ICP-MS

Inductively Coupled Plasma Mass Spectrometry

Co-funded by the Horizon 2020 Framework Programme of the European Union
under the grant N° *952306*

Definitions

ICP-MS

Analytical technique developed to analyse elements using Mass Spectrometry of ions generated by an Inductively Coupled Plasma

Mass Spectrometry

Separation and Quantification by measurement of the intensity of mass charge ratios of atoms or molecules

Atoms and Isotopes

Atom = **a nucleus** and an **electron cloud**

The **nucleus** = group of **neutrons** and **protons**

	Charge	**Mass**
Protons	+ 1,6 10^{-19} c	1 amu
Neutrons	0	1 amu

The **electron cloud** = group of electrons

	Charge	Mass
Electrons	- 1,6 10^{-19} c	+/- 0 amu

An atom is electrically neutral, i.e. the number of electrons is equal to the number of protons

Atoms, Isotopes and Atomic Mass

Example: Copper

Atomic Number: 29 but 2 isotopes

	^{63}Cu (69.2 %)	^{65}Cu (30.8 %)
Protons	29	29
Neutrons	34	36

Result: the atomic Mass (Mean) equal to

$$(69.2/100 \times 63) + (30.8/100 \times 65) = 63.6 \text{ a.m.u.}$$

First Ionization Potential

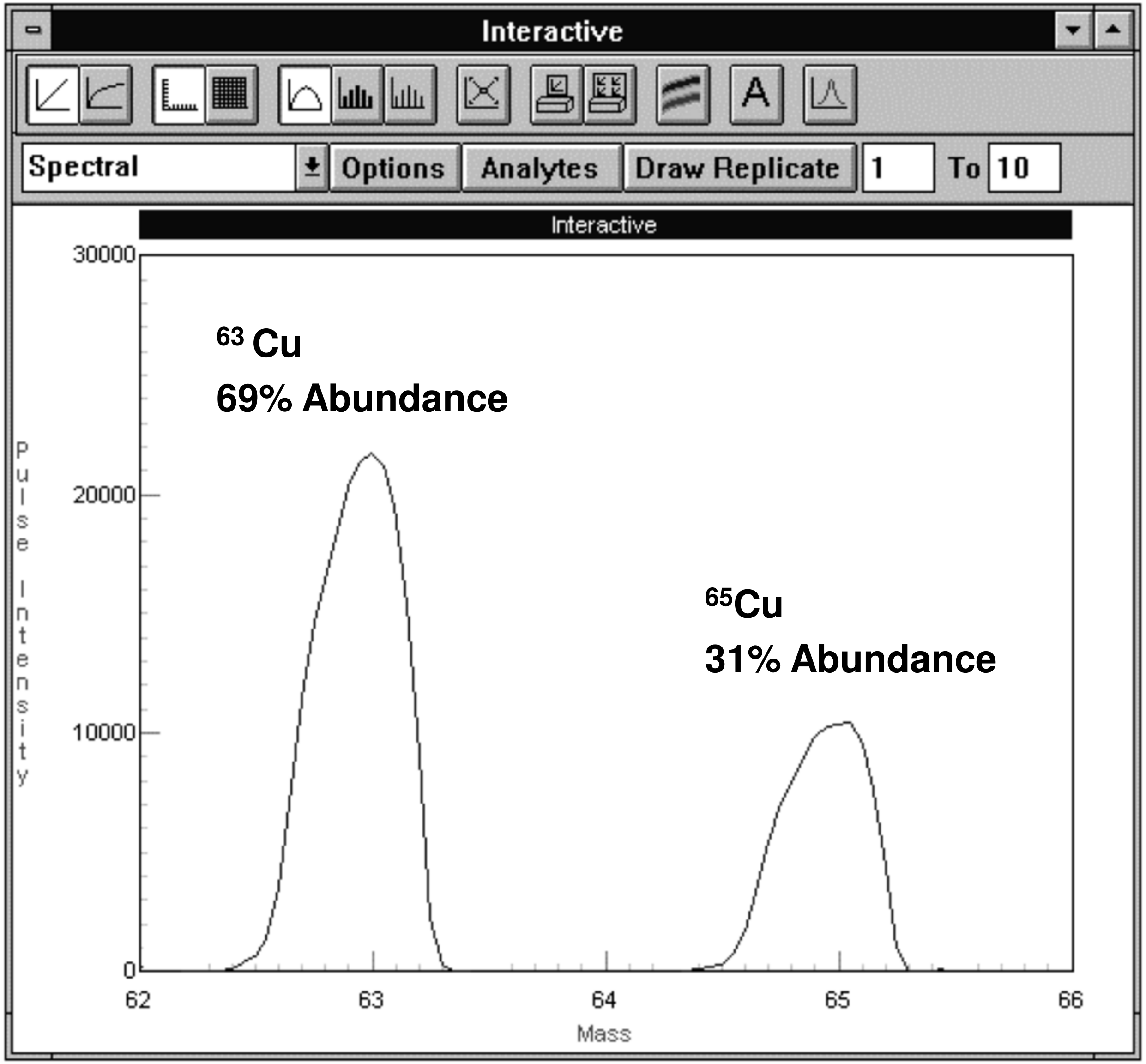
1 **H** 13,598																	2 **He** 24,587
3 **Li** 5,392	4 **Be** 9,323											5 **B** 8,298	6 **C** 11,260	7 **N** 14,534	8 **O** 13,618	9 **F** 17,423	10 **Ne** 21,565
11 **Na** 5,139	12 **Mg** 7,646											13 **Al** 5,986	14 **Si** 8,152	15 **P** 10,487	16 **S** 10,360	17 **Cl** 12,968	18 **Ar** 15,760
19 **K** 4,341	20 **Ca** 6,113	21 **Sc** 6,561	22 **Ti** 6,828	23 **V** 6,746	24 **Cr** 6,767	25 **Mn** 7,434	26 **Fe** 7,902	27 **Co** 7,881	28 **Ni** 7,640	29 **Cu** 7,726	30 **Zn** 9,394	31 **Ga** 5,999	32 **Ge** 7,900	33 **As** 9,815	34 **Se** 9,752	35 **Br** 11,814	36 **Kr** 14,000
37 **Rb** 4,177	38 **Sr** 5,695	39 **Y** 6,217	40 **Zr** 6,634	41 **Nb** 6,759	42 **Mo** 7,092	43 **Tc** 7,28	44 **Ru** 7,361	45 **Rh** 7,459	46 **Pd** 8,337	47 **Ag** 7,576	48 **Cd** 8,994	49 **In** 5,786	50 **Sn** 7,344	51 **Sb** 8,64	52 **Te** 9,010	53 **I** 10,451	54 **Xe** 12,130
55 **Cs** 3,894	56 **Ba** 5,212	57 – 71 **L**	72 **Hf** 6,825	73 **Ta** 7,89	74 **W** 7,98	75 **Re** 7,88	76 **Os** 8,7	77 **Ir** 9,1	78 **Pt** 9,0	79 **Au** 9,226	80 **Hg** 10,438	81 **Tl** 6,108	82 **Pb** 7,417	83 **Bi** 7,289	84 **Po** 8,417	85 **At** 9,5	86 **Rn** 10,749
87 **Fr**	88 **Ra** 5,279	89 - 103 **A**															

L Lanthanides	57 **La** 5,577	58 **Ce** 5,539	59 **Pr** 5,464	60 **Nd** 5,525	61 **Pm** 5,55	62 **Sm** 5,644	63 **Eu** 5,670	64 **Gd** 6,150	65 **Tb** 5,864	66 **Dy** 5,939	67 **Ho** 6,022	68 **Er** 6,108	69 **Tm** 6,184	70 **Yb** 6,254	71 **Lu** 5,426
A Actinides	89 **Ac** 5,17	90 **Th** 6,08	91 **Pa** 5,89	92 **U** 6,19	93 **Np** 6,266	94 **Pu** 6,06	95 **Am** 5,993	96 **Cm** 6,02	97 **Bk** 6,23	98 **Cf** 6,30	99 **Es** 6,42	100 **Fm** 6,50	101 **Md** 6,58	102 **No** 6,65	103 **Lr**

Isotopes and Mass Spectra

If we consider a single ionization, the m/z ratio is equal to the m, then isotopes of an element could be separated according to their masses.

In a first approximation, the sensitivity of the different isotopes is only proportional to isotopic abundances.



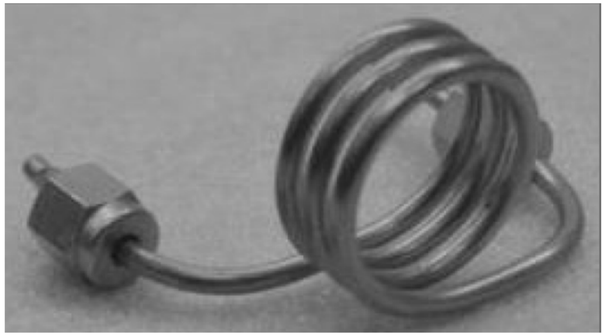
What is a plasma?

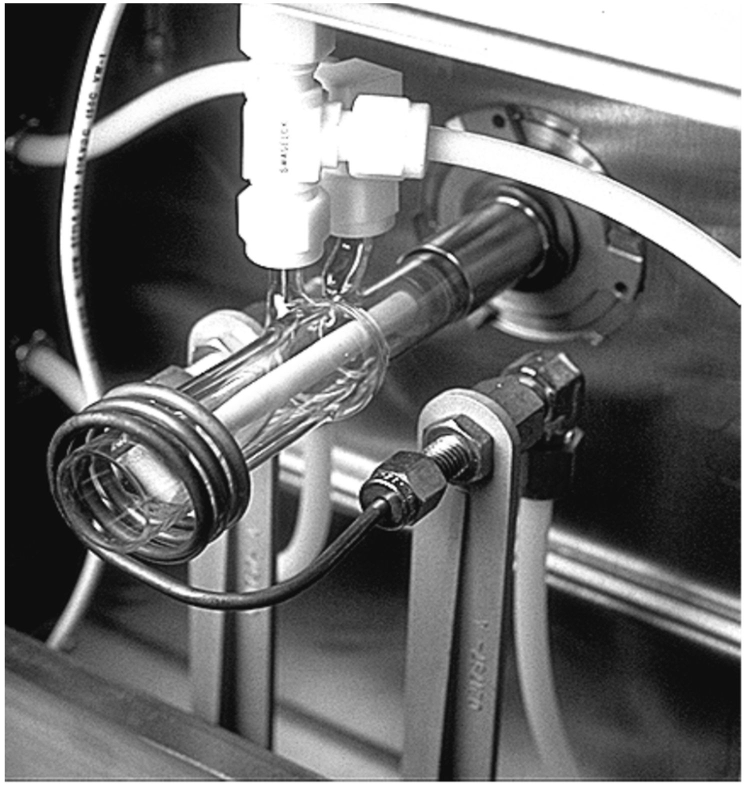
A **plasma** is an ionised gas but globally electrically neutral, and characterised by the presence of free electrons. Practically, all ionised gas could be considered as a plasma.

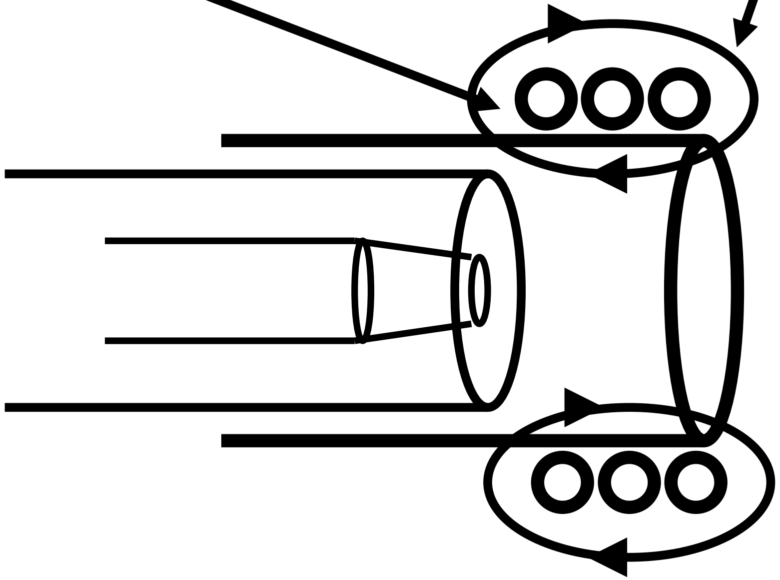
We are also talking about the 4th state of matter

