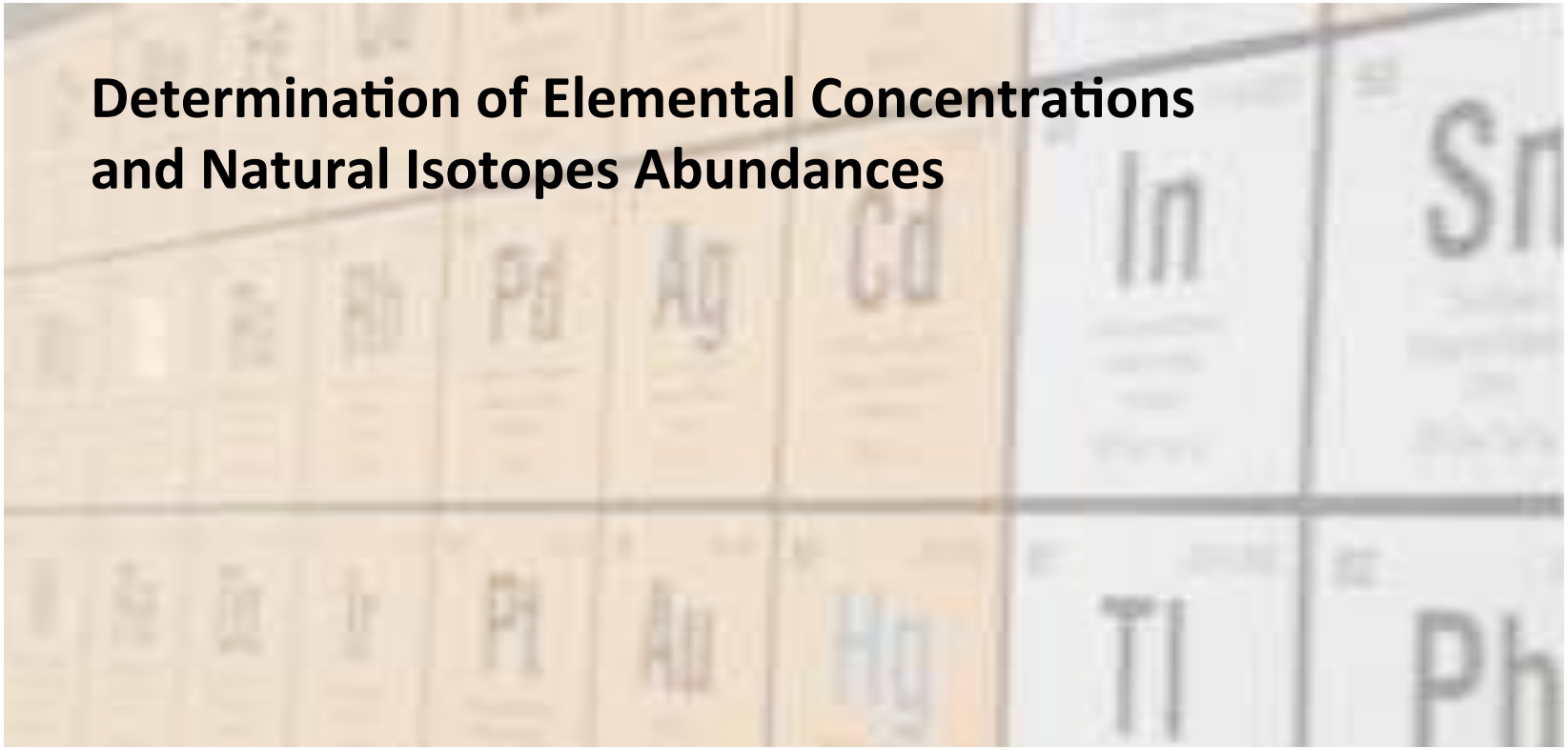
CZECH REPUBLIC
DEVELOPMENT COOPERATION

Analytical Methods for Environmental Geochemistry



Determination of Elemental Concentrations and Natural Isotopes Abundances

Overview - Analytical Methods

- **Basic Terms (Definitions, etc.)**
- **Atomic Spectroscopy**
  - **Optical Spectroscopy**
    - Atomic absorption spectroscopy (AAS)
    - Atomic emission spectroscopy (AES)
    - Inductively coupled plasma atomic emission spectroscopy (ICP AES)
  - **Mass Spectroscopy**
    - Mass spectrometry with inductively coupled plasma
    - Single collector mass spectrometry
    - Multicollector mass spectrometry
  - **Data Processing - Construction of Calibration Curves**
- **Isotope Analysis**
    - TIMS (Thermal ionisation mass spectrometry)
    - MC ICP MS (Multicollector Induct. Coupled plasma mass spectrometry)

Basic Terms

Instrumental analysis *is a field of analytical chemistry that investigates analytes using scientific (analytical) instruments.*

Instrument *is an equipment capable to convert a specific sample property to analogue (continuous) or digital (discrete-time) response or signal, which is then compared the signal or response of a specific standard.*

Sample *is our study material with specific characteristics and measureable properties, and it can be divided into* ***analyte*** *and sample* ***matrix****.*

Analyte *is a substance or chemical constituent that is of our interest in an analytical procedure.*

Matrix *the rest of sample composition which is not measured but must be monitored due to effect of interference, etc.*

Interference *is false response of sample matrix being read as an analyte signal.*

Atomic Spectroscopy

Atomic Spectroscopy (AS) *is a method for the determination of elemental composition by using* ***OPTICAL*** *(electromagnetic) or* ***MASS*** *spectrum of analyte.*

- **Optical Spectroscopy (OS)** – electrons exist in specific energy levels within an atom. These levels have defined energies (i.e. energy quantum) which can be either emitted or absorbed by an atom depending if the electrons being moved to higher or lower energetic levels. Specifically, the **energy (E)** is emitted if the electrons are moved to lower energy level, and this emission is always in a form of an energy quantum.

Max Plank's Equation:

h = Plank's constant

f = frequency

$$E = hf = \frac{hc}{\lambda}$$

E = Energy

c = speed of light

λ = wavelength

- **Mass Spectroscopy (MS)** – consists of an ion source, a mass analyzer, and a detector. Identification by **mass-to-charge (m/z) ratio** and concentrations by the number of ions detected (signal). The ion sources facilitate the ionization of a sample.

Optical Spectroscopy – Principles

Adsorption – Emission - Fluorescence

Atomic <u>Adsorption</u> Spectrometry (AAS) *is a technique to determine the concentration of an analyte in a sample (elemental analyses).*

Principles:

- Comparative method - requires standards with known concentration - **the relation between the measured absorbance (A) and concentration (c) must be known**

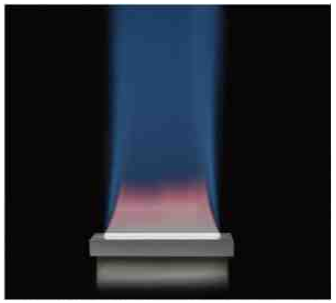
- Sample is atomized in atomizer and the electrons absorbed (and excited to higher energy state) with a defined quantity of energy. **The amount of energy is element specific and according to Lambert-Beer Law,** which relates an **absorbance (A)** to an elemental concentration, according to:

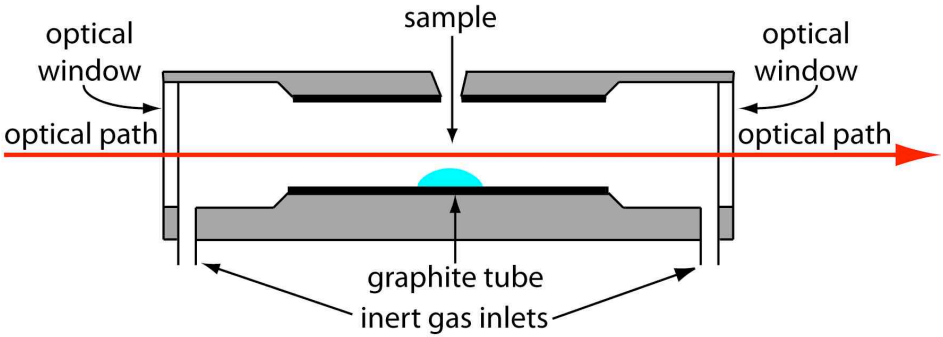
$$A = \epsilon . l . c$$

ε = absorbtivity of an dye (L/g/cm)
l = is the length of the light path (cm)
c = the concentration of the dye in solution (g/L)

Optical Spectroscopy – Atomizers

Flames or Graphite furnace (Electrothermal) atomizers





- **Flame Atomizers**

The oldest and most commonly used is **AAS** (Atomic Adsorption Spectroscopy) that uses either an air-acetylene (2300 °C), or nitrous oxide-acetylene (2700 °C), flames

The processes in a flame:

- **Desolvation** (drying) – the solvent is evaporated and the dry sample and nano-particles remain
- **Vaporization** (transfer to the gaseous phase) – the solid particles are converted into gaseous molecules
- **Atomization** – the molecules are dissociated into free atoms

Optical Spectroscopy – Atomizers

Graphite Furnace (Electrothermal) atomizer

- **Electrothermal AAS (ET or GF AAS)** graphite furnace atomizers, use heat generated via ohmic resistance, with a controlled temperature in the individual heating steps.

Furnaces are very small, typically about 20 mm in length and 5mm inner diameter. A measured volume (typically 10–50 µL) or a weighed mass (typically around 1 mg) of a solid sample are introduced into the graphite tube and subject to heating.

The processes in a graphite furnance:

- **Drying** – the solvent is evaporated
- **Pyrolysis** – the majority of the matrix constituents is removed
- **Atomization** – the analyte element is released to the gaseous phase
- **Cleaning** – eventual residues in the graphite tube are removed at high temperature.

Advantages: solid, liquid or gaseous samples, higher sensitivity, is 2–3 orders of magnitude higher than that of flame AAS, determinations in the low µg L^{-1} range.

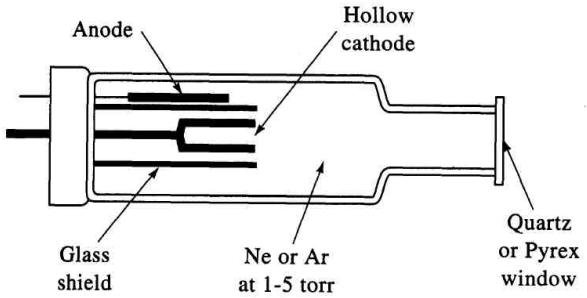
Hence this **GF AAS** method is very robust and almost without interferences.

