Characterization of Catalysts and Surfaces

Elemental Analysis
(ICP, AAS etc.)

Fall Semester 2016

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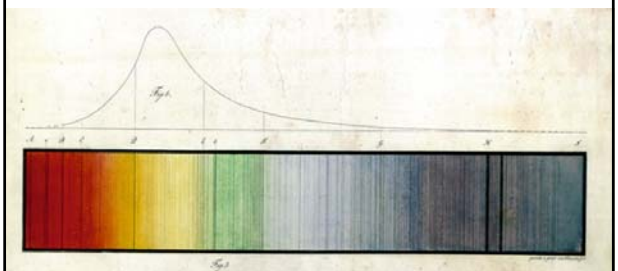
Outline

- Instrumental Methods for Determination of the Elements
  - Atomic Absorption Spectrometry - AAS
  - Inductively Coupled Plasma Optical Emission Spectrometry - ICPOES
  - Inductively Coupled Plasma Mass Spectrometry - ICPMS
- Sample Preparation Techniques
- Considerations for Quantitative Analysis

Common Aspects

- Solution-based Techniques
  - Usually aqueous
  - Usually acidified (HNO_3, HCl; 1-10 Vol.%)
  - Digestion of solids required
- Calibration required
  - External standards / Standard Addition
  - Matrix-matching may be required
  - Internal standards (when applicable)

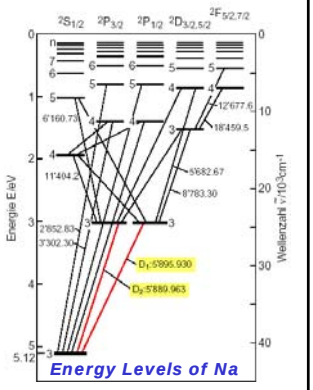
Atomic Absorption Spectrometry



Gaseous atoms can absorb electromagnetic radiation corresponding to the ΔE of their electronic states

Atomic Absorption

- Photons of sufficient energy excite electrons to higher levels
- Excitation is most likely for "resonant" photon, i.e.: hν = ΔE



Energy Levels of Na

Atomic Absorption Spectrometry

The magnitude of this absorption is given by ***Lambert-Beer's*** *law:*

$$I = I_0 e^{-\varepsilon_\lambda L c}$$

$$E = \lg \frac{I_0}{I} = \varepsilon_\lambda L c$$

I: Intensity registered in presence of an absorber (analyte atom)
I_0: Intensity registered in absence of an absorber (analyte atom)
ε_λ: Absorption coefficient
λ: Wavelength registered
L: Observation path length
c: Concentration of the analyte
E: Extinction (evaluated signal)

AAS (and ICPOES) operate in the UV-VIS range, ≈ 200 – 800 nm

Atomic Absorption Spectrometry

So what do we need for an AAS Experiment?

1) Gaseous Atoms → Flame or Furnace

2) Photon source → line- or continuous
(ideally resonant hν) (HCL, EDL or arc)

3) Optical Spectrometer
(Monochromator, Detector)

Atomic Absorption Spectrometry

Flame Atomizer

Oxidants: Air, N_2O, O_2
Fuel: Acetylene, H_2, CH_4, C_3H_8

Oxidant	Fuel	T, °C
Air	CH_4	1875
Air	C_2H_2	1930
Air	H_2	2045
Air	Acetylene	2300
N_2O	Acetylene	2750
O_2	H_2	2660
O_2	Acetylene	3100

Furnace Atomizer

Electrically heated up to 2700 °C

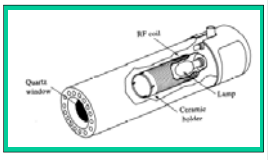
Atomic Absorption Spectrometry

Line Sources

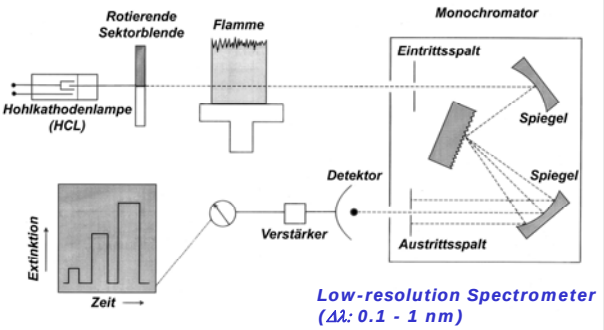
Element-specific emission spectra

Hollow Cathode Lamp
HCL

Electrodeless Discharge Lamp
EDL



Atomic Absorption Spectrometry



Low-resolution Spectrometer
(Δλ: 0.1 - 1 nm)

