

DAY 1 (Afternoon)

Instrumentation

- **A Mass Spectrometry : ICP-MS**
 - A1- Source : ICP
 - A2- Vacuum
 - A3- Ion optics
 - A4- Mass Spectrometer
 - A5- Detector
 - A6- Instruments comparison

- **B Sample introduction:**
 - B1- Solid analysis: Laser Ablation
 - Principle of laser
 - Description of a Nd-YAG laser:
 - Bean attenuator
 - Harmonic crystals
 - Beam expander
 - Operating Parameters
 - B2- Liquid analysis:
 - Nebulizer
 - Spray chamber
 - Desolvation unit

Instrumentation

A- Mass Spectrometry : ICP-MS

A1- Source : Inductively Coupled Plasma

Inductively Coupled Plasma is used as emission sources for the mass spectrometer.

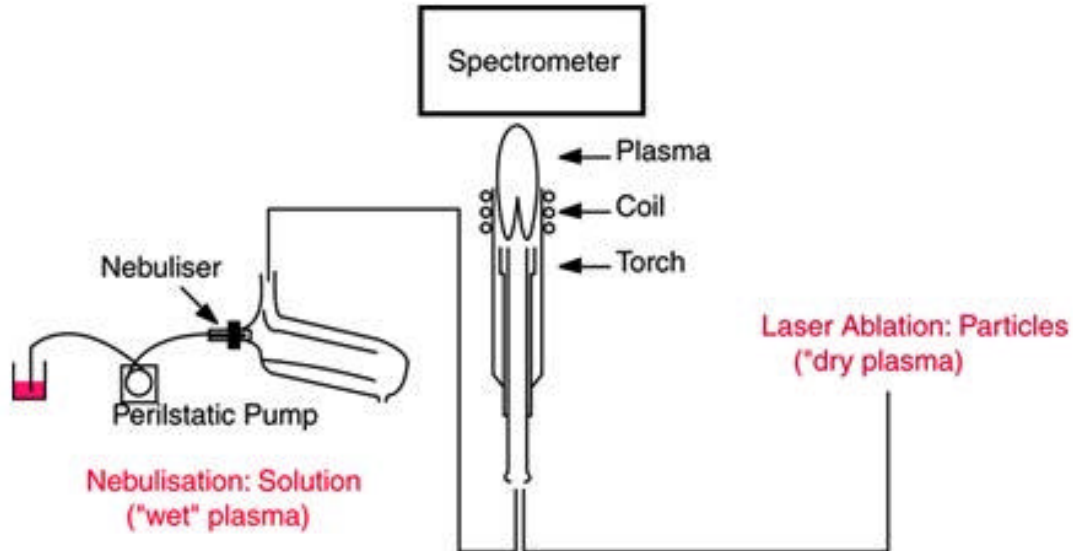


Figure 2.1 : Schematic representation of the two mode of sample introduction in the ICP.

The plasma could be "wet" if solution is introduced into the torch, which produces a large amount of interference, by oxides formation. This plasma could also be "dry" by using a laser ablation sampling device, which leads to a reduction in the level of oxide interferences. Sample introduction system will be detailed later on.

* Torch, Coil and plasma generation: The base of ICP source

Torch

The torch is made of three concentric glass tubes through which argon is blowing. The outermost tube carry the cool gas (13-15 l/min), which is responsible for the main supply of Ar to the plasma. The cool gas help also to stabilise the plasma and finally cool the outer glass jacket of the torch made of fused silicate (melting point 1700C, see information on glassware below). The middle tube is made for the auxiliary gas (1-2 l/min). The role of the auxiliary gas is to lift the plasma off the injector and once again avoid torch-melting problems. The gas flow to the cool and auxiliary gas is injected tangentially in order to create a vortex and stabilise the plasma. The Fassel torch (most common type of torch on the market) is design to produce a stable torroidal plasma, through the centre of which the sample aerosol (sample gas 0.8 – 1 l/mn) is injected. Most of the sample introduction system for solution (including the torch) is made of fused silica or borosilicate glasses, for its specific resistance to heating stress and its purity. Commercial glasses may be divided into soda–lime–silica glasses and special glasses, most of the tonnage produced being of the former class. Such glasses are made from three main materials—sand (silicon dioxide, or SiO_2), limestone (calcium carbonate, or CaCO_3), and sodium carbonate (Na_2CO_3). **Fused silica** itself is an excellent glass, but, as the melting point of sand (crystalline silica) is above 1,700° C (3,092° F) and as it is very expensive to attain such high temperatures, its uses are restricted to those in which its superior properties—chemical inertness and the ability to withstand sudden changes of temperature—are so important that the cost is justified. Nevertheless the production of fused silica glass is quite a large industry; it is manufactured in various qualities, and when intended for optical purposes the raw material used is rock crystal rather than quartz sand. When ordinary glass is

subjected to a sudden change of temperature, stresses are produced in it that render it liable to fracture; by reducing its coefficient of thermal expansion, however, it is possible to make it much less susceptible to thermal shock. The glass with the lowest expansion coefficient is fused silica. Another well-known example is the borosilicate glass used for making domestic cookware, which has an expansion coefficient only one-third that of the typical soda–lime–silica glass. In order to effect this reduction, much of the sodium oxide added as a flux is replaced by boric oxide (B_2O_3) and some of the lime by alumina.

Coil

The coil is made of 2 or 3 turns of copper tube through which is circulating water, for cooling purpose. The coil is made of copper for its thermal conductivity property. The coil is wrapped around the end of the torch and connected to a radio-frequency power generator. This creates oscillating RF magnetic fields within the Ar flowing through the torch.

Plasma generation:

First the Ar gas has to be seeded with a few electron by an electric discharge from a Tesla coil. These electrons are subjected to intense oscillations by the radio-frequency magnetic fields generated by the coil. Collisions that occur between the free electrons and atoms of Ar gas cause further ionisation. Each particle formed in the Ar gas is subjected to a magnetic field that cause it to travel in annular paths within the torch, However other Ar atoms doesn't follow the current doughnut like flow which is responsible for ohmic heating of the gas. Through this process, temperature could rise up to 10,000 K.

In conclusion, in ICP spectrometry, the plasma (luminous volume of partially ionised gas) is generated from radio-frequency magnetic fields induced by a copper coil, which is wound around the top of a glass torch.

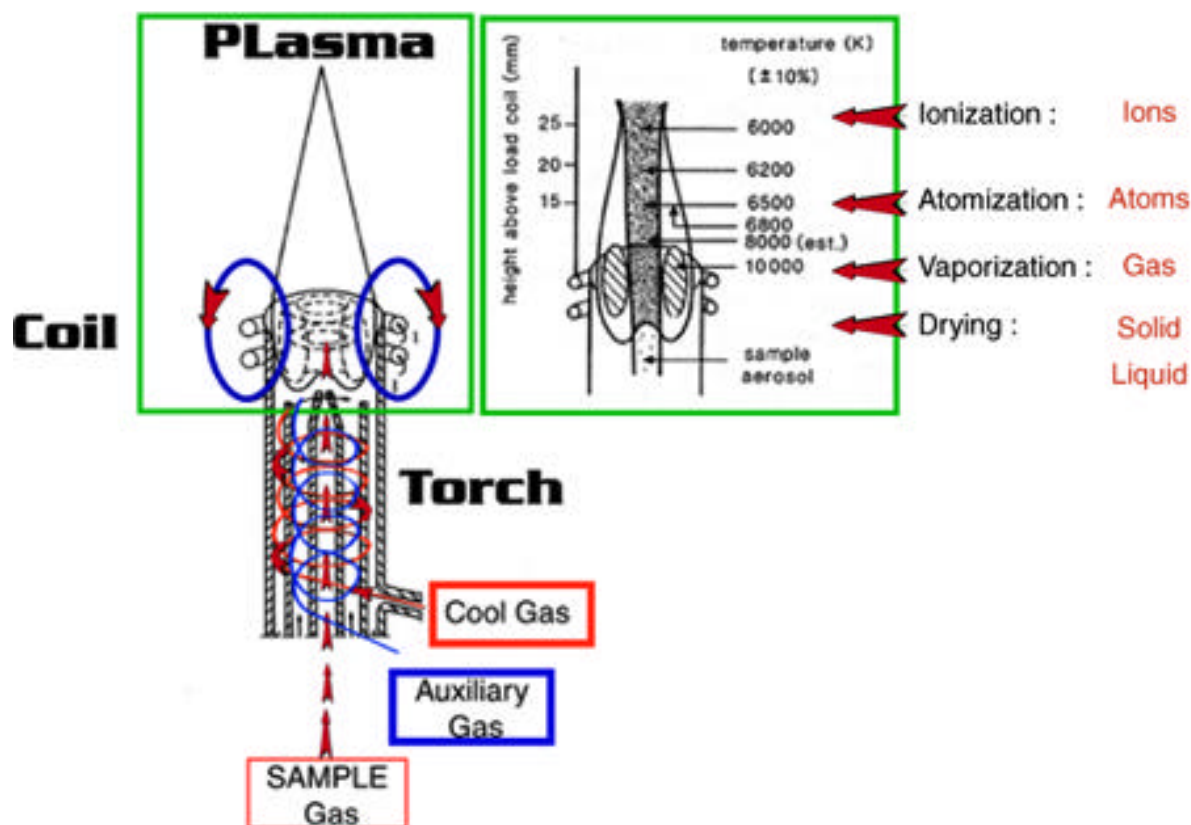


Figure 2.2 : Schematic of an Inductively Coupled Plasma system.

