Inorganic Mass Spectrometry: operating principles, instrumentation and applications

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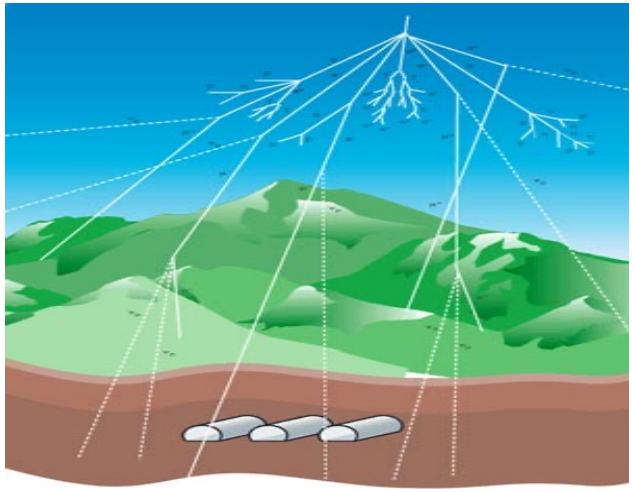
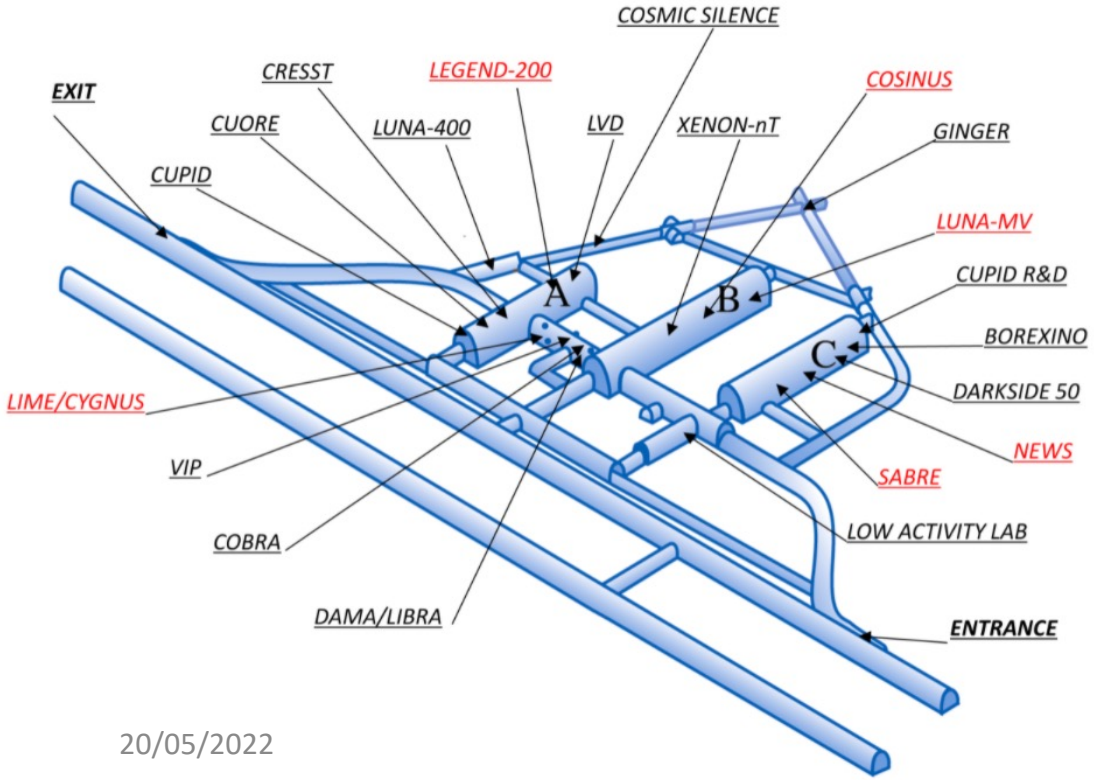
Milano Bicocca - 18 maggio 2022

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?
- Applications
- Conclusions

Gran Sasso National Laboratory





The LNGS underground laboratory provides the necessary **ultra-low radioactive background** to detect extremely rare events

Cosmic ray flux reduction: ≈10^6

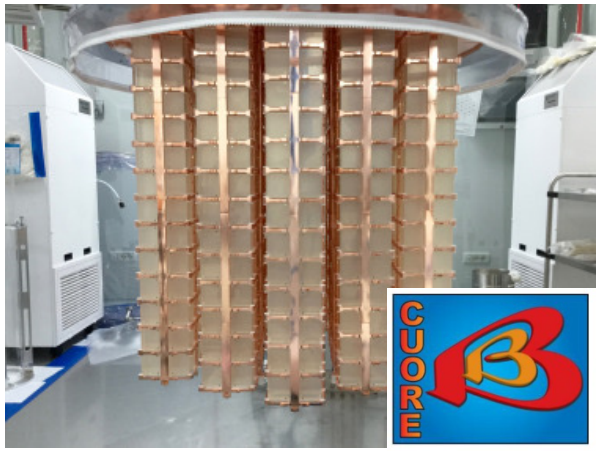
Neutron flux reduction: ≈10^3

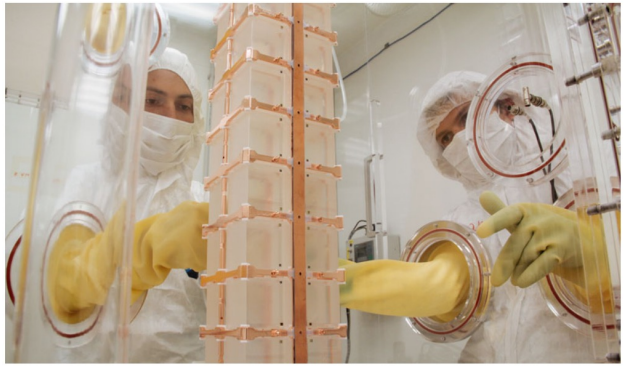
- Selection of **highly radio-pure materials**

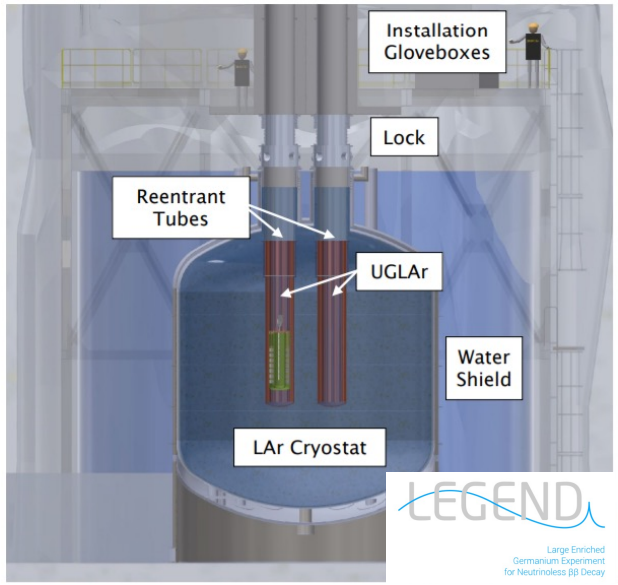
K Pb Th U

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

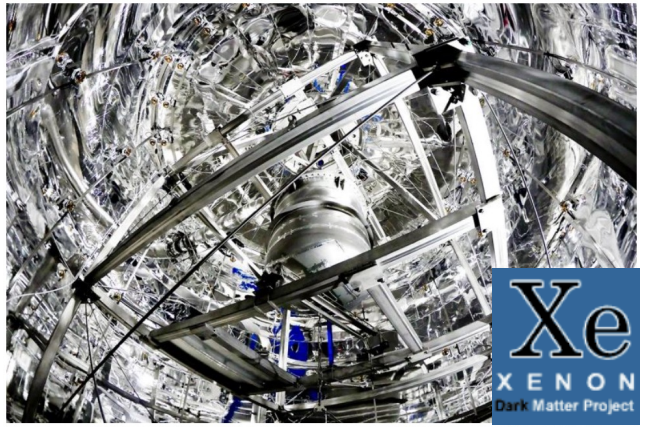
Neutrinoless double beta decay







Dark Matter



An extremely low radioactive background is the common feature of all experiments

Background rate & feasibility: the LEGEND example

Neutrinoless double-beta decay half-life discovery potential as a function of exposure and background rate in LEGEND experiment.

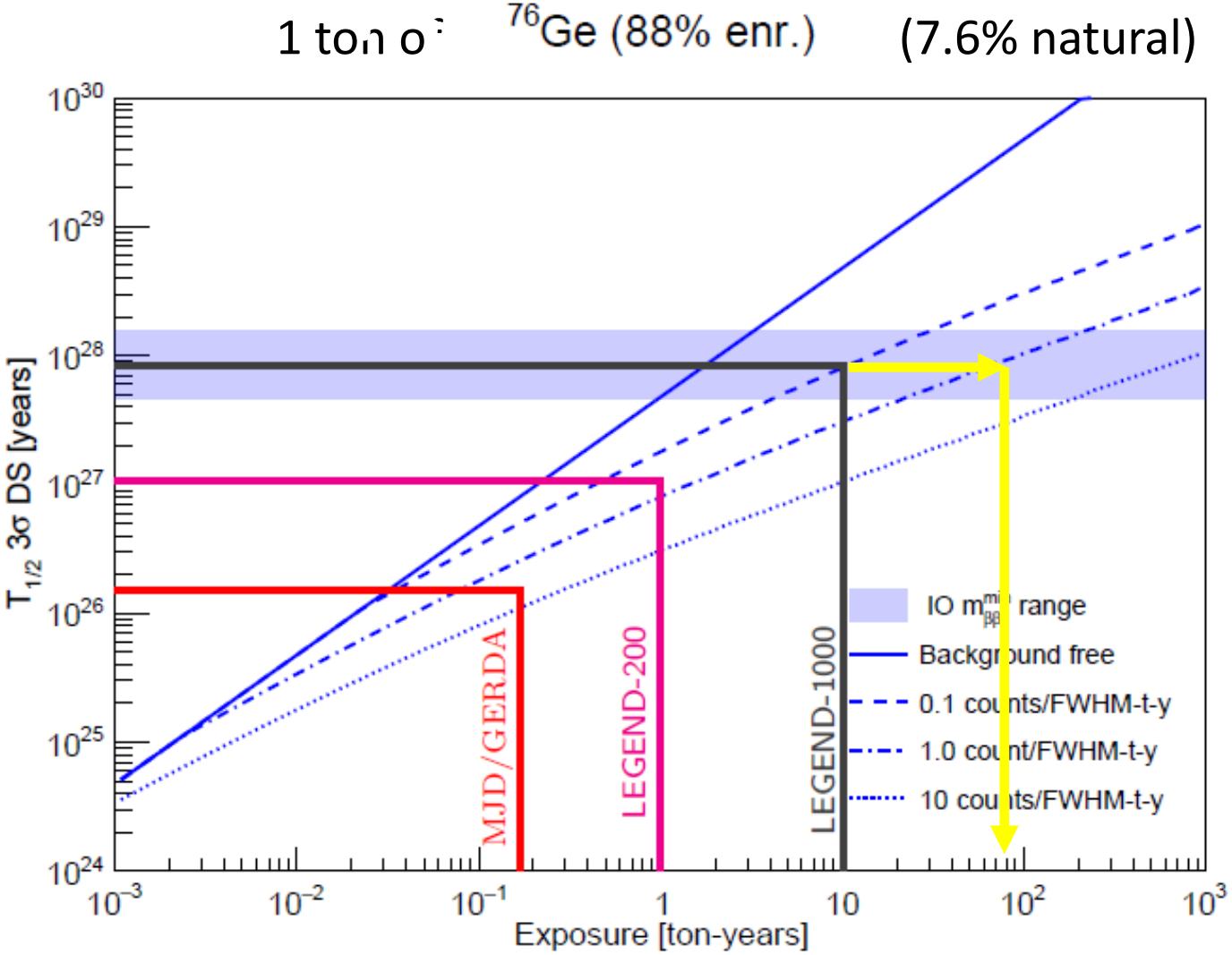
The sensitivity is proportional with exposure:

- The detector mass cannot increase indefinitely (costly: 100 Keuro/Kg)
- The data taking period must be reasonable

The background drives the sensitivity: an increase of a factor 10

0.1 c/t*y → **1 c/t*y**

Means to increase from 10 to almost 100 years exposure for 1 ton!

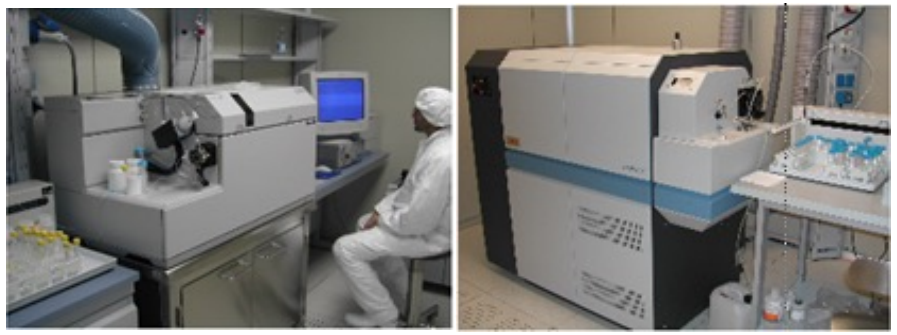


Ultra-low level radioactivity measurement facilities

STELLA (SubTErranean Low Level Assay)

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

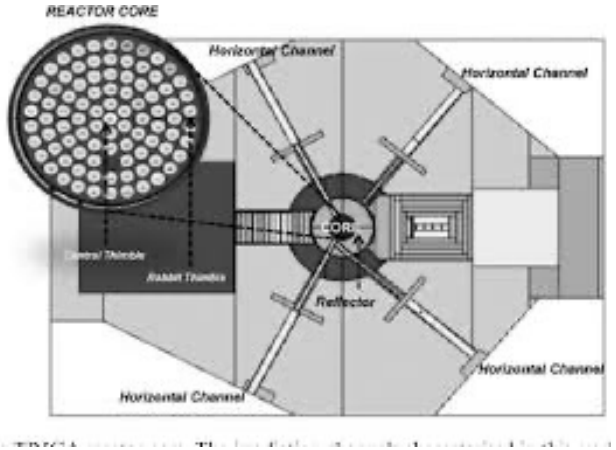
ICP-Mass Spectrometry



- **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

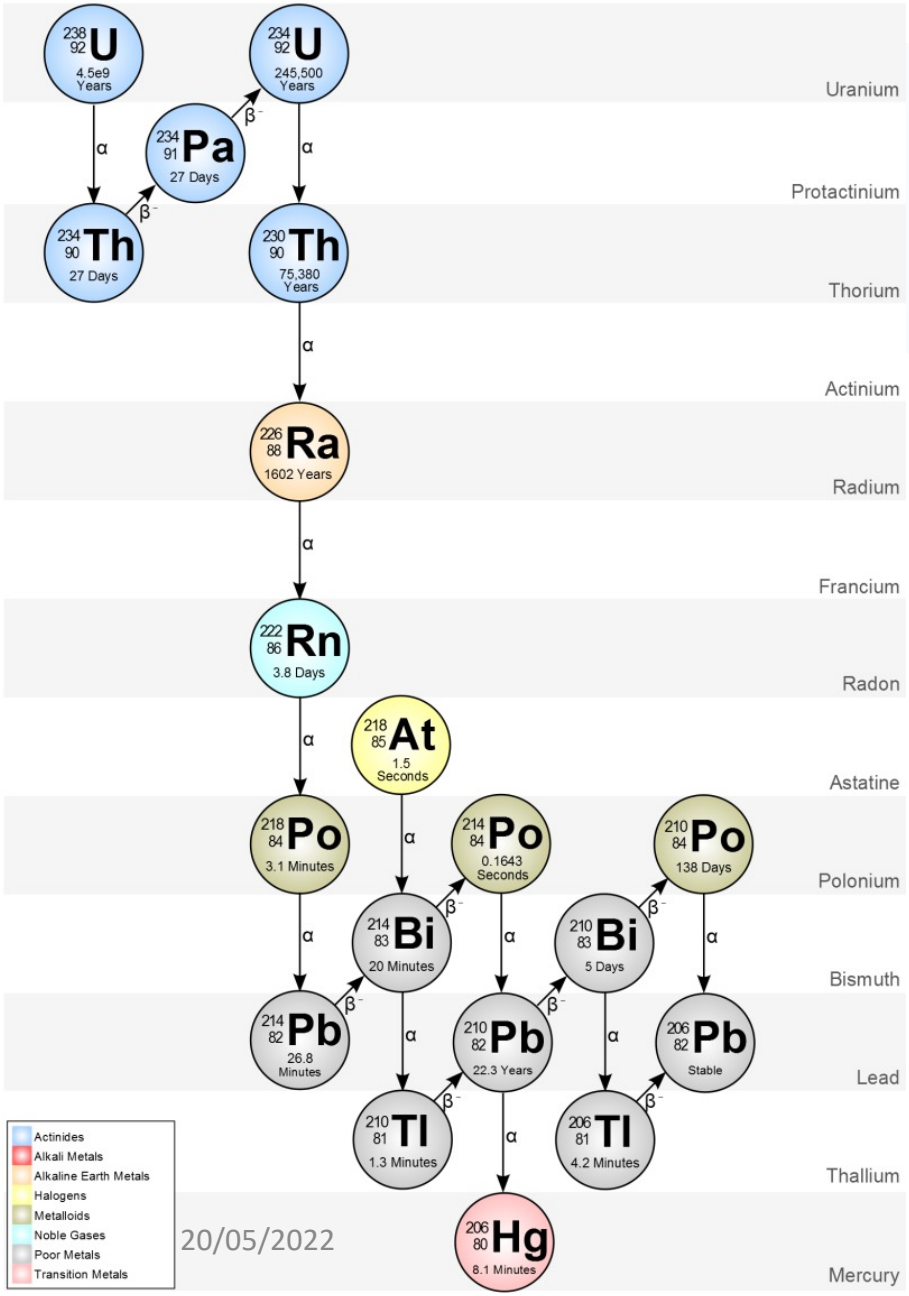
Mass spectrometry measures the concentration of radionuclides (number nuclides/mass)