Atomic Absorption Spectrometry

Spectral Interferences

Absorption (atomic or molecular)
Scattered radiation
→ Background correction required:
D_2-Lamp, Zeeman-effect

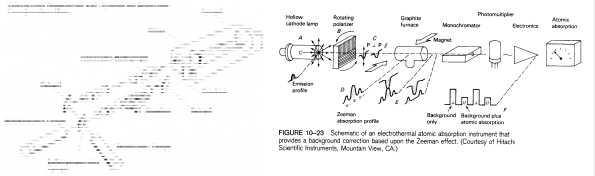
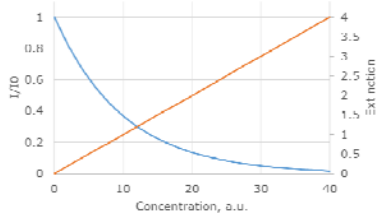


FIGURE 10–23 Schematic of an electrothermal atomic absorption instrument that provides a background correction based upon the Zeeman effect. (Courtesy of Hitachi Scientific Instruments, Mountain View, CA.)

Atomic Absorption Spectrometry

Limited dynamic range

Small change of I/I_0 when the extinction exceeds ≈ 1
→ Higher uncertainty of the concentration.

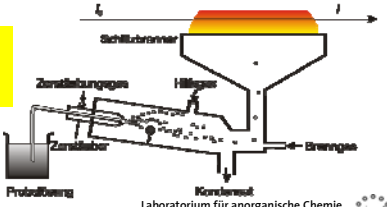


Atomic Absorption Spectrometry

Flame AAS Principle

Sample is nebulized and aerosol transferred to burner.
Optimization:
- Fuel/Oxidant gas flow rates
- Observation height

Temperature
Particle formation
Residence time

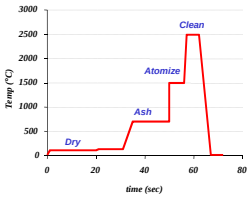


Atomic Absorption Spectrometry

Furnace AAS

Sample is pipetted into furnace (addition of modifier) and T-program started.
Optimization:
- T-program: Drying, Ashing, Atomization, Cleaning
- Modifier type and amount

Separation of Analyte from sample matrix and Solvent.
Efficient vaporization.



Common Modifiers:
$Mg(NO_3)_2$, $Pd(NO_3)_2$,$NH_4H_2PO_4$

Atomic Absorption Spectrometry

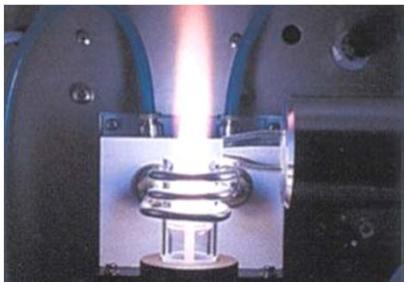
Characteristics

	Flame AAS	Furnace AAS
Sample Volume	mL	µL
Analysis Time	seconds	minutes
Calibration[1]	Ext./Std.Add.	Std.Add.
Limits of Detection[2]	0.1 – 1000 µg/L	0.001 -10 µg/L
Repeatability[3]	1-5 %	1-5 %

1: Ext: External Calibration, Std.Add.: Standard Addition
2: Depends on Element, Matrix, Analysis Time
3: For Concentrations > 100×LOD

ICP-Optical Emission Spectrometry

ICP: Inductively Coupled Plasma
An Rf-powered electrodeless gas (Ar) discharge,
reaching Temperatures of 10000K



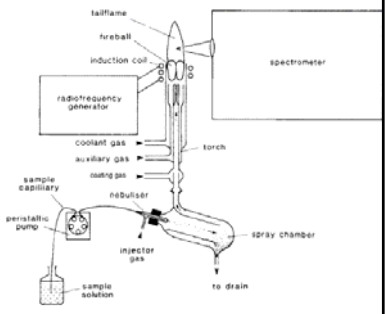
ICP-Optical Emission Spectrometry

Setup

Nebulizer Gas: ≈ 1 L/min Ar
Auxiliary Gas: ≈ 1 L/min Ar
Coolant Gas: ≈ 14 L/min Ar