Why plasma is good?

Ar plasma ICP is so popular mainly because the source is under atmospheric conditions. There are no vacuum required in the sample introduction area by opposition to an other common analytical technique such as Thermal Ionisation. Therefore the sample output is significantly greater.

Atomization:

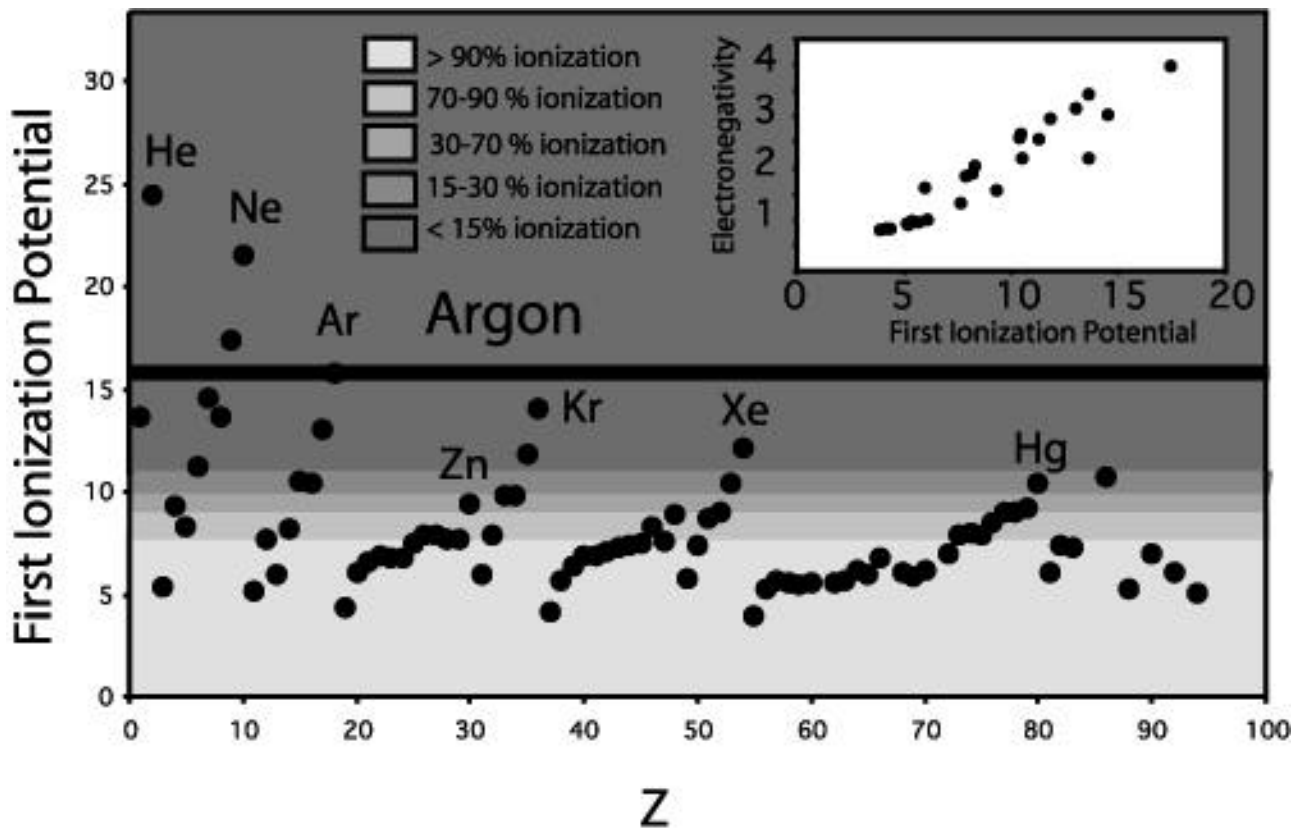
Due to the high temperature (8000 K) inside the plasma fireball, where the sample aerosol is drawn, the sample is rapidly desolvated, volatilised and atomized. Thus most molecular ion species are nearly undetectable.

Ionization:

Ar ICP is a weakly ionised plasma (around 0,1% ionised). However, the plasma inside an ICP is also very efficient to ionise the sample. The Argon plasma is buffered by the first ionisation energy of the Ar (15,76 eV) and can easily ionized elements, which have lower ionization energies. In other words the average energy for an atmospheric pressure Ar plasma is dominated by the first ionization potential of Ar (15,76 eV). Elements with their first ionization potential below that value, will be singly charge positive ions. Most of the elements have their first ionization energy below the first ionization potential of the Ar (Table 2.1). The second ionization potential of most of the elements is higher and doubly charged particles are unlikely to be significantly present in an ICP. The degree of ionization for most metal is greater than 90% in the Ar ICP. However, less than 50% ionization is achieved for non-metals with the same source (for example Cl would be ionized at about 1%).

AN	Ionization potential		AN	Ionization potential	
	I	II		I	II
18 Ar	15.76	27.62	7 N	14.53	29.59
47 Ag	7.57	21.48	11 Na	5.14	47.29
13 Al	5.98	18.82	41 Nb	6.88	14.32
33 As	9.81	18.63	60 Nd	5.51	
79 Au	9.22	20.5	10 Ne	21.56	41.07
5 B	8.30	25.15	28 Ni	7.63	18.15
56 Ba	5.21	10.00	8 O	13.61	35.11
4 Be	9.32	18.21	76 Os	8.5	17
83 Bi	7.29	16.68	15 P	10.48	19.72
35 Br	11.84	21.6	82 Pb	7.42	15.03
6 C	11.26	24.38	46 Pd	8.33	19.42
20 Ca	6.11	11.87	59 Pr	5.46	
48 Cd	8.99	16.90	78 Pt	9.0	18.56
58 Ce	5.6	12.3	94 Pu	5.1	
17 Cl	13.01	23.8	88 Ra	5.28	10.14
27 Co	7.86	17.05	37 Rb	4.18	27.5
24 Cr	6.76	16.49	75 Re	7.87	16.6
55 Cs	3.89	25.1	45 Rh	7.46	18.07
29 Cu	7.72	20.29	86 Rn	10.75	
66 Dy	6.8		44 Ru	7.36	16.76
68 Er	6.08		16 S	10.36	23.4
63 Eu	5.67	11.24	51 Sb	8.64	16.5
9 F	17.42	34.98	21 Sc	6.54	12.8
26 Fe	7.87	16.18	34 Se	9.75	21.5
31 Ga	6	20.57	14 Si	8.15	16.34
64 Gd	6.16	12	62 Sm	5.6	11.2
32 Ge	7.88	15.93	50 Sn	7.34	14.63
1 H	13.59		38 Sr	5.69	11.03
2 He	24.48	54.40	73 Ta	7.88	16.2
72 Hf	7	14.9	65 Tb	5.98	
80 Hg	10.43	18.75	43 Tc	7.28	15.26
53 I	10.45	19.13	52 Te	9.01	18.6
49 In	5.79	18.86	90 Th	6.95	
77 Ir	9		22 Ti	6.82	13.57
19 K	4.34	31.81	81 Tl	6.11	20.42
36 Kr	13.99	24.56	69 Tm	5.81	
57 La	5.61	11.43	92 U	6.08	
3 Li	5.39	75.62	23 V	6.74	14.65
71 Lu		14.7	74 W	7.98	17.7
12 Mg	7.64	15.03	54 Xe	12.13	21.2
25 Mn	7.43	15.64	39 Y	6.38	12.23
42 Mo	7.10	16.15	70 Yb	6.2	12.10
			30 Zn	9.39	17.96
			40 Zr	6.84	13.13

Table 2.1 : First and second ionization potential of the elements. Data from Wesat (1973). I, first ionization energy (eV), figure in bold indicate elements that cannot be ionized by an argon plasma. II, second ionization energy (eV), figure in bold indicates elements that can form doubly-charged ions in an argon plasma.



