Laser Ablation ICP-MS technique for rare event experiments

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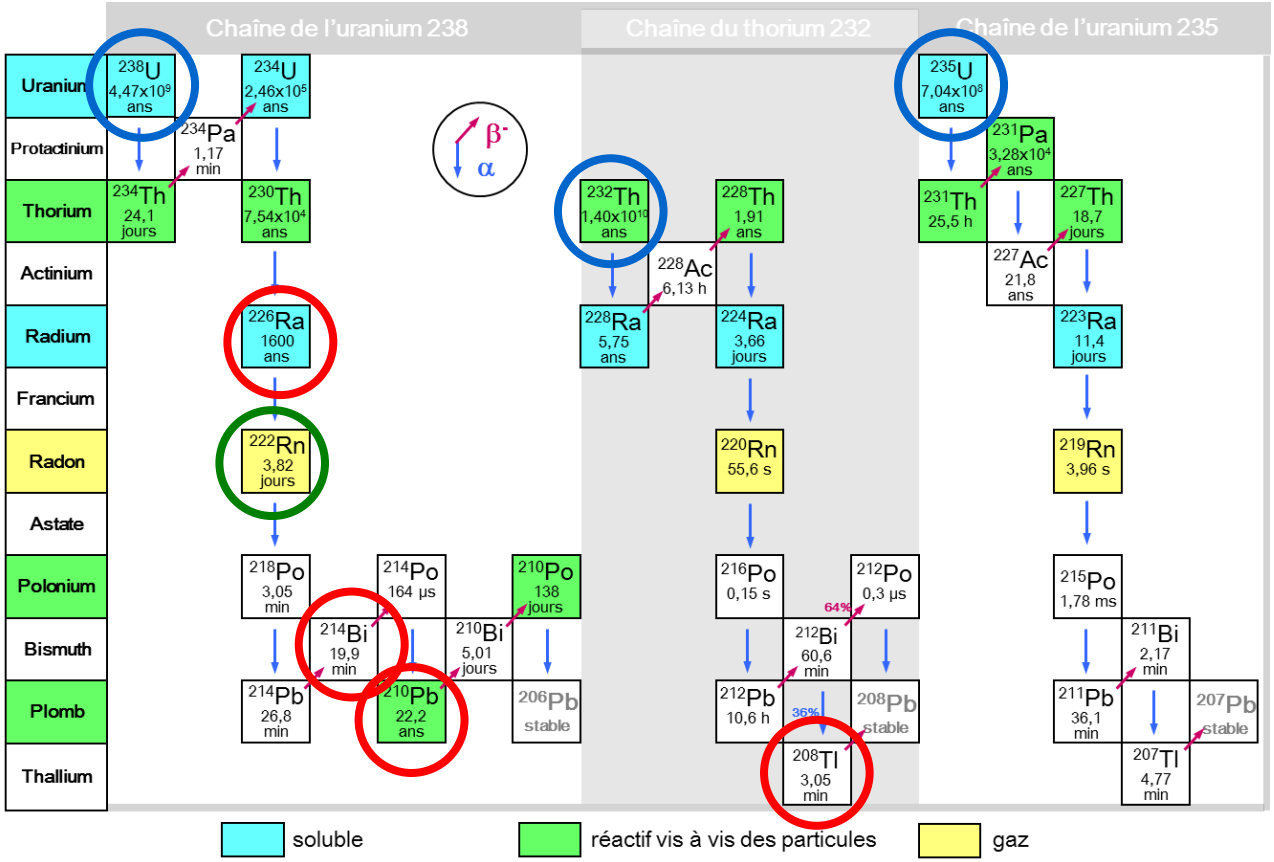
Outline

- ✓ Description of the ICPMS and Laser Ablation ICP-MS techniques
- ✓ Application to samples of interest for rare event experiments

Natural radioactivity : our main ennemy!

✓ Primordial radioactivity, cosmogenics, man-made radioactivity



✓ Long-lived isotopes~10^9 y (head of the $^{238}U/^{232}Th$ chains and ^{40}K)

→ NAA, ICPMS, LA-ICPMS techniques

✓ Medium and short-lived isotopes ≤10^5 y (**^{226}Ra, ^{214}Bi, ^{210}Pb, ^{208}Tl, ^{60}Co,…)**

→ low background γ/α/β spectroscopy techniques

✓ Gaseous isotopes (**^{222}Rn)**

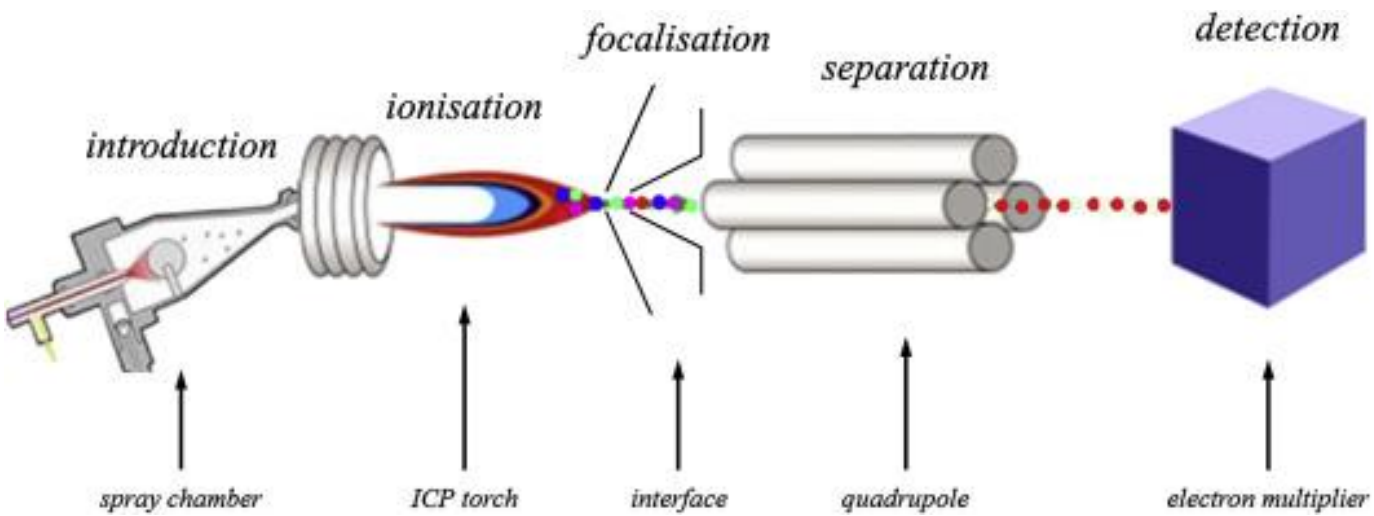
→ Dedicated techniques

→ Complementary techniques to screen all the critical materials for rare event expts

Principle of the ICP-MS technique

Inductively coupled plasma mass spectrometry (ICP-MS)