Rf-Power: 100o -1500 W
Rf Frequency: 27, 40 MHz

Sample uptake: ≈ 1 mL/min
Nebulizer Efficiency: 3 – 5 %



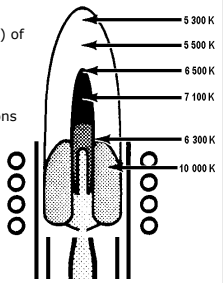
ICP-Optical Emission Spectrometry

Characteristics

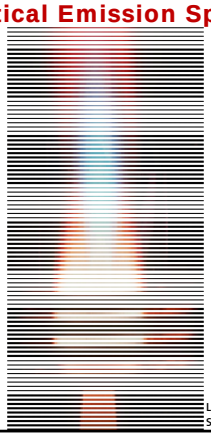
Sample aerosol is injected in a narrow region (≈2 mm) of very high Temperature:

- → Efficient atomization
- → Ionization
- → Generation of electronically excited Atoms and Ions

Relaxation of excited states leads to detecable emission signals

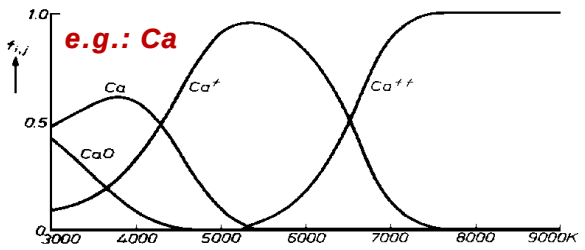


ICP-Optical Emission Spectrometry



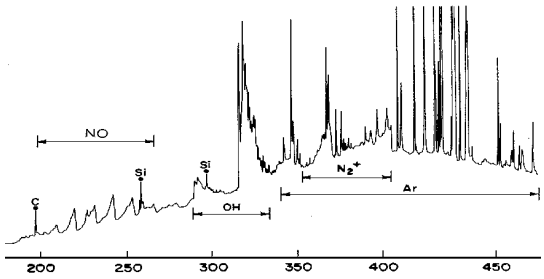
ICP-Optical Emission Spectrometry

Elemental Species vs. T



ICP-Optical Emission Spectrometry

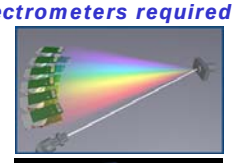
ICP Background Emission



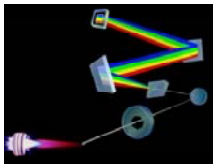
ICP-Optical Emission Spectrometry

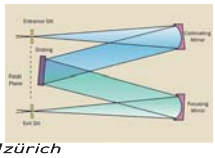
High-resolution Optical Spectrometers required

$\Delta\lambda$: ≈ 10s of pm
Polychromators providing simultaneous access to the UV-VIS spectral range (≈130/180 – 800 nm)
→ Paschen Runge Setup
→ Echelle Configuration



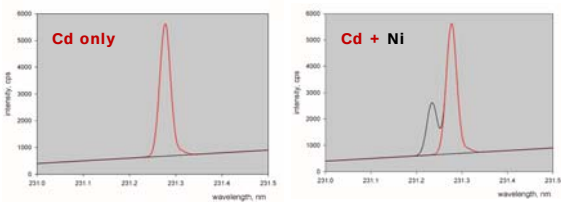
Monochromators
→ Czerny Turner Configuration
(barely used in current instruments)





ICP-Optical Emission Spectrometry

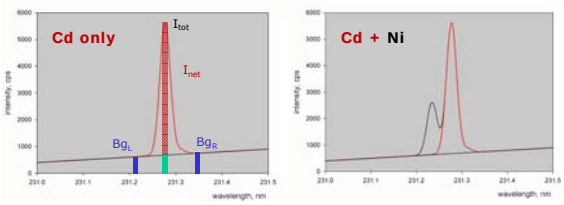
High-resolution Optical Spectrometers required



Identification and Correction of Spectral interferences

ICP-Optical Emission Spectrometry

Simultaneous Spectrometers advantageous

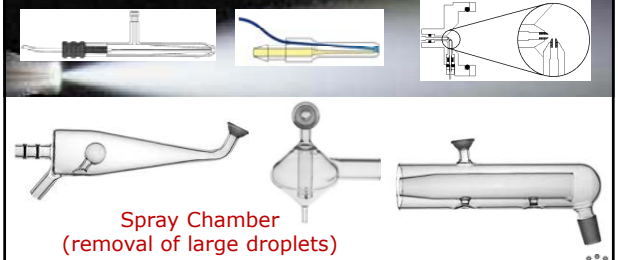


- **Correlated acquisition allows for better compensation of fluctuating baseline and interference signals.**
- **Internal Standard(s) can be monitored simultaneously**