Why plasma is bad ?

- Interferences: Apart from isobaric overlap, recombination of ions leads to the formation of interferences. There are different types of interferences:
 - The argon plasma: Ar^+ , Ar_2^+
 - Polyatomic species: Contribution from the solvent and combination with the analyte species: (H_2O^+ , H_3O^+ , OH^+ , ArH^+ etc....). Incomplete dissociation of the sample matrix will lead to recombination in the plasma tail, usually in the form of oxide MO^+ (or MO_2^+ , MO_3^+). The oxide formation will depend on the oxide bond strength of the element (quite high for REE for example).
 - Air entrainment and gas impurity (N^+ , O_2^+ , NO_2^+ , etc...)
 - Material eroded from the cones (isotopes of Ni, Cu, Mo etc...)

- Space Charge effect and Mass Bias:

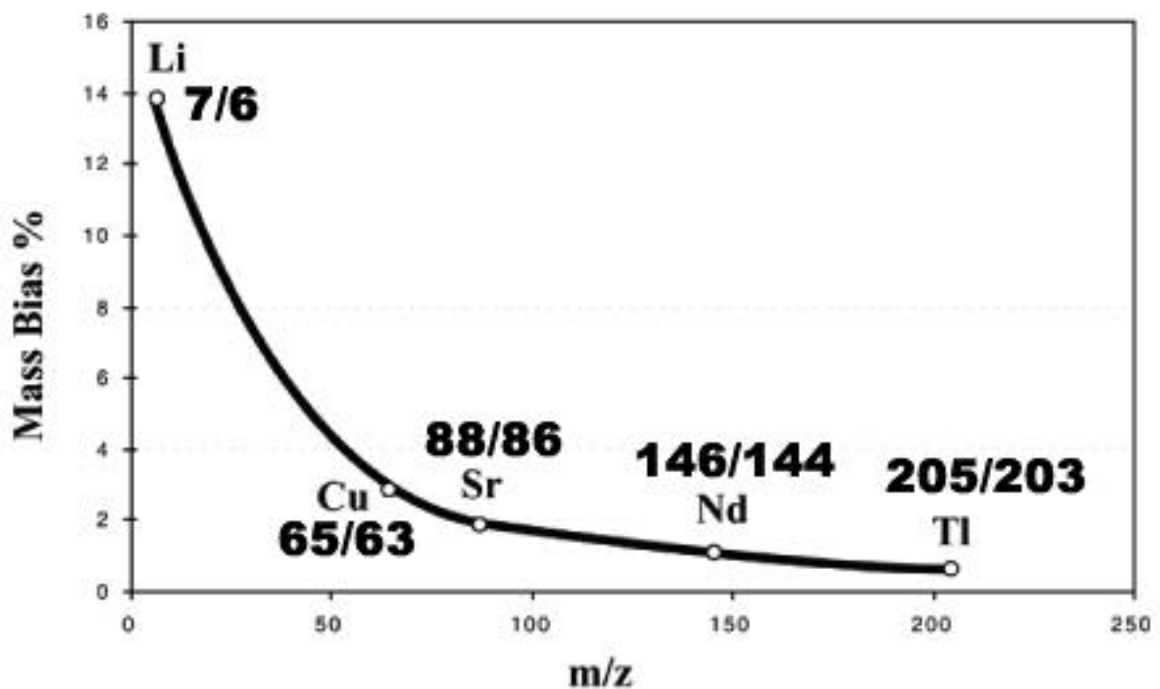


Figure 2.3: Effect of the mass bias on the measurement of several isotopic ratios across the mass range (e.g. Li7/Li6). The values for Li and Cu are not compared to the true ratio. Expected deviation for these two elements should be higher.

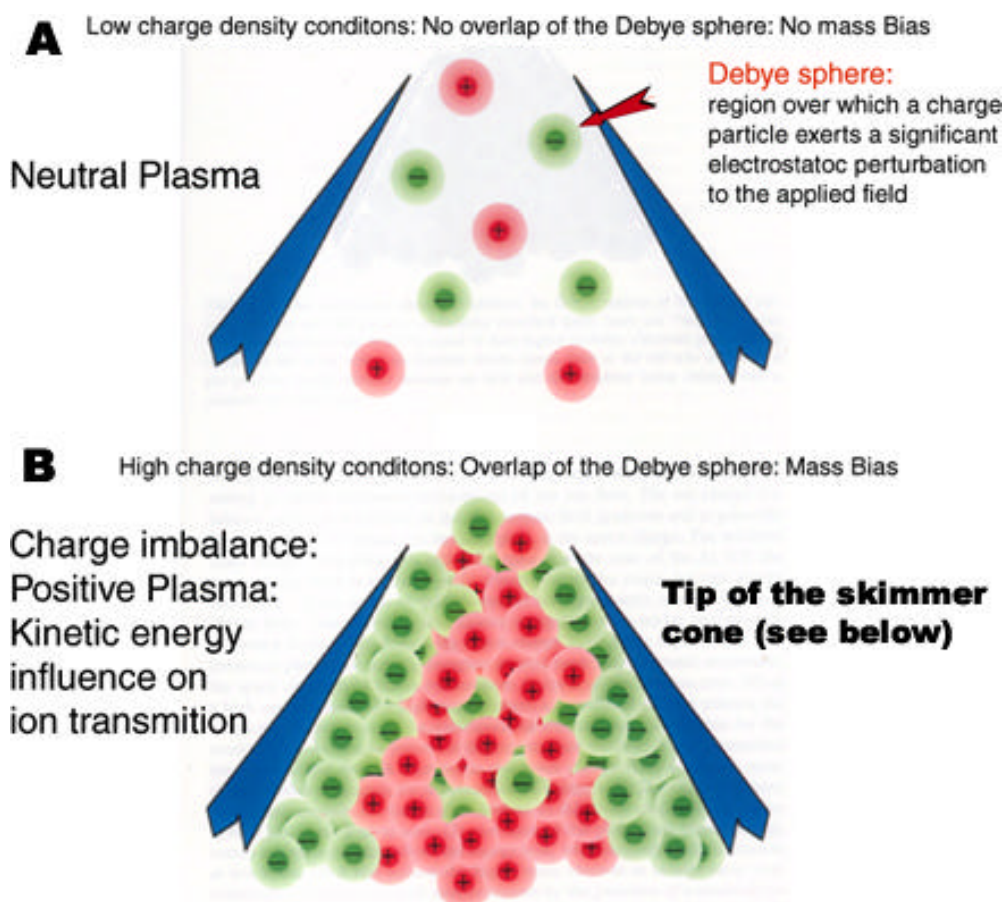


Figure 2.4: Comparison between a neutral plasma (A) and a charge imbalance plasma (normal plasma) on the space charge ratio (Montaser, 1998).

*** Cone:**

Hot argon and sample ions (8000K) are accelerated through the sample cone orifice to produce a supersonic jet of gas in the expansion chamber. The skimmer cone pierces the back of the supersonic jet and extracts a small proportion of the plasma gas. The ions are therefore sucked by the vacuum in the interface area and accelerate about 10 times the speed of sound (300m/s). Cones are made of nickel most of the time, but they could also be made of Pt, Cu or Al. It has to have a high thermal conductivity, otherwise it will melt. A high melting point is therefore important and it finally should be as hard as possible. However thermal conductivity seems to be the best criteria on a performance/price ratio and Al cone seems to be the best choice.

	Thermal conductivity (W per m per K)	Melting point (degrees C)	hardness
Al	237	660	soft
Cu	401	1083	soft
Ni	90,9	1453	hard
Pt	71,6	1772	hard

Table 2.2 : Thermal conductivity, melting point and hardness of different types of cones.

