH^-]^3=1\cdot10^{-38}\,mol^4/l^4)$ 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 Spectroscopic Methods

2.2.1 Atomic Emission Spectroscopy (AES)

2.2.2 Atomic Absorption Spectroscopy (AAS)

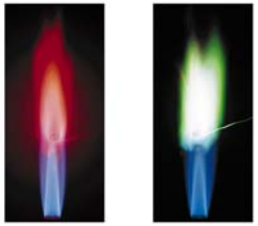
2.2.3 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

2.2.4 X-Ray Fluorescence Spectroscopy (XRF)

2.2.5 Scanning Electron Microscopy-Energy - Dispersive X-Ray Fluorescence Spectroscopy (SEM-EDX)

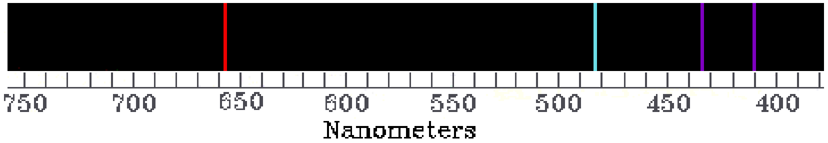
2.3 Spectroscopic Methods

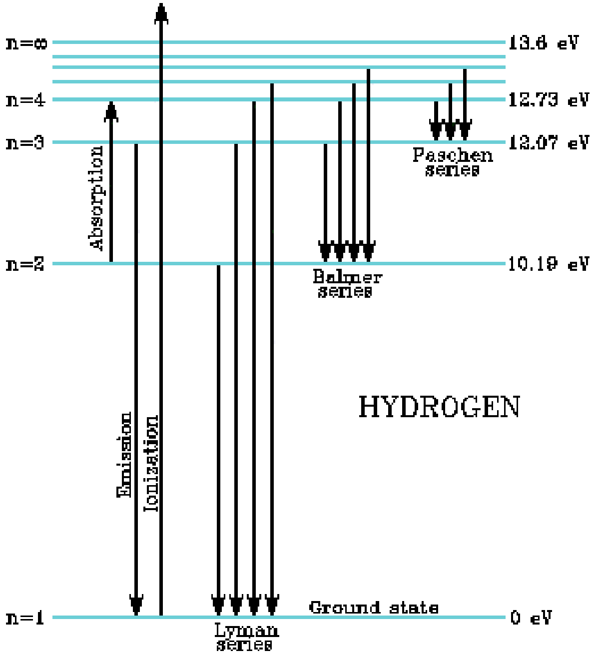
2.2.1 Atomic Emission Spectroscopy



- **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 (visible lines = Balmer series)





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

intensity of an emission line

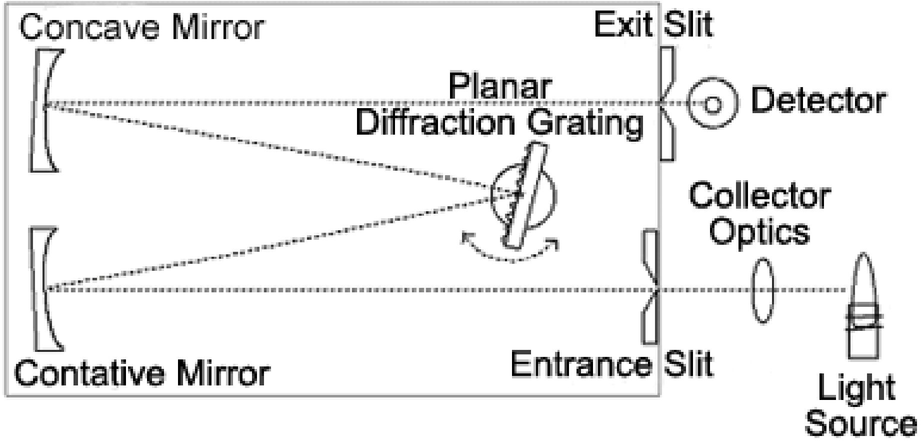
$$I = \Phi\left(\frac{h \cdot c \cdot g_m \cdot A \cdot N}{4\pi \cdot \lambda \cdot Z}\right) \cdot \exp\left(\frac{-E_m}{kT}\right)$$

- **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

2.2.1 Atomic Emission Spectroscopy

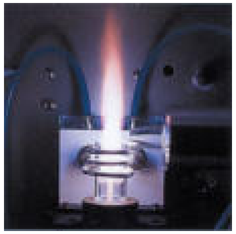
instrumentation



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:

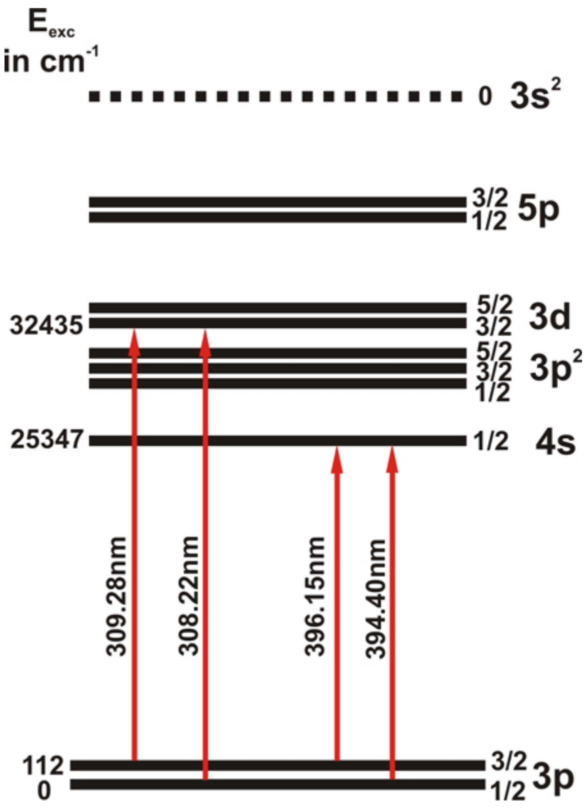
- **flame AES – low cost system for alkali and earth alkaline metals**
- **ICP AES – suited for any sample that can be brought into solution**
- **arc AES – with photographic plate for qualitative overview analysis**
- **spark AES – unsurpassable for metal analysis (steel, alloys)**
- **laser ablation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

2.3 Spectroscopic Methods

2.2.2 Atomic Absorption Spectroscopy

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

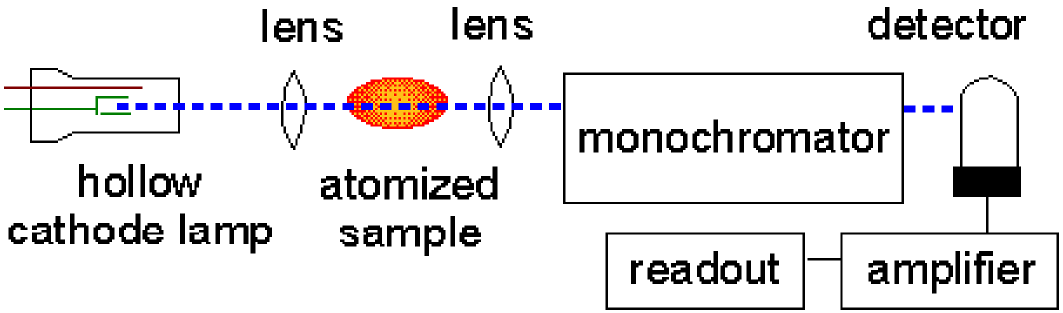
ground and excited states of Al and optical transitions used for AAS



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



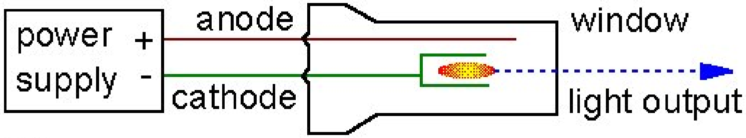
2.3 Spectroscopic Methods

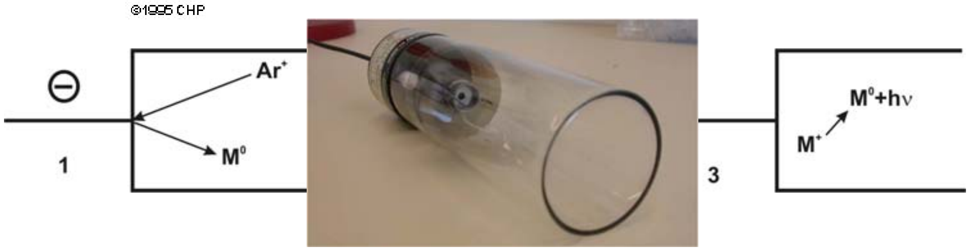
2.2.2 Atomic Absorption Spectroscopy

radiation source

- atomic absorption lines are very small $(\Delta\lambda \leq 0.005\,\text{nm}) \Rightarrow$ narrow excitation lines required
- hollow cathode lamp filled with Ar (~5 Torr) $\Rightarrow$ discharge in cathode cup
- cup-shaped cathode made from the element to be determined $\Rightarrow$ emission of sharp de-excitation lines

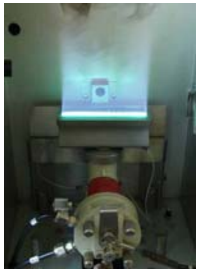
working principle of hollow cathode lamps





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 $\Rightarrow$ drying, ashing, atomization, cleaning
- transient signals
- liquid and solid samples

2.3 Spectroscopic Methods

2.2.2 Atomic Absorption Spectroscopy

interferences in atomic absorption spectroscopy

- flame and furnace AAS are sensitive to matrix interferences ⇒ i.e. matrix constituents (anything but the analyte) influence the analyte signal
- there are two types of interferences ⇒ 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) ⇒ hotter N_2O flame (La buffer)
- large amounts of easily ionized elements (alkali metals) modifies the equilibrium between atoms and ions ⇒ adding excess of Cs
- loss of volatile analyte species during the ashing process in GF-AAS (e.g. $ZnCl_2$) ⇒ adding of matrix modifiers

$$NH_4NO_3 + NaCl \rightarrow NH_4Cl + NaNO_3$$

spectral interferences

- two spectral lines overlap within the band pass of the dispersive element (e.g. $\Delta\lambda_d \approx 0.1$nm, Cd 228.802nm and As 228.812nm) ⇒ 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