Optical Spectroscopy – Radiation Sources

Line sources (produce narrow bands with specific wavelengths)

Emit the spectrum of an analyte in the form of lines that are narrower than the absorption lines.

Hollow cathode lamps - made for specific element(s) that are being determined, so for different groups of elements (e.g. alkali metals) a different lamp has to be used.

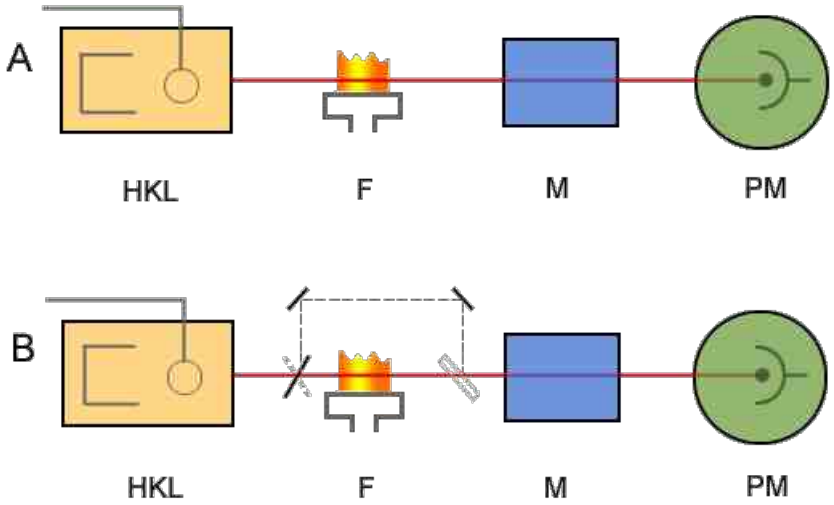


Continuous sources (produce broad range of wavelengths)

Emit a continuum spectrum and therefore high resolution monochromator is used to choose the specific spectra (a more sensitive optical device needed).

Optical Spectroscopy – Principles of AAS

Schematic diagram of AAS (Atomic Adsorption Spectrometer)
with a flame (F) atomizer and set of cathode lamps for different elements



Optical Spectroscopy – Principles of AES (OES)

Atomic emission spectroscopy (AES) uses the intensity of light emitted from a **flame**, **plasma**, **arc**, or **spark** at a particular wavelength to determine the quantity (i.e. concentration) of an element in a sample.

The wavelength *of the atomic spectral line is unique for a specific element*

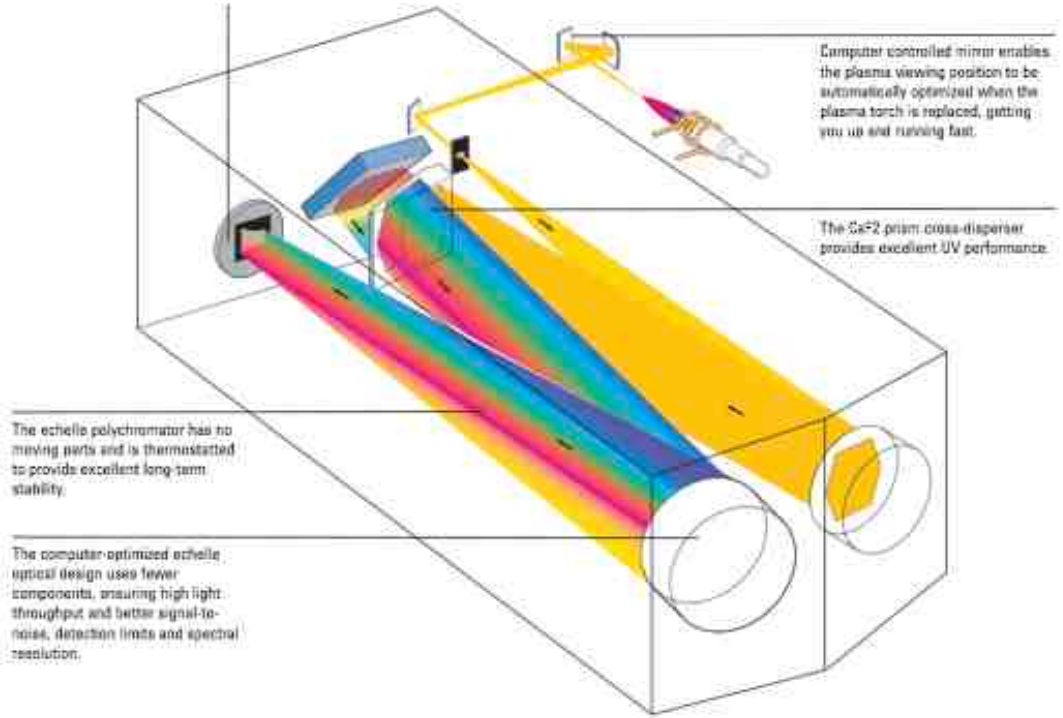
The intensity *of the emitted light is proportional to the element concentration*

Principles

The thermal energy of the source excites the atoms into higher energy levels (i.e., excited states) that subsequently **emit light when they return to the ground state**. The emitted light does not have a continuum therefore is expressed as **an atomic spectral lines specific for given element**

Possible problems of AES (OES): Sometimes two or more lines overlap for two or more elements, causing so-called **spectral interferences**

Optical Spectroscopy – Principles of AES (OES)

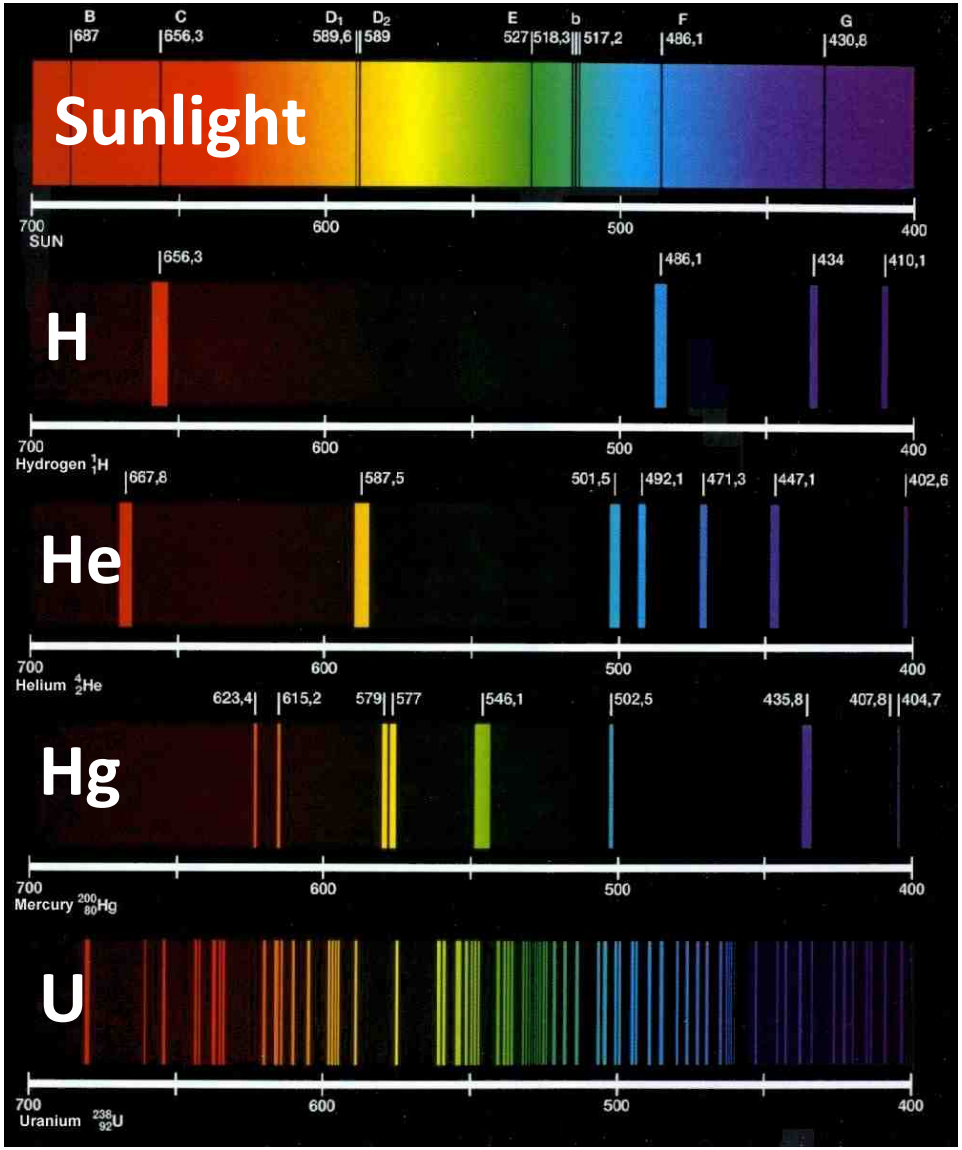


Agilent ICP-OES Spectrometer

Elements become excited and the electrons emit energy at a characteristic wavelength, and emitted light is then measured by optical spectrometry.

Optical (atomic) emission spectrometry (OES or AES), is a very sensitive technique for quantification of elements (dissolved ions) in natural samples

Optical Spectroscopy – Principles of AES (OES)



Atomic Optical Spectra

Continuous Spectra:

Basically all wavelength are visible

Line (Band) Spectra:

Specific for individual elements and these are produced when a cathode lamp (e.g. a sodium vapour lamp) is placed between the source and optical prism.

Pros and Cons of Adsorption (AAS) vs. Emission (AES)

AAS (Adsorption Technique)

Advantages: less interference problems due to specific adsorption spectra lines, in combination with ETA (electrothermal atomization) this method can also have quite low detection limits

Disadvantages: requirements for many lamps depending on the number of elements that are measured (two, three or four combination lamps exist), not simultaneous determination, generaly lower detection limits than AES

AES (Emission Technique)

Advantages: simultaneous determination of numerous elements, no need for any lamp, the lowest price for an acquisition and operation costs.