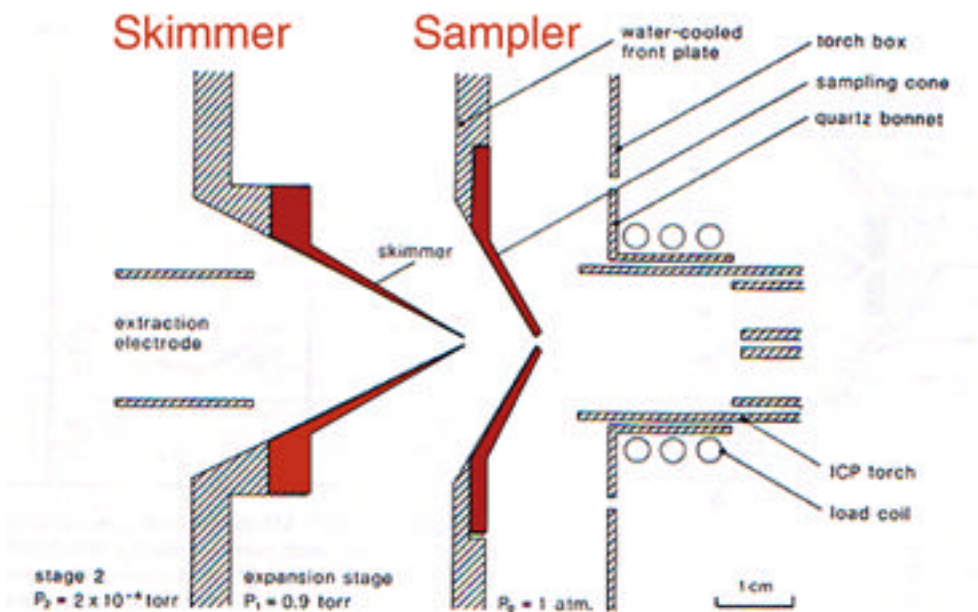


Figure 2.5: Configuration of sampling cone, expansion stage and skimmer cone designed for continuum sampling operation (Date and Gray, 1982).

A2- Vacuum

A high vacuum is required in order to facilitate the travel of the ion, otherwise they will collide with other particles under atmospheric pressure (0.1 micron, Table 2.3). Pressure down to 10^{-6} to 10^{-8} Torr (table 2.4) are required to properly focus in ion beam inside a mass spectrometer.

Vacuum pumps are required to remove the air from the system. **Mechanical rotary pumps** are used to first lower the pressure. They are based upon a simple mechanical system in which an eccentric rotor isolates a volume of the system gas, and using oil to make gas tight seals pushes this volume of gas out of the system to the ambient atmosphere. Through this process the oil gets contaminated and needs to be changed periodically.

In front of a mechanical pump, a **Turbo Molecular** pump is usually use to improve the vacuum. The pump has to be very clean and consists of jet engine turbine blades. As residual gas molecules get close to a blade, they are hit by the blade and forced towards the next blades and finally go into the rotary pump.

Pressure (torr)	Mean free Path
760 (1atm) - Sample introduction area	0.1 μ m
10 ⁻⁵ - Optic area	5m
10 ⁻⁷ - Analyser area	500m
10 ⁻⁸ - MC-ICP with ionic pump	5000m

Table 2.3: Mean free path distances as a function of the system pressure (from Longerich and Diegor, 2001).

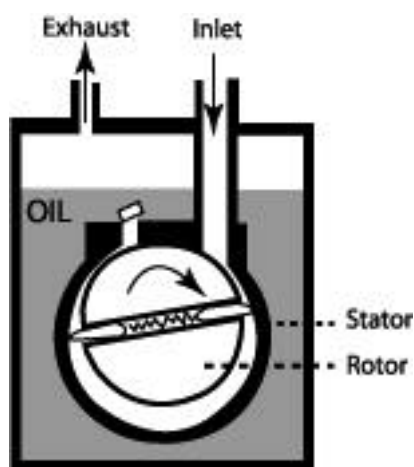


Figure 2.6: Schematic diagram of a mechanical rotary pump (from Potts, 1987)

	bar	psi	Torr	Pascal
1 bar	1	14.5	750	100000
1psi	0.0689	1	51.7	6895
1 torr	0.00133	0.0193	1	133
1 pascal	0.00001	0.000145	0.0075	1

Table 2.4: Units of pressure measurements (Longerich and Diegor, 2001).

A3- Ion optics (Acceleration – Focus)

* Extraction, Initial Focus

Ions extracted from this gas are accelerated, focussed and shaped in the mass spectrometer interface using ions lenses. The proportion of ions, sampled from the plasma, that reach the detector is very small (1 in 10^6 - 10^8) and usually a high gain ion detection system is essential if low limits of detection are to be achieved.

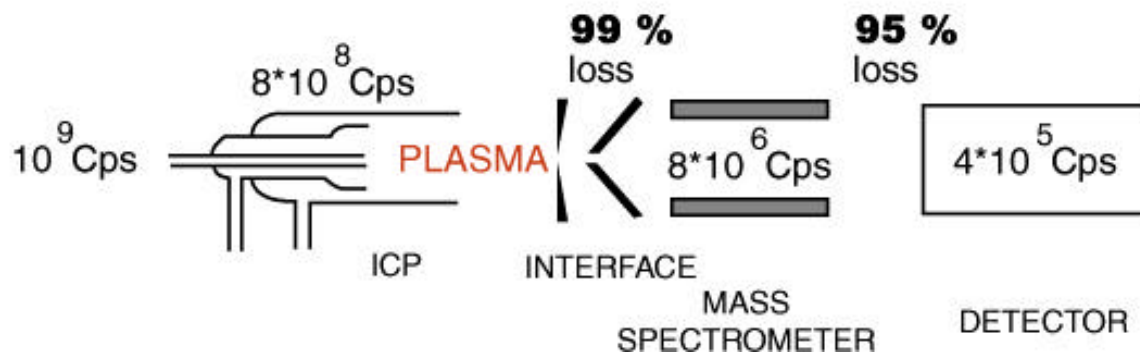


Figure 2.7: Ion transmission efficiency in a typical ICP-MS.

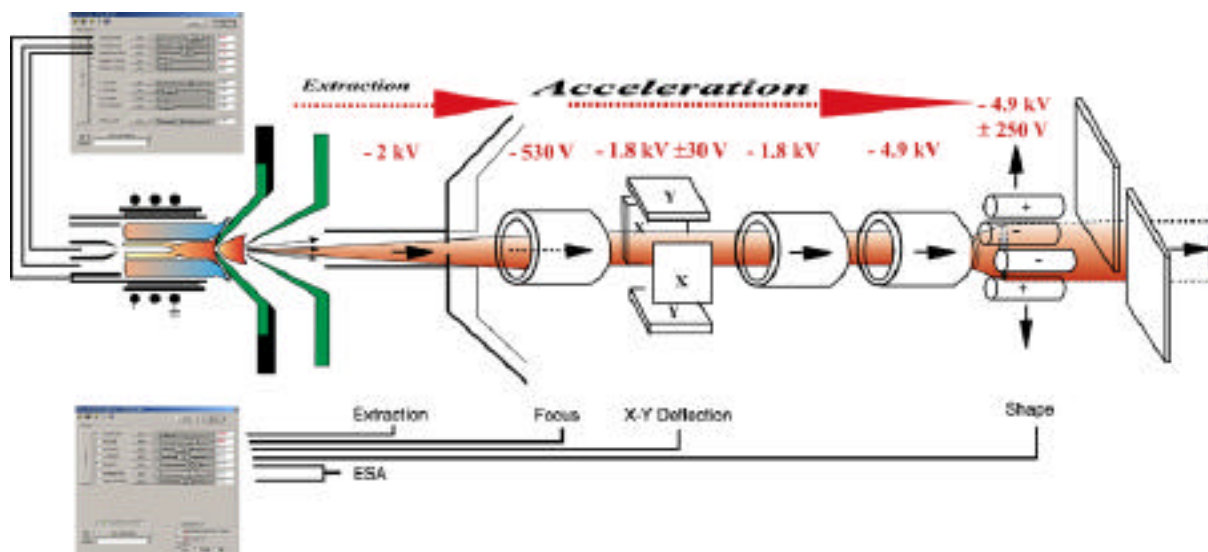


Figure 2.8: First extraction and focussing lenses assembly in the Neptune and Element (Finnigan TM). Ions are extracted at -2 kV and accelerated up to -5 kV (Neptune) or -8 kV (Element) before the first slit.