ICP-Optical Emission Spectrometry

Sample Introduction Methods

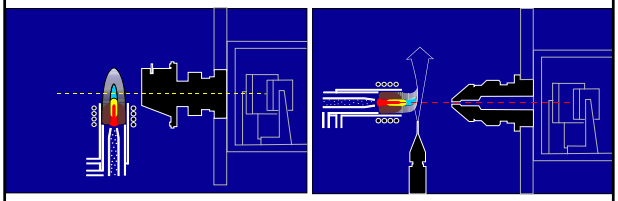
Pneumatic Nebulizer
(aerosol generation)



Spray Chamber
(removal of large droplets)

ICP-Optical Emission Spectrometry

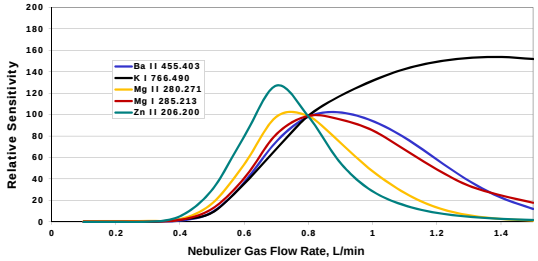
Plasma View: Radial vs. Axial



Robust against Matrix	≈ 10x higher Sensitivity
Simpler Setup	Lower Background
Lower Analyte Sensitivity	Better LODs
	Stronger Matrix Dependence

ICP-Optical Emission Spectrometry

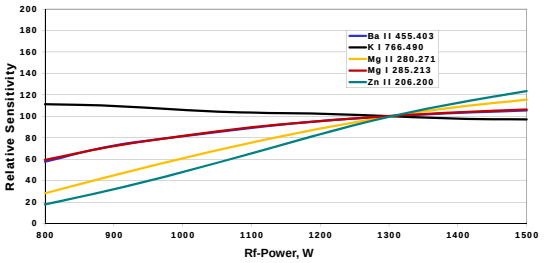
Optimization



I: Atom Line, II: Ion Line

ICP-Optical Emission Spectrometry

Optimization



I: Atom Line, II: Ion Line

ICP-Optical Emission Spectrometry

Effects of Increasing Plasma Temperature:

- More efficient vaporization and excitation
  - Higher Analyte Signal
  - Less Matrix Effects
  - More Potential Spectral Interferences
- Increasing degree of ionization
  - More intense Ion Lines
  - Less intense Atom Lines
  - More Potential Spectral Interferences
- Increasing background emission
  - Lower Signal / Noise
- Mechanical Stress / Erosion of the Torch

ICP-Optical Emission Spectrometry

Typical Limits of Detection

Pneumatic Nebulizer, Radial Plasma View

> 10 µg/l
1- 10 µg/l
0.1 - 1 µg/l

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra																

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

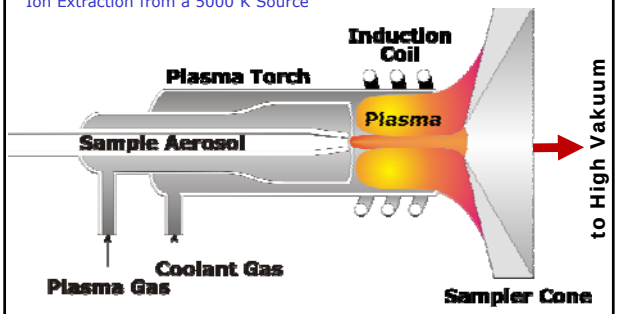
ICP-Optical Emission Spectrometry

Limitations:

- **Sample Composition can Influence Emission Signal**
  - **More pronounced with Axial View**
  - **Enhancment and Suppression can occur**
- **Line-rich Spectra from many Transition Elements**
  - **Interference Control Mandatory**
  - **Background Signals may vary between Samples**
- **Deposition of dissolved Solids can cause Memory Effects**
  - **Long Rinse Times**
  - **Application-Specific Sample Introduction Systems**