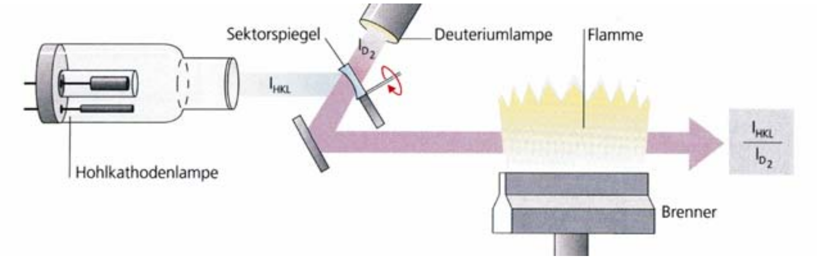
2.3 Spectroscopic Methods

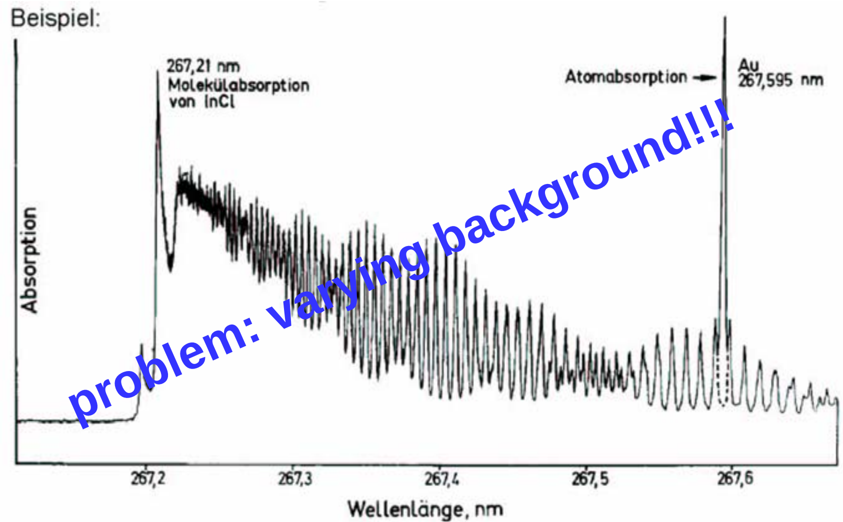
2.2.2 Atomic Absorption Spectroscopy

deuterium background correction

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

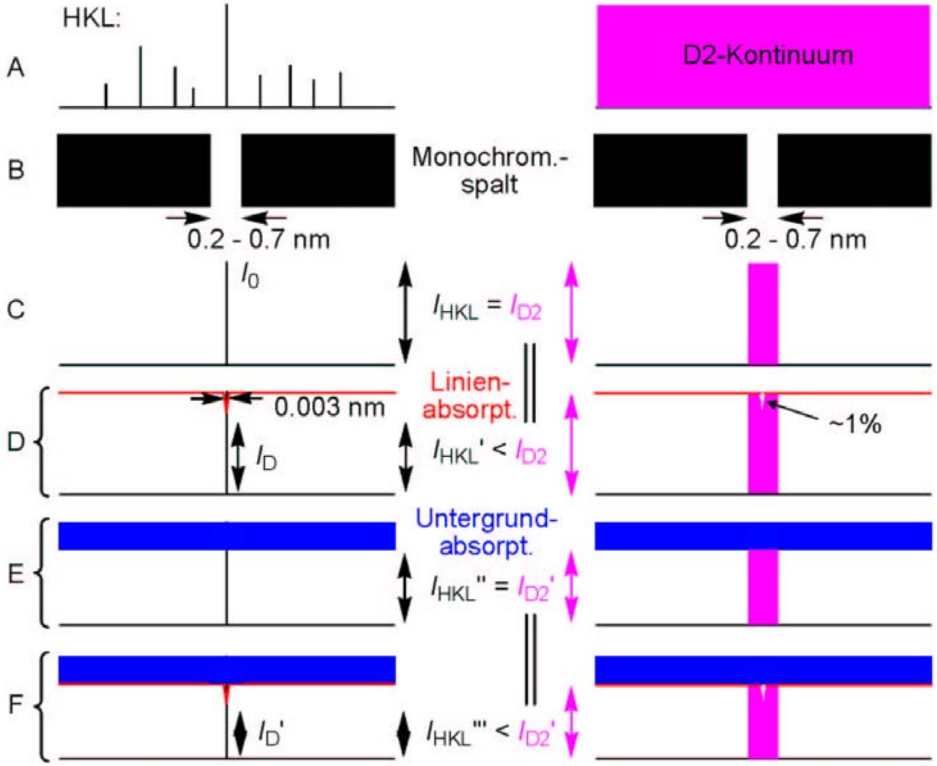
setup sketch





problem: varying background!!!

working principle



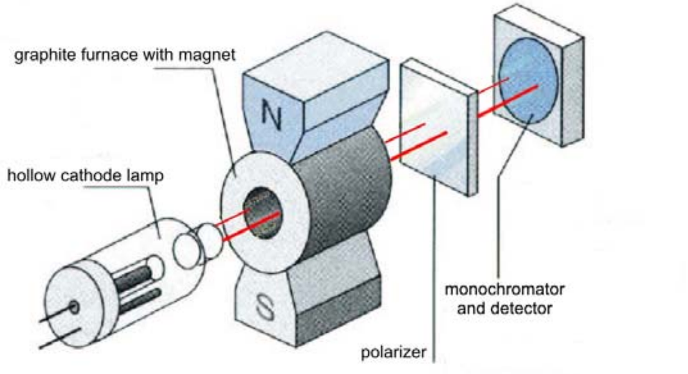
2.3 Spectroscopic Methods

2.2.2 Atomic Absorption Spectroscopy

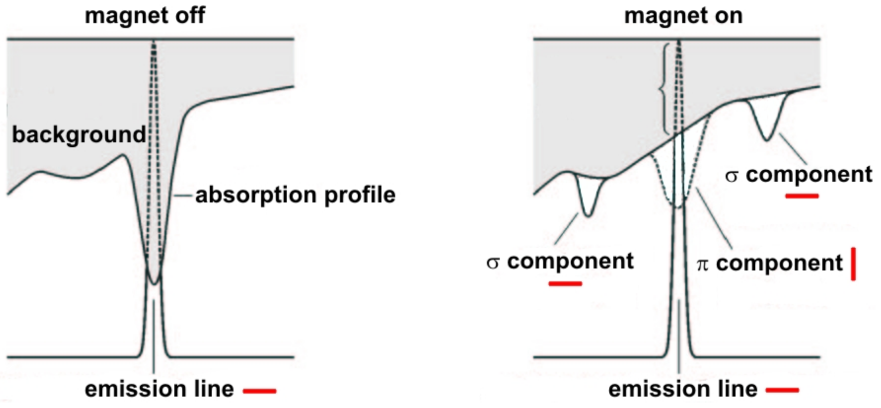
Zeeman background correction

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

setup sketch

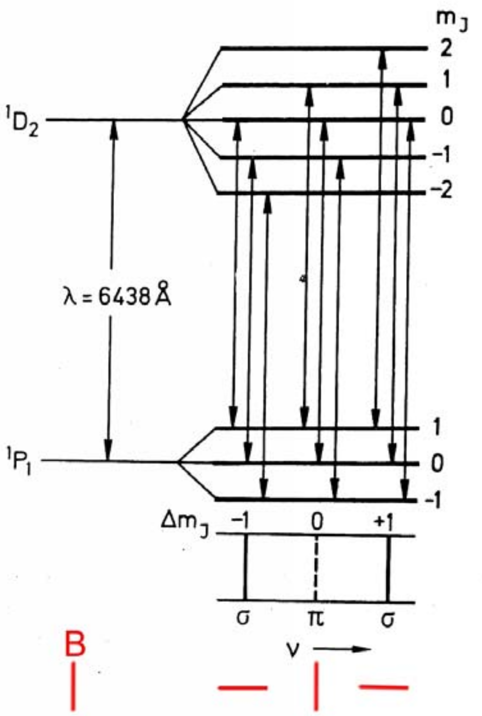


working principle



normal Zeeman effect (S=0)

(e.g. Cd atoms)



2.3 Spectroscopic Methods

2.2.2 Atomic Absorption Spectroscopy

analytical performance

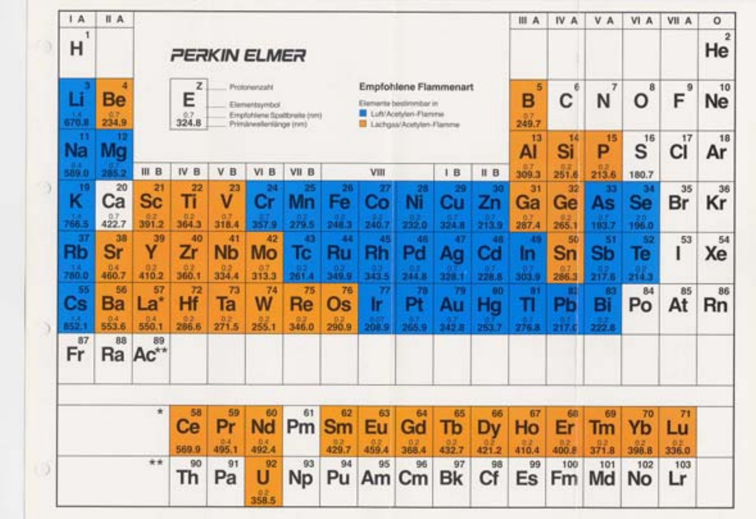
- ➢ AAS is most popular among the instrumental methods for elemental analysis