Disadvantages: many spectral and non-spectral interferences, the lowest detection limits (lower than AAS), limitations for specific elements analysis

ICP OES (Plasma Source Technique)

Advantages: excellent detection limit, multi-element capability (fully simultaneous determination), at least 70 elements (metals, non-metals), low non-spectral interferences (hydrides, etc.) and a stable and reproducible signal.

disadvantages: spectral interferences (many emission lines), high costs and operating expense and the fact that samples typically must be in solution.

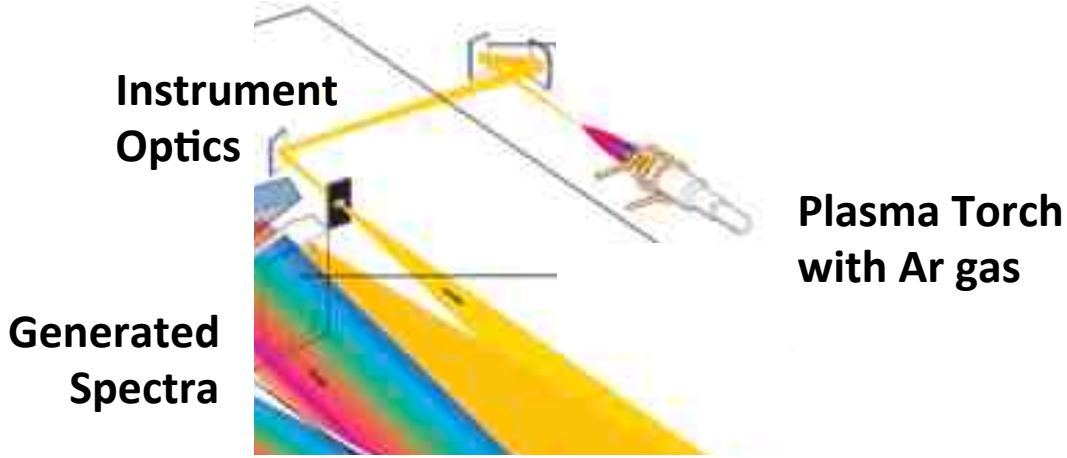
Principles of ICP OES

Inductively coupled plasma (ICP) optical emission spectroscopy (OES)

This technique uses an inductively coupled **plasma as the source for sample ionization and atomic excitation**, and commonly used carrying gas is Ar.

Principle of plasma generation:

In a **plasma torch** (3 concentric quartz tubes, see below) the plasmatic state of Argon (Ar) gas is maintain by **RF-generator** through load coil (inductor). The ignition of plasma is done by an **electric spark** through Tesla's transformer.



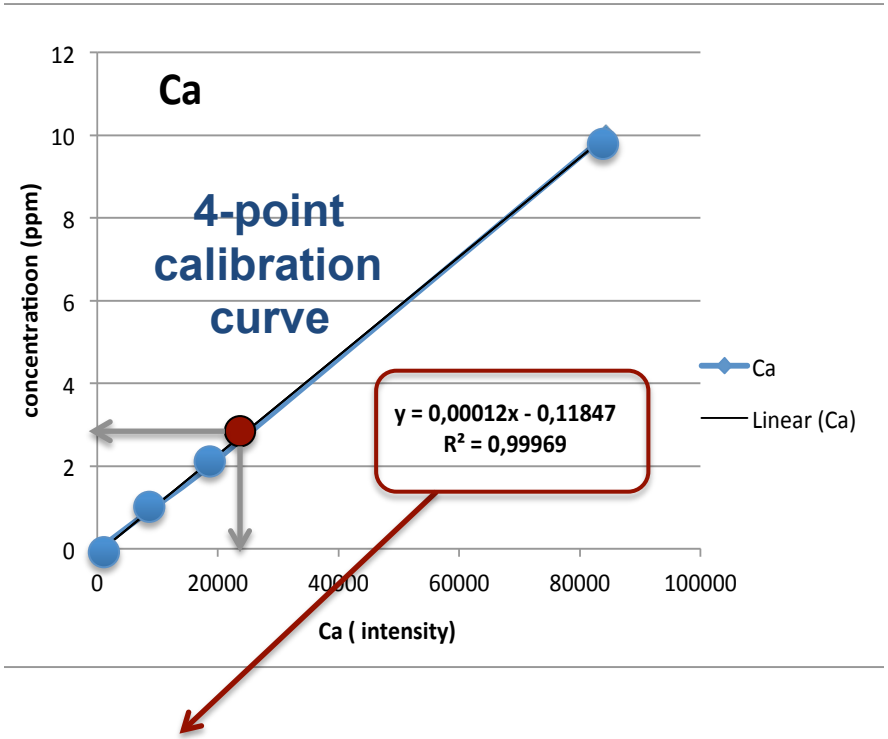
Processing of raw data from ICP OES

Construction of a ‘calibration curve’ and calculation of elemental concentrations

calibration curve concentration (ppm)	Measured INTENSITY (ion counts, raw data)			
	Ca	Mg	Na	K
0	259	14	15108	259
1	9400	2827	295333	33394
2	18575	5469	557544	74445
10	84355	24754	2484030	420180

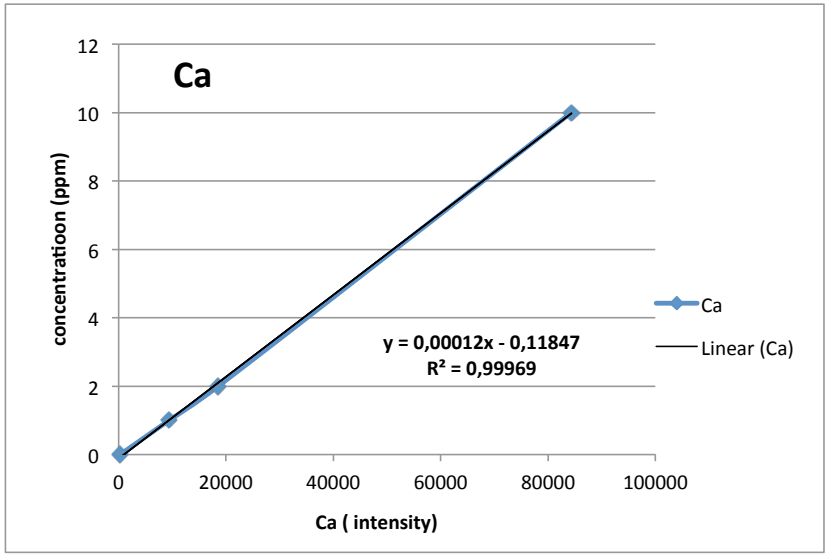
Sample	Ca	Mg	Na	K
NW Nist 1640a	21332,700	2945,800	153353,000	5232,000

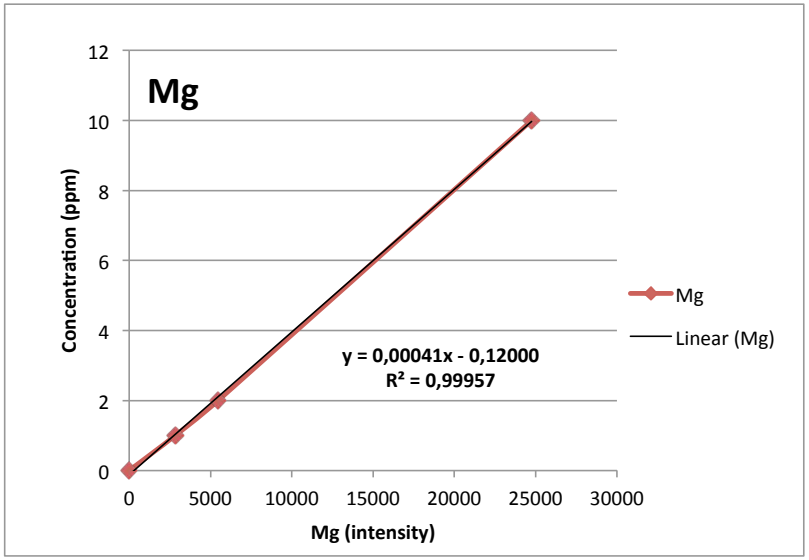
Calculated CONCENTRATIONS (ppm)				
Sample	Ca	Mg	Na	K
NW Nist 1640a	2,441	1,088	0,441	0,249

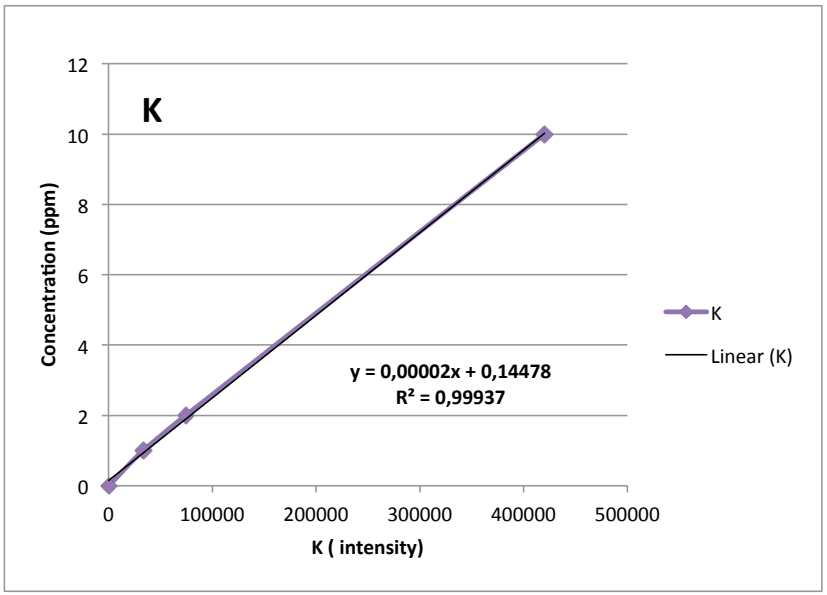


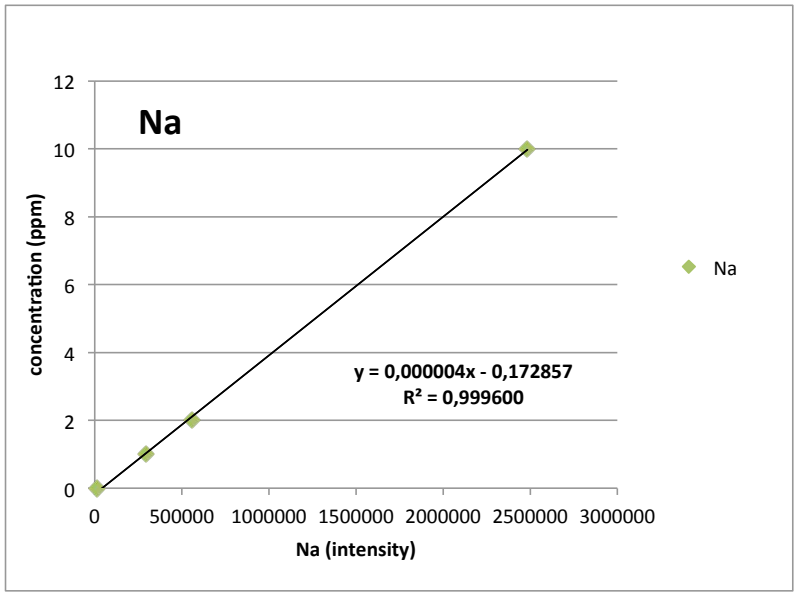
Ca (ppm) = 0.00012 * (*Intensity signal*) – 0.11847