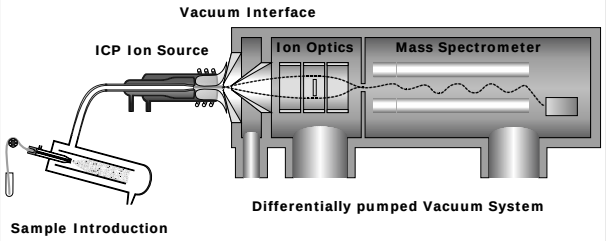
ICP-Mass Spectrometry

Ion Extraction from a 5000 K Source



ICP-Mass Spectrometry

Setup



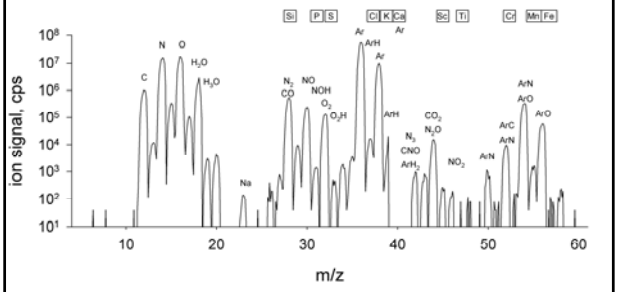
ICP-Mass Spectrometry

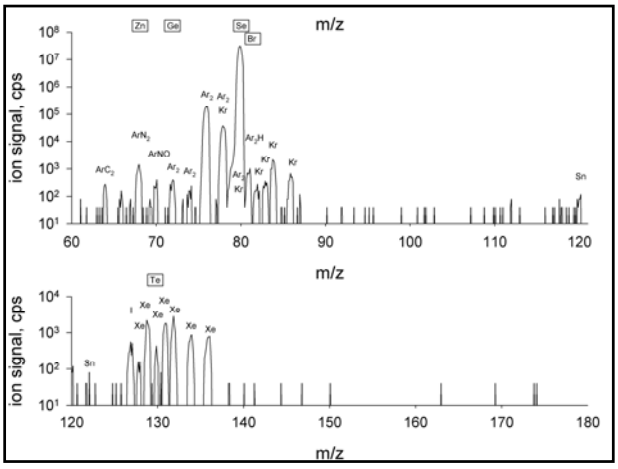
Why ICPMS?

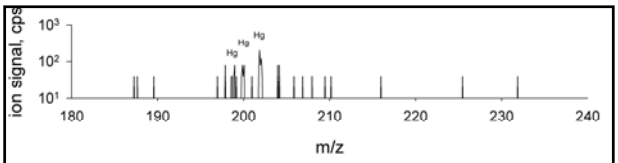
- **Eventually lowest instrumental background**
- **High ion yield for most elements**
  - **→ Low Limits of Detection**
- **Less, and easier to predict spectral inerferences**
- **Isotope Information**
- **Various Sample Introduction Methods**
- **Up to 12 Orders of Magnitude Linear Dynamic Range**

ICP-Mass Spectrometry

Intrumental Background







Typical Background Contributions:

→Plasma Gas: Ar^+, Ar_2^+ $Ar^{(2-4)+}$ etc.

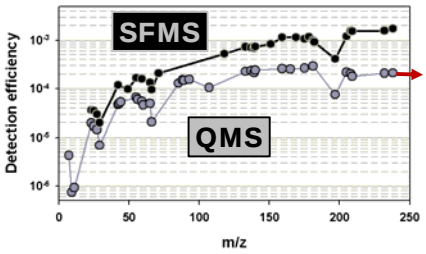
→Impurities in the Gas and ambient Air:
C^+, N^+,O^+,H_2O^+ Kr^+, Xe^+, (Hg^+, Sn^+, Pb^+)

→Deposits in Torch, Interface:
Alkaline Metals (e.g. Na^+), Sample Matrix, Si^+

→Molecular and Cluster Ions:
C_2^+, N_2^+, $C_xO_y^+$, $N_xO_y^+$, $Ar_yH_x^+$, ArC_x^+, ArN_x^+, ArO_x^+, ArN_x^+.....

ICP-Mass Spectrometry

Ion Yield



1 ion detected requires 20000 atoms in the source

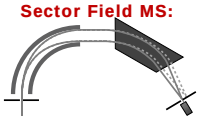
ICP-Mass Spectrometry

MS Types

Quadrupole MS:

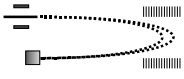
Ion Transmission: Moderate
Mass Resolving Power: 0.7 m/z
Acquisition: Sequential (0.1 ms / peak)

Sector Field MS:



Ion Transmission: High
Mass Resolving Power: 300 – 12000
Acquisition: Slow Sequential
(0.1 ms – 300 ms/ peak)

Time of Flight MS:

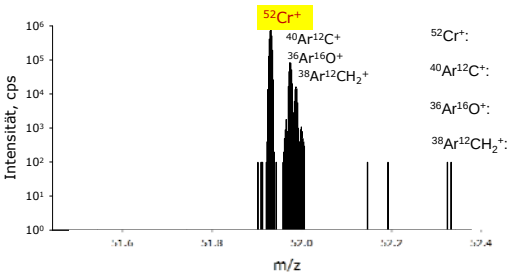


Ion Transmission: Moderate
Mass Resolving Power: ≈4000
Acquisition: Simultaneous
Measurement Speed:0.033 ms / Spectrum