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

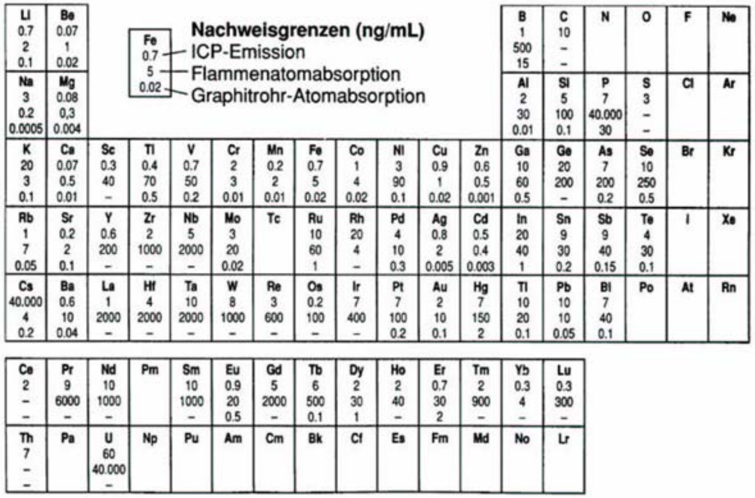


PERKIN ELMER

E (Z, 0.7, 324.8): 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	VIII	VIII	I B	II B	III A	IV A	V A	VI A	VII A	O
1 H																	2 He
3 Li 🟦 670.8	4 Be 🟧 234.9											5 B 🟧 249.7	6 C	7 N	8 O	9 F	10 Ne
11 Na 🟦 589.0	12 Mg 🟦 285.2											13 Al 🟧 309.3	14 Si 🟧 251.6	15 P 🟧 213.6	16 S 180.7	17 Cl	18 Ar
19 K 🟦 766.5	20 Ca 422.7	21 Sc 🟧 391.2	22 Ti 🟧 364.3	23 V 🟧 318.4	24 Cr 🟦 357.9	25 Mn 🟦 279.5	26 Fe 🟦 248.3	27 Co 🟦 240.7	28 Ni 🟦 232.0	29 Cu 🟦 324.8	30 Zn 🟦 213.9	31 Ga 🟧 287.4	32 Ge 🟧 265.1	33 As 🟦 193.7	34 Se 🟦 196.0	35 Br	36 Kr
37 Rb 🟦 780.0	38 Sr 🟧 460.7	39 Y 🟧 410.2	40 Zr 🟧 360.1	41 Nb 🟧 334.4	42 Mo 🟧 313.3	43 Tc 🟦 261.4	44 Ru 🟦 349.9	45 Rh 🟦 343.5	46 Pd 🟦 244.8	47 Ag 🟦 328.1	48 Cd 🟦 228.8	49 In 🟦 303.9	50 Sn 🟧 286.3	51 Sb 🟦 217.6	52 Te 🟦 214.3	53 I	54 Xe
55 Cs 🟦 852.1	56 Ba 🟧 553.6	57 La* 🟧 550.1	72 Hf 🟧 286.6	73 Ta 🟧 271.5	74 W 🟧 255.1	75 Re 🟧 346.0	76 Os 🟧 290.9	77 Ir 🟦 208.9	78 Pt 🟦 265.9	79 Au 🟦 242.8	80 Hg 🟦 253.7	81 Tl 🟦 276.8	82 Pb 🟦 217.0	83 Bi 🟦 222.8	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac**															
		*	58 Ce 🟧 569.9	59 Pr 🟧 495.1	60 Nd 🟧 492.4	61 Pm	62 Sm 🟧 429.7	63 Eu 🟧 459.4	64 Gd 🟧 368.4	65 Tb 🟧 432.7	66 Dy 🟧 421.2	67 Ho 🟧 410.4	68 Er 🟧 400.8	69 Tm 🟧 371.8	70 Yb 🟧 398.8	71 Lu 🟧 336.0	
		**	90 Th	91 Pa	92 U 🟧 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

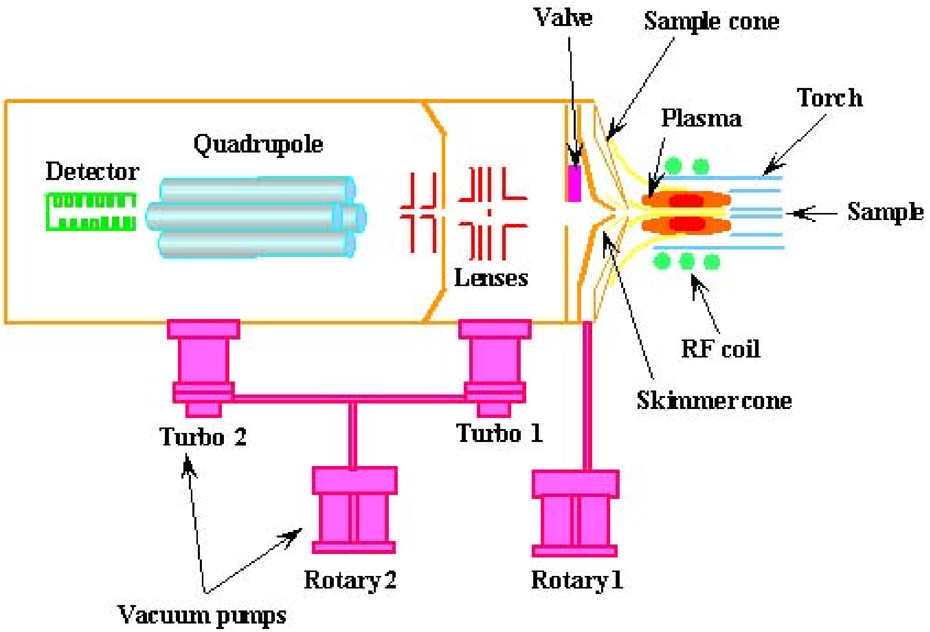
Li 0.7 2 0.1	Be 0.07 1 0.02											B 1 500 15	C 10 – –	N	O	F	Ne
Na 3 0.2 0.0005	Mg 0.08 0,3 0.004											Al 2 30 0.01	Si 5 100 0.1	P 7 40.000 30	S 3 – –	Cl	Ar
K 20 3 0.1	Ca 0.07 0.5 0.01	Sc 0.3 40 –	Ti 0.4 70 0.5	V 0.7 50 0.2	Cr 2 3 0.01	Mn 0.2 2 0.01	Fe 0.7 5 0.02	Co 1 4 0.02	Ni 3 90 0.1	Cu 0.9 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

2.2.3 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 ⇒ **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

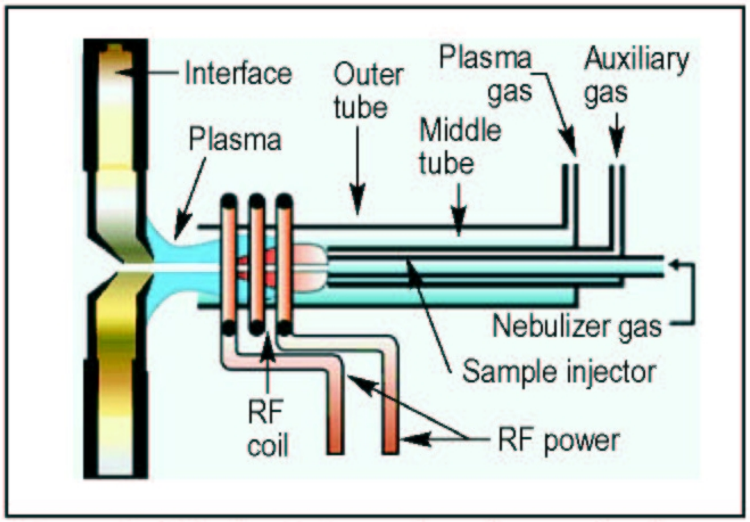
  solid samples

2.2.3 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

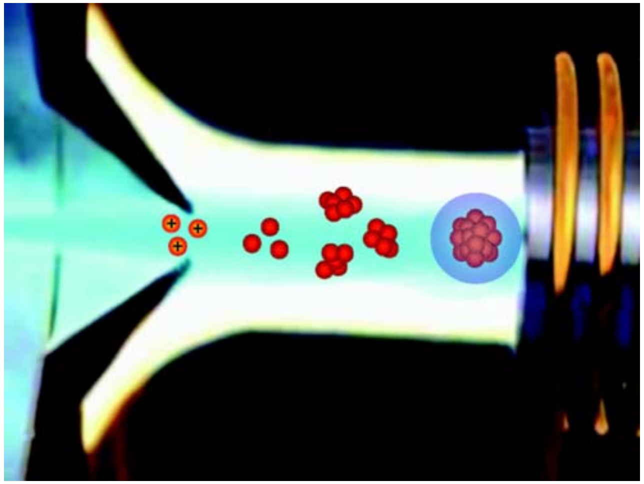


- ICP works under atmospheric pressure, MS under high vacuum ⇒ differentially pumped interface required
- typical RF frequencies 27 or 40 MHz
- power consumption 1 – 5 kW

2.3 Spectroscopic Methods

2.2.3 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 describes degree of ionization in a plasma



Saha equation

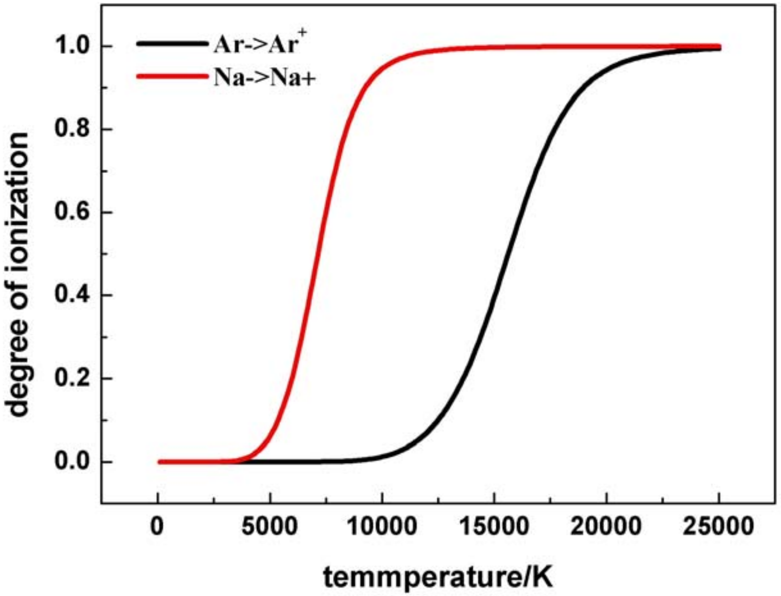
$$\frac{n_{i+1} \cdot n_e}{n_i} = \frac{2}{\Lambda^3} \frac{g_{i+1}}{g_i} \exp\left[-\frac{(\varepsilon_{i+1} - \varepsilon_i)}{k_B T} \right]$$

thermal de Broglie wavelength

$$\Lambda = \sqrt{\frac{h^2}{2\pi m_e k_B T}}$$

- 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

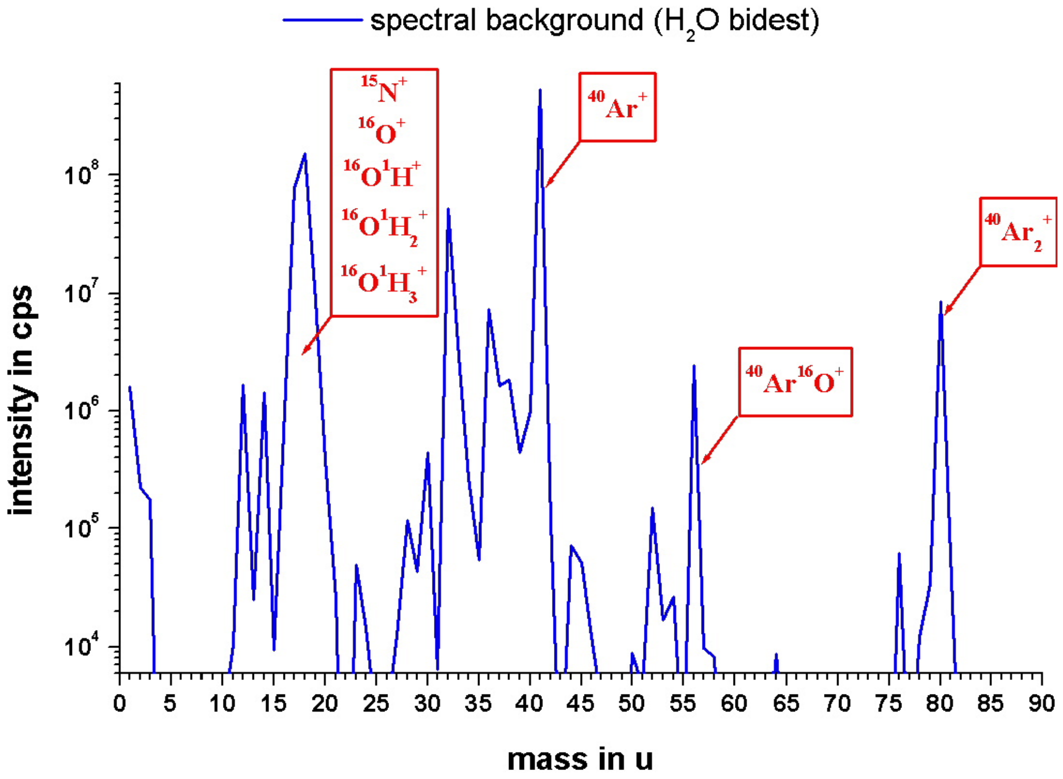
2.2.3 Inductively Coupled Plasma Mass Spectrometry

