Use of Inorganic Mass Spectrometry for the screening of radio-pure material

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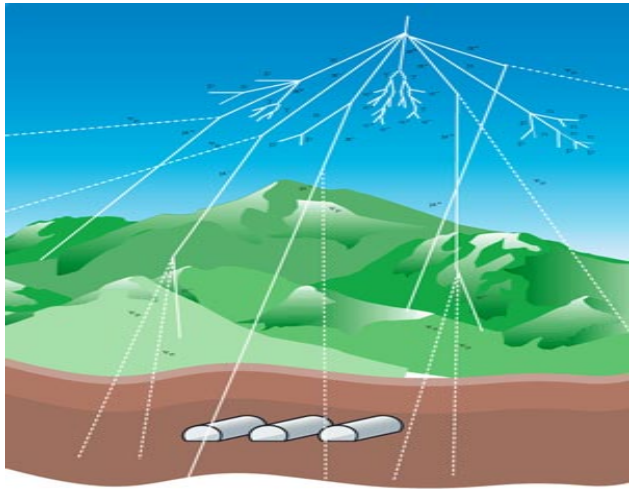
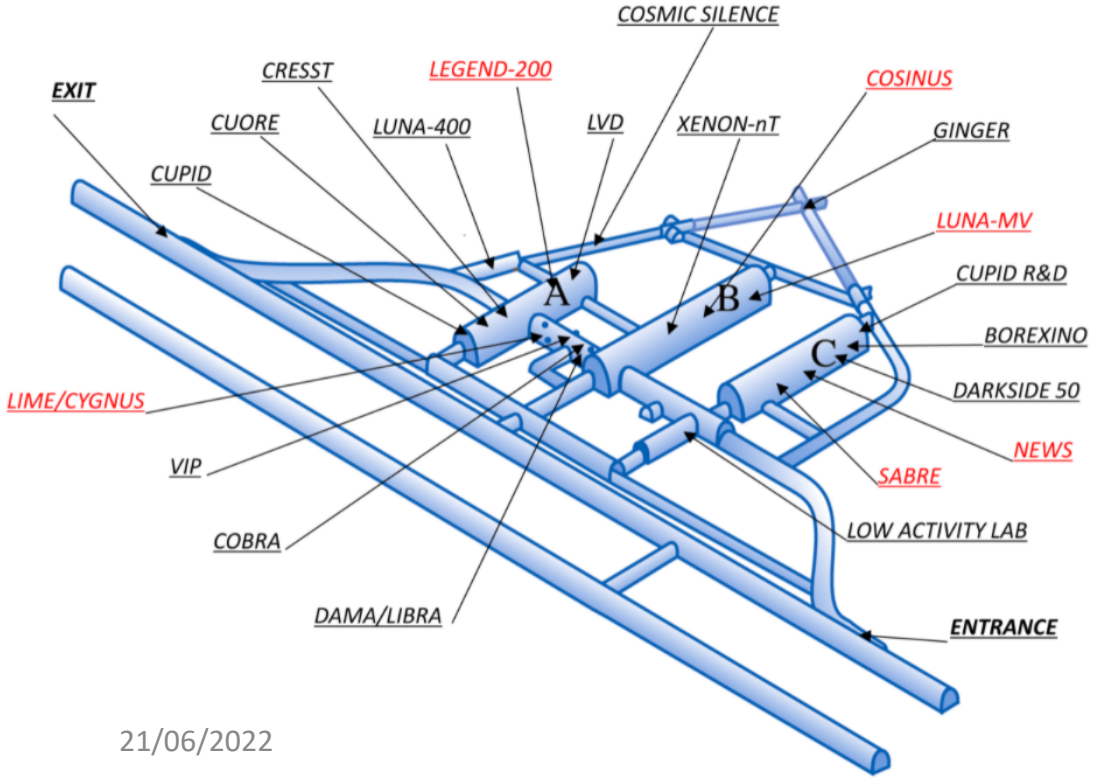
Outline

- Gran Sasso National Laboratory (LNGS)
- The relevance of background
- Ultra-low level radioactivity measurement facilities at LNGS: Gamma ray & ICP-MS
- What is mass spectrometry?
- ICP-MS potentiality and limiting factor
- Applications

Gran Sasso National Laboratory





The LNGS underground laboratory provides the necessary **ultra-low radioactive background**

to detect extremely rare events

Cosmic ray flux reduction: $\approx 10^6$

Neutron flux reduction: $\approx 10^3$

- Selection of **highly radio-pure materials**

K Pb Th U

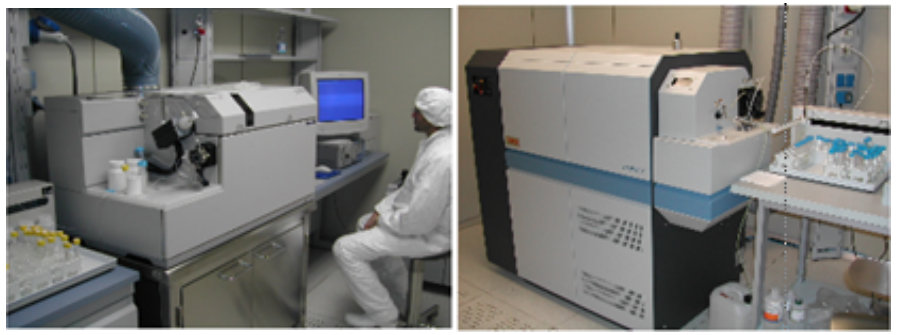
Neutron Activation Analysis, γ-Ray Spectrometry, ICP-Mass Spectrometry

Ultra-low level radioactivity measurement facilities

STELLA (SubTErranean Low Level Assay)

- **ϒ-ray spectrometry with high purity Ge detectors (HPGE)**
- α spectrometry with Silicon PIPS detectors
- Liquid scintillation counters

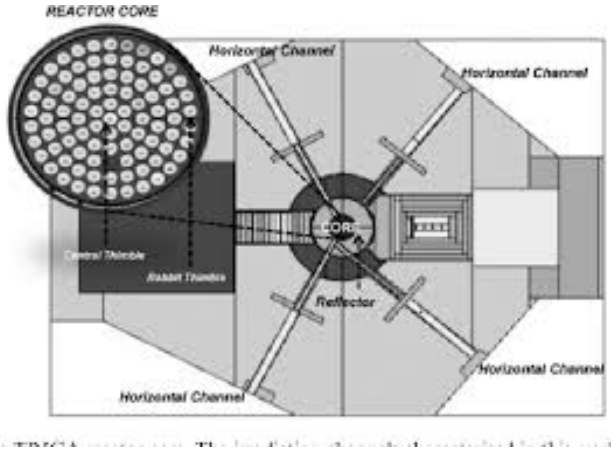
ICP-Mass Spectrometry



- **Quadrupole and double focusing ICPMS**
- ISO 6 Clean room
- Reagent purification systems
- Sample treatment device

Neutron Activation Analysis (NAA) Pavia

- TRIGA Mark II reactor Pavia University
- Radio-Chemical Lab
- HPGE at Milan INFN&University



Radiometric techniques are sensitive to the radiation emitted by radionuclide decay

Sensitivity f($T_{1/2}$, Energy ϒ-ray line, branching ratio, sample mass, time of measurement)

ULL-GRS Ultra Low Level Gamma Ray Spectrometry

+ Sample treatment free
+ Non destructive technique
- Sensitivity depend on the sample mass (Kg)
- Long measurement time is requested to achieve high sensitivity (weeks)
- Bulk measurement/homogeneous material

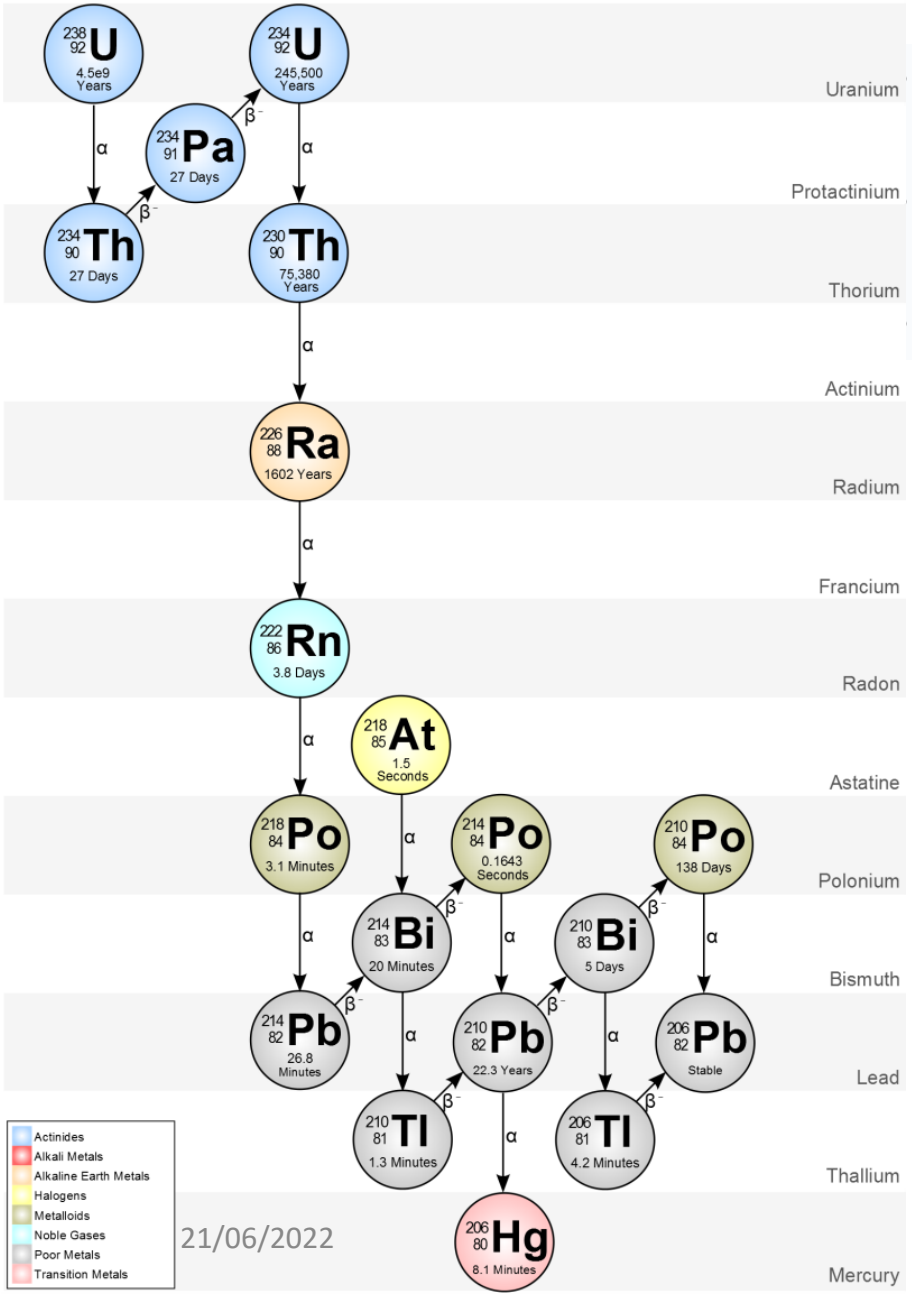
Mass spectrometry measures the concentration of radionuclides (number nuclides/mass)

ICP-MS Quadrupole Mass Analyzer equipped with collision cell
HR-ICP-MS High resolution ICP-MS

+ Small sample (g)
+ Relatively quick measurement
- Sample treatment is mandatory and delicate
- Destructive technique