Construction of ‘calibration curves’ from data



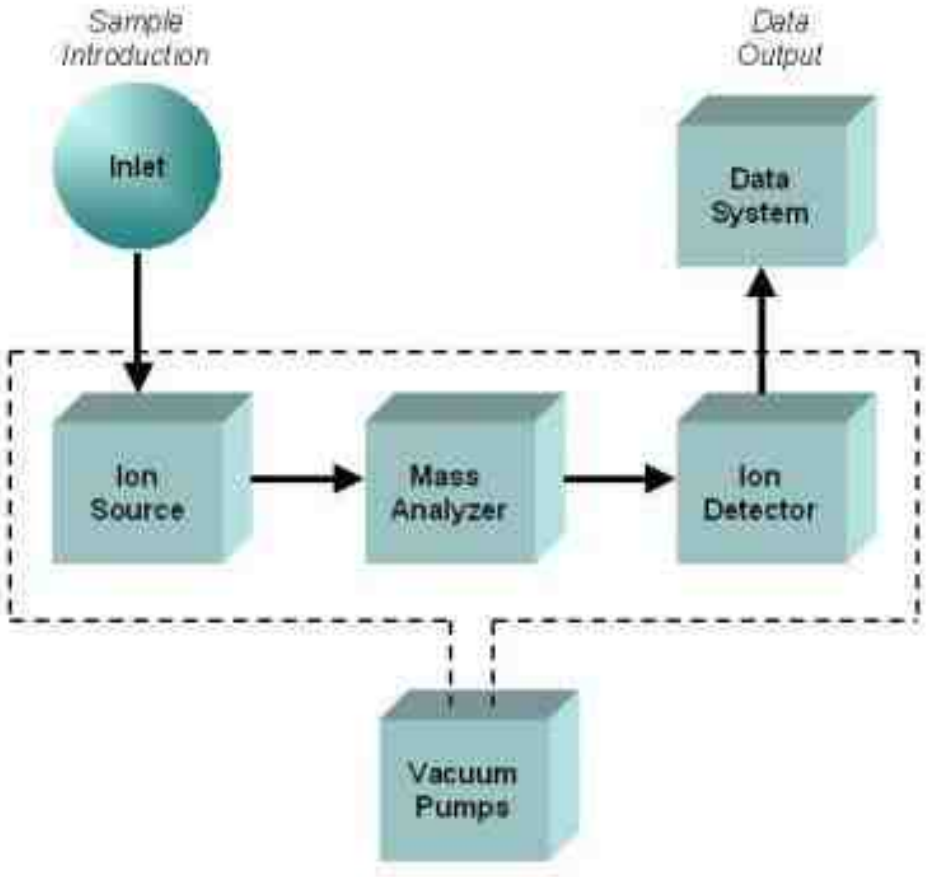






Atomic Mass Spectroscopy – Principles

Simplified Diagram of Mass Spectrometer



Ion Sources:

Inductively coupled plasma (ICP)

Thermal source (TIMS)

Mass analyzers:

Quadrupole

Pros: lower price, fast scan,

Cons: low resolution, non-simultaneous determination)

Magnetic sector

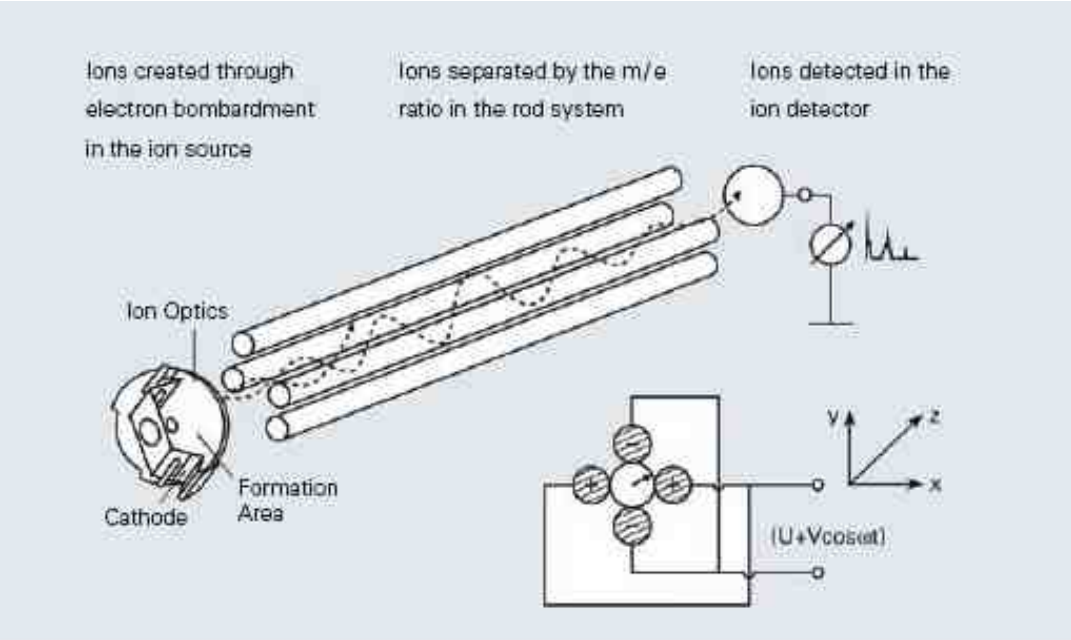
Pros: high resolution ability, simultaneous ability with multiple detector layout

Cons: the highest price, big size.

Mass Analyzers – Quadrupole

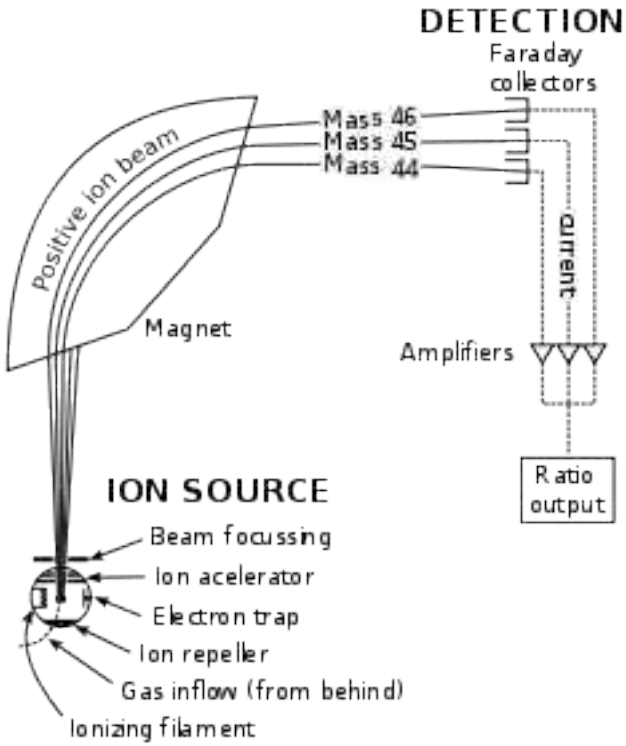
Quadrupole: Four parallel metal rods, a radio frequency (RF) voltage is applied between one pair of rods and the other. A direct current voltage (DC) is then superimposed on the RF voltage. Only ions of a certain mass-to-charge ratio will reach the detector for a given ratio of voltages: other ions have unstable trajectories and will collide with the rods and are discharged.

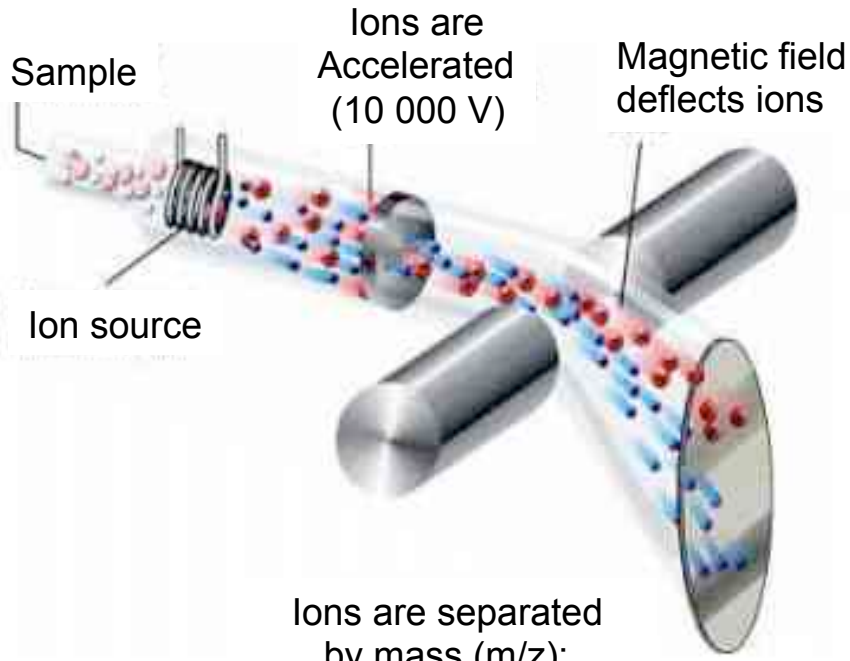
Quadrupole System:



Mass Analyzers – Magnetic Sector

Magnetic sector field instrument: the ion trajectory is curved by a magnetic field due to different **mass-to-charge ratio** (**specific *m/z* ratio**) of these ions traveling through the magnetic field. The trajectory of lighter ions is curved more than for the heavier ions (see below).