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



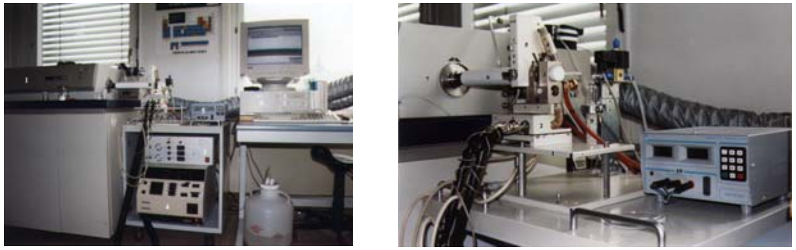
- spectral interferences cause a high background ⇒ higher decision limit for disturbed analytes (e.g. x_d(Fe)≈10 µg/l, x_d(Ag)≈0.03 µg/l)

2.3 Spectroscopic Methods

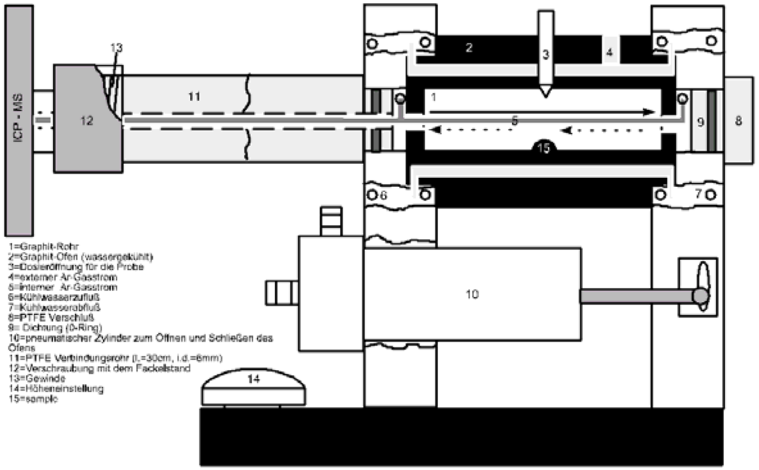
2.2.3 ETV – ICP – MS

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

setup picture

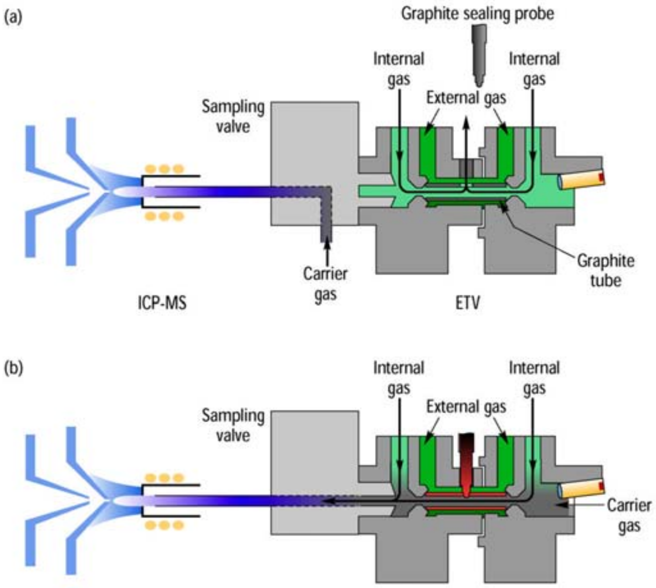


scheme of the ETV unit



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 (0-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

2.2.3 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

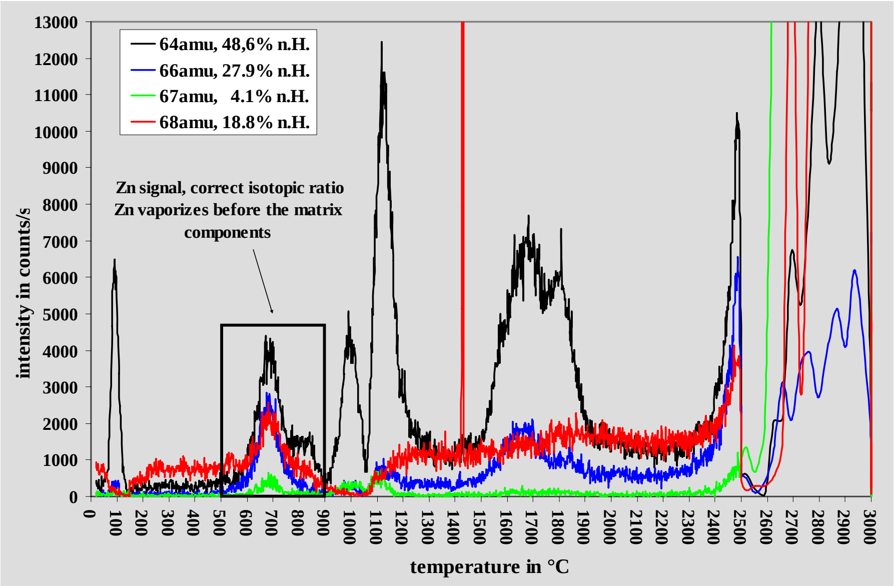
ion	64 u	66 u	67 u	68 u	concentration in seawater
Zn^{2+}	48.6% n.a.	27.9% n.a.	4.1% n.a.	18.8% n.a.	~1 ng/ml
Cl^-			$^{35}Cl^{16}O^{16}O^+$	$^{35}Cl^{16}O^{17}O^+$	ca. 16 mg/l
SO_4^{2-}	$^{32}S^{16}O^{16}O^+$ $^{32}S^{32}S^+$	$^{34}S^{16}O^{16}O^+$ $^{32}S^{34}S^+$ $^{33}S^{33}S^+$ $^{32}S^{17}O^{17}O^+$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

2.2.3 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)

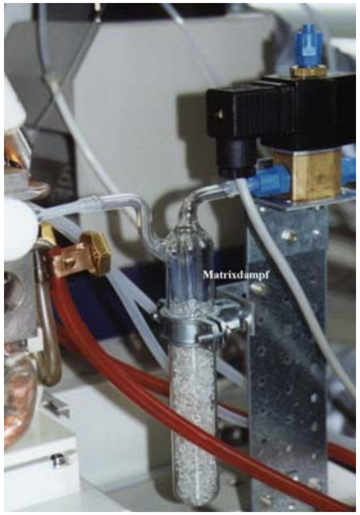
application to the Zn in seawater problem



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



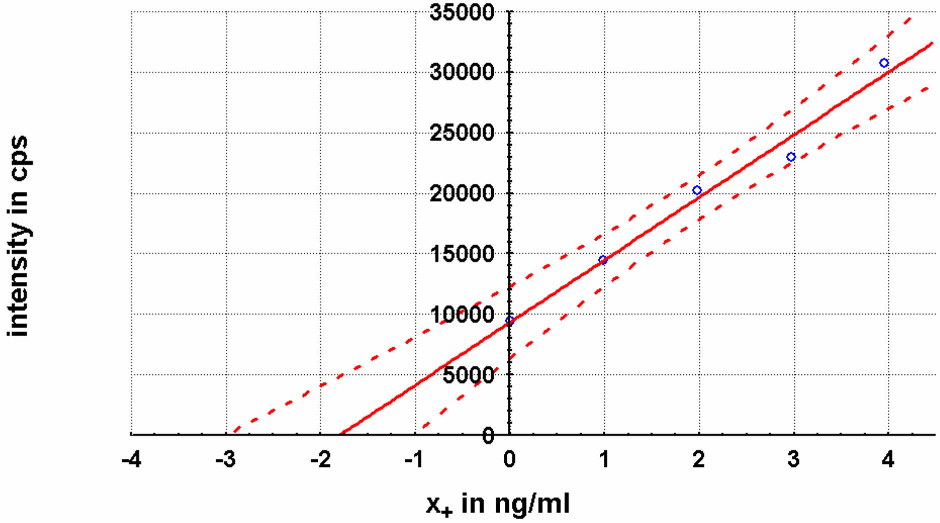
2.3 Spectroscopic Methods

2.2.3 ETV – ICP – MS

- if matrix matched calibration samples are not available ⇒ 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 ($y = f(x_+) = 0 \Rightarrow x_A$)

