ICP-MS measurements of ultra-low level radioactivity in solid material and comparison with γ-spectrometry within the CUPID experiment

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ICRM-LLRMT, September 26-30 2016, Seattle (WA)

Gran Sasso National Laboratory (LNGS):

The largest and most advanced underground facility in the world, currently hosting ≈16 experiments

Italy

Gran Sasso mountain

LNGS underground facility

1400 m of rock (3600 mwe):
-cosmic ray flux reduction 10^6
-neutron flux reduction 10^4

An ideal environment for ultra-low background physics experiments

LNGS facilities for radio-pure material selection

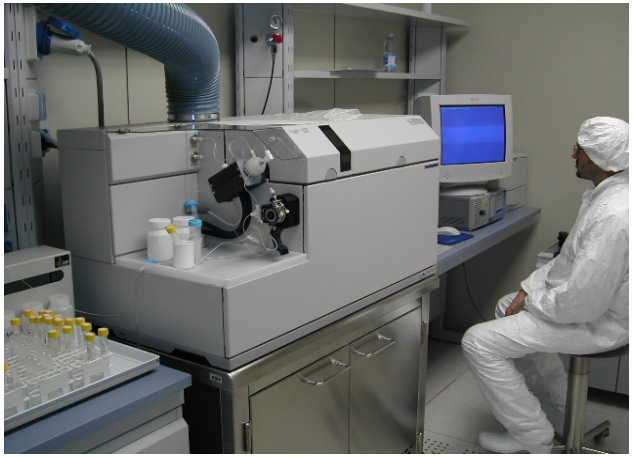
STELLA: SubTErranean Low Level Assay

(Matthias Laubenstein)

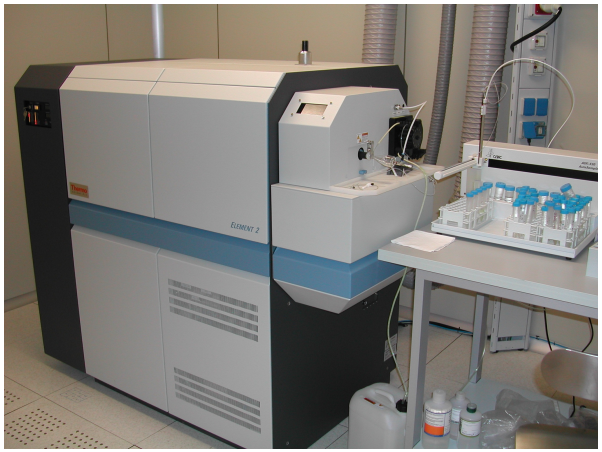
- High Purity Germanium HPGe Detectors – γ spectrometry
- α- spectrometry with silicon detectors
- Liquid Scintillation Counters

Ultra-trace ICP MS laboratory:

(Stefano Nisi, Maria Laura di Vacri)



Agilent 7500a quadrupole mass analyzer



Thermo Element 2 double focusing high resolution mass analyzer

- ISO6 class clean room
- APEX desolvation system
- Sub-boiling distillation system for reagent purification
- High temperature oven for dry ashing technique

OUR CHALLENGE:

Develop analytical procedures to
improve detection limits in ICP MS material radiopurity assay,
in order to meet physics experiments requirements

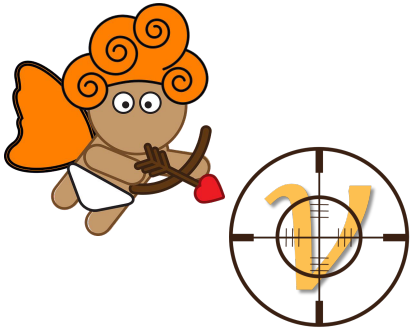
Limiting factors:

-Lack of validated methods and reference materials (unusual matrices)
-Isobaric interferences
-Background (we are looking for very very low concentrations!)
-High risk of contamination during sample preparation
-Sensitivity
-Required dilution factor (the instrument does not tolerate high matrix content)