Naturally present in the sun, milky way, lightning, northern lights…

Plasma Genesis

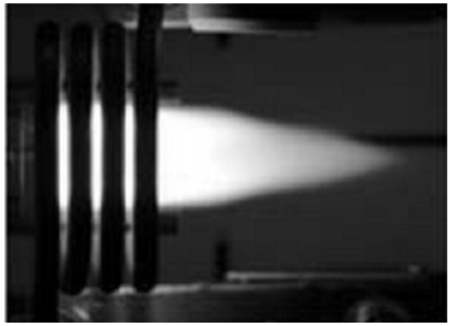




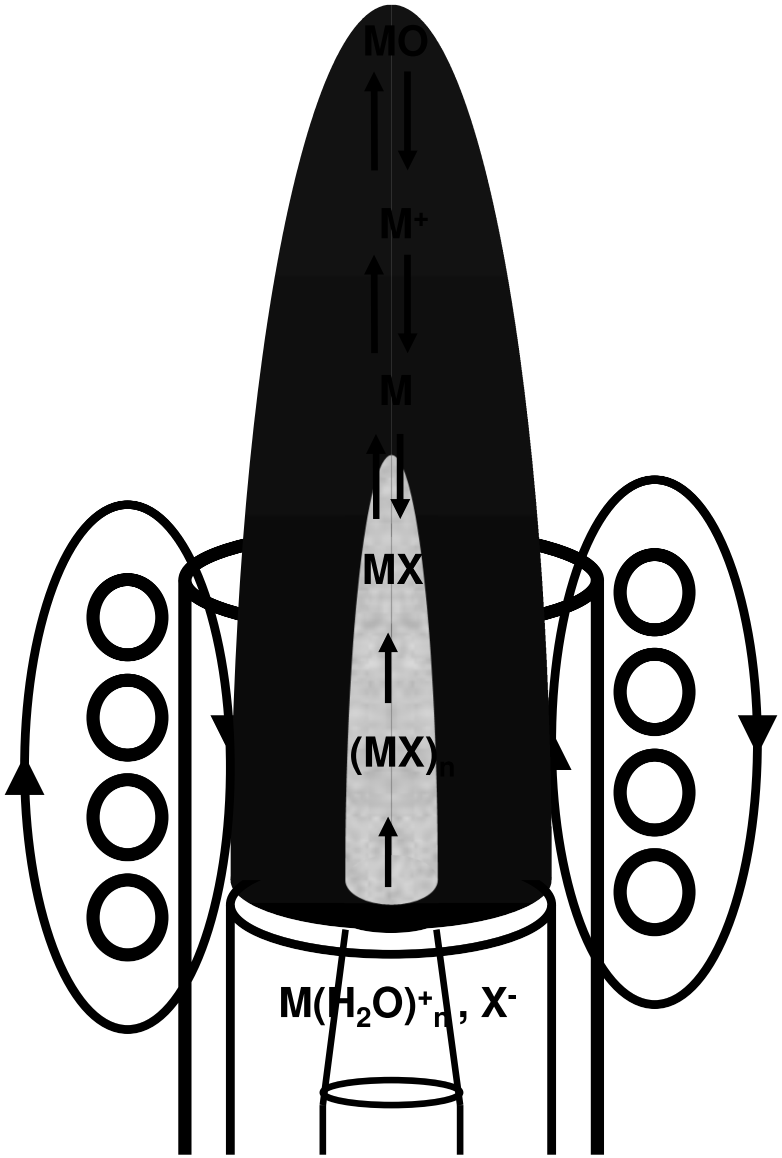


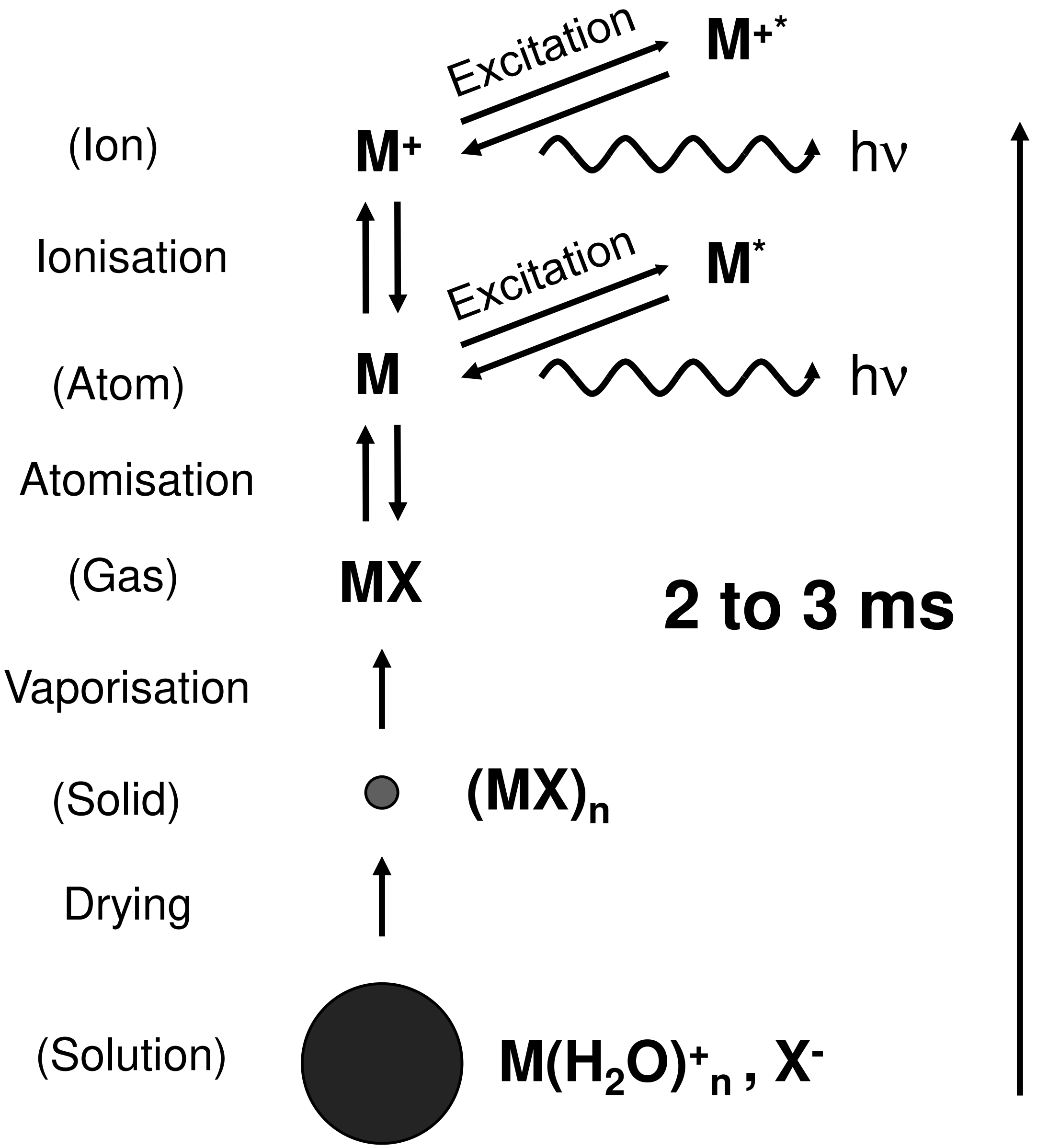
Magnetic field (H)

Coil (AC – High Frequency)



Plasma: Sample Behaviour





Excitation → M^{+*}

(Ion) M^+ ← hν

Ionisation

Excitation → M^*

(Atom) M ← hν

Atomisation

(Gas) MX

2 to 3 ms

Vaporisation

(Solid) $(MX)_n$

Drying

(Solution) $M(H_2O)^+_n$, X^-

Conclusions on the Plasma

- Most elements are ionised at 90 % in the 6000^{o}C of an ICP.
- Exceptions:
  - As: 52 %
  - Se: 33 %
  - S: 14 %
  - F: 9x10^{-4} %

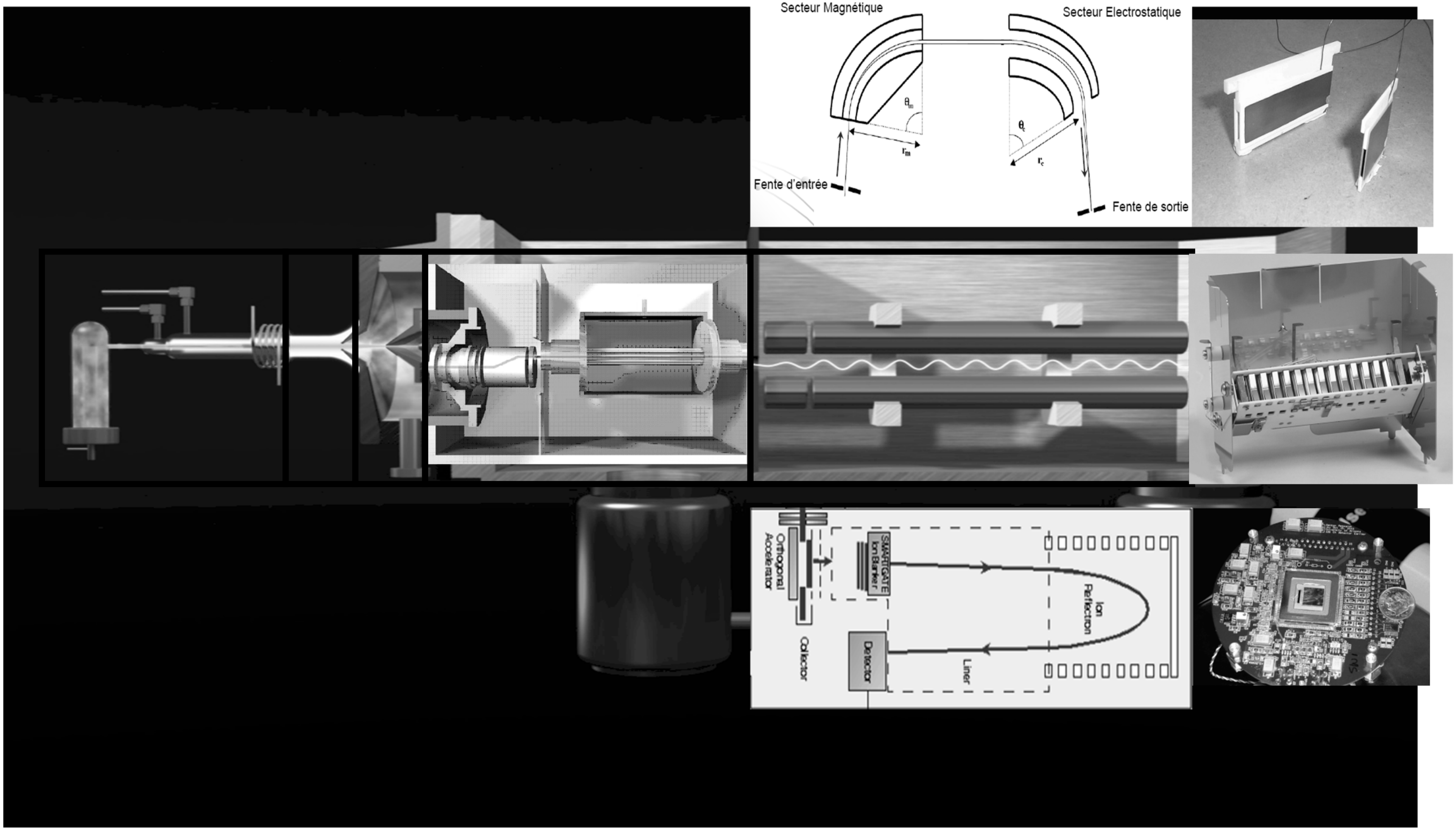
- Single charged positive ions predominate

- Only a small population of double charged ions
  - Main Example: Ba = 1 - 2 % of Ba^{++} and Ce^{++}

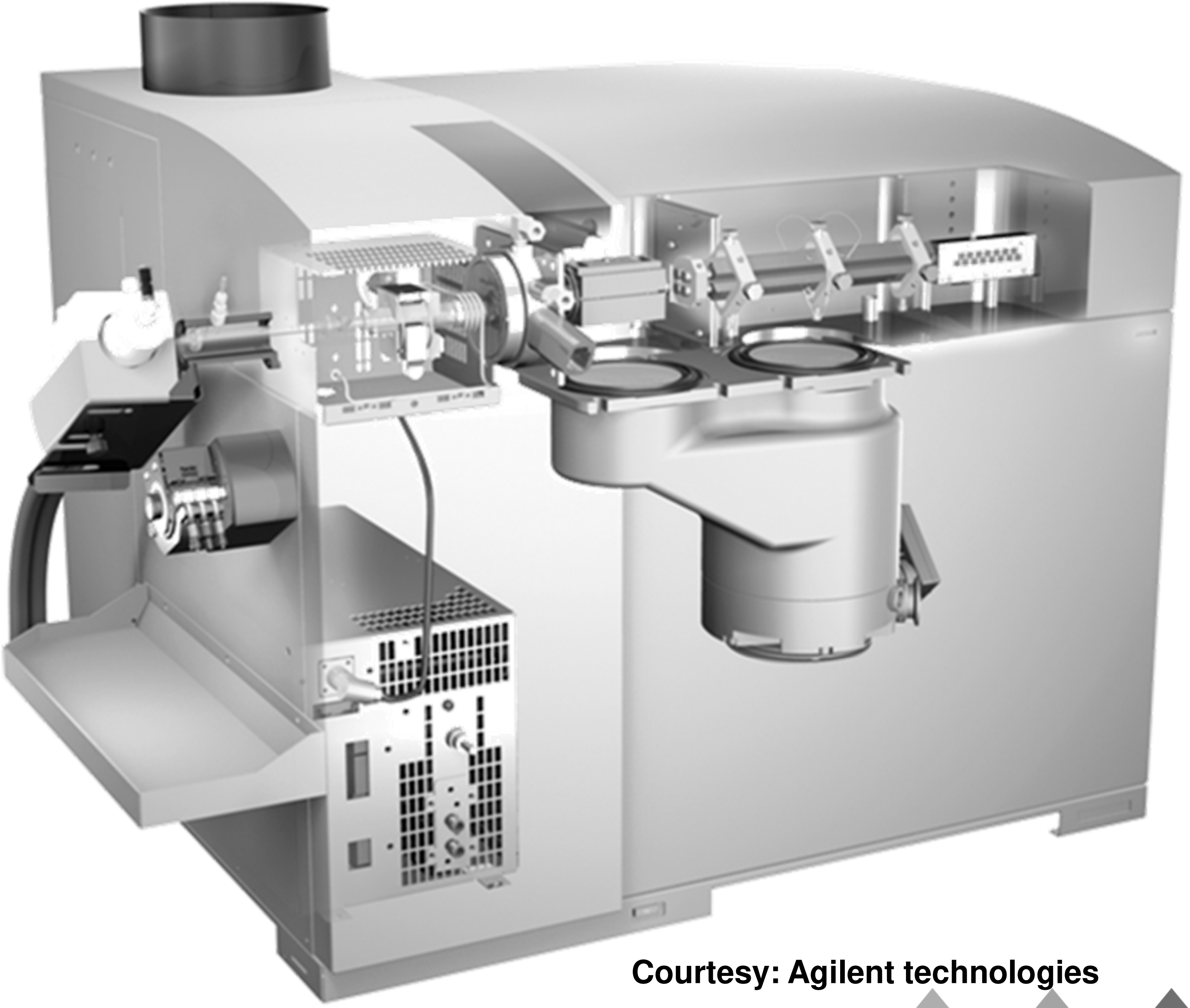
Components of an ICP-MS

- Sample introduction system
- Ionization source (Plasma)
- Ion extraction system (Interface)
- Ion focusing system (Ion optics)
- Mass filter (Mass spectrometer)
- Ion detection system (Detector)

Components of an ICP-MS

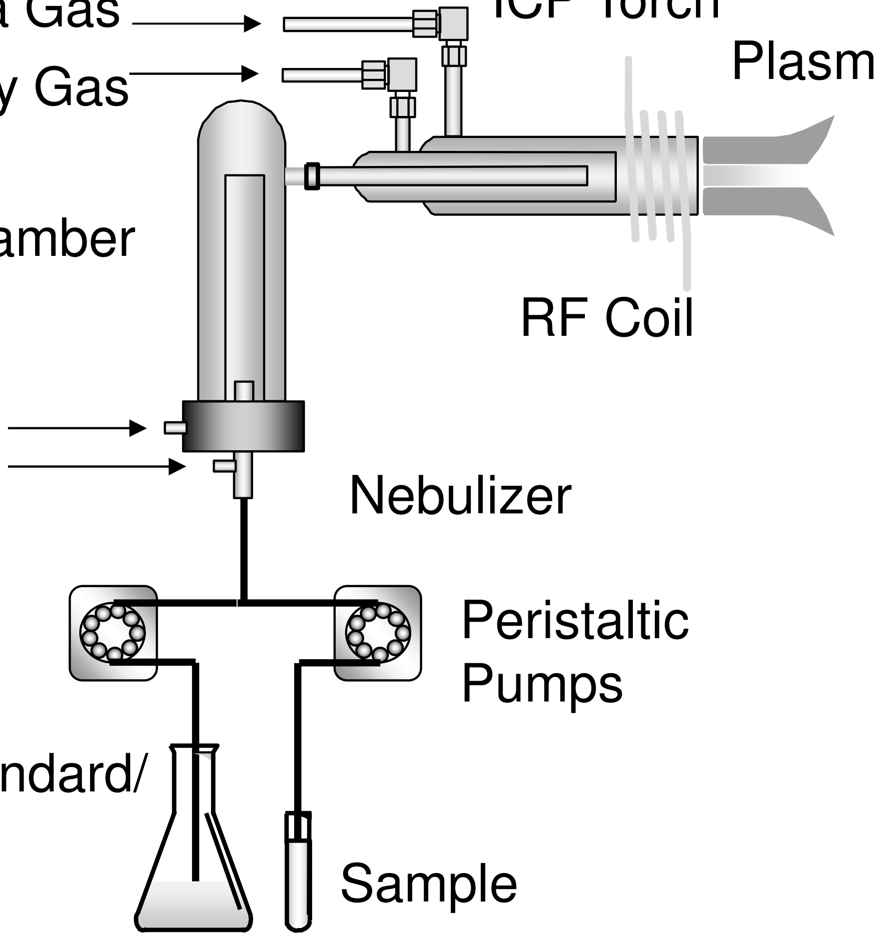


Overview of an ICP-Q-MS



Courtesy: Agilent technologies

Sample Introduction



Plasma Gas

ICP Torch

Plasma

Auxiliary Gas

Peltier Cooled Spray Chamber

RF Coil

Blend Gas

Carrier Gas

Nebulizer

Peristaltic
Pumps

Internal Standard/
Diluent

Sample

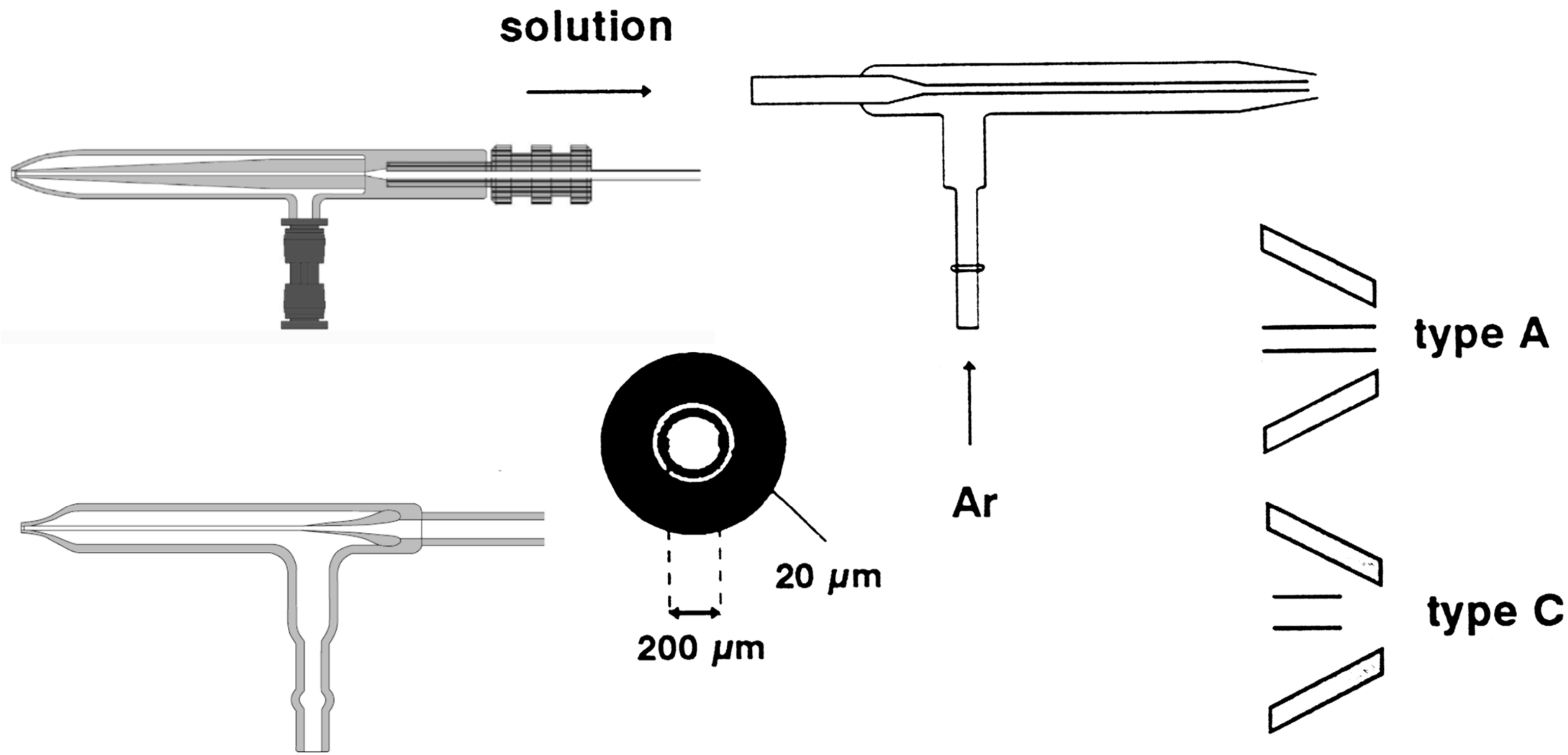
Nebulizers

Must generate a fine and steady spray (i.e. < 10 µm)

To be used with or without spray chamber regarding the design

Concentric Nebulizer Type

Operating principle : The sample is introduced into a capillary tube by a peristaltic pump or by auto-suction. The concentric gas flow around the capillary nebulizes the sample.



