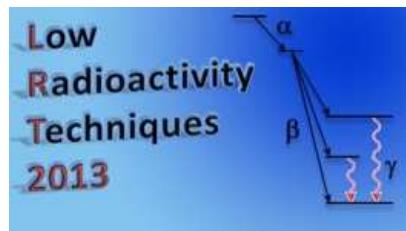
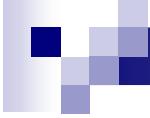




ICP MS measurement of natural radioactivity at LNGS

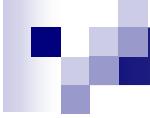


Stefano Nisi
Chemistry and Chemical Plants Service
Gran Sasso National Laboratory



Outline

- LNGS Chemistry & Chemical Plants Service
- MS technique
- LNGS ICPMS instrumentation overview
- Ultra trace level measurements
- Examples of application

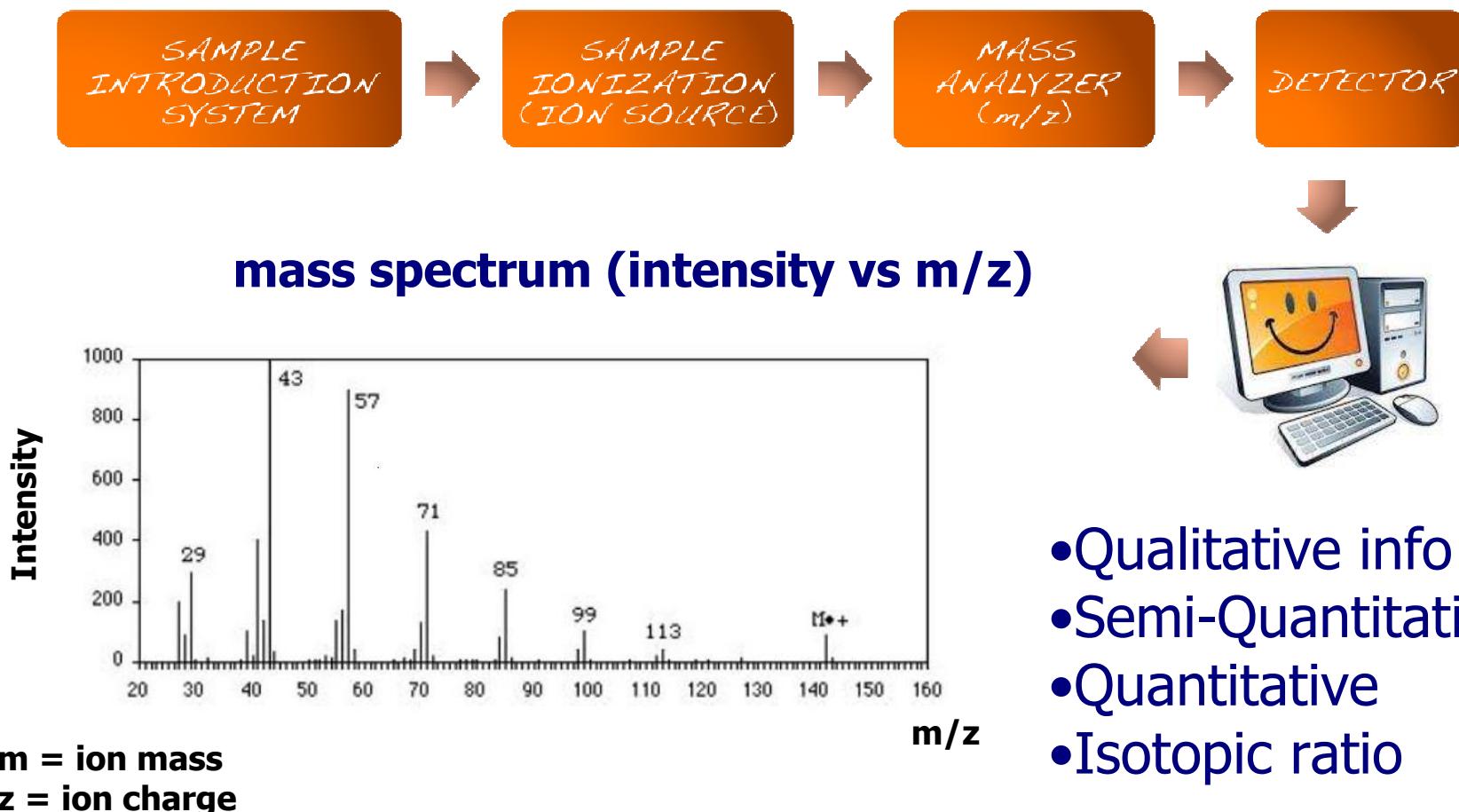


Chemistry & Chemical plants Service