Our current ICP MS detection limits:

Sample	Liquid	Metals (solid)		Plastic (solid)
		Dissolution and dilution	Analyte separation	
Element	**[pg g^{-1}]**	**[pg g^{-1}]**	**[pg g^{-1}]**	**[pg g^{-1}]**
K	50	5×10^4	-	5×10^4
Pb	0.5	500	-	100
Th	0.05	**50**	**1.0**	10
U	0.05	**50**	**0.5**	10

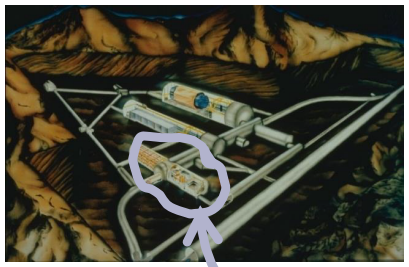
Aim of this work:



Develop an analytical procedure to meet **CUPID** requirements in copper assay for Th and U

CUPID: CUORE Upgrade with Particle IDentification
arXiv:1504.03612v1

Ambitious target: 10 meV sensitivity on the effective Majorana mass → Very demanding background requirements!

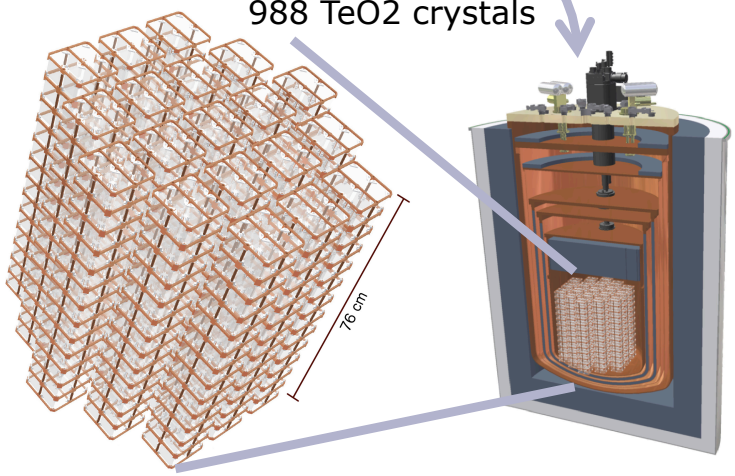


CUORE
T=10 mK
988 TeO2 crystals

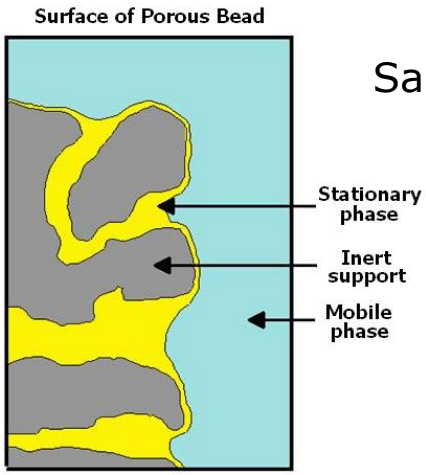
COPPER:

CUPID background budget *	ICP MS detection limits
1 – 0.1 [pg g^{-1}]	50 [pg g^{-1}]

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



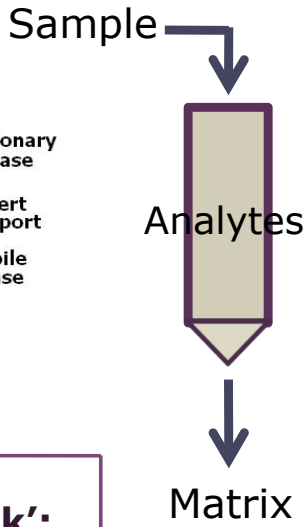
Extraction chromatography for Th and U chemical separation:



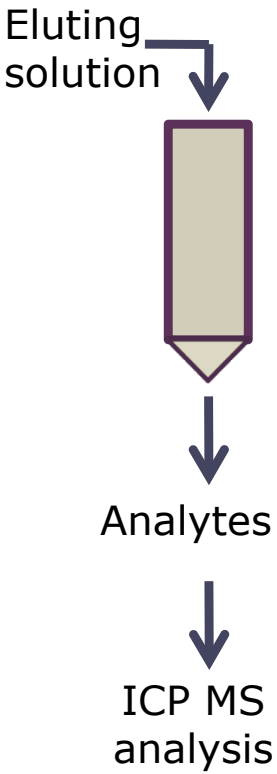
Capacity factor k':

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

Step 1:



Step 2:



Advantages:

- Matrix removal
- Low instrument contamination
- Reduced risk of interferences
- Reduced matrix effect
- Analyte pre-concentration
- Reduced dilution factor
- Higher sensitivity

Disadvantages:

- Time consuming
- Risk of contamination
- Column background

Th and U low-level assay in electroformed copper

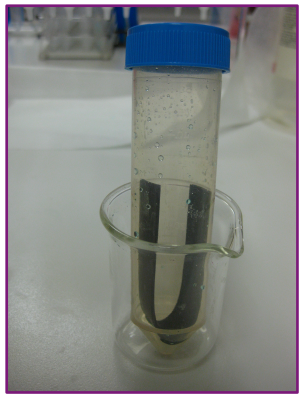
- Electroformed copper produced at Canfranc Laboratory (Silvia Borjabad Sanchez)

-Weight: 31 g. Dimensions: (120×12.6×2.3) mm^3

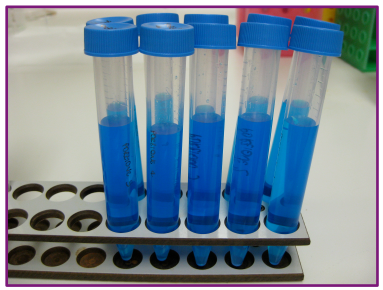
-Preliminary cleaning with 5% citric acid (surface contamination)

-Dissolution in UP HNO_3 solution (5 M, 30 mL). Several controlled etching steps (depth profile analysis):

	Step 1	**Step 2**	**Step 3**
Dissolved Cu [g]	3.35	3.66	3.70
Removed layer [μm]	≈100	≈110	≈110

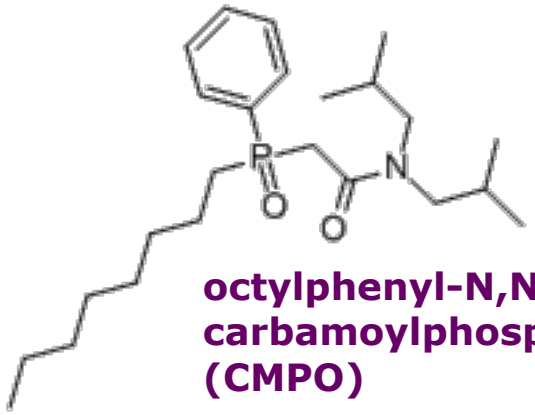


Electroformed copper slab in a clean vial

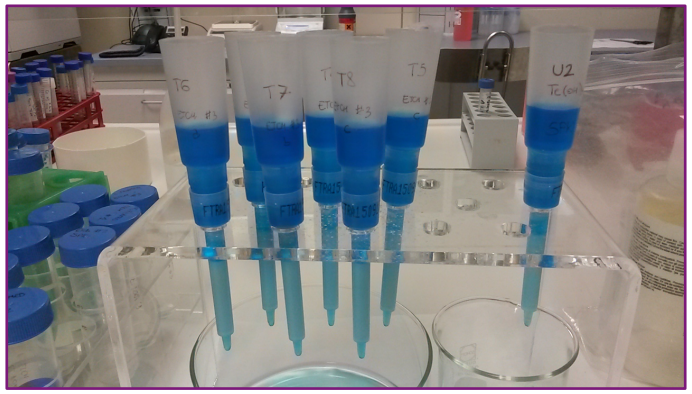


Solutions of dissolved copper

Th and U extraction: TRU® resin (Triskem)