- ✓ Sample usually dissolved by acids in ultrapure water (liquid phase)
- ✓ Liquid samples to formate aerosol in nebulizer
- ✓ Introduction of aerosols into an argon plasma at T>6000 K, decomposition of the molecules and ionization
- ✓ Ions extracted from the plasma into mass spectrometer region and detected by an electron multiplier sensor



Note: very difficult to measure ^{40}K due to ^{40}Ar used for plasma

Sample preparation and sensitivity

Several equipments are needed for the pre-treatment of the sample without any contamination

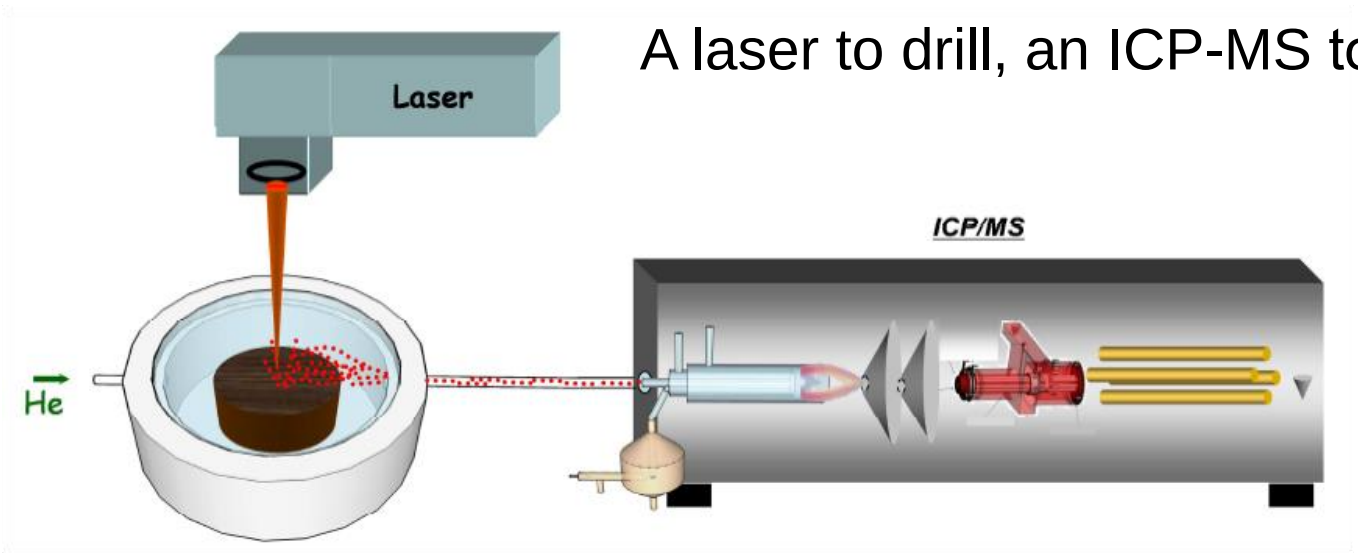
- ✓ Class 10000 clean room
- ✓ Ultra-pure deionized water, nitric acid, microwave digestion, ultra-sonic cleaner…

→ it is critical to have ultra-clean vessel and acids for blank test in order to reach a sub-10^{-12} g/g sensitivity for U/Th in critical materials

→ Not extensively developed in France for our field but several installation around the world (for example PNNL, USA)

Principle of Laser Ablation ICP-MS

Concept: to replace the chemical preparation of a sample by using a laser in ablation mode



A laser to drill, an ICP-MS to count…

Main advantages of LA-ICPMS: small risk of sample contamination and fast access to the spatial distribution of the U/Th radionuclides

A bit of history

1983 1985 1990 1995 2000 2005 2010 2015 2020

Big Bang
(first ICPMS)

694 nm, Nanosecond, 10 Hz, *(Gray et al,1985)*

1064 nm, Nanosecond, 10 Hz, *(Arrowsmith et al, 1987)*

266 nm, Nanosecond, 20 Hz *(Chenery et al, 1993)*

213 nm, Nanosecond, 20 Hz *(Jeffries et al, 1998)*

193 nm, Nanosecond, 20 Hz *(Geertsen et al, 1994)*

785 nm, Femto, 10 Hz *(Russo et al 2002)*

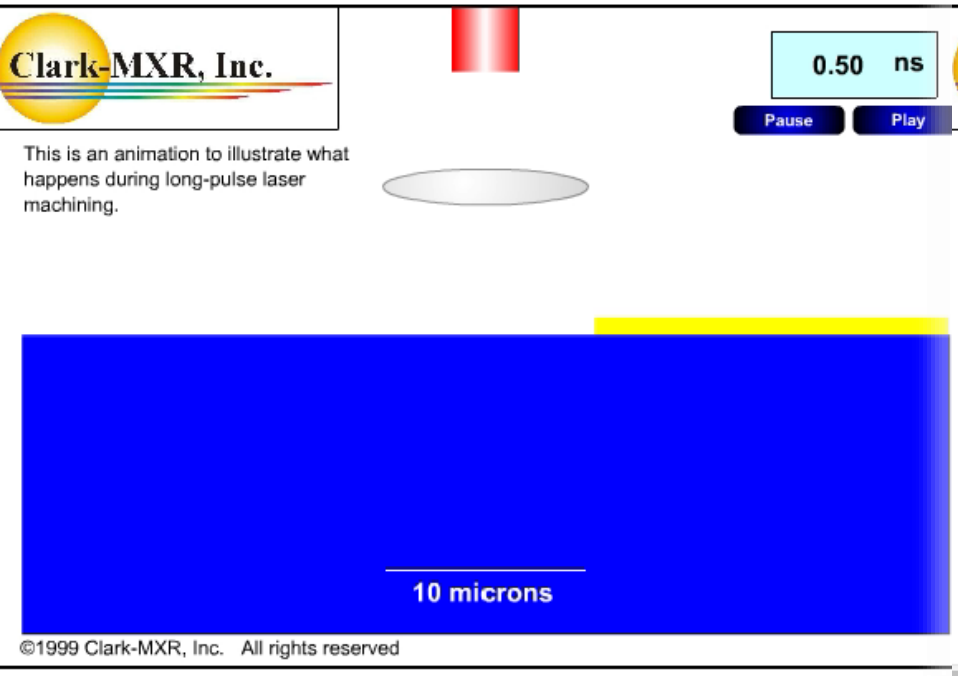
266/196 nm, Femto, 20 Hz *(Poitrasson et al 2003)*

1030 nm, Femto, 10 kHz
(Pécheyran et al 2005)

257 nm, Femto, 100 kHz,
(Pécheyran et al, 2013)