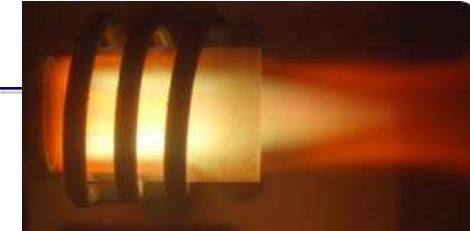
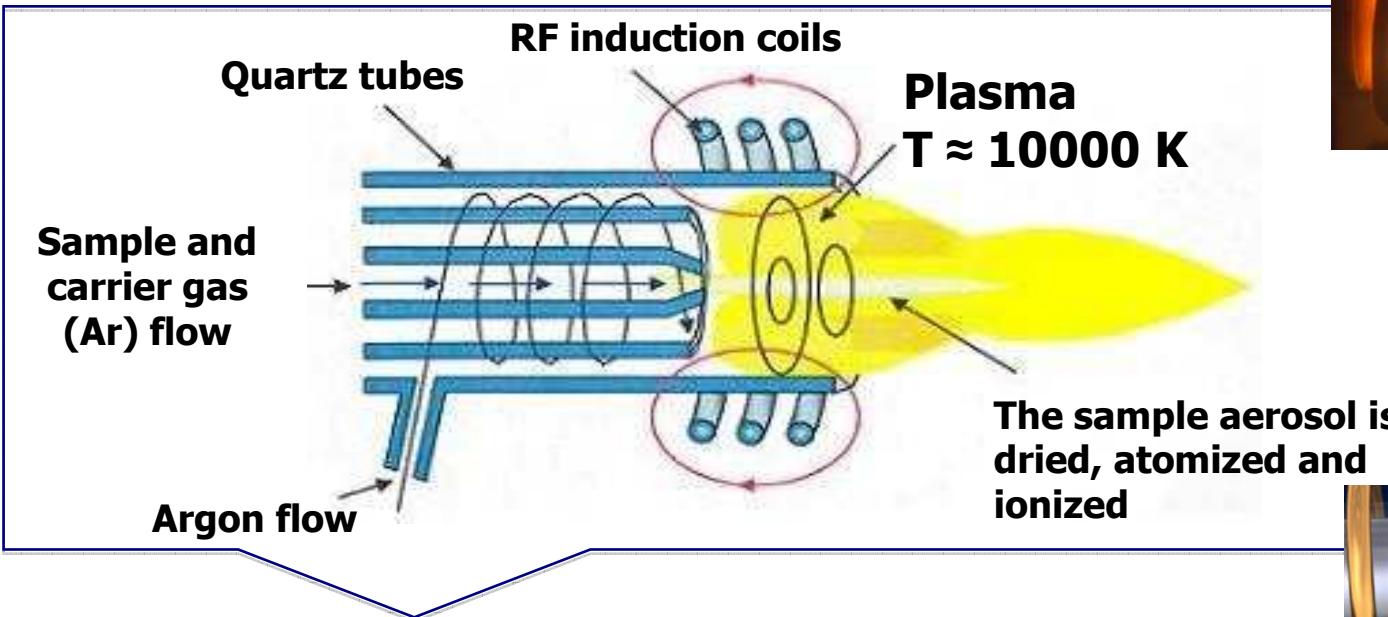
- Technical support to the LNGS experiments for designing and handling chemical plants
- Cleaning of small mechanical and electronic parts for experimental apparatus
- Cleaning of samples for radioactive background by mean γ -ray
- Help for purchasing reagents and chemical compounds for the experiments
- Support to researchers for chemical activity inside the LNGS chem lab
- Analytical measurements

What is mass spectrometry?