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



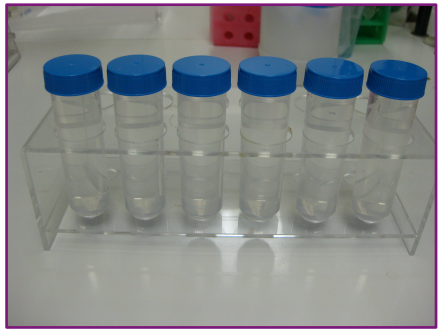
Procedure:

1. preliminary cleaning of the columns: 0.1 M ammonium oxalate, 25 mL, 3 days.
2. column rinse: 4.5 M HNO_3, 5 mL
3. sample loading: ≈10% Cu solution, 13 mL
4. column rinse for matrix removal: 4.5 M HNO_3, 7 mL
5. Th and U elution: 0.1 M ammonium oxalate, 7 mL
6. ICP MS analysis

Reduction of background and contamination risk:

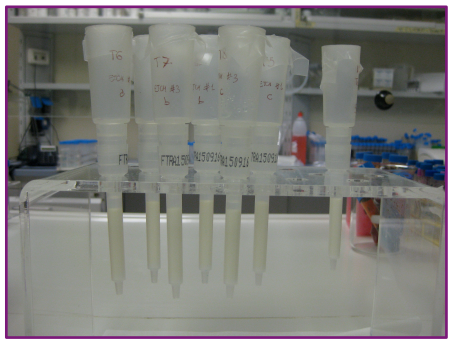
- Work in clean room (ISO6 class)

- Preliminary cleaning (2% UP HNO3 solutions + rinsing with MilliQ - 18.2 MΩ cm – water) and check of all vials and labware involved in the analysis



- Preliminary rinsing (ammonium oxalate 0.1 M for 3 days, total 15 mL) and check of the chromatographic extraction columns contribution to background

- Procedure blanks and sample solutions collected, respectively, in the same (previously checked) vial



Results:

Analytical method:

	DL* (in solid Cu)	Recovery
	[pg g^{-1}]	%
Th	1.5	90.0 ± 0.6
U	0.7	97.9 ± 6.1

*DL = 3 × BLKStdDev, N=6

Rinsing HNO_3 volume	Cu separation efficiency
[mL]	[%]
7	99.90 ± 0.04
20	99.99 ± 0.01

Sample analysis:

	Step 3		Step 1	
	[pg g^{-1}]	[µBq Kg^{-1}]	[pg g^{-1}]	[µBq Kg^{-1}]
Th	< 1.5	< 6.09	27.7 ± 0.7	113 ± 3
U	< 0.7	< 8.71	2.20 ± 0.06	27.4 ± 0.7

(N=3, 95% C.L.)

More about the sample: comparison with the starting raw copper

	Starting copper	Electroformed copper
	[pg g^{-1}]	[pg g^{-1}]
Th	< 15	< 1.5
U	< 5	< 0.7

(Bulk analysis. Starting copper was measured when our DL were still a little worse)

	Starting copper	Electroformed copper	Removal efficiency
	[ng g^{-1}]	[ng g^{-1}]	[%]
Fe	13×10^3	< 3×10^3	> 76.9
Co	1.6×10^3	< 1	> 99.9
Ag	1.0×10^3	240	76.0
Sn	19×10^3	< 5	> 99.9
Sb	1.9×10^3	< 5	> 99.7
Pb	49×10^3	< 50	>99.9
Bi	180	< 5	> 97.2

Gamma spectrometry* – ICP MS comparison

Electroformed copper sample:

	ICP MS		γ –SPECTROMETRY *
	Step 3 (bulk)	**Step 1 (surface, ≈100 μm)**	**Total contamination (508.9 g)**
	[pg g^{-1}]	**[pg g^{-1}]**	**[pg g^{-1}]**
Th	< 1.5	27.7 ± 0.7	< 290 (^{228}Th)
U	< 0.7	2.20 ± 0.06	< 85 (^{226}Ra)

Starting copper sample:

	ICP MS	γ –SPECTROMETRY *
		(10.6 kg of sample)
	[pg g^{-1}]	**[pg g^{-1}]**
Th	< 15	<16 (^{228}Th)
U	< 5	< 8.4 (^{226}Ra)

* γ- spectrometric measurements performed at the LNGS STELLA laboratory by Matthias Laubenstein

* 68% C.L.