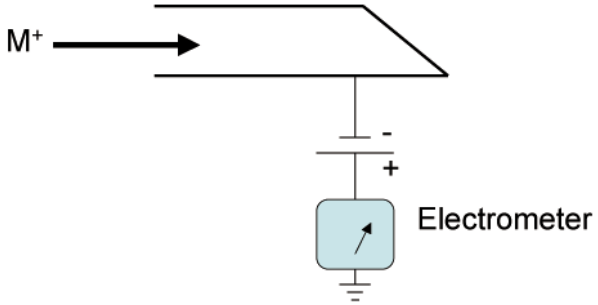




Ions are separated by mass (m/z):
light = more deflected
heavy = less deflected

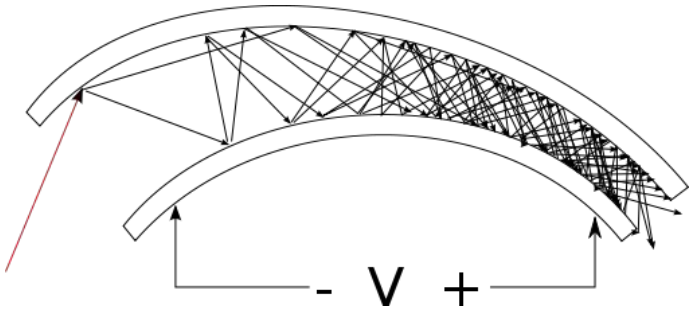
Detectors in Mass Spectrometry

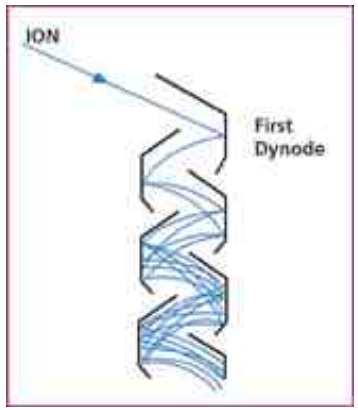
Faraday Cups - is basically a metal (conductive) cup designed to trap charged particles (ions) in a vacuum. The resulting currents can be then measured and used to determine the number of ions or electrons hitting the Faraday cup.



Secondary Electron Multipliers (SEM) - When the ions hit a surface, it can cause a cascade release of the electrons from the outermost area of the atom (i.e. release of secondary electrons).

SEM Design:





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Analytical Methods for Isotopes: TIMS and MC ICP MS

LECTURE 2: Arba Minch, Ethiopia, Oct 15, 2014

Basic Terms, and Definitions

Mass Number – is a total number of protons and neutrons in the nucleus

Atomic Number – reflects a total number of protons in the nucleus

Nuclide – is a type of an atom of certain element characterized by the number of protons (p^+) and neutrons (n^0) in the nucleus of an atom

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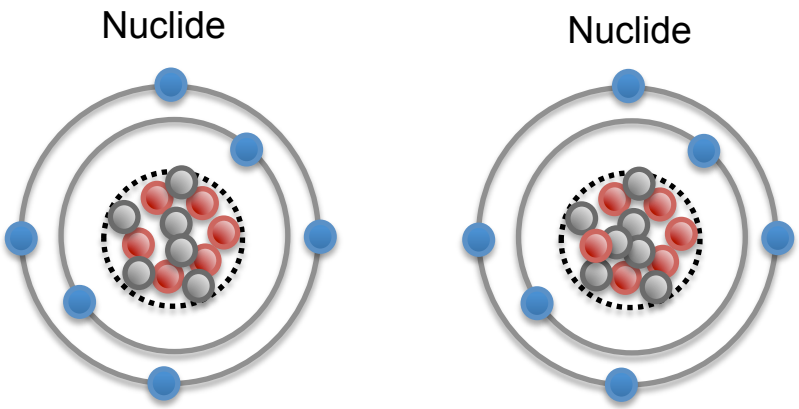
Carbon Isotopes

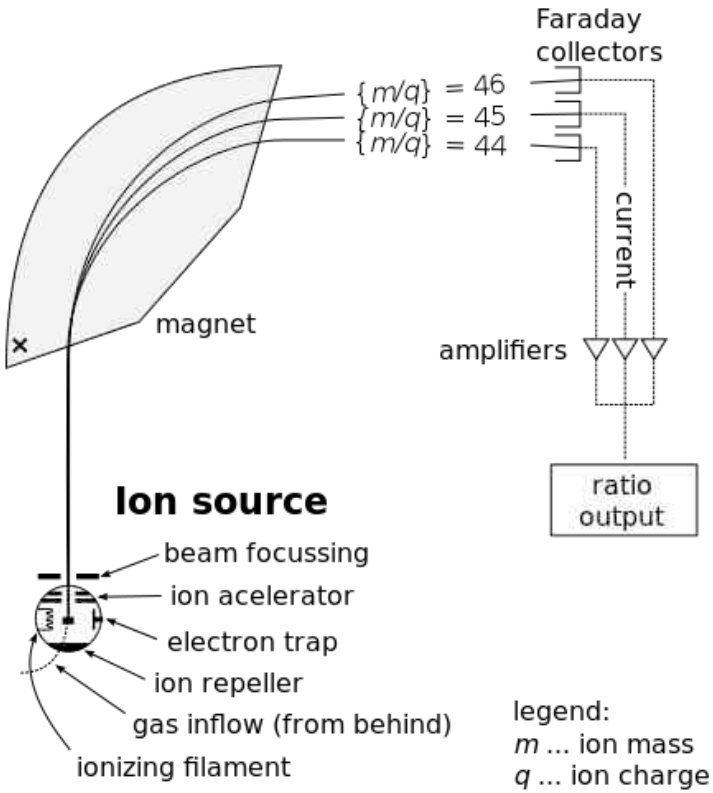


Isotopes – of certain element have the same number of protons (p^+), but distinct number of neutrons (n^0)

Analytical Methods for Isotopes

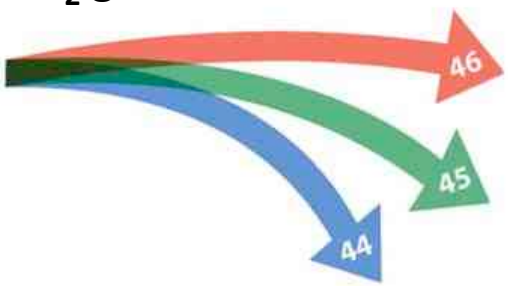
Isotopes – an 'isotope' of any given element is an atom with the same number of protons but a different number of neutrons, resulting in a different mass

Mass Spectrometry (MS) – an analytical technique that produces spectra of the masses of atoms or molecules. The spectra are used to determine the elemental or isotopic signature of a sample



In a typical MS procedure, a sample, which may be solid, liquid, or gas, is **ionized**. The ions are **separated (deflected)** according to their **mass-to-charge ratio (m/q)**

CO_2 gas



Heavy species

46 (^{12}C, ^{16}O, ^{18}O)

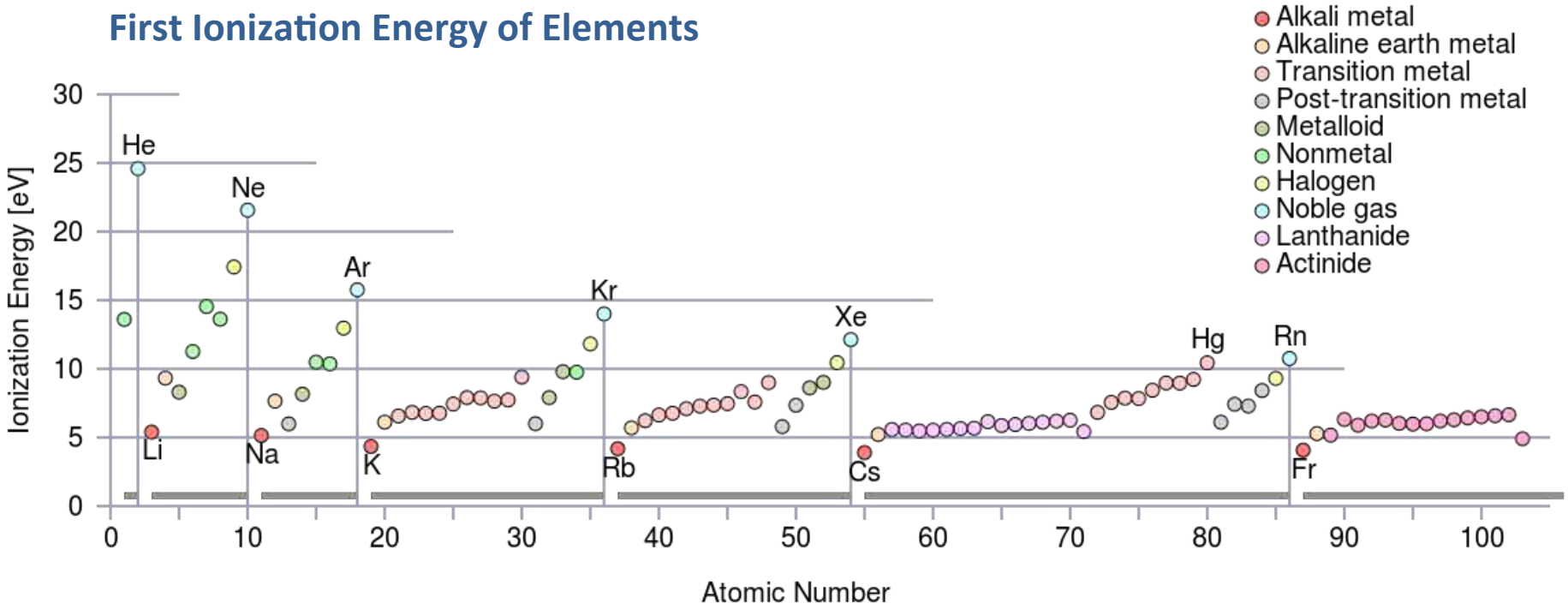
45 (^{13}C, ^{16}O, ^{16}O)