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 a decay chain is in **secular equilibrium**

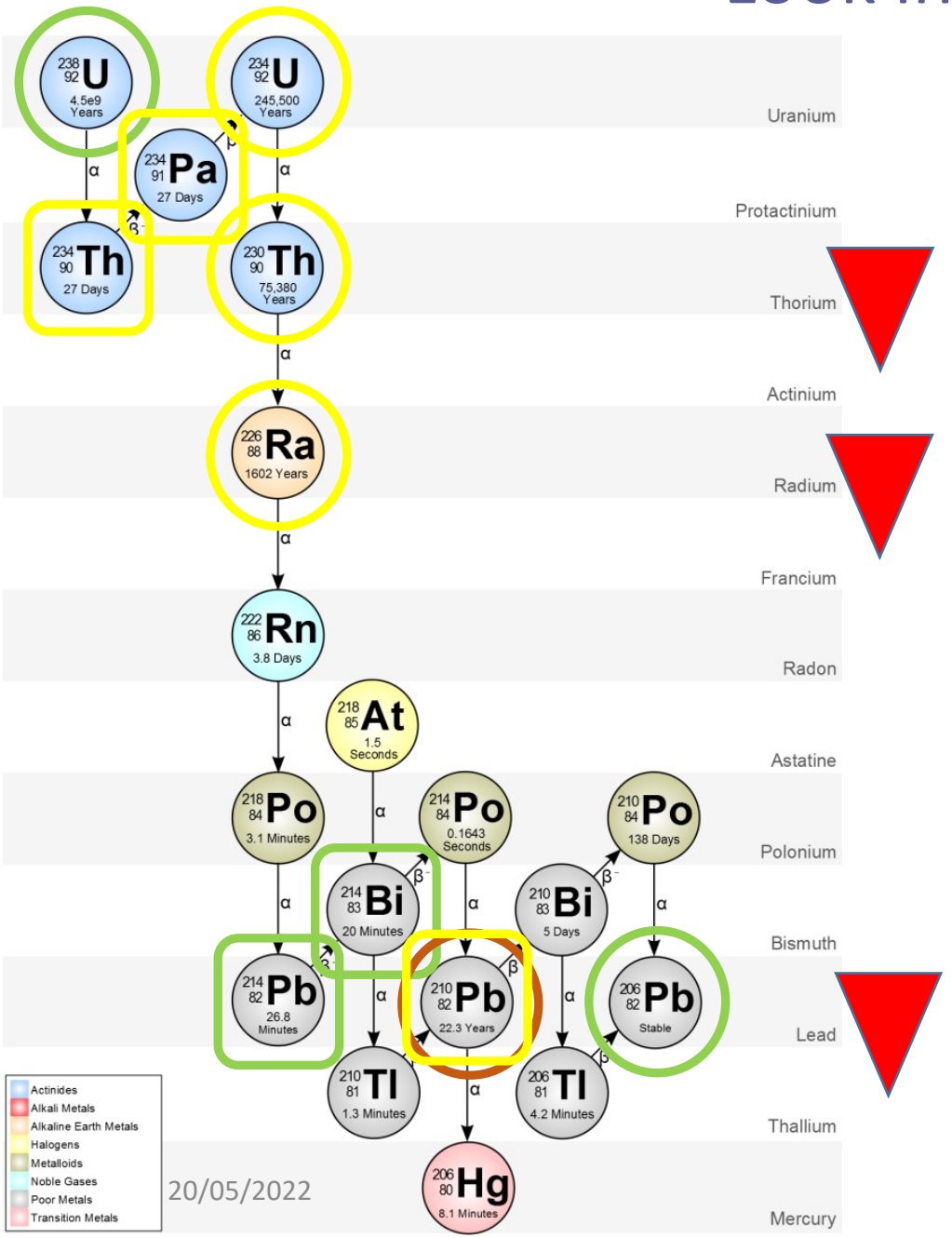
the number of atoms that decays for each nuclide per unit time is the same.

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

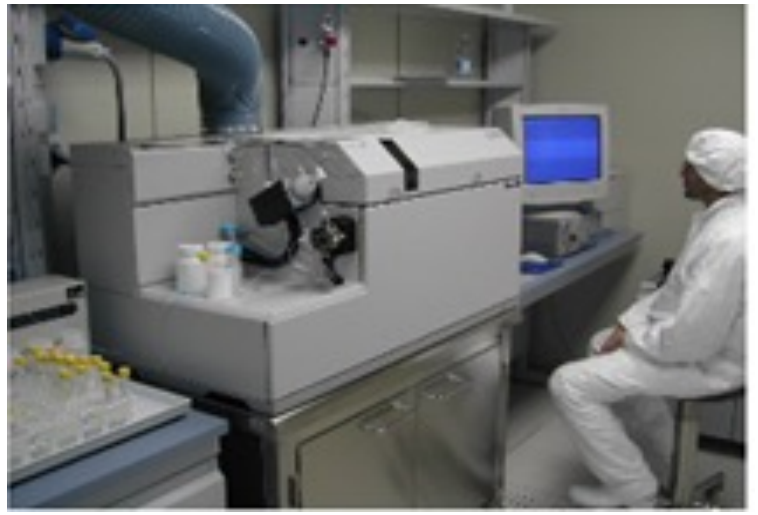
their concentrations are inversely proportional to $T_{1/2}$

Radiometric techniques and mass spectrometry are intrinsically complementary

Look inside the decay chains



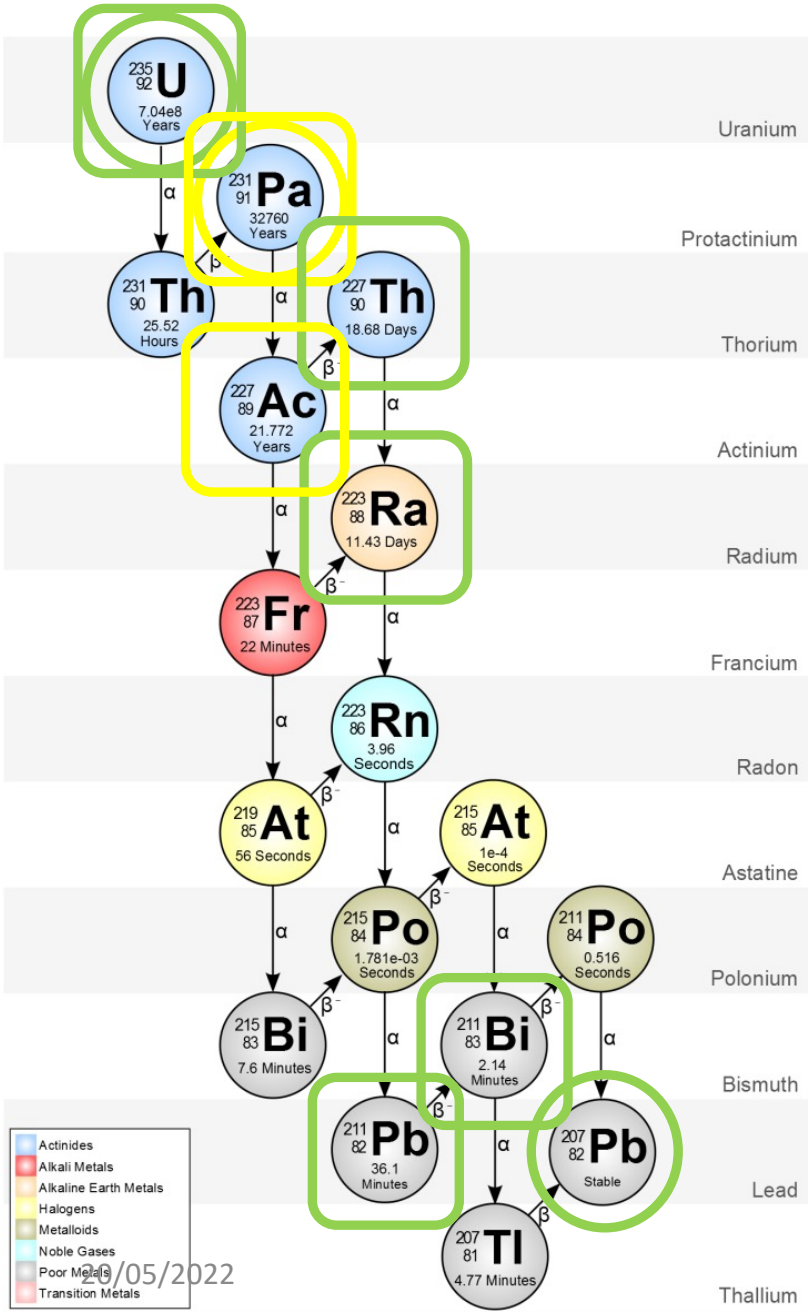
ICP-MS



Chemical & physical behaviour different for the nuclides

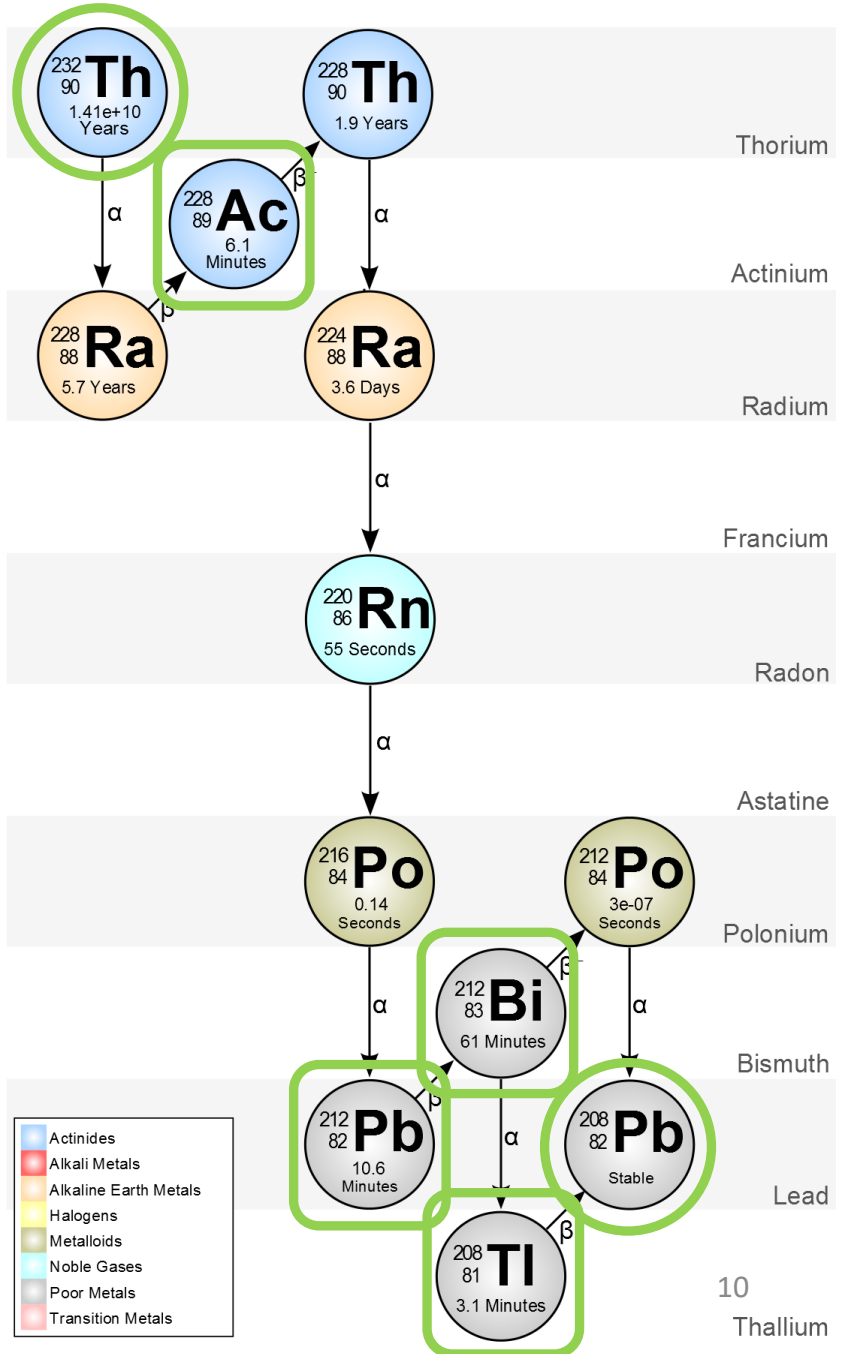
γ-ray Spectrometry

Others natural decay chains



ICP-MS

γ-Ray Spectrometry



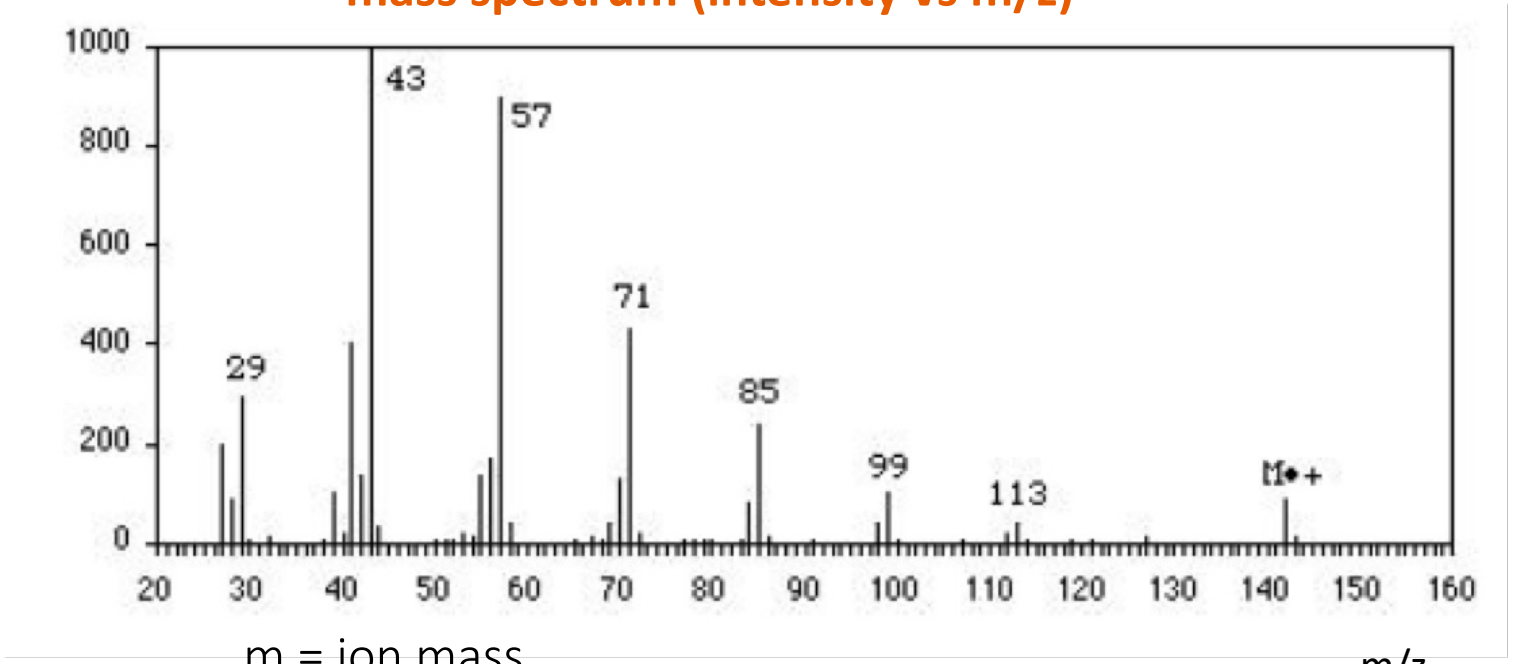
What is the mass spectrometry?