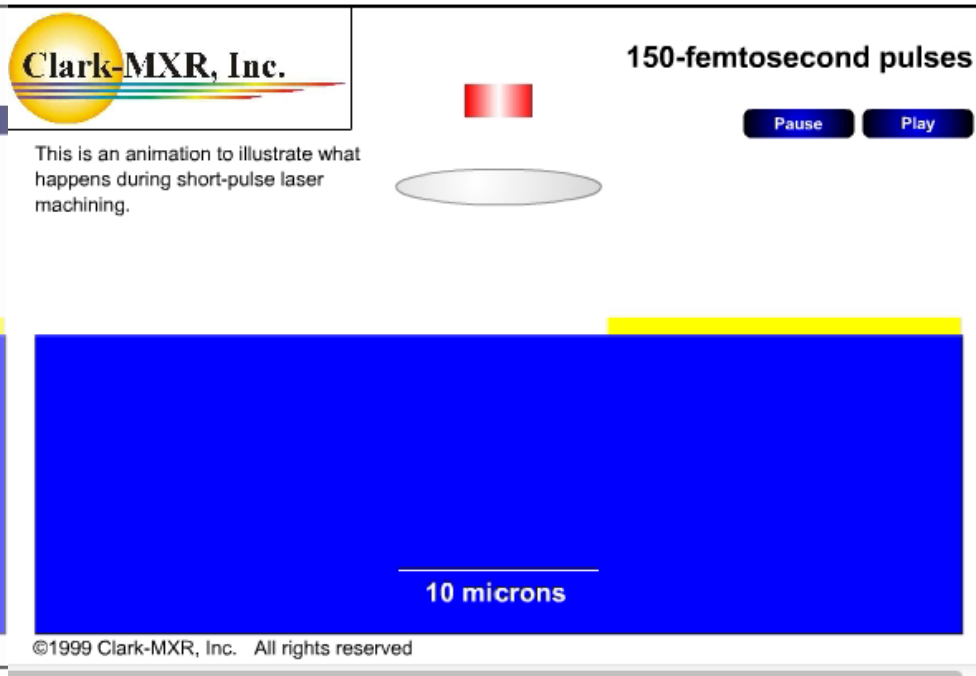
Nano versus femto laser

« Long » laser pulse duration ~ 10^{-9} s



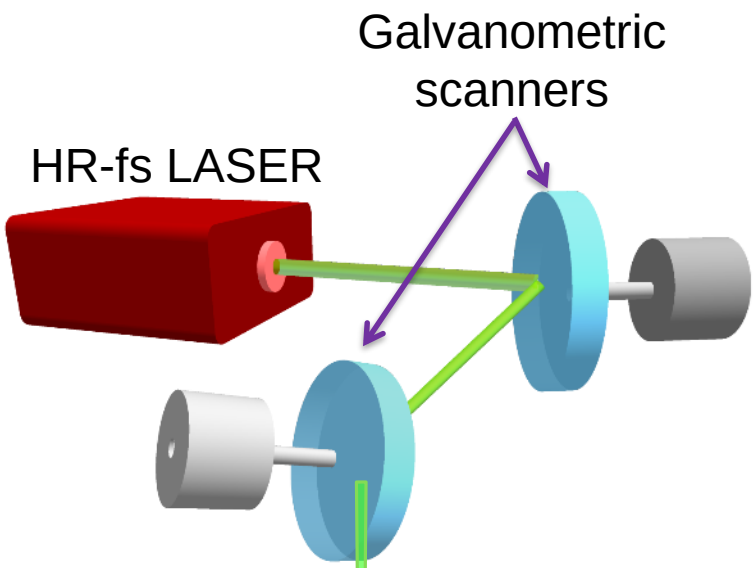
- Thermal effects
- Systematical effects (larger size of particles, fractionation, redeposition)
- Uncertainties on depth/volume ablated

Short laser pulse duration ~ 10^{-13} s



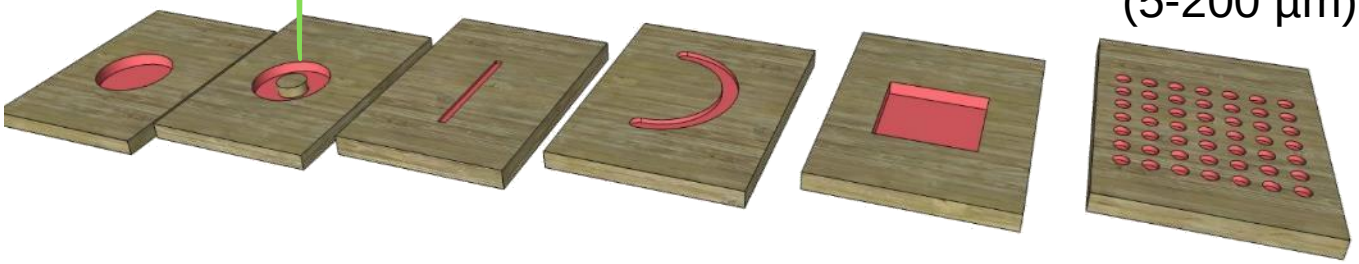
- No thermal effects
- Less systematical effects (small size of particles, negligible fractionation effect)
- High depth resolution

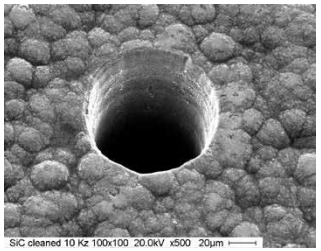
Shaping technique of the fs laser beam



Possibility to move in 2D the sample and/or the laser beam in order to fit with the morphology of the sample

- Size of the beam ~10 µm
- High repetition rate <100 kHz
- Translation speed < 2 m/s





Advantages of the UV fs LA-ICPMS

- ✓ Alternative method to classical ICPMS
  - Direct and fast analysis without chemical preparation
  - Smaller risk of sample contamination
  - Access to the refractory matrix samples

- ✓ Poweful tool for micro-analysis
  - Quasi non-destructive technique
  - Micro-analysis from few µm to few 1000 µm
  - 2D mapping to study the homogeneity of a given surface
  - High precision depth profile (sub µm)

Bottleneck of LA-ICPMS: quantification

The mass of ablated sample depends on:

- ✓ the laser: energy, wavelength, duration of the pulse, rate of laser shots, beam diameter
- ✓ the sample: optical, mechanical and thermal properties

→ using a UV fs laser is limiting strongly systematical effects (fractionation, small size of the particles for a more accurate atomization/ionization efficiency measurement,…)

→ need of a reference material similar to the sample of interest

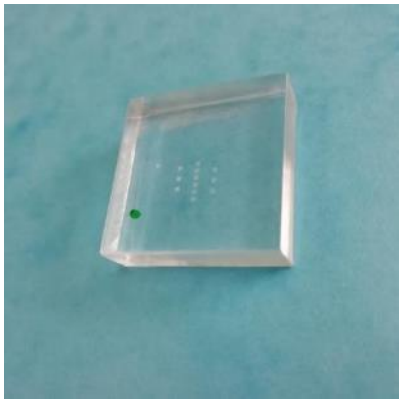
Collaboration between CENBG & IPREM

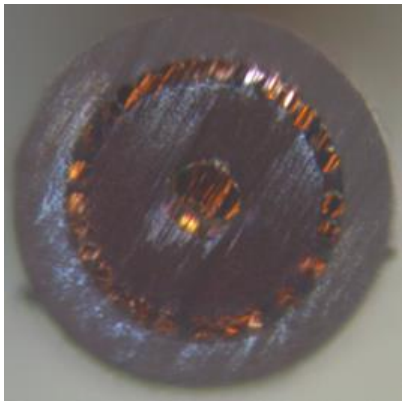
- CENBG involved for many years in neutrino physics with low background measurements expertize