* Zoom lenses

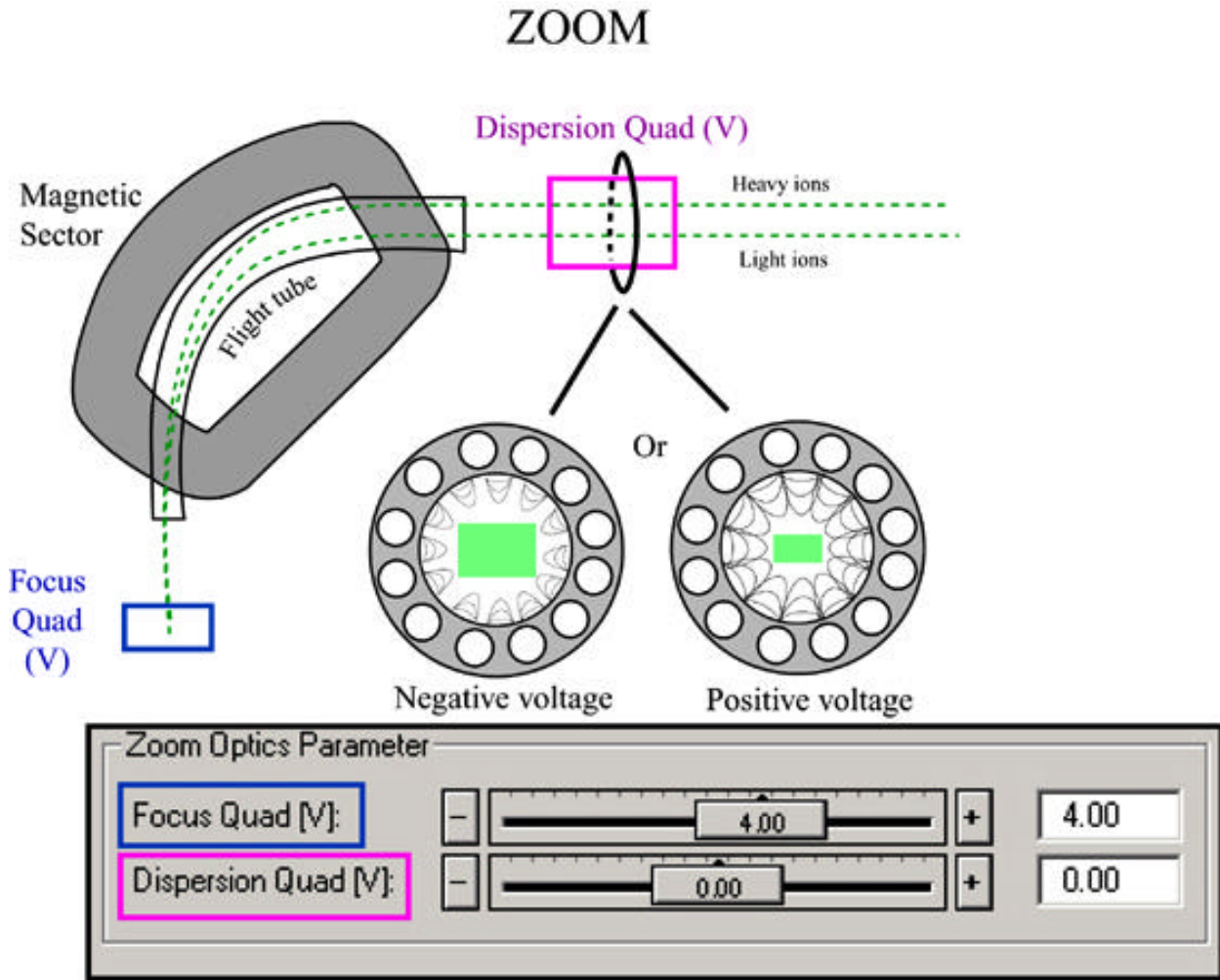


Figure 2.9: Schematic of the zoom lens assembly of the Neptune. The focus quad, focus the ion beam while the dispersion quad expand or shrink the beam while keeping the ions in focus.

* Retardation Potential Quadrupole

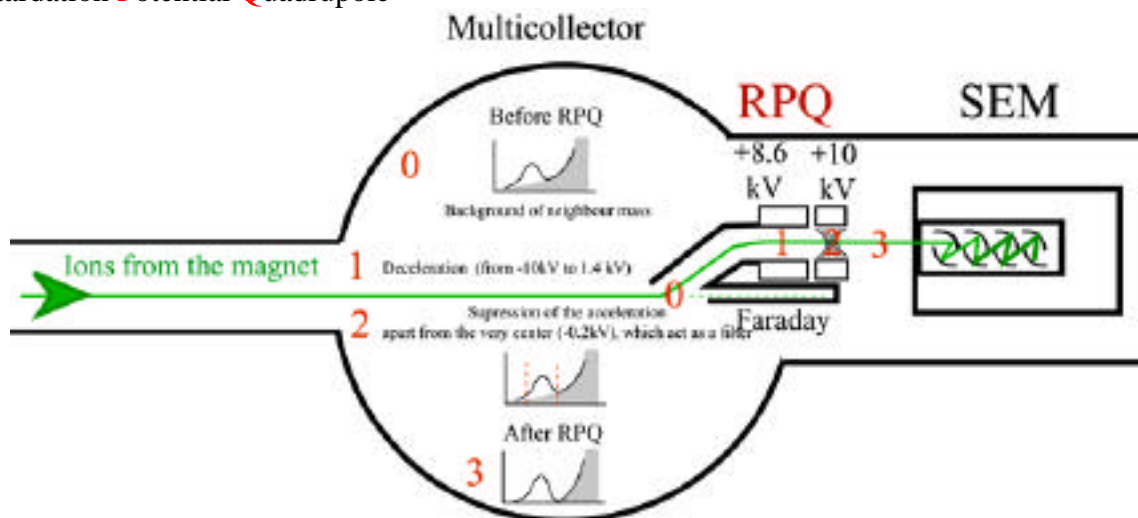


Figure 2.10: Schematic of the RPQ system, which reduce the tailing effect of abundant isotope on nearby less abundance isotopes (e.g., ^{232}Th on ^{230}Th , or ^{238}U on ^{234}U).

A4- Mass Spectrometer (ESA – Magnet)

Two main types of mass spectrometers are used in ICP-MS.

The most popular is the **quadrupole mass filter**.

By varying the electric signals to a quadrupole it is possible to transmit only ions within a very small m/z ratios (other ions are neutralised and carried away as uncharged particles). A quadrupole mass filter consists of four parallel metal rods. Two opposite rods have an applied potential of $(U+V\cos(\omega t))$ and the other two rods have a potential of $-(U+V\cos(\omega t))$, where U is a dc voltage and $V\cos(\omega t)$ is an ac voltage. The applied voltages affect the trajectory of ions travelling down the flight path centred between the four rods. For

The other type of instrument is a magnetic sector (with a radii of r), which simultaneously disperses ions (of charge = e and velocity = v) by a magnetic field (field strength = H) as a function of their m/z ratio between the poles of a magnet.

The function of the mass analyser is :
 -to separate the ions according to their mass to charge ratio.
 -to focus the ion beam through the zoom optic and to the multicollector system.

A moving particle, inside a magnet, has a force F .

$$\mathbf{F} = q\mathbf{v} \times \mathbf{B} \quad (1)$$

B : magnetic field, v : particle velocity, q : charge of the particle.

given dc and ac voltages, only ions of a certain mass-to-charge ratio pass through the quadrupole filter and all other ions are thrown out of their original path. A mass spectrum is obtained by monitoring the ions passing through the quadrupole filter as the voltages on the rods are varied.

