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

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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)

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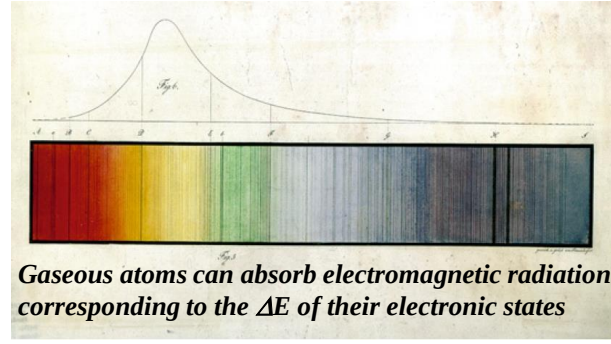
Atomic Absorption Spectrometry



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

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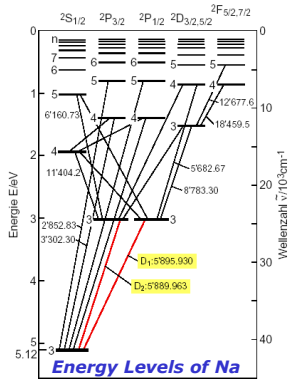
Atomic Absorption

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



Energy Levels of Na

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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

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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

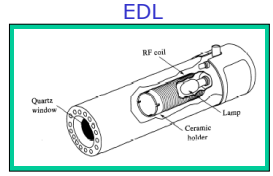
Atomic Absorption Spectrometry

Line Sources

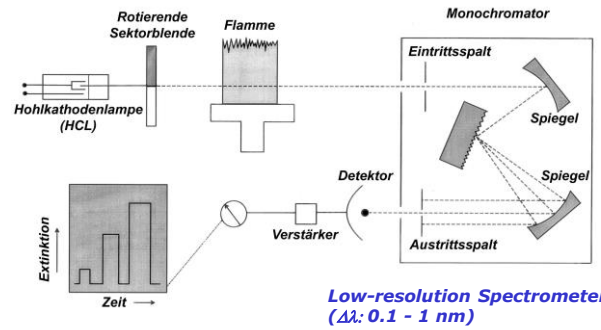
Element-specific emission spectra

Hollow Cathode Lamp
HCL

Electrodeless Discharge Lamp
EDL



Atomic Absorption Spectrometry

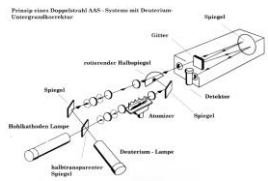


Low-resolution Spectrometer (Δλ: 0.1 - 1 nm)

Atomic Absorption Spectrometry

Spectral Interferences

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



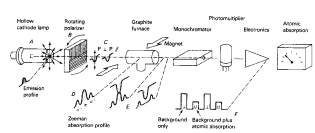
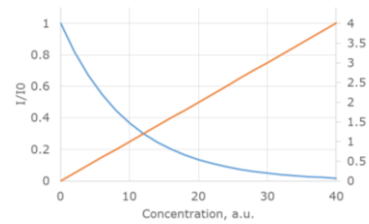


FIGURE 10–23 Schematic of an electrothermal atomic absorption instrument that provides a background correction based upon the Zeeman effect. (Courtesy of Hitachi Scientific Instruments, Mountain View, CA.)