R&MS are often applied both to check secular equilibrium of decay chain

Look inside the decay chains



^{238}U is the parent of its decay chain

^{206}Pb is a stable nuclide, the finish line of the chain

In between there are many radionuclides, all undergoing α&β decay processes

If the **secular equilibrium is respected**

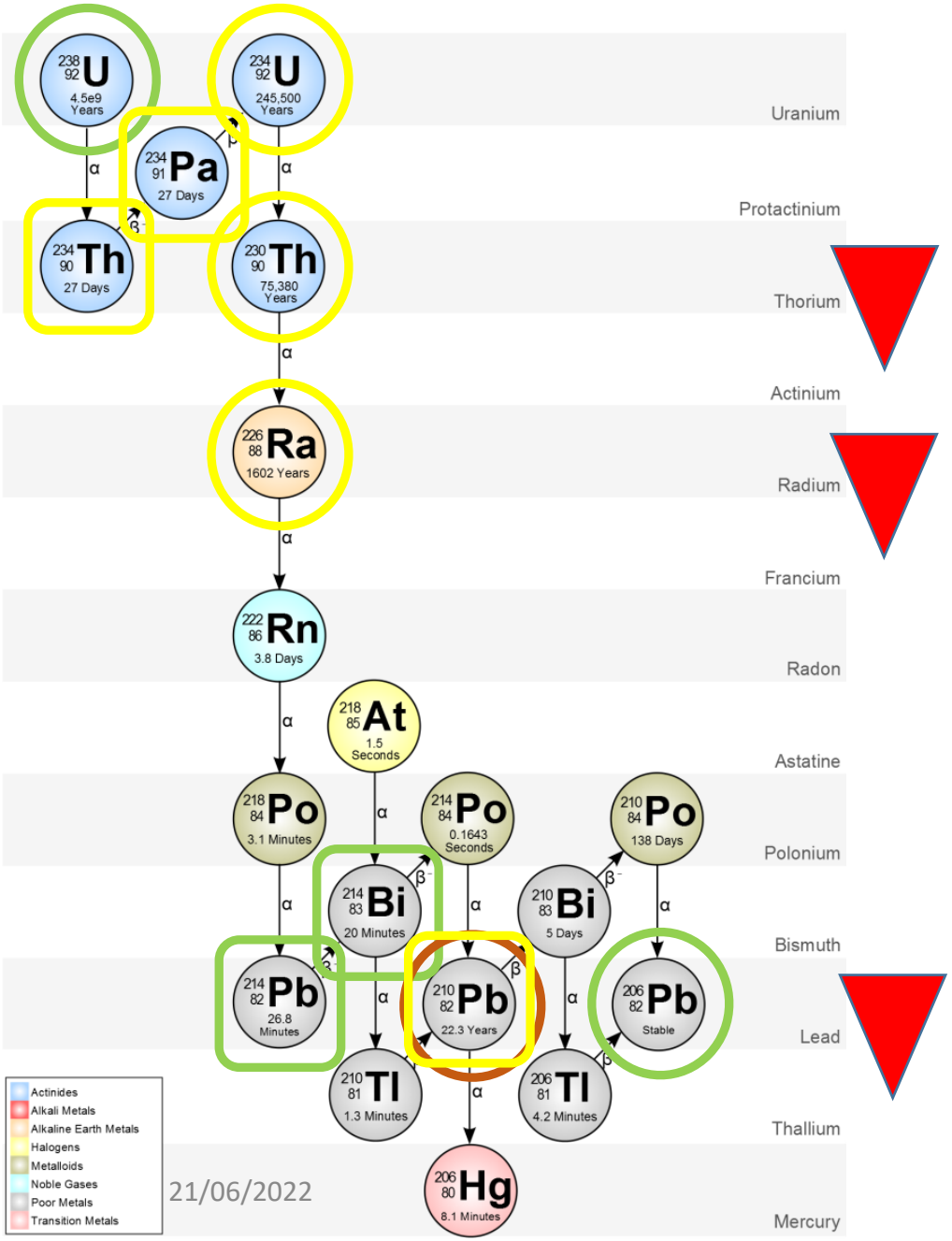
the number of atoms that decays for each nuclide per unit time is the same.

But the half-life time ($T_{1/2}$) is characteristic for each nuclide

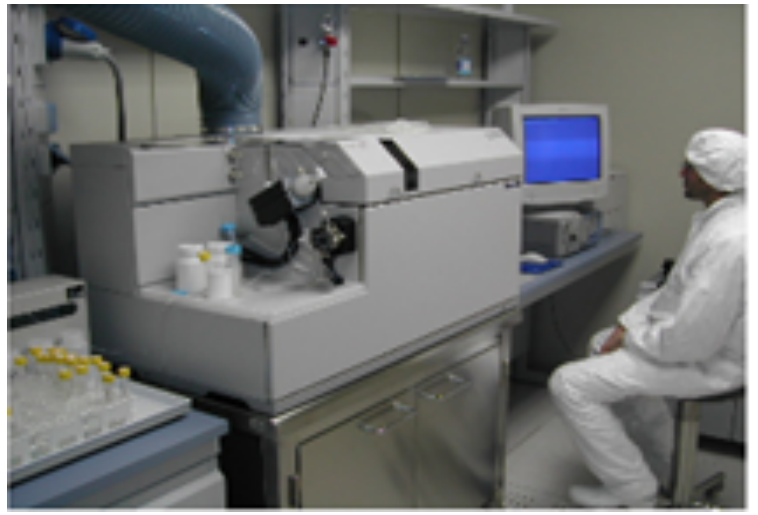
their concentrations are inversely proportional to $T_{1/2}$

