Mass Spectrometry facility at LNGS for the screening of radio-pure material

S. Nisi

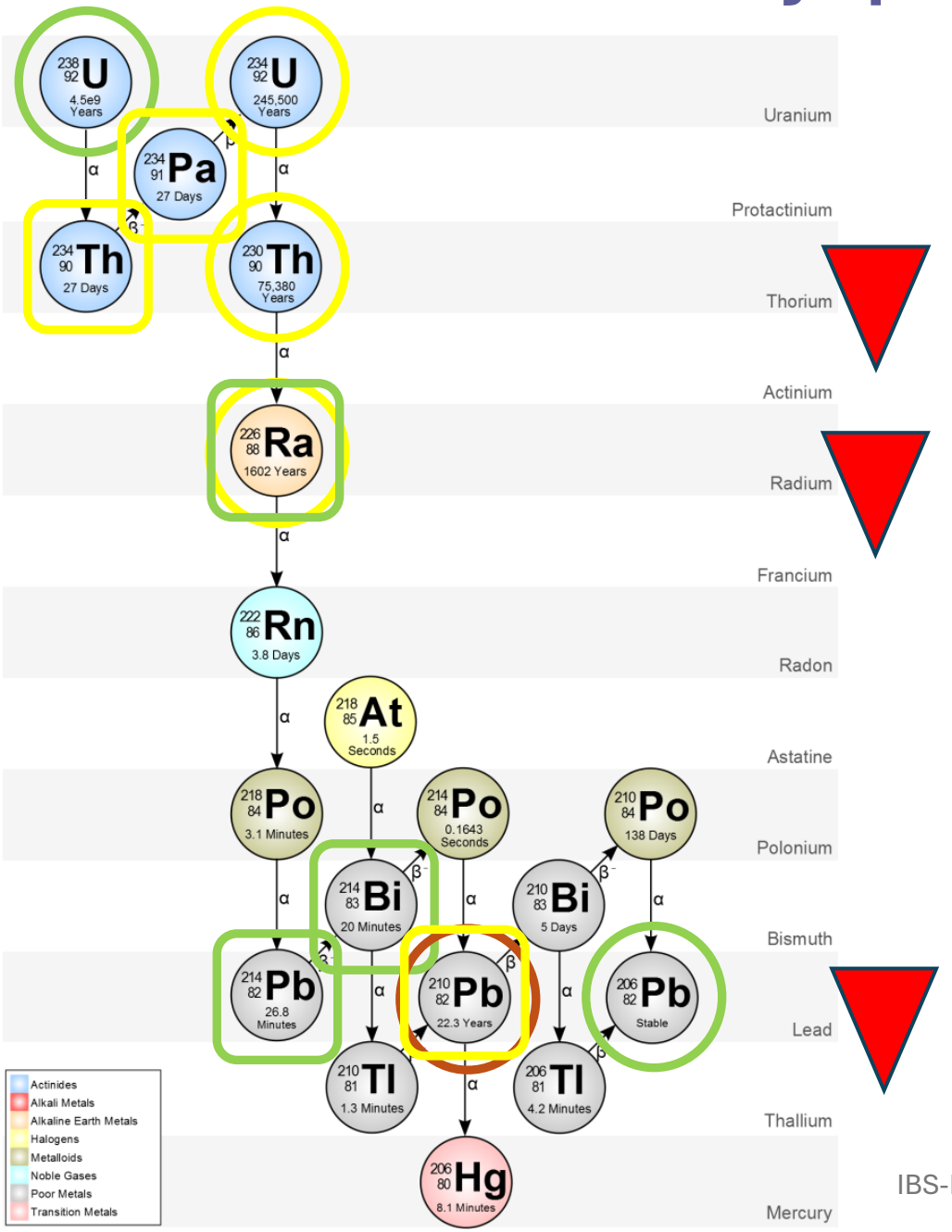
Laboratori Nazionali del Gran Sasso

Chemistry Department

stefano.nisi@lngs.infn.it

IBS-INFN Global Research Center, Daejeon

ICP-MS and Y-ray spectrometry: intrinsic complementary



ICP-MS

Chemical & physical behaviour different for the nuclides
Rupture of SE is possible

γ-ray Spectrometry

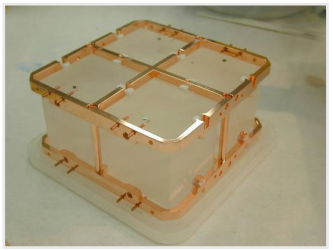
LRT's performance comparison

		ICPMS LNGS (LSC)	ULB GRS LNGS (LSC)	ULB GRS+NAA LENA-Pavia
		Primordial parents	Y emettitors	Primordial parents
		Surface/bulk	BulK	Surface/bulk
Destructive		Yes	No	Yes
DL (Cu sample)	[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

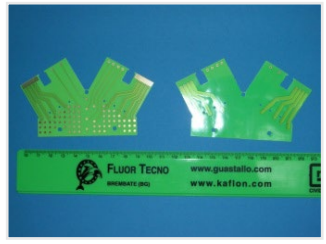
Screening material examples

≈ 200 Complex samples/year
- Hundreds ready samples/ year (water and reagents)



Crystal and raw material

Metal & alloy



Heterogeneous material

(PCB)

Sensitivity for copper		
	pg/g	**uBq/Kg**
Th	0,5	2,0
U	0,2	2,4
Sensitivity for UP water		
^{226}Ra	0,000002	70
Th	0,005	0,02
U	0,005	0,06
K in NaI crystal		
K	3000	90

Issues in ICP-MS ultra-trace analysis

- **Isobaric interferences:** polyatomic species, isotopes of different elements and double charged ions ($^{38}Ar^{1}H^{+}$ on K^{+}, $^{184}W^{16}O_3^{+}$ on ^{232}Th)

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

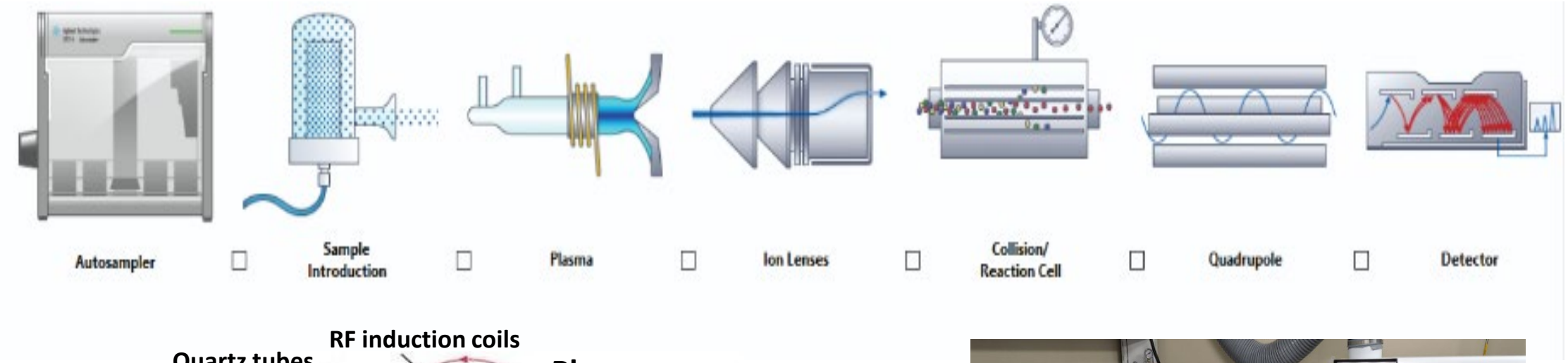
- **Background** instrumental and method. Vial conditioning, ultrapure reagent, Clean room)

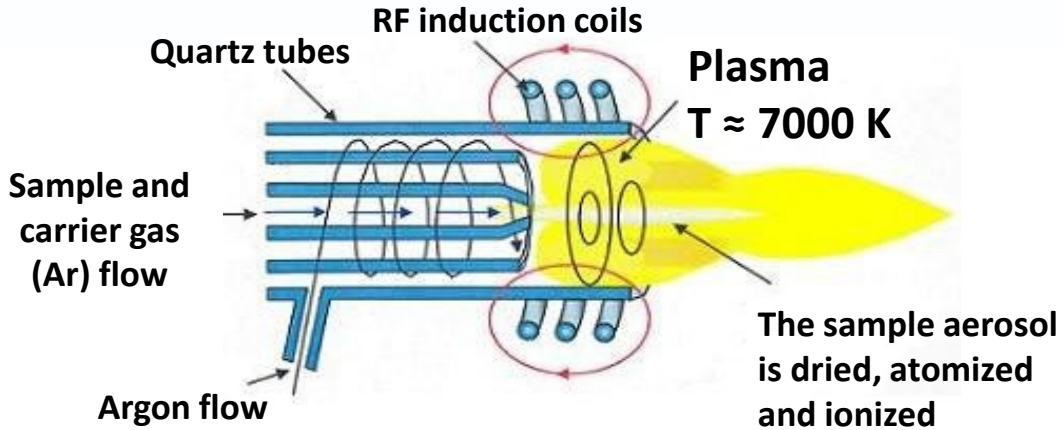
- **Risk of contamination** during sample preparation and measurement (we are looking for very very low concentrations!!!)

- **Lack of Certified Reference Material** (spike technique, method validation, inter-calibration)

ICP mass spectrometers @ LNGS

ICP QMS (quadrupole mass analyzer) – Agilent 7850

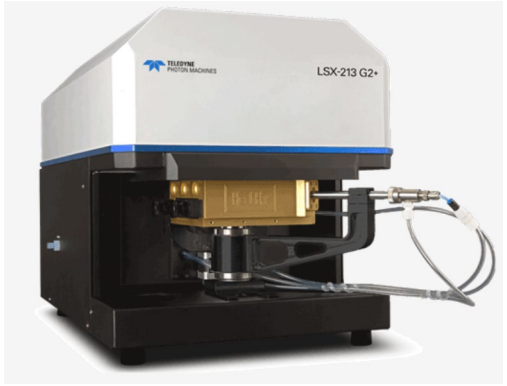


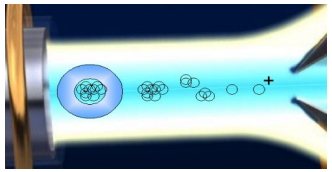


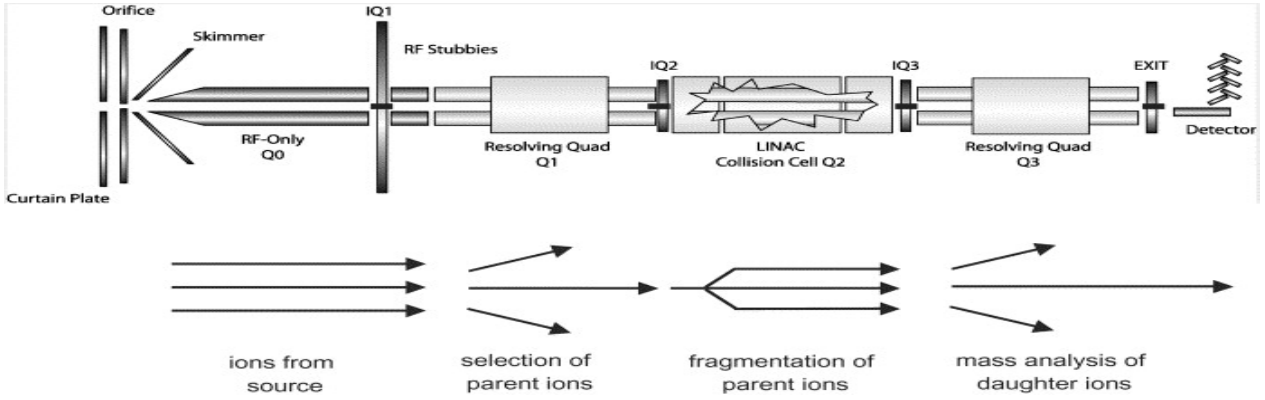
General use to avoid contamination and memory effect for QQQ-ICP-MS and HR-ICP-MS