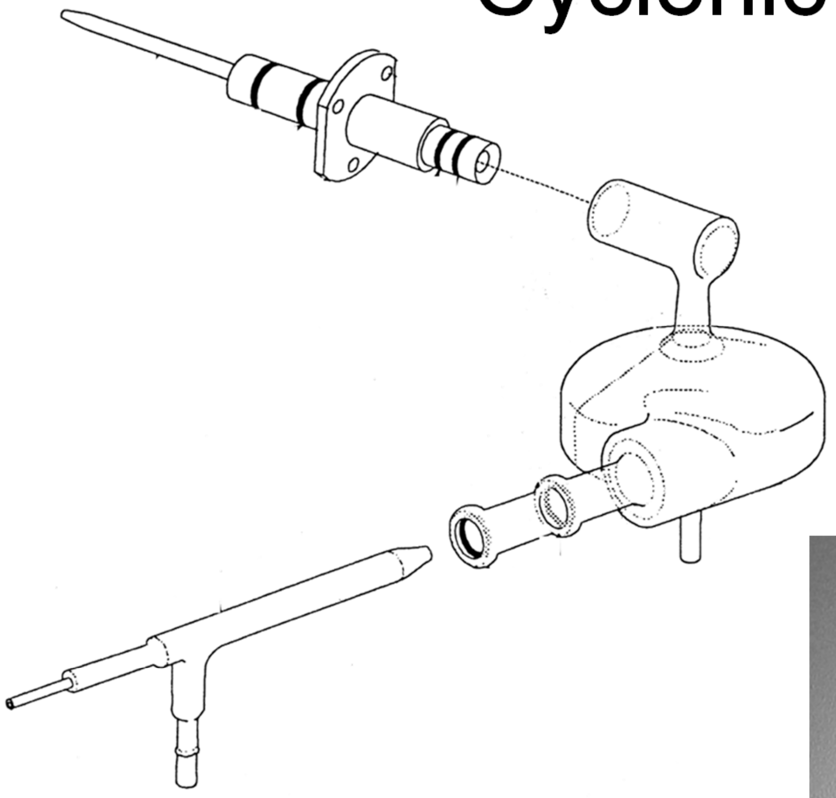
Spray Chamber

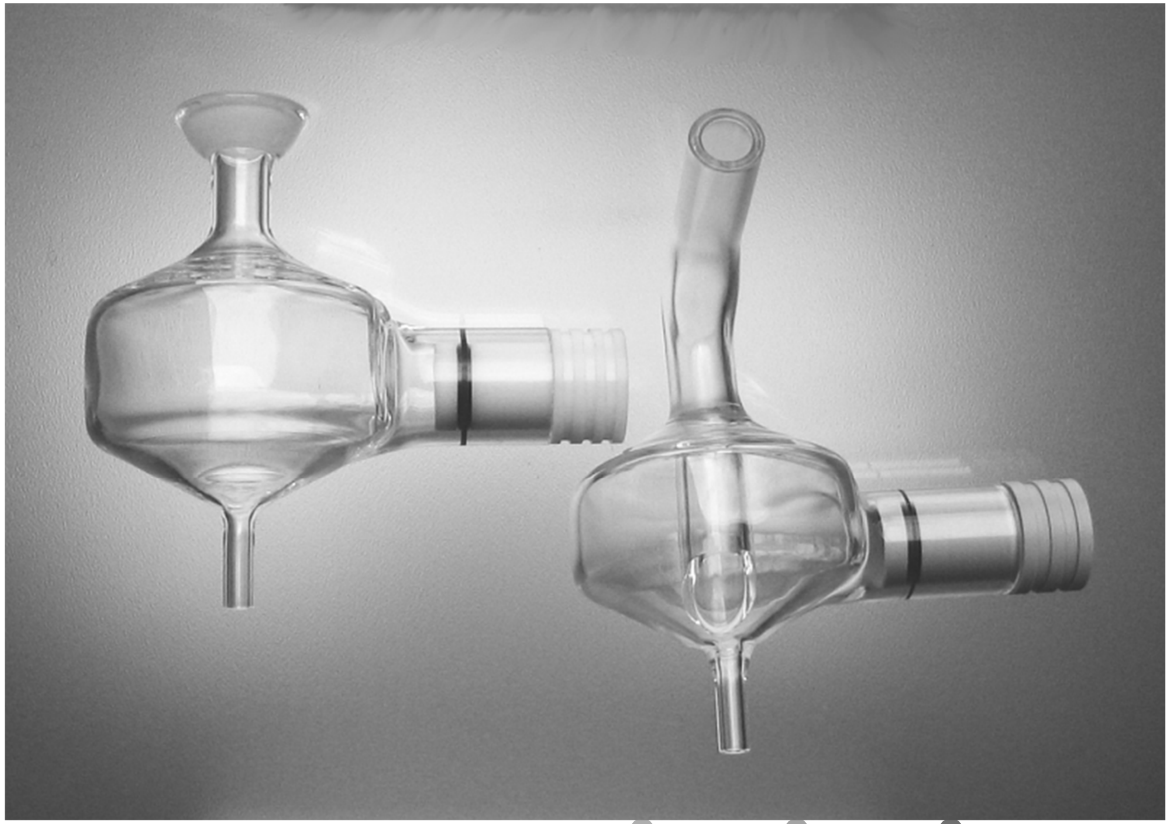
Target : to stop the greatest droplets (> 10 µm).

3 designs:

- Single pass with impact bead
- Scott (Double Pass)
- Cyclonic (Baffle or unbaffled)

Cyclonic Spray Chamber





Interface

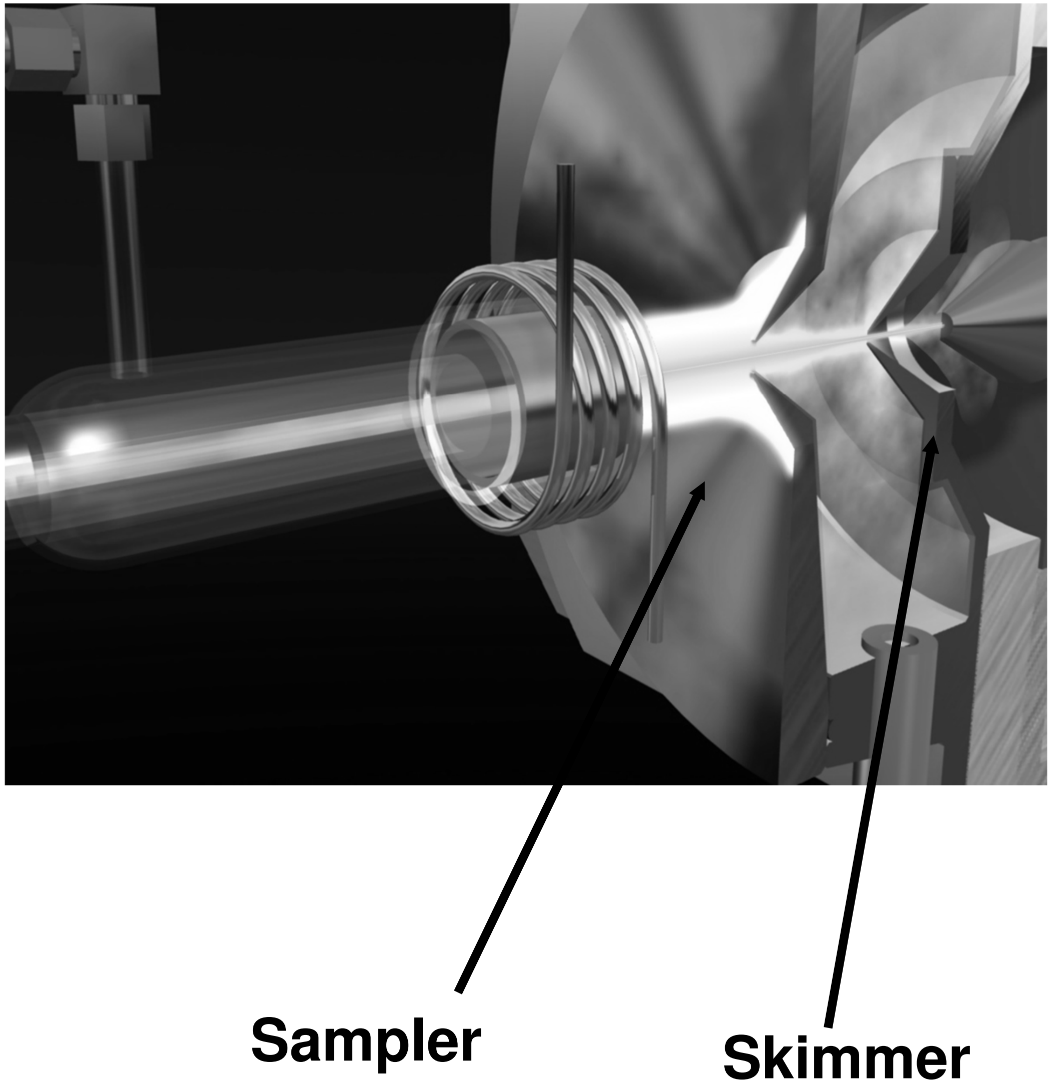
2 or 3 cones:

- **Sampling or sampler**
- **Skimming or skimmer**
- **Hyper-skimmer**

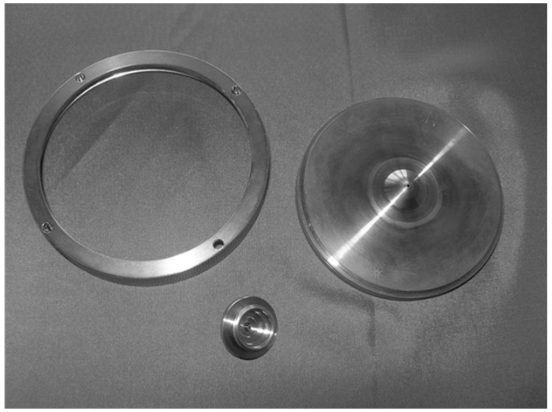
Allow introduction of ions into the vacuum chamber

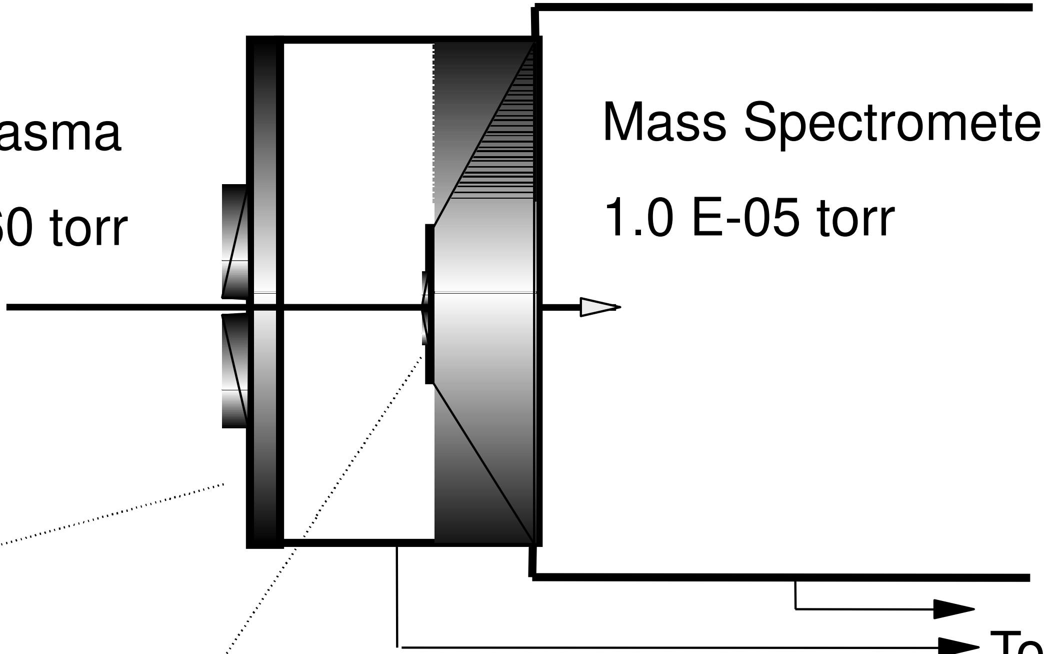
Material : Nickel

Platinum (Cupper, Aluminium)



Interface





Interface

1.0 E-02 torr

Plasma

760 torr

Mass Spectrometer

1.0 E-05 torr

Sampler Cone

+/- 1 mm orifice

Skimmer Cone

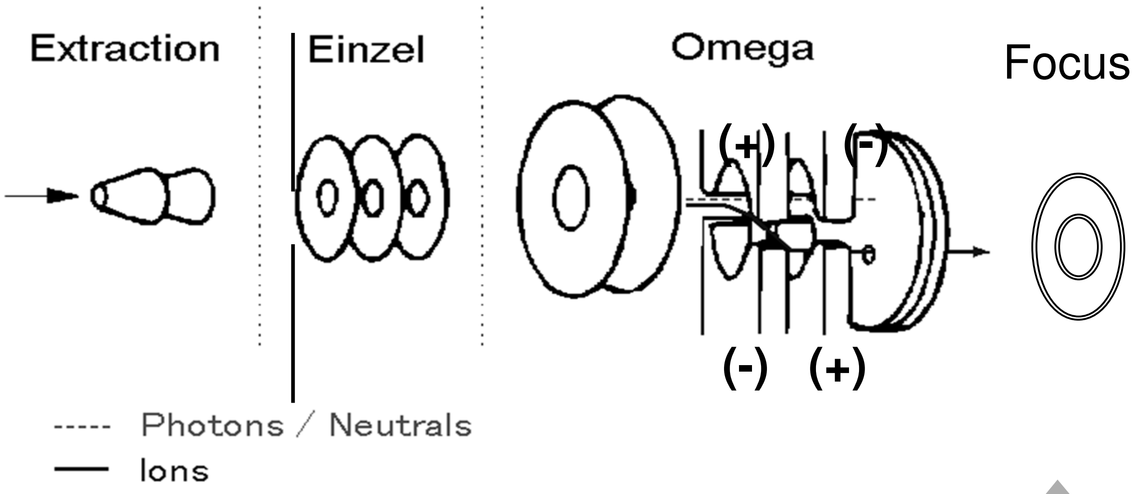
0.4 - 1 mm orifice

To pumps

Ion Lens System

Serves to focus ions coming from the skimmer into the mass filter. Rejects neutral atoms and minimizes the passage of any photons from ICP.