- Collaboration initiated in 2019 with IPREM laboratory in Pau, world-wide experts in LA-ICPMS using fs lasers

- Goal: to use LA-ICPMS for quantitative ultra-low level measurements of U/Th and mapping of materials for rare event experiments

Tests performed on acrylic samples and µ-coaxial cable

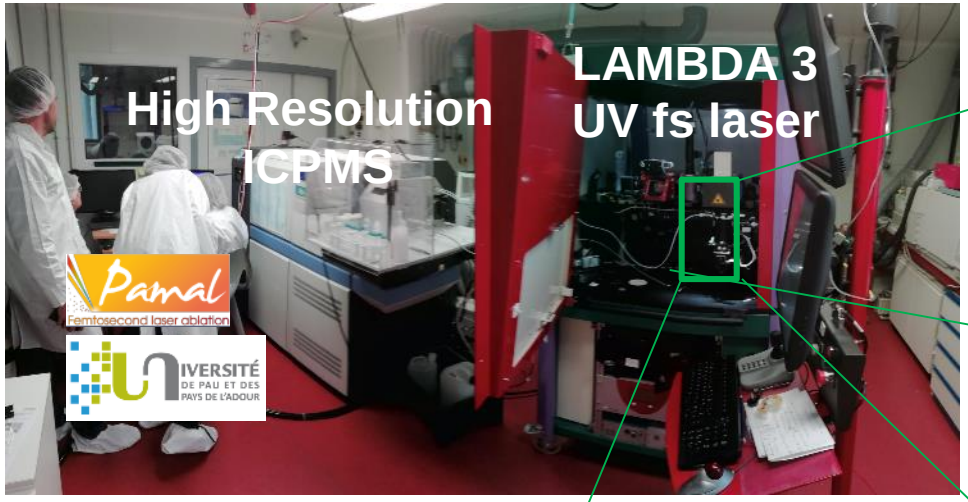


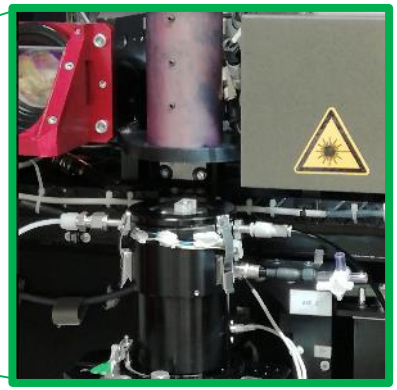


Collaboration between CENBG & IPREM

UV fs laser ablation HR-ICPMS @ Pau

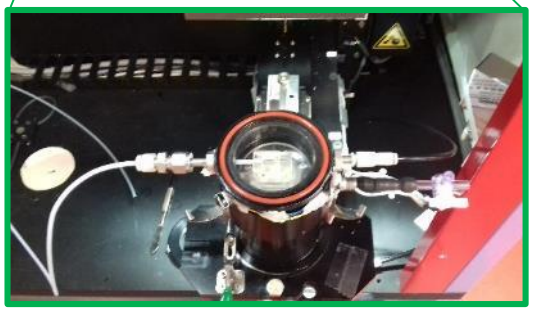
Unique in the world. 100% made in Aquitaine region (France)





ICPMS

- High Resolution ICPMS with jet interface (most sensitive ICPMS)
- m/Δm~300-10000
- Optimized for U/Th

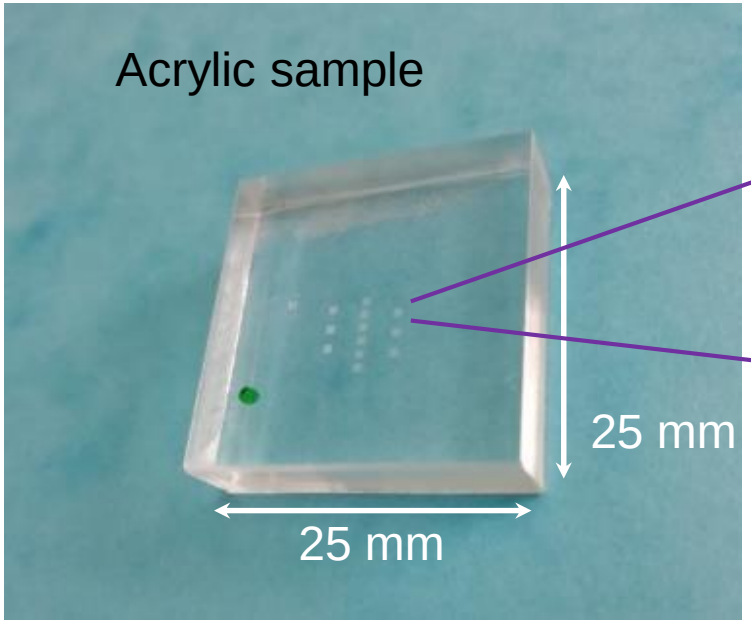


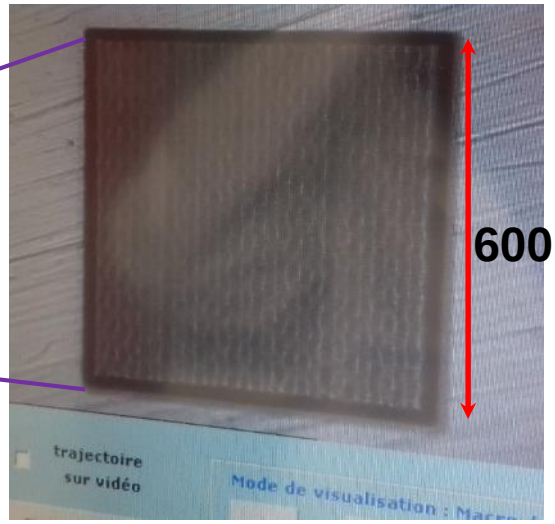
Laser ablation cell (sample size limitation)

UV fs laser :

- λ=257 ns
- Pulse duration: 360 fs
- Energy per pulse: few µJ
- Frequency: 0-300 kHz
- Spot size: 5-10 µm
- Speed of the scan: <2 m/s