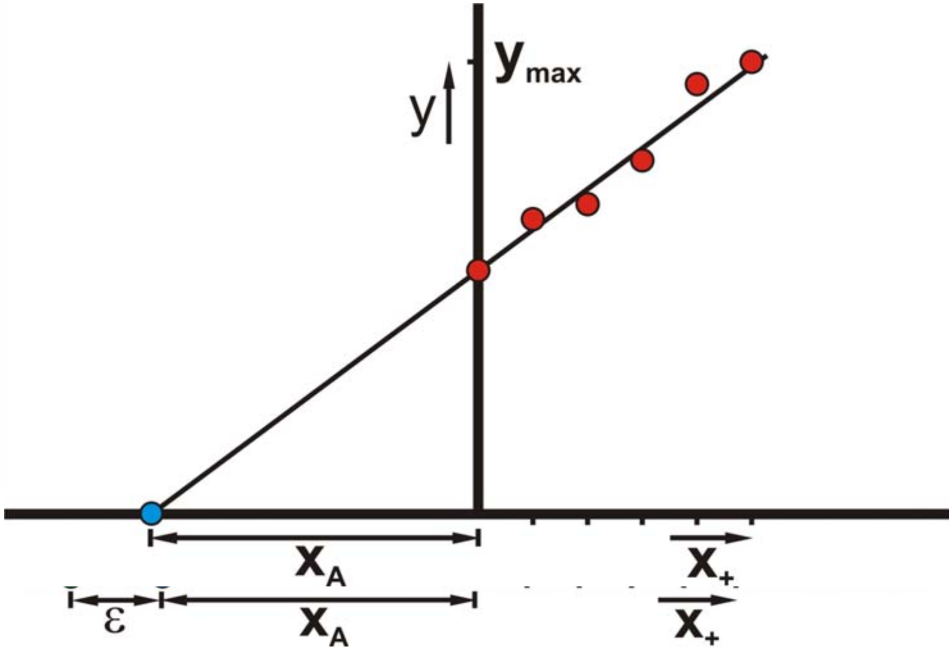
Zn in seawater by ETV-ICP-MS

standard addition



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

certified value: 1.24 ng/ml



2.3 Spectroscopic Methods

2.2.3 Inductively Coupled Plasma Mass Spectrometry

analytical performance of ICP-MS

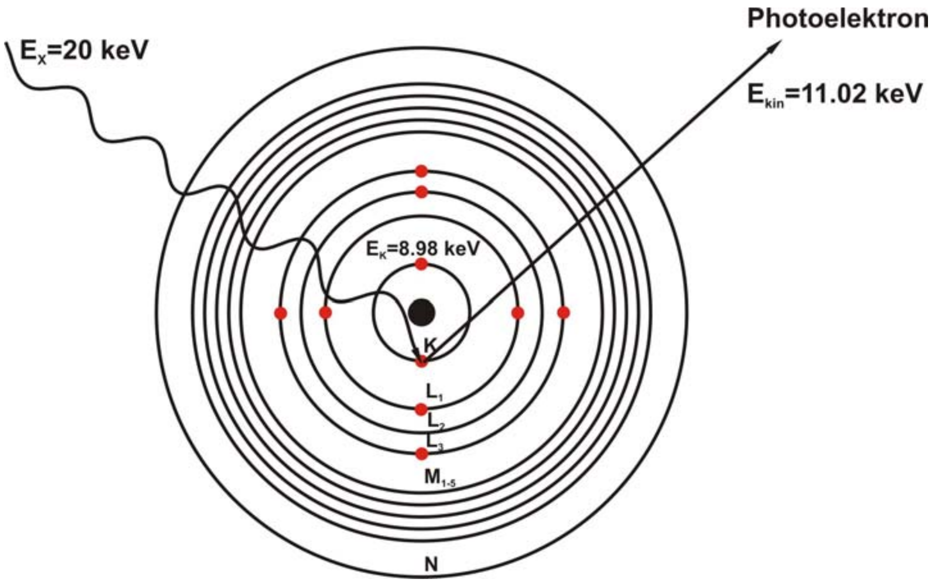
- multi-element method (more than 20 analytes in parallel)
- good performance in precision (a few percent), accuracy, number of determinable elements, decision limit (depending on the instrument 0.01-100 ng/l) and sample throughput
- linear dynamic range ⇒ 3-5 orders of magnitude
- difficult for elements 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) ⇒ high innovative potential

2.3 Spectroscopic Methods

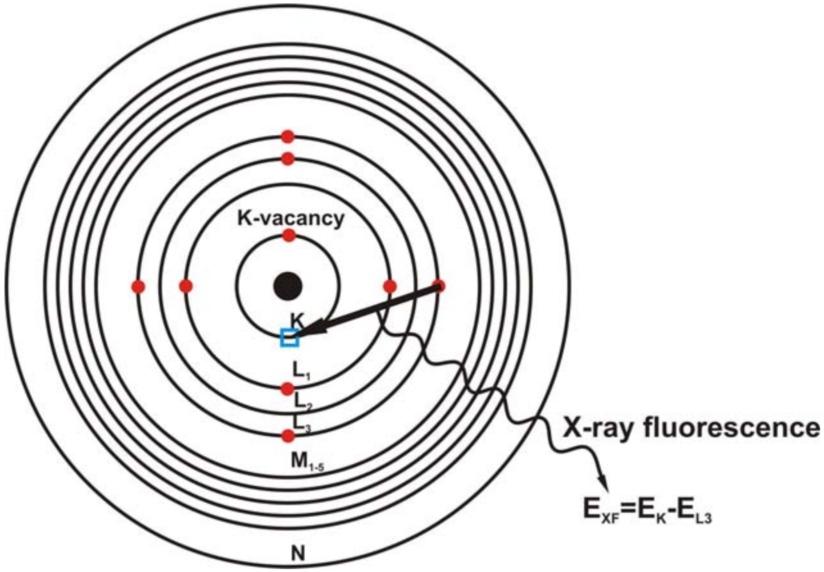
2.2.4 X-Ray Fluorescence Spectroscopy

- **instrumental analytical technique for the elemental analysis of solids and liquids**
- **wide concentration ranges (ppm - %), minimal sample preparation, boron-uranium**
- **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



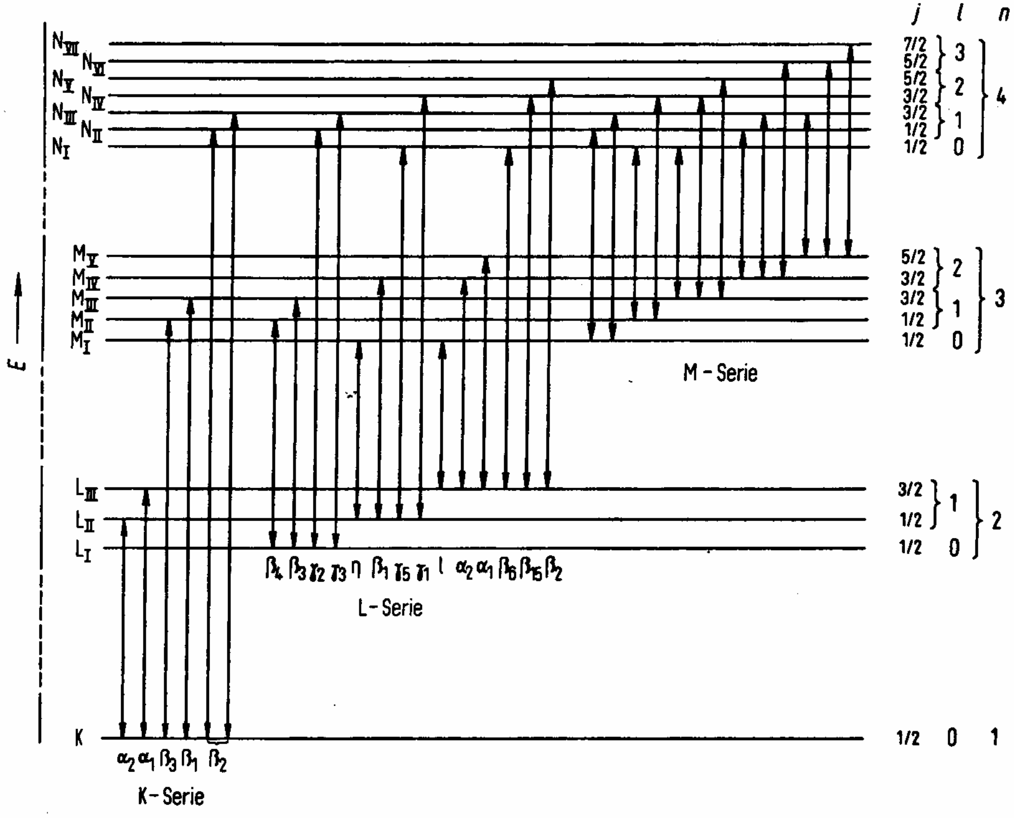
energetic relaxation by X-ray fluorescence

2.3 Spectroscopic Methods

2.2.4 X-Ray Fluorescence Spectroscopy

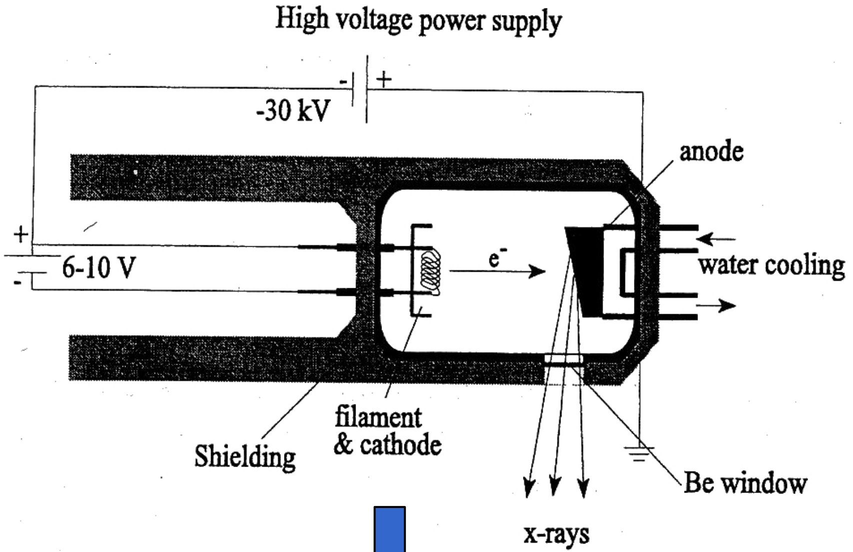
- **transitions are governed by quantum mechanical selection rules (Δn>1, Δl=⌖1, Δj=0,⌖1)**
- **K – lines originate from vacancies in the K – shell, L – lines from vacancies in the L – shell …**
- **denotation of lines:**
  i) IUPAC notation – Fe KL$_3$
  ii) Siegbahn notation – Fe α1
- **line intensities 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$_{5,4}$)**

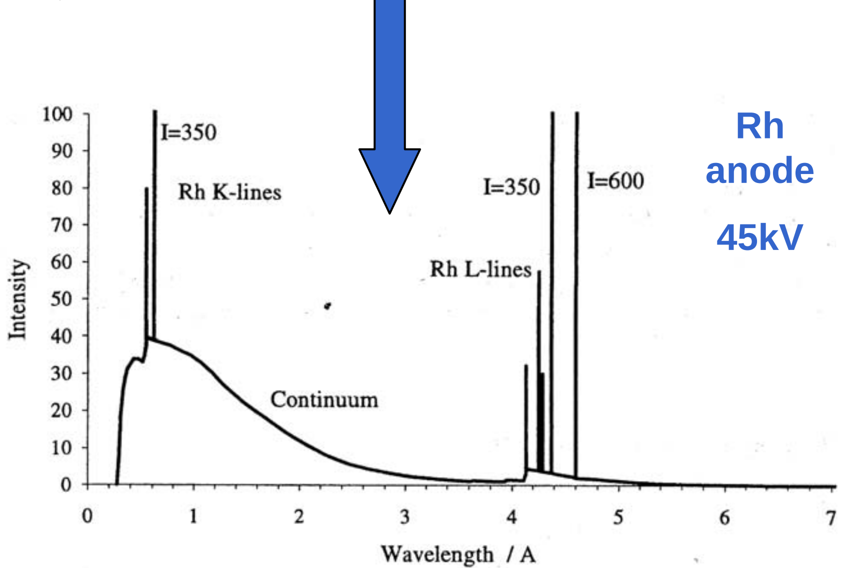
atomic energy levels and allowed transitions