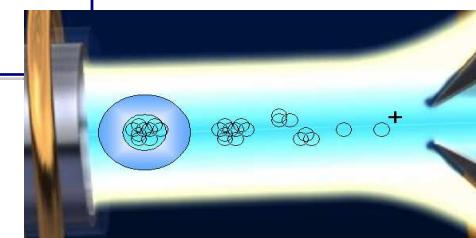
- Identification and quantification of molecules and elements



Inductively Coupled Plasma Mass Spectrometry (ICP MS)



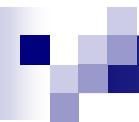
High energy!



Plasma torch ion source

Elemental analysis

- Complete (almost):
- Desolvation
- Atomization
- Ionization



Measurable elements

H																	He
Li	Be																
Na	Mg																
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw				

- AA / ICP / ICP-MS
- ICP / ICP-MS
- Radioactive
- Not Measurable
- Unstable Elements

Ultra - trace

Trace

majors...

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

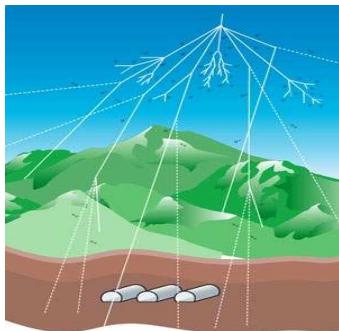
1ppt
(10^{-12} g/g)

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

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

Why ICP MS @ LNGS?

Detection of extremely weak events



1400 m of rock (3600 mwe)