ICP mass spectrometers @ LNGS

LA-ICP-QQQMS (quadrupole mass analyzer) – Agilent8900



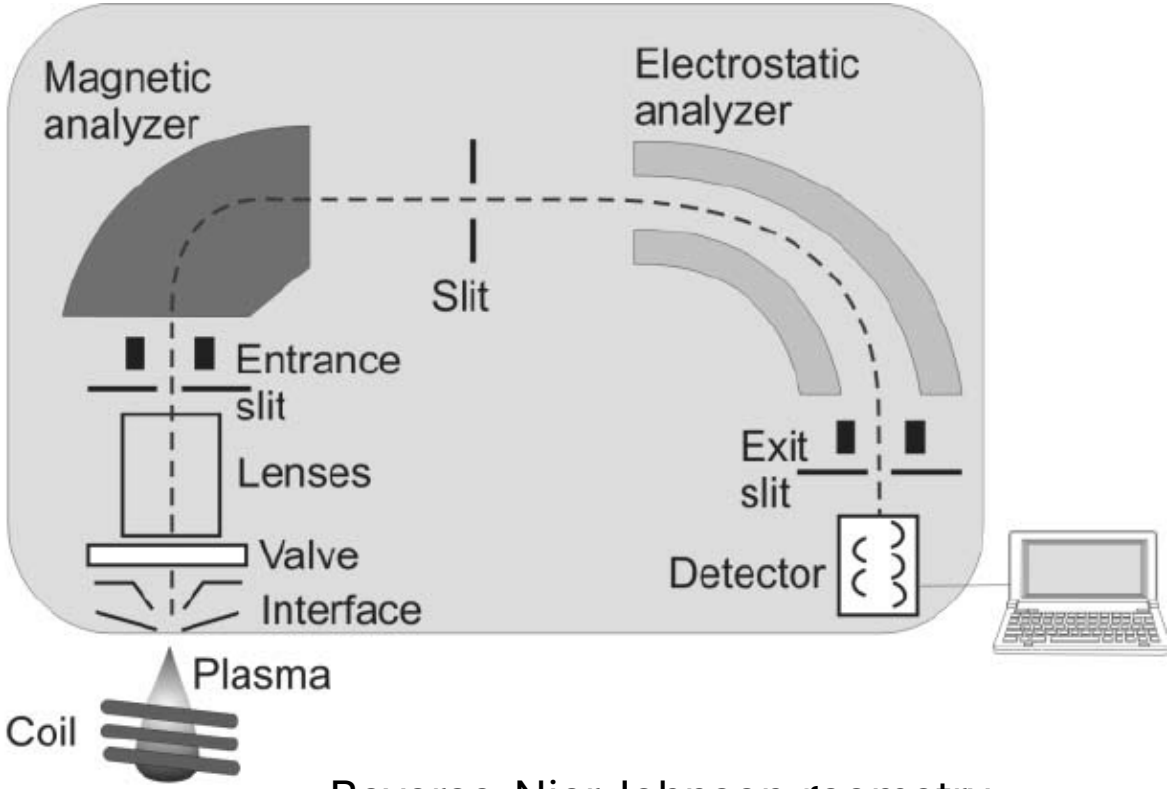




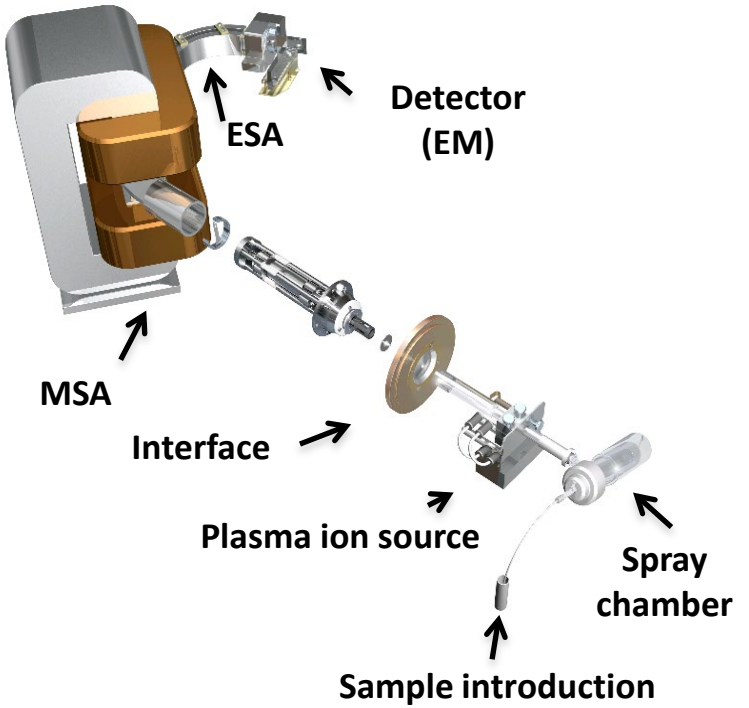
Installed at beginning 2025

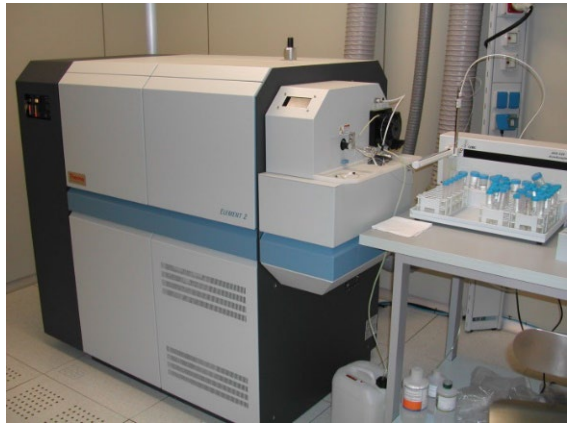
- **Typically used with laser ablation system to analyse of solid sample**
- **Spatial distribution and depth concentration profile**
- **Specific application requiring reaction gases (H_2, O_2, NH_3...)**

Sector Field ICP-Mass Spectrometer



Reverse Nier-Johnson geometry





The strengths of double focusing ICP-MS are sensitivity and the mass resolution

Drawbacks in ICP-MS ^{39}K measurement in NaI

Dilution is requested (at least 100)

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

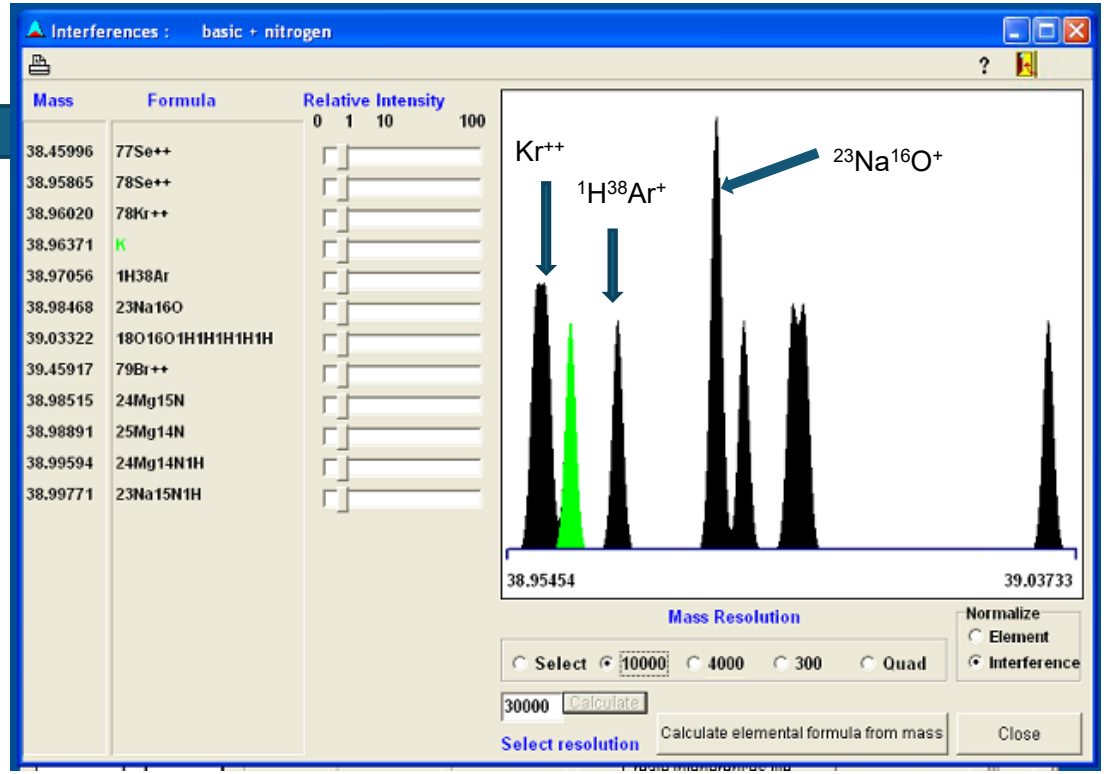
Contamination risk

- 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	

	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 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	27 ± 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

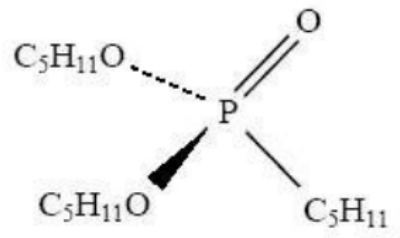
Without matrix separation, the DLs achieved in different labs using different instrumentation are at ppb level

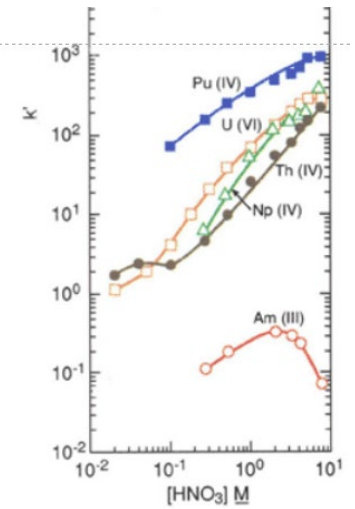
Development of new ICP-MS method for radiopurity assay of lead

Literature (Hoppe et al. 2014)

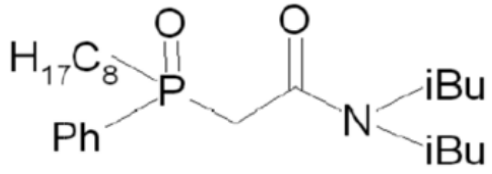
- Th U pre-concentration based on chromatographic resin UTEVA
- Recovery 45% for Th 12% for U
- Use of ^{229}Th and ^{233}U used as tracers
- Detection limit: 0,23 ng·kg^{-1} for Th 0,5 ng·kg^{-1} for U

UTEVA
Dipentyl Pentyl Phosphate

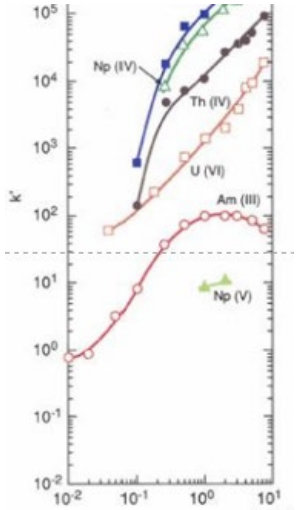




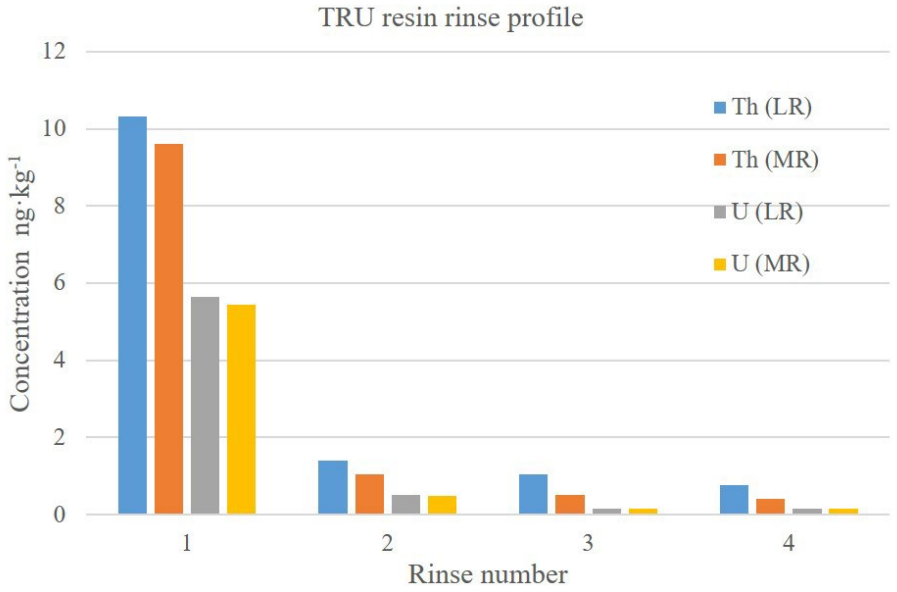
TRU
CMPO+TBP
(Carboamoyl Phosphine Ox
+ Tributylphosphate)