Conclusions and perspectives:

- Excellent DL in thorium and uranium ICP MS assay in solid copper for low background applications.

- Work is in progress to further improve these DL. Tests have been performed and results are so far promising for an improvement of a factor ≈5.

- 5% citric acid bath is not sufficient to totally remove surface contamination (due to handling and cutting operations) from the electroformed copper piece.

- The electroforming process performed at Canfranc laboratory resulted to be efficient for copper purification for several elements of interest.

- The comparison ICP MS - gamma spectrometric measurements demonstrates that the techniques are in agreement and complementary.

Thank you!

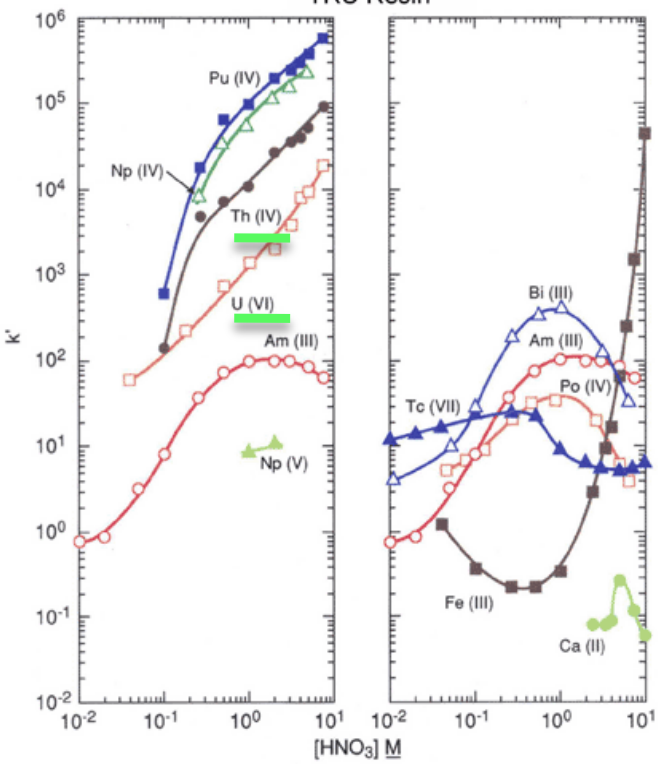
BACK UP SLIDES:

TRU resin:

TRU column specifics	
Stationary phase	CMPO/TBP (ρ= 0.37 g/mL)
Inert support	Amberlite™ XAD-7
Grain dimension	100-150 µm
Vs	0.167 mL/mL bed
Vs/Vm	0.257
Vm (FCV)	0.65 mL/mL bed