Cosmic ray flux reduction: 10^6

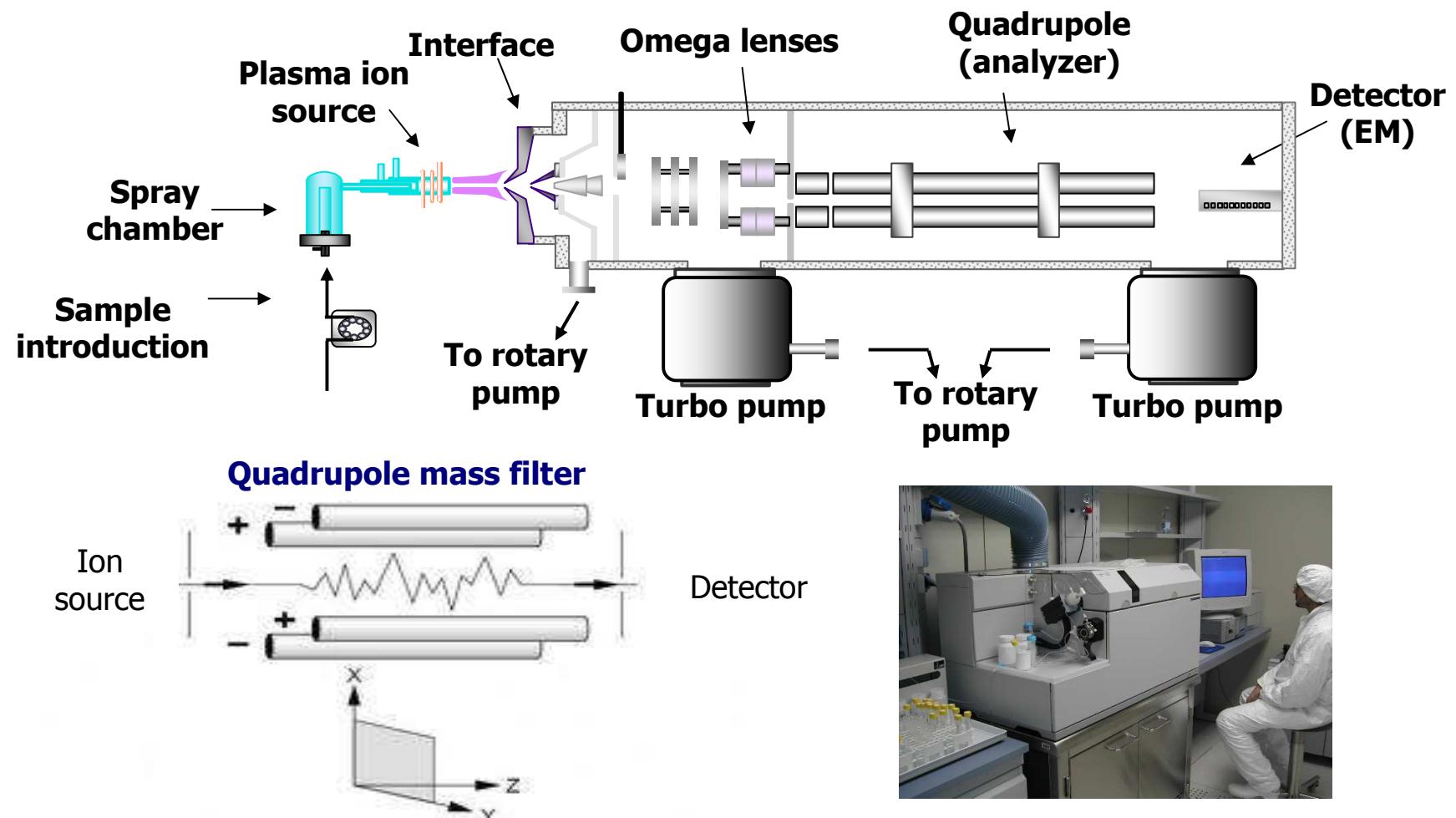
Neutron flux reduction: 10^4

- The underground facility provides the necessary **low radioactive background**
- Selection of **highly radio-pure materials**