Atomic Absorption Spectrometry

Limited dynamic range

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

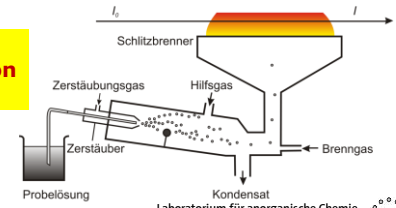


Atomic Absorption Spectrometry

Flame AAS Principle

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

Temperature
Particle formation
Residence time



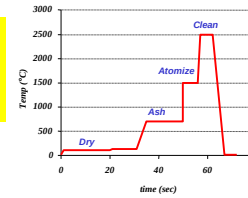
Atomic Absorption Spectrometry

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

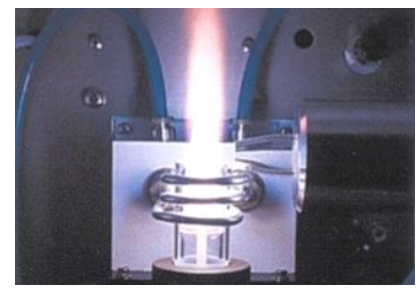
Characteristics

	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



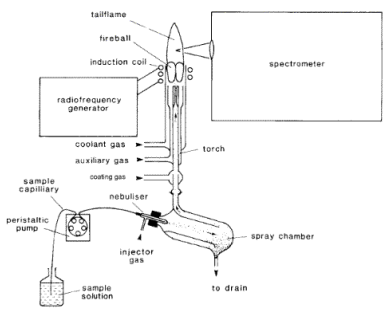
ICP-Optical Emission Spectrometry

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 %



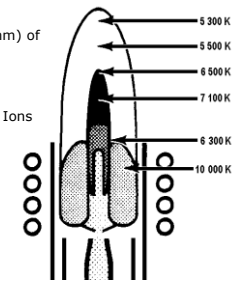
ICP-Optical Emission Spectrometry

Characteristics

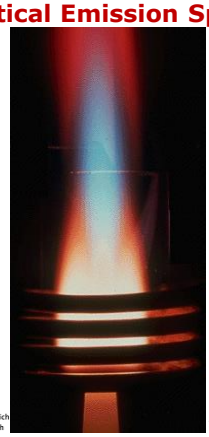
Sample aerosol is injected in a narrow region (≈2 mm) of very high Temperature:

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

Relaxation of excited states leads to detecable emission signals

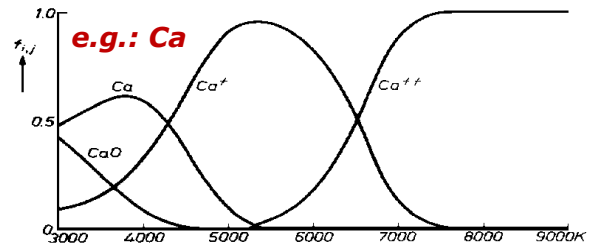


ICP-Optical Emission Spectrometry



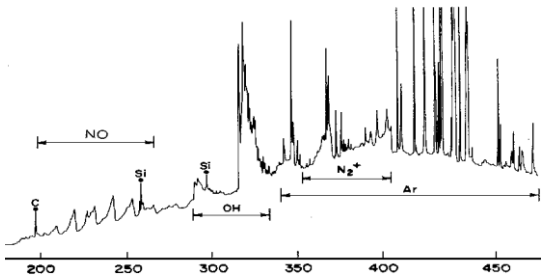
ICP-Optical Emission Spectrometry

Elemental Species vs. T



ICP-Optical Emission Spectrometry

ICP Background Emission

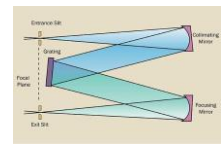


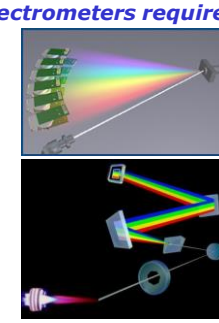
ICP-Optical Emission Spectrometry

High-resolution Optical Spectrometers required

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

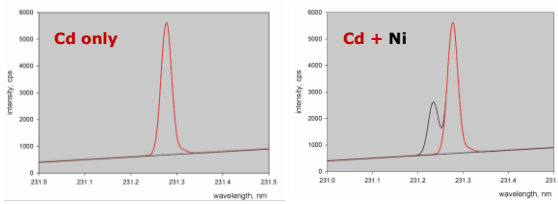
Monochromators
→ Czerny Turner Configuration
(barely used in current instruments)





ICP-Optical Emission Spectrometry

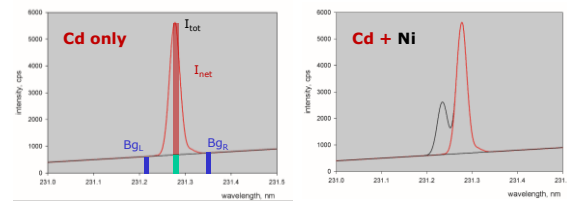
High-resolution Optical Spectrometers required