Light species

44 (^{12}C, ^{16}O, ^{16}O)

Analytical Methods for Isotopes

Ionization - is the process by which an atom or a molecule acquires a negative or positive charge by gaining or losing electrons (e^-)



Ionization energy of an atom or molecule describes the amount of energy required to remove an electron from the atom or molecule in the gaseous state

$$\mathbf{X + energy \rightarrow X^+ + e^-}$$

Types of Ionization Methods for Isotope Analysis

Inductively coupled plasma (ICP) sources

ICP (MS) uses plasma to atomize introduced sample by stripping the outer electrons from the atoms at high plasma temperatures (~10 000 C). Plasma gas is typically argon (Ar), because Ar has very high first ionization energy (> 15 eV)

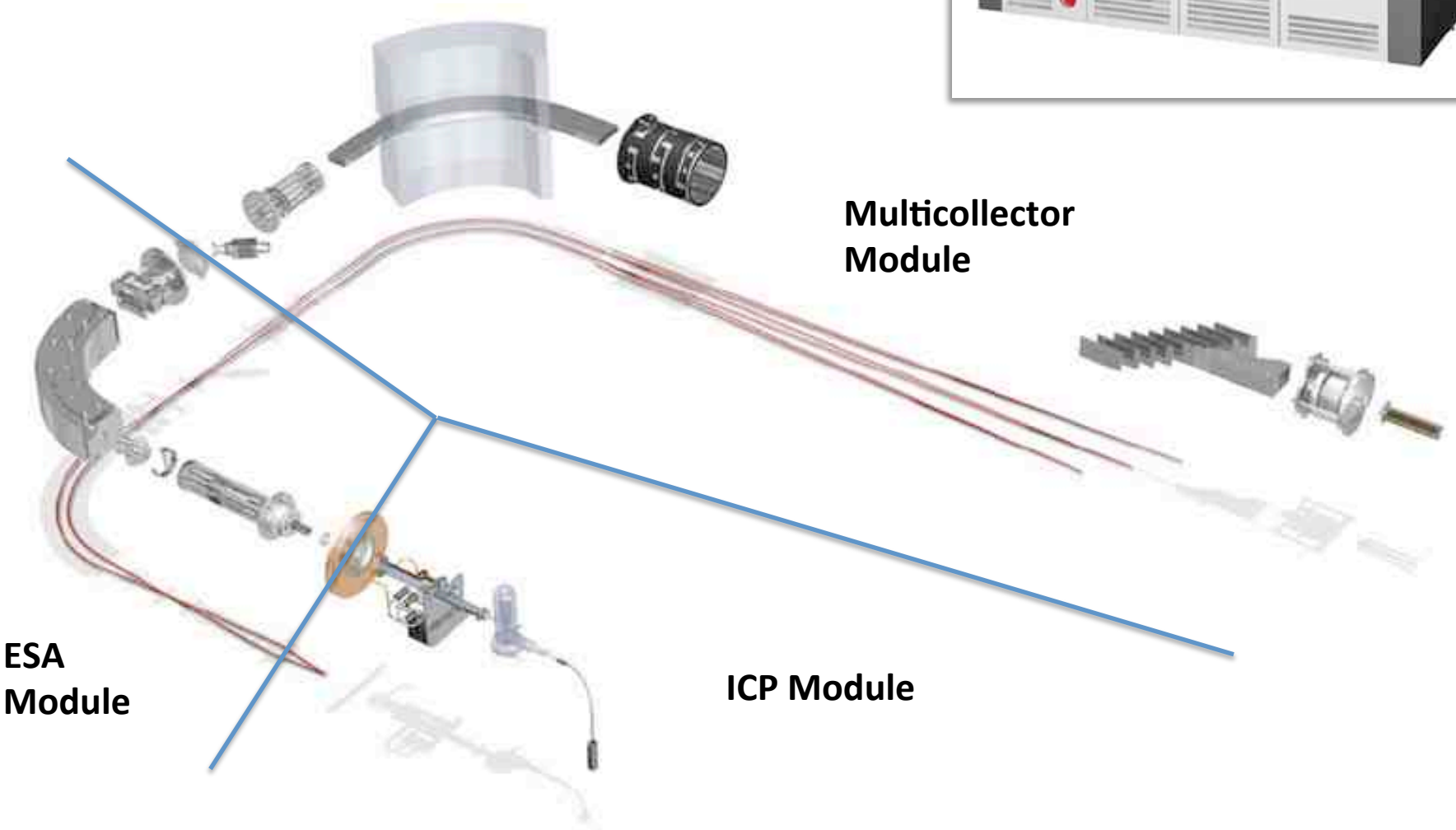
Thermal Ionization (TI) sources

TI (MS) uses metal filaments (Re, Ta, W) which are heated to higher temperatures (> 1200 C), which ionize a solid sample by stripping the outer electrons from the atoms.

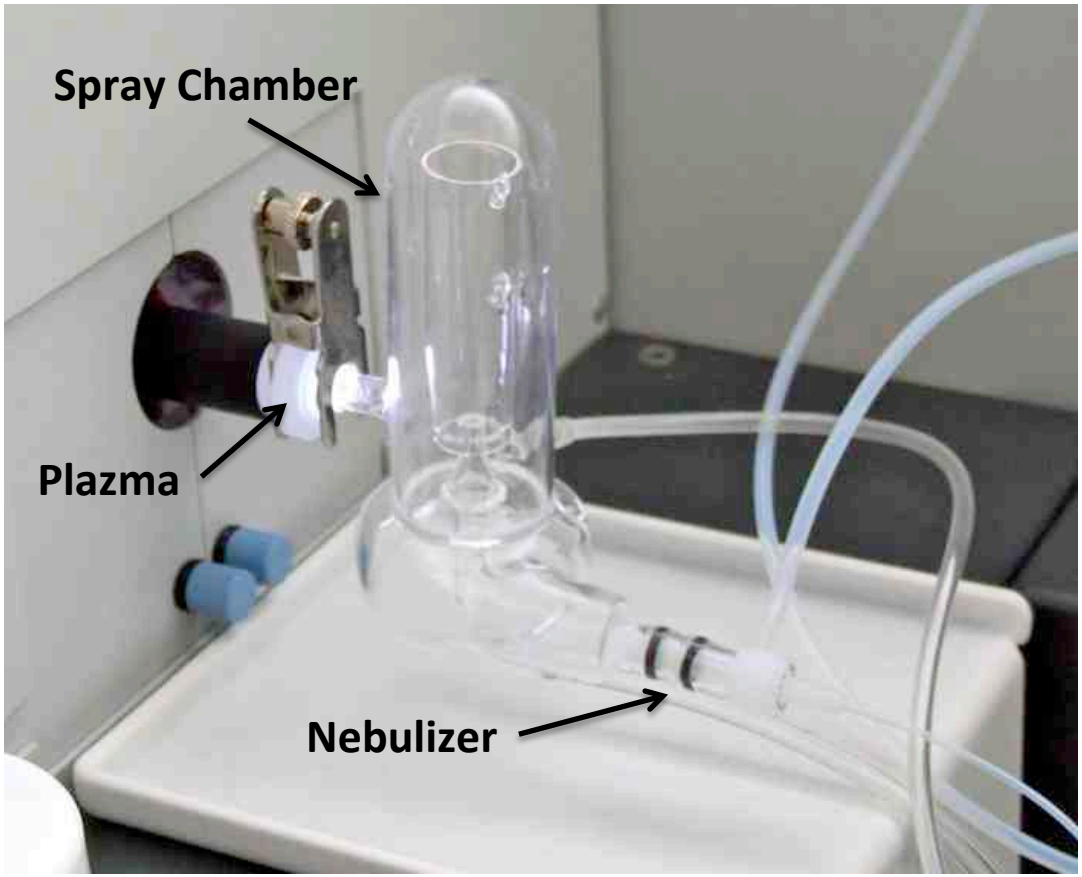
Other popular ionization techniques include:

Laser Ablation / Ionization (LA-MS)
Secondary Ionization (SI-MS), or Electron Impact (EI-MS)

Inductively coupled plasma (ICP) MS



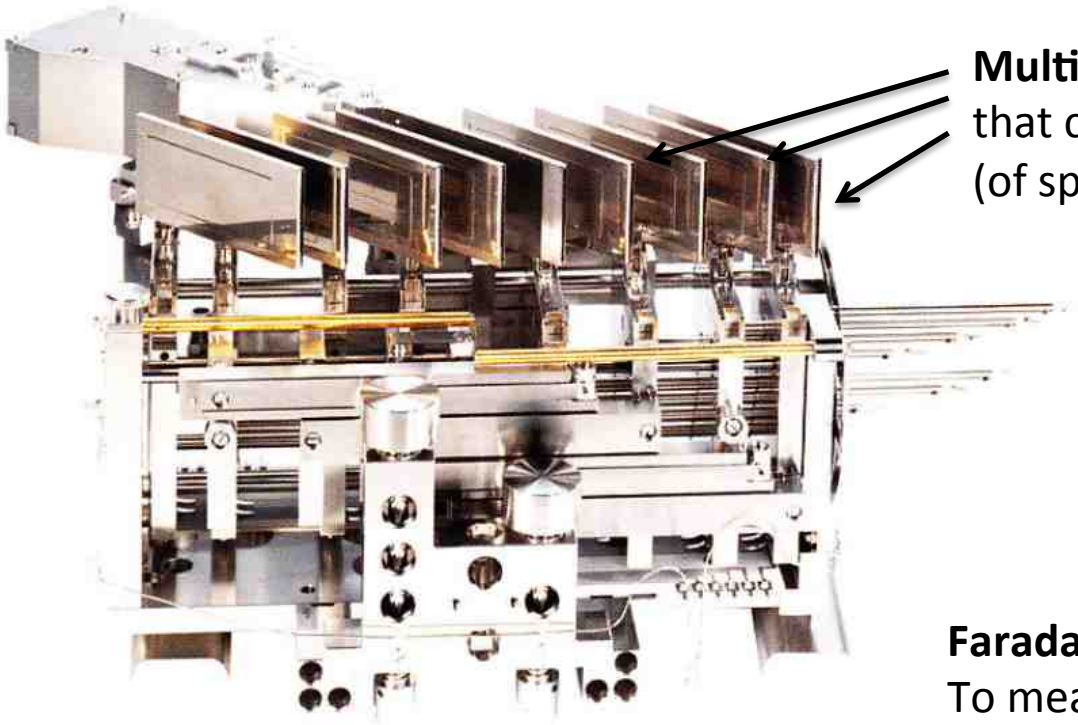
Sample Introduction - Inductively coupled plasma (ICP) MS