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 ⇒ effective water or air cooling required
- quantitative work ⇒ stable filament heating and accelerating voltage required





Rh anode

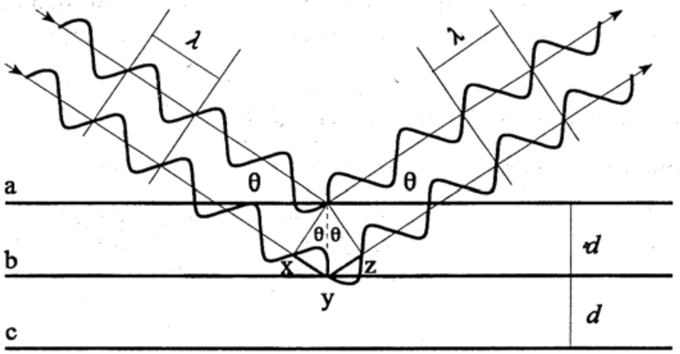
45kV

2.3 Spectroscopic Methods

2.2.4 X-Ray Fluorescence Spectroscopy

instrumentation – wavelength dispersive instruments (WDXRF)

- irradiated sample emits polychromatic X-rays

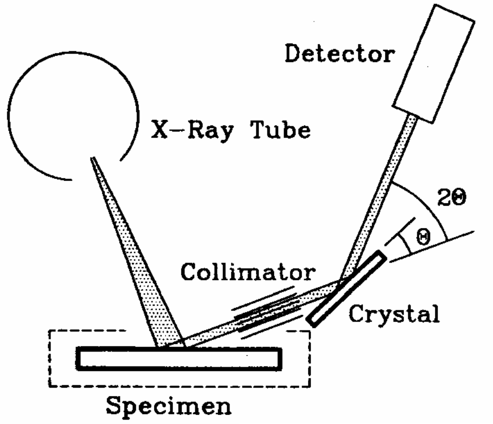


- crystal as dispersive element
- wavelength selection according to Bragg’s law

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

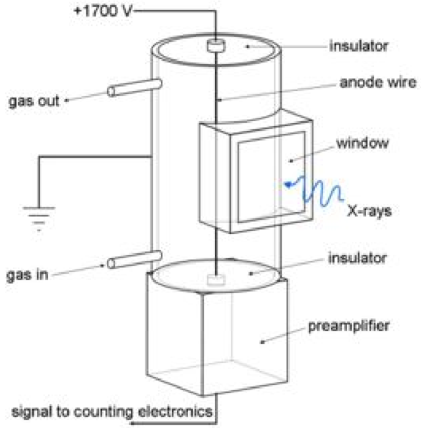
- wavelength scan by varying θ ⇒ rotation of the crystal with respect to the incoming beam

geometric arrangement

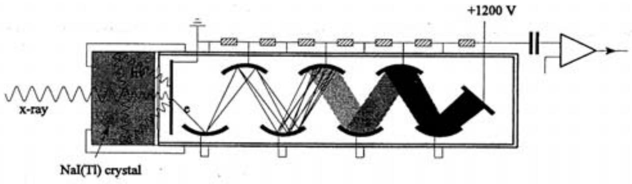


detector

flow proportional counter for low energetic X-rays (<6.2 keV)



scintillation counter for high energetic X-rays (>6.2keV)

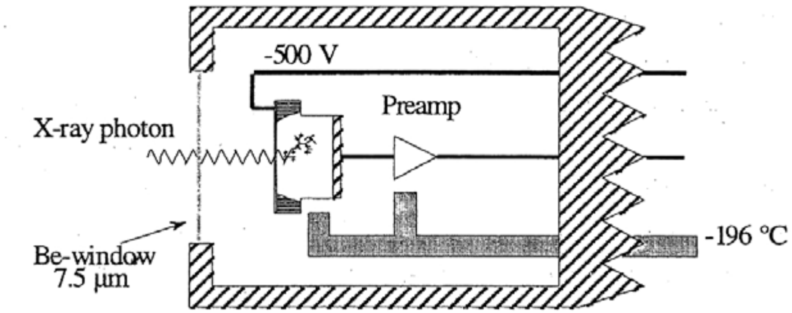


2.3 Spectroscopic Methods

2.2.4 X-Ray Fluorescence Spectroscopy

instrumentation – energy dispersive instruments (EDXRF)

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



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

example

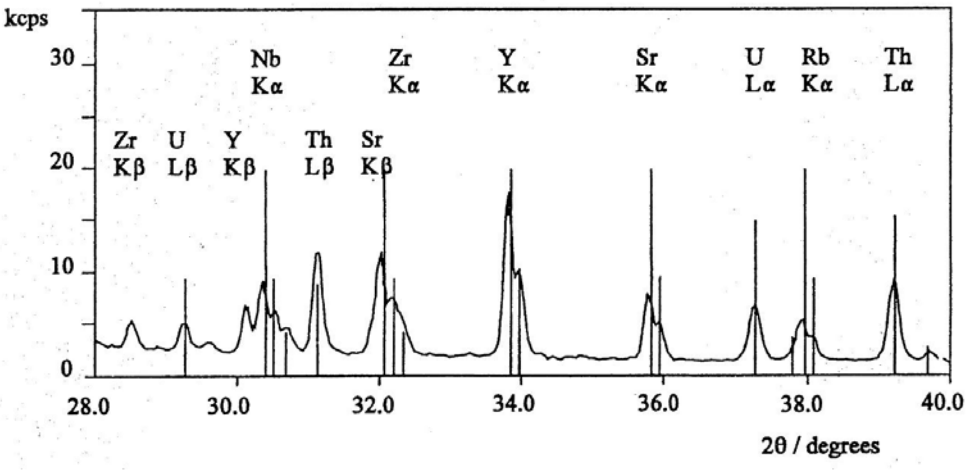
- an Fe K-L3,2 X-ray photon (E=6.400keV) hits a Si detector
- energy to create 1 electron – hole pair = 3.85eV ⇒ creation of 1662 ehp’s
- the preamplifier converts this current in voltage pulse of e.g. 32mV
- a connected ADC translates the amplified pulse height into a digital number, e.g. 320 ⇒ channel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

2.3 Spectroscopic Methods

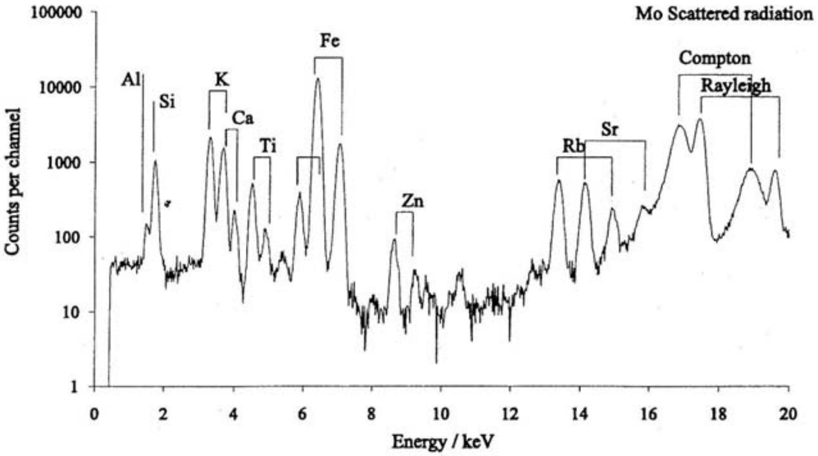
2.2.4 X-Ray Fluorescence Spectroscopy

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

qualitative analysis by XRF



WD-XRF



ED-XRF

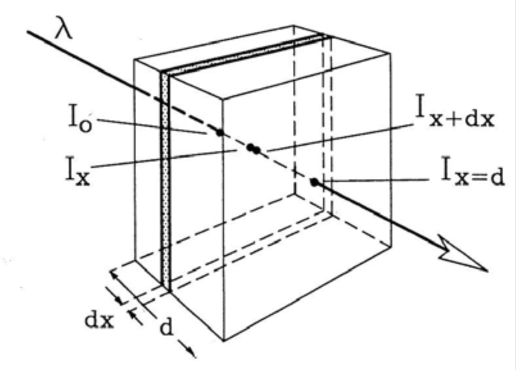
2.3 Spectroscopic Methods

2.2.4 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

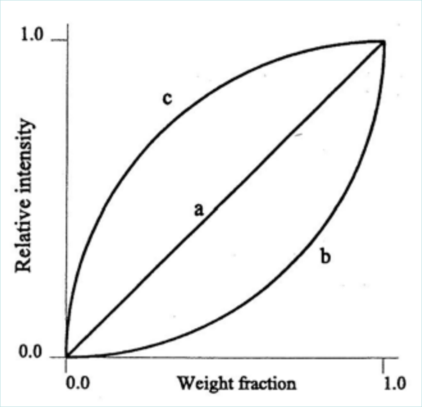
quantitative analysis complicated by

x-ray attenuation



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

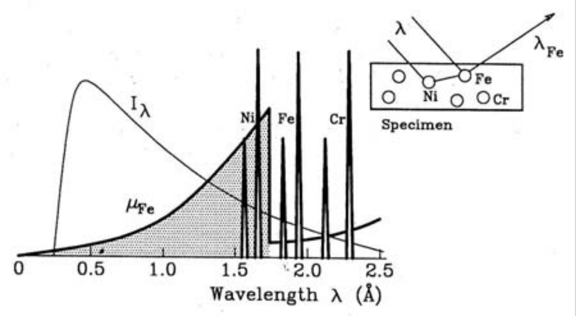
$$\mu_{sample} = \sum_i w_i \mu_i$$



a) no matrix effect
b) attenuation
c) enhancement

fundamental parameters approach (implemented in software)