ICP-Mass Spectrometry

High-Resolution Advantage

At least 5 different Species in a 1 m/z Mass Window



$^{52}Cr^+$: 51.93996

$^{40}Ar^{12}C^+$: 51.961833

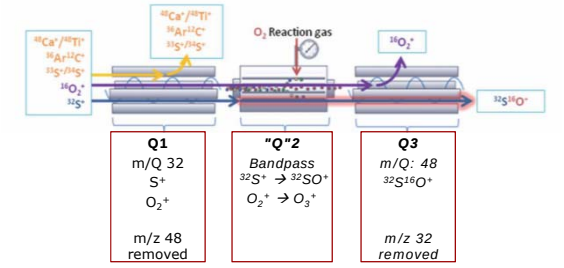
$^{36}Ar^{16}O^+$: 51.961911

$^{38}Ar^{12}CH_2^+$: 51.977832

ICP-Mass Spectrometry

"High Mass Resolution" with Quadrupole MS

Chemical manipulation of the Ion Beam Composition:
Ion-Molecule Reactions, MS-MS mode



ICP-Mass Spectrometry

Limitations

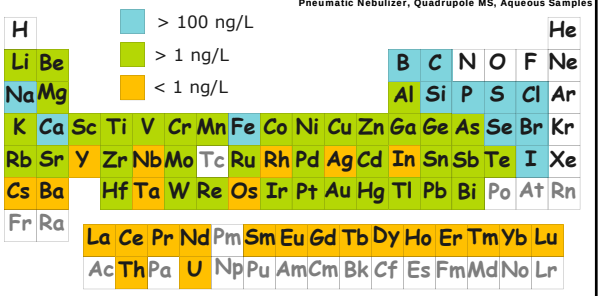
Matrix Effects are more severe:

- **Spectral Interferences**
  - **Limits the Choice of Solvents**
    (H_2SO_4, H_3PO_4 should be avoided, HCl only when absolutely needed)
- **Deposits at Vacuum Interface can cause Instrument Drift**
  - **Limits the Content of dissolved Solids**
    (1 g/L generally considered maximum)
- **«Space Charge» Effects from high Ion Currents**
- **Changes in Ion Yield:**
  - **Signal Suppression (e.g. Easily Ionized Elements)**
  - **Signal Enhancement (e.g. changes in Space Charge)**

ICP-Mass Spectrometry

Typical Limits of Detection

Pneumatic Nebulizer, Quadrupole MS, Aqueous Samples



ICP-based Spectrometries

Characteristics

	OES	MS
Sample Volume	mL	µL-mL
Analysis Time	seconds	seconds
Matrix Tolerance[1]	high (%)	low (<0.1%)
Calibration[2]	Ext./Std.Add.	Ext./Std.Add./ID
Repeatability[3]	1-5%	1-5%
Dynamic Range	10^6	10^9-10^{12}

1: Values in Brackets indicate the tolerable Dissolved Solids Content
2: Ext: External Calibration, Std.Add.: Standard Addition, ID: Isotope Dilution
3: For Concentrations > 50×LOD

Calibration

Methods

- **External Calibration**
  - **Synthetic Solutions of the Analyte(s)**
  - **Matrix-Matching may be required**
  - **Internal Standards recommended (ICP-based methods)**
- **Standard Addition**
  - **Addition of Synthetic Solutions of the Analyte(s) to Aliquots of the Sample**
  - **Ideal Matrix-Matching**
  - **Time-consuming**
- **Isotope Dilution**
  - **Only with MS**

Calibration

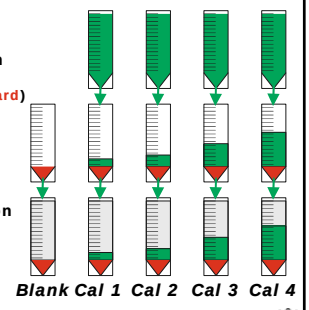
External Calibration

Known Amounts of Primary Standard(s) are filled into clean vials
(eventually with an Internal Standard)

Ideal to use different Supplies

Dilution to desired Concentration using a suitable Solvent

Mix!