LA-ICPMS for acrylic samples





2D scan of a square of 600x600 µm^2 with a laser spot of 8 µm

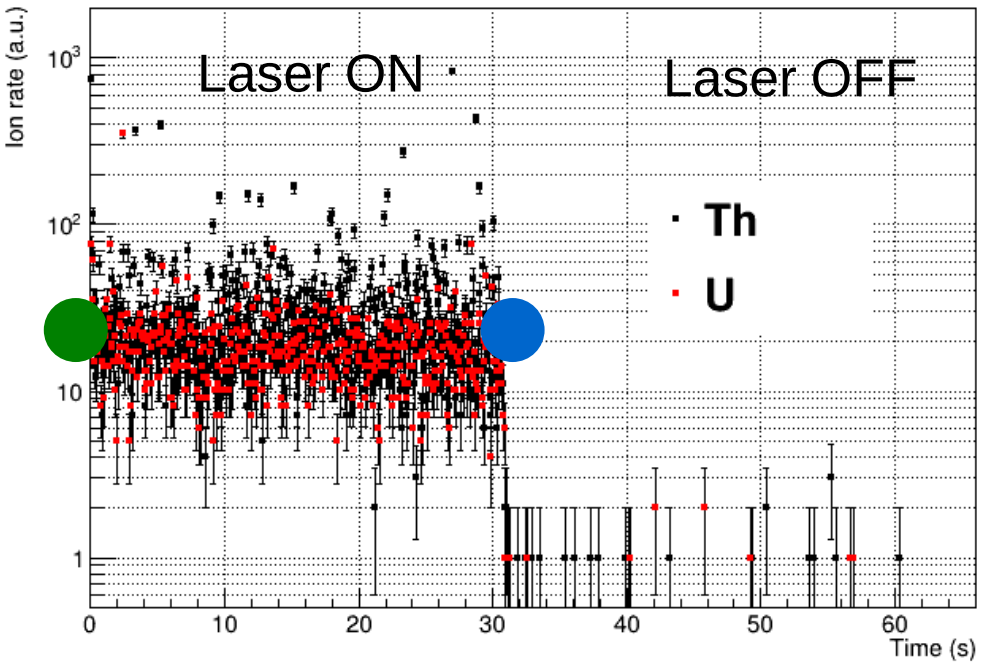
UV fs laser features :

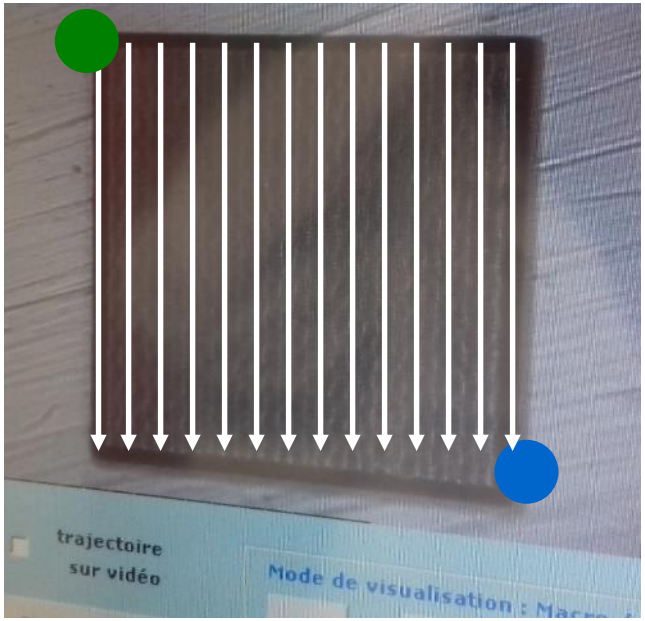
- λ=257 nm
- Duration: 360 fs
- Energy: ~ µJ/pulse
- Frequency: ~few 100Hz
- Spot size: 8 µm

What are the level of U and Th impurities on the surface and in the bulk of the acrylic sample ?

Protocol of measurement

sample background





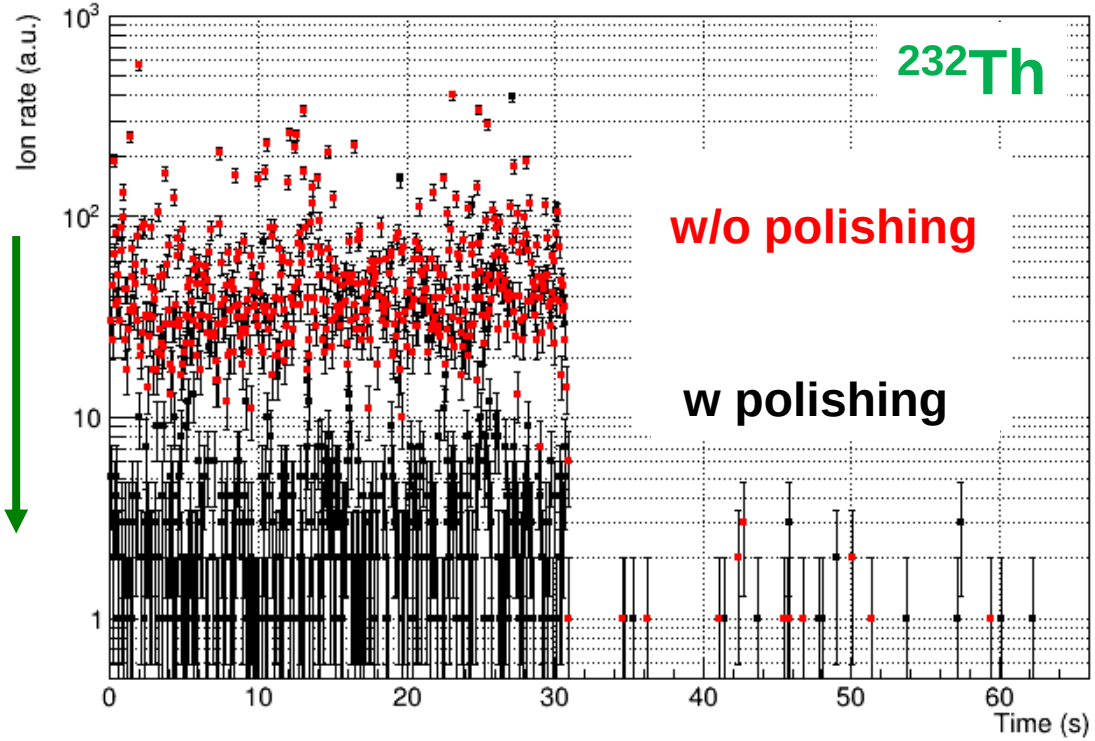
- Only 30 seconds to scan a square of 600x600 µm^2
- Background measurement performed just after during a similar duration

Acrylic: polished or not polished ?

Example of two acrylic samples measured:

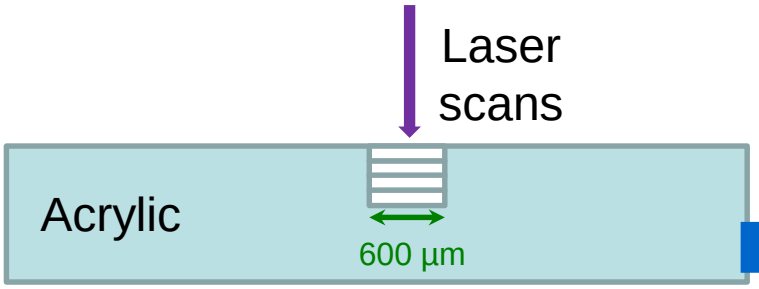
- one **with polishing** process applied on the top surface
- one **without polishing**

One order of magnitude !