Radiometric techniques and mass spectrometry are intrinsically complementary

Look inside the decay chains



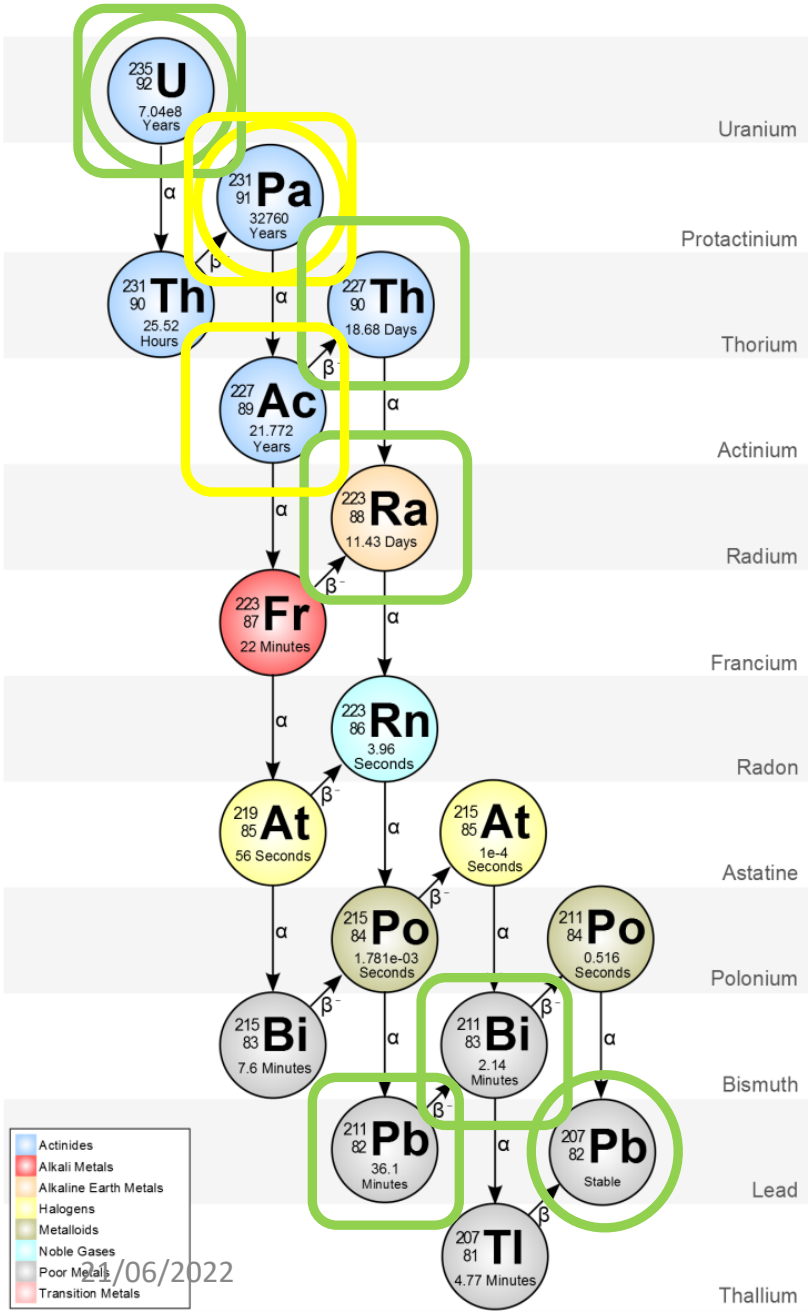
ICP-MS



Chemical & physical behaviour different for the nuclides

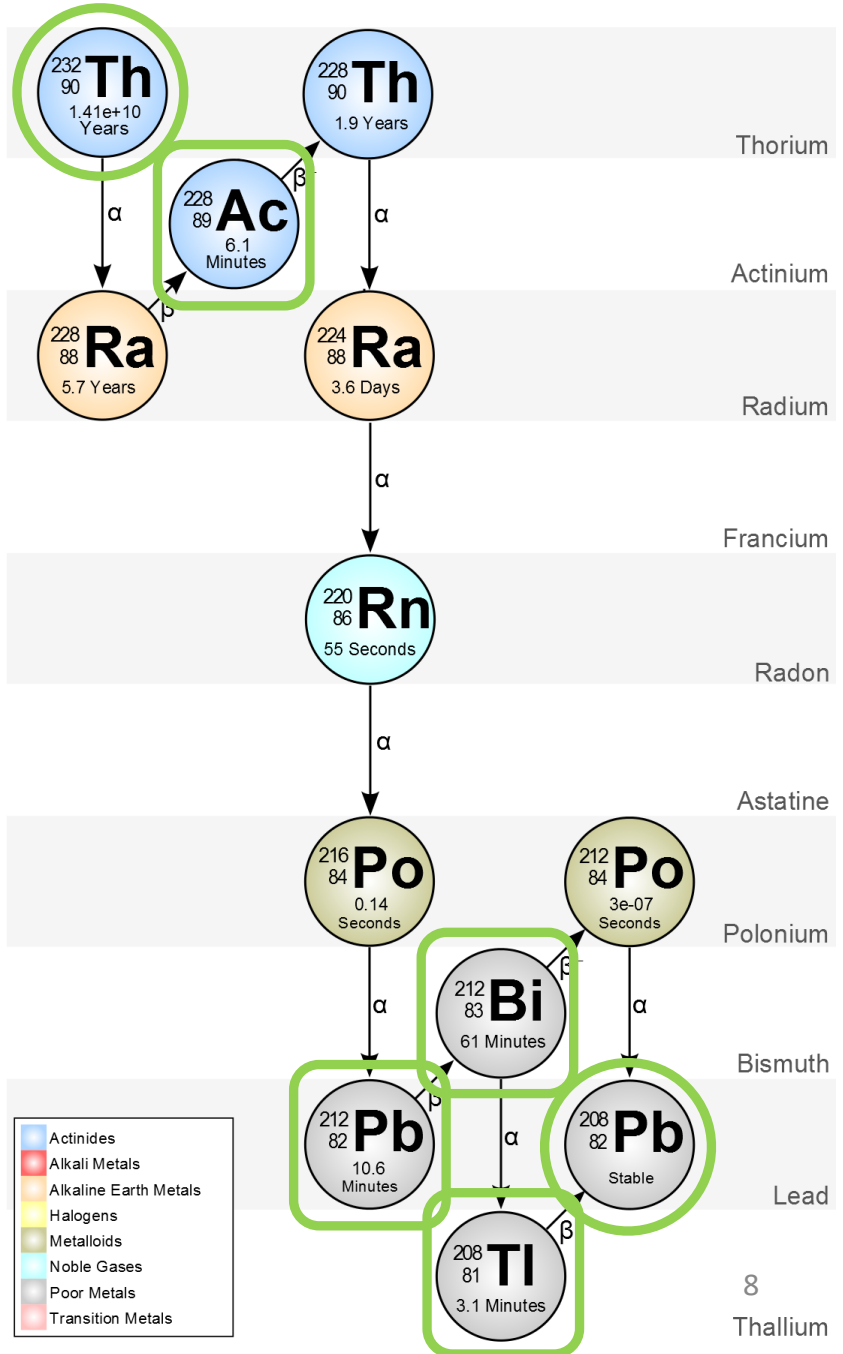
γ-ray Spectrometry

Others natural decay chains



ICP-MS

γ-Ray Spectrometry



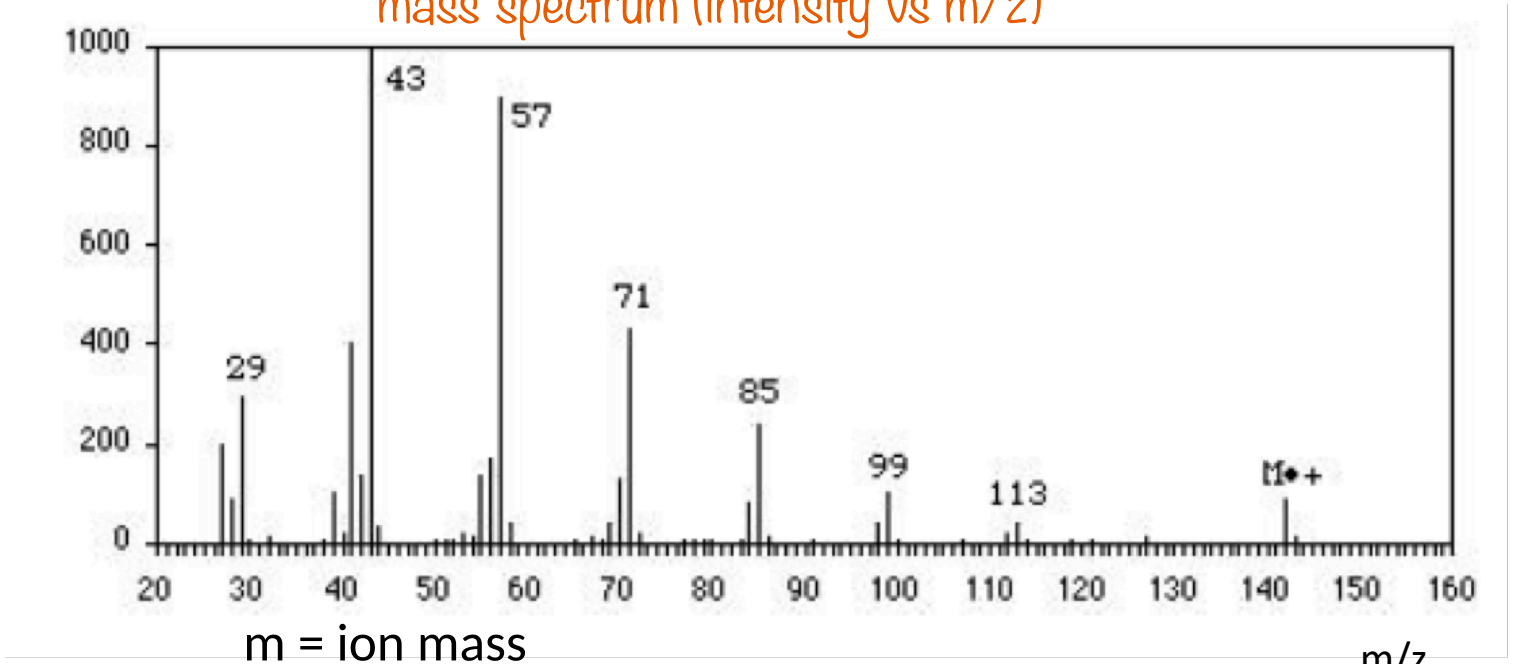
What is the mass spectrometry?

- Identification and quantification of molecules and elements

SAMPLE INTRODUCTION SYSTEM → SAMPLE IONIZATION (ION SOURCE) → MASS ANALYZER (m/z) → DETECTOR

Intensity

mass spectrum (intensity vs m/z)



m = ion mass

z = ion charge

- Qualitative info
- Semi-Quantitative
- Quantitative
- Isotopic ratio

Mass Spectrometry History

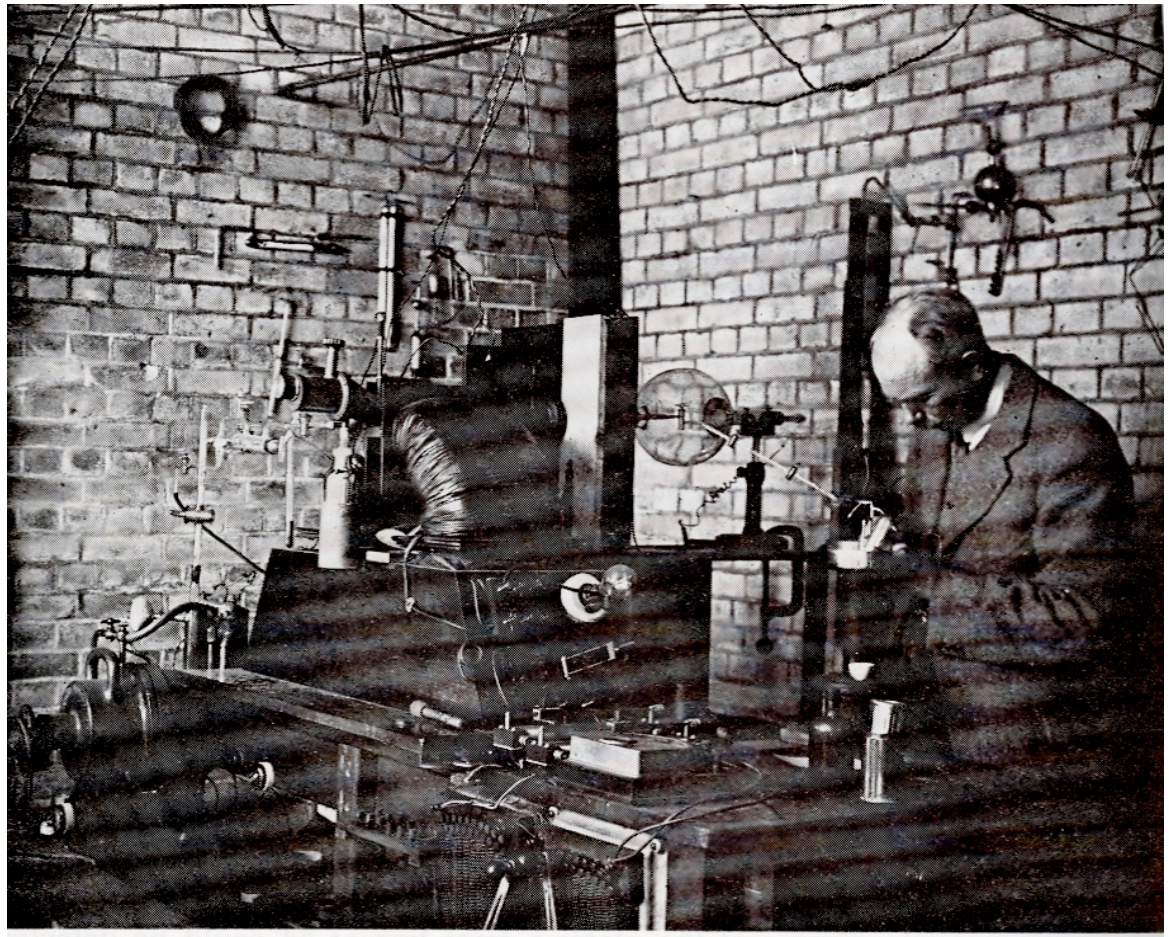
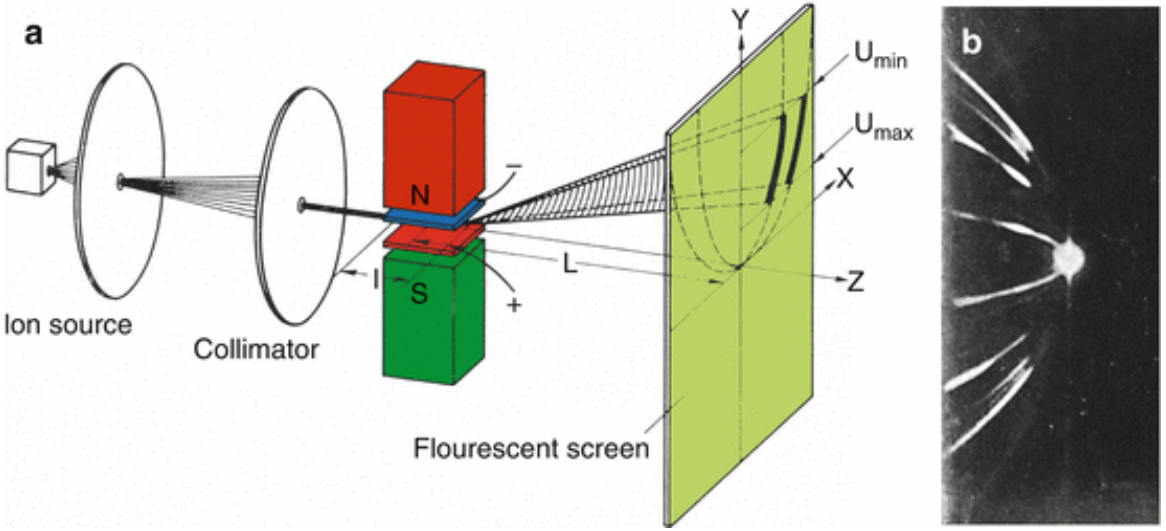
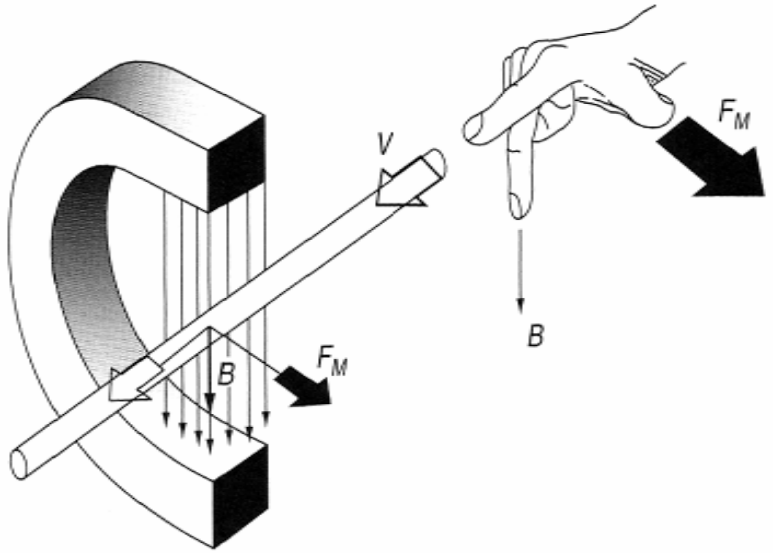


Plate 1. F. W. Aston with second mass spectrograph.