Identification and Correction of Spectral interferences

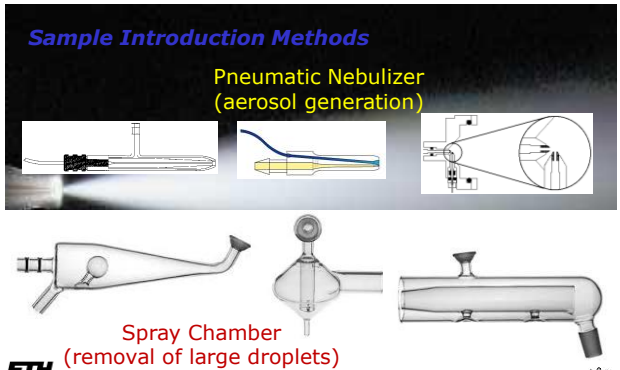
ICP-Optical Emission Spectrometry

Simultaneous Spectrometers advantageous



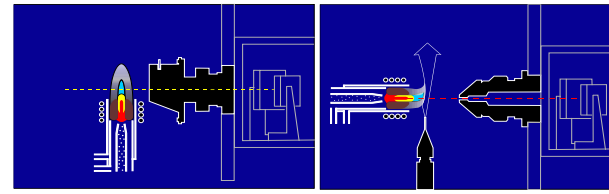
- **Correlated acquisition allows for better compensation of fluctuating baseline and interference signals.**
- **Internal Standard(s) can be monitored simultaneously**

ICP-Optical Emission Spectrometry



ICP-Optical Emission Spectrometry

Plasma View: Radial vs. Axial

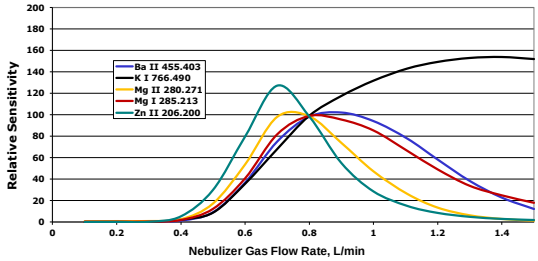


Robust against Matrix
Simpler Setup
Lower Analyte Sensitivity

≈ 10x higher Sensitivity
Lower Background
Better LODs
Stronger Matrix Dependence

ICP-Optical Emission Spectrometry

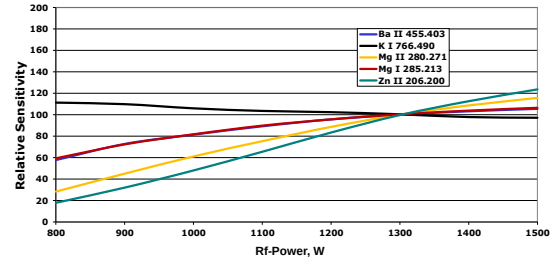
Optimization



I: Atom Line, II: Ion Line

ICP-Optical Emission Spectrometry

Optimization



I: Atom Line, II: Ion Line

ICP-Optical Emission Spectrometry

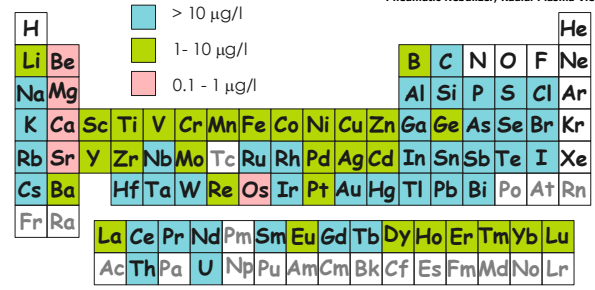
Effects of Increasing Plasma Temperature:

- **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



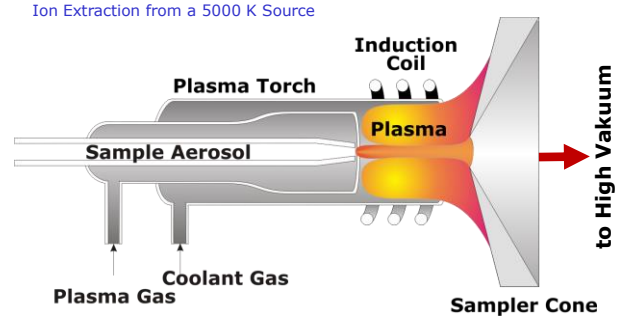
ICP-Optical Emission Spectrometry

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



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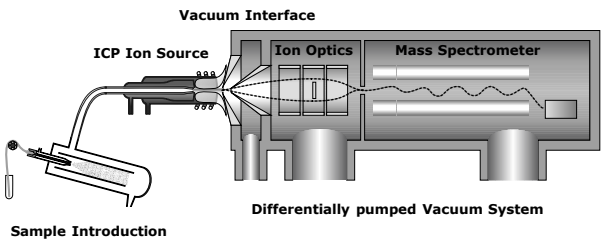
ICP-Mass Spectrometry

Setup



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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**

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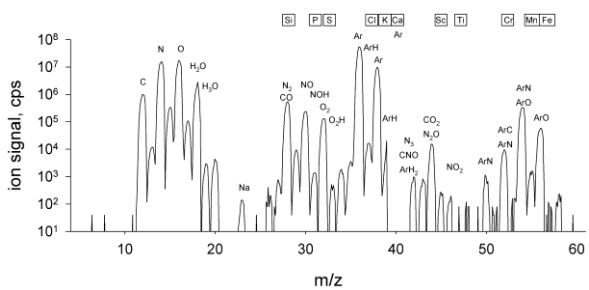
ICP-Mass Spectrometry

Intrumental Background



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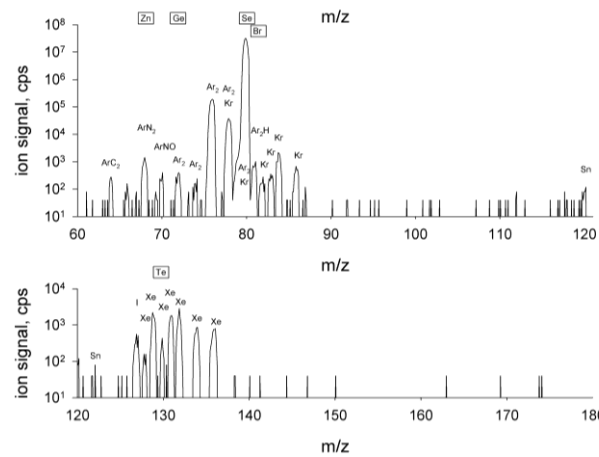
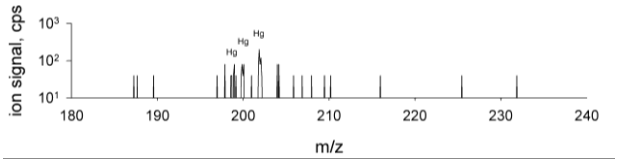




Typical Background Contributions:

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

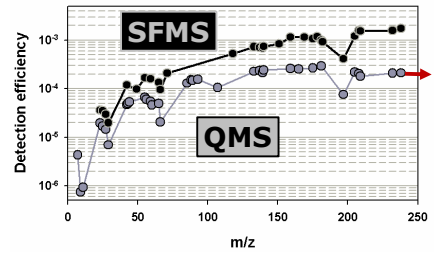
→Impurities in the Gas and ambient Air:
C^+, N^+,O^+,H_2O^+ Kr^+, Xe^+, (Hg^+, Sn^+, Pb^+)

→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



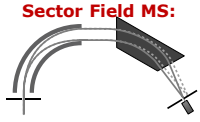
1 ion detected requires 20000 atoms in the source

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)