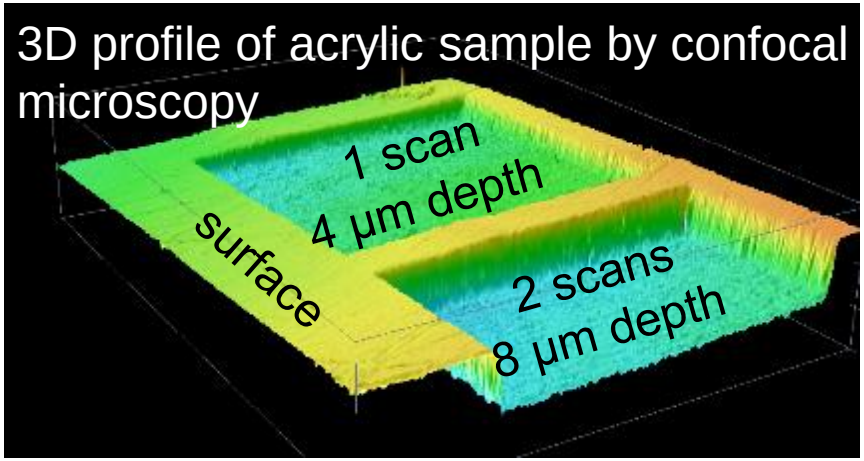


→ very powerful tool to measure the U/Th contamination and to choose the best surface treatment of a given material

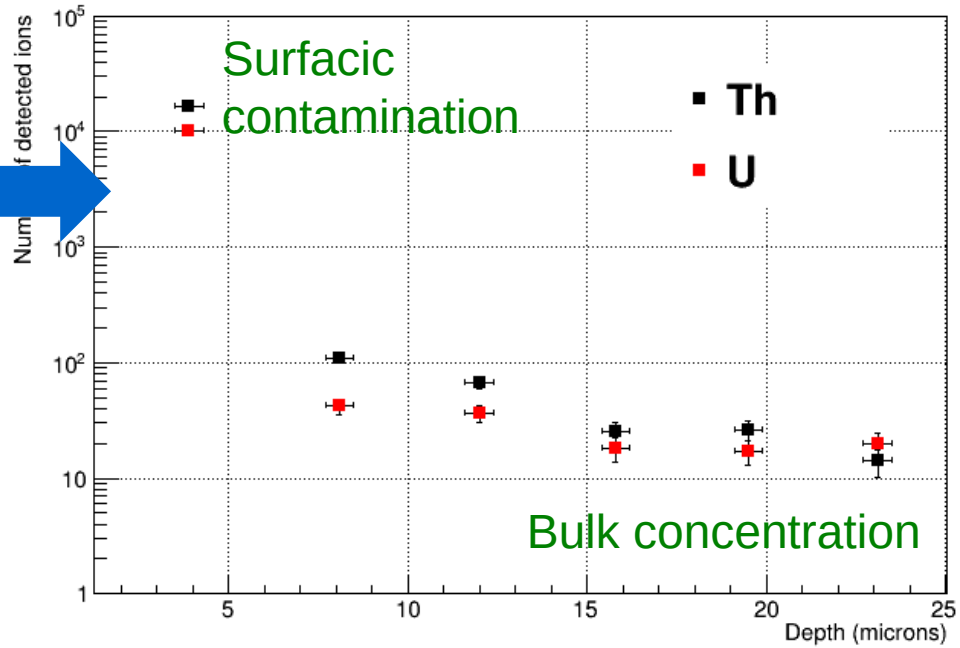
Depth profile of U/Th concentration



Several 2D laser scans
to explore the Z-axis



Good reproducibility of the ablated volume after several scans



→ U and Th contamination of the acrylic is located at the surface in the first 4 µm

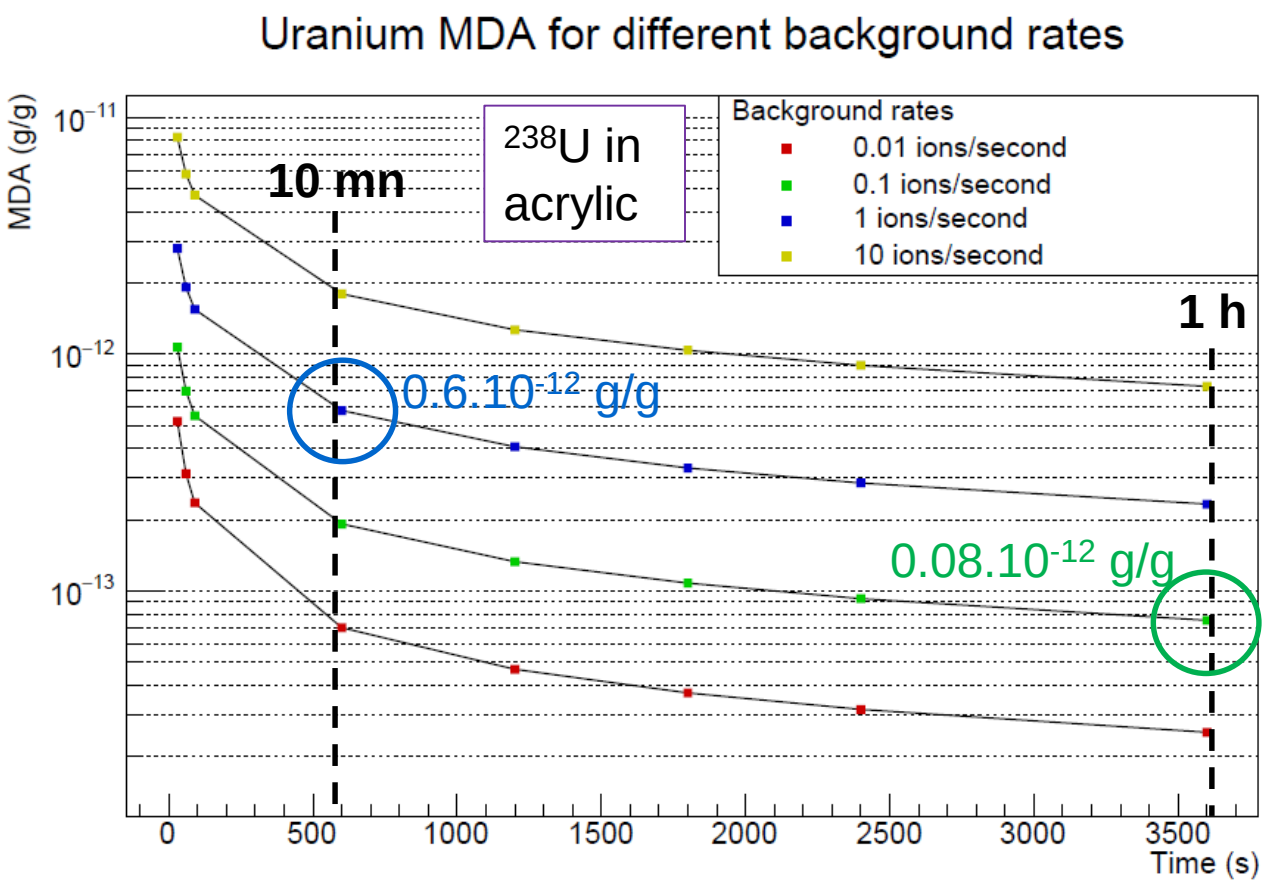
How to be quantitative in g/g ?