- 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)

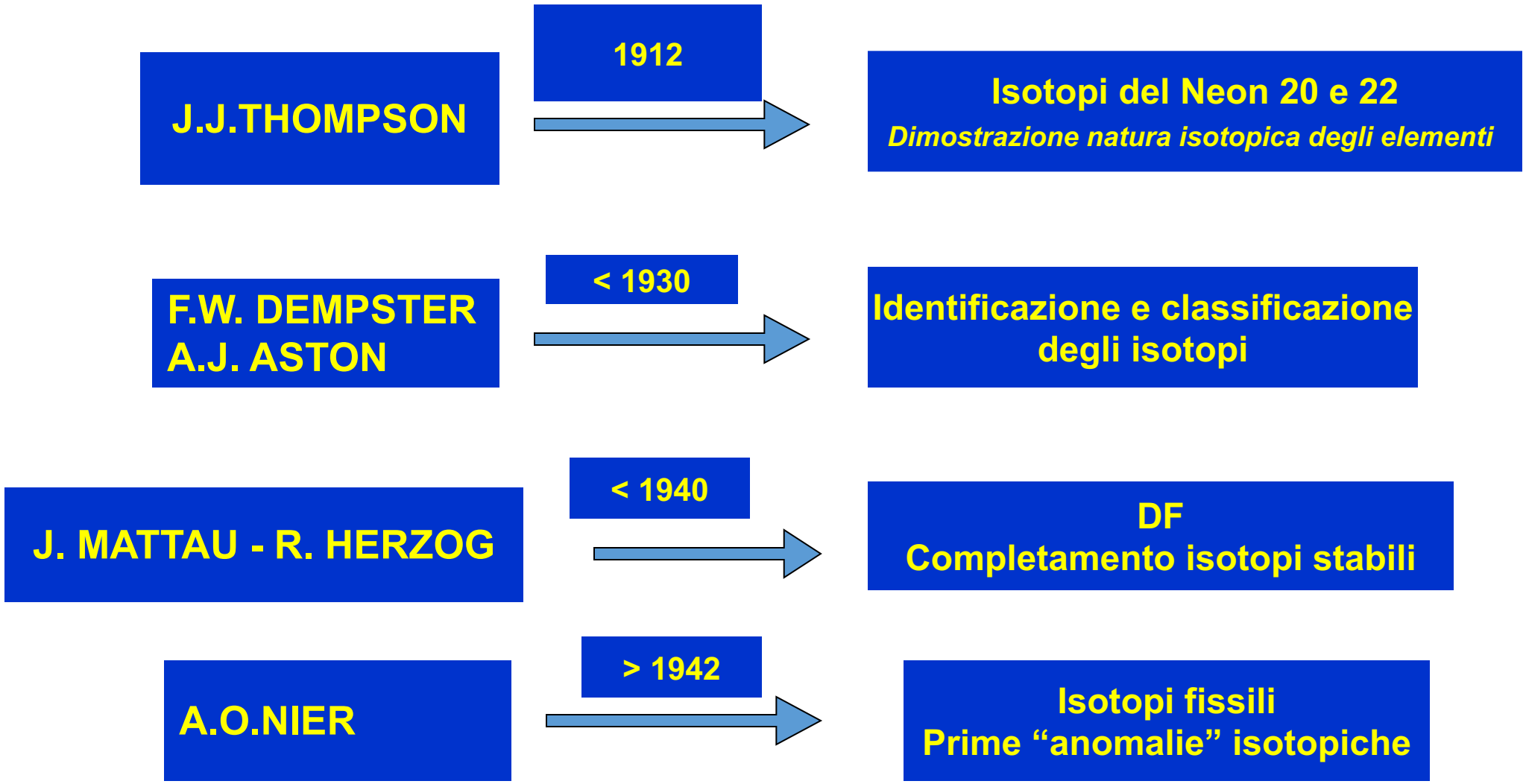


m = ion mass

z = ion charge

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

RIFERIMENTI STORICI



RIFERIMENTI STORICI

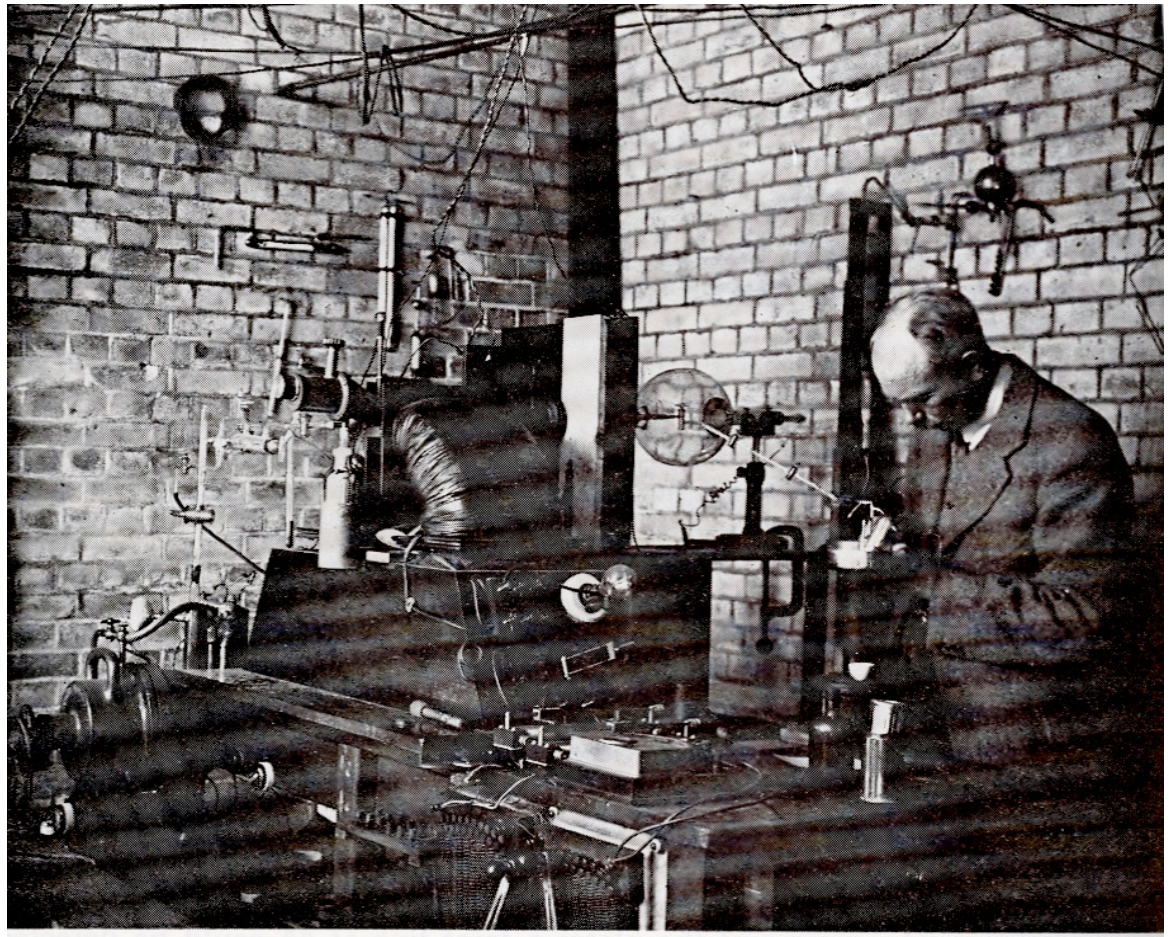
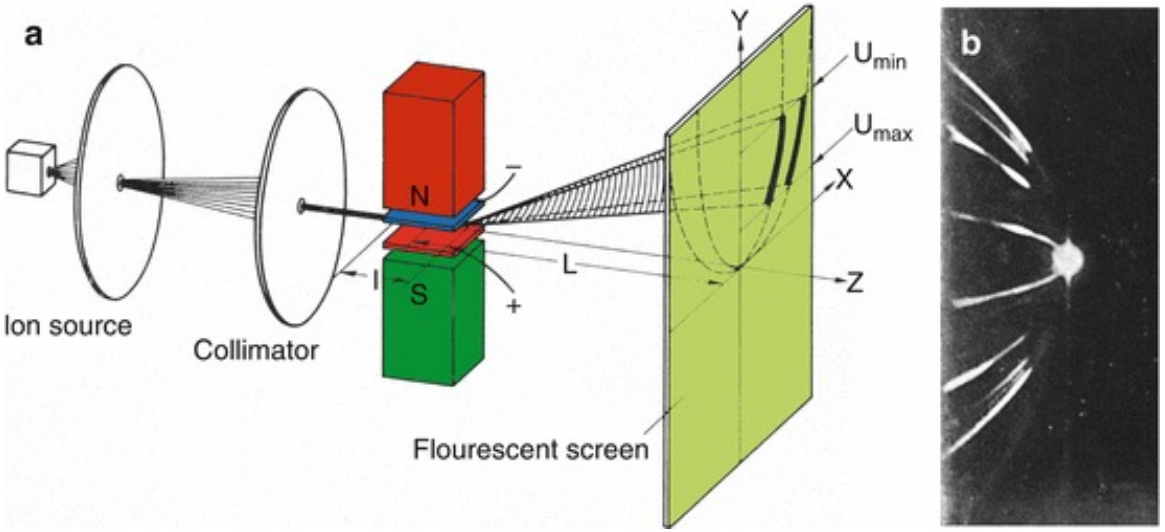
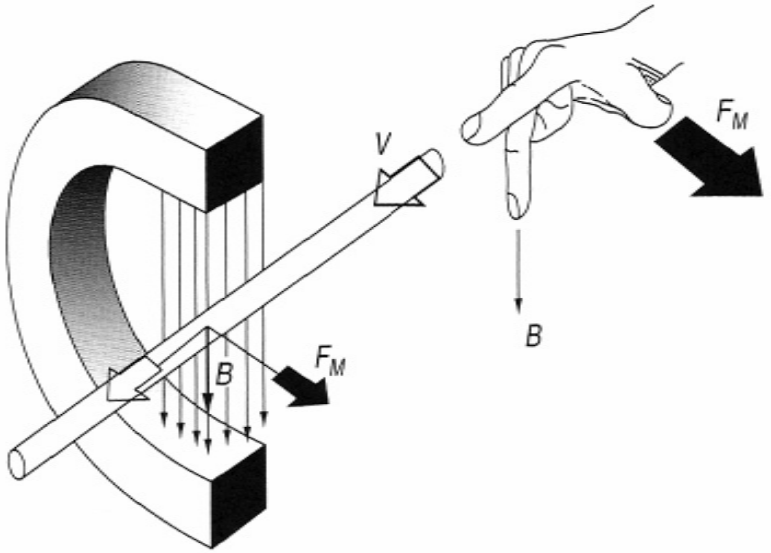


Plate 1. F. W. Aston with second mass spectrograph.



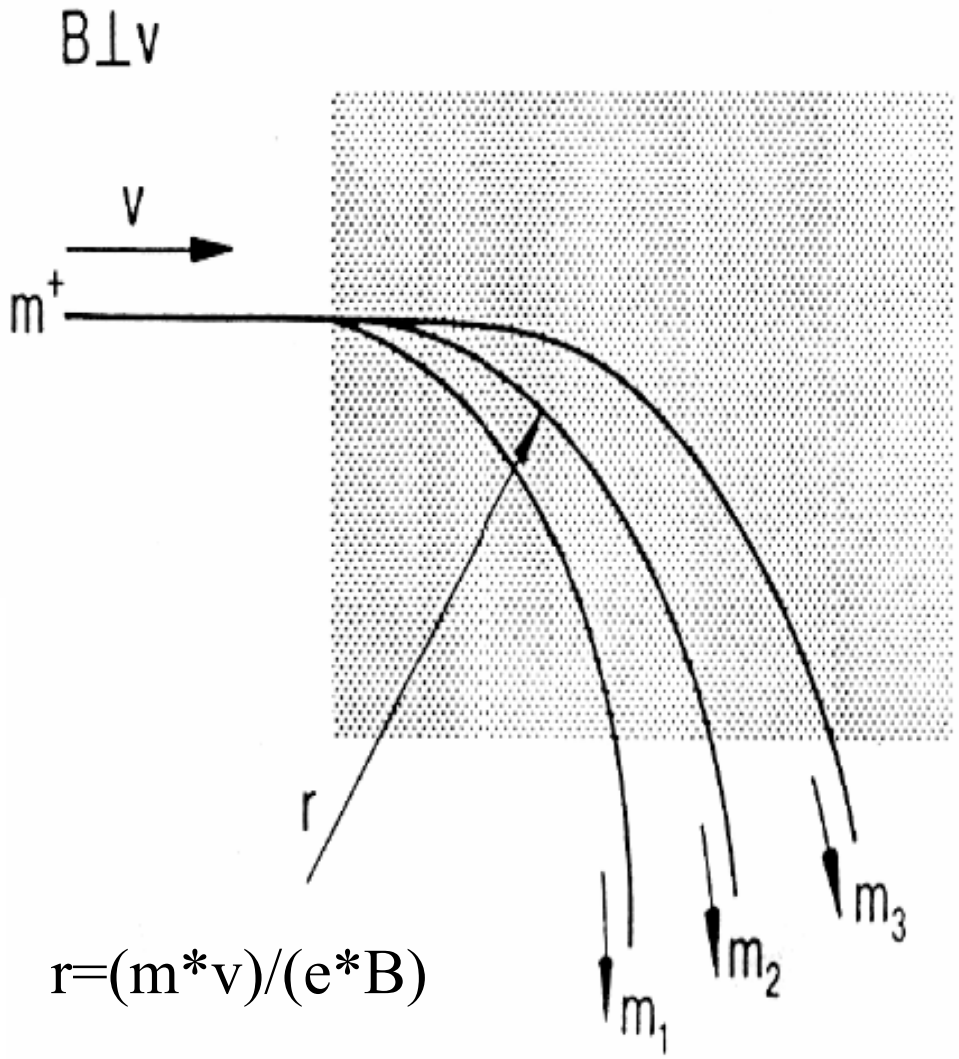
Ion source = discharge tube

Operating principle of magnet sector



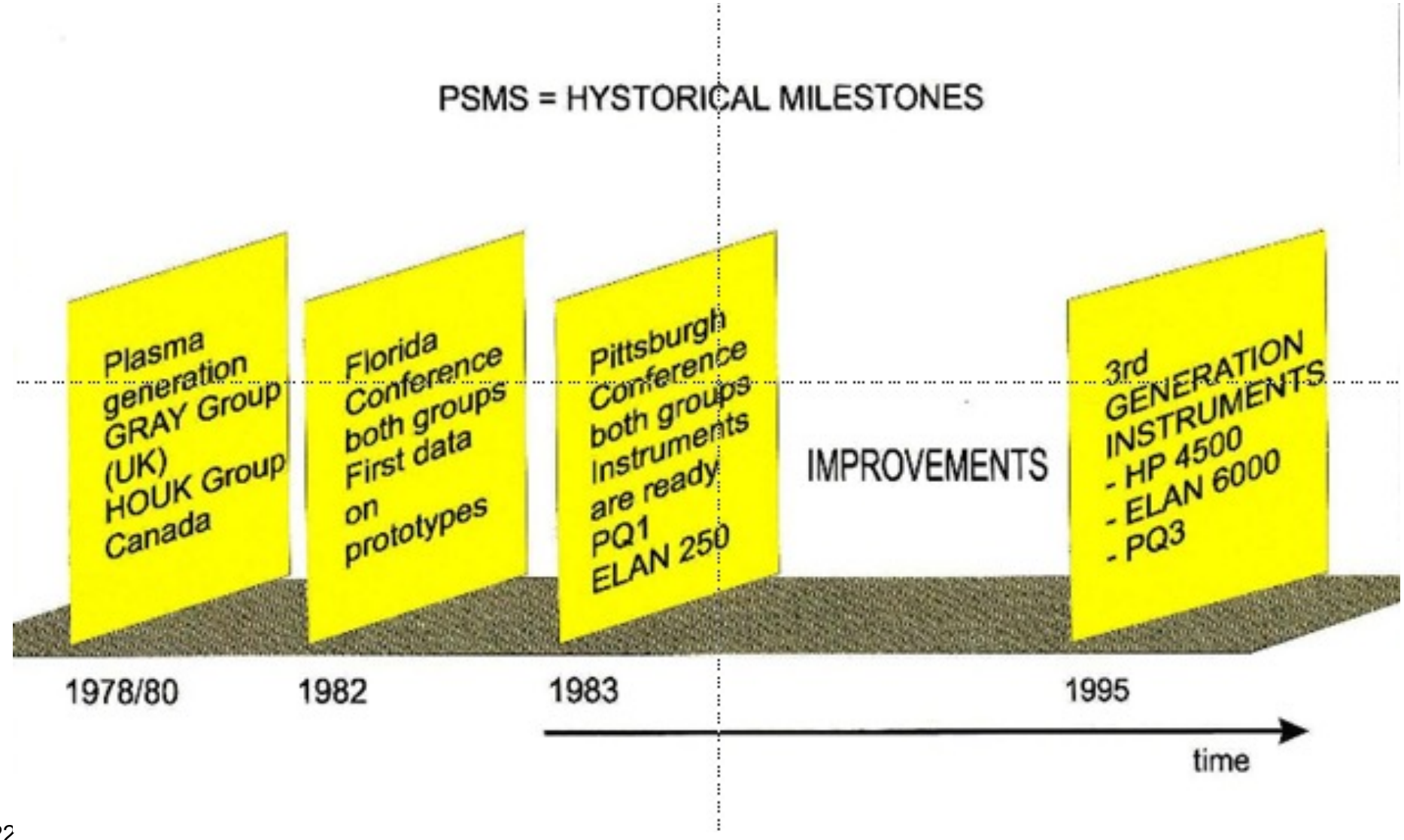
Lorentz force: $F_L = q(E + v \times B)$