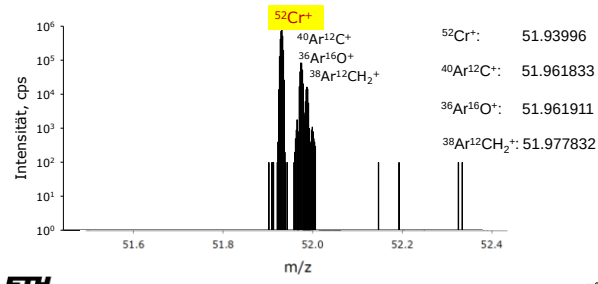


Time of Flight MS: Ion Transmission: Moderate
Mass Resolving Power: ≈4000
Acquisition: Simultaneous
Measurement Speed:0.033 ms / Spectrum

ICP-Mass Spectrometry

High-Resolution Advantage

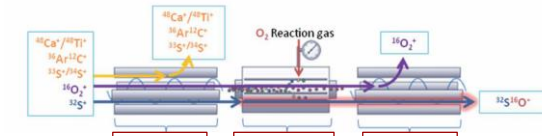
At least 5 different Species in a 1 m/z Mass Window



ICP-Mass Spectrometry

"High Mass Resolution" with Quadrupole MS

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



Q1	**"Q"2**	**Q3**
m/Q 32 S^+ O_2^+ m/z 48 removed	*Bandpass* $^{32}S^+ \rightarrow {}^{32}SO^+$ $O_2^+ \rightarrow O_3^+$	*m/Q: 48* $^{32}S^{16}O^+$ *m/z 32 removed*

ICP-Mass Spectrometry

Limitations

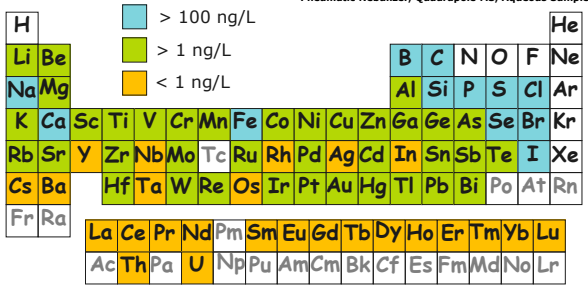
Matrix Effects are more severe:

- **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

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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**

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Calibration

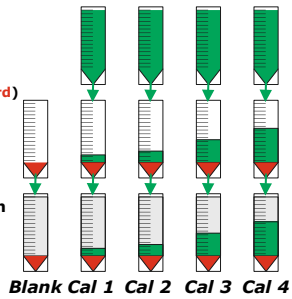
External Calibration

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!



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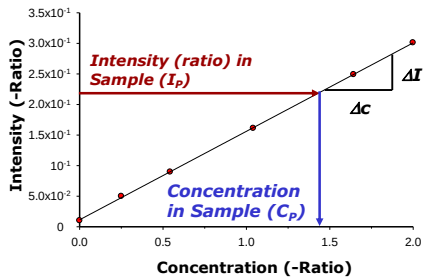
Calibration

External Calibration

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

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



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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***

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Calibration

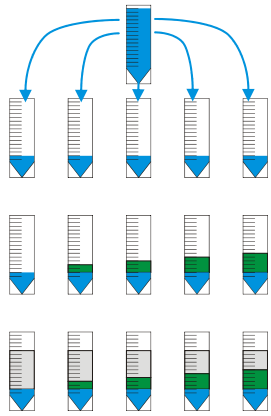
Standard Additions

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!