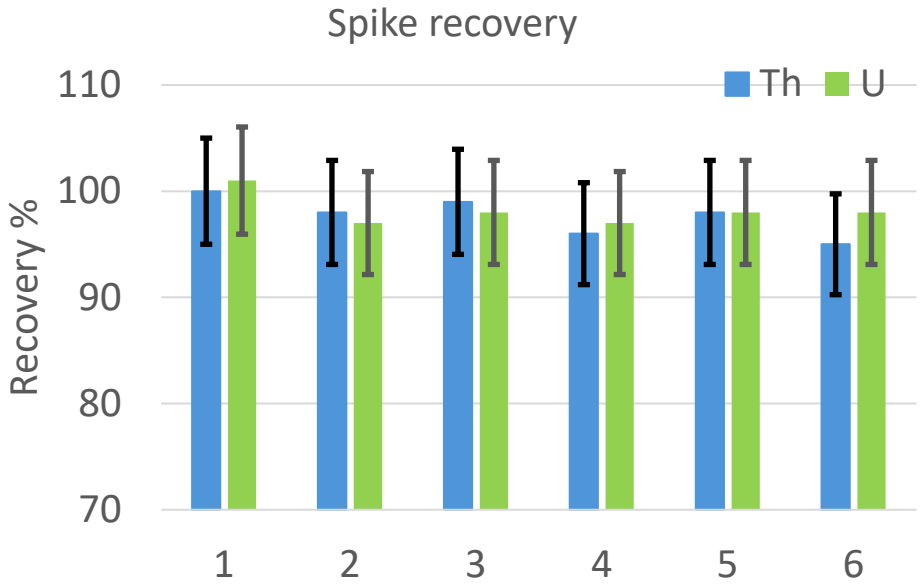


Development of method **based on TRU** resin (ammonium oxalate as eluting solution) to improve the recovery for Th and U resulting in a rapid and reliable measurement **without use of artificial isotopes**



Validation & Performance of the method





Process Blank & DLs ($3\sigma_{BLK}$)

	Average	ST Dev	DL
	pg·g^{-1}	pg·g^{-1}	pg·g^{-1}
^{232}Th (LR)	0.50	0.05	0.5
^{232}Th (MR)	0.49	0.06	0.5
^{238}U (LR)	0.32	0.02	0.2
^{238}U (MR)	0.31	0.02	0.2

- TRU resin has been used for long time at LNGS to preconcentrate Th and U from several material (Cu, Steel, GSO, …)
- Proper preparation of the column is crucial
- Recovery is 98 ± 2 for both (Th and U)
- Pb removal is very efficient (>99,95%)
- Process blanks are quite low and very reproducible
- Excellent DLs: 0,5 pg·g^{-1} for Th, 0,2 pg·g^{-1} for U
- DLs are driven by the blank of the process (LR=MR)

Hundred kg of archaeological Pb: ICP-MS-Gamma-Ray comparison

Decay chain [μBq kg^{-1}]	Isotope	Activity [μBq kg^{-1}]
^{232}Th (*24±8)	^{228}Ac	40±20
	^{212}Pb	<210
	^{212}Bi	<140
	^{208}Tl	<23
^{238}U (*100±30)	^{214}Pb	100±40
	^{214}Bi	<20
	^{235}U	<760
	^{40}K	<270
	^{137}Cs	<8.0
	^{207}Bi	<13
	^{202}Tl	60±5

*ICP-MS

- 4 ingots of archaeological Pb were re-casted producing pieces to fit the HPGe detector to maximize the efficiency
- 97.3 kg of Lead were measured by Gamma ray for 68 days.
- Gamma-ray and ICP-MS results agree for Th and U chains.
- The secular equilibrium is OK.

Archaeological lead is suitable to produce low background $PbWO_4$ cryogenic detectors

GRC: perspectives

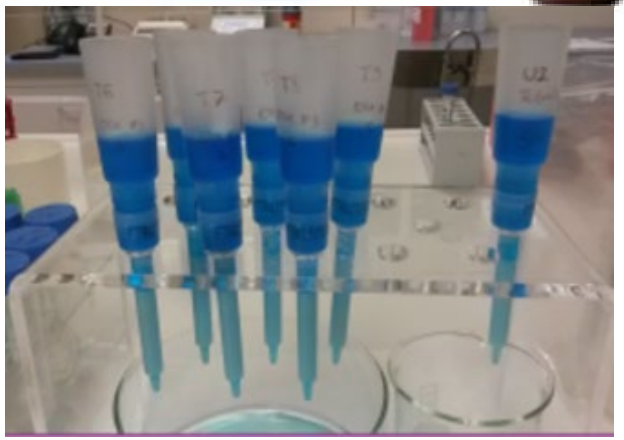
Sharing knowledge and skills helps improve analytical capacity

- Accelerates R&D
- Helps the validation of the method
- Represents an opportunity for intercalibration
- Increases the reliability of the data

GRC: action plan

- Selection some samples of material of interest for particle physics
- Defining a common procedure for sample cleanup
- Establishing a common analytical method to be applied in different labs
- Measuring sample by mean ICP-MS and Y-ray spectrometry in different labs
- Results comparison

Thank you



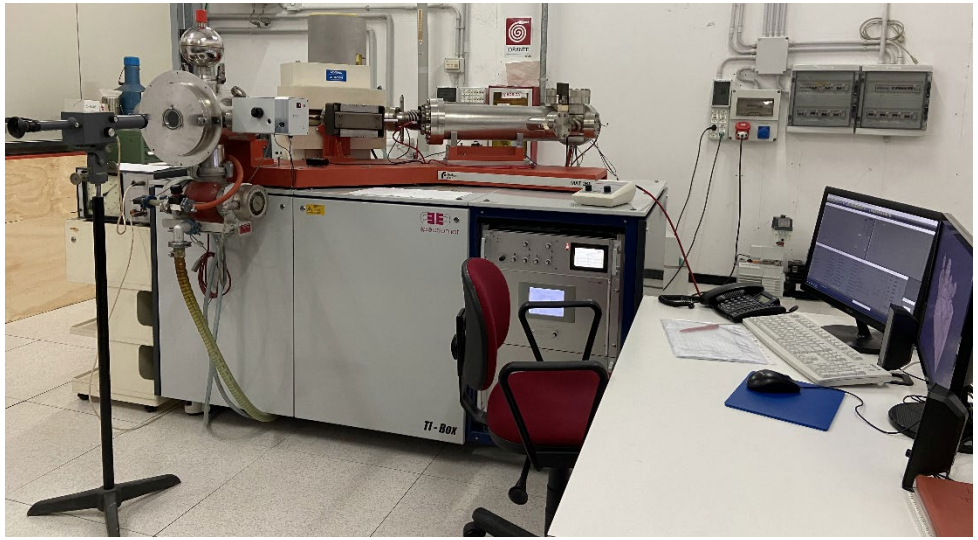
Sample preparation

Instrumentation

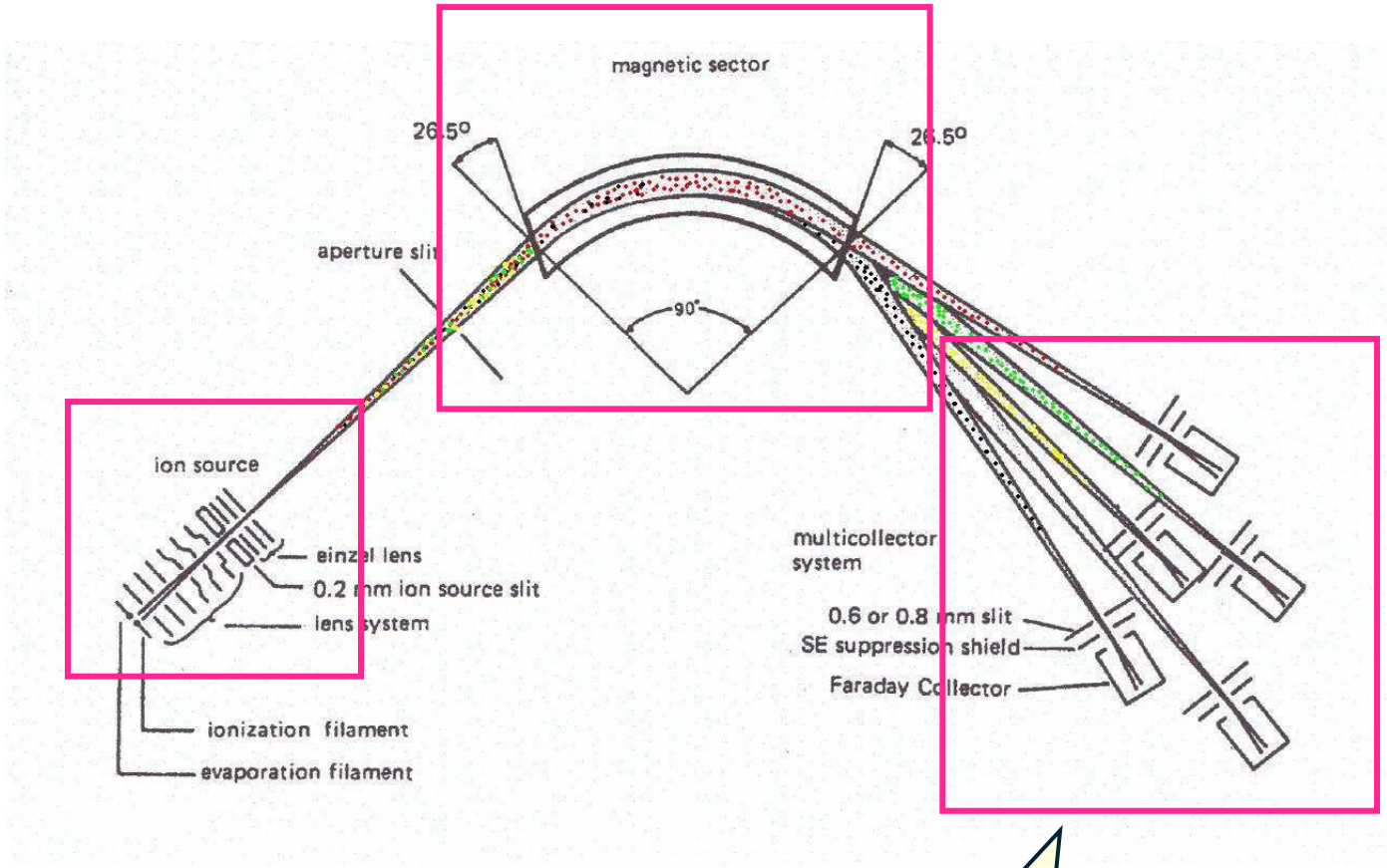
“Clean chemistry”

Thank you for your attention

Analisi isotopiche ad alta precisione con TIMS a collettore multiplo

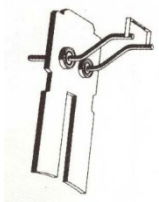


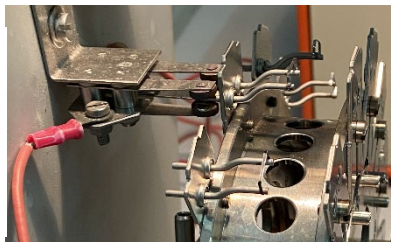
TIMS MAT 261 Thermo Finnigan

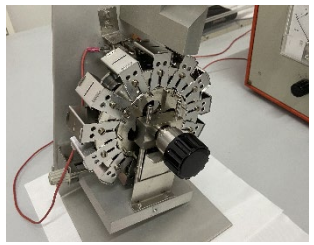


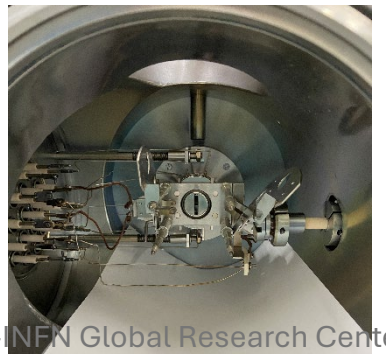
Discriminazione tra rapporti isotopici <0.01%