Centrifugal force: $Fc = \frac{m \cdot v^2}{r}$

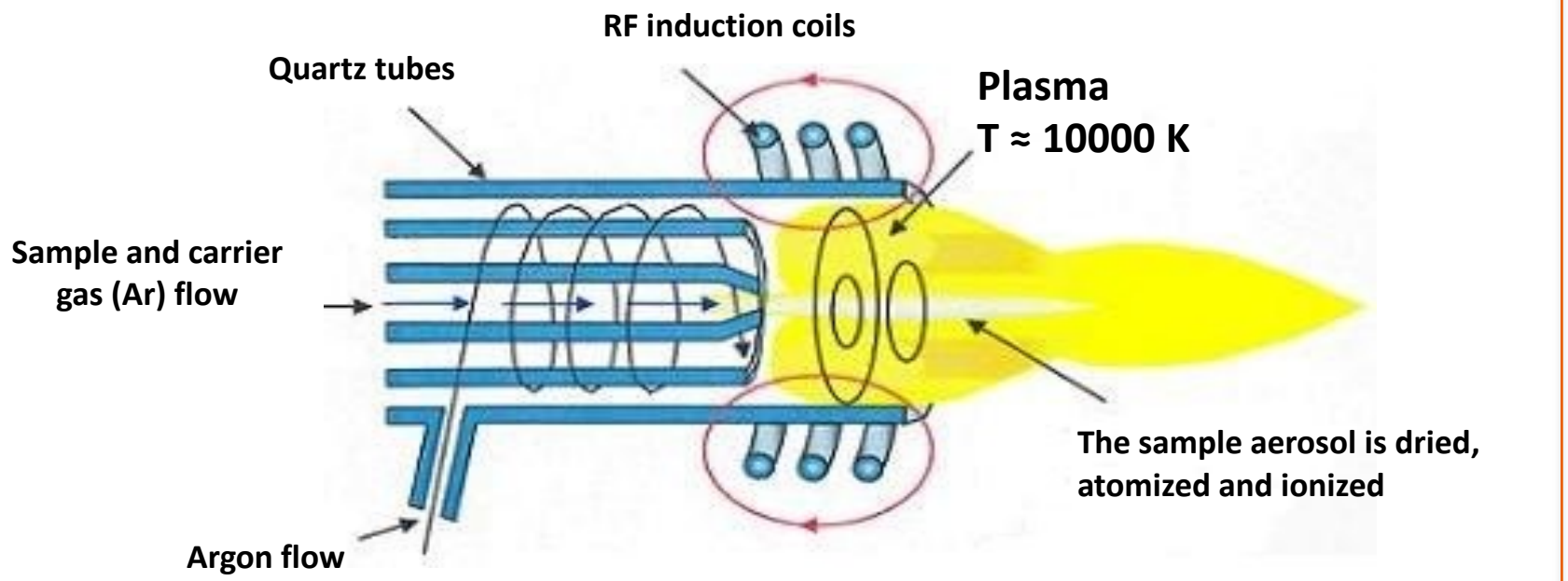


r=(m*v)/(e*B)

Plasma Source Mass Spectrometry: historical milestone

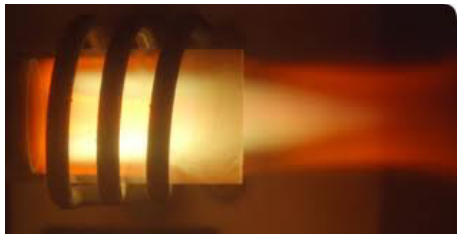


Inductively Coupled Plasma Mass Spectrometry

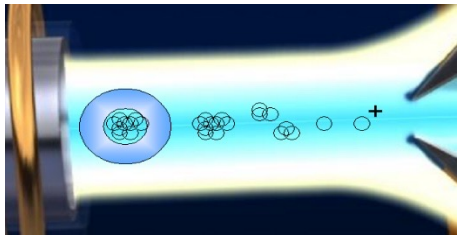


Plasma torch ion source

Plasma is capable to ionize almost all chemical elements

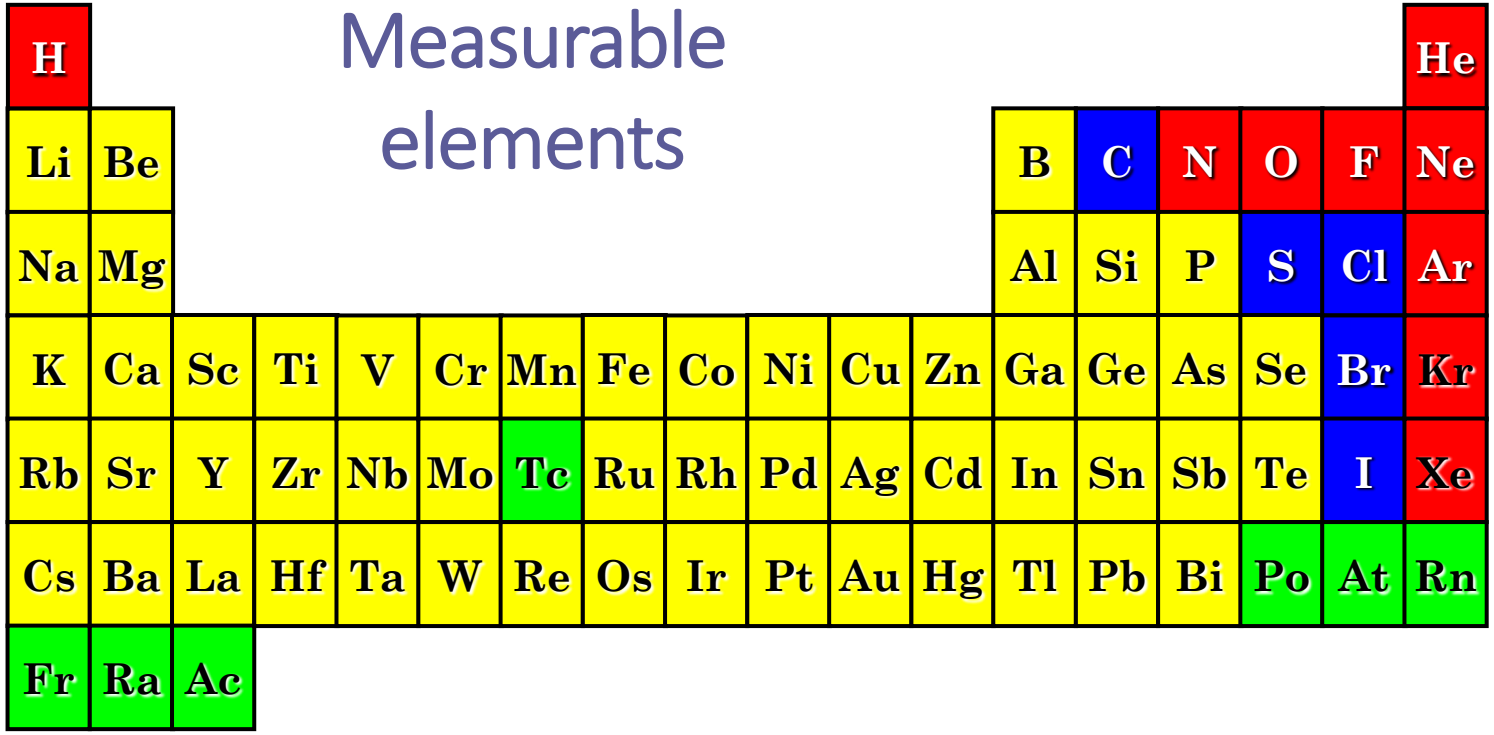


High energy!



Complete (almost):
- Desolvation
- Atomization
- Ionization

Measurable elements



AA / ICP / ICP-MS

ICP / ICP-MS

Radioactive

Not Measurable

Unstable Elements

Ultra - trace ... Trace ... majors...

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

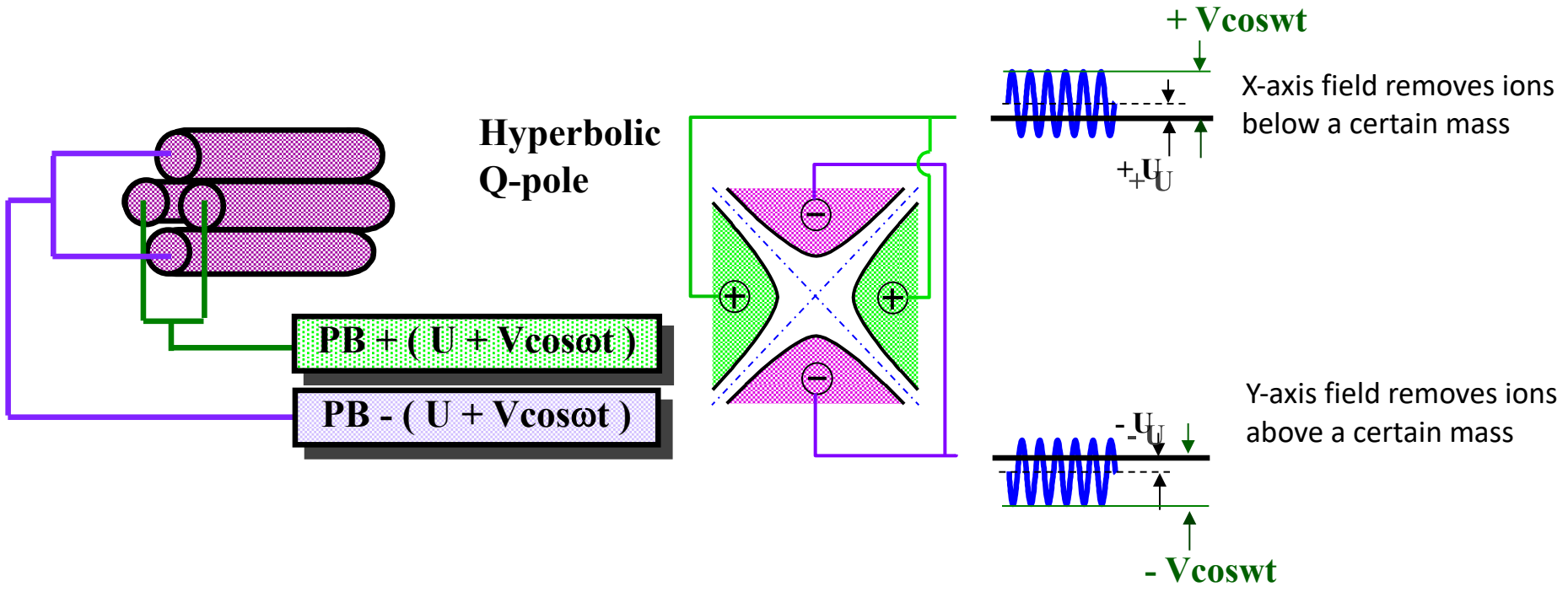
1ppt (10^{-12} g/g)