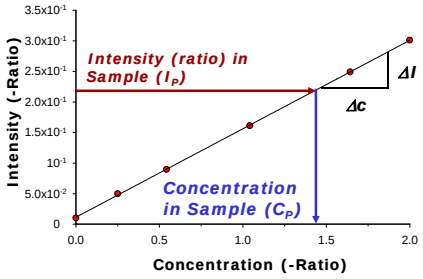


Calibration

External Calibration

$$C_P = \frac{I_P - I_0}{S}$$

$$S = \frac{\Delta I}{\Delta C}$$



Calibration

External Calibration

+ *Simple*
+ *Practically all Elements accessible*
+ *Practically all Sample Types accessible*
+ *Internal Standard can be easily included*
+ *Concentration range only limited by Solubilities*

- *Spectral Interferences need to be absent or corrected for*
- *Matrix Effects and Instrument Drift have to be monitored and corrected for*

Calibration

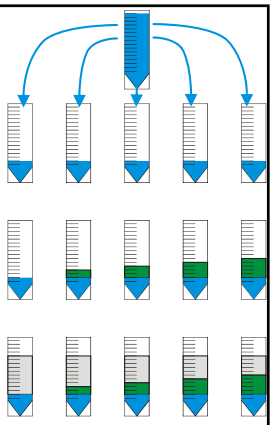
Standard Additions

Sample splitted to identical Aliquots
→ minimum 3, ideal 5

Addition of known amounts of a Standard Solution

Dilution to desired Concentration using a suitable Solvent

Mix!



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Calibration

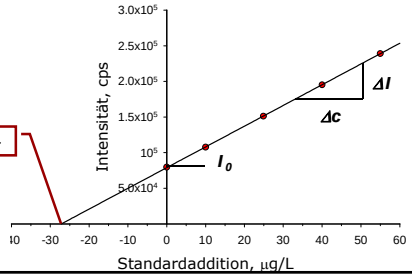
Standard Additions

Round Roin Test
IMEP-16, IRMM
Pb in Wine

$$C_P = \frac{I_0}{S}$$

$$S = \frac{\Delta I}{\Delta C}$$

27.15 ± 0.45 µg/L



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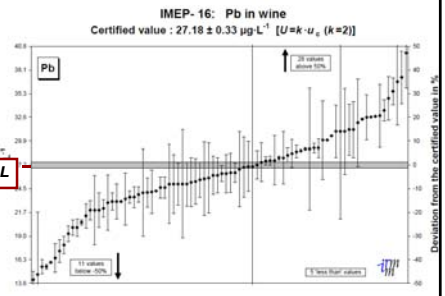
Calibration

Standard Additions



27.15 ± 0.45 µg/L

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Calibration

Standard Additions

+ *Matrix Effects can be eliminated*

- *Spectral Interferences need to be absent or corrected for*
- *Labour intensive*
- *Approximate Concentration needs to be known*
- *Long measurement times*
- *Instrument Drift is not compensated for (may require another internal Standard)*

Calibration

Isotope Dilution (MS only)

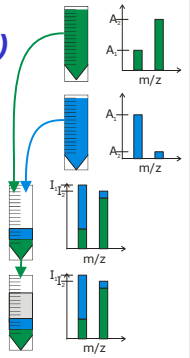
Unknown Sample with «Natural» Isotope Ratio

Isotopically enriched Standard

Aliquots of exactly known amount are mixed

Dilution to desired Concentration using a suitable Solvent

Mix!

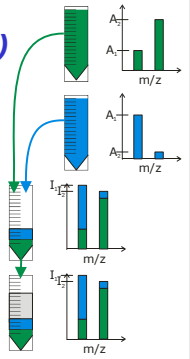


Calibration

Isotope Dilution (MS only)

$$R_P = \frac{A_{1P}}{A_{2P}} \qquad R_S = \frac{A_{1S}}{A_{2S}} \qquad R_M = \frac{I_{1M}}{I_{2M}}$$

$$C_P = C_S \times \frac{V_S}{V_P} \times \frac{R_S - R_M}{R_M - R_P} \times \frac{A_{1P}}{A_{1S}}$$



Calibration

Isotope Dilution (MS only)

+ *"Goldstandard" of Calibration*
+ *Optimum internal Standard*
+ *Ideal Compensation of Matrix Effects*
+ *SI-Traceable*

- *High experimental Effort*
- *Not Applicable with Mono-Isotopic Elements*
- *Spectral Interferences must be absent or corrected for*
- *Enriched Standards not readily available*
- *Instrument Drift not easily compensated for*

Sample Preparation

Aqueous Solutions

Stabilization of the Elements in Solution

→ *Usually Acidification with HNO_3 (Saturation of Cation-Exchange positions of the Container and Sample Introduction)*

→ *Specific Stabilizers may be required, depending on Chemistry*

Dilution to suitable matrix concentration

→ *Depends on Analytical Method*

Addition of Internal Standard(s)

Sample Preparation

Organic Solvents

High variability of Viscosity, Surface Tension and Evaporation Rates causes issues with Nebulization