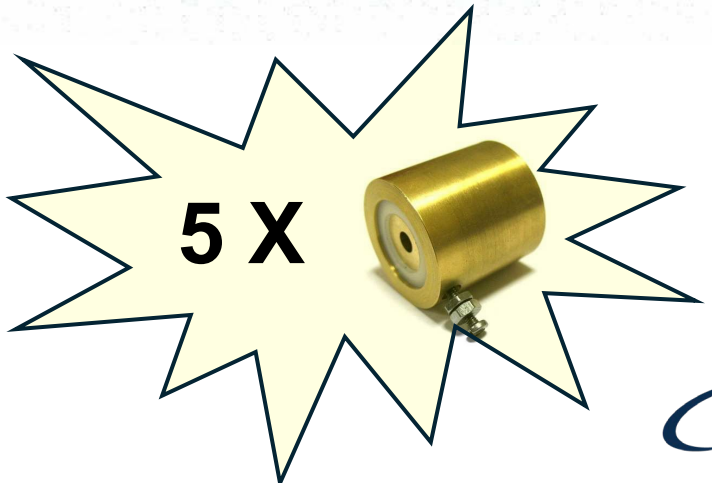
Precisione interna >**0.005%**





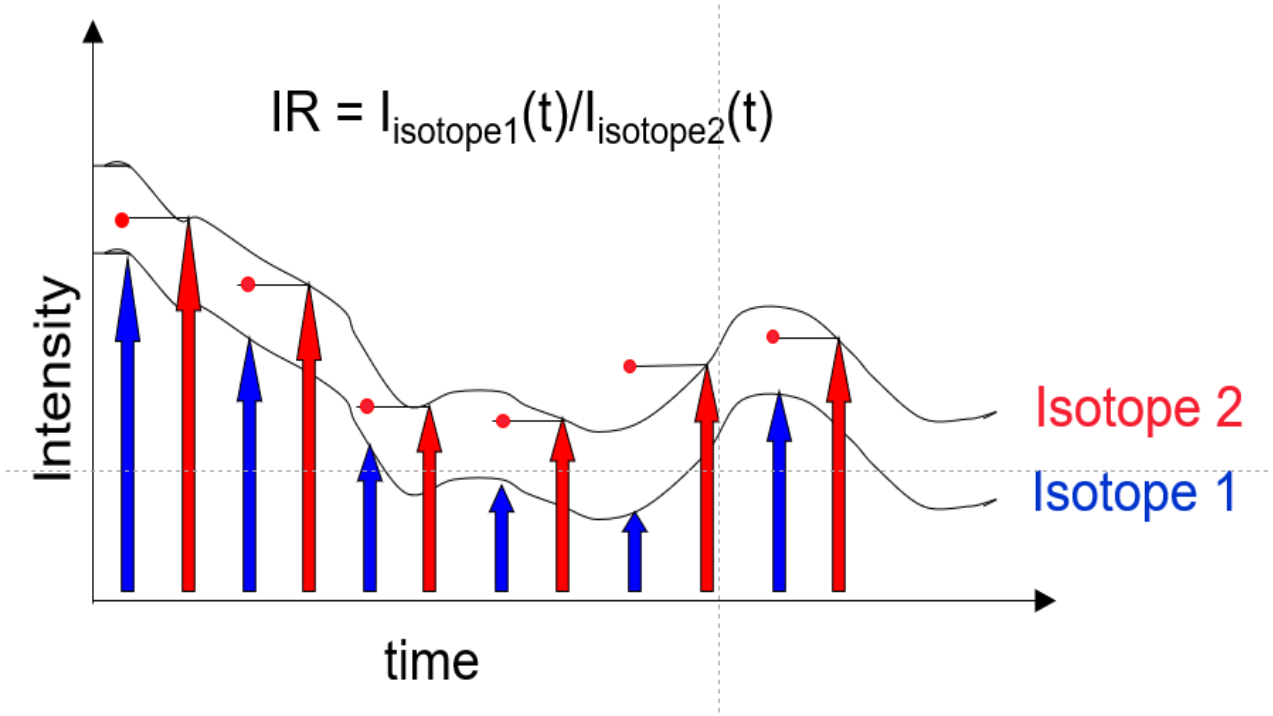






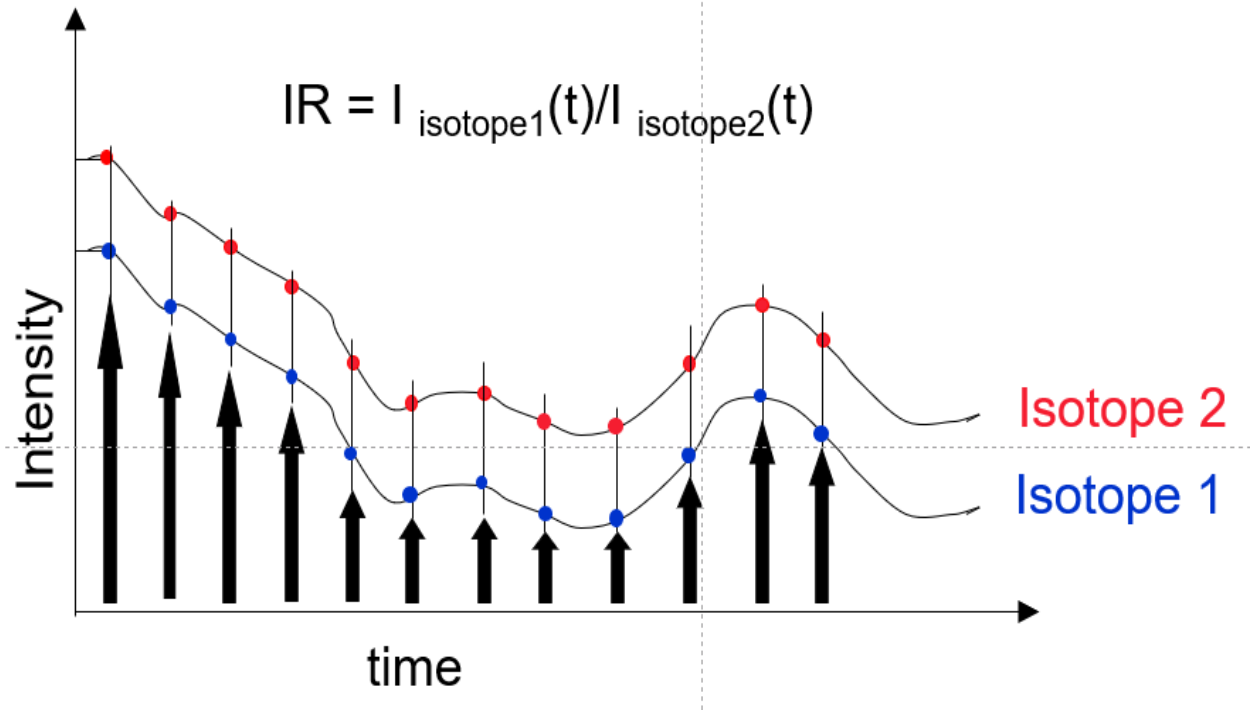
Misure isotopiche: vantaggi del rivelatore a collettore multiplo

Collettore singolo: misura sequenziale



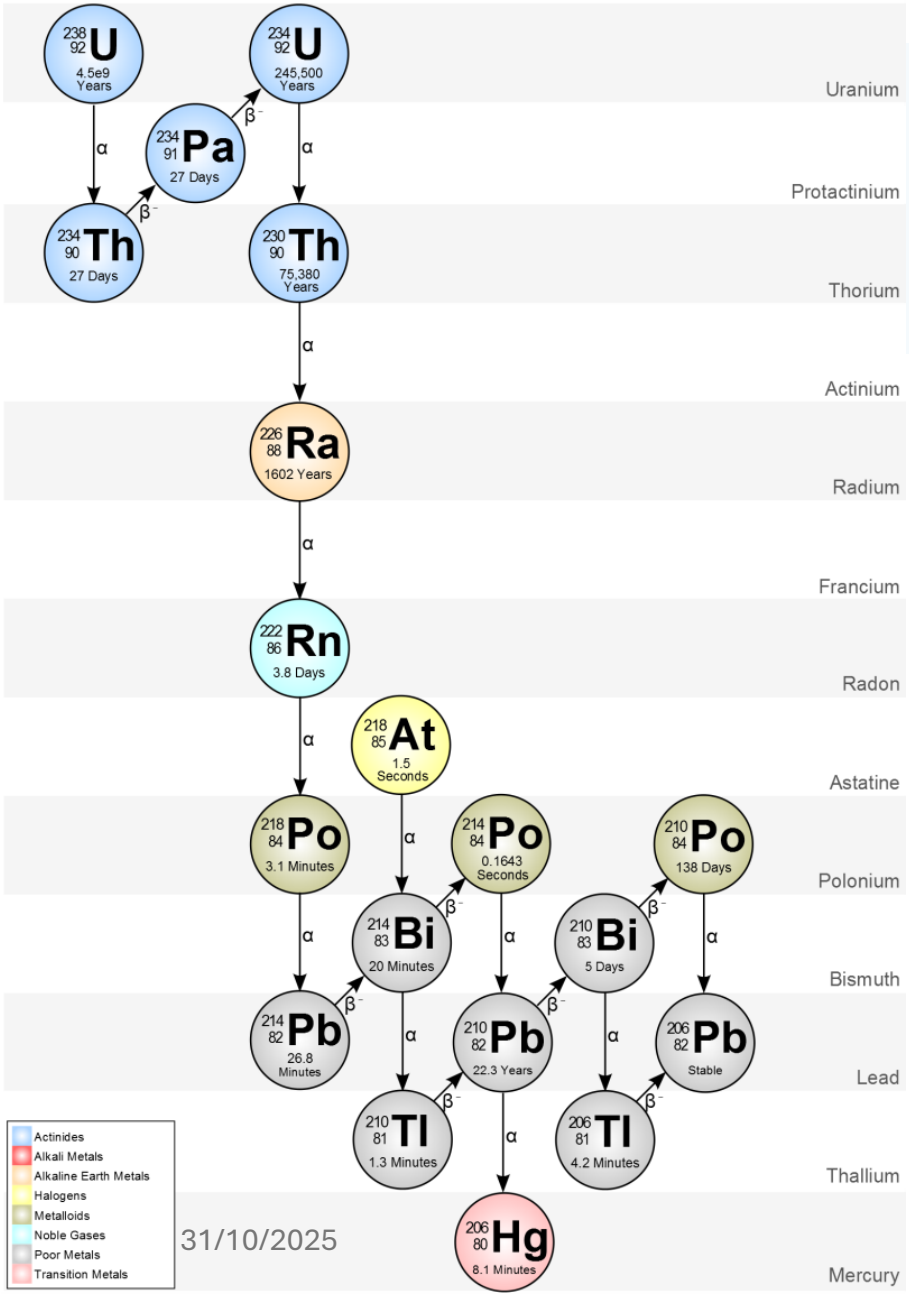
Accuratezza e precisione sono influenzate dalla stabilità del segnale