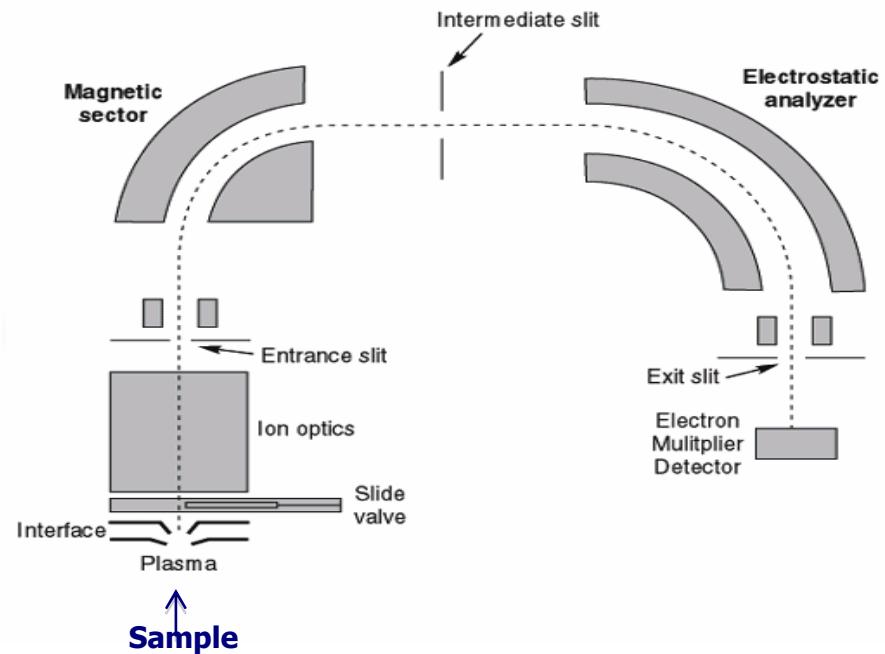
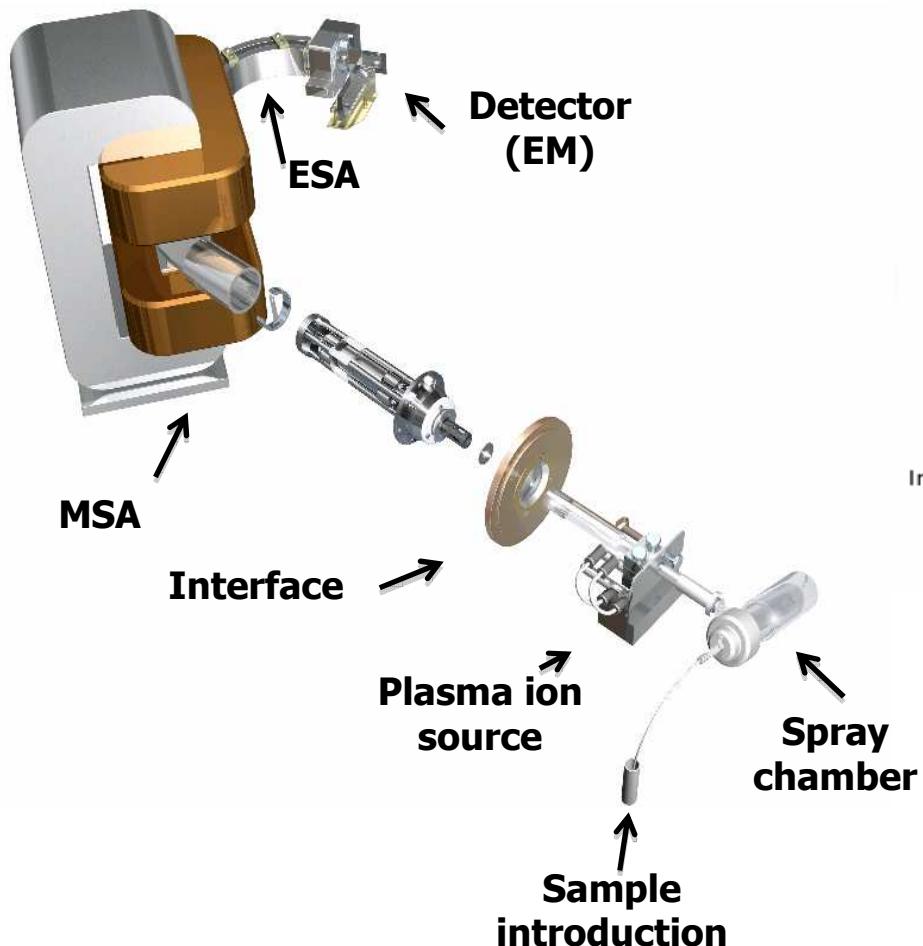


Two ICP mass spectrometers @ LNGS

-ICP QMS (quadrupole mass analyzer) – Agilent 7500a



- High Resolution ICP MS (double focusing mass analyzer) Thermo Element2



**Double focusing mass analyzer
(MSA + ESA)**

Ultra trace level measurement

some issues....

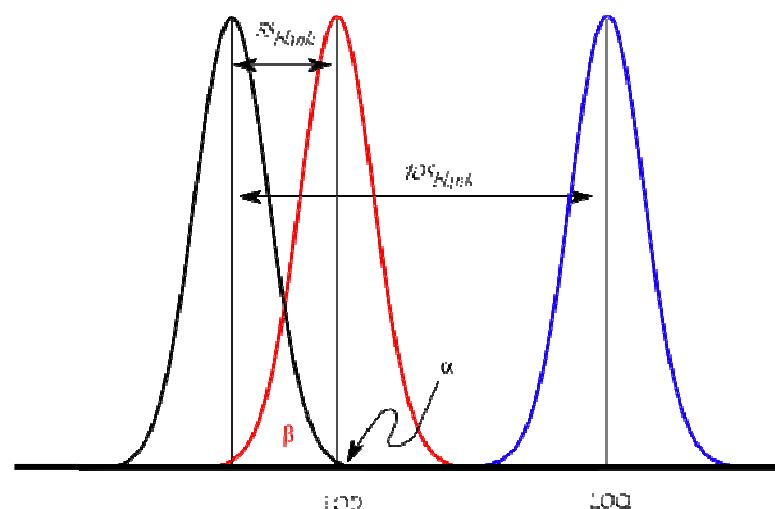
- Risk of contamination
- No validated method available
- Poor availability of Certified Reference Material
- Signal lower than LOQ