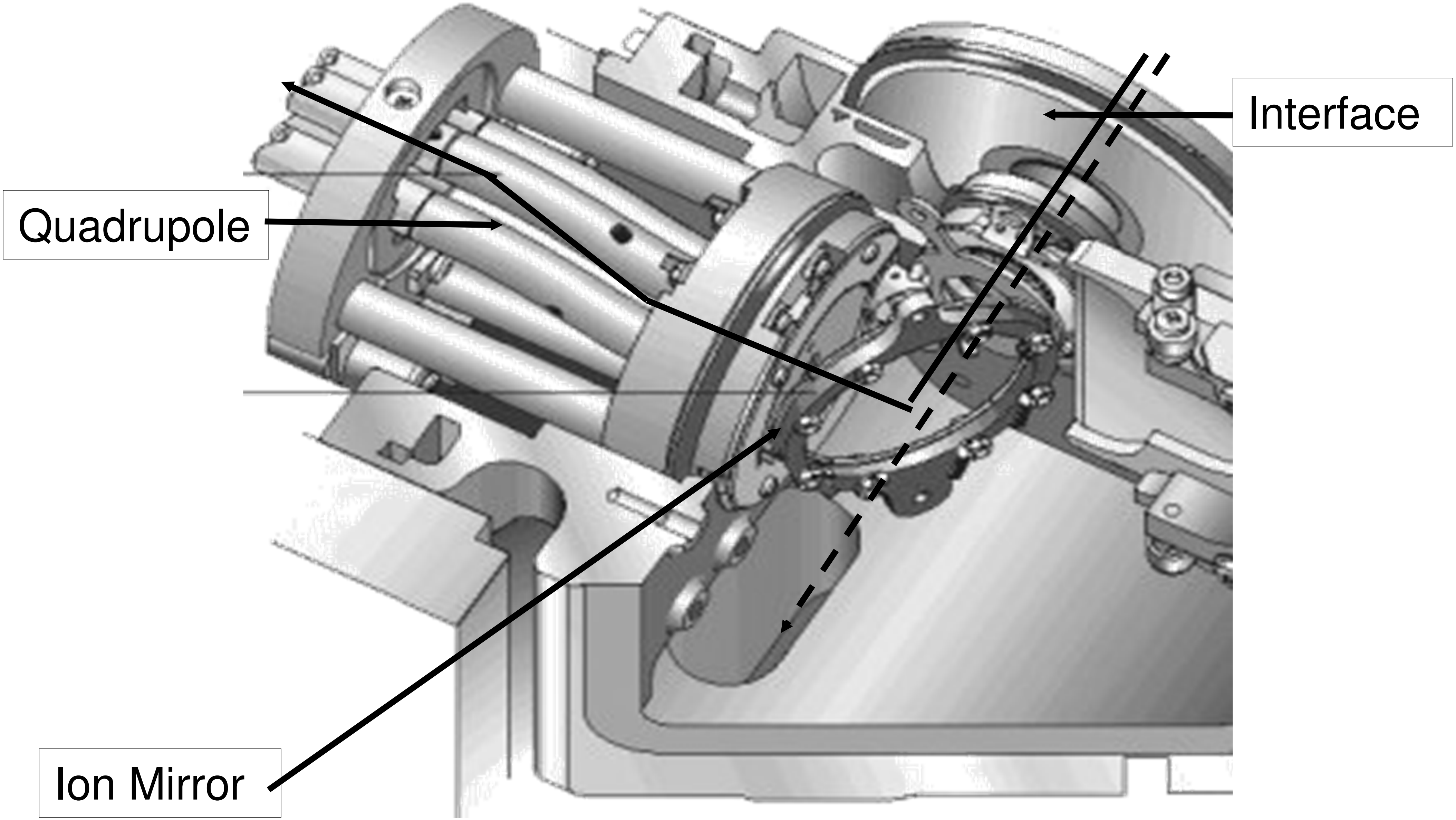
- **Extraction** - Extract and accelerate ions from the plasma
- **Einzel** - Collimate and focus ion beam
- **Deflection** - Bend ion beam to eliminate photons and neutrals
- **Focus** - Refocus ion beam
- …



Electrostatic Lenses

- Ions, photons and neutrals all enter the spectrometer through the interface
  - the detector is sensitive to photons/neutrals, as well as ions
- Ions are charged particles
  - can be deflected using electric fields
- Photons travel in straight lines
- If ions can be deflected off-axis, they will be separated from non-charged species (photons/neutrals)

Ionic optics: Focusing Mirror



Interface

Quadrupole

Ion Mirror

Mass Filter

Inorganic Mass Spectrometer

- $m/z < 300$
- Measurement of concentrations with accuracy and repeatability (absence of isobaric interference)
- Measurement of traces and ultra-traces: ppb in a solid

  ng / L in a solution
- Measurement of isotope ratios, including isotopic dilution.

Main Types of Mass Spectrometers

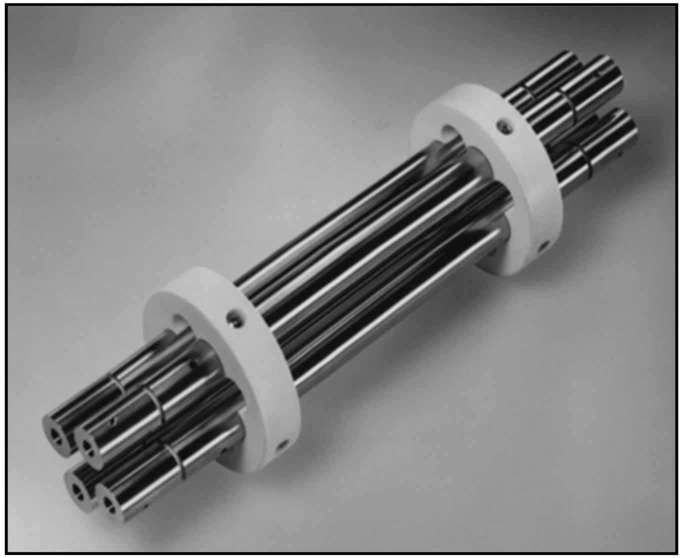
- **Mass filtration:**
    - Quadrupole filter

- **Selection in space:**
    - Sector (s)

- **Selection over time:**
    - Flight time

Quadrupole Filter

- 4 rods of section ideally elliptical or circular (for practical reasons with a radius r = 1.144 r °)



- Internal diameter, 2 r° (6 to 8 mm)
- Bar length
- Materials (golden ceramic, tungsten, etc.)
- High Frequency (1.5 to 3 MHz)

Quadrupole Filter

$$\Phi_0 = (Bias) + U + V \cos \omega t$$

Where :

Offset, **Bias** : Direct voltage applied identically to each of the rods

U: DC applied to each pairs of rods

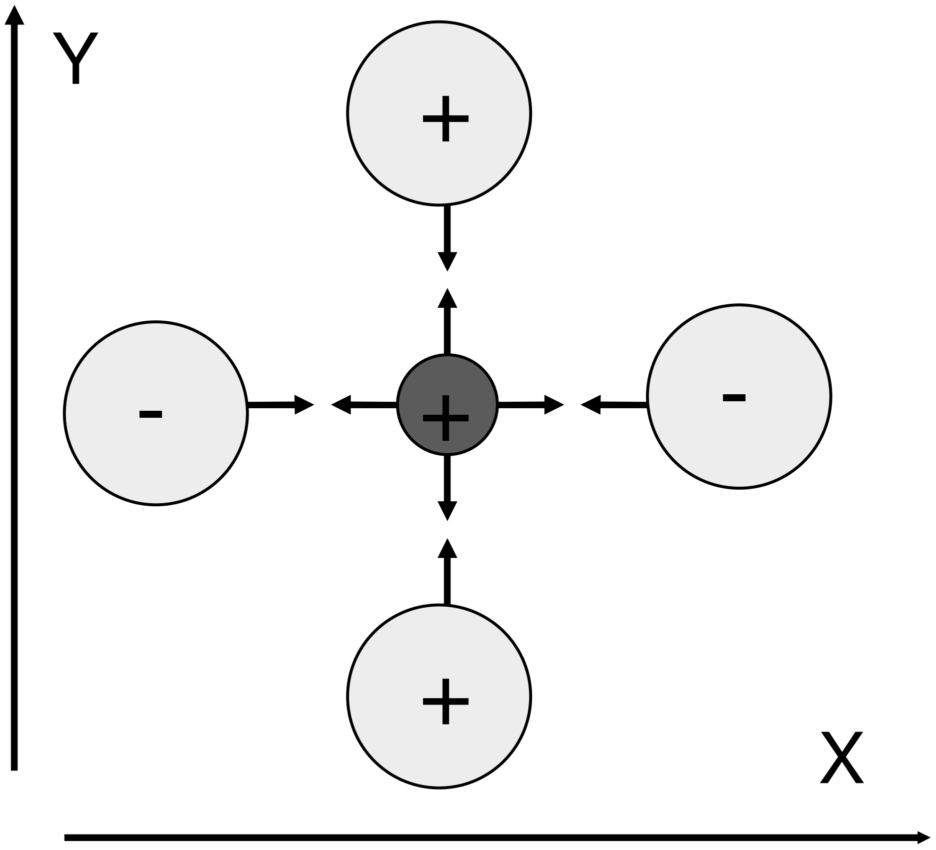
V: RF applied to each pairs of rods

with $|\mathbf{V}| > |\mathbf{U}|$

$\omega = 2\Pi\nu$ where ν = frequency (fixed)

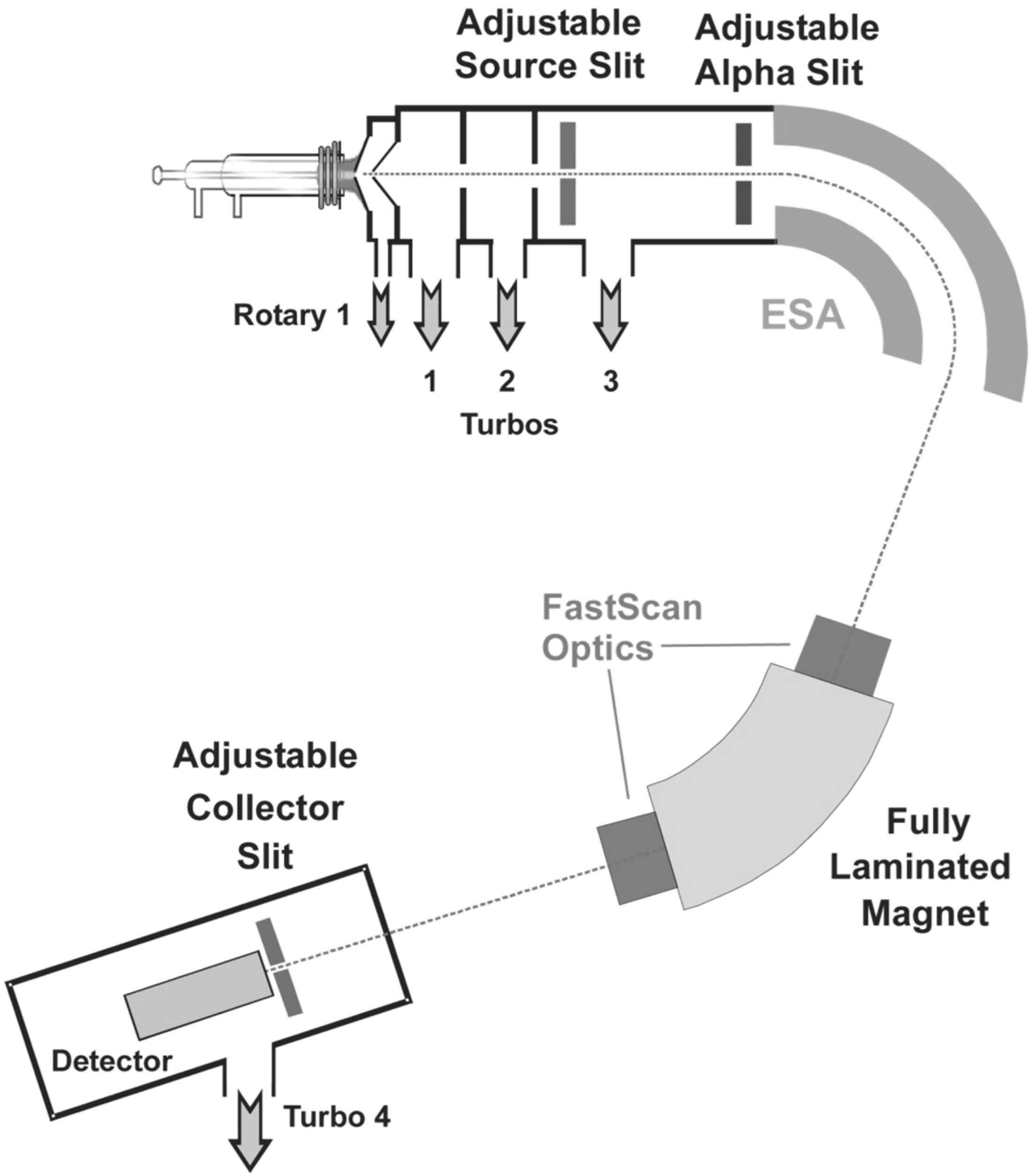
Quadrupole Filter

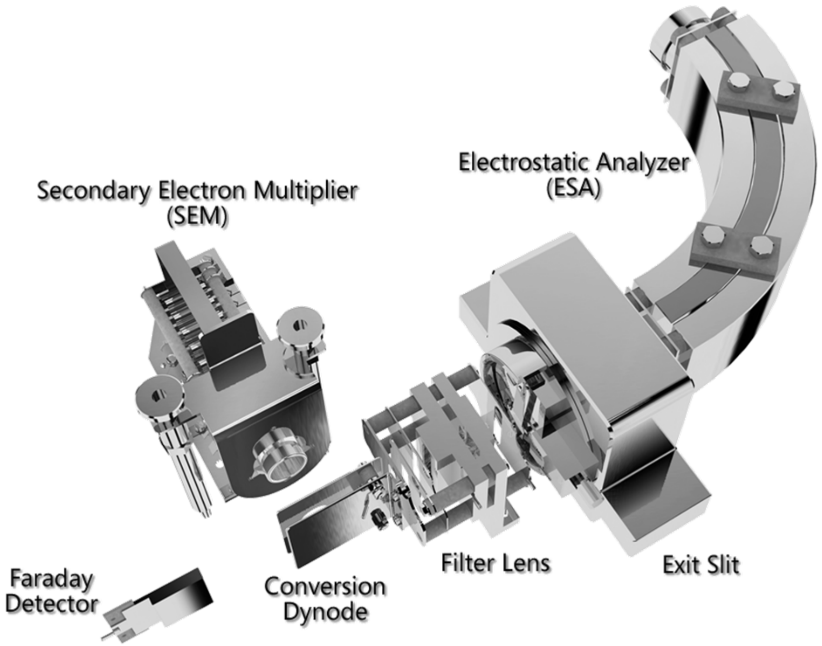
For a given field ϕ_0,



If m / z is the right value, the restoring force in the X and Y planes will exactly compensate for the attraction of the bars presenting a back and forth trajectory in the X plane and in the Y plane, i.e. in the end more or less helical.