Collettore multiplo: misurasimultanea



Accuratezza e precisione non dipendono da fluttuazioni della sorgente

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**

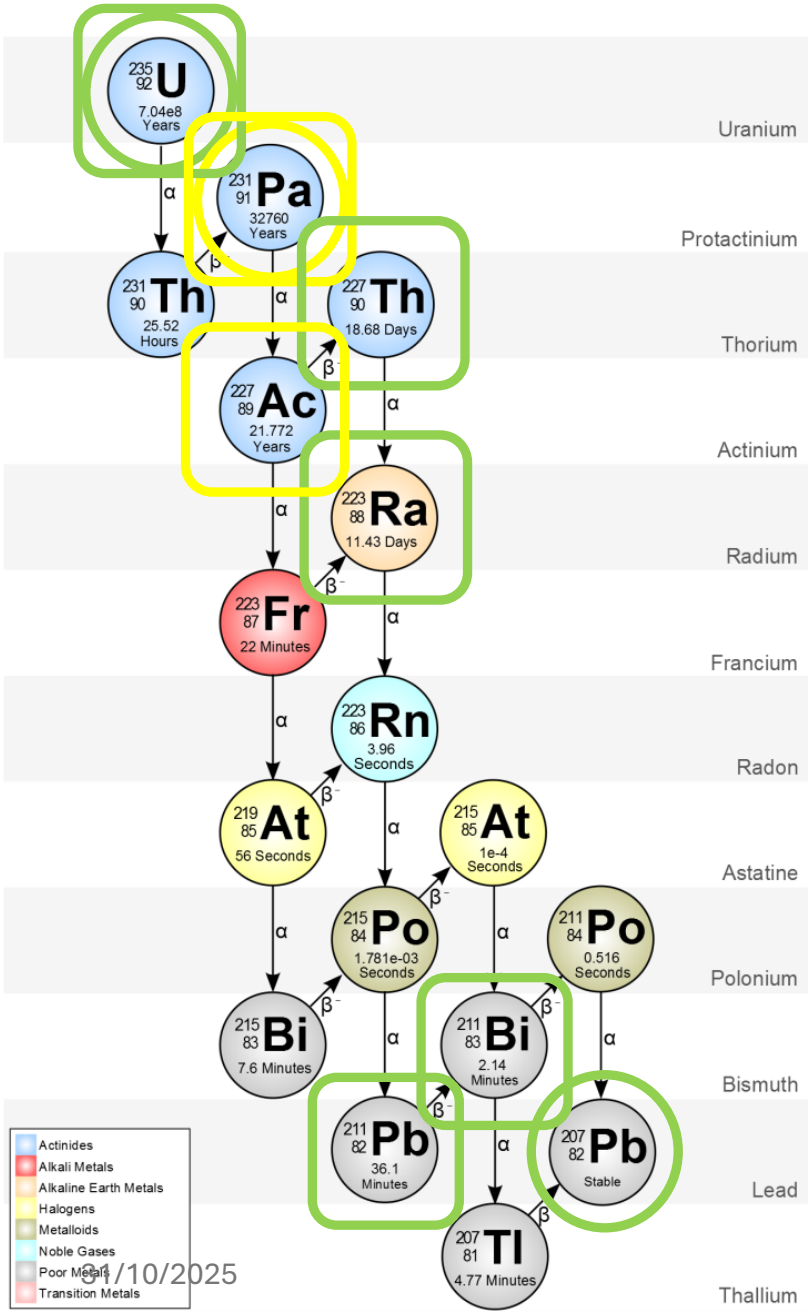
the number of atoms that decays for each nuclide per unit time is the same.

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

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

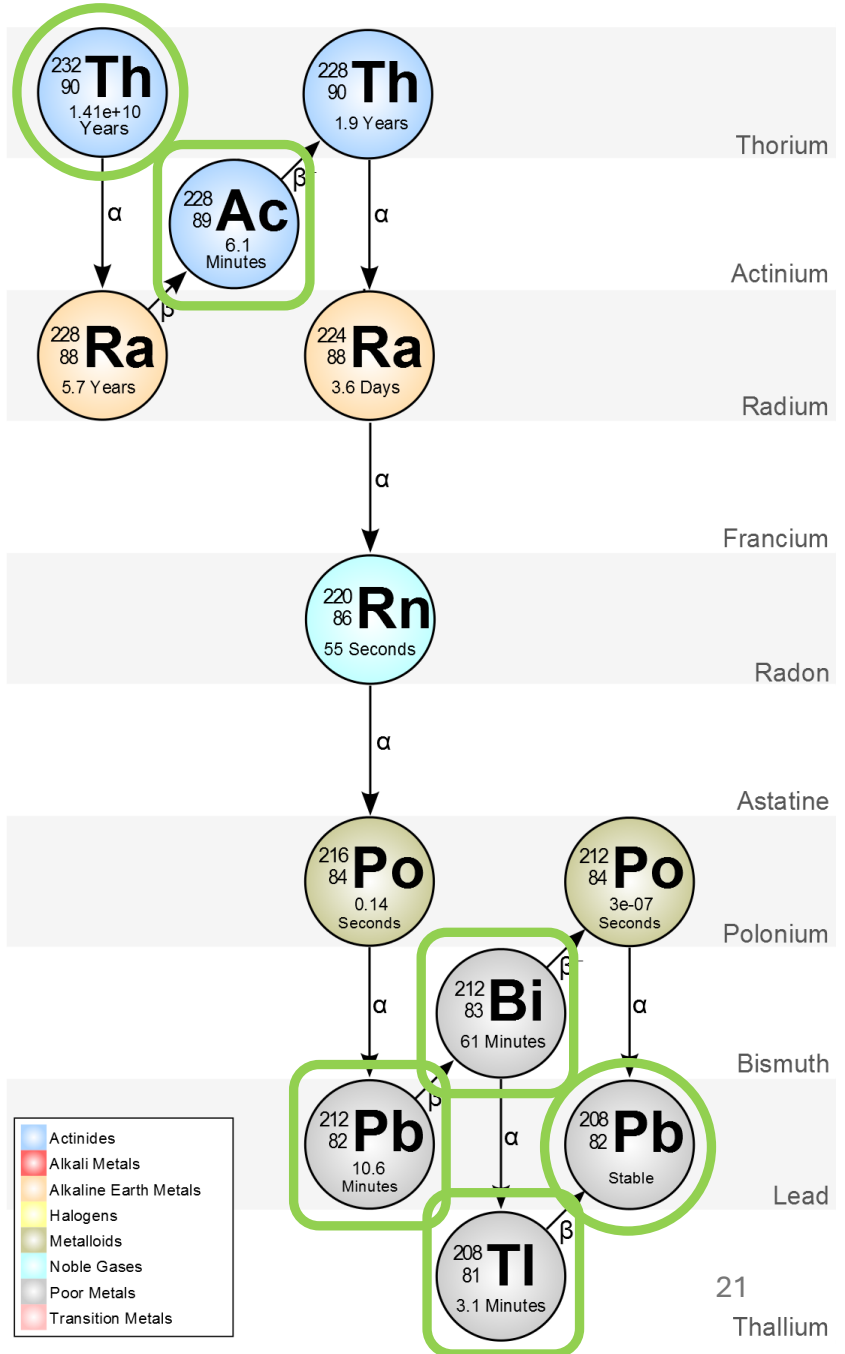
Radiometric techniques and mass spectrometry are intrinsically complementary

Others natural decay chains



ICP-MS

γ-Ray Spectrometry



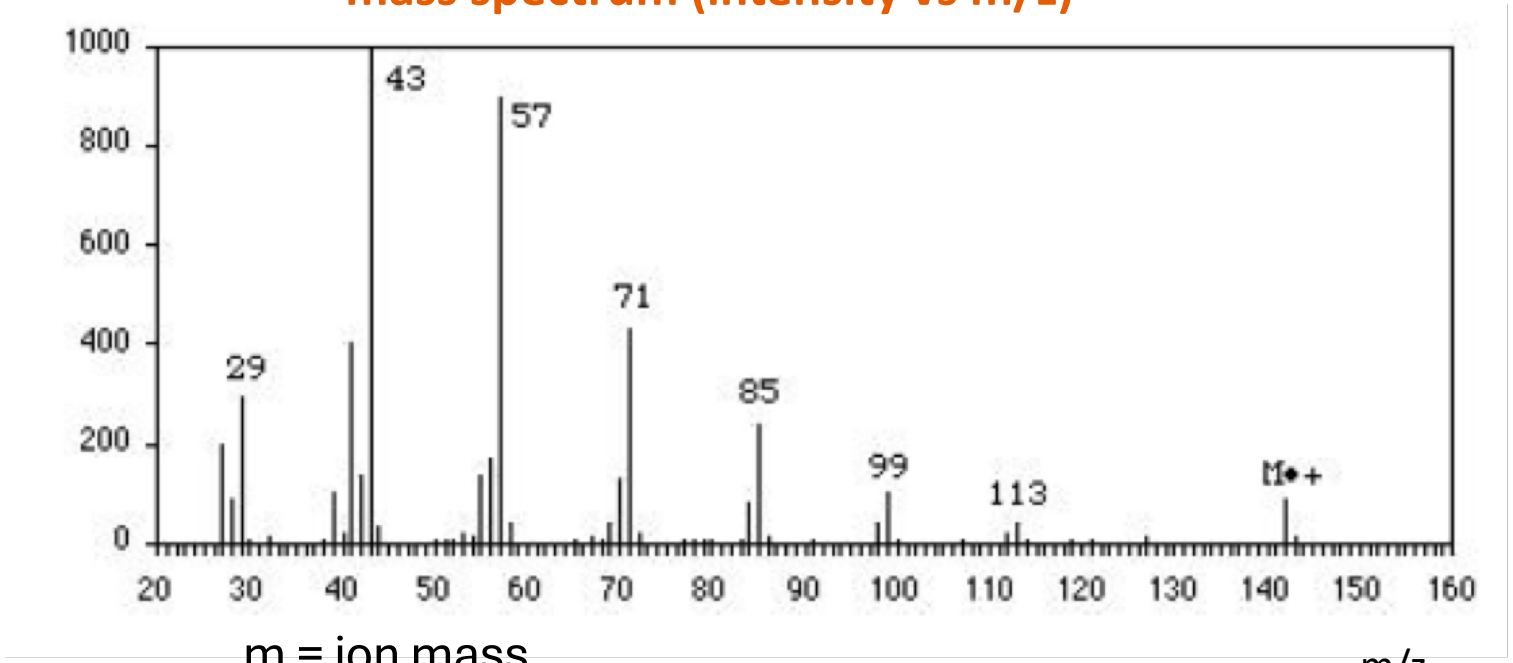
What is the mass spectrometry?

- 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)

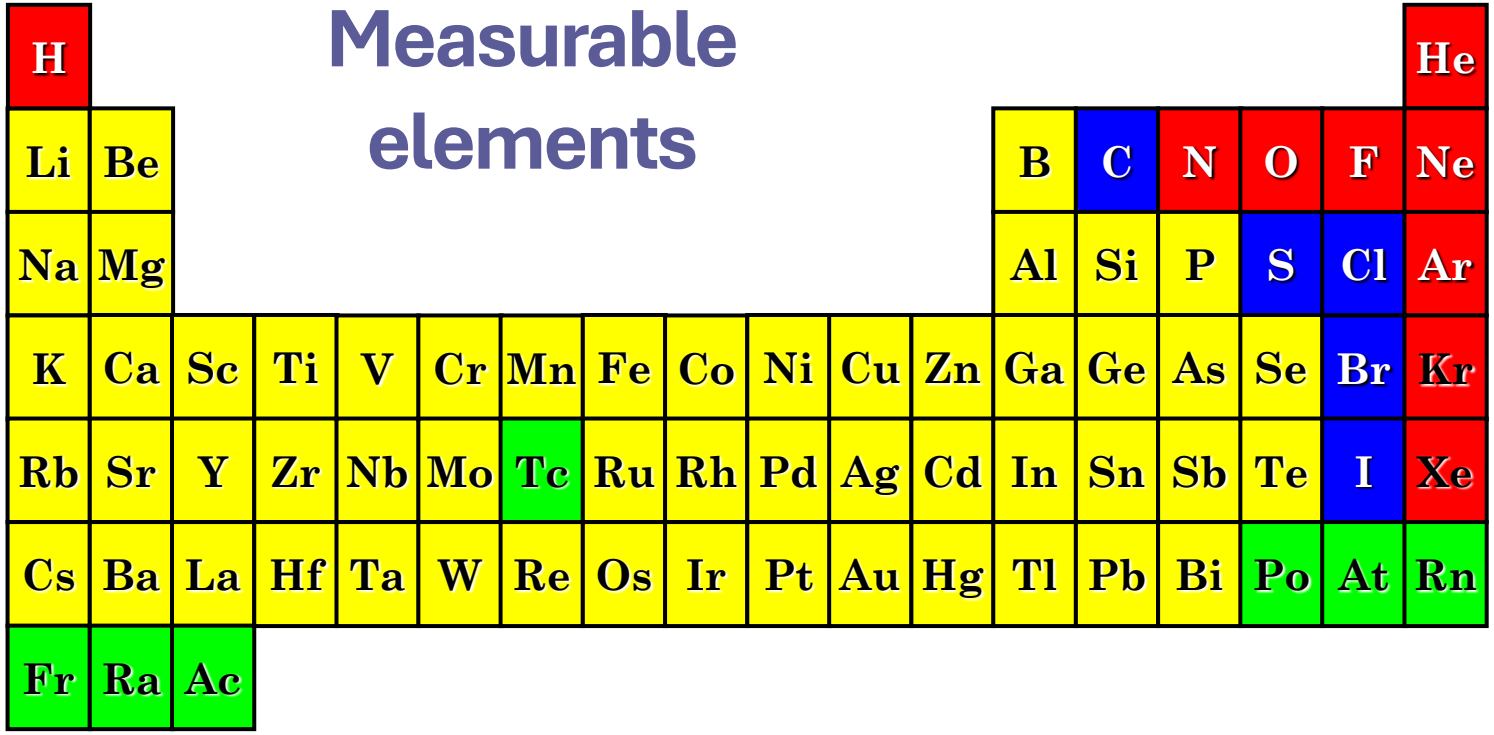


m = ion mass

z = ion charge

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

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

Measurement of K in NaI crystal

DM Direct detection experiments sensitivity = f(radioactivity background)