→ *Sample uptake Rate needs to be controlled*

Calibration Standards not readily available

ICP methods are less tolerant to Organic Solvents

→ *Digestion*

→ *Addition of trace amounts O_2 to the ICP to avoid Soot formation*

Sample Preparation

Solids

Conventional Methods require Digestion using a suitable Reagents

Most frequently an Acid Cocktail

→ ***HNO_3 (HCl, HF if necessary; H_2SO_4 should be avoided)***

Suitable Digestion Methods are available for most Materials

→ ***Reagents and Digestion Vials need to be of sufficient Purity***

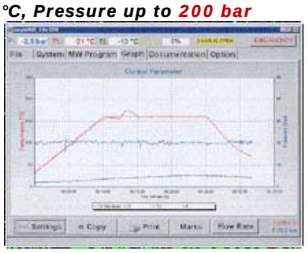
Direct Solids analysis using Laser Ablation ICPMS or Solid Sampling GFAAS

Sample Preparation

Common Digestion Methods

Microwave assisted High Pressure, High Temperature Digestion

→ ***Temperature up to 200 °C, Pressure up to 200 bar***



Sample Preparation

Common Digestion Methods

Oven-heated High Temperature, High Pressure Systems

Sample Preparation

Common Digestion Methods

All Material in Contact with Sample and Reagents must be Inert and Clean

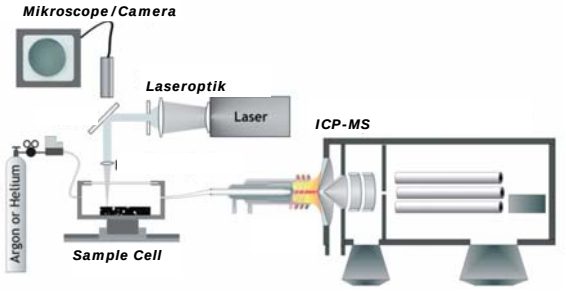
- → ***Mostly Fluoropolymers: PTFE, PFA, etc.***
- → ***(Quartz)***

Evolution of Gas (e.g. Oxidation of Organic Material) can lead to sudden Pressure Jump

- → ***Sample loss via the Safety Relief Valve / Rupture Disk***
- → ***Potential Safety Hazard***

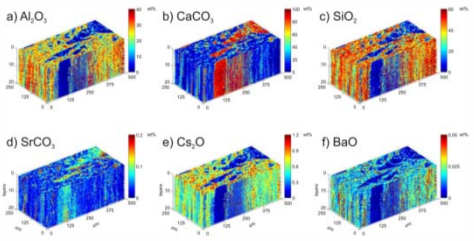
Sample Preparation

Direct Solid Sampling with LA



Sample Preparation

Direct Solid Sampling with LA



2-D and 3-D Element Distributions at 5 µm Spatial Resolution

Method Development

Considerations

- ***Accuracy of the Analysis***
- ***Concentration Range***
- ***Techniques used***
- ***Reproducibility***
- ***Sample Throughput***
- ***Cost***

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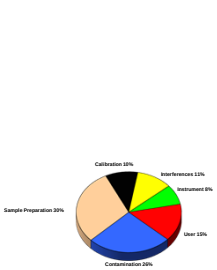
Method Development

Sources of Error in Trace Element Analysis



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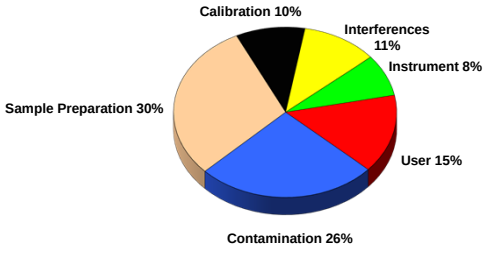
Method Development

Sources of Error in Trace Element Analysis



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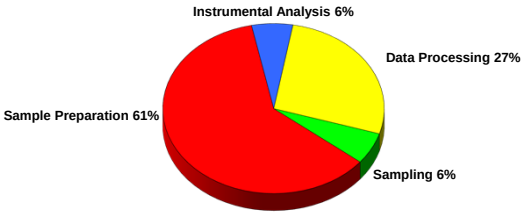
Method Development

Time Spent



Method Development

Validation

Ensuring Representative Analytical Results

- → ***Validate Representativeness of Subsamples***
  - ***Sampling Theory***
- → ***Validate Accuracy of Calibration***
  - ***Recovery Check Analyses***
  - ***Serial Dilution***
  - ***Matrix Evaluation***
  - ***Analysis of Certified Reference Materials***
- → ***Evaluate Reproducibility of Results***
  - ***Duplicate Analyses (randomized)***
  - ***Repeated Calibration***