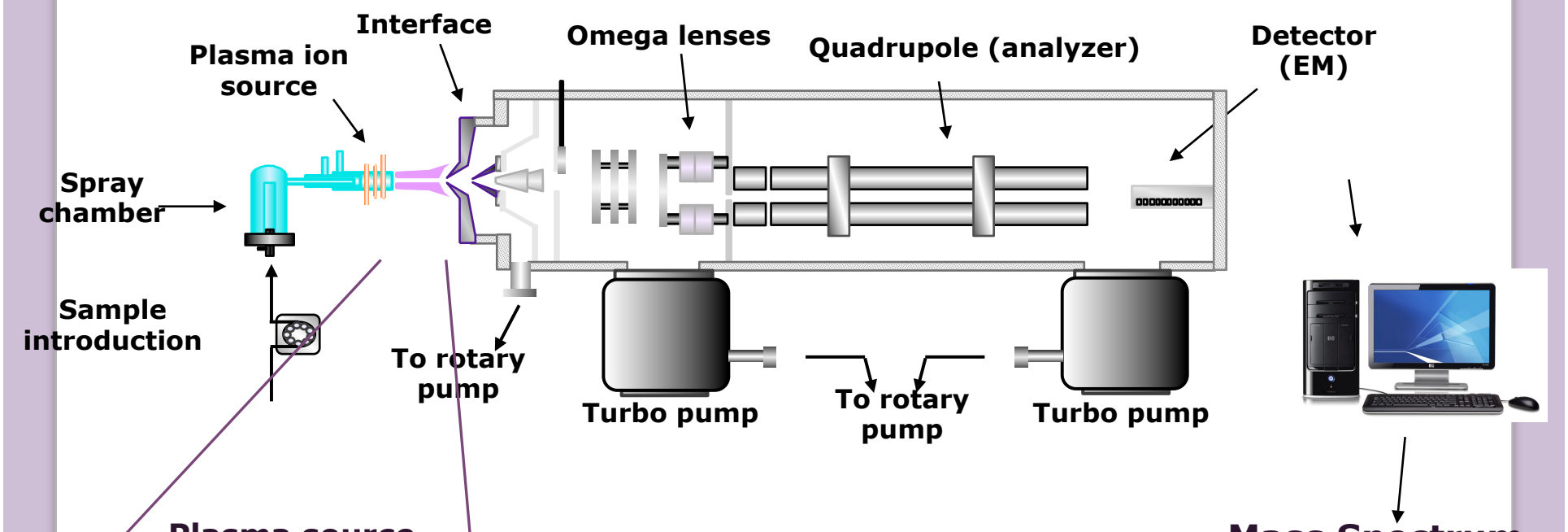
Figure 2

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

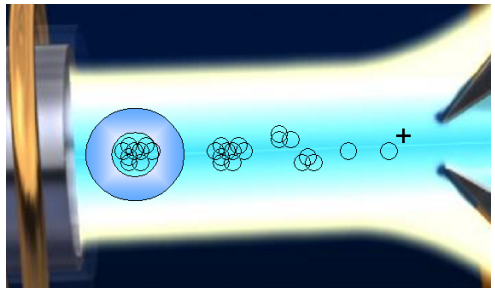


Horwitz, et al. (HP193)

ICP MS: trace element analysis

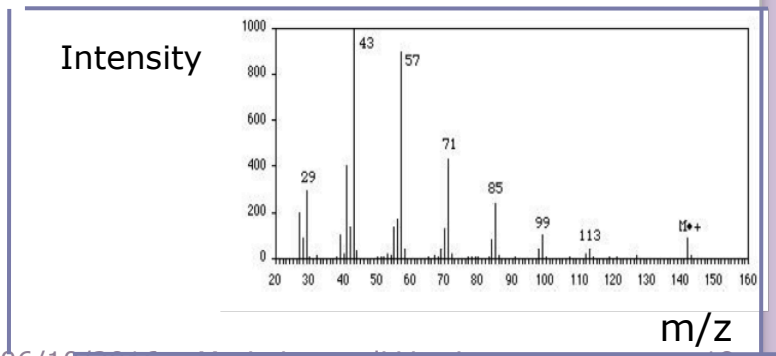


Plasma source (10000 K)



1. The aerosol is dried
2. Particles are decomposed to atoms
3. Atoms are ionized

Mass Spectrum



Measurable elements with ICP MS

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
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)