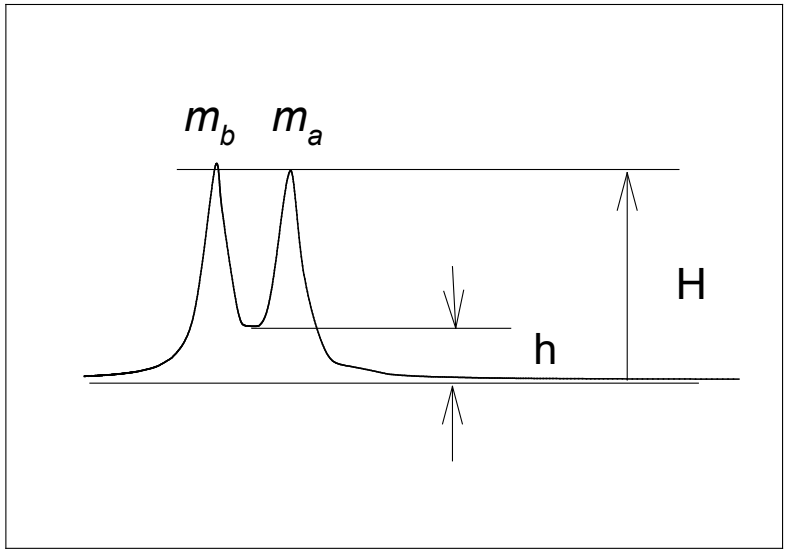
Some experiments looking for DM evidence are using or developing **NaI crystal-based detectors**

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).**

Mass resolution power

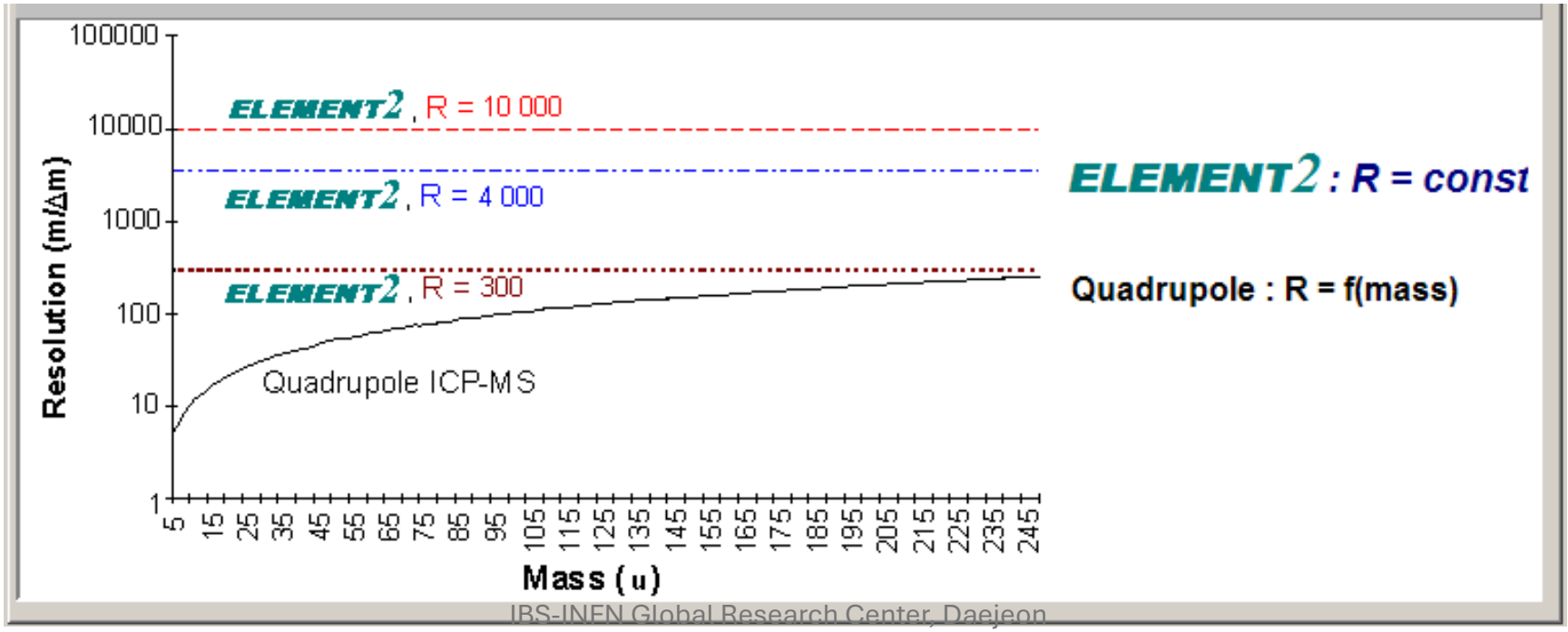


When two adjacent peaks m_a and m_b with comparable intensitiy and

h<10%H

the resolution is defined as the ratio:

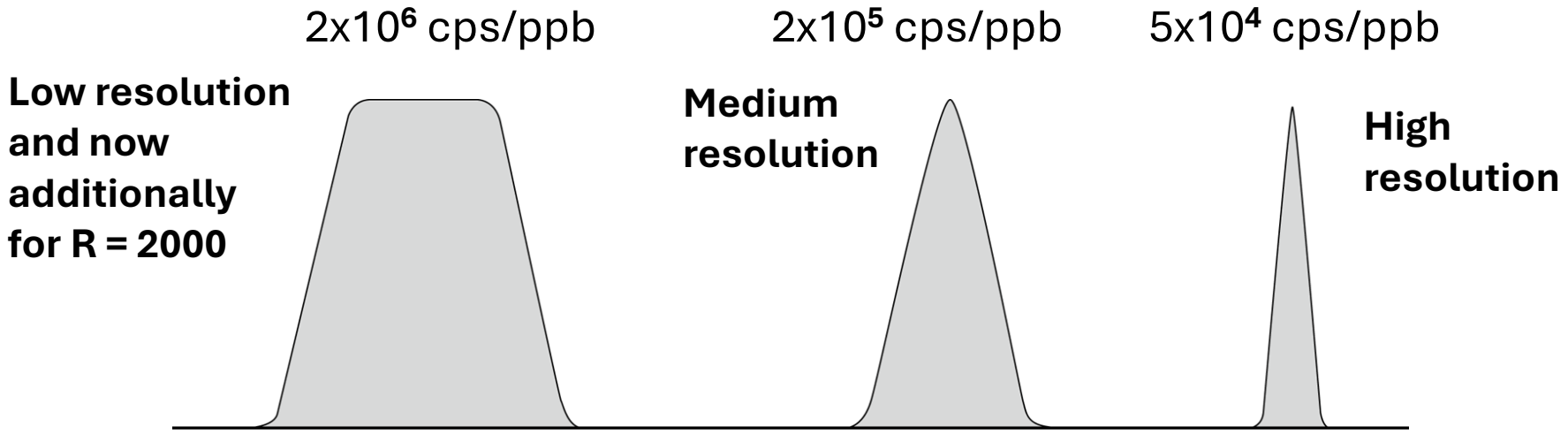
$$R = m / (m_a - m_b)$$



Low-Medium-High Resolution: peak shape

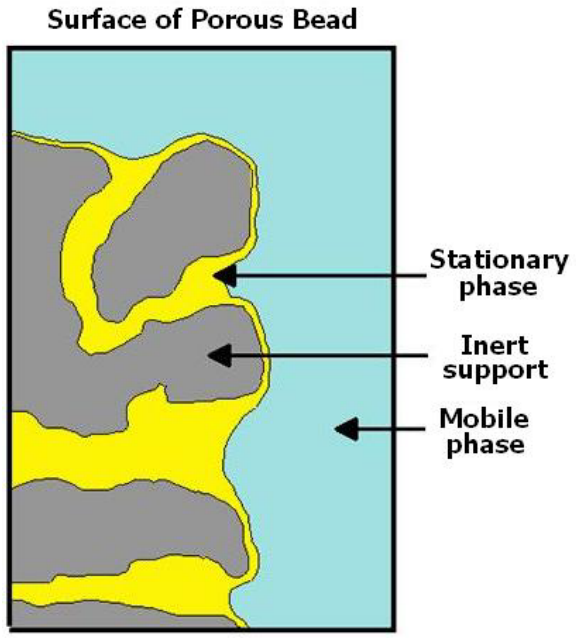
- Using the Low Resolution mode the sensitivity is the highest and the top of the peaks are flat. This is a successful approach for many isotopic systems also

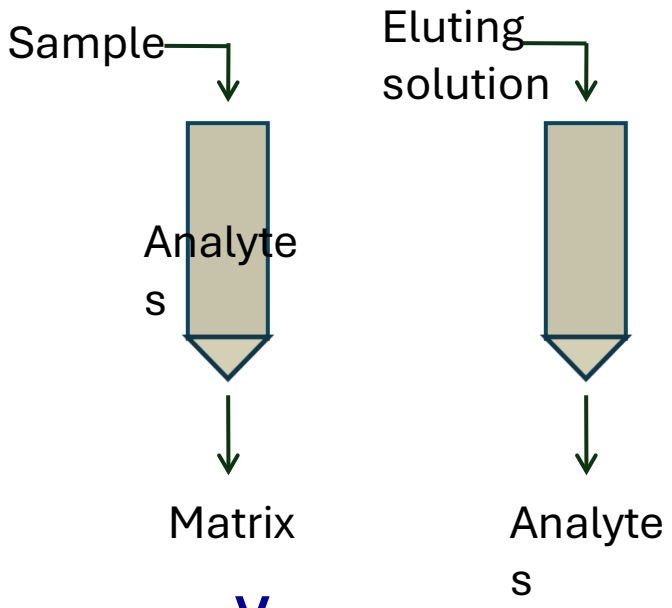
- In higher resolution the peaks have triangular shape, the resolution rise up, but the sensitivity degrease



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

Extraction chromathography





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

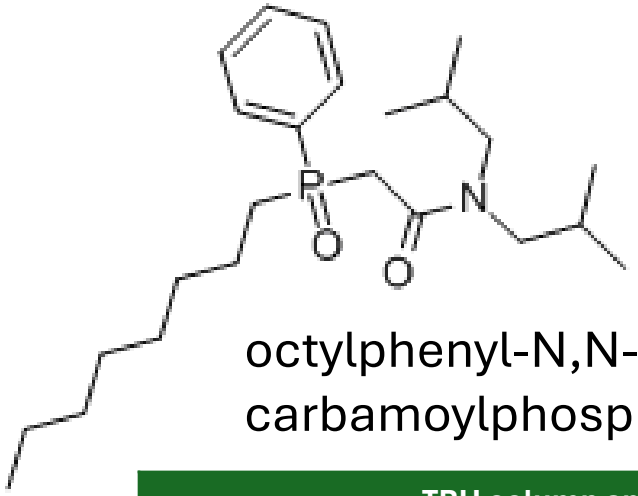
Advantages:

- Matrix removal
- Analyte pre-concentration

Disadvantages:

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

TRU resin (Triskem®)