Detection Limit

$$DL = 3 \cdot SD_{BLK} \cdot C_{STD} / (I_{STD} - I_{BLK})$$

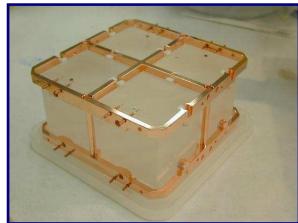
LOQ Limit of quantification

$$LOQ = 10 \cdot SD_{BLK} \cdot C_{STD} / (I_{STD} - I_{BLK})$$

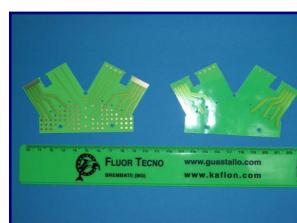


MAINLY: low radioactivity measurements

- **≈200 samples/year (complex matrices)**
- **few hundreds samples/year (reagents and water)**



Cu, TeO₂ and reagents
-CUORE-



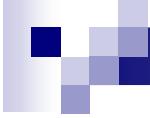
Printed Circuit Board (PCB)
-GERDA-



Metals and alloys
-GERDA, XENON, DARK SIDE-



Al-Mylar insulating foils
-XENON, DARK SIDE-



OUR CHALLENGE:

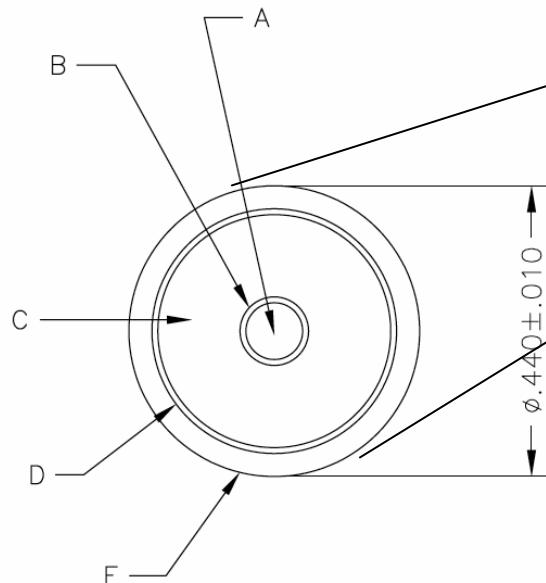
Achievement of better and better detection limits

10^{-15} g/g (ppq) in water samples
 10^{-11} g/g (ppt) in solid samples

Measurement of Th and U in a high voltage (HV) cable (DARK SIDE experiment)

Composite material

- A. #12 AWG (19/25) T.C.
- B. Semicon polyethylene
- C. Insulating polyethylene
- D. Braided shield
- E. PVC jacket



Measurement of the radioactivity background coming from each of the different components

Separation and mineralization of the five components



Metallic components

Dissolution in acidic solution



Plastic components

Burning @ high temperature
(700°C for three hours) in clean
quartz crucibles



Results:

	External jacket (black PVC)	Braided shield (metal)	Insulating PE (white)	Semicon PE (black)	AWG wires (metal)
Th [ppb]	21.0 ± 6	0.50 ± 0.15	0.045 ± 0.014	0.104 ± 0.031	<0.2
U [ppb]	9.0 ± 3	<0.1	0.023 ± 0.007	0.035 ± 0.011	<0.2