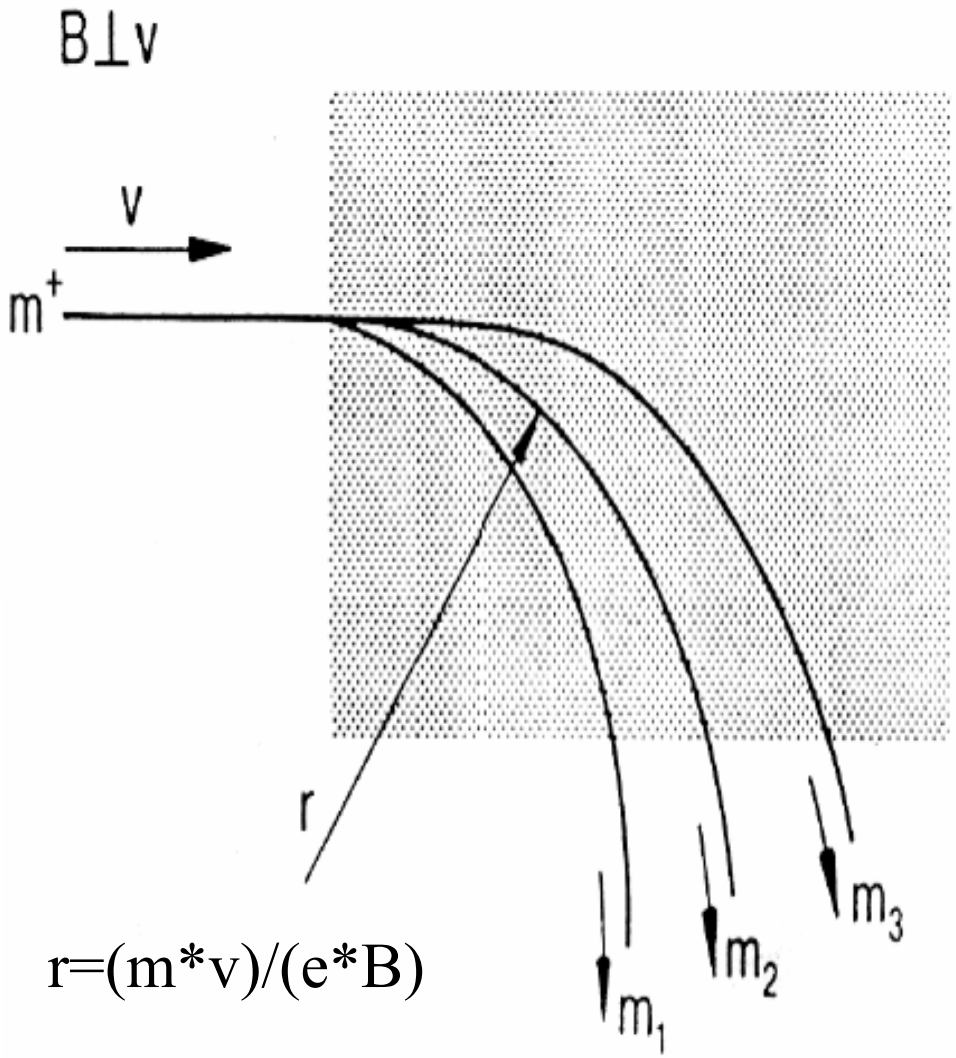
Ion source = discharge tube
Mass analizer =magnet
Detector = Fluorescent screen

Operating principle of magnet sector



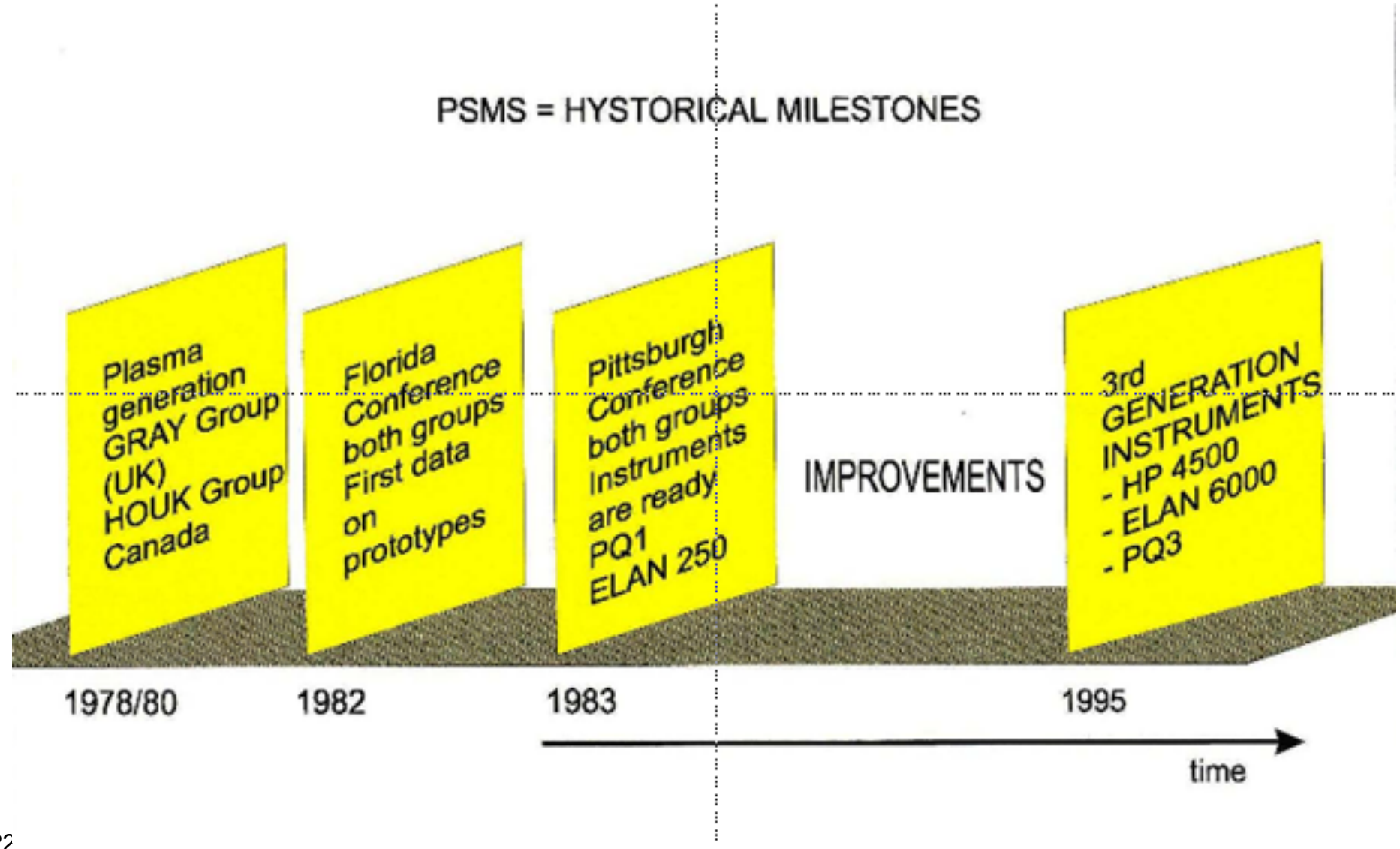
Lorentz force: $F_L = q(E + v \times B)$

Centrifugal force:

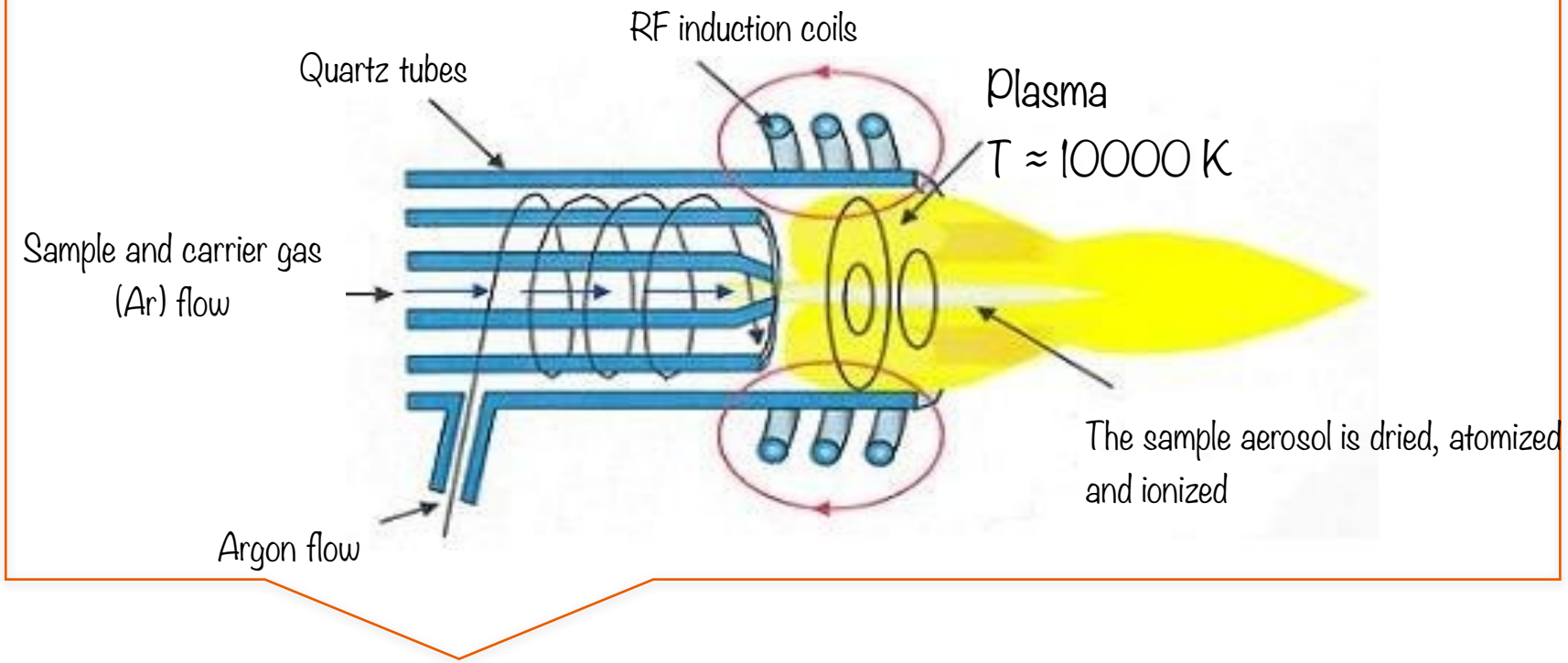


$r = (m*v)/(e*B)$

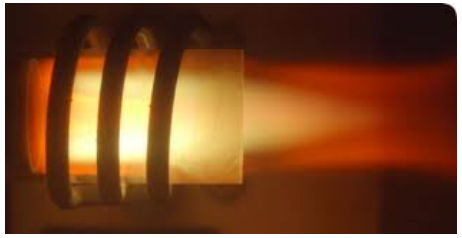
Plasma Source Mass Spectrometry: historical milestone



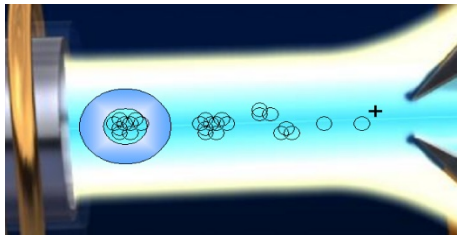
Inductively Coupled Plasma Mass Spectrometry