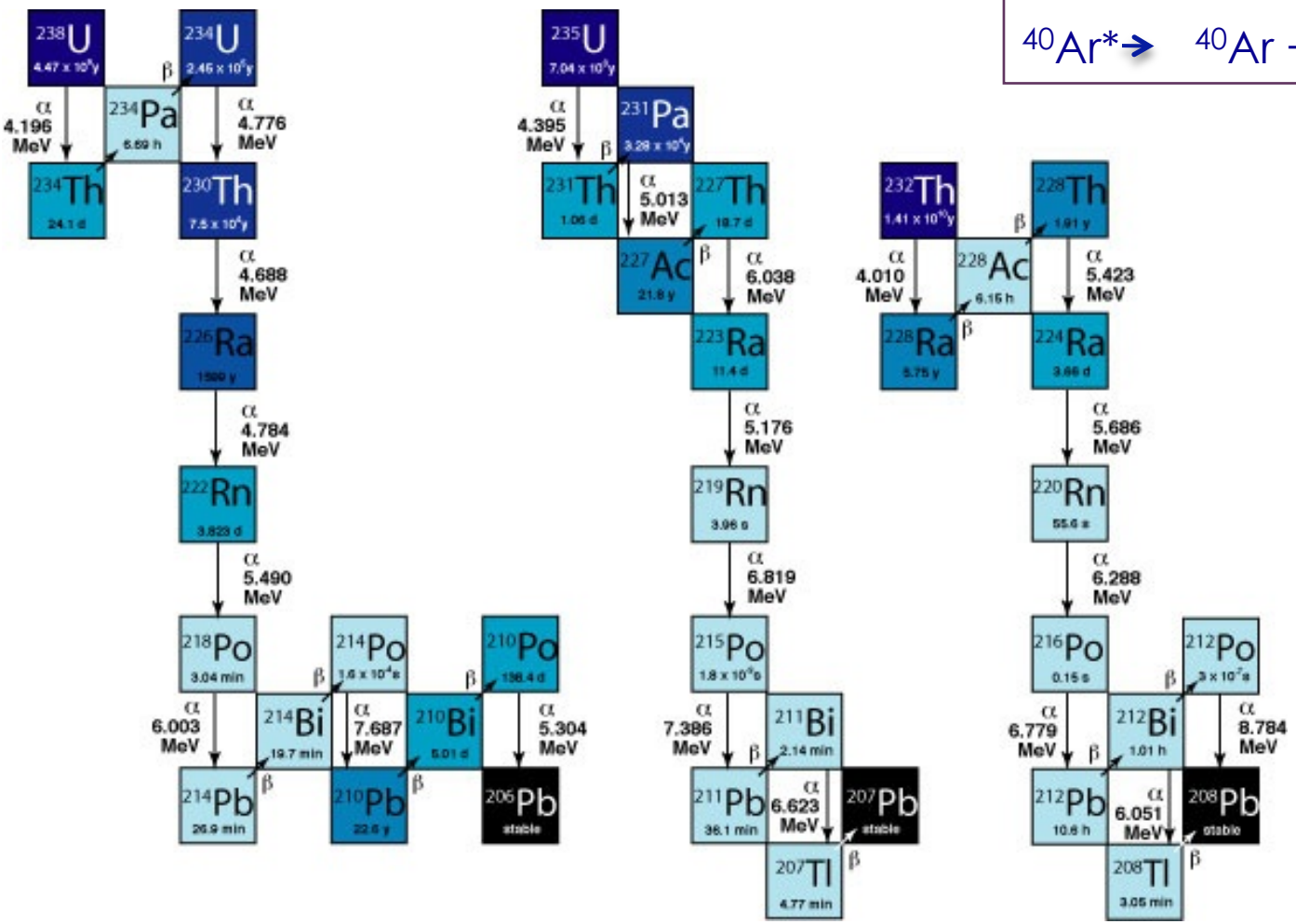
1ppm (10^{-6} g/g)