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

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

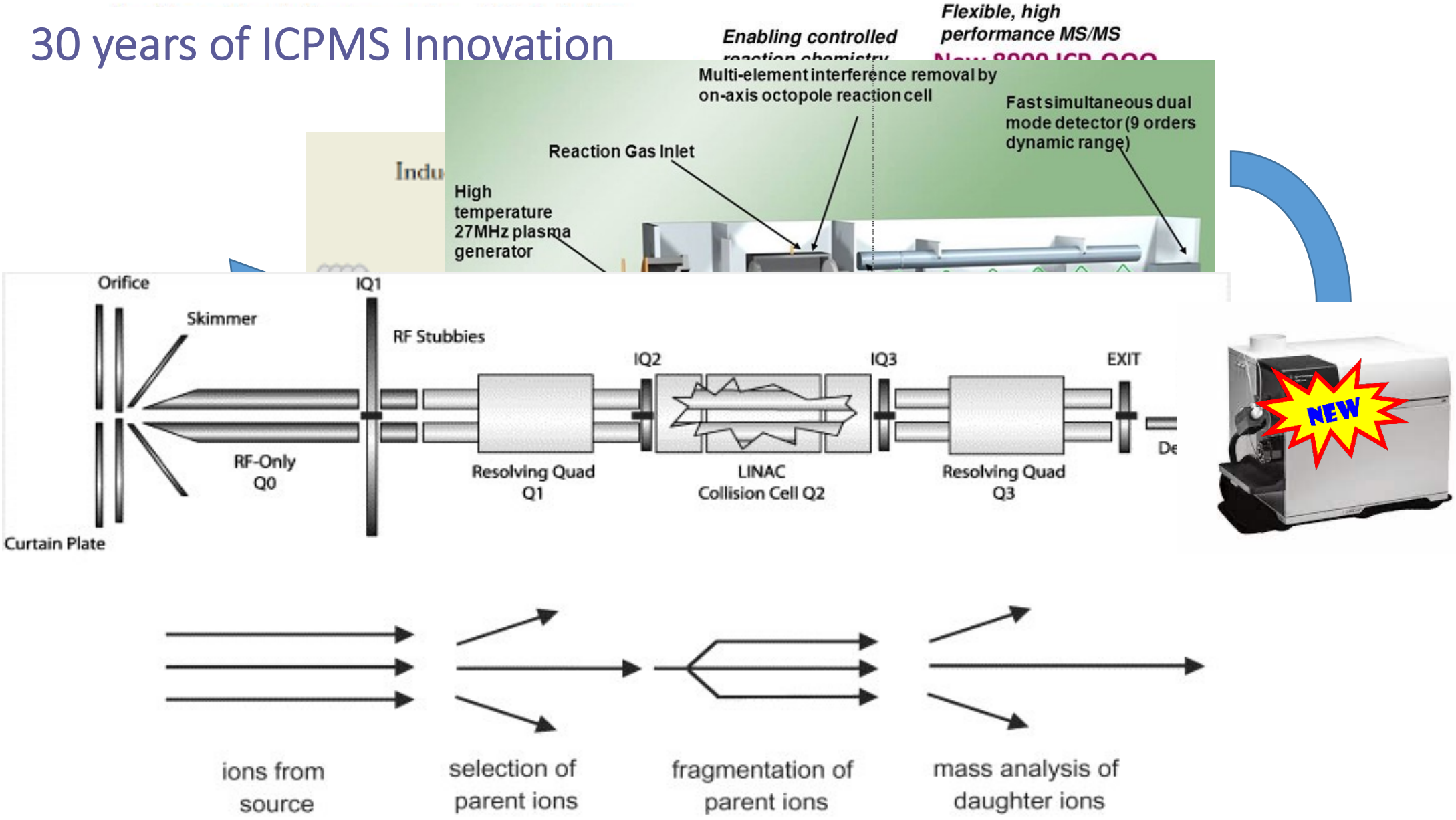
Quadrupole Theory

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



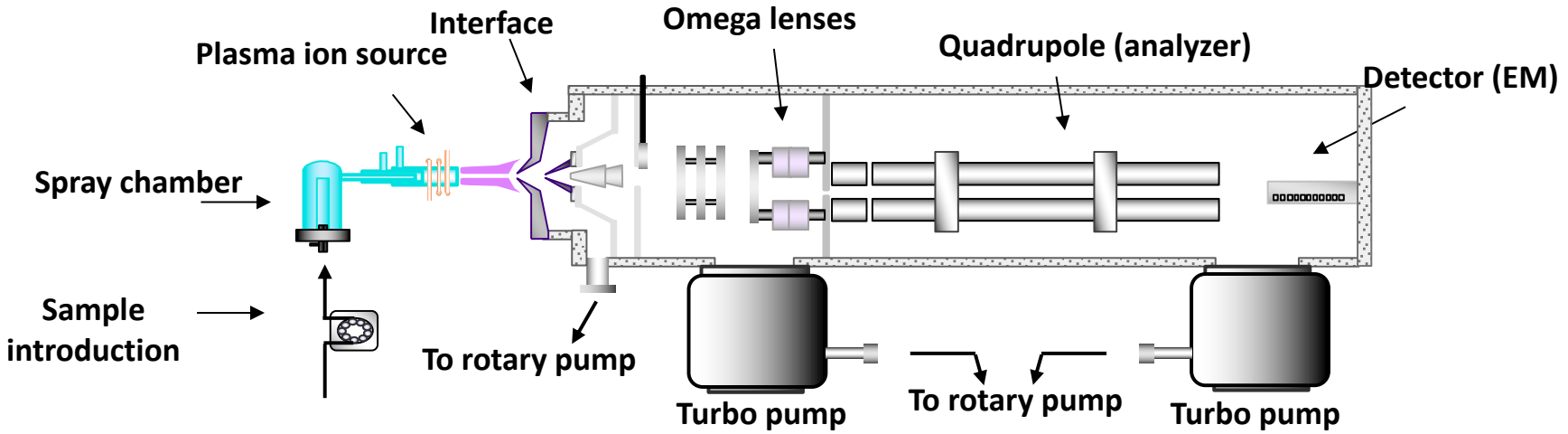
For a given combination of RF and DC voltages, the quadrupole only lets ions of a **specific mass** pass through to the detector. (In fact, quadrupole filter works on mass/charge ratio, not mass)

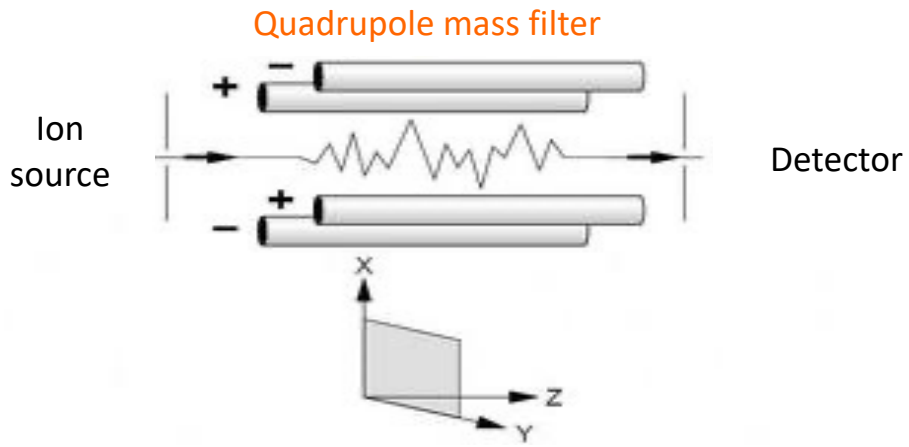
30 years of ICPMS Innovation

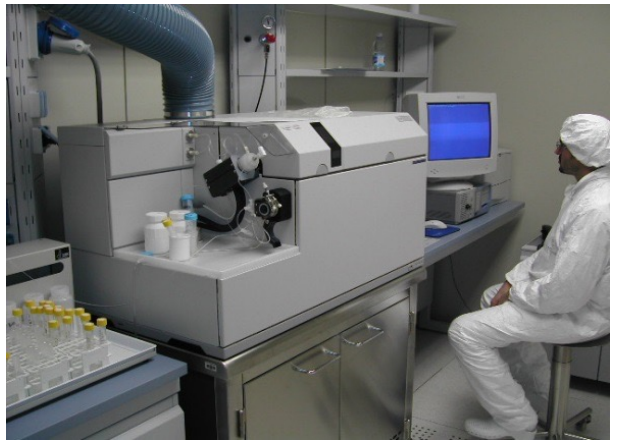


Two ICP mass spectrometers @ LNGS

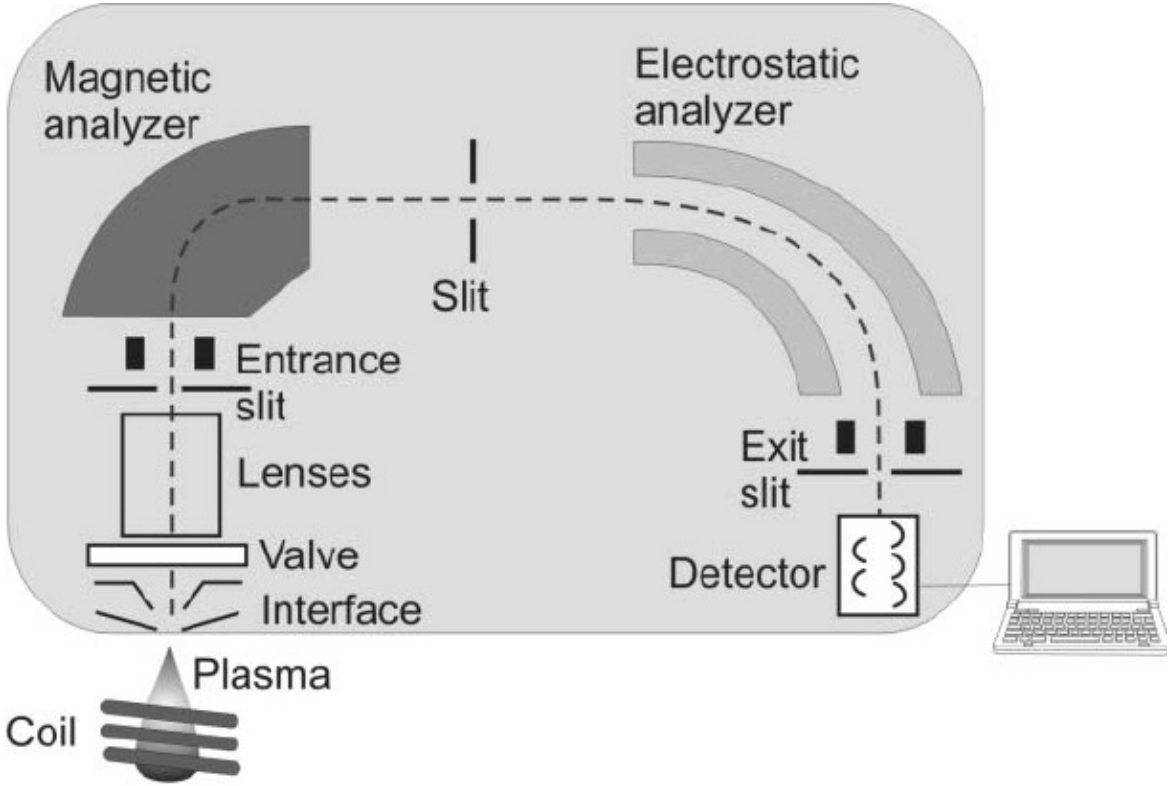
ICP QMS (quadrupole mass analyzer) – Agilent 7850

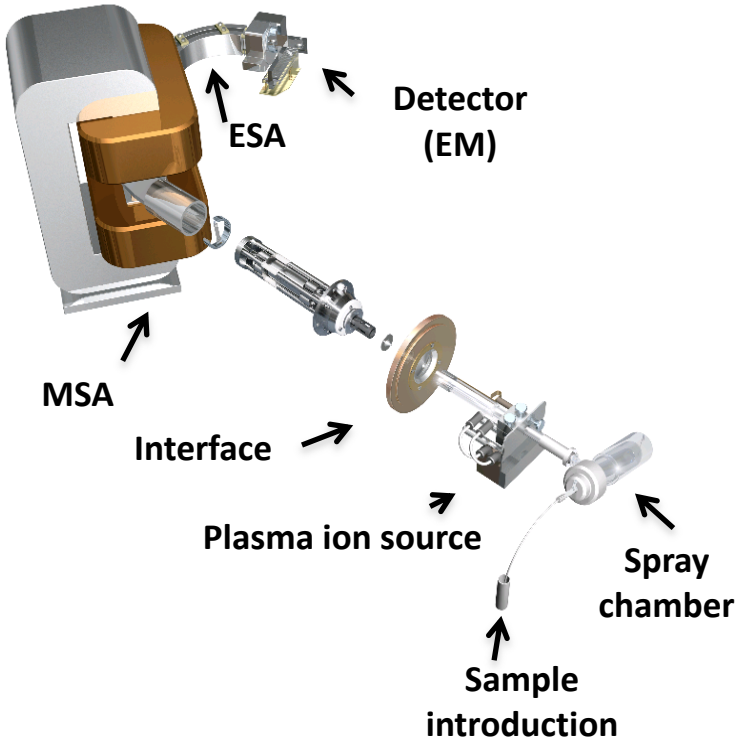






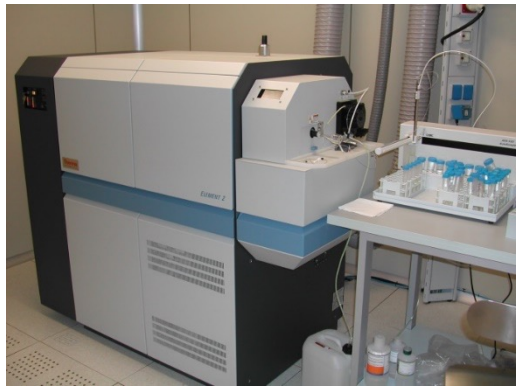
Sector Field ICP Mass Spectrometer





Reverse Nier-Johnson geometry

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

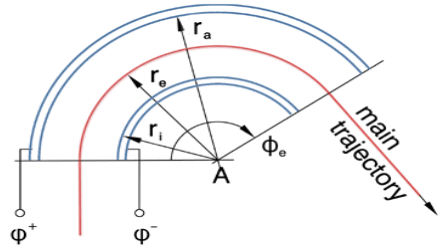


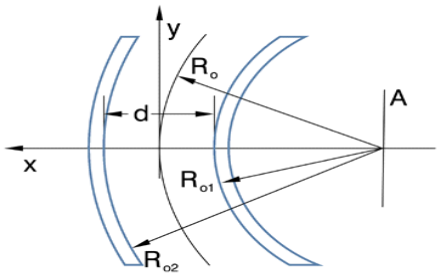
Electrostatic Sector

$$E_{kin} = q \cdot U_0$$

$$r_e = \frac{2 \cdot E_{kin}}{q \cdot E} \qquad E_{kin} = \frac{r_e \cdot E \cdot q}{2}$$

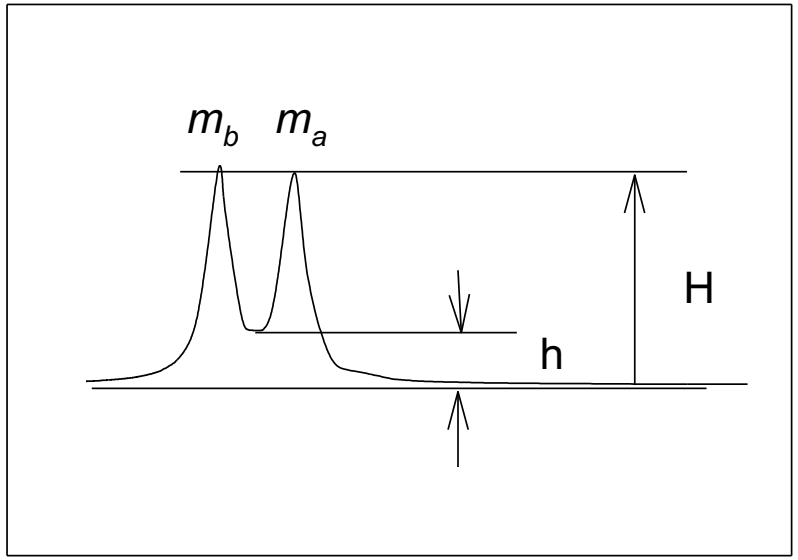
$$dE_{kin} = \frac{E \cdot q}{2} \cdot dr_e$$





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

Mass resolution power

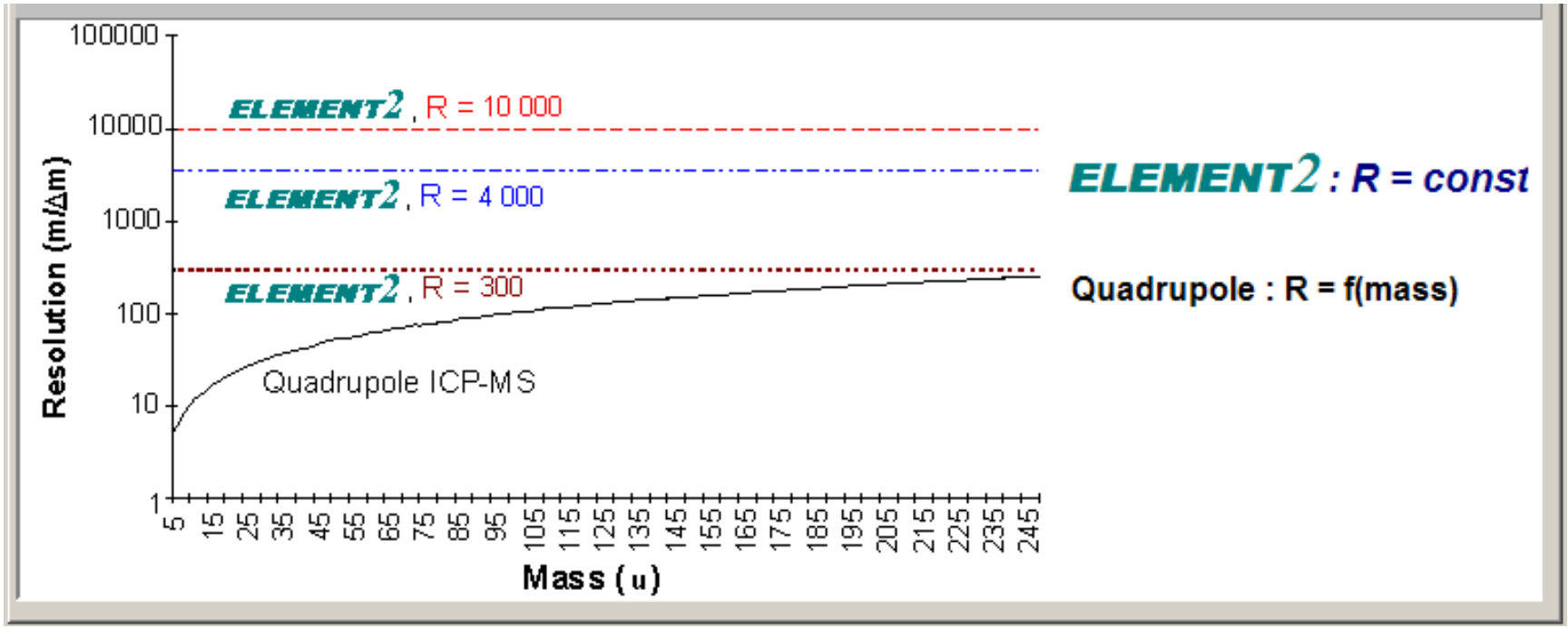


When two adjacent peaks m_a and m_b with comparable intensitiy and

h<10%H

the resolution is defined as the ratio:

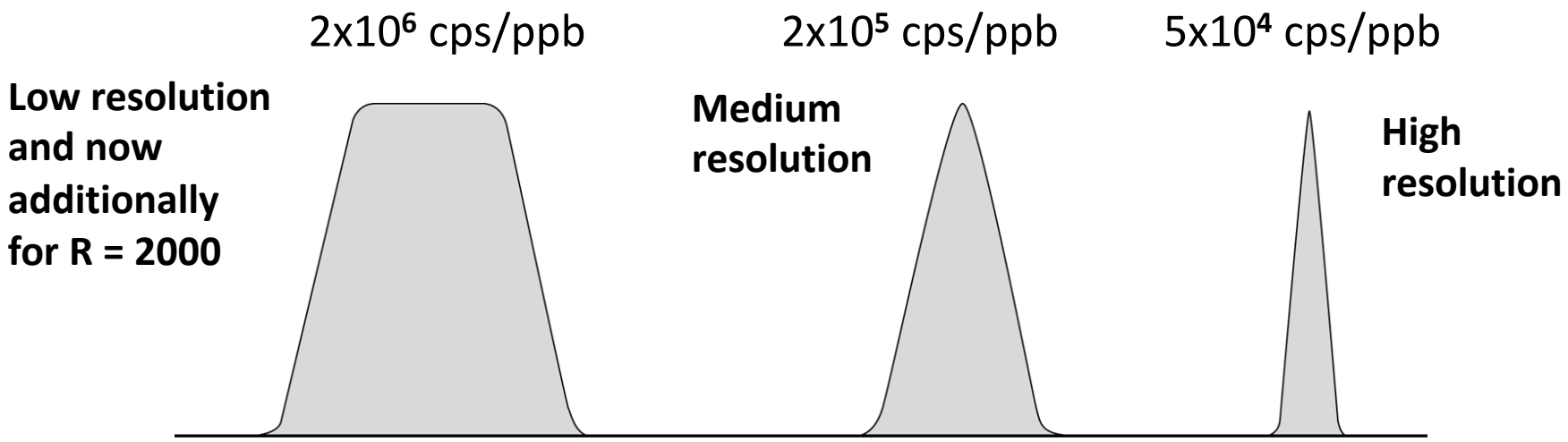
$$R = m / (m_a - m_b)$$

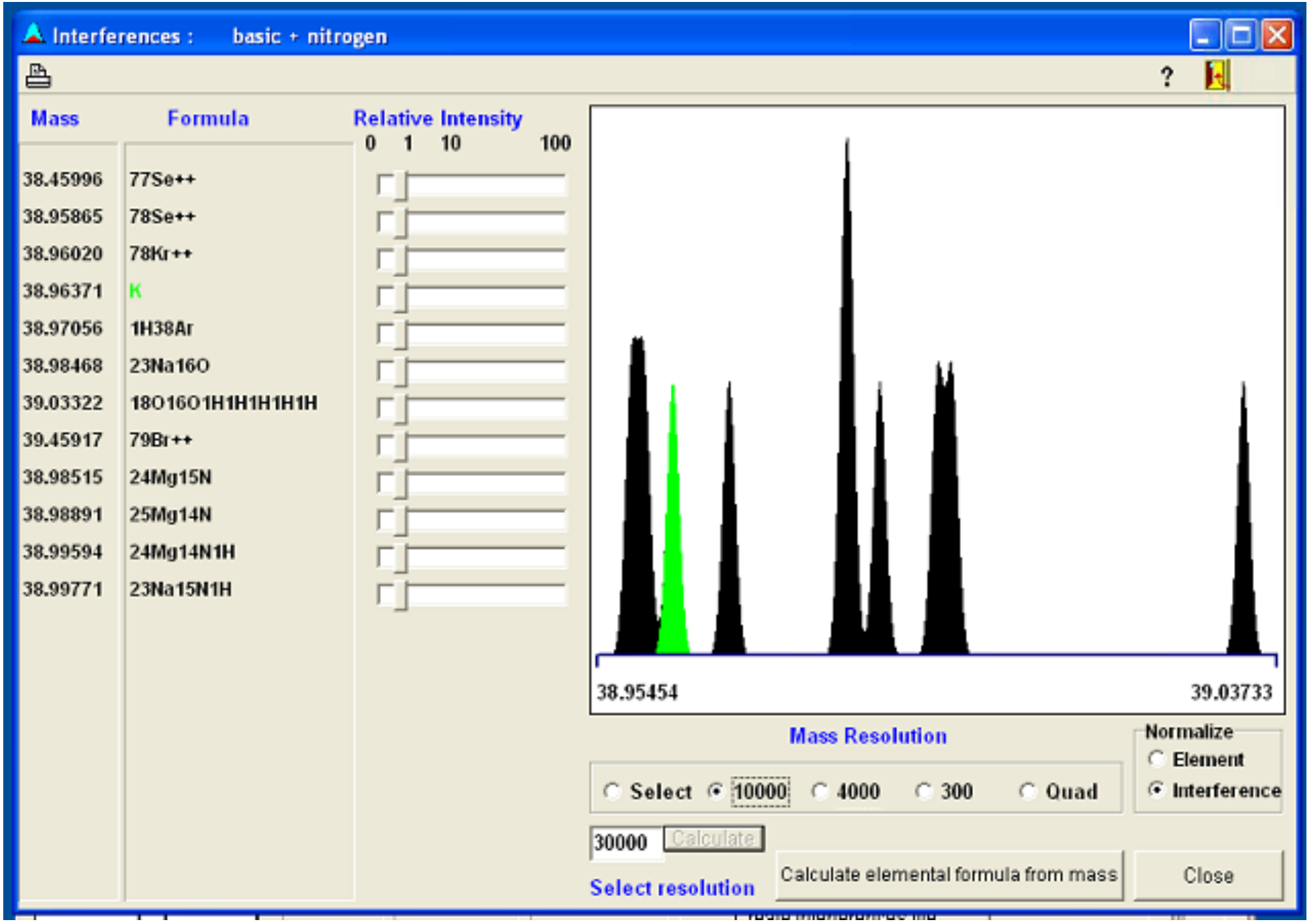


Low-Medium-High Resolution: peak shape

- 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




Interferences : basic + nitrogen
Mass
Formula
Relative Intensity
0 1 10 100
38.45996 77Se++
38.95865 78Se++
38.96020 78Kr++
38.96371 K
38.97056 1H38Ar
38.98468 23Na16O
39.03322 18O16O1H1H1H1H1H
39.45917 79Br++
38.98515 24Mg15N
38.98891 25Mg14N
38.99594 24Mg14N1H
38.99771 23Na15N1H
38.95454
39.03733
Mass Resolution
Select
10000
4000
300
Quad
Normalize
Element
Interference
30000
Calculate
Select resolution
Calculate elemental formula from mass
Close

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**

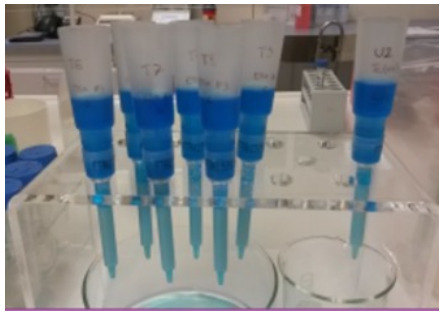
- **Background** (instrumental and method)

- 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”

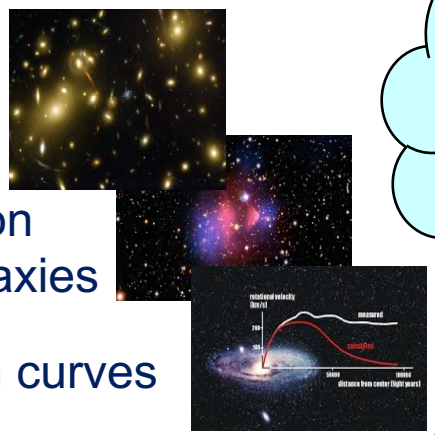
Measurement of K in NaI crystal for Dark Matter

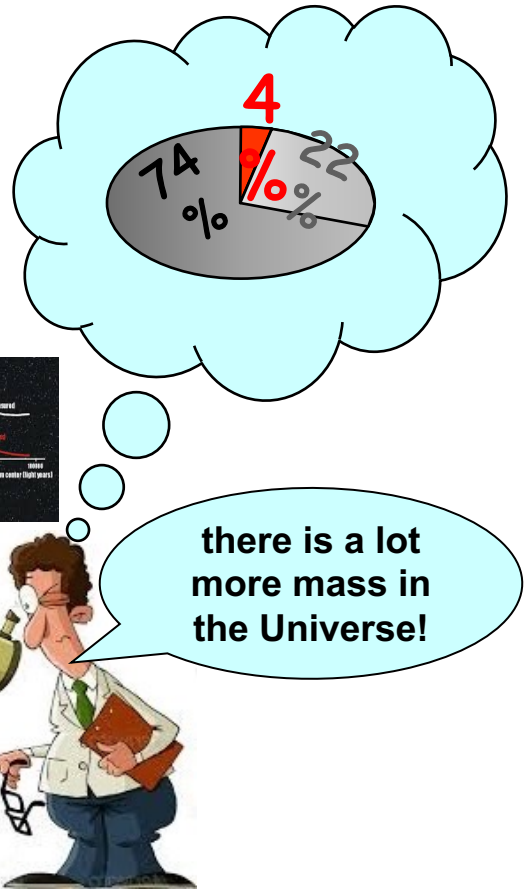
Observational evidence

Gravitational lensing

Gravitational effect on observed speed of galaxies

Galaxy rotation curves





?

Dark matter = Subatomic particles → **WIMPs are most popular candidates**

Many experiments aim to test this hypothesis

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)

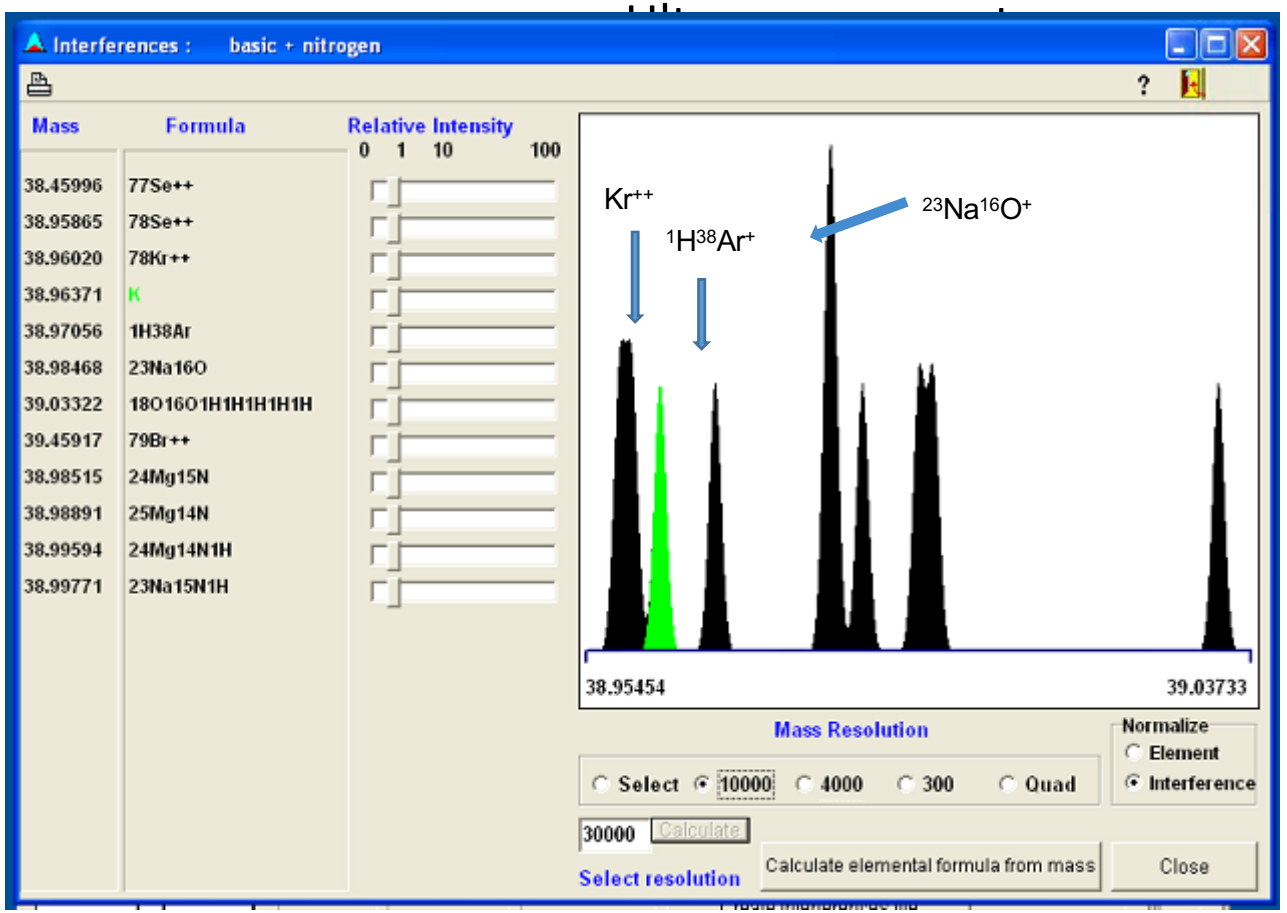
- Sensitivity reduction
- Matrix effect (St. Add.method)

Contamination risk

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	

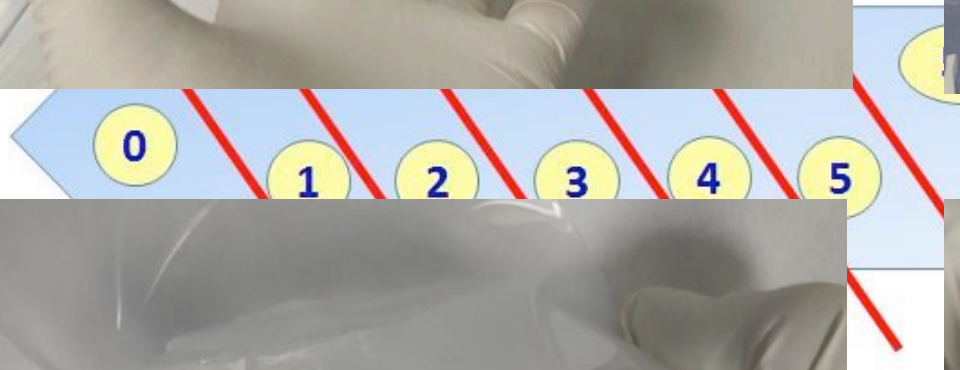
	Mass (amu)	Resolution
$^{78}Kr^{++}$	38.96020	11100
$^{39}K^{+}$	38.96371	
$^{1}H^{38}Ar^{+}$	38.97056	5690
$^{23}Na^{16}O^{+}$	38.98468	1860

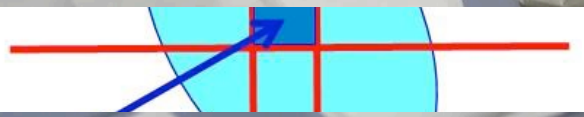


HR-ICP-MS: Hot plasma vs cool plasma

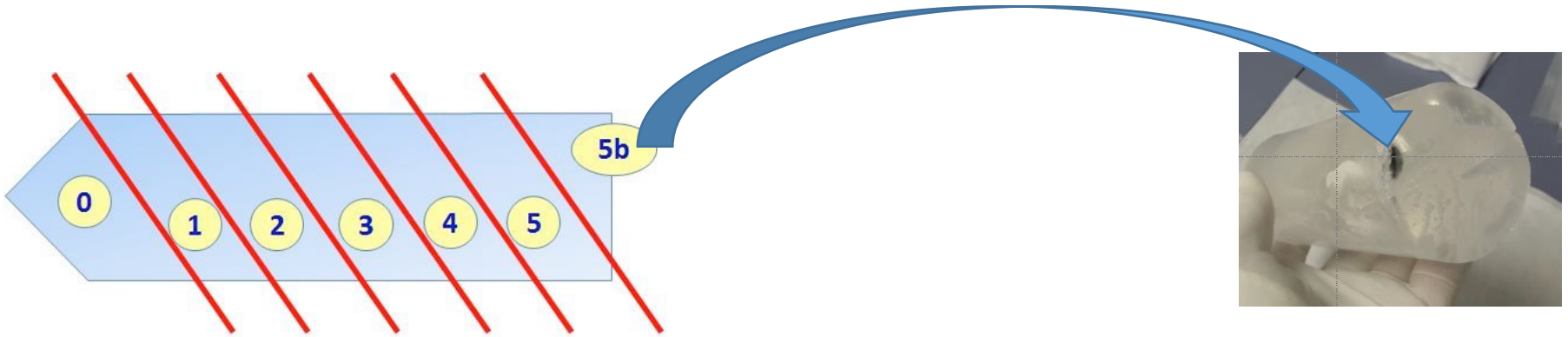
	Hot plasma	Cool Plasma
RF Power [w]	1282	583
Resolution [m/Δm]	10000	10000
Sample per peak [n]	30	30
Integration window [%]	40	40
K Sensitivity [cps/ppb] Pure water	6000	3000
K sensitivity [cps/ppb] matrix (1% of NaI)	3000	300
Background [cps]	100	10
Detection Limit [ng K/g NaI]	3	5