ICP-MS High Resolution





Action of a Magnetic Sector

When the ions of charge z, of speed v are subjected to a magnetic field H, they undergo a force F:

$$F = H.z.v$$

Under the influence of this force, the ion deflects and acquires a circular path of radius r, with a centripetal force *F*:

$$F = \frac{m.v^2}{r}$$

And then

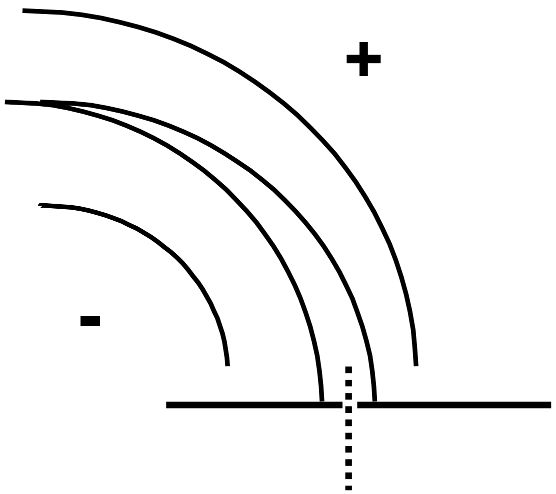
$$r = \frac{m.v}{z.H}$$

Action of an Electrostatic Field

The action of an electrostatic field leads to a force F:

$$F = z.E = \frac{m.v^2}{r}$$

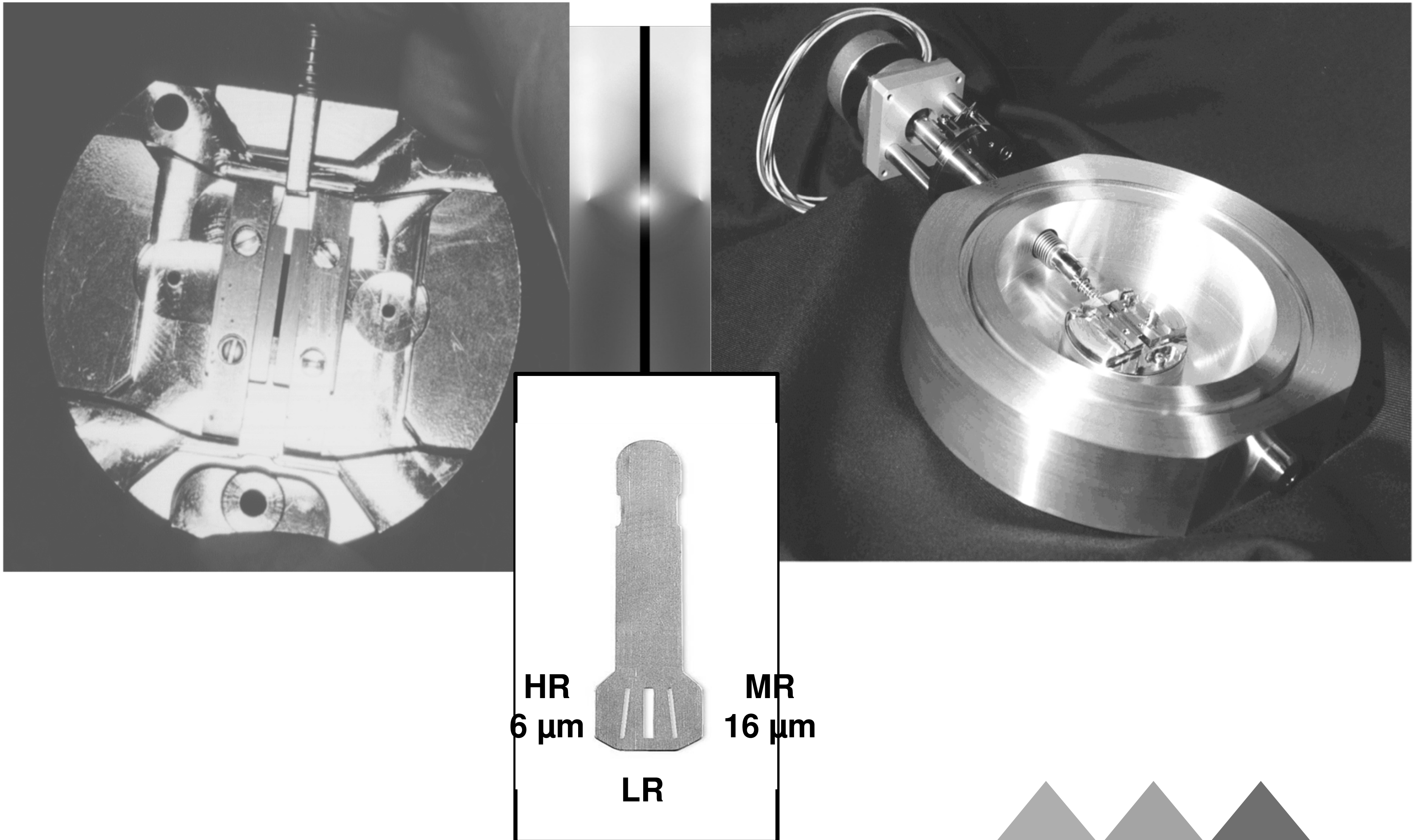
$$r = \frac{2.\mathrm{Ke}}{z.E}$$



Using an exit slit, we isolate a fraction of the beam of uniform energy, whatever the mass of the ion

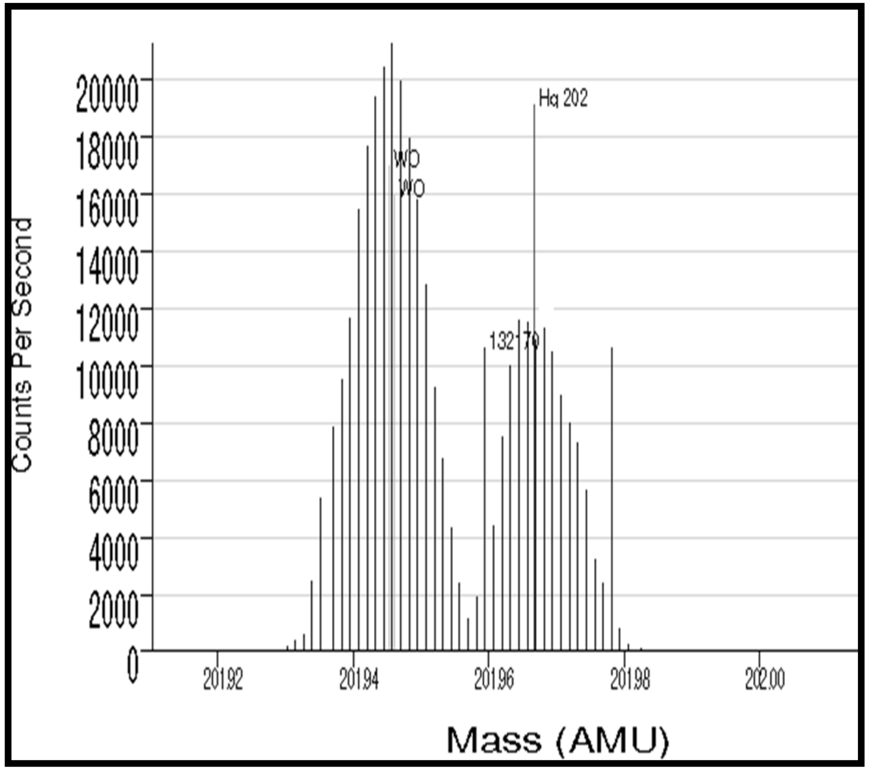
Resolving Power : Exit Slit

Adjustable between 400 and over 10,000 Resolving Power

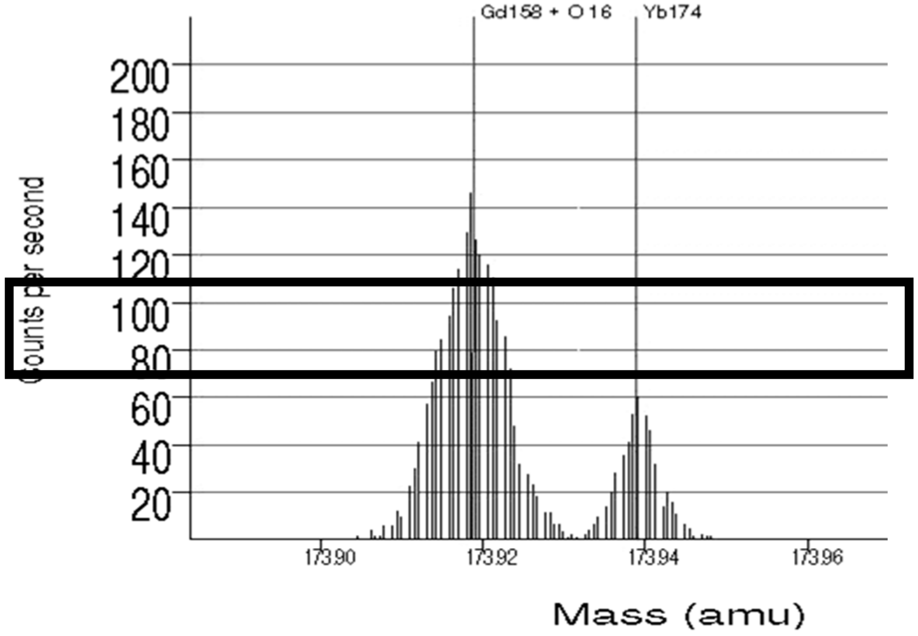


High Resolution

Resolving Power: over 10,000

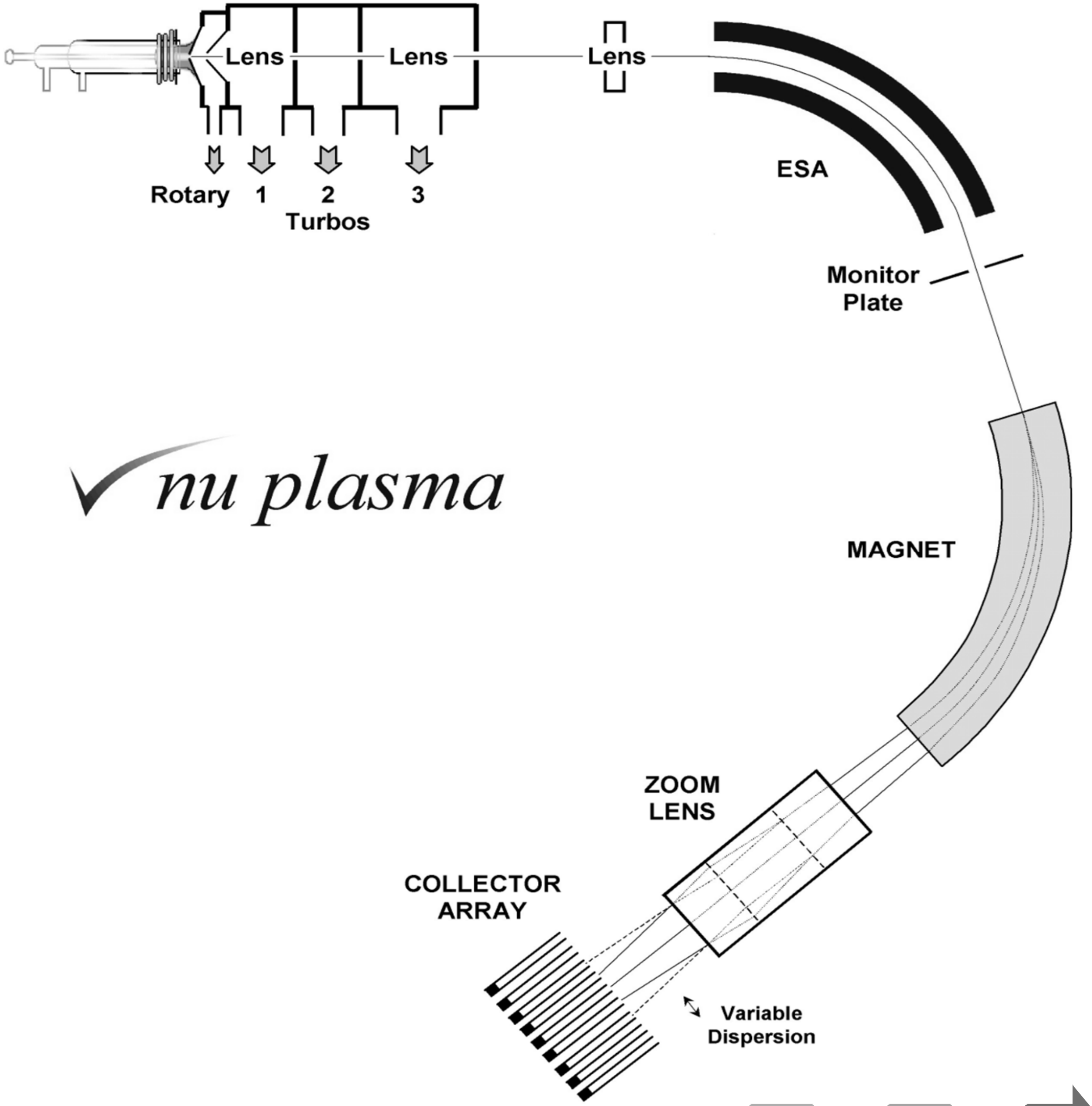


^{202}Hg separated from ^{186}W^{16}O et 11 000 of RP



50 ppt Yb in 0.1% GdO (PR 13 500)

ICP-MC-MS High Resolution



nu plasma

The Time of Flight

Taking into account that:

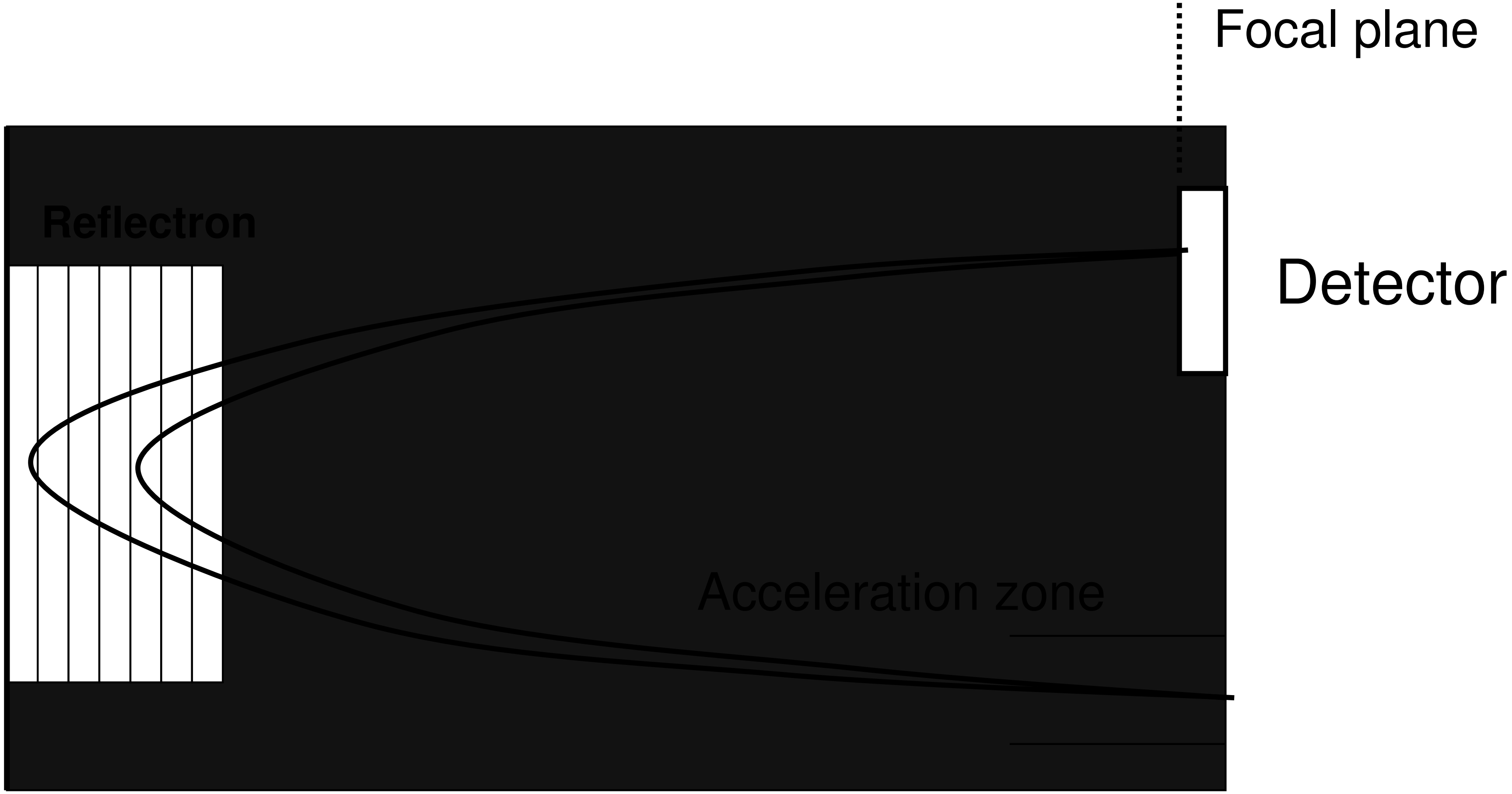
$$E = \frac{1}{2} m.v^2$$

The flight time t is therefore equal to:

$$t = L\left[\frac{m}{2E}\right]^{1/2}$$

The time of flight is therefore proportional to the square root of the mass.