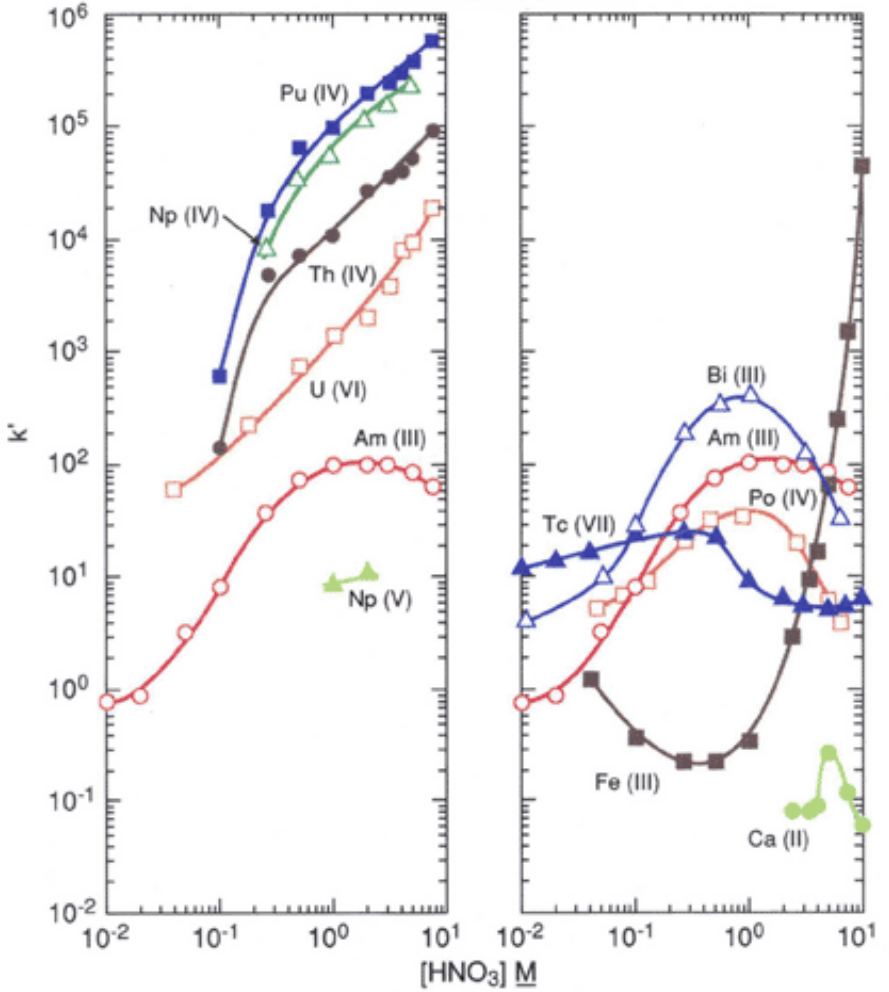


octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide (CMPO)

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

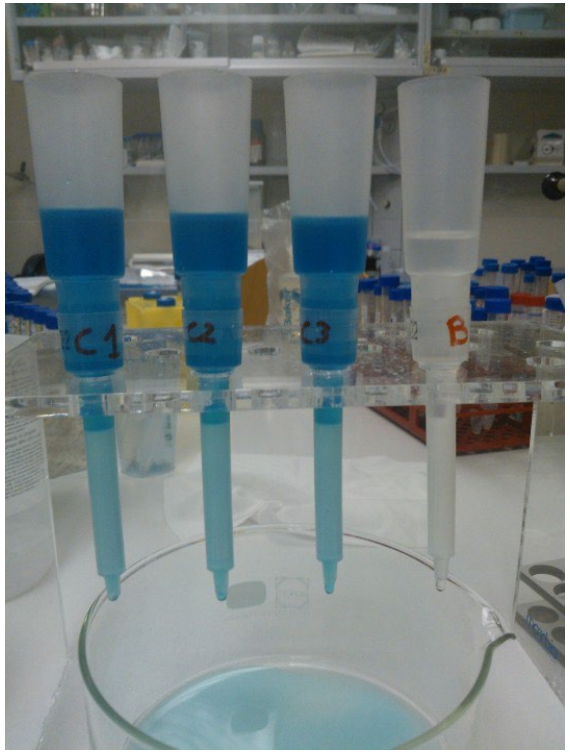
- Work in clean room (class 1000-ISO6)

-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

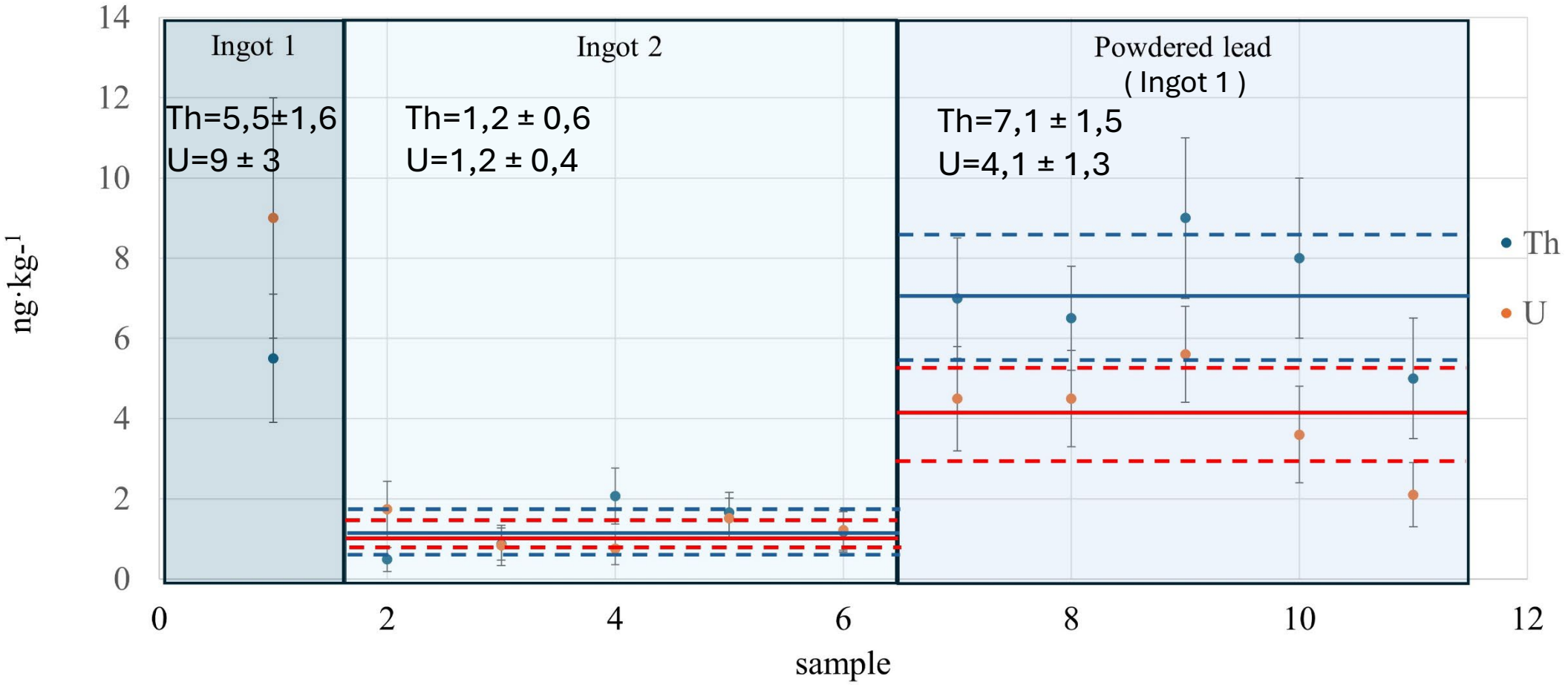
*DL = 3 × BLKStdDev

Cu separation efficiency:

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

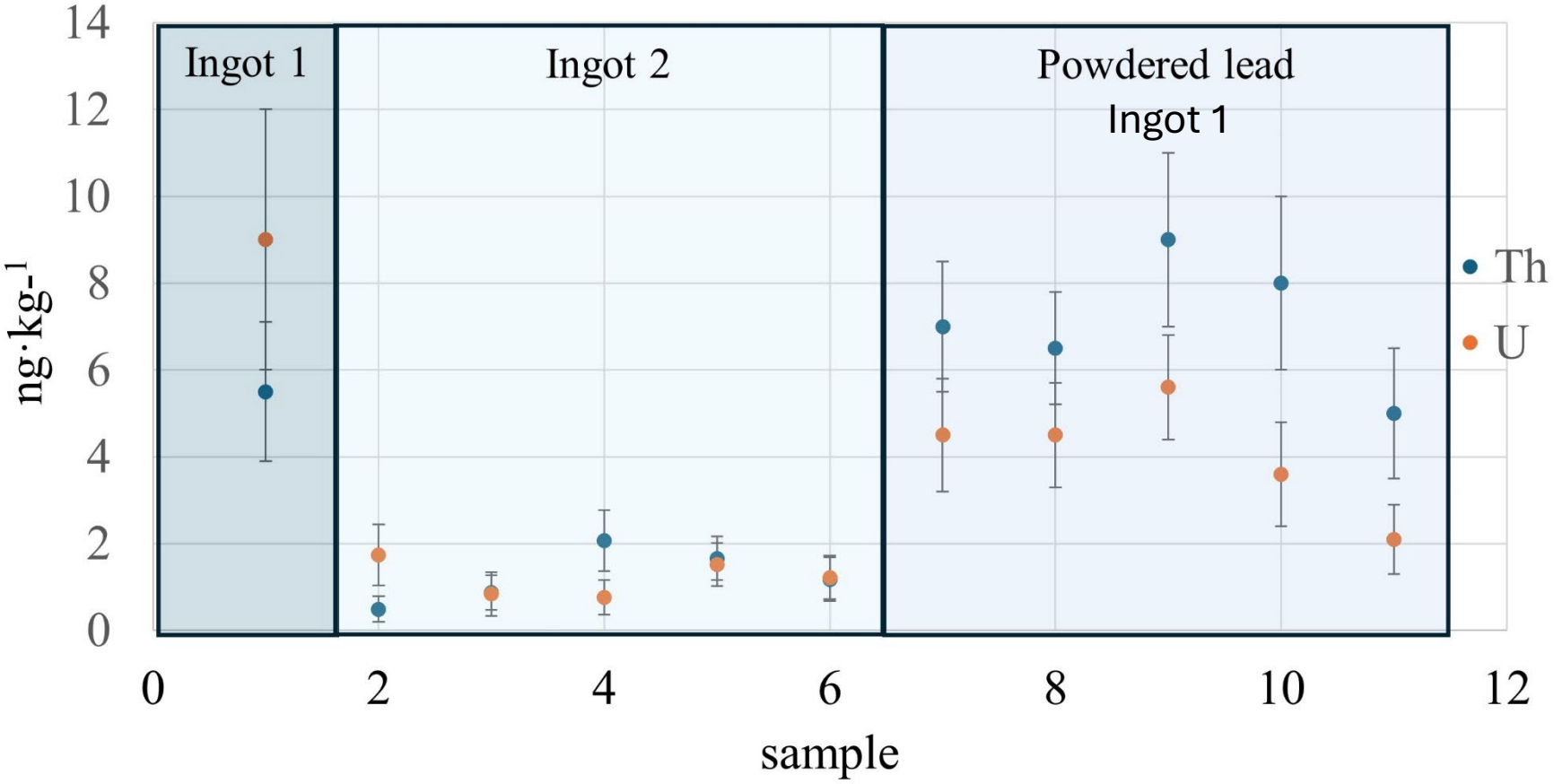
	DL	Recovery %
Th	**very good**	**excellent**
U	**excellent**	**excellent**

Th and U determined by ICP-MS in archaeological lead samples



Th and U concentration given as arithmetic mean (solid line) and expanded uncertainty $U_{CRM} = k \cdot u_{CRM}$ (k = 1) (dotted).