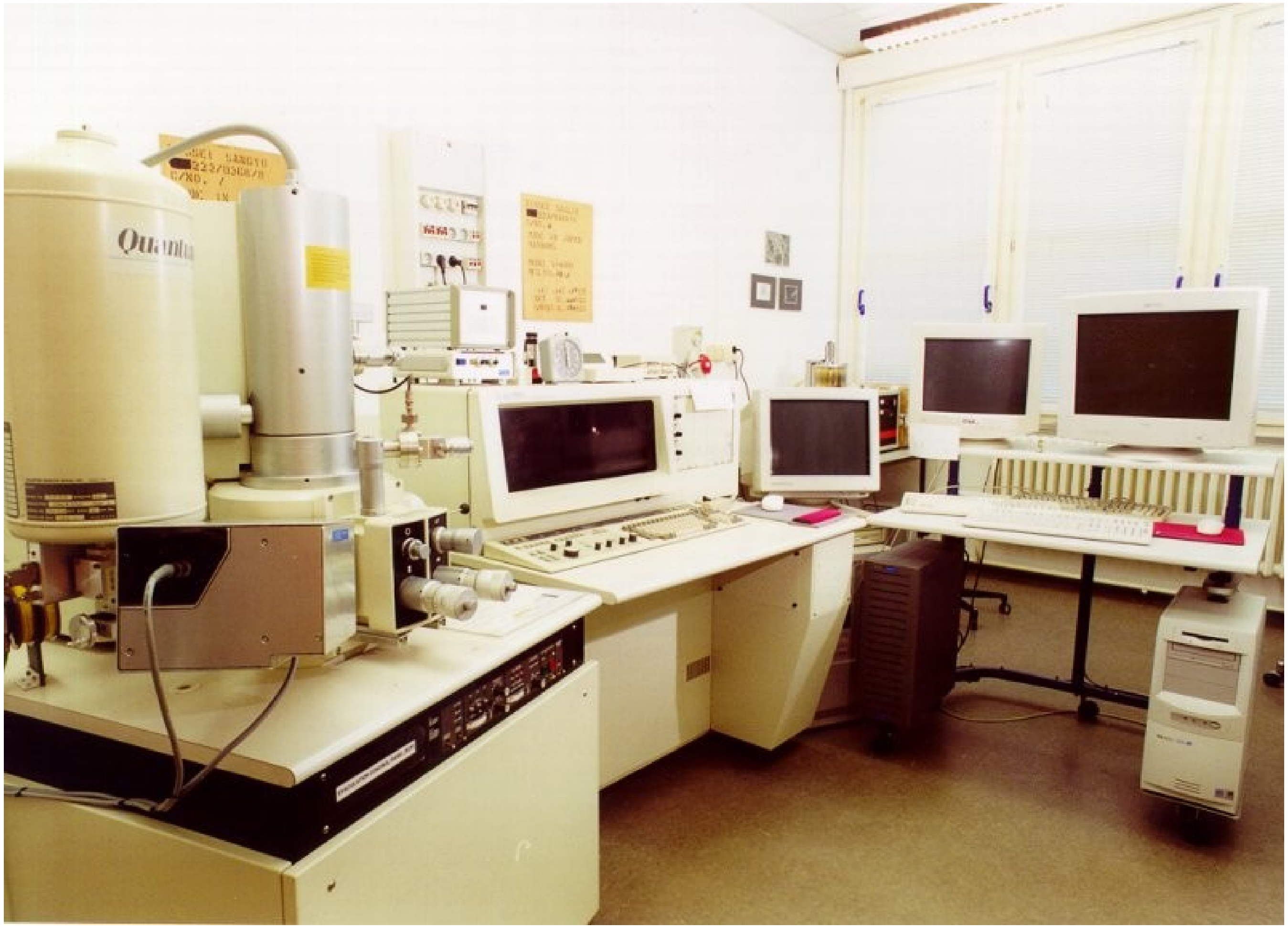
x-ray enhancement



- 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

2.2.5 SEM-EDX

SEM-EDX at the Fritz-Haber-Institute
(Inorganic Chemistry Department)

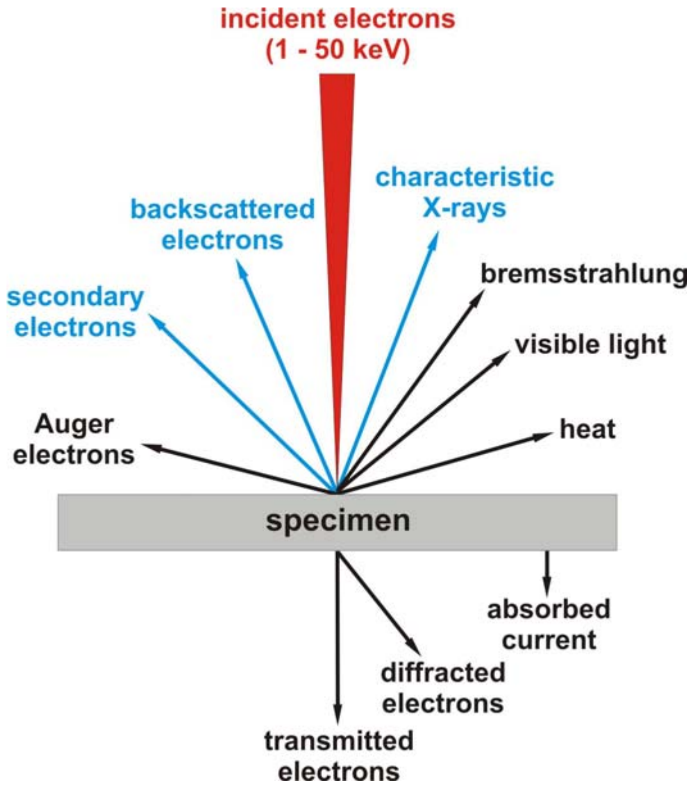


2.3 Spectroscopic Methods

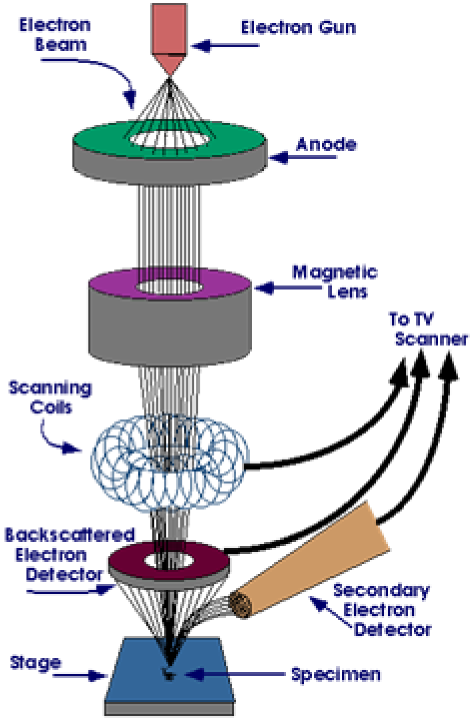
2.2.5 SEM-EDX

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

electron sample interaction



SEM instrumentation

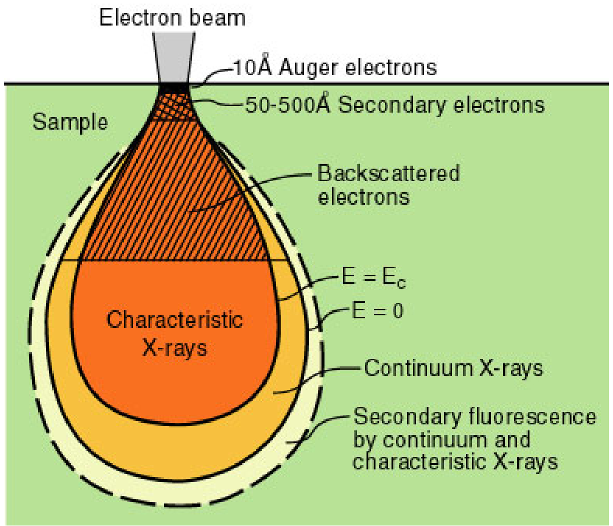


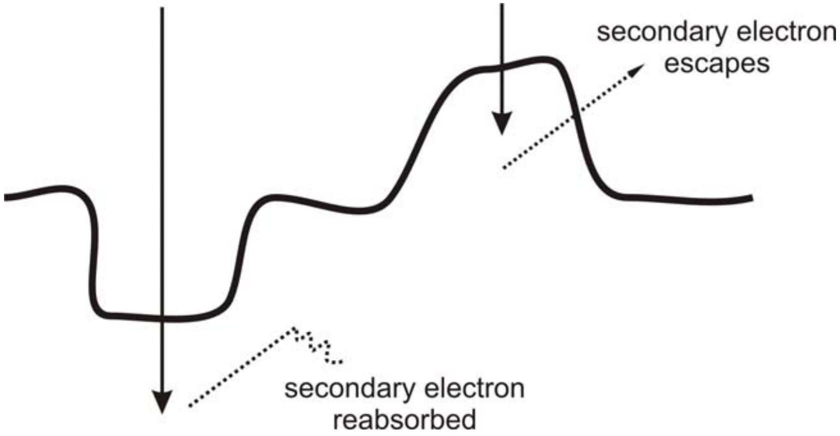
- **topographic sample image by synchronizing the TV – scanner with the scanning coils**
- **X-ray detection by a solid – state detector (Si single crystal) as in XRF (not shown above)**

2.3 Spectroscopic Methods

2.2.5 SEM-EDX

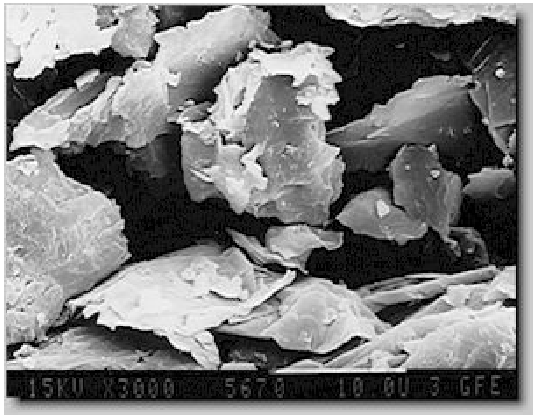
information depths, spatial resolution





- 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

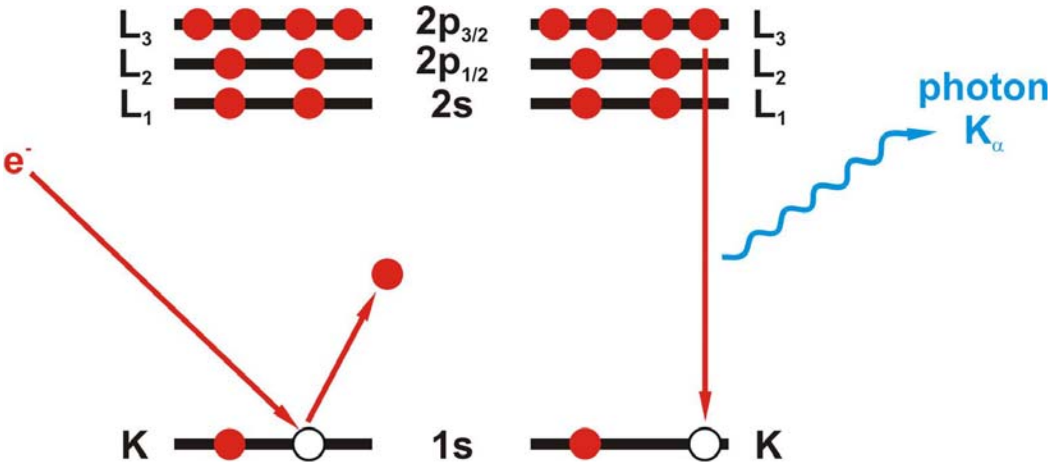


synthetic graphite (25keV, ×3000)