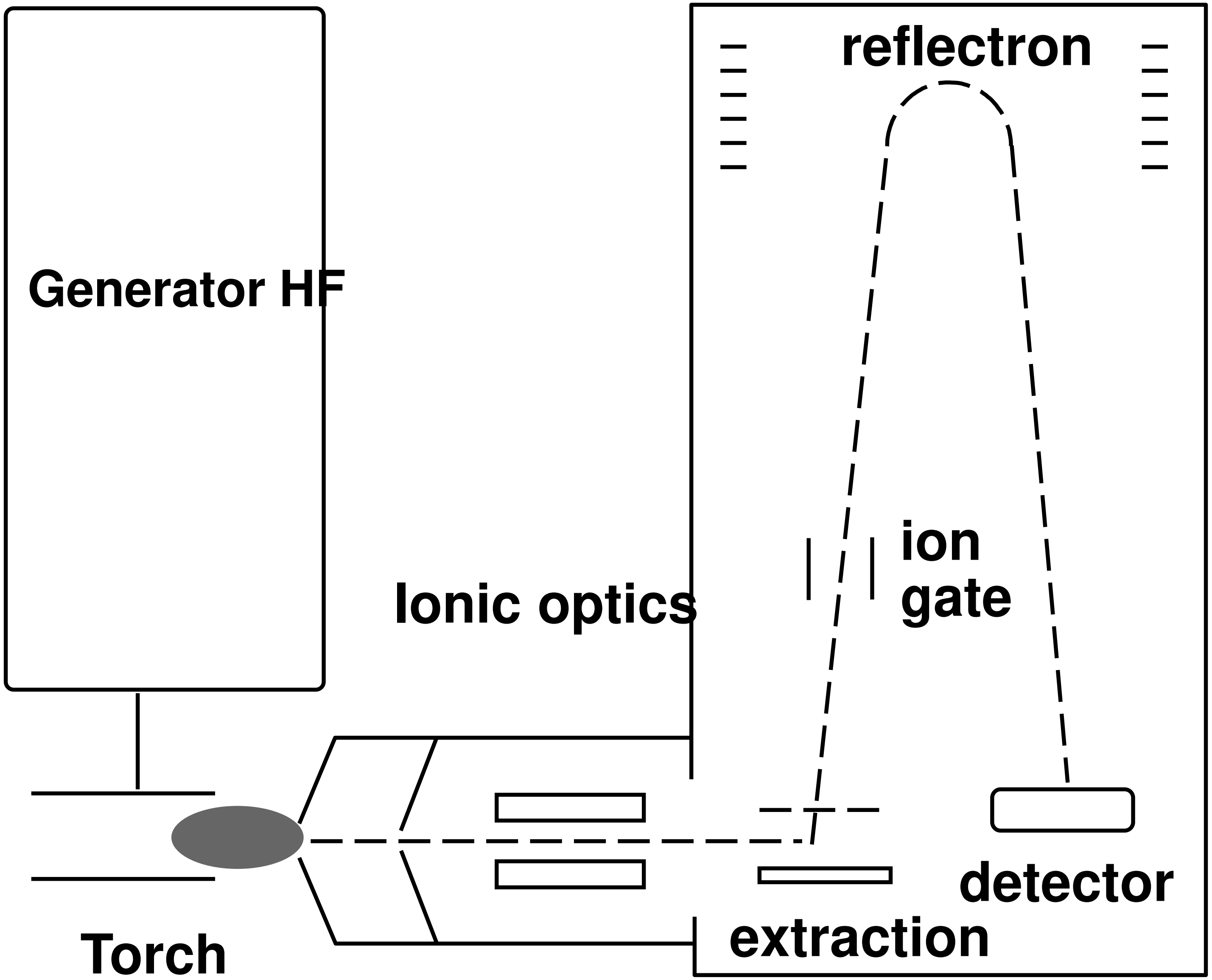
ICP-TOF-MS : Reflectron/ Ion mirror



— X mass ion, slightly faster

— X mass ion, slightly slower

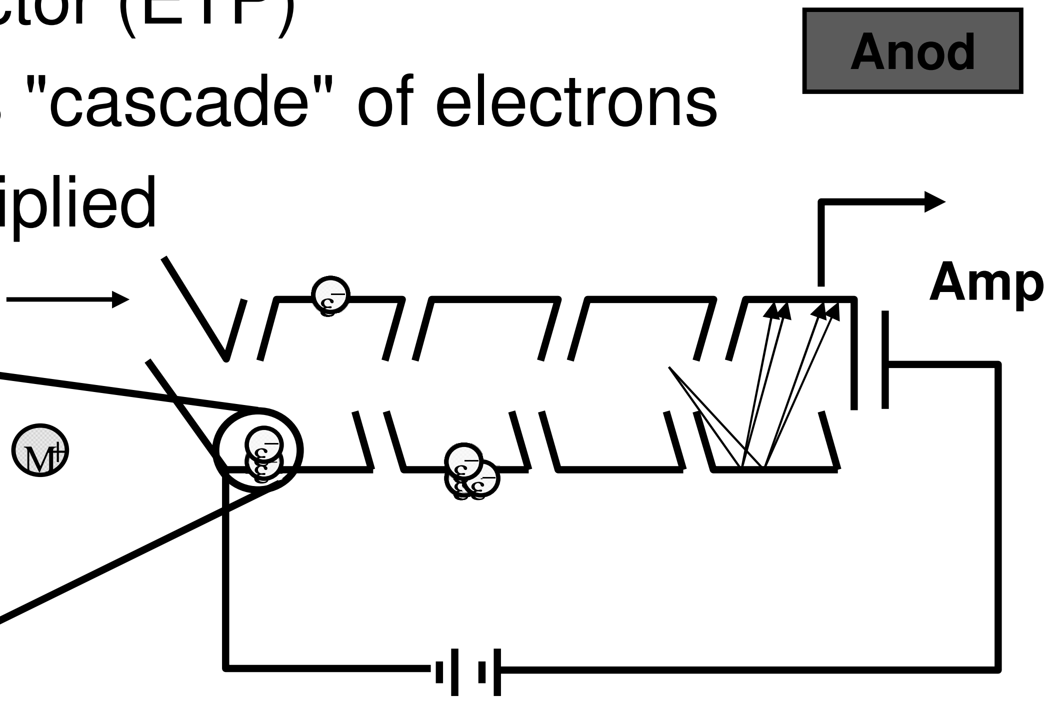
Design of a system ICP-TOF-MS

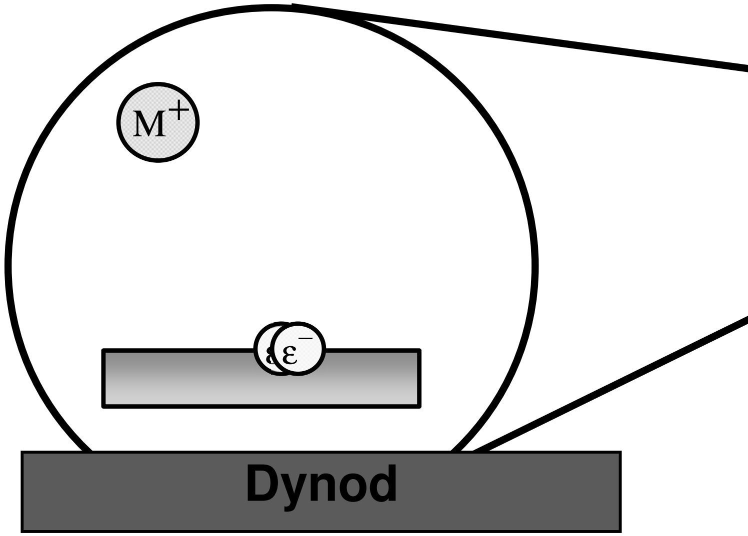


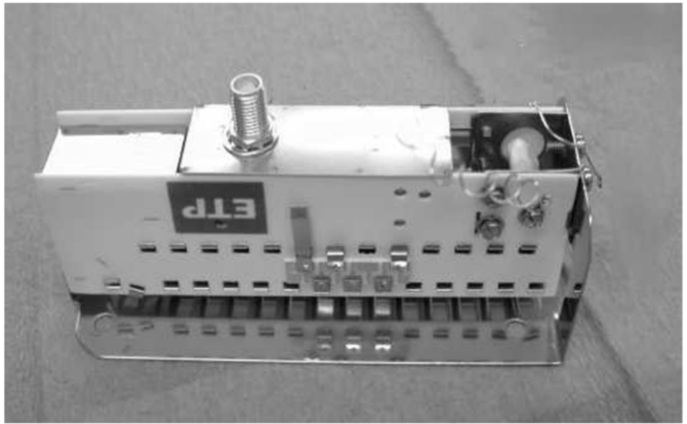
The Electron Multiplier

- Electron multiplier
    - discrete dynode detector (ETP)
        - each dynode gives "cascade" of electrons

          => signal is multiplied







ICP-MS Analyses

Calibration Types

All Atomic Spectrometry techniques are comparative techniques involving calibration

- External calibration
- Standards additions
- (Internal calibration)

- Isotopic dilution (and ratio)

Semi-Quantitative Analysis

Useful to determine :

- The elements present and estimate the contribution of major species to the intensity of each mass
- Potential interference
- Optimal sample dilution
- Which isotope to use in order to avoid interference and select the appropriate internal standard

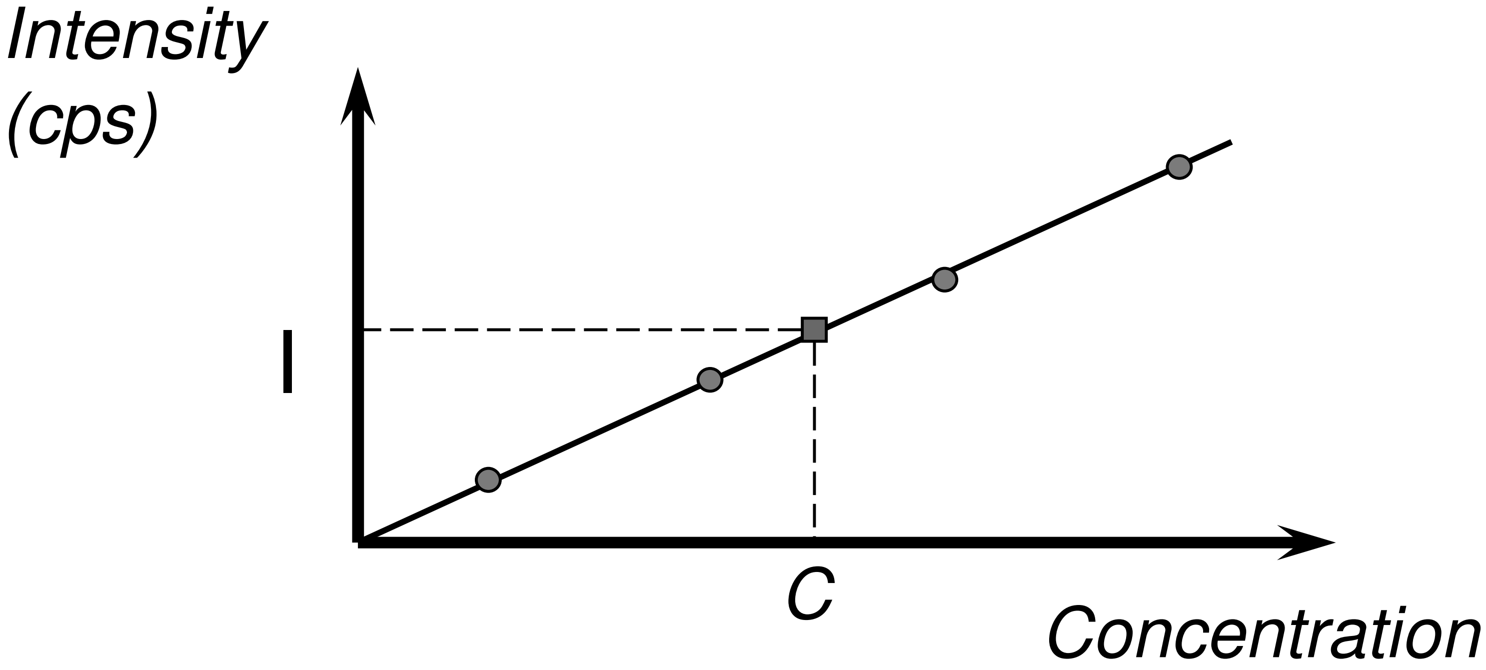
Quantitative Analysis

Analytical Comparison

=> Calibration

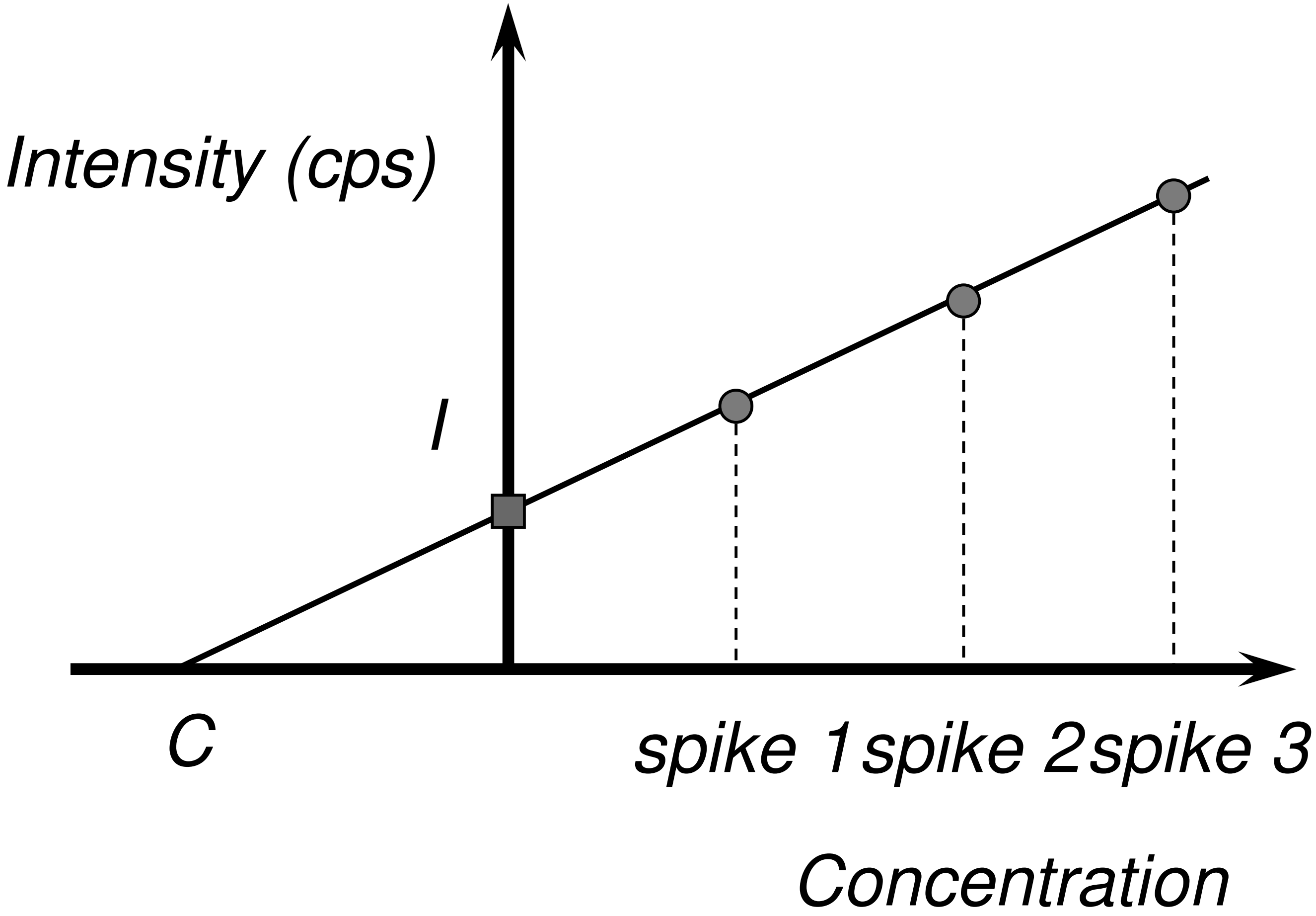
=> Representativity of the standards vs samples