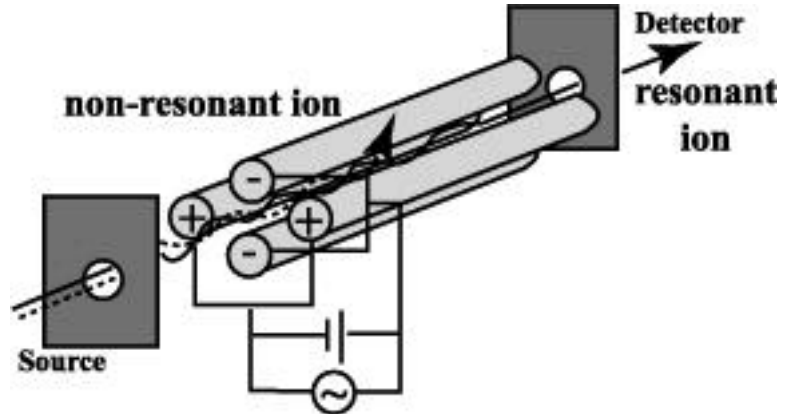


Figure 2.11: Schematic of a quadrupole filter

Since the particle is also moving in a circular path :

$$F = m \frac{v^2}{r} \quad (2)$$

The velocity of the particle can be determined from its energy :

$$(1) \text{ in } (2) \quad m \frac{v^2}{r} = qv \times B \quad (3)$$

$$Vq = \frac{1}{2} mv^2 \quad \text{or} \quad v^2 = 2 \frac{Vq}{m} \quad (4)$$

$$(4) \text{ in } (3) \quad \frac{m}{q} = \frac{B^2 r^2}{2V}$$

The mass/charge ratio (m/q) of a given heavy element will move along longer radius for a given radius curvature of a magnet (r), accelerating potential (v) and magnetic field (B).

Most magnetic sector mass spectrometers are usually single focussing (TIMS or ICP-MS with collision cell) but an electrostatic analyser (with a radii of r_2 and a field strength of E/d) is sometimes necessary in ICP-MS in order to separate ions (with a charge = e) with different kinetic energies.

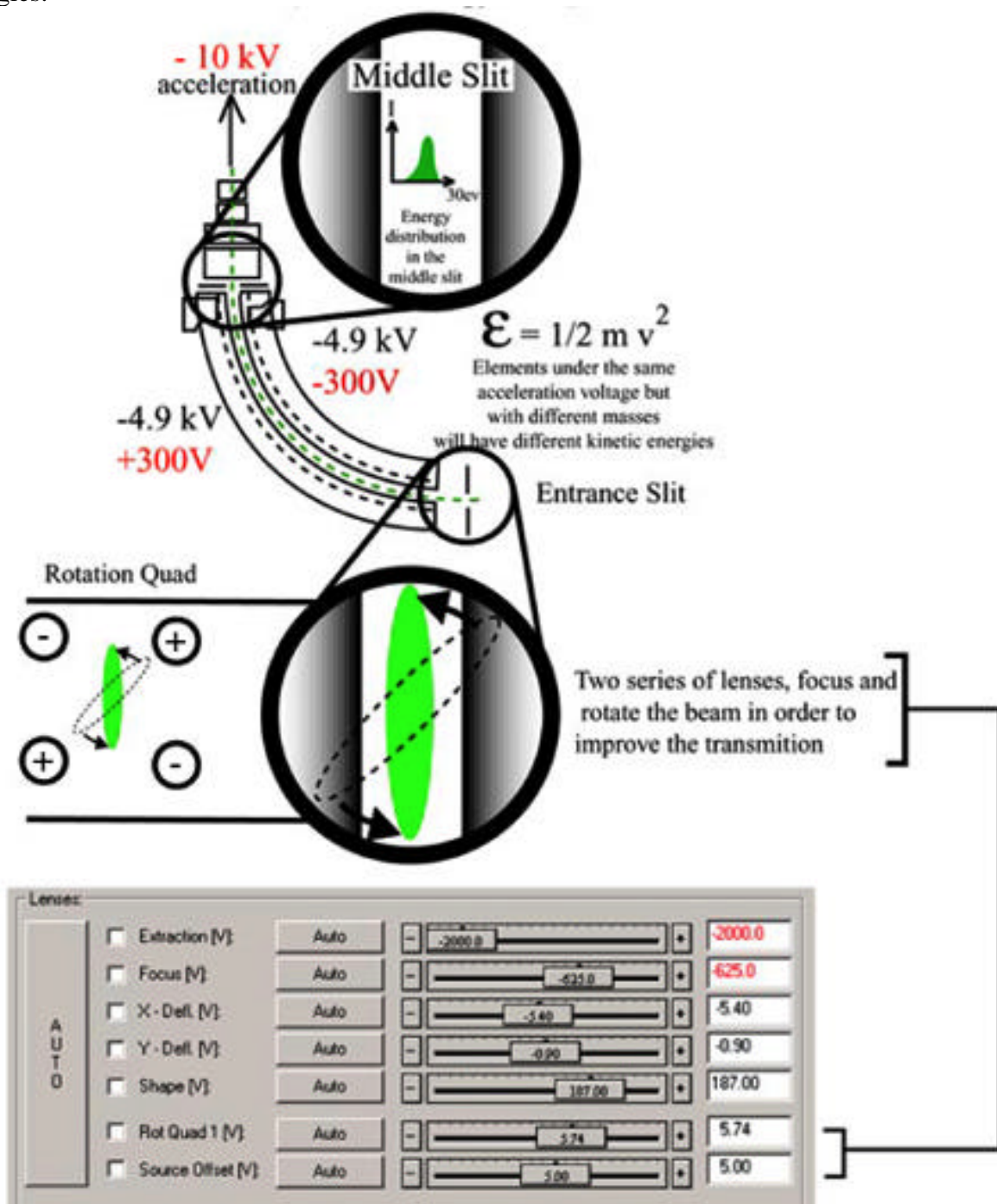


Figure 2.13: Schematic of the electric sector from the Element.

When the magnetic sector is located before the electrostatic analyser the instrument is in Reverse Geometry (RG) in comparison to Nier-Johnson Forward Geometry. The ion beam generated at the interface is transmitted into a magnetic sector where it undergoes mass dispersion. Then the electrostatic sector brings the ion beam of filtered kinetic energy into focus through the exit slit. Moreover double focussing mass spectrometers have a Higher Resolution (HR) in comparison to quadrupole mass filters, which is important for reducing the level of polyatomic ion interferences introduced to the mass spectrometer by the ICP.

A5- Detector (SEM, Faraday)

Doubly focussed ions are counted using a **Secondary Electron Multiplier**, which consists of a series of biased dynodes that eject secondary electrons when they are struck by an ion. They therefore multiply the ion current and can be used in analog or digital mode.

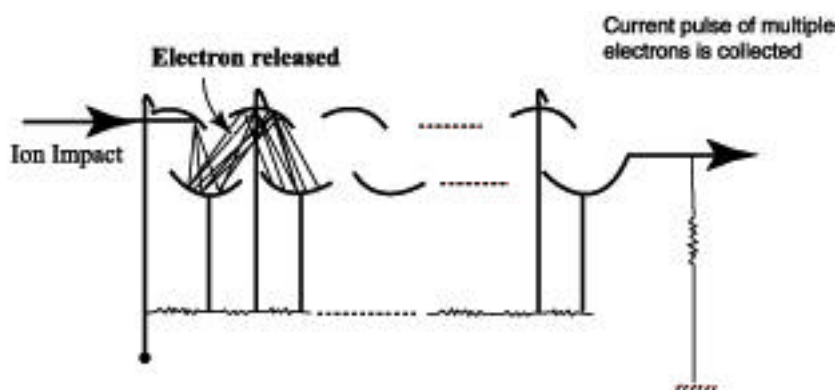


Figure 2.14 : Schematic of an electron multiplier ion beam detector (Beynon and Brenton, 1982)

Other types of double focussing mass spectrometers use a multi-collector assembly, which consists of eight independently adjustable **Faraday collectors** and one fixed axial Faraday collector. The disadvantage of this system is the high ion count rate required by the Faraday collector.

Since a Faraday cup can only be used in an analog mode it is less sensitive than secondary electron multiplier that are capable of operating in pulse-counting mode.

Hence, limit of detection are high.

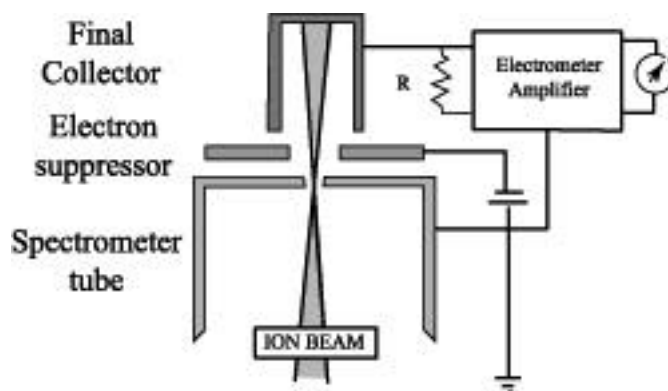


Figure 2.15: Faraday cage ion beam detector (White 1968). Each positive ions are collected in the yellow bucket, and each of them are responsible for the movement of an electron through the resistor: Measurement of the potential difference in the resistor is proportional to the ion current.