Calibration

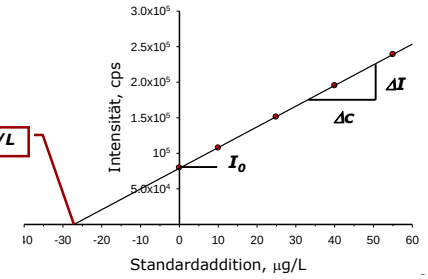
Standard Additions

Round Roin Test IMEP-16, IRMM Pb in Wine

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

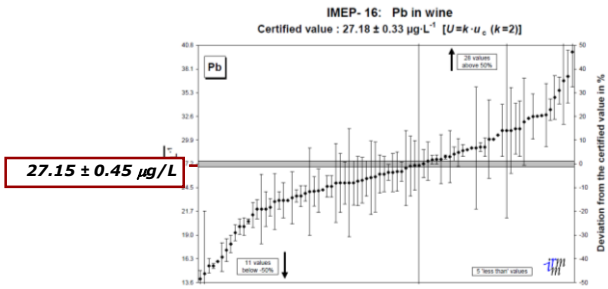
$$S = \frac{\Delta I}{\Delta C}$$

27.15 ± 0.45 µg/L



Calibration

Standard Additions



27.15 ± 0.45 µg/L

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)

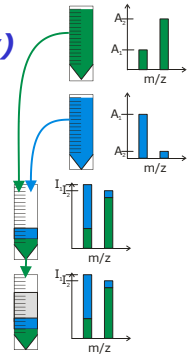
Unknown Sample with «Natural» Isotope Ratio

Isotopically enriched Standard

Aliquots of exactly known amount are mixed

Dilution to desired Concentration using a suitable Solvent

Mix!

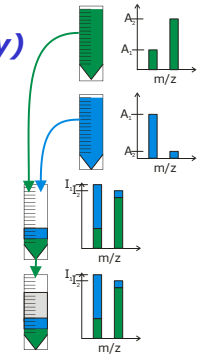


Calibration

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)

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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*

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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

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Sample Preparation

Common Digestion Methods

Microwave assisted High Pressure, High Temperature Digestion

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

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Sample Preparation

Common Digestion Methods

Oven-heated High Temperature, High Pressure Systems

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Sample Preparation

Common Digestion Methods

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

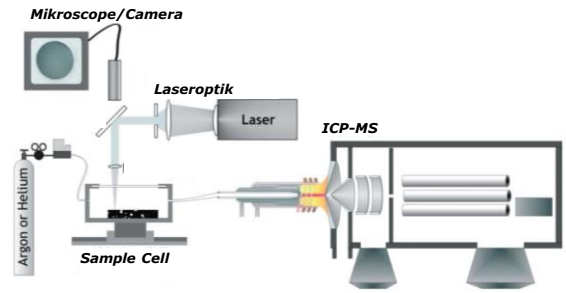
- → ***Mostly Fluoropolymers: PTFE, PFA, etc.***
- → ***(Quartz)***

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***

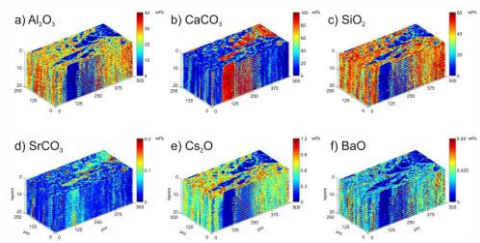
Sample Preparation

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

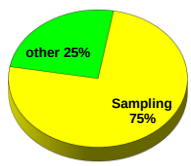
Reproducibility

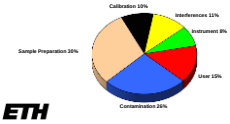
Sample Throughput

Cost

Method Development

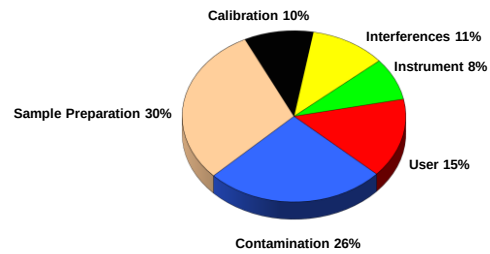
Sources of Error in Trace Element Analysis





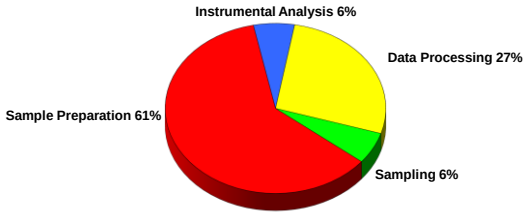
Method Development

Sources of Error in Trace Element Analysis



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***

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