$$C_m(U) = \frac{m(U)}{m(sample)} = \frac{M(U)/N_A \times N_{ions} / \varepsilon}{\rho \times V_{ablated}}$$

- ✓ To know precisely the background in order to derive the net count N_{ions} of U/Th ions
- ✓ To have a reference material at known low U/Th concentration → to measure the overall efficiency ε from ablation to ion counting
- ✓ To know precisely the ablated mass → by confocal microscopy to measure *a posteriori* the depth and thus the ablated volume $V_{ablated}$

Sensitivity of LA-ICPMS technique

- ✓ Assuming 0.2% efficiency, 2 µg/mn of ablated mass of acrylic
- ✓ Minimum detectable activity in g/g vs time (proportionnal to mass) for different background rates



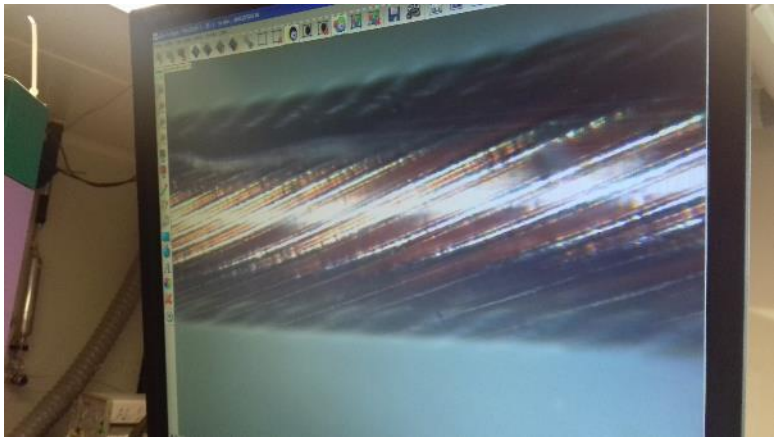
→ sub-10^{-12} g/g level reached within 10 mn @ 1 ion/s background rate

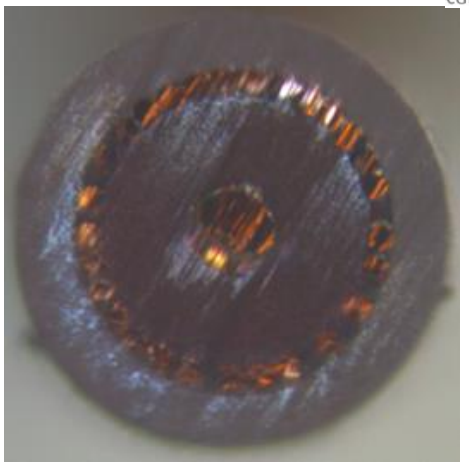
→ sub-10^{-13} g/g level reached within 1 h @ 0.1 ion/s background rate

→ Opportunity to measure tens of samples per day at the sub-ppt level with LA-ICPMS !

2D mapping of a µ-coaxial cable

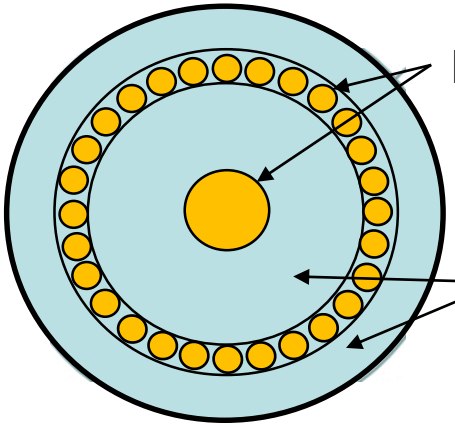
µ-coaxial cable produced by the AXON company (France)





400 µm

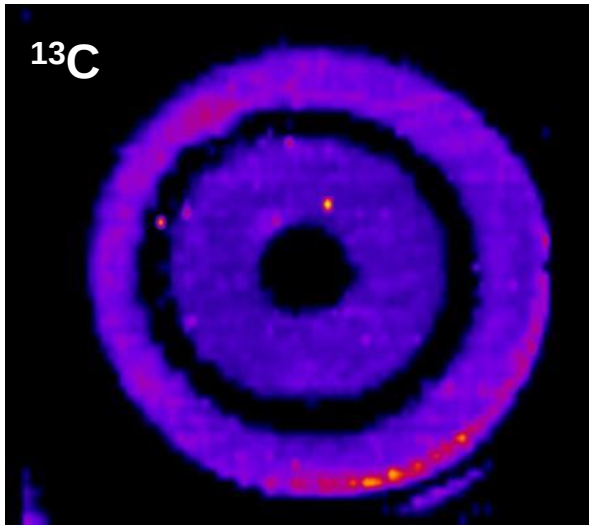
- λ=257 ns
- Duration: 360 fs
- Energy per pulse: few µJ
- Frequency/cadence: few 10 Hz
- Spot size: 8 µm

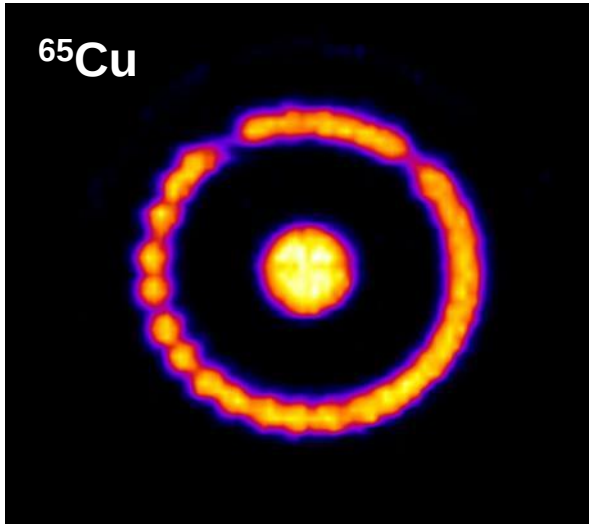


400 µm

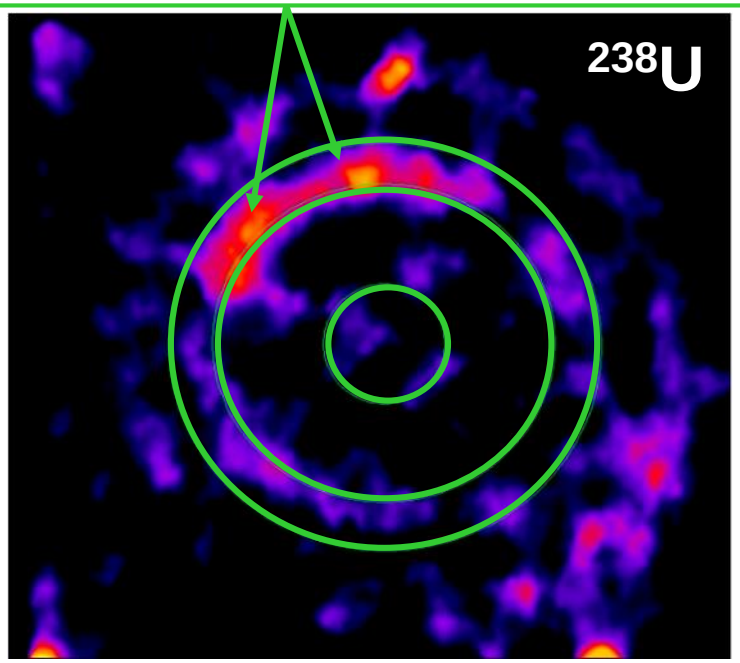
What is the U/Th mapping impurities on the section of the cable ?