External Calibration



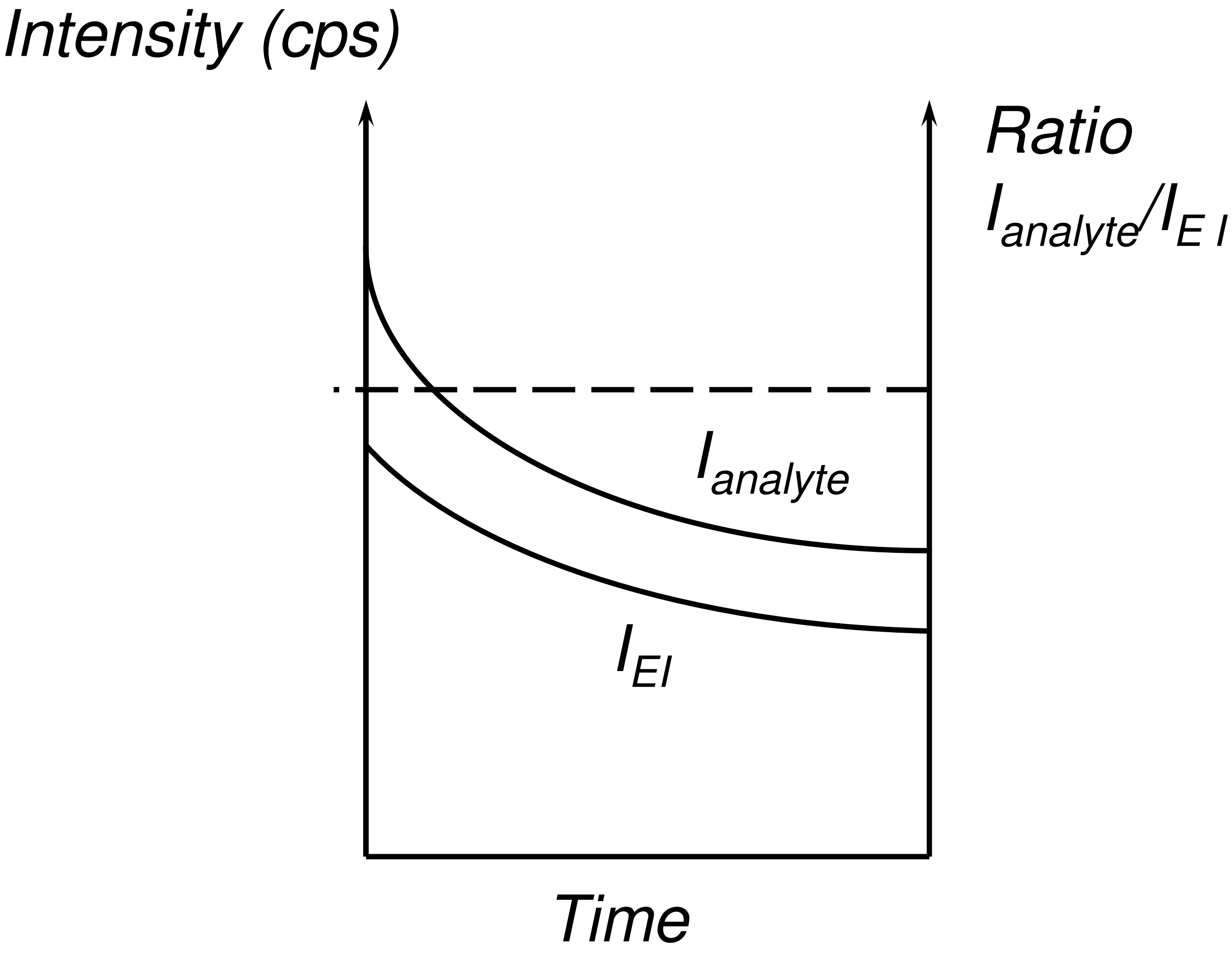
- Easy to handle
- Limited by Matrix effects

Standard Addition



- Optimal if matrix effects
- Spike should be limited
- Good precision for close concentrations
- Difficult
- Linearity

Internal Standard



How the Internal Standards Work

- Added to each sample, standard and blank at identical concentration
- System therefore expects identical response from ISTDs in each solution
- Ratio of measured ISTD response to expected ISTD response is used to correct the response of the non-internal standard elements accordingly.

The Role of Internal Standards

Correct for variations in response due to:

Matrix Effects

- Transport effects
- Nebulization effects
- Ionization effects
- Space-charge effects

Instrument Drift

Choice of the Internal Standard

It is assumed that the IS elements behave in the same way that the analytes do in the plasma when using this correction. Therefore, selecting the appropriate IS element is very important.

These are the things to take into consideration:

- The element is not present in the sample solution.
- The mass number is close to that of the analyte.
- The ionization potential is similar to that of the analyte.
- Chemical characteristics

The ionization potential matching is extremely important for analytes with high ionization potentials.

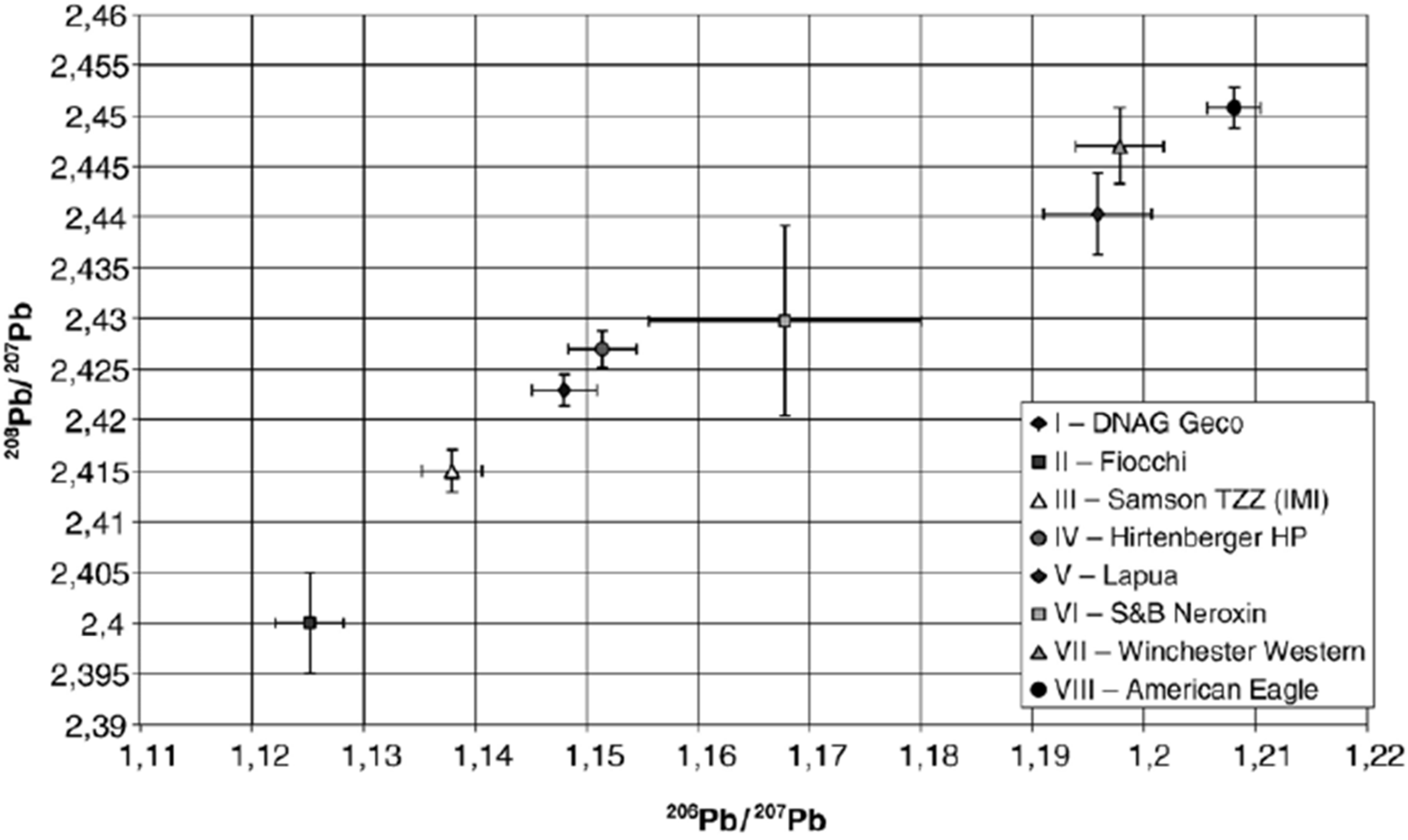
Elements that are commonly used as IS are:

^{6}Li, Sc, Ge, Y, Rh, In, Tb, Ho, Bi, Re

Isotopic Ratio Analysis

- Isotope ratio analysis is used to measure the relative amount of two (or more) isotopes of the same element
- Results are expressed as the ratio of the intensity of a specific isotope to the intensity of a reference isotope
- No calibration is required
- Accuracy is in the range of 0.1% to 2% and depends on the number of counts and the isotope ratio measured

Example: GSR



2,46
2,455
2,45
2,445
2,44
2,435
2,43
2,425
2,42
2,415
2,41
2,405
2,4
2,395
2,39
^{208}Pb/^{207}Pb
1,11
1,12
1,13
1,14
1,15
1,16
1,17
1,18
1,19
1,2
1,21
1,22
^{206}Pb/^{207}Pb
◆ I – DNAG Geco
■ II – Fiocchi
△ III – Samson TZZ (IMI)
● IV – Hirtenberger HP
◆ V – Lapua
■ VI – S&B Neroxin
▲ VII – Winchester Western
● VIII – American Eagle

Isotopic Dilution

- The determination of the concentration is based on the measurement of the intensity ratio of two isotopes of the same element in the sample
- The sample must be spiked with a known amount of an enriched stable isotope which changes the natural isotope ratio of the element
- The spiked isotope is used for calibration

Isotopic Dilution

Pros

- High accuracy
- Calibration and internal calibration are performed with an isotope of the same element
- Automatic compensation for analyte lost during sample preparation
- Automatic compensation for chemical and physical interferences (matrix effects)
- No conventional external calibration required

Isotopic Dilution

Cons

- Need for enriched stable isotopes
- The standard of the stable isotope must be accurately certified
- Depending on the element or enrichment level, this standard can be very expensive
- Both the reference isotope and the analyte isotope must be free of spectral interference
- Not applicable to mono-isotopic elements (yet...)

Isotopic Dilution
Accuracy and Precision

Sample : 50 µg/l Ni in 10% HF

Run	Total Quant	Quant	Isotope Dilution
1	57.5	48.93	50.07
2	57.5	49.93	49.62
3	57.8	48.97	49.32
4	54.4	48.98	49.54
5	54.1	49.97	49.53
mean	56.3	49.36	49.62
recovery [%]	112.6	98.14	99.24

Interferences

Interferences in ICP-MS

- Non-spectroscopic Interferences

  Result from the matrix or the analyzed element

  > Physical
  > Concentration in dissolved solids
  > Space charge effect
  > Ionization Suppression / Exaltation
  > Speciation Influence
  > Memory effect

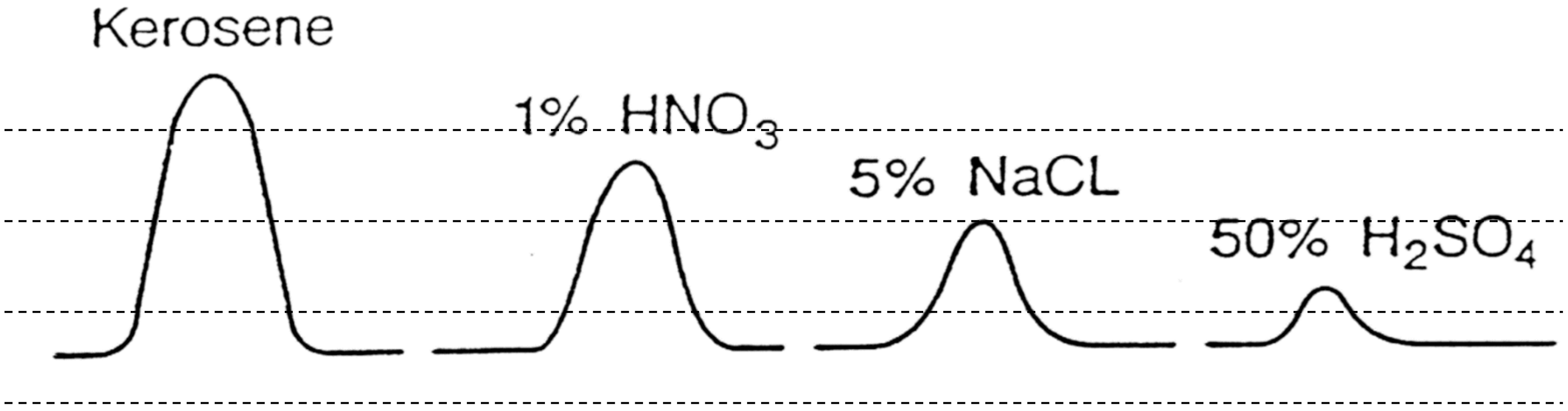
- Mass Spectroscopic Interferences

  Inability to separate same nominal masses

Effect of Dissolved Solids or acid concentration

- Signal suppression
- Deposits on sampler and skimmer cones
- Deposits on ion optics

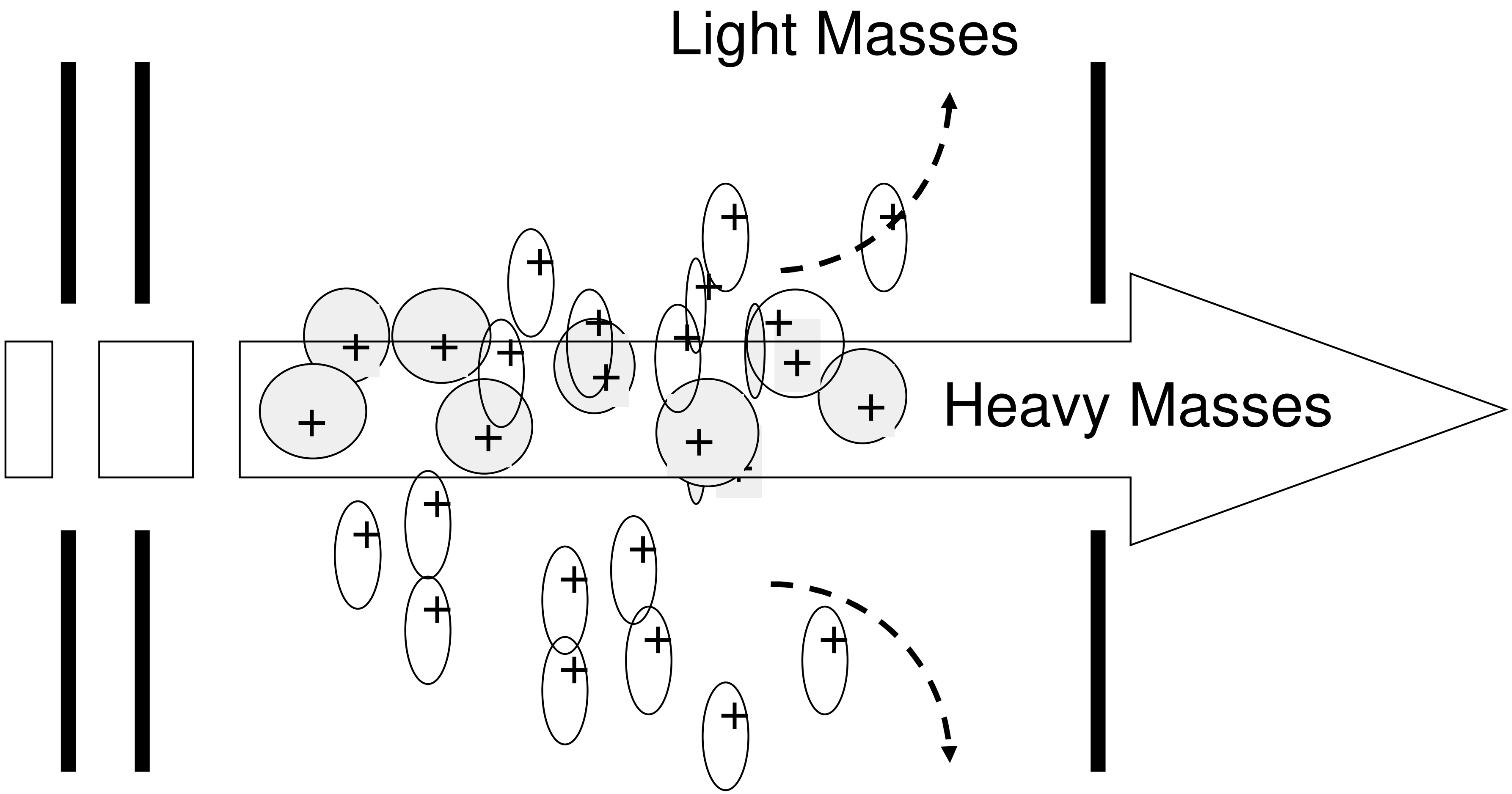
2 mg/l in Cu



Non-spectroscopic interferences: Physical - Resolutions

- Imitate the composition of the sample matrix in the standards - "Matrix matching"
- Acid matrix generally quite easy to reconstitute
- Difficult with regard to the matrix of the sample
- Use of internal standard
- Calibrate by standard additions