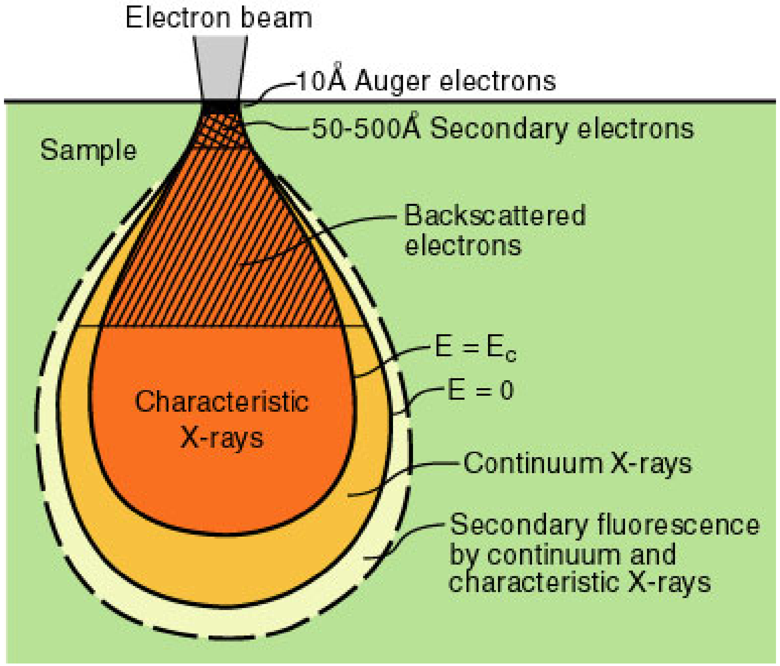
2.3 Spectroscopic Methods

2.2.5 SEM-EDX

X – ray generation



information depths, spatial resolution



- X-ray generation process similar to XRF
- X-ray spatial resolution much lower than by secondary electrons
- information depth from characteristic X-rays in µm range

2.3 Spectroscopic Methods

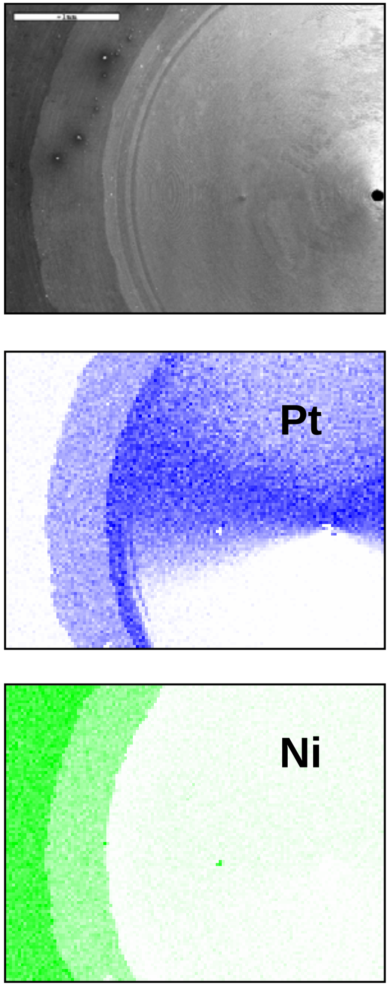
2.2.5 SEM-EDX

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 $\Rightarrow$ 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

<table>
<tr><th colspan="4">analytical methods</th></tr>
<tr><td rowspan="3">absolute methods</td><td colspan="3">relative methods</td></tr>
<tr><td rowspan="2">definite methods</td><td colspan="2">reference methods</td></tr>
<tr><td>direct RM</td><td>indirect RM</td></tr>
<tr><td colspan="3">$y = b\cdot x$</td><td rowspan="2">$y = f(x)$
$y = a+bx$</td></tr>
<tr><td>$b = F$</td><td>$b = k\cdot F$</td><td>$b = y_r/x_r$</td></tr>
</table>

gravimetry

$$m_{A_qB_p} = \underset{\overset{\downarrow}{b}}{\boxed{\frac{M_{A_qB_p}}{q\cdot M_A}}}\cdot m_A$$

photometry

$$A_\lambda = \overset{\overset{b}{\uparrow}}{\boxed{\varepsilon_\lambda \cdot d}}\cdot c_A$$

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

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

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

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

- verbal: with a probability of P is the concentration x of the analyte A in the concentration range $\overline{x} \pm \Delta\overline{x}$
- 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

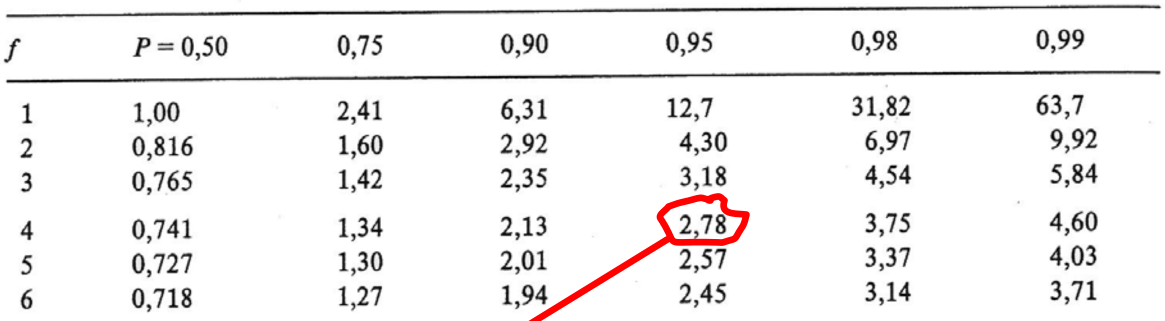
example 1: gravimetric determination of Fe_2O_3 in an iron ore

- **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) $\Rightarrow$ 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

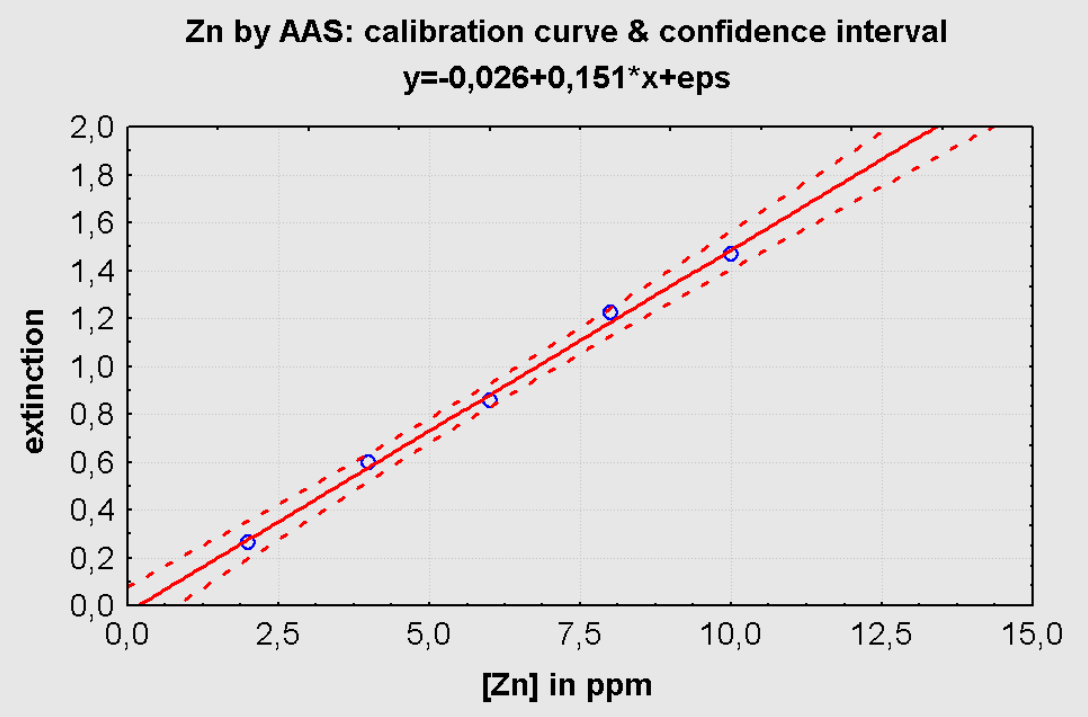
$$y = \hat{a} + b\hat{x}$$

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

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

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

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



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

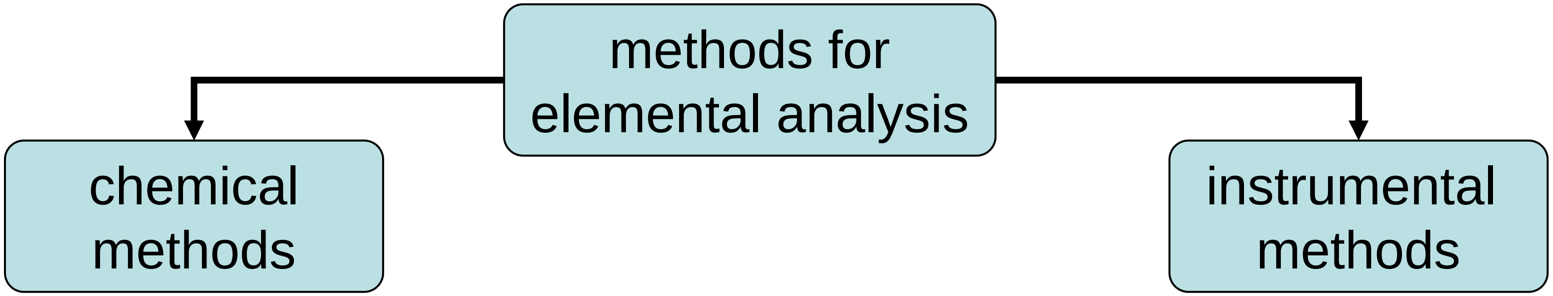
- calculation of $$\Delta\bar{x} = t(P, f)\cdot\frac{s_0}{\hat{b}}\cdot\sqrt{\frac{1}{m} + \frac{1}{n_p} + \frac{\left(\bar{x} - \bar{\bar{x}}\right)^2}{\sum_i \left(x_i - \bar{\bar{x}}\right)^2}}$$

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

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

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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Chemical (Elemental) Analysis

Thank You For Your Attention