Plasma torch ion source



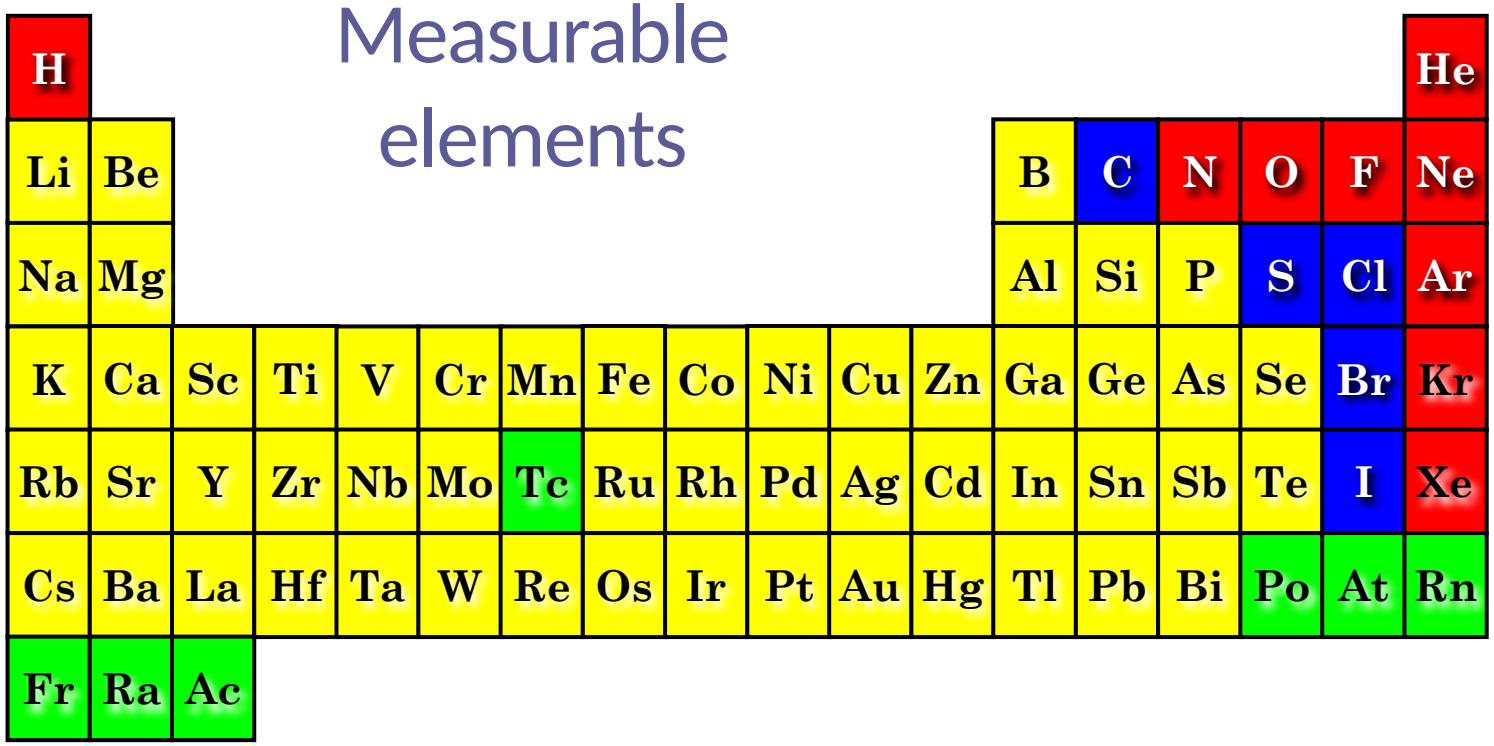
High energy!



Complete (almost):
- Desolvation
- Atomization
- Ionization

<u>Plasma is capable to ionize almost all chemical elements</u>

Measurable elements



AA / ICP / ICP-MS

ICP / ICP-MS

Radioactive

Not Measurable

Unstable Elements

Ultra - trace

Trace

majors...

1ppq (10^{-15} g/g)

1ppt (10^{-12} g/g)

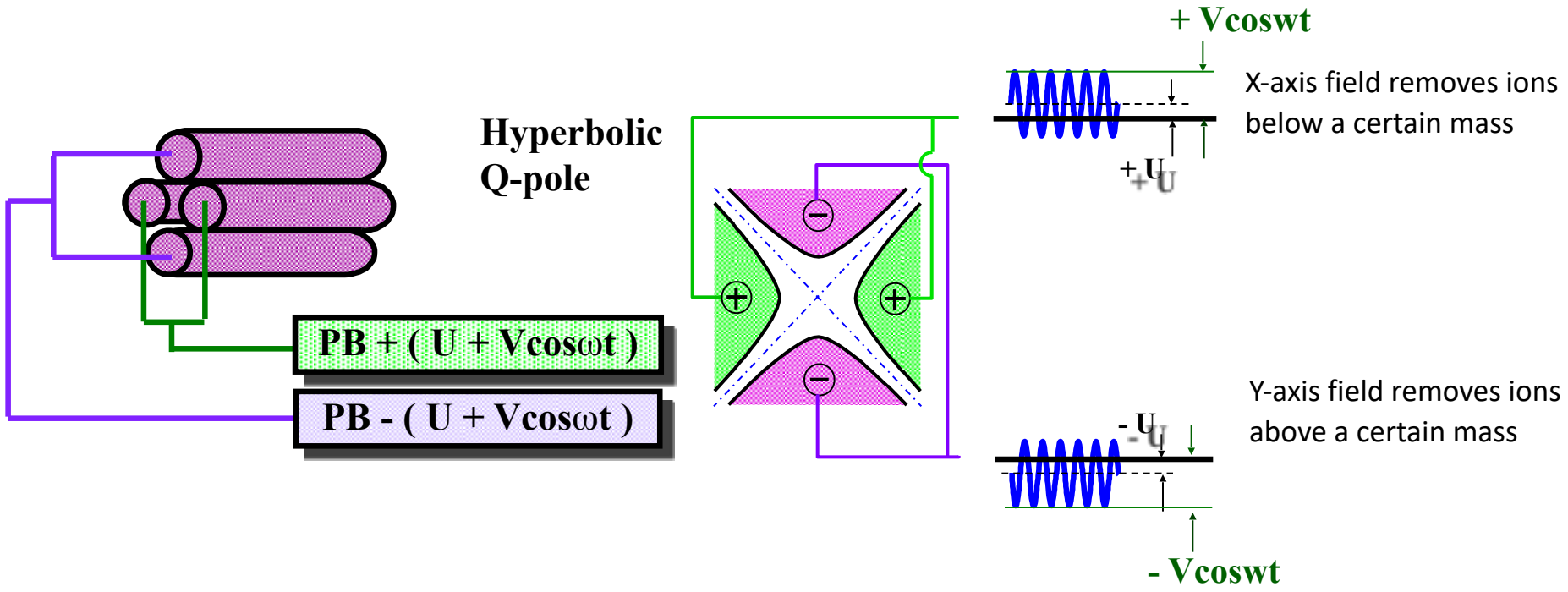
1ppb (10^{-9} g/g)

1ppm (10^{-6} g/g)

INFN

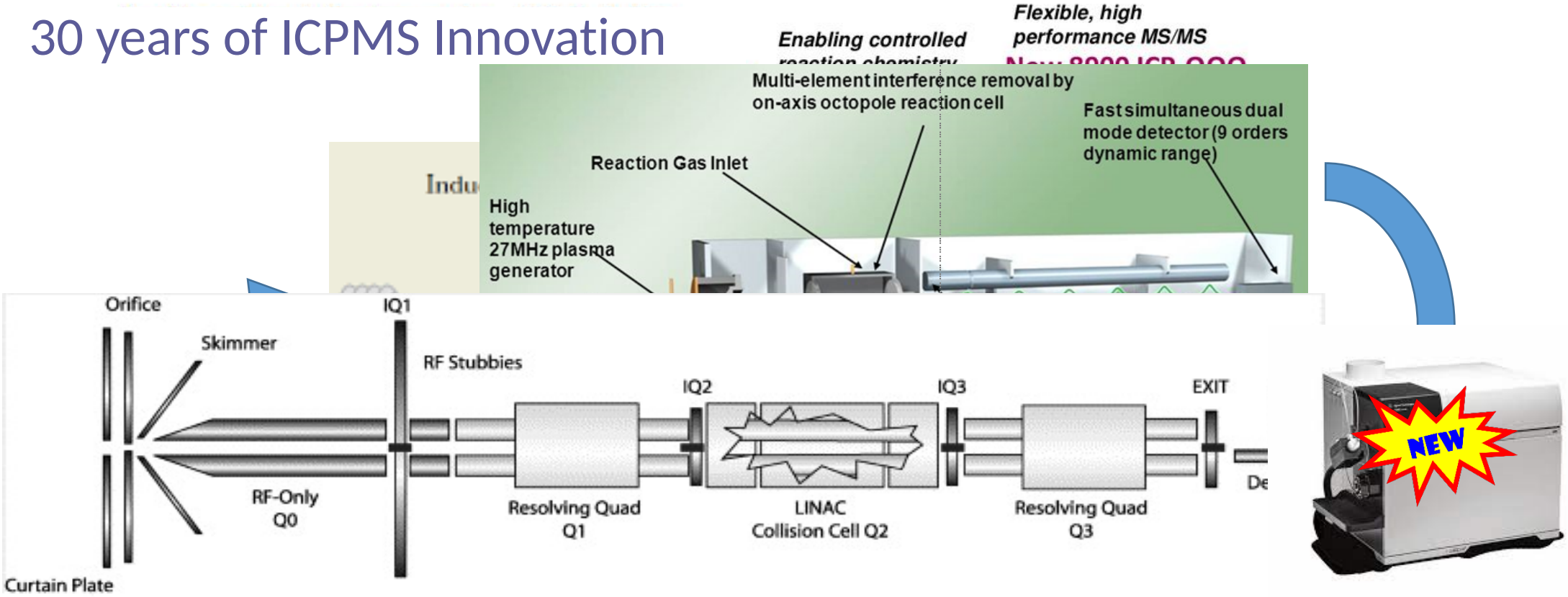
Quadrupole Theory

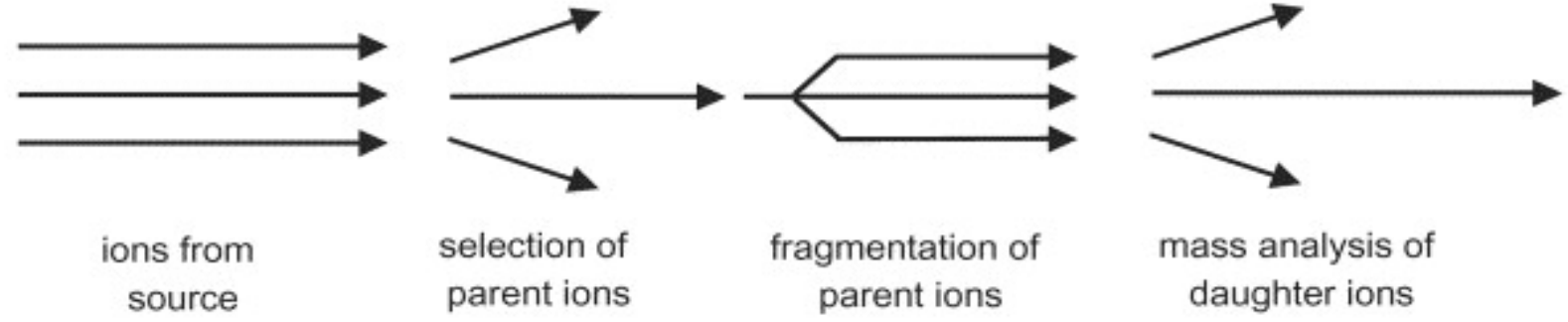
Consists of four Hyperbolic rod supplied with DC current and radio frequency



For a given combination of RF and DC voltages, the quadrupole only lets ions of a **specific mass** pass through to the detector. (In fact, mass spectrometer works on mass/charge ratio, not mass)

30 years of ICPMS Innovation





Issues in ICP MS ultra-trace analysis

- Isobaric interferences: polyatomic species, isotopes of different elements and double charged ions

- Sensitivity, especially for solid samples (the instrument does not tolerate high matrix content, dilution is necessary) and **matrix effect**

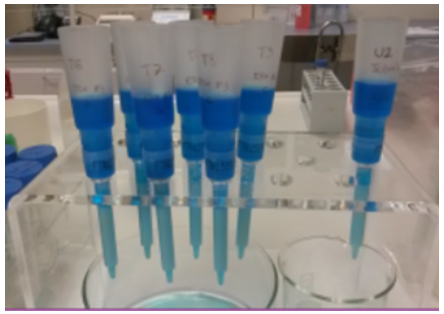
- Background (instrumental due to cross contamination and reagent, vials …)

- High **risk of contamination** during sample preparation and measurement (we are looking for very very low concentrations!!!)