Crystal sampling procedure





Study of the impurity distribution



Sample	0 NOSE	1	2	3	4	5 TAIL	5B
K ppb	**230**	**320**	**360**	**340**	**350**	**1415**	**------**
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
K ppb	**10.2**	**11.5**	**11.2**	**11.6**	**11.6**	**13.3**	**-----**

Cry **ST Powder**
Hot plasma

Cry N1 **UP Powder**
Hot plasma

Cry N2 **UP Powder**
Cool plasma

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

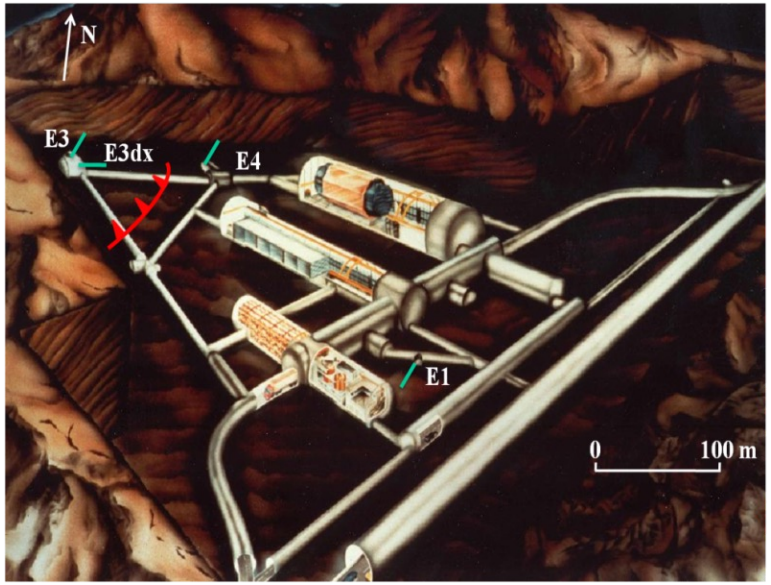
Without matrix separation the DLs achieved in different labs using several instrumentation are at ppb level

Environmental Radioactivity Monitoring for Earth Sciences carried out at LNGS

In the framework of ERMES thousands 1-L groundwater samples have been weekly collected since 2008 at ten different sites located in the underground laboratory (Plastino et al. 2010; Plastino et al. 2011; Ciarletti et al. 2015)

One target of the project was the study of ^{226}Ra time series

- Small amount of sample available
- High number of samples
- High sensitivity needed
- High precision requested



We proposed to optimize a method for ICP-MS ^{226}Ra measurement

ICP-MS ^{226}Ra measurement

- **Low concentration of ^{226}Ra in water**

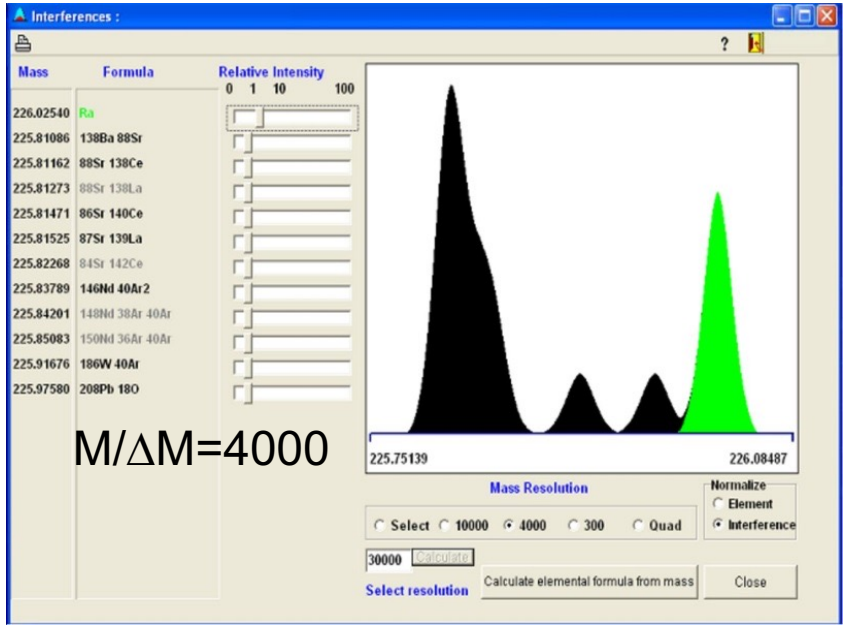
expected radium concentrations are in the range 0.1-1 ppq (<36mBq/Kg)

- Sample preconcentration
- APEX-Q system
- Acquisition Method

- **Spectral interference**

due to polyatomic species (Epov et al 2003)

	Mass (amu)	Resolution
$^{88}Sr^{138}Ba$	225.8106	1050
$^{86}Sr^{140}Ce$	225.8147	1070
$^{87}Sr^{139}La$	225.8152	1075
$^{40}Ar^{40}Ar^{146}Nd$	225.8379	1200
^{226}Ra	226.0254	



- **Matrix effect**

high concentration of some elements (Ca,Mg, Na) affects the instrumental response

- chemical separation
- Internal calibration

^{226}Ra: sample treatment optimization

(Lariviere et al. 2005, Copia et al. 2015)

- AG-50W-X8
- Sr*resin

Procedure steps:

1.Pre-wash and conditioning

2.Sample load

3.Wash: HCl

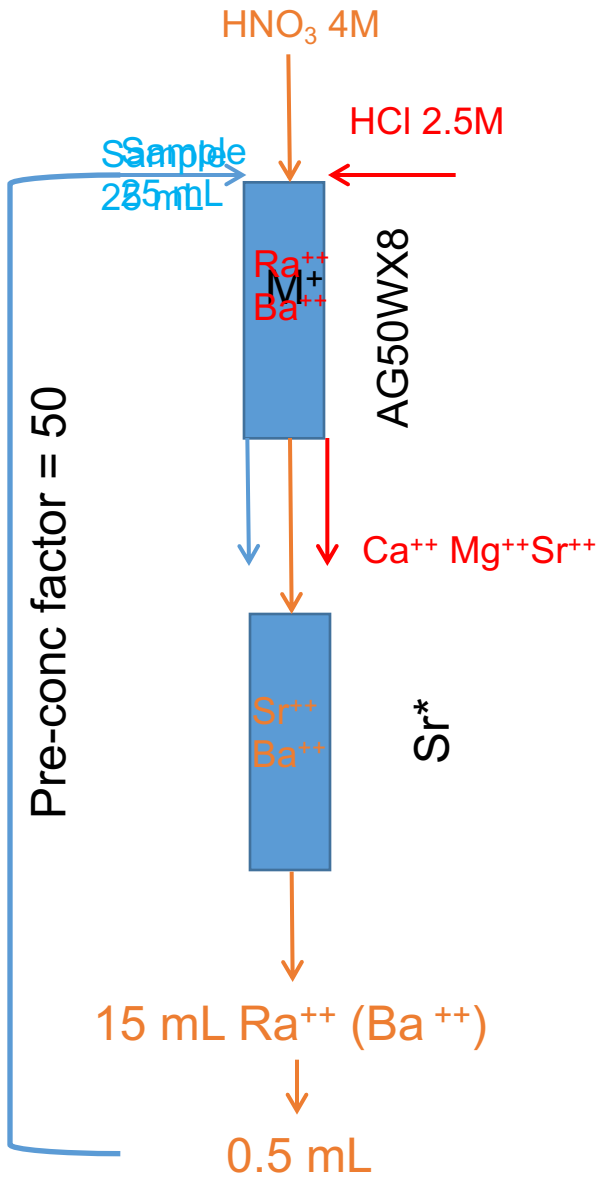
4.Ra elution: HNO_3

Sample load

Series connection

5.Rinse

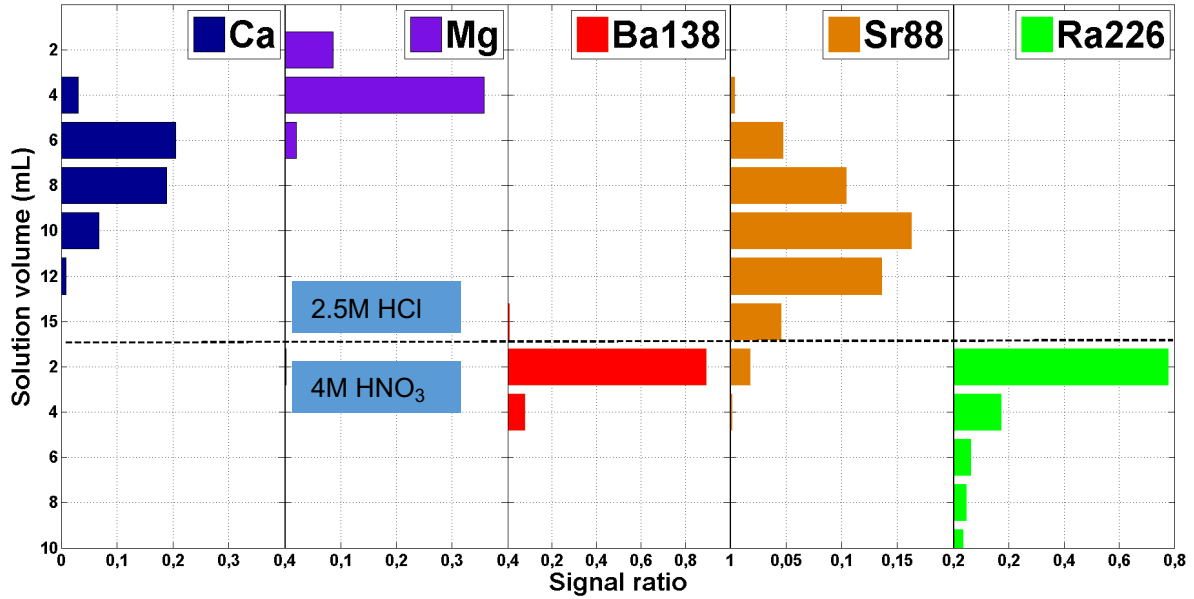
Step 3	Recovery eff. (%)	Separation efficiency (%)			
HCl M	^{226}Ra	^{43}Ca	^{25}Mg	^{88}Sr	^{138}Ba
1.7	86.9	68	98.2	19.8	23.4
2.5	100	99.7	99.9	96.4	12.1
4	64.2	99.8	99.9	99.7	96.2
6	9.1	99.8	99.9	99.6	76.4



Elution profiles for Ca, Mg, Ba, Sr, and Ra

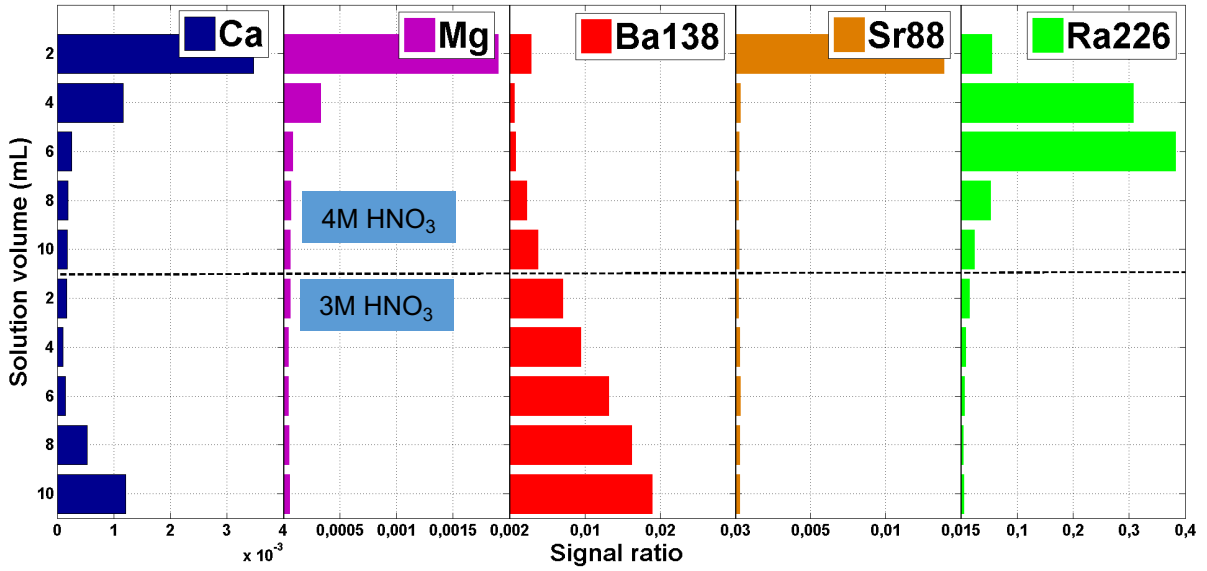
Cationic exchange resin

- high efficiency removal for Ca and Mg >99,7 %
- Good separation for Sr 96.6 %
- Poor for Ba



Sr Resin

- Improves Sr separation to >99 %
- Increases Ba separation to >95 %
- Rinse with 3M HNO_3 complete the Ra recovery



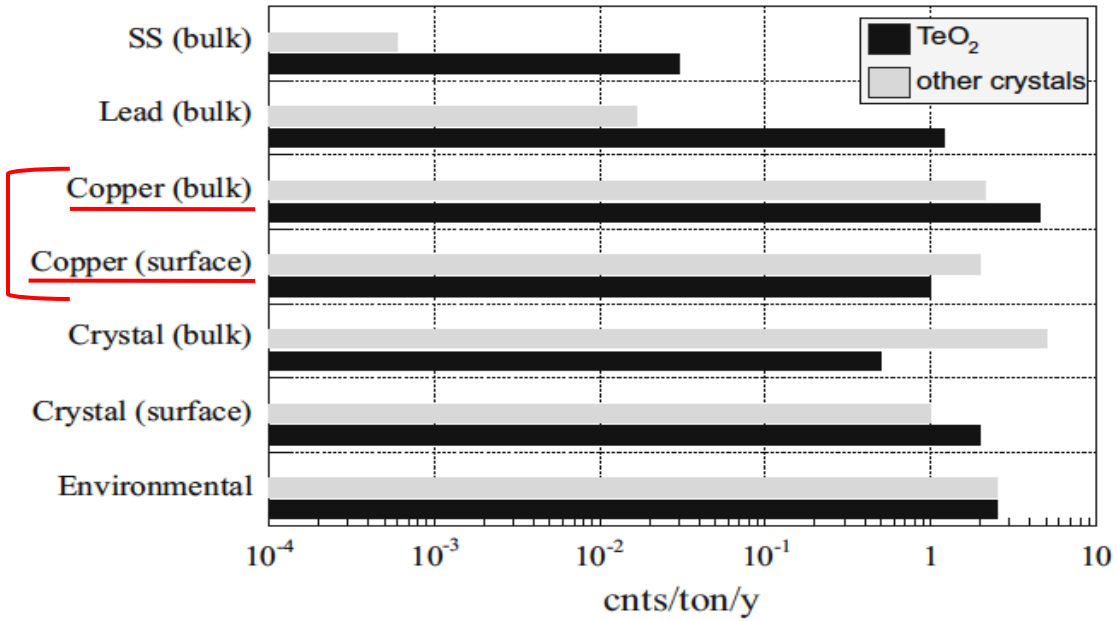
Method performance

- The developed method resulted to be relatively fast and economic then suitable for the measurement of large number samples
- An excellent sensitivity was achieved. **DL = $2*10^{-18}$ g mL^{-1}** (25 mL sample) thank to the improvements in the separation and pre-concentration techniques (PF=50)
- The Ra recovery was completely satisfactory **R_E= (100±3) %**
- The method has proved to be reliable, reproducible and robust

The proposed methodic allowed the reliable measurements of the ^{226}Ra concentration in the different sites of LNGS and the Ra time series analysis