A6- Instrument comparisons

a- Mass Spectrometry at the mineralogy department of Frankfurt University
Double focussing mass spectrometers (The Finnigan Element TM)

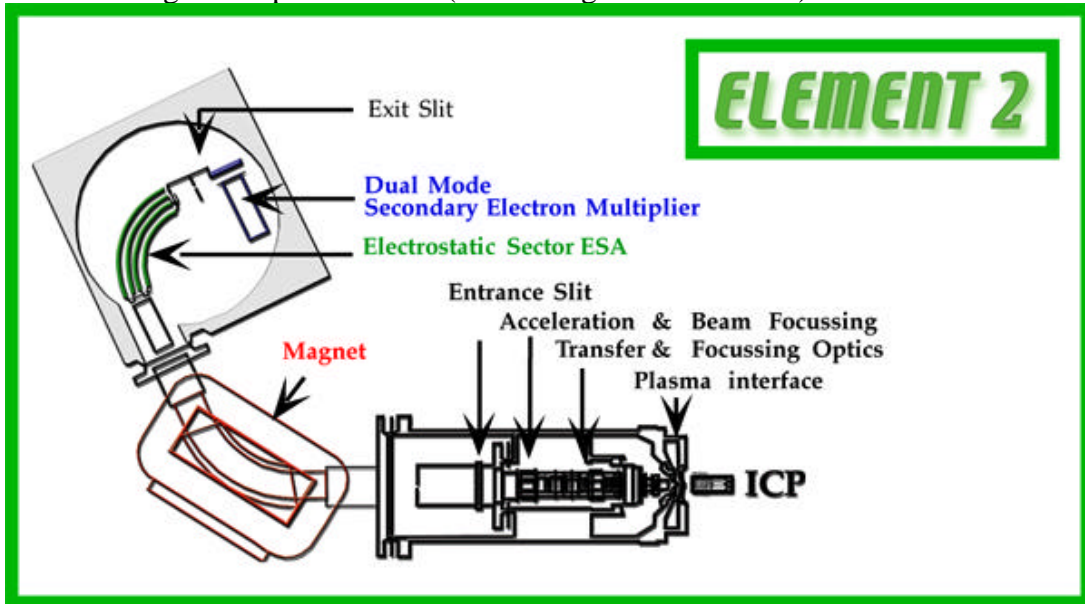


Figure 2.17: Schematic diagram of a Reverse Geometry High Resolution-ICP-MS instrument (the Finnigan ELEMENT, divided into three main parts: (1) the ICP with the interface (cones and ion optics); (2) the analyser (magnetic sector and electrostatic analyser); (3) the detector (secondary electron multiplier: SEM).

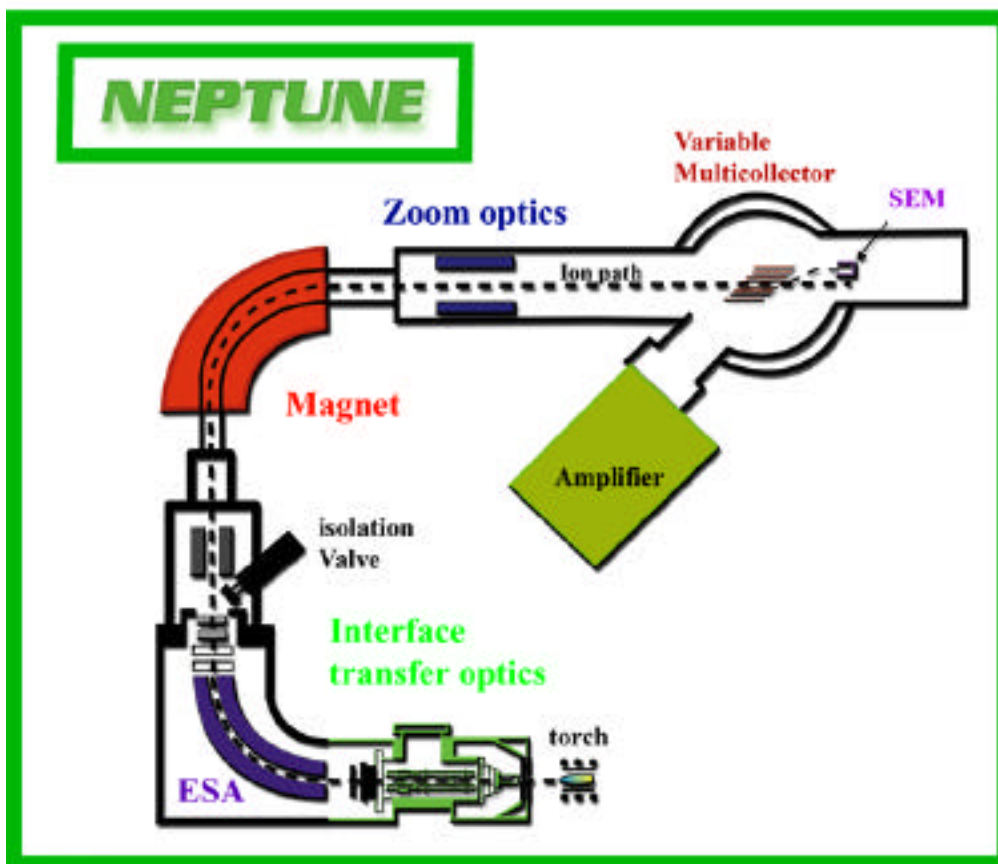


Figure 2.18: Schematic of a Multi Collector ICP-MS (The Finnigan Neptune™), divided gain into three parts; (1) the ICP interface, (2) the analyser (ESA and magnet), (3) the detector (multiple Faraday cups).

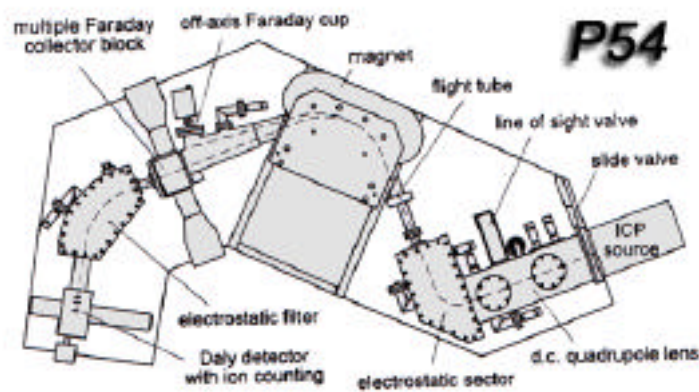
The use of the magnetic sector mass spectrometers offer lots of advantages in terms of (1) resolution; (2) peak shape (3) background.

(1) In comparison to quadrupole mass filters, double focussing mass spectrometers permit variable resolution using three sets of slit positions ($M/M= 300, 3000, 7500$) which is important for reducing the level of polyatomic ion interferences introduced to the mass spectrometer by the ICP. This is critical for the accurate quantification of elements such as P, S, As, K, Ca and the transition elements that can exhibit significant isobaric interferences.

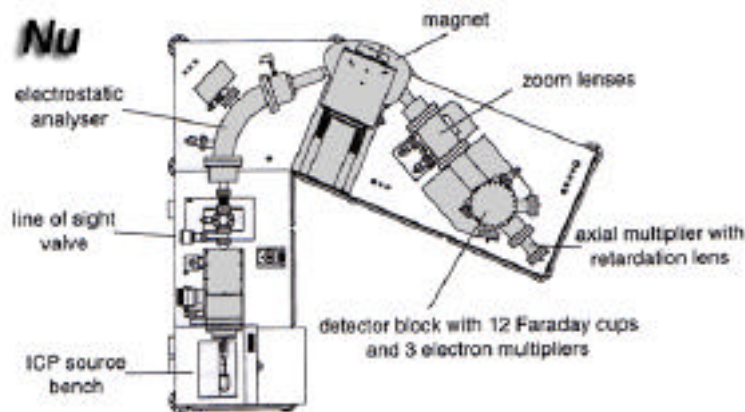
(2) The flat topped peak shape obtained using stable magnetic sector instruments allows better precision for isotope ratio measurements in comparison to the gaussian peak shape produced by quadrupole-based instruments designed for scanning over a relatively large mass range.