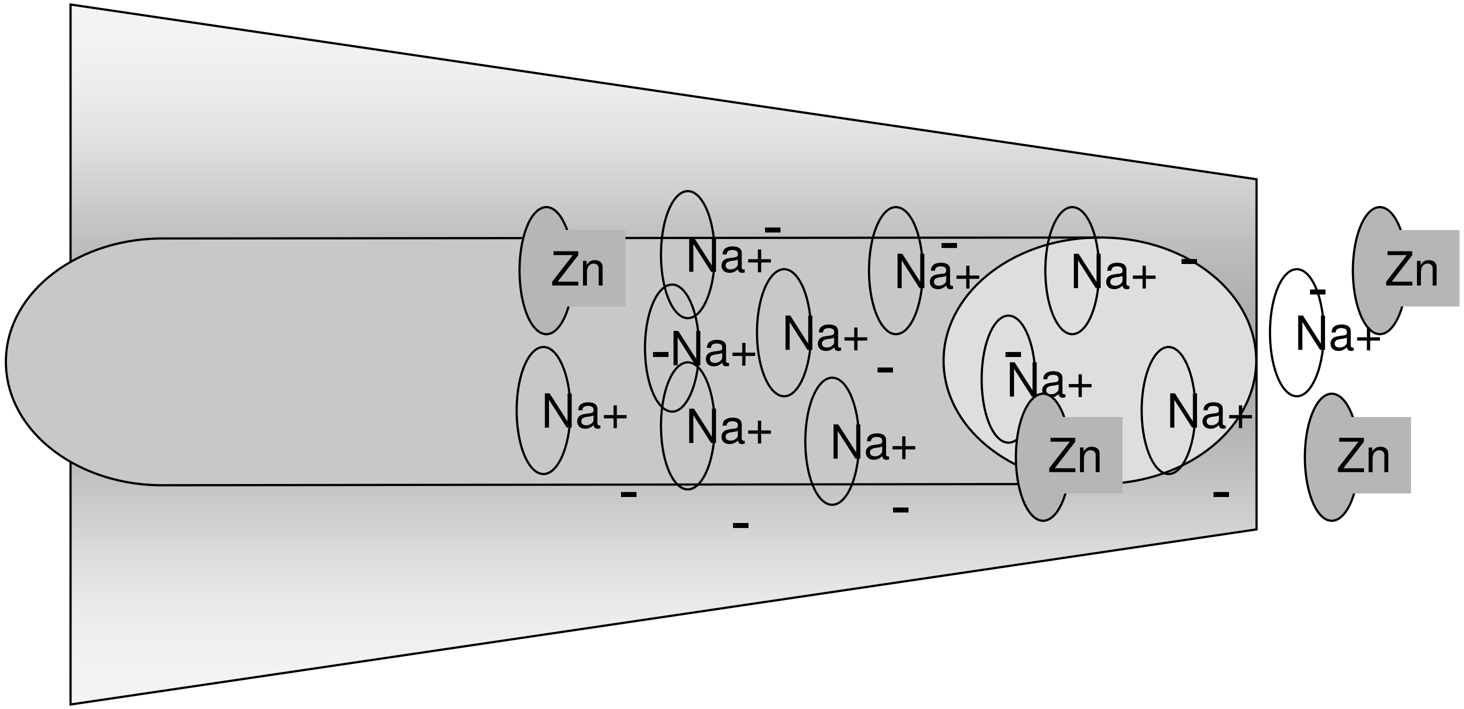
Space Charge Interface and Lens Region



Resolution of Non-spectroscopic Interferences
Space - Charge Effect

- Sample dilution
- Use of an internal standard of mass similar to the analyte
- Elimination of the matrix (Preparation of the sample, ETV ...)
- Imitation of the composition of the sample matrix in the standards - "Matrix matching"
- Calibration by standard additions

Ionization Suppression Plasma Region



$$Na \Rightarrow Na^{+} + e^{-}$$

$$Zn^{+} + e^{-} \Rightarrow Zn$$

- Ex: High Na concentration depresses the signal

Resolution of Non-spectroscopic Interferences

Ionization Suppression / Enhancement

- Sample dilution
- Elimination of the matrix (Preparation of the sample, ETV ...)
- Imitation of the composition of the sample matrix in the standards - "Matrix matching"
- Use of an internal standard of ionization potential similar to the analyte
- Calibration by standard additions

Mass Spectroscopic Interferences

- Isobaric
- Polyatomic
  - Argides
  - Oxides
  - Other (i.e. Chlorides, Hydrides, etc.)
- Doubly-charged
- Abundance in sensitivity

Isobaric Interferences

Interference generated by an isotope associated with an element different from the analyte, but with a mass / charge ratio sufficiently close to that of the analyte that it cannot be separated by the mass filter (quadrupole)

	Isotopic Abundance				
	46	**47**	**48**	**49**	**50**
Ca	**0,003**		**0,187**		
Ti	**8,0**	**7,3**	**73,8**	**5,5**	**5,4**

Isobaric Interferences: Solutions

- Choice of another non-interfered isotope (^{44}Ca instead of ^{40}Ca <> ^{40}Ar)

Impossible for mono-isotopic elements

- Elimination of the matrix (Preparation of the sample, ETV ...)

- Instrument optimization to minimize interference

- Correction equation

- Collisional / reaction mechanism

Polyatomic Interferences

- Polyatomic ion generated by the association of 2 (see more) isotopes creating an interference with the mass / charge ratio of the element analysed

Examples:

- $^{14}N_2^+$ < > $^{28}Si^+$
- $^{40}Ar^{16}O^+$ < > $^{56}Fe^+$
- $^{40}Ar^{35}Cl^+$ < > $^{75}As^+$

Polyatomic Interferences: Solutions

- Choice of another non-interfered isotope
    - Impossible for mono-isotopic elements
- Optimize instrument to minimize interference
    - Oxides, doubly-charged ions
- Elimination of the matrix (Preparation of the sample, ETV ...)
- Correction equation
- Collisional / reaction mechanism

Interferences related to doubly charged ions

Interference generated by an isotope associated with another element than the analyte, but with a mass / charge ratio divided by two due to a double ionization

Example: $^{138}\mathrm{Ba}^{++}$ < > $^{69}\mathrm{Ga}^{+}$

$^{46}\mathrm{Ti}^{++}$ < > $^{23}\mathrm{Na}^{+}$

Interferences related to doubly charged ions

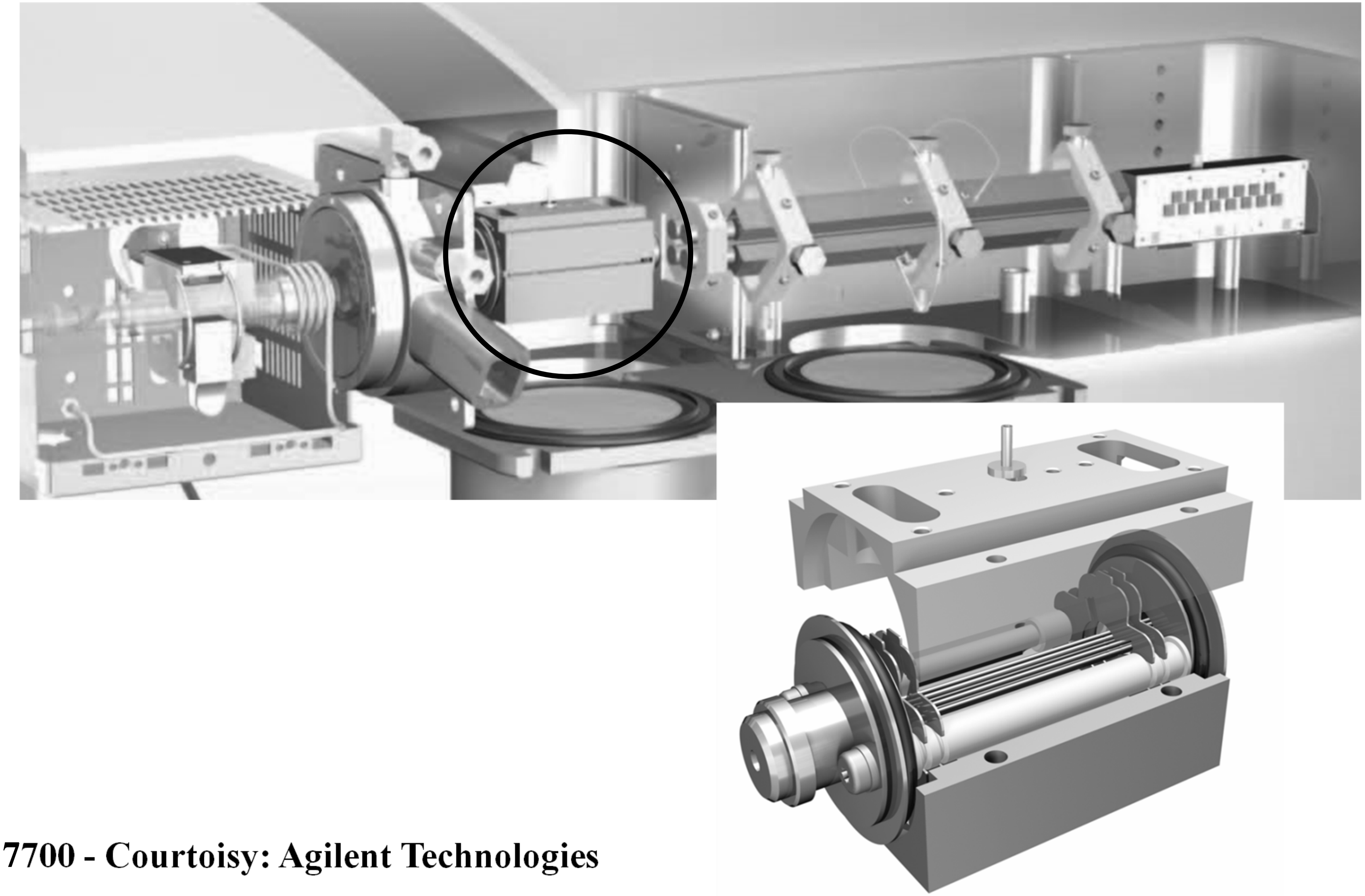
- Optimization of the rate of double charges on the Barium

  (lowest 2nd ionization potential)

- Choice of another non-interfering isotope

  (Ex: ^{71}Ga instead of ^{69}Ga)

Collision Reaction System



ORS – 7700 - Courtoisy: Agilent Technologies

Collision Reaction Cells : Operating Principle

Injection of a pressurized and potentially reactive gas

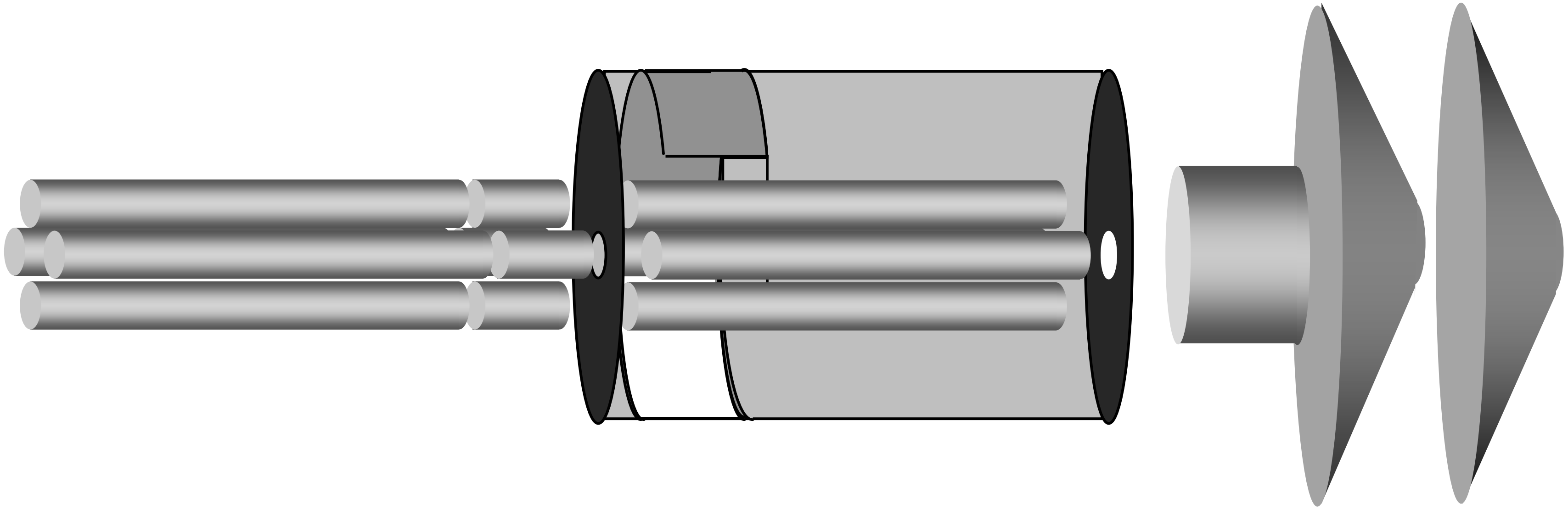
- which chemically or physically modifies an isobaric ion or polyatomic in a different ion which no longer interferes or that we can eliminate, or

- which combines with the analyte to form a polyatomic ion which can then be analysed on another mass Interference free

This device is inserted

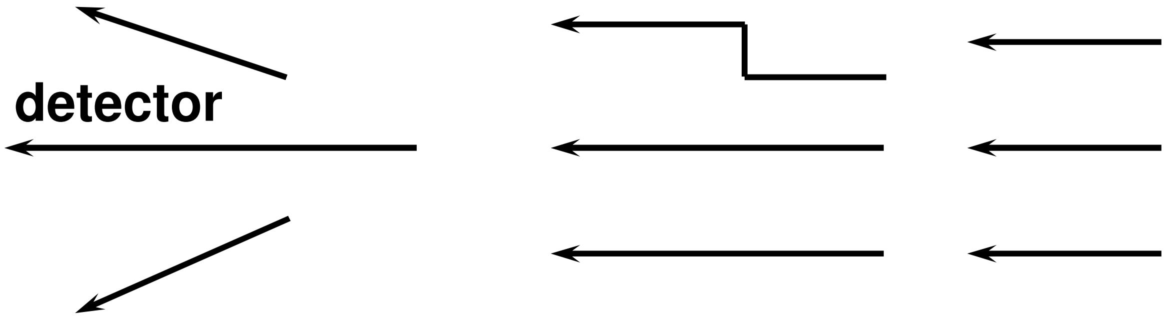
- between the device interface and the mass filter
- or between two mass filters

CRC: device operation



Mass Analyser

CR Volume



Isobaric Interferences

ions through detector

analyte

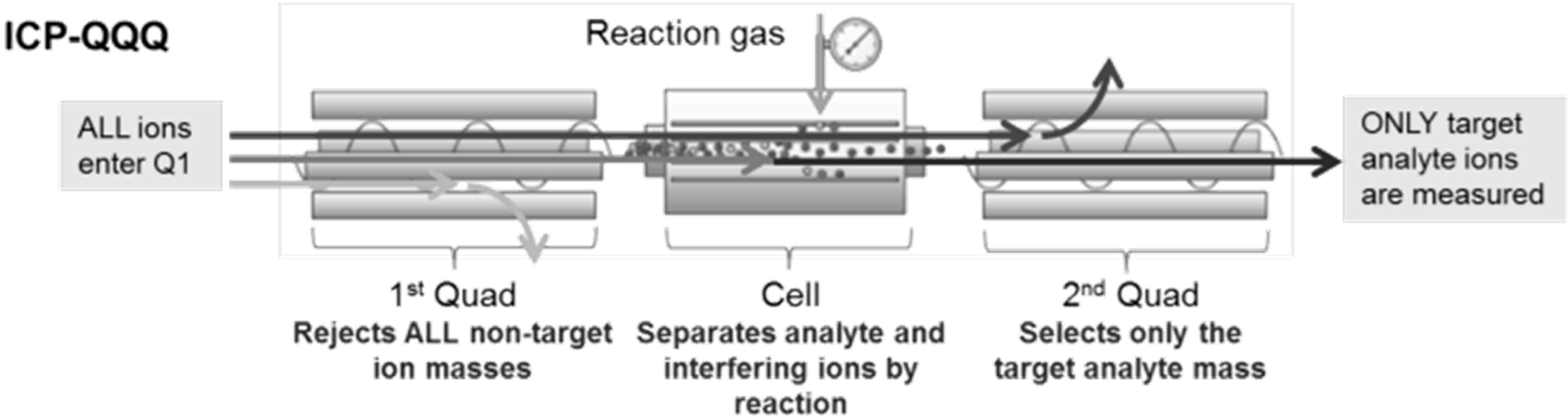
others m/z

Analysis of the mass of transmitted ions

conversion of reactive ions

The specific chemistry of the cell is dependent on the nature and density of the reaction gas, as well as the electric fields present in the cell (close to interstellar chemistry)

Mass filter: Triple quadrupole Elimination of interfering constituents



Courtesy : Agilent Technologies

ICP / MS Analyses : Pros and Cons

PROS

- Excellent detection limits
- Multi-elementary
- High productivity (routine)
- Analysis cost / element
- Rapid semi-quantitative analyses
- Easily interpretable mass spectra
- Isotope analyses
- Accepts a large number of sample introduction modes,
- Dynamic range (10^4- 10^8)

CONS

- Investment cost
- Operator qualification
- Maintenance cost and consumable
- Not recommended for the analysis of samples that are too concentrated (memory effect, cone plugging, etc.)
- Possible interferences but well identified and often correctable.
- Dynamic range(10^4 - 10^8)