Th and U measured content in the five components of the HV cable

Composition:

- PVC jacket: 25.6%_w
- Braided shield: 21.1%_w
- Insulating PE: 32.8%_w
- Semicon PE: 3.7%_w
- AWG wires: 16.8%_w

	ICP MS	γ-spectroscopy
Th [ppb]	5.5 ± 1.6	7 ± 1
U [ppb]	2.3 ± 0.7	4.78 ± 0.34

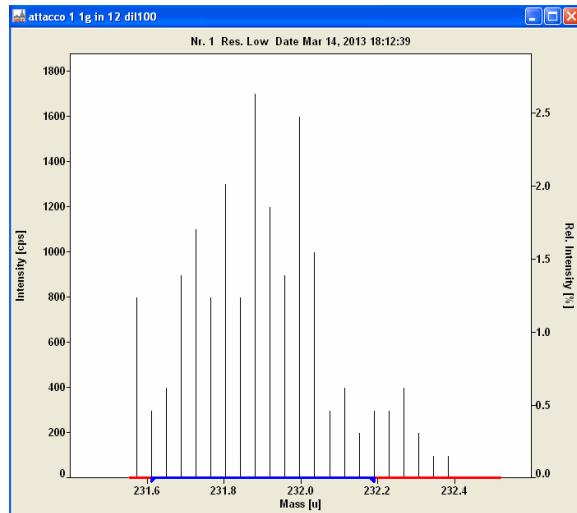
Th and U contamination of the whole cable

Th & U measurement in stainless steel samples (XENON experiment)

Dissolution in acidic solution
DF~1500

	DL [ppb] $3SD_{BLK}$	LOQ [ppb] $10SD_{BLK}$
Th	0.07	0.24
U	0.20	0.63

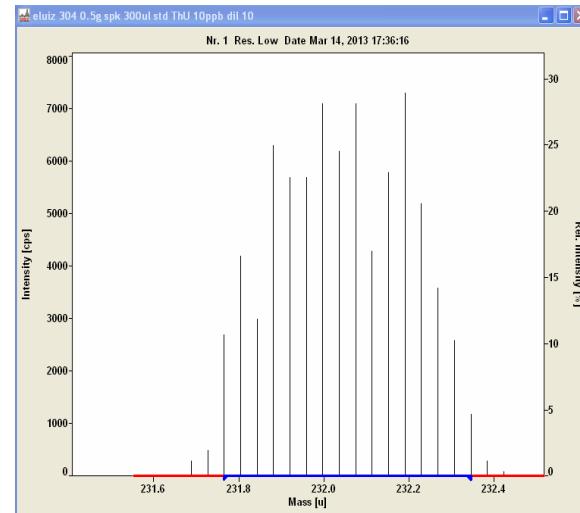
Th peak shape (LR)