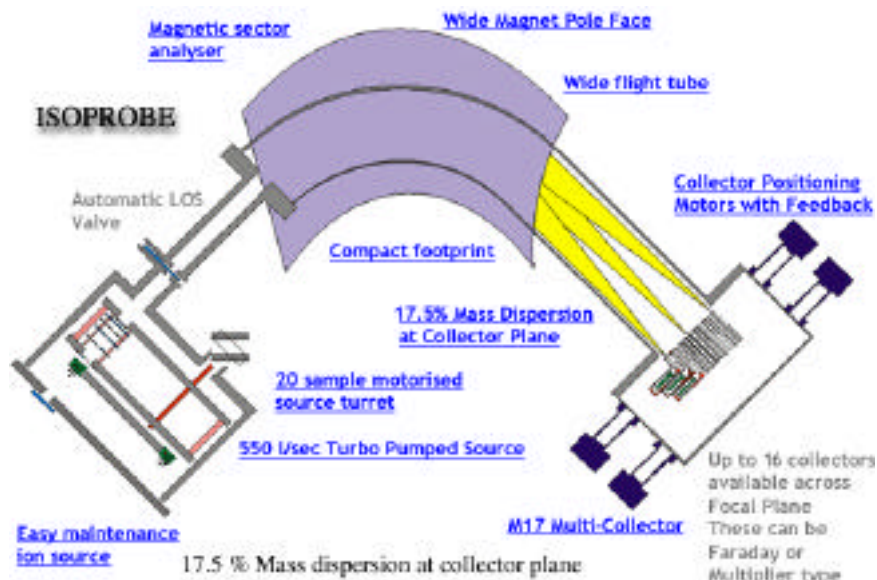
(3) The curvature of the optical axis of the double-focusing geometry greatly reduces the photon background derived from the ICP torch without reducing sensitivity. For heavy masses, the background counting rate is negligible (< 0.2 cps) which significantly increases signal/noise and provides enhanced limits of detection.

b-Comparison between different MC-ICP-MS used in Earth Sciences



8 adjustable Faraday cups with a Daly detector behind the central cup. Additional high mass collector for large differences in mass (10%)



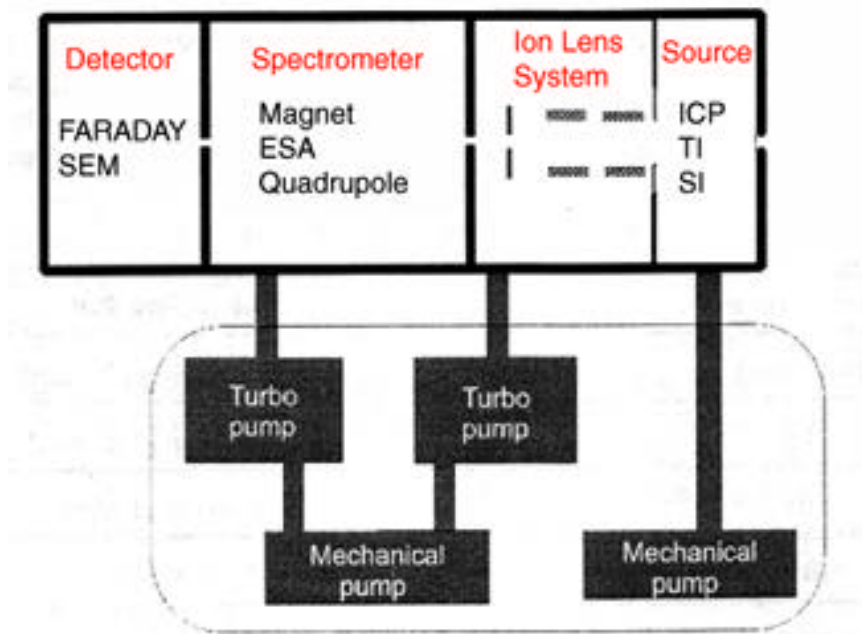


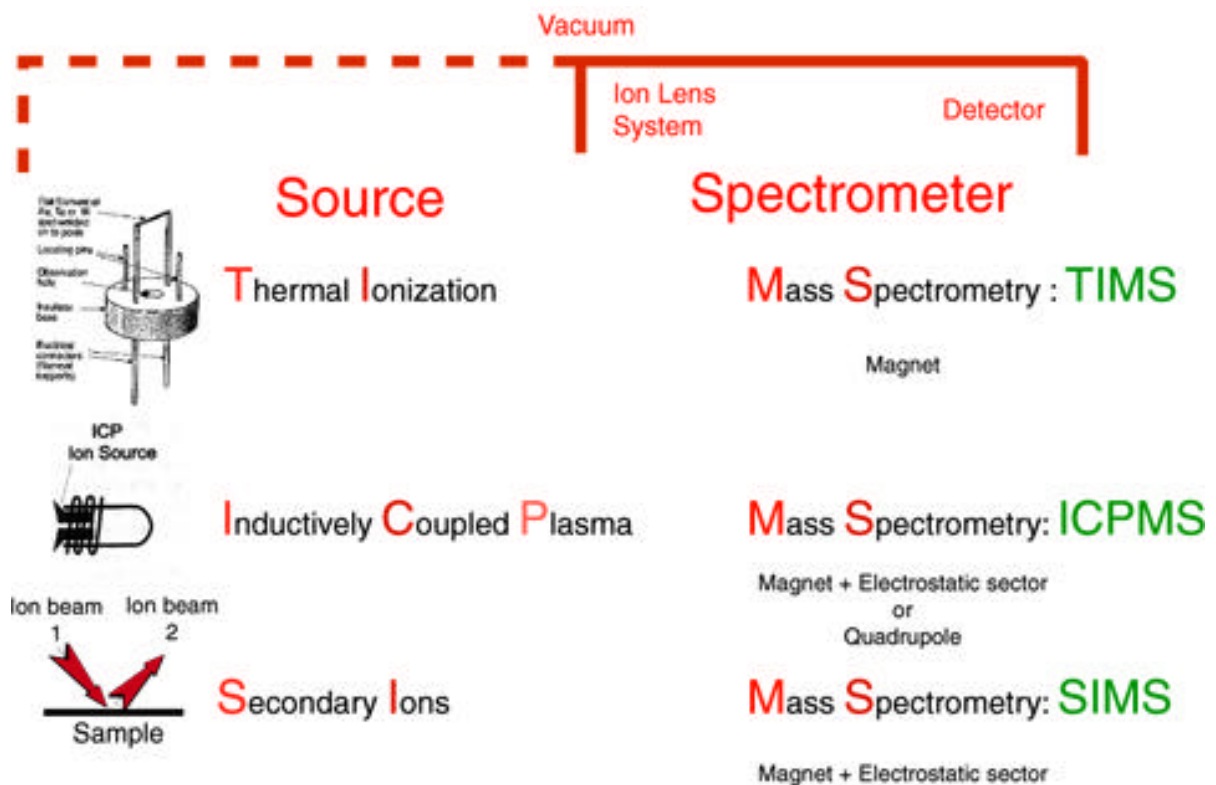
Single focussing

Hexapole collision cell for the reduction of the energy spread of the ions (no need for ESA).

c- Comparison between different techniques of Mass Spectrometry used in Earth Sciences.

Figure 2.19: Most of the analytical technique used in Earth Sciences could be divided into 5 main units. (1) – a source, which ionise the elements (thermal ionization, ICP or secondary ions); (2) a ion lens system for extracting, accelerating and focussing the ions; (3) one or two analysers dependant on the spread in kinetic energy creates by the source; (4) a system of detector (single SEM or multiple Faraday); (5) a vacuum system, which may include the source, dependant on the ionization technique.





d- The laser ablation tool of the future !!: TOF

A time-of-flight (TOF) mass spectrometer uses the differences in transit time through a drift region to separate ions of different masses. It operates in a pulsed mode so ions must be produced or extracted in pulses. An electric field accelerates all ions into a field-free drift region with a kinetic energy of qV , where q is the ion charge and V is the applied voltage. Since the ion kinetic energy is $\frac{1}{2}mv^2$, lighter ions have a higher velocity than heavier ions and reach the detector at the end of the drift region sooner.

$$K.E. = qV$$

$$\frac{1}{2} mv^2 = qV$$

$$V = \left(\frac{2qV}{m}\right)^{1/2}$$

The transit time (t) through the drift tube is L/V where L is the length of the drift tube.

$$t=L / \left(\frac{2V}{m/q}\right)^{1/2}$$

(taken from SCIMEDIA: <http://www.rmsb.u-bordeaux2.fr/rmsb/ms/tof.html>)