Th &U in copper used for the CUPID experimental set up

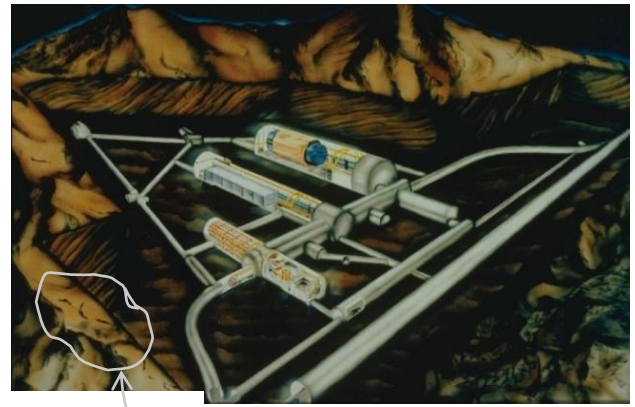
Copper is envisaged to be one of the materials for CUPID detector assembling



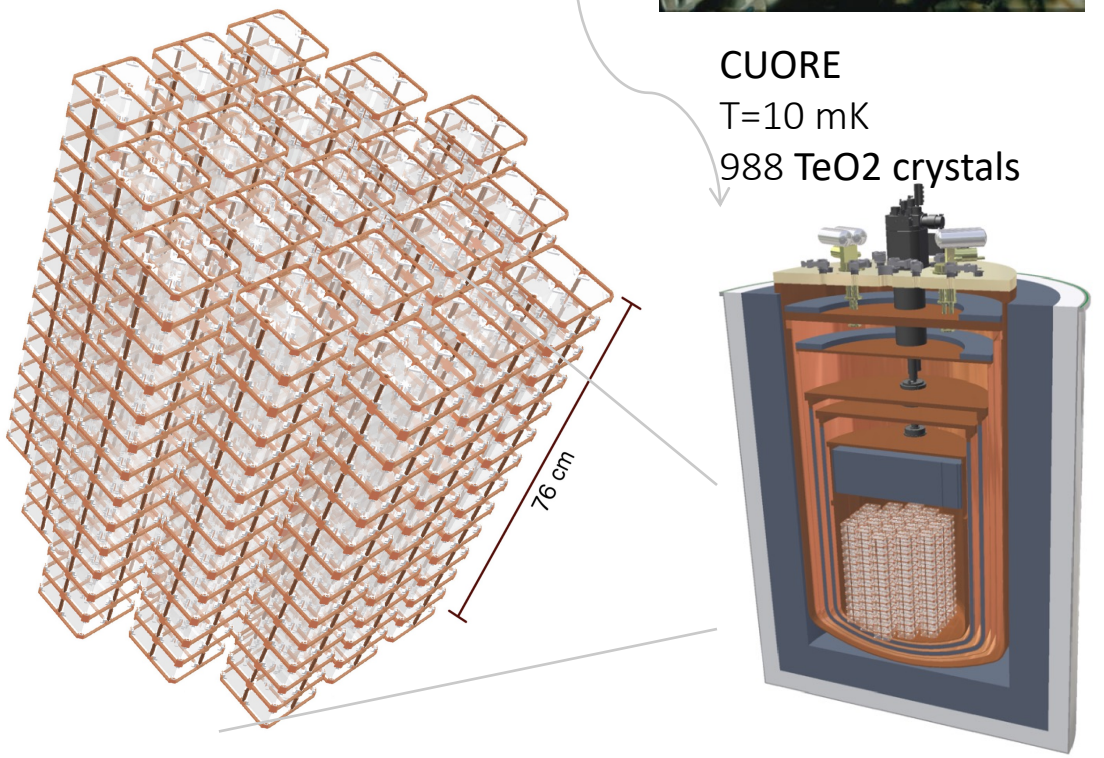
Background budget (upper limits)

Eur. Phys. J. C (2014) 74:3096

This translates in contamination level of the order of **ppt** or **fraction of ppt** of **Th and U in copper**



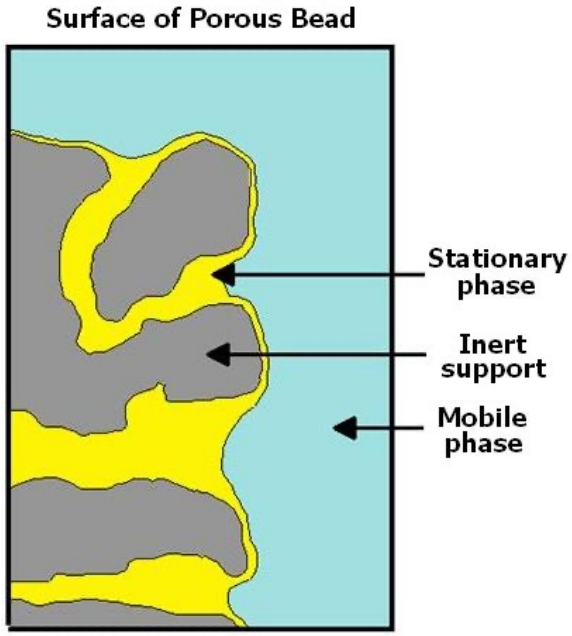
CUORE
T=10 mK
988 TeO2 crystals

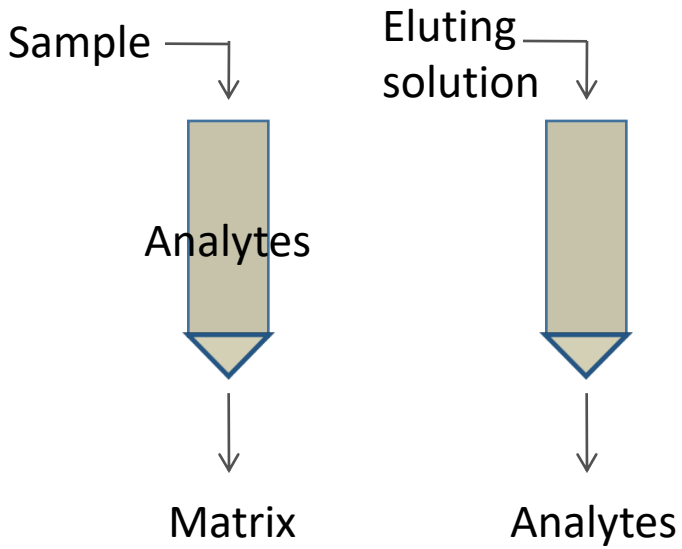


Purpose of this work

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

Extraction chromathography





Capacity factor k': $k' = D \frac{V_s}{V_m}$

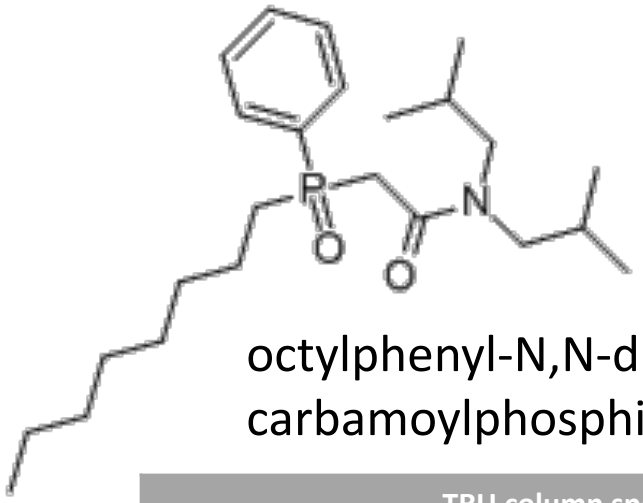
Advantages:

- Matrix removal
- Analyte pre-concentration

Disadvantages:

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

TRU resin (Triskem®)

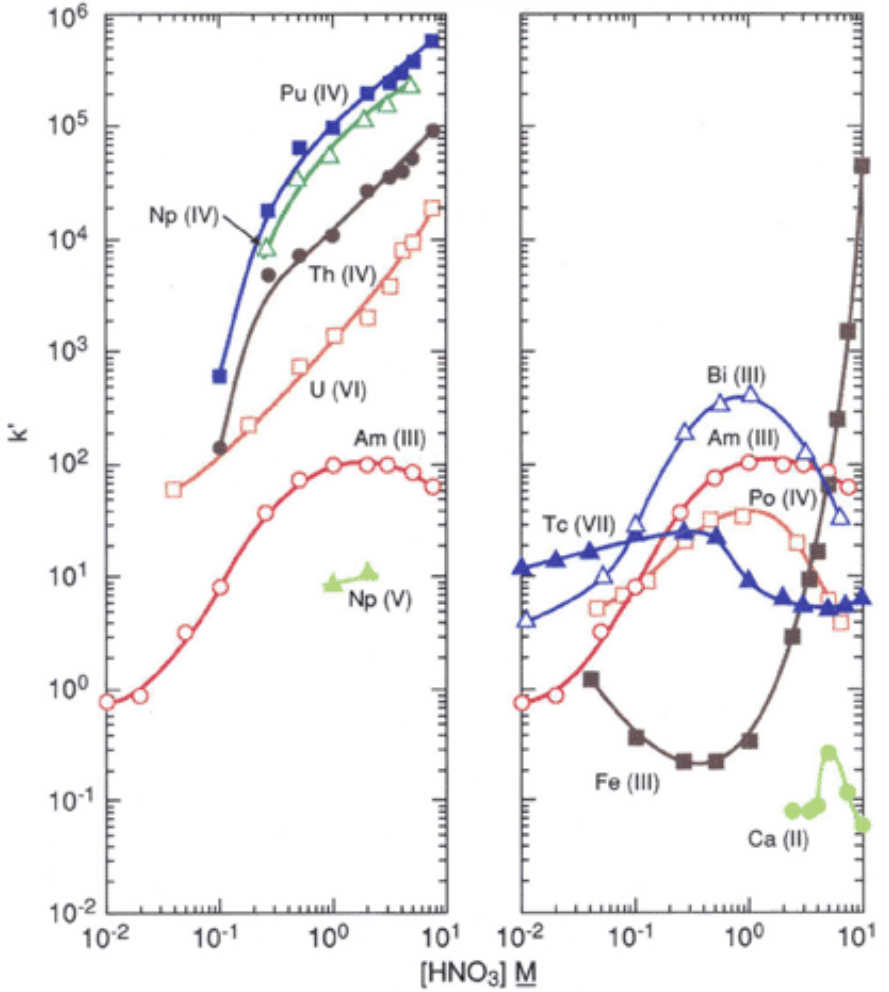


octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide (CMPO)

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

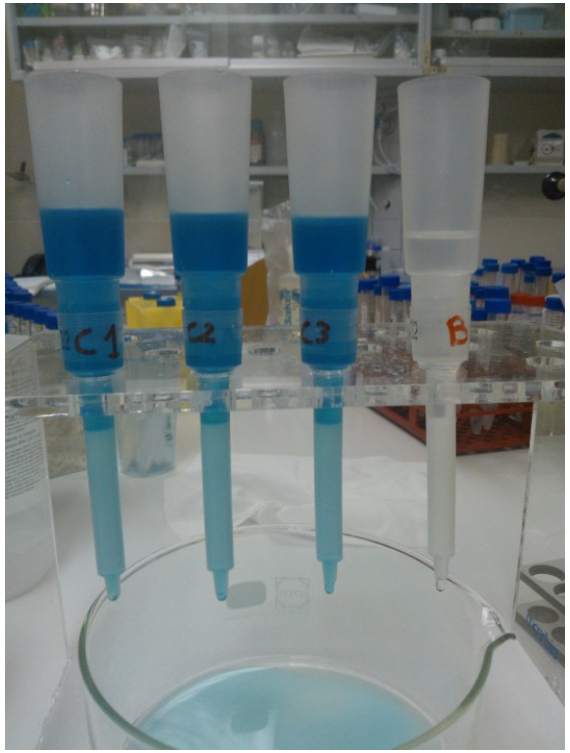
- Work in clean room (class 1000-ISO6)

-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

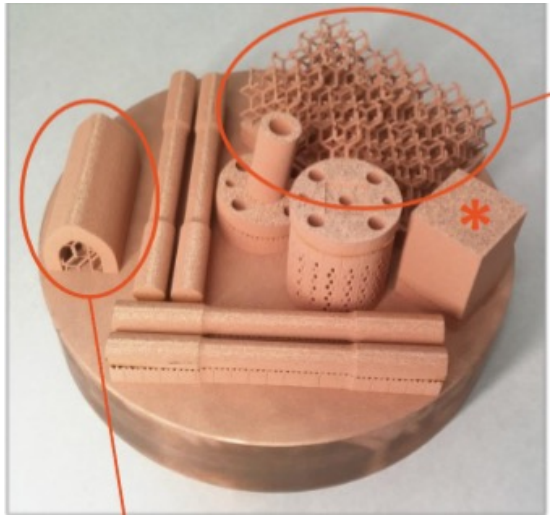
		ICPMS LNGS (LSC)	ULL GRS LNGS (LSC)	ULLGS+NAA LENA-Pavia
		Primordial parents	ϒ emettitors	Primordial parents
		Surface/bulk	BulK	Surface/bulk
Destructive		Yes	No	Yes
DL	[10^{-12}g/g]	Th=0.5 U=0.5	Th= 10-20 U= 10-20	Th(^{233}Pa)= 0.1 U(^{239}Np)= 3-5
Sample size	[g]	0.1-10	1-10000	100
Sample treatment		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)

Additive Manufacturing: Future Outlook in Designing Pure Metal Components for Particles Detectors

AM allows to produce parts:

- Complex geometries
- High Resolution
- Hollow components
- W/o final traditional machining
- W/o surface cleaning
- Mass save of a factor about 2-3
- Components number reduction

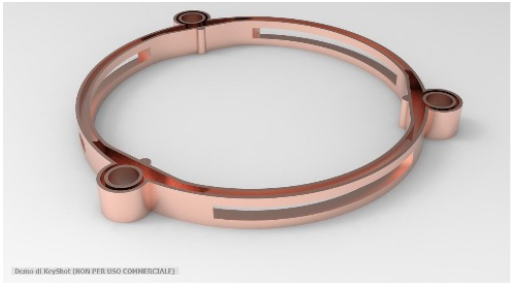


Crystal Holder

Traditional CNC
mass=27g

AD same supports
mass=11g

M/3 !



AD new design
mass=9g

Ultrapure Copper component production process

Starting copper

Copper
Electtroforming

Cu powder production (µm)

3D printing

Raw Cu

Relatively good quality Cu is available on the market

EF Purification efficiency has been already tested

Contamination of atomization must be investigated but...

Contamination risk has been **preliminary** checked

Quality control along the flow
Th U sub-ppt (uBq/Kg) level

Different LRTs are available: **ICPMS**, ULL-GRS, NAA

Study of purification effect for EF at LSC

Element	Mass		CURAW2ET.D [ng/g]		CUEF2ET.D [ng/g]		Removal efficiency [%]	
Mn	55	ppb	21		<10		>	52.38
Fe	57	ppb	13,000		<3000		>	76.92
Co	59	ppb	1,600		<1		>	99.94
Ni	60	ppb	26,000		<10		>	99.96
Zn	68	ppb	70,000		<10		>	99.99
Ge	72	ppb	5.6		<1		>	82.14
As	75	ppb	1,300		<100		>	92.31
Ag	107	ppb	1,000		240			76.00
Cd	110	ppb	520		<5		>	99.04
In	115	ppb	75		<2		>	97.33
Sn	118	ppb	19,000		<5		>	99.97
Sb	121	ppb	1,900		<5		>	99.74
Te	125	ppb	66		<5		>	92.42
Pb	208	ppb	49,000		<50		>	99.90
Bi	209	ppb	180		<5		>	97.22
Th	232	ppb	<0.01		<0.001			---
U	238	ppb	<0.005		<0.001			---

Valori misurati in modo Semi-Quantitativo incertezza=25%

Th ed U dopo separazione di matrice e preconcentrazione mediante estrazione cromatografica selettiva

Conclusioni

- La spettrometria di massa ICP è una tecnica estremamente versatile, molto valida anche per lo screening dei materiali radiopuri

- L'uso combinato di spettrometria di massa e metodi radiometrici fornisce un quadro più completo sul campione e sulla verifica dell'equilibrio secolare

- Ovunque sia importante elevata purezza chimica (es. Crescita di un cristallo, polvere 3D ect) l'ICP-MS è una tecnica fondamentale (l'analisi Semi-Quantitativa è un potente strumento analitico)

- L'ICP-MS oltre che un valido strumento analitico indipendente si presta anche come tecnica di supporto per l'ottimizzazione dei metodi, inclusi quelli che prevedono altre tecniche (ad esempio NAA)

- Grazie alla sua rapidità di analisi e l'impiego di una quantità minima di campione è una tecnica adatta al controllo di qualità (anche sul singolo lotto)

- La preparazione del campione è determinante per la sensibilità e l'affidabilità della misura finale

- L'accoppiamento LA-ICP-MS allarga ulteriormente i campi d'impiego (analisi su campioni solidi senza trattamento del campione, studi contaminazione superficiale, mappa delle concentrazioni)