Accurate mass
232.0375 amu

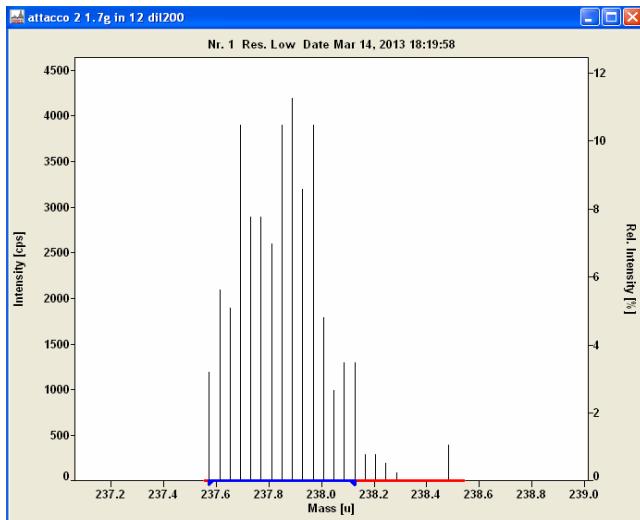
Diluted sample
231.8844

Th STD solution
232.0388





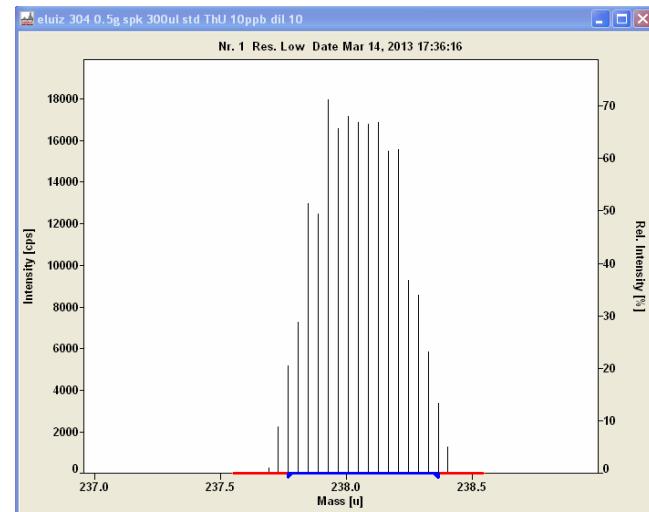
U peak shape (LR)



Accurate mass
238.0502 amu

Diluted sample
237.8445

U STD solution
238.0564



Evidence of isobaric interferences!

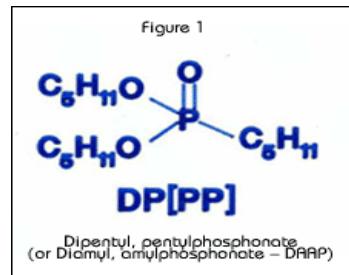
Investigations about the nature of the interference are still in progress

Th & U Chromatographic Extraction

AISI 304	Reference value	Measured value	Separation efficiency
	[%]	[%]	[%]
V		0.1	99.83
Cr	18/20	18	99.99
Mn	2	1.9	99.99
Fe		70	99.95
Co		0.15	99.99
Ni	8/10,5	7.5	99.99



UTEVA resin from Triskem based on the capability of DAAP to complex Th and U



	DL[ppb] $3SD_{BLK}$	LOQ[ppb] $10SD_{BLK}$
Th	0.012	0.04
U	0.014	0.05

AISI 316 Stainless Steel 56 mm thick				
	UTEVA treated (LR)	UTEVA treated (MR)	Not extracted (LR)	Not extracted (MR)
Th [ppt]	2213	2153	3628	2274
U [ppt]	387	381	2690	537
AISI 316Ti Stainless Steel , Melt 528194				
Th [ppt]	49	51	2192	<200
U [ppt]	97	117	1782	231

Dissolution in acidic solution DF~1500

- + relatively fast
- + information about all elements
- High DL
- Only MR reliable

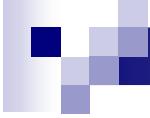
Th, U Chrom. Extr. DF ~150

- + Better DL
- + Interferences solved
- + Instrumental contamination clearly reduced
- Time consuming

ICP-MS/ γ -Ray Spectroscopy comparison

Samples	^{232}Th	^{228}Ra	^{228}Th	^{238}U	^{238}U	^{235}U	^{226}Ra
Stainless Steel AISI 316Ti, Melt 528194	0.2	<5.5	<3.8	1.2	<200	<2.9	<0.54
Stainless Steel 5 mm AISI 316, lot A2002778	0.4	<0.97	<0.5	4	<29	<1.8	<0.55
Stainless Steel 56 mm AISI 316	9	6.1 ± 1.1	12 ± 0.8	5	<109	<4.2	6.1 ± 0.6

All values are expressed in **mB/Kg**.
ICP MS measurements uncertainty is about 30%



Conclusions

- ICPMS is a fundamental technique for the experiments searching for rare events at LNGS
- By the application of both ICP MS and ULL GRS it is possible to have more complete and complementary information
- The study and development of new sample preparation procedures allow the achievement of better and better detection limits and reliable analysis