Samples are introduced into MC-ICP-MS for isotope analysis as **liquids** (in 2% HNO3)

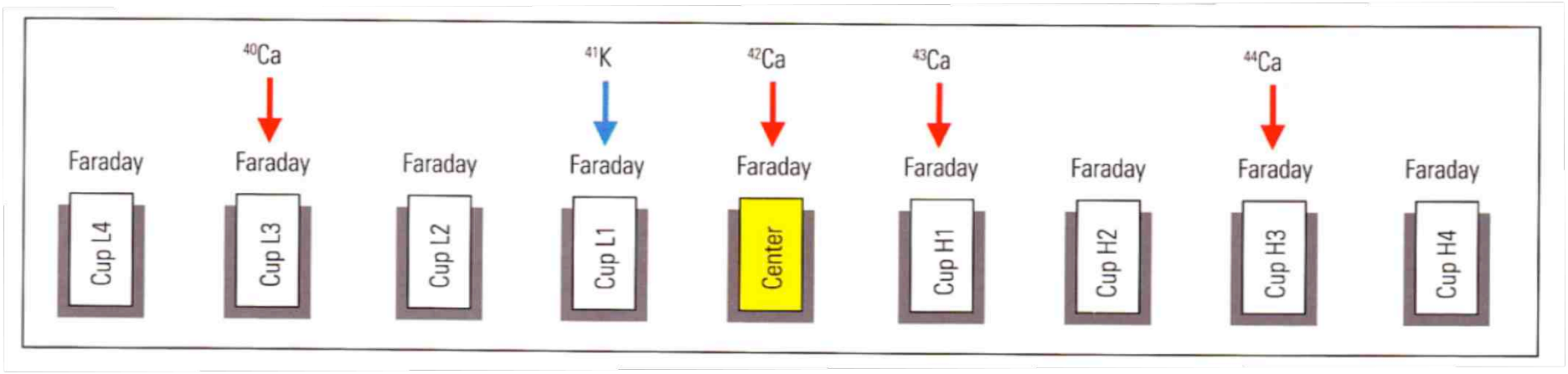
Nebulizer and **spray chamber** generates an aerosols which are then ionized in **plasma**

Ion Detection System - Inductively coupled plasma (ICP) MS



Multiple Faraday Cups
that collect ion beams
(of specific isotopes)

Faraday Cups Set-Up
To measure Calcium isotopes



Thermal Ionization (TI-MS)

Magnet
810 mm magnet dispersion
Laminated and water cooled
Mass range: 4-310 amu @ ±10 kV

Dynamic Zoom Lens
For optimized peak
overlap adjustment

Variable Multi-Collector
For up to 9 Faradays plus 8 MIC
Mass dispersion 17%
Adjustment precision < 5 µm

RPQ-IC (optional)
For abundance
sensitivity < 10 ppb

Virtual Amplifier
All resistors 10^{11} Ω
50 V dynamic range
Housing evacuated
Amplifiers and matrix
temperature stabilized

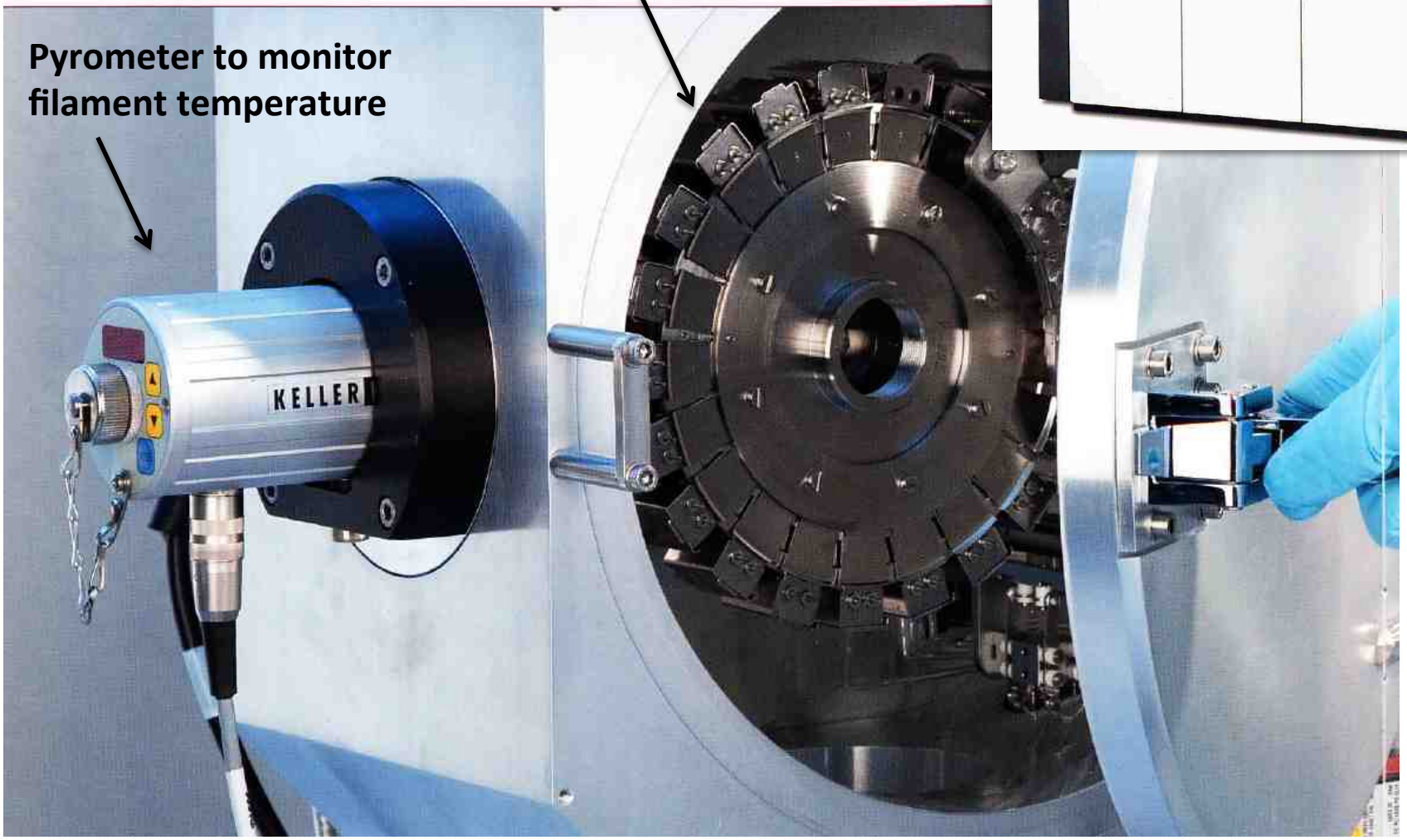
TI - Source and Magazine
10 kV positive / negative ions
21-Sample magazine with clip-in filaments
Double or single filaments

Ion Counting
For smallest signals low dark noise

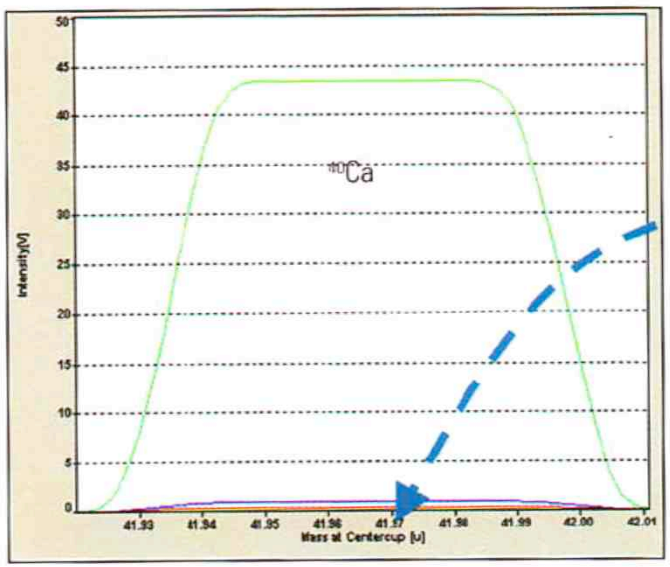
Thermal Ionization (TI-MS)

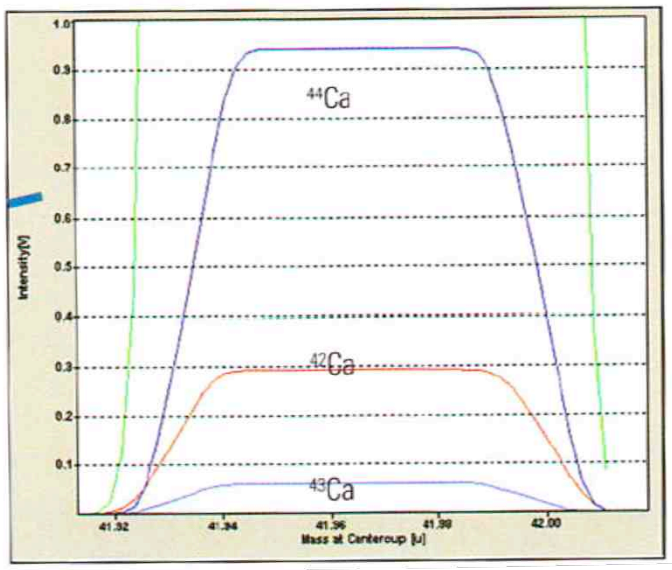
Solid samples
on metal filaments

Pyrometer to monitor
filament temperature



Measured Ion Beams (i.e. Calcium Isotope Signals)





Ca-Intensities @ 10^{11} Ω:

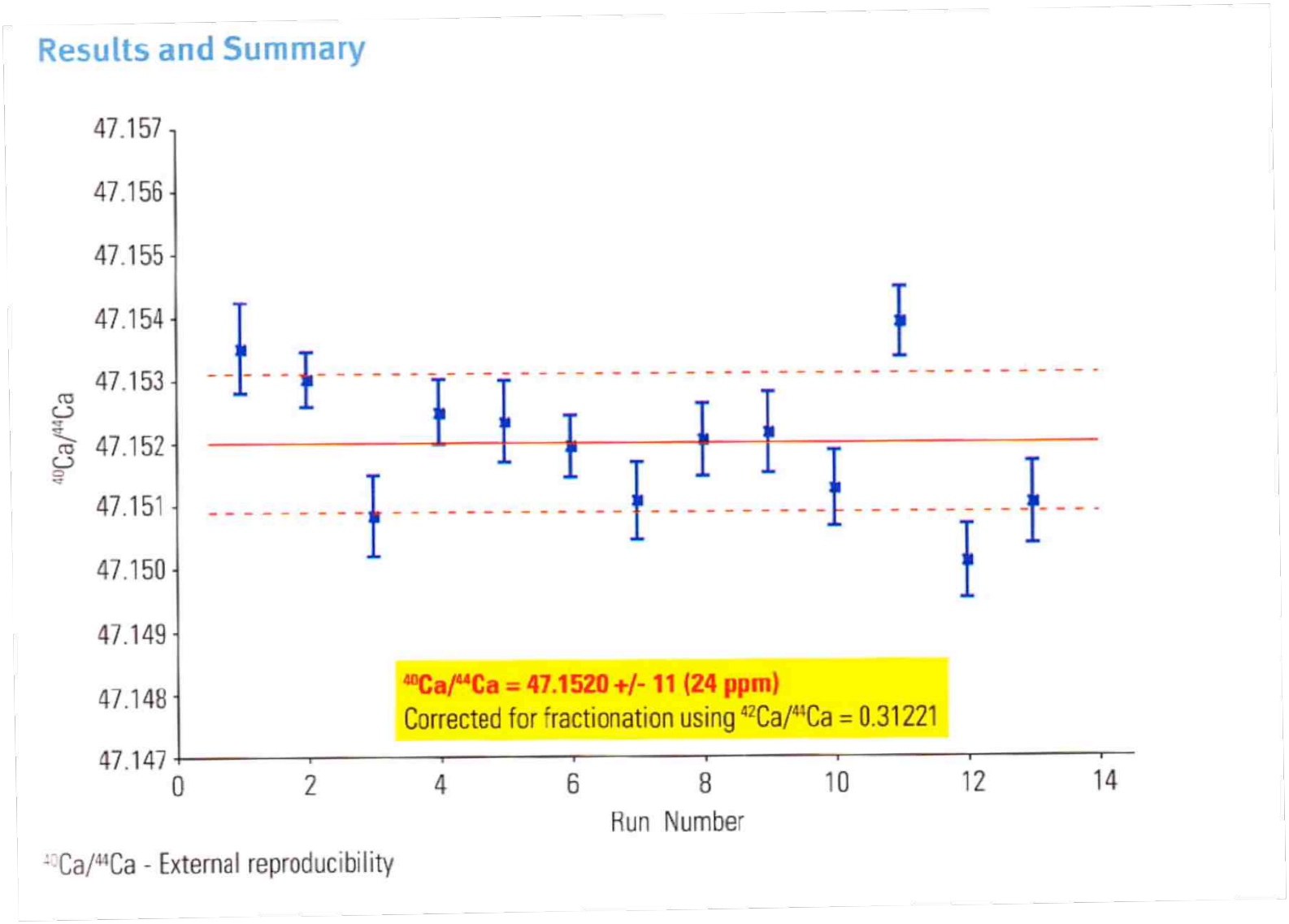
^{40}Ca → 45 V

^{42}Ca → 0.3 V

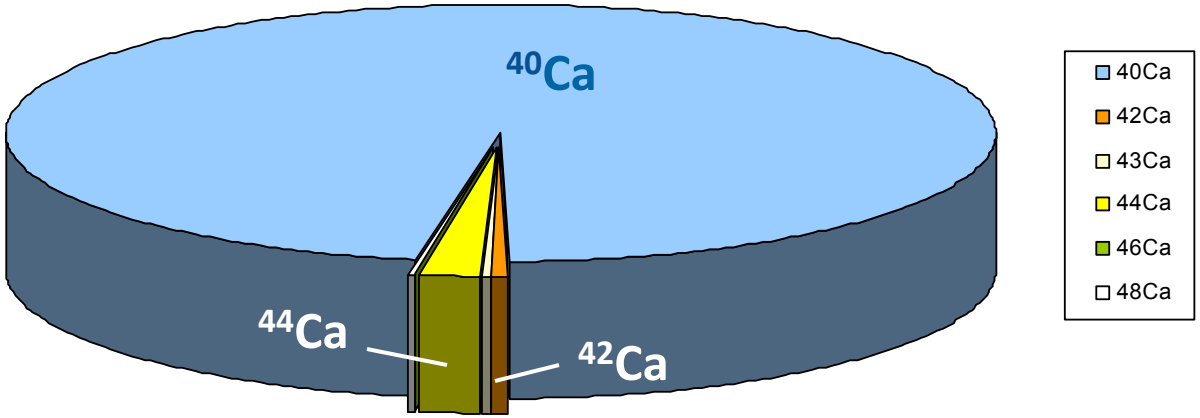
^{43}Ca → 0.06V

^{44}Ca → 0.95 V

Measured Calcium Isotope Composition ($^{40}Ca/^{44}Ca$ ratios)



Expressing measured $^{44}Ca/^{40}Ca$ ratios as DELTA (δ) variations



Delta Normalization ($\delta^{44/40}Ca$) of raw isotope data relative to standard:

$$\delta^{40/44}Ca = \left[\frac{^{44}Ca/^{40}Ca_{SAMPLE}}{^{44}Ca/^{40}Ca_{STANDARD}} - 1 \right] * 1000$$

As isotope variations in $^{44}Ca/^{40}Ca$ ratios of natural samples are small, we express our results as **delta ($\delta^{44/40}Ca$)** variations **in parts per mil (‰)** relative to an isotope standard (e.g., NIST material, or modern seawater)

Expressing measured $^{40}Ca/^{44}Ca$ ratios as DELTA (δ) variations

$^{44}Ca/^{40}Ca_{STANDARD} = 0.021208$ ($^{40}Ca/^{44}Ca_{STANDARD} = 47.152$)

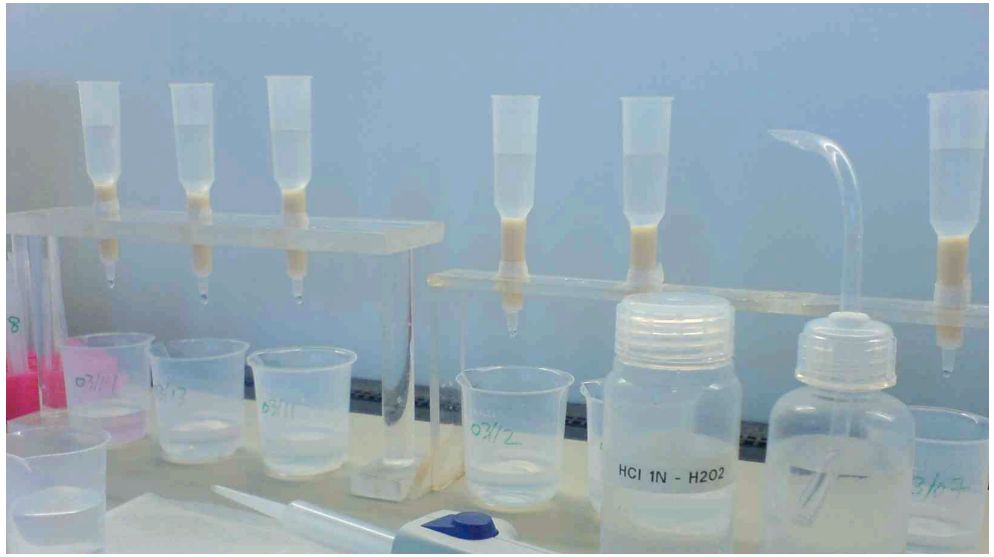
	$\delta^{44/40}Ca = 0$ ‰	$\delta^{44/40}Ca = +1$ ‰	$\delta^{44/40}Ca = -1$ ‰
	Ca in a sample and a standard are isotopically IDENTICAL	**Ca in a sample is isotopically HEAVIER (has more 44Ca) than the standard**	**Ca in a sample is isotopically LIGHTER (has less 44Ca) than the standard**
$\frac{^{44}Ca/^{40}Ca_{SAMPLE}}{^{44}Ca/^{40}Ca_{STD}}$ =	$\frac{0.021208}{0.021208}$	$= \frac{0.021229}{0.021208}$	$= \frac{0.021187}{0.021208}$

As these small changes in $^{44}Ca/^{40}Ca$ ratios of natural samples are occurring on **the FORTH or the FIFTH decimal places** it is more convenient for us to express these small variations as delta values ($\delta^{44/40}$**Ca**) in per mil (‰) units

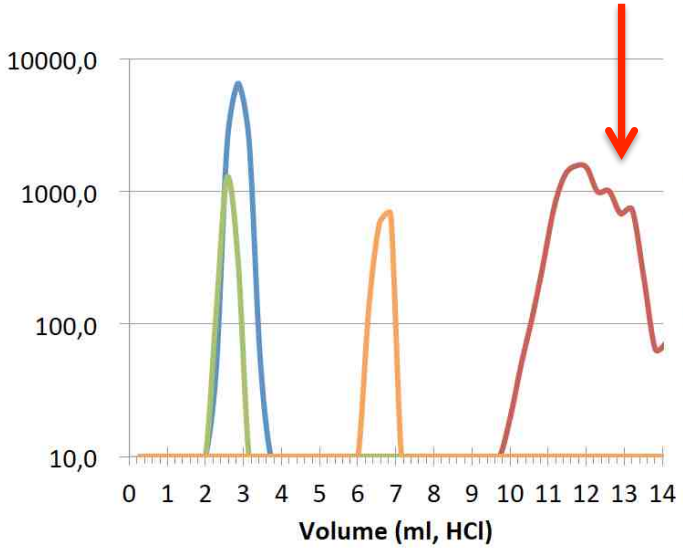
Chemical Separation – An Important Step prior to Isotope Analysis

1) Sample Weighing

2) Dissolution in acids



3) Eluent Chromatography – Purification of Ca on columns



Analysis of Ca Isotopes

Typical Elution Curves for specific elements