ICPMS Ultra Trace measurement “triangle”

Instrumentation

Sample preparation

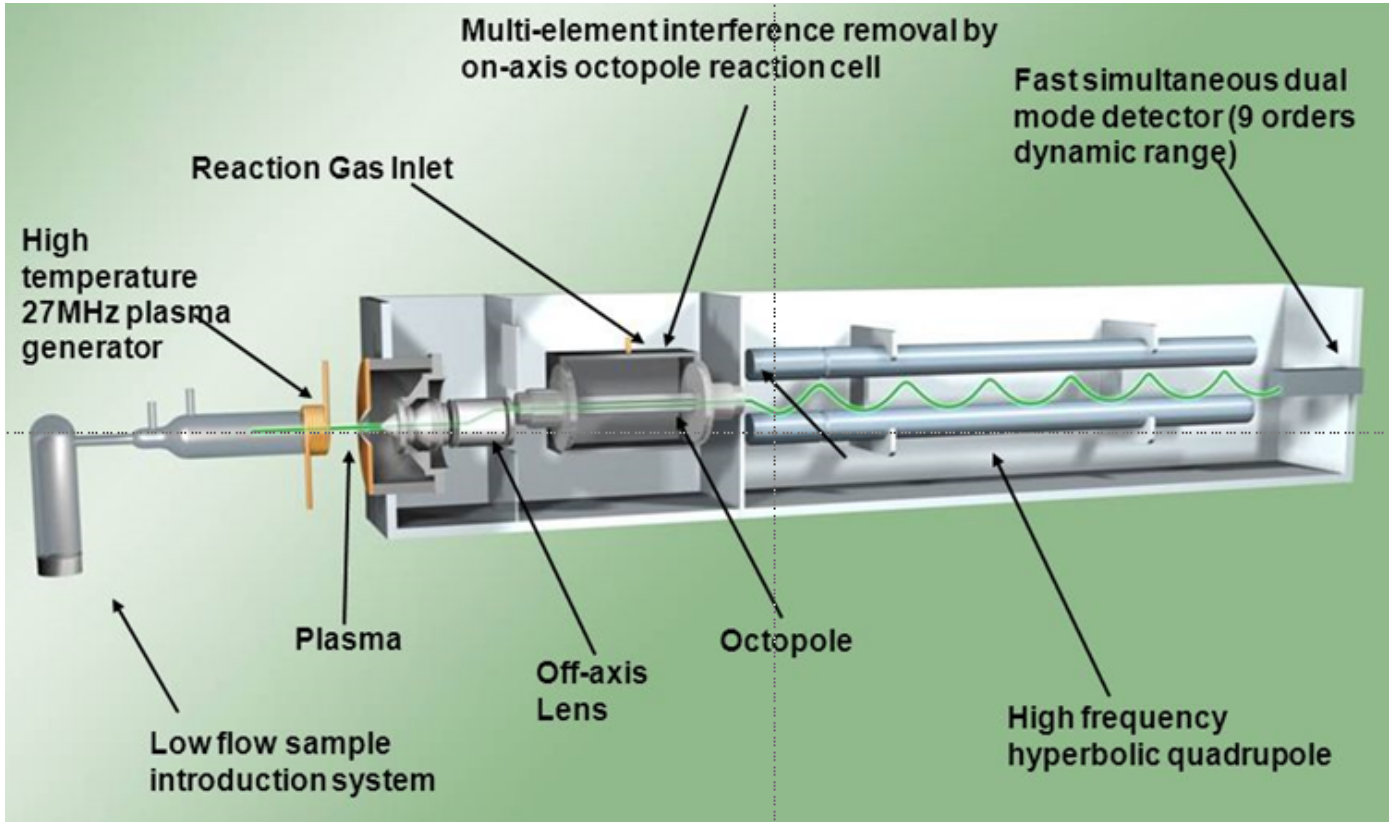


Ultra trace

“Clean chemistry”

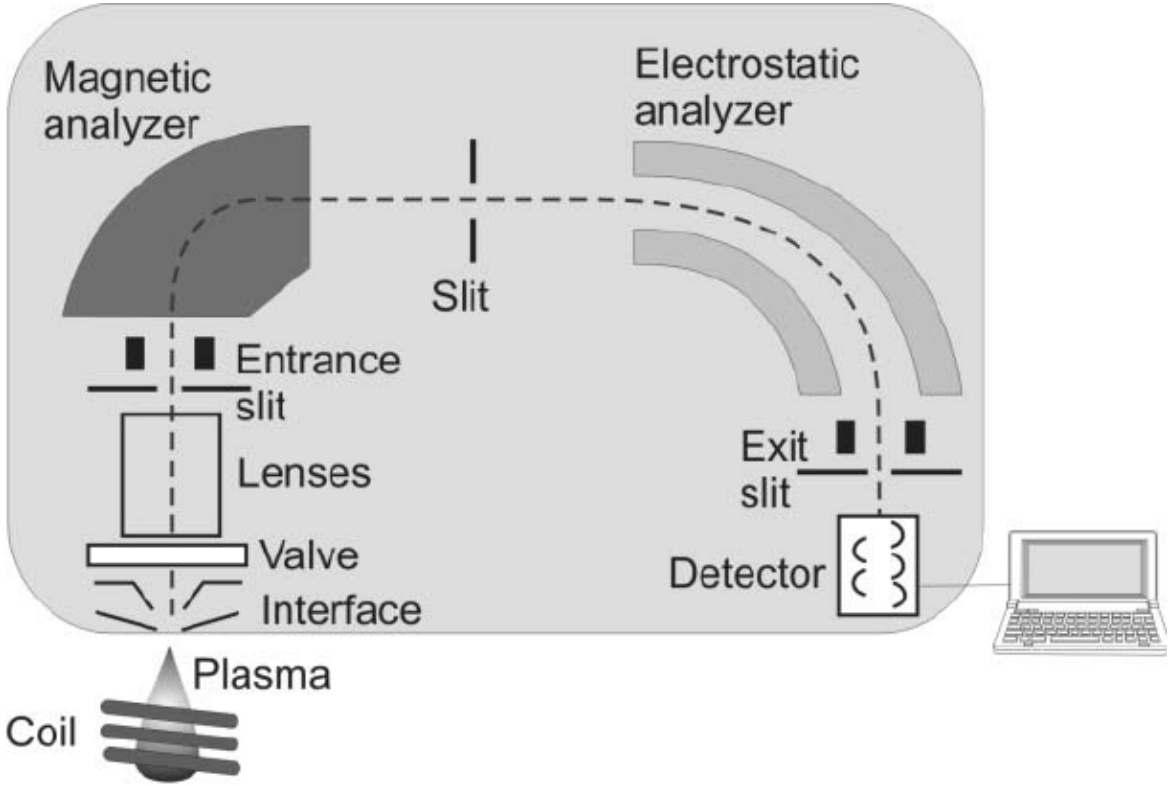
Two ICP mass spectrometers @ LNGS

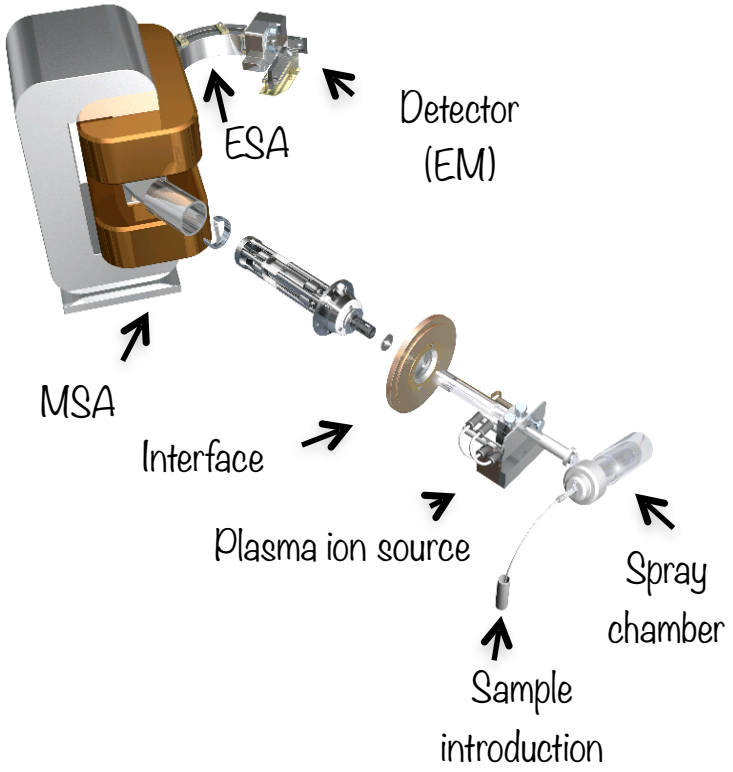
ICP QMS (quadrupole mass analyzer) – Agilent 7850



The polyatomic species interfering with the analytes are removed in the collision cell

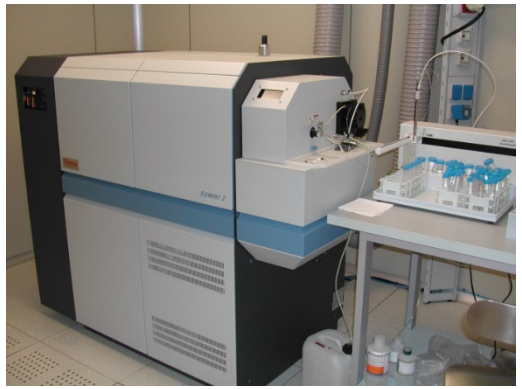
Double focusing ICP Mass Spectrometer



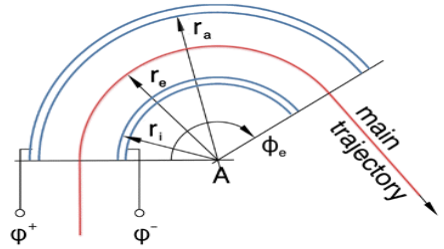


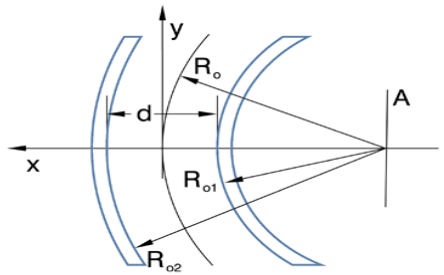
Reverse Nier-Johnson geometry

The peculiarity of double focusing ICPMS are sensitivity and **the mass resolution**



Electrostatic Sector





- No Mass Dispersion
- Slit at particular radius r, the system acts as an energy filter.

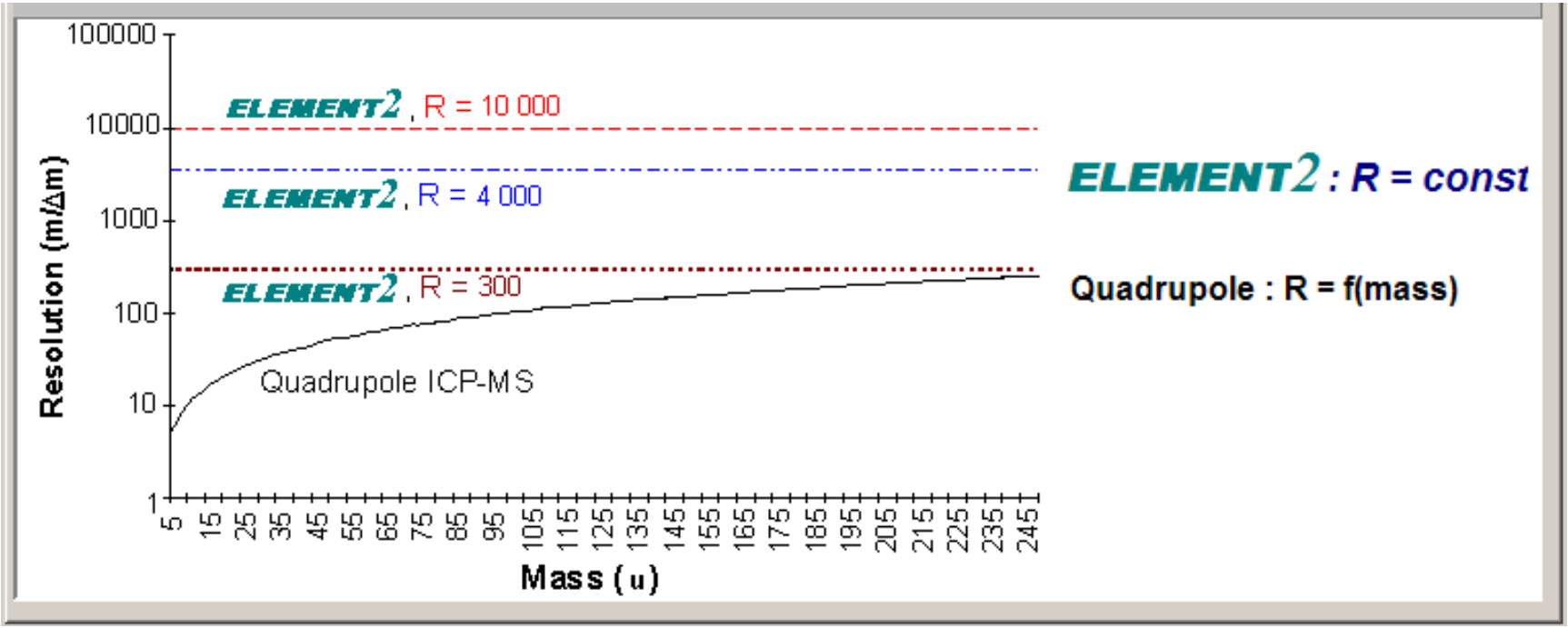
Mass resolution power

When two adjacent peaks m_a and m_b with comparable intensitiy and

h<10%H

the resolution is defined as the ratio:

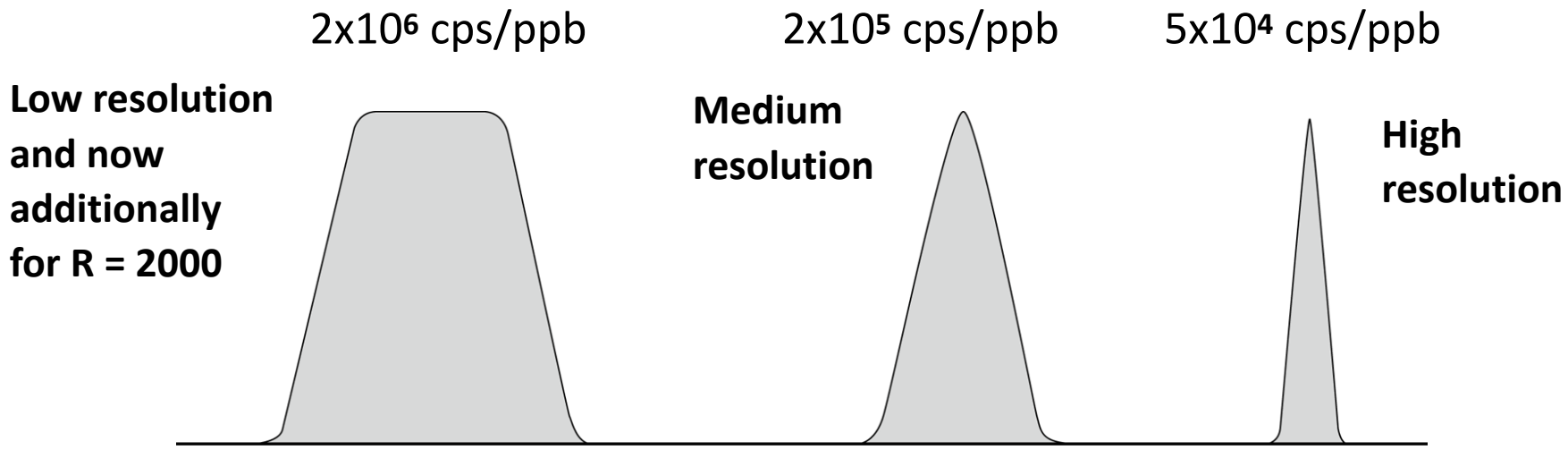
$$R = m / (m_a - m_b)$$



Low-Medium-High Resolution: peak shape

- Using the Low Resolution mode, the sensitivity is the highest and the top of the peaks are flat. This is a successful approach for many isotopic systems also

- In higher resolution the peaks have triangular shape, the resolution rise up, but the sensitivity degrease



Measurement of K in NaI crystal

DM Direct detection experiments sensitivity = f(radioactivity background)

Some experiments looking for DM evidence are using or developing **NaI crystal-based detectors**

K is the most critical natural radio contaminant for Na due to their chemical affinity

The K final background budget is 10 ppb

The development of a high sensitivity analytical method is required in order to have a quick and reliable tool for NaI crystal production process monitoring **(Detection Limit=ppb level).**

Drawbacks in ICP-MS ^{39}K measurement

Dilution is requested (at least 100)

- Sensitivity reduction
- Matrix effect (St. Add.method)

Contamination risk

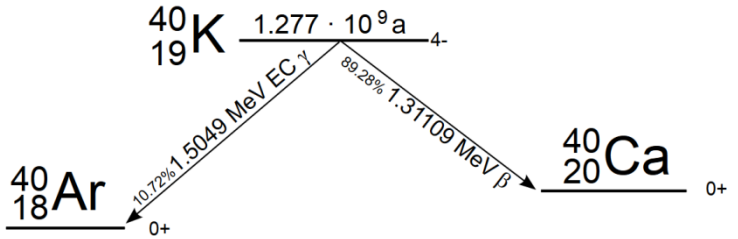
- Ultrapure reagents
- ISO6 Clean room
- Vials conditioning

Isobaric interferences

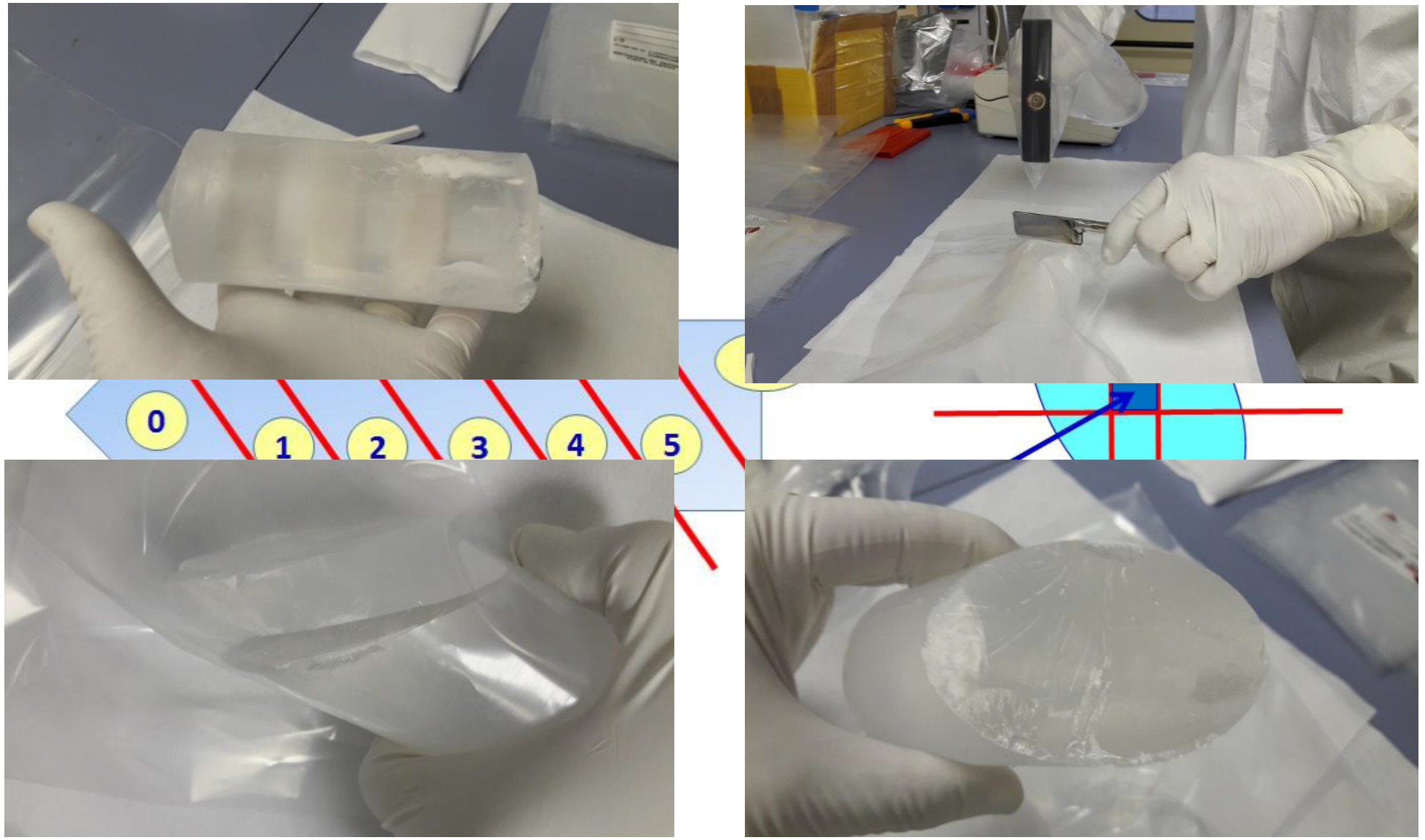
	33	34	35	36	37	38	39	40	41
S	0.76	4.29		0.02					
Cl			75.78		24.22				
Ar				0.337		0.063		99.60	
K							93.26	0.012	6.730
Ca								96.94	

- Chemical separation is hard
- Collision cell ICP-MS (Cool pl.)
- **HR-ICP-MS Hot/Cool Plasma Element II Thermofisher**

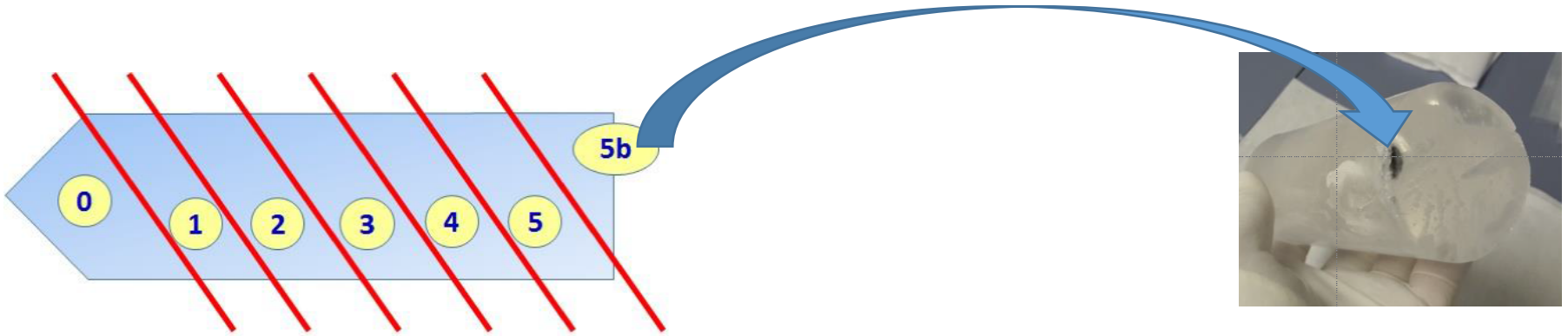
	Mass (amu)	Resolution
$^{78}Kr^{++}$	38.96020	11100
$^{39}K^{+}$	38.96371	
$^{1}H^{38}Ar^{+}$	38.97056	5690
$^{23}Na^{16}O^{+}$	38.98468	1860



Crystal sampling procedure



Study of the impurity distribution



Sample	0 NOSE	1	2	3	4	5 TAIL	5B
Cry **ST Powder** Hot plasma							
K ppb	**230**	**320**	**360**	**340**	**350**	**1415**	**------**
Cry N1 **UP Powder** Hot plasma							
K ppb	**<15**	**<15**	**<15**	**<15**	**<15**	**120**	**360**
Th ppt	<1	<1	<1	<1	<2	<1	280
U ppt	<1	<1	<1	<1	<1	<2	130
Cry N2 **UP Powder** Cool plasma							
K ppb	**10.2**	**11.5**	**11.2**	**11.6**	**11.6**	**13.3**	**-----**