Th and U determined by ICP-MS in archaeological lead samples



- Homogeneity inside ingot 2
- Modest heterogeneity between ingots
- Powdered Lead obtained from Ingot 1 comparable

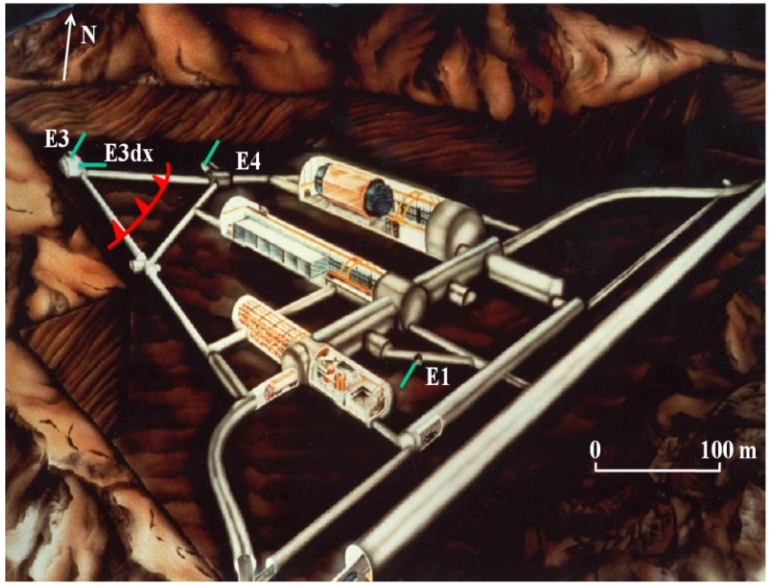
Concentration values shown with their combined standard uncertainties

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

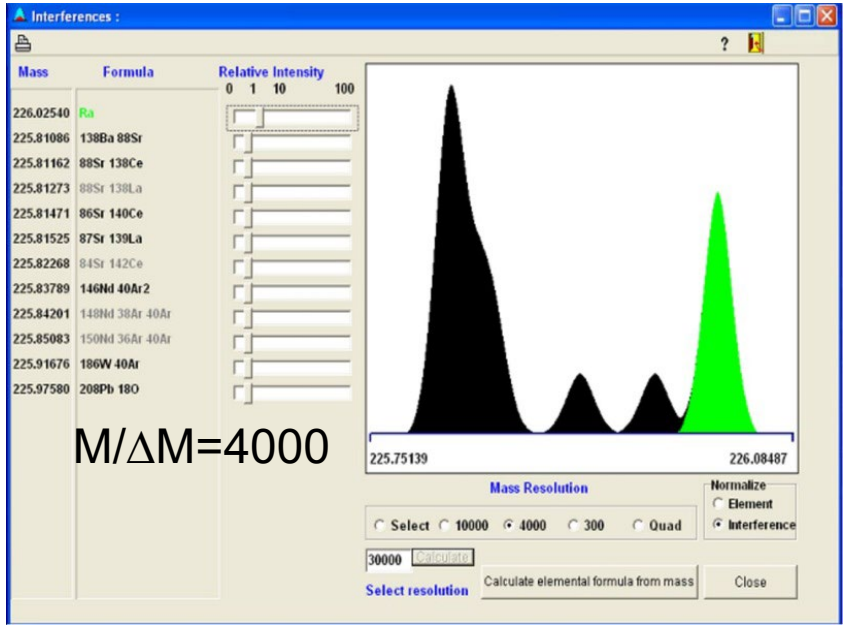
ICP-MS ^{226}Ra measurement

- **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)

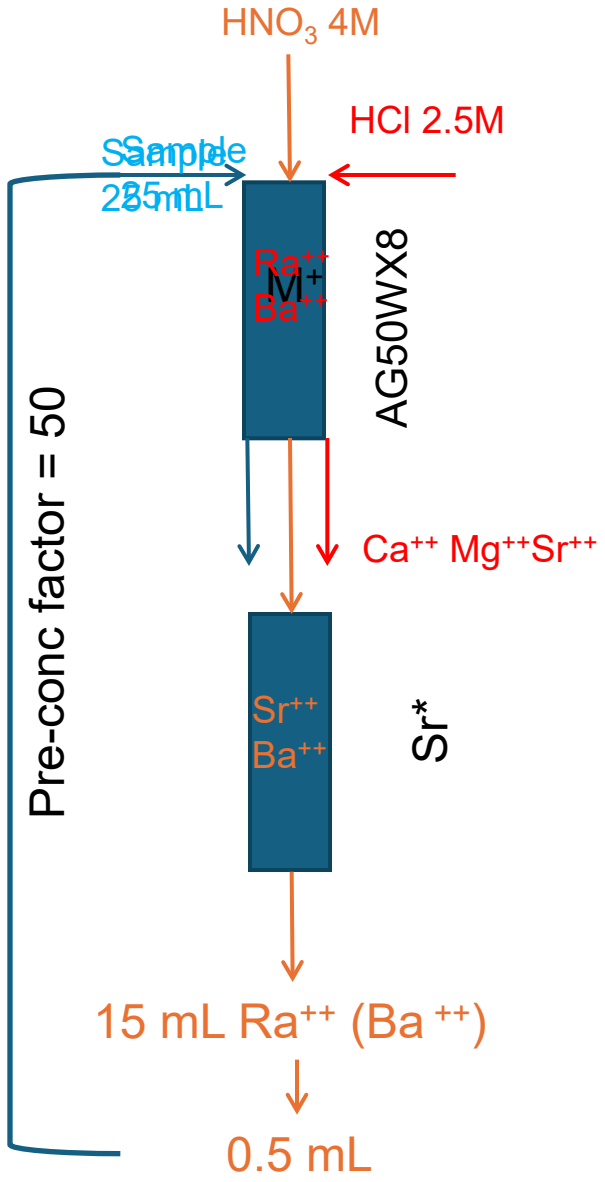
- AG-50W-X8
- Sr*resin

Procedure steps:

1. Pre-wash and conditioning
2. Sample load
3. Wash: HCl
4. Ra elution: HNO_3
   Sample load
5. Rinse

Series connection

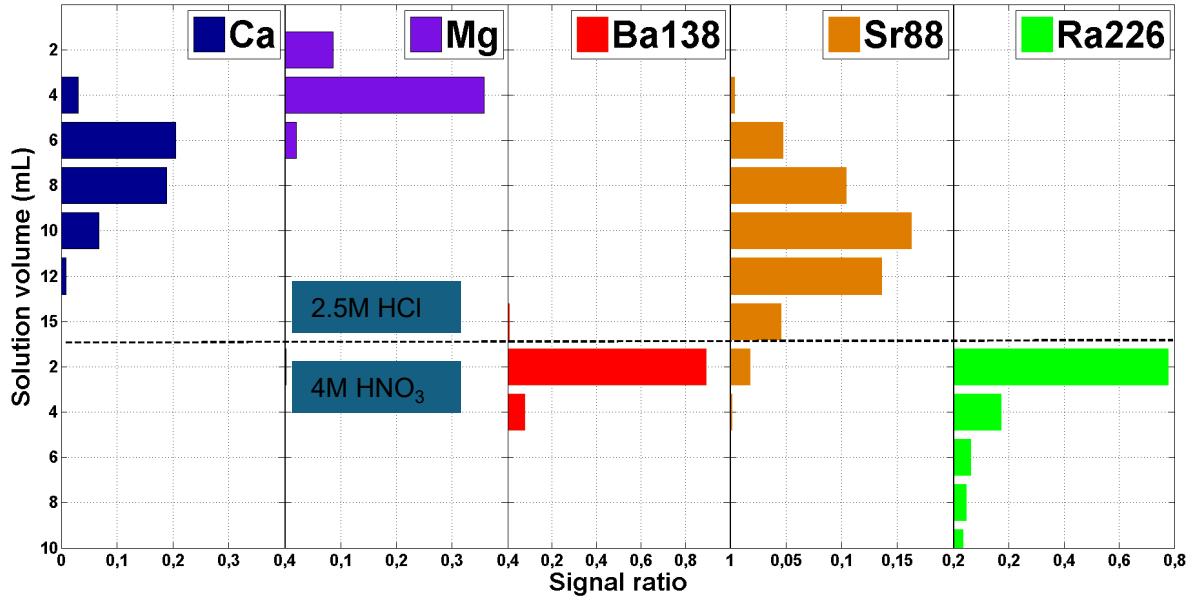
Step 3	Recovery eff. (%)	Separation efficiency (%)			
HCl M	^{226}Ra	^{43}Ca	^{25}Mg	^{88}Sr	^{138}Ba
1.7	86.9	68	98.2	19.8	23.4
2.5	100	99.7	99.9	96.4	12.1
4	64.2	99.8	99.9	99.7	96.2
6	9.1	99.8	99.9	99.6	76.4



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

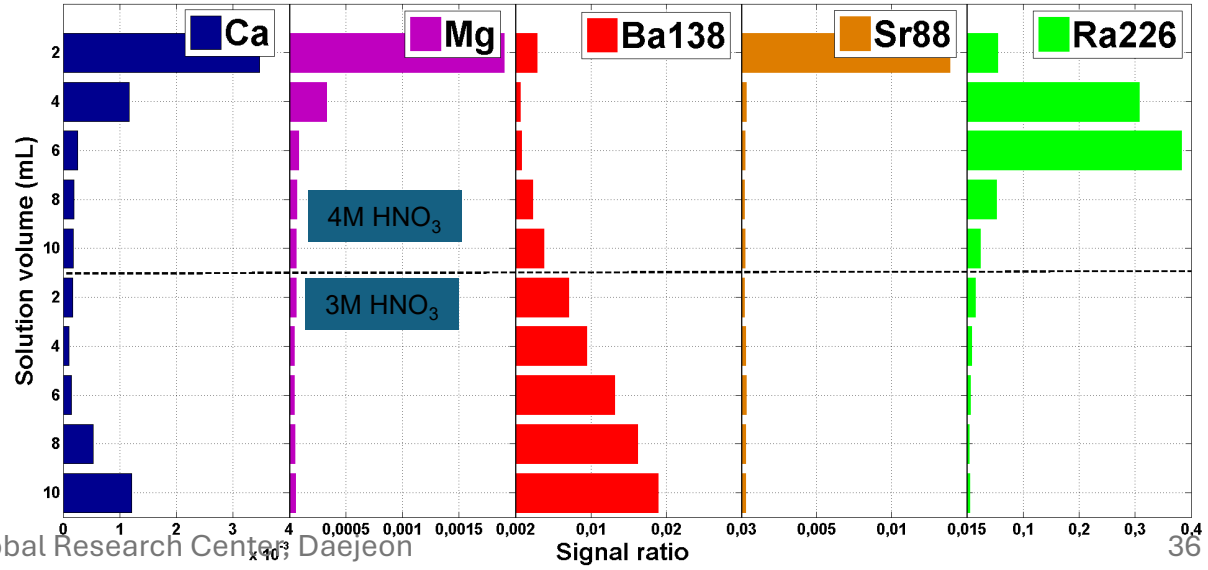
Cationic exchange resin

- 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

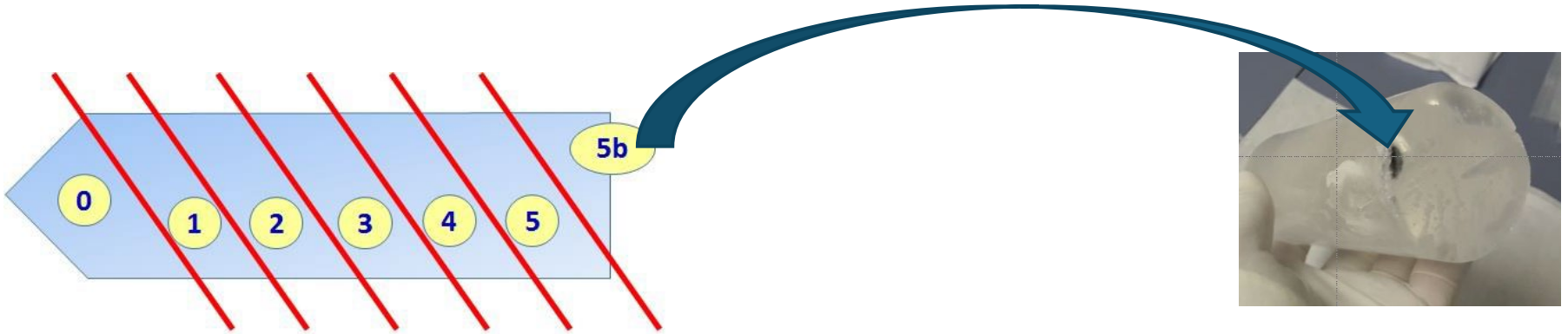


Method performance

- 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

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 %

Radiometric techniques are sensitive to the radiation emitted by radionuclide decay

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

ULB-GRS Ultra Low-Background Gamma Ray Spectrometry

+ Sample treatment free
+ Nondestructive 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