2D mapping of a µ-coaxial cable





U contamination observed in some of the copper wires !



Complementarity of the techniques:

- fs LA HR-ICPMS able to identify where the contamination comes from
- classical ICPMS able to measure it more quantitatively

Summary

- ✓ fs laser ablation ICPMS is a complementary technique to ICPMS
  - No chemical preparation
  - Fast analysis
  - Spatial information for micro-analysis

- ✓ Promising applications of LA-ICPMS to measure low U/Th concentrations in various samples of interest
  - A tool to select the best surface treatment
  - A tool to scan the surfacic homogeneity in U/Th of the sample and to identify possible contaminated region/material
  - A tool to map the U/Th concentration in 3D
  - Achievable sensitivity at the sub-10^{-12} g/g level with only few tens of µg (precise quantification methods still in development)

Discussion

- ESR-EquipEx+ application PLATTO (**PL**atform for elemental and isotopic **ATTO**-trace analysis) submitted in 2020 by CENBG/IPREM institutes to develop new instruments for several applications (including rare event experiments) → unfortunately not successful

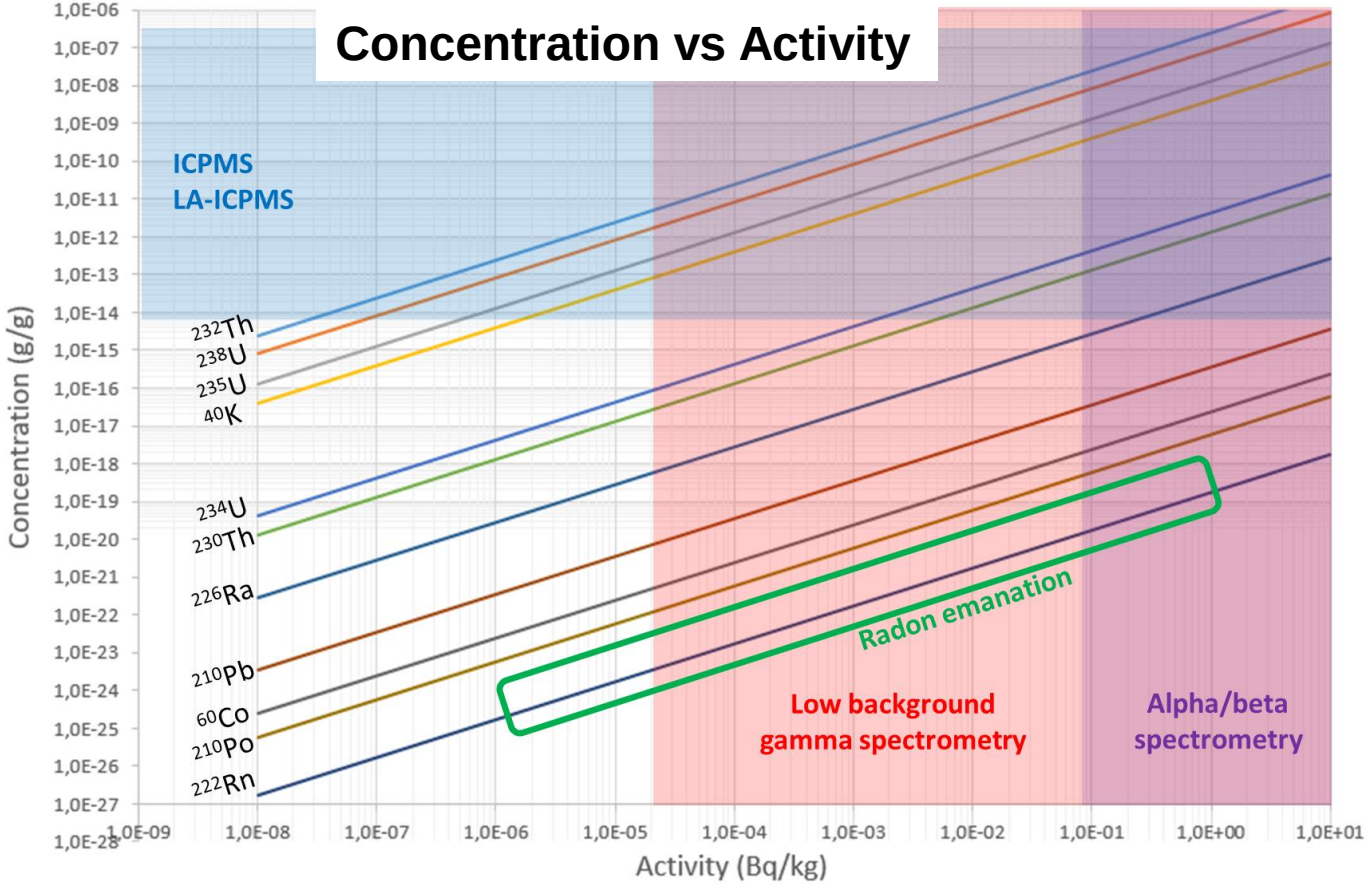
- Discussion needed in our community to promote these techniques (ICPMS and LA-ICPMS especially) in the future at CNRS in France for dark matter searches, neutrinoless double beta decay and solar neutrino experiments

Thank you for your attention

Comparison of the techniques

Techniques	Typical time (day)	Mass (g)	Typical limit of detection for U/Th (10^{-12} g/g)	Chemical preparation	Sensitive to surface contamination	Mapping in 2D	Sensitive to secular equib.	Comments
Ultra low γ spectrometry	~30	~10^3	10	No	No	No	Yes	Sensitive to short-lived isotopes Limited sensitivity
Neutron Activation Analysis (NAA)	~10-30	~10-100	0.1-1	No	Yes/No	No	No	Possibility to irradiate several samples Sensitive to ^{40}K Sensitive to interferences
ICPMS	~0.5	~0.1-10	0.1-1	Yes	Yes/No	No	No	Very mature technique Chemical preparation Not sensitive to ^{40}K
LA-ICPMS	**~0.1**	**~10^{-4}**	**0.1-1**	**No**	**Yes**	**Yes**	**No**	2D spatial mapping Possibility to measure ten samples/day Not sensitive to ^{40}K

Mass spectrometry vs γ/α/β spectroscopy



- ✓ Mass spectrometry: well-suited for long-lived isotopes to reach concentration $<10^{-12}$ g/g
- ✓ Gamma spectroscopy: well-suited for short-lived isotopes to reach activity >10 µBq/kg