The uncertainty of the reported concentration values is about 10-25 %

HR-ICP-MS performance

Detection limit calculated with 3*SD_{BLK6} for NaI solid=3ppb

Recovery test

	B5	B5+13.25	Mesured	Recovery %
ppb	13.3 ± 2.5	26.5 ± 3	28 ± 5	**105 ± 25**

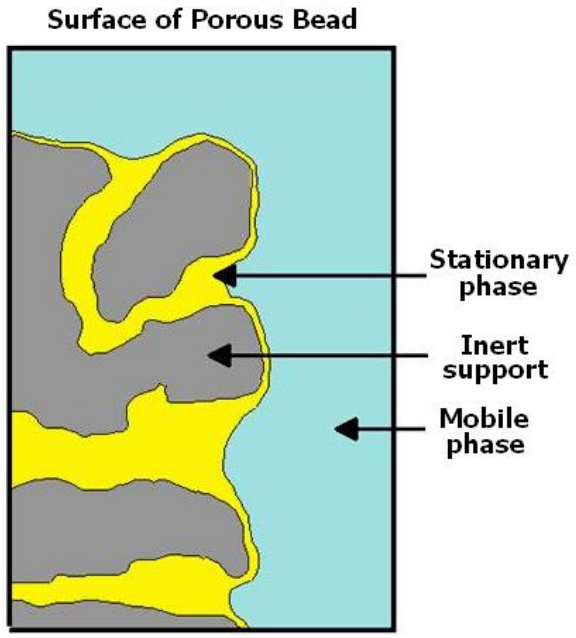
Techniques and labs comparison

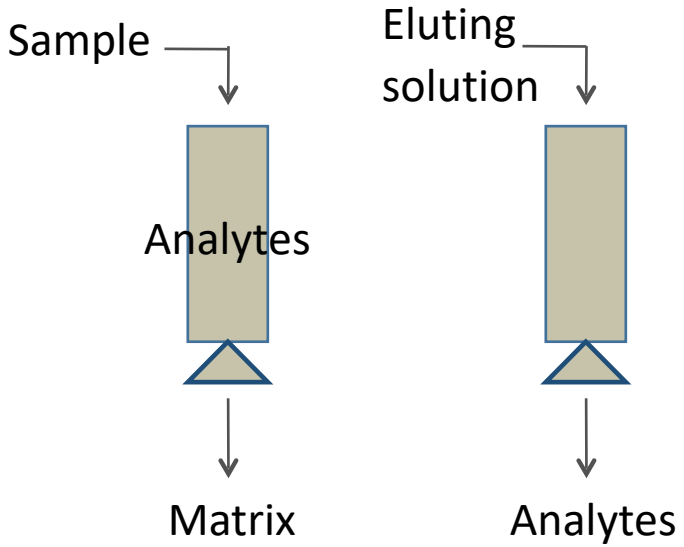
Technique	Laboratory	DL [ppb]
HR-ICP-MS	LNGS	3
ICP-QMS	SICCAS	10
ICP-OES	Ametek R&D	5
ICP-QQQ-MS	PNNL	0.6

Without matrix separation, the DLs achieved in different labs using different instrumentation are at ppb level

Development of an analytical procedure for the improvement of ICP MS detection limits for Th and U in copper

Extraction chromathography





Capacity factor k':

$$k' = D \frac{V_s}{V_m}$$

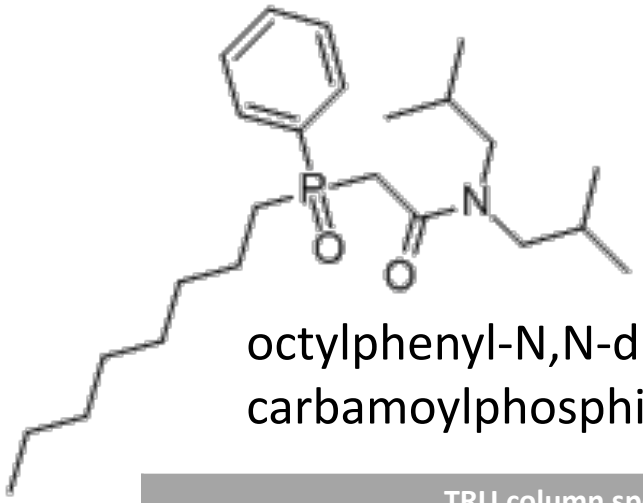
Advantages:

- Matrix removal
- Analyte pre-concentration

Disadvantages:

- Time consuming
- Reagents
- Risk of contamination
- Higher amount of sample

TRU resin (Triskem®)

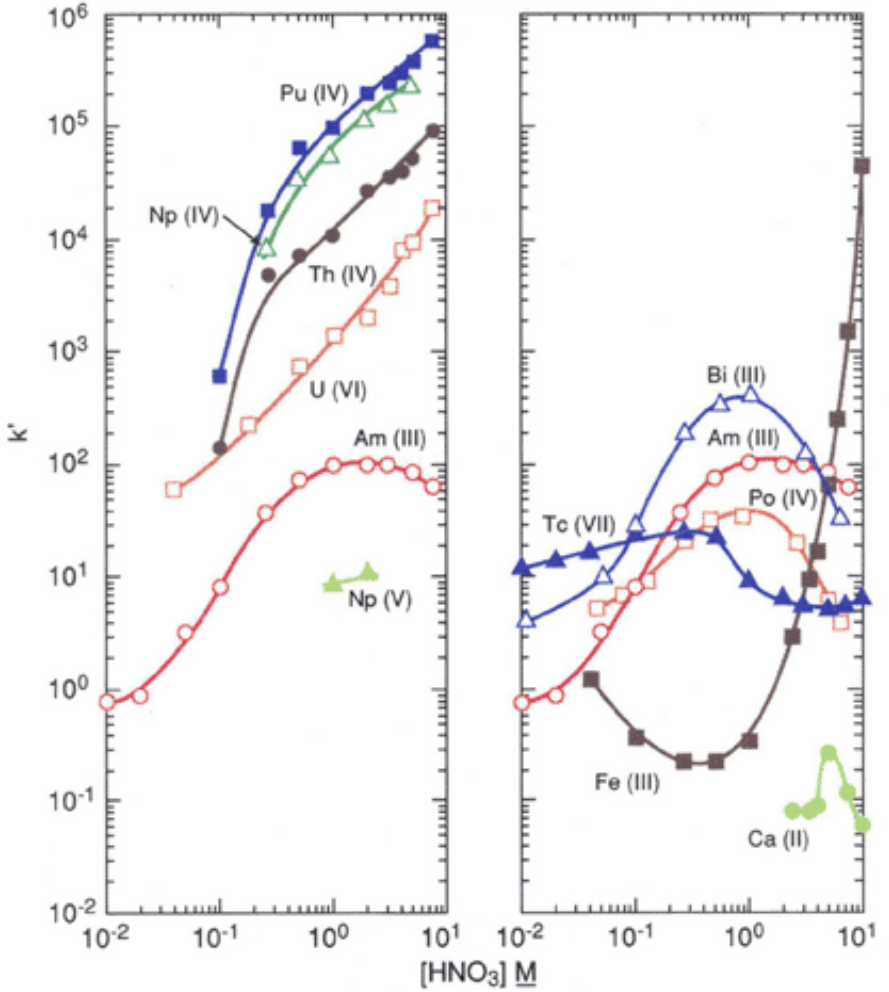


octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide (CMPO)

TRU column specifics	
Stationary phase	CMPO/TBP (ρ= 0.37 g/mL)
Inert support	
Grain dimension	100-150 µm
CMPO content	
Vs	
Vs/Vm	
Vm (FCV)	

Figure 2

Acid dependency of k' for various ions at 23-25°C.
TRU Resin



Horwitz, et al. (HP193)

Experimental

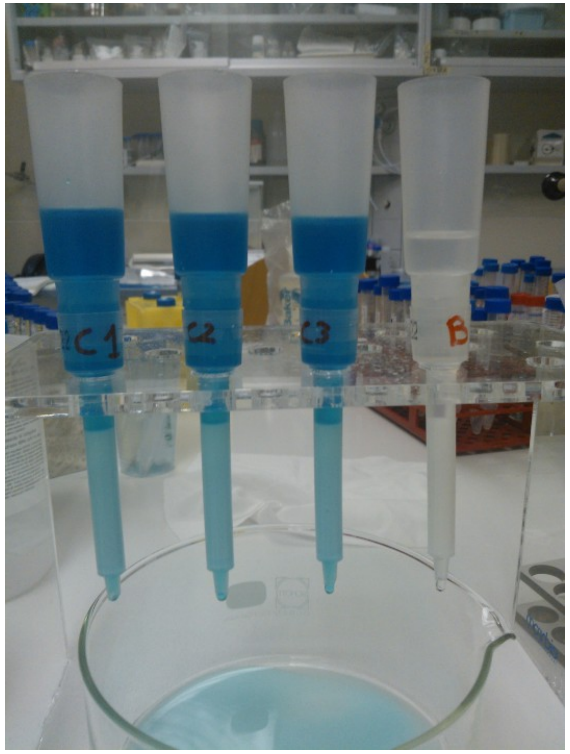
- Work in clean room (class 1000-ISO6)

-Preliminary cleaning of all vials and labware involved in the analysis (10% UP HNO3 solutions + rinsing with MilliQ - 18.2 MΩ*cm – water)

- Dissolution in UP HNO_3 solution

- Several controlled etching steps: removal of likely contaminated surface and bulk analysis / depth profile

- Analytes separation and pre-concentration using extraction chromatographic columns loaded with selective resins



TRU results

Sample solution:

10% Cu in 4M HNO3

Th and U chromatographic extraction:

1.Resin pre-wash and conditioning (0.1M ammonium oxalate)

2. Rinse (4M HNO3, 5 mL)

3. Sample load (10 mL)

4. Rinse (4M HNO3, 5 mL)

5. Th and U elution (0.1M ammonium oxalate 10 mL)

Solution 5 analyzed undiluted

Total Dilution Factor: ≈10

(vs ≈1500 without pre-concentration)

	DL* (in solid Cu)	Recovery %
Th	2.6 ppt	90.0 ± 0.6
U	0.8 ppt	97.9 ± 6.1

*DL = 3 × BLKStdDev

Cu separation efficiency: >99%

	Measured in Cu sample
Th	4.6 ± 1.3
U	1.0 ± 0.3

	DL	Recovery %
Th	very good	excellent
U	**excellent**	**excellent**

LRT performance comparison

		ICPMS LNGS (LSC)	ULL GRS LNGS (LSC)	ULLGS+NAA LENA-Pavia
		Primordial parents	ϒ emettitors	Primordial parents
		Surface/bulk	BulK	Surface/bulk
Destructive		Yes	No	Yes
DL	[10^{-12}g/g]	Th=0.5 U=0.5	Th= 10-20 U= 10-20	Th(^{233}Pa)= 0.1 U(^{239}Np)= 3-5
Sample size	[g]	0.1-10	1-10000	100
Sample treatment		Contamination **risk not negligeble**	Almost free	Hot sample handling **Low cont risk**
Analysis Time		days	weeks	days-week

R&MS are often applied both to check secolar equilibrium of decay chain
ICP-MS allows to perform the quality control of each single part (or lot)

Final remarks

- The next generation of experiments focuses to detect rare low-energy events needs «zero background» conditions in fact the residual radioactive background rate drives the feasibility of the experiments in terms of detector mass (cost) and length of data taking period.

- ICP mass spectrometry is an extremely versatile technique: it is a very powerful tool also for the screening of radiopure materials and whenever high chemical purity is important (eg. Crystal growth, 3D powder ect)

- The sample treatment plays a fundamental role in order to achieve excellent sensitivity

- Thanks to its rapidity of analysis and the use of a minimum amount of sample, it is a technique suitable for quality control (even on a single lot)

- ICPMS allows to discriminate the contamination contributes for inhomogeneous material (for example PCB trace/support/components)

- The combination of γ-ray and ICP-MS analyses allows to determine the background with the best sensitivity and to check for secular equilibrium over the lifetime of the experiment.