Natural radioactivity

$^{40}K \rightarrow {}^{40}Ca + e^- + \nu_e$

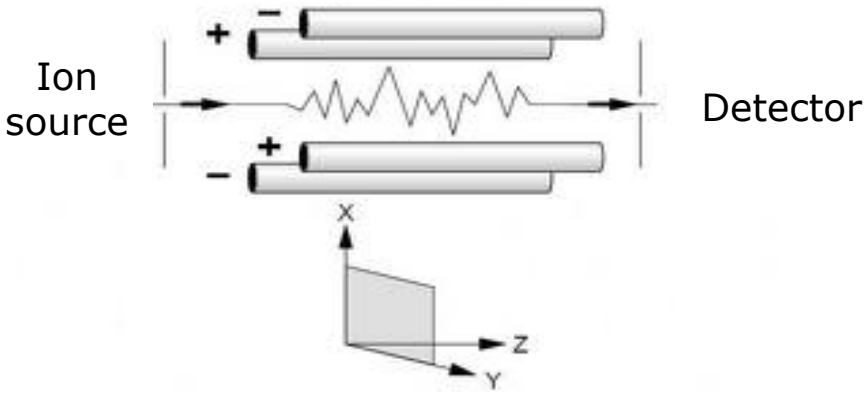
$^{40}Ca + e^- \rightarrow {}^{40}Ar^* + \nu_e$

$^{40}Ar^* \rightarrow {}^{40}Ar + \gamma$



Mass analyzers

Quadrupole mass filter

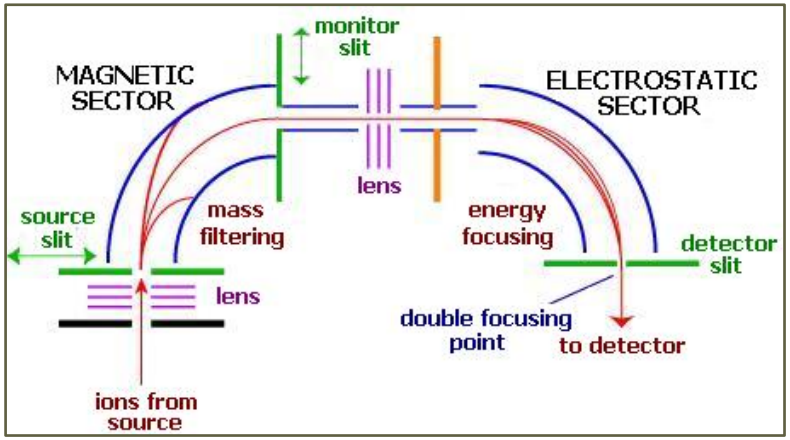


RESOLUTION POWER

$R = \Delta M/M$

R ≈ 300 low resolution
R ≈ 4000 medium resolution
R ≈ 10000 high resolution

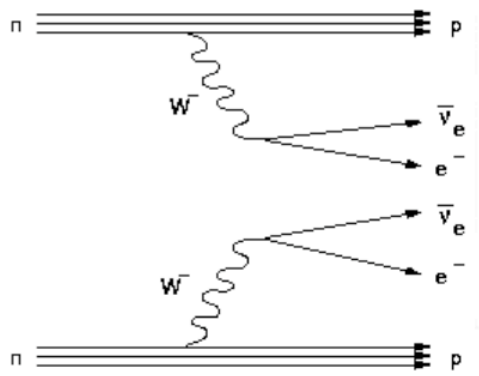
Double focusing mass analyzer (MSA + ESA) High Resolution Mass Spectrometry



2νββ:

$$ {}^{A}_{Z}X \xrightarrow{\beta^-\beta^-} {}^{A}_{Z+2}Y + 2e^- + 2\bar{\nu}_e $$

$$ {}^{A}_{Z}X \xrightarrow{\beta^+\beta^+} {}^{A}_{Z-2}Y + 2e^+ + 2\nu_e $$



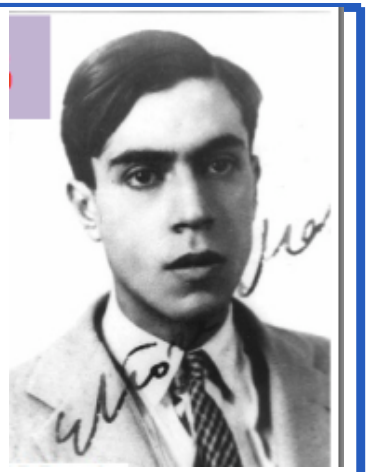
$\Delta L = 0$

Admitted by the Standard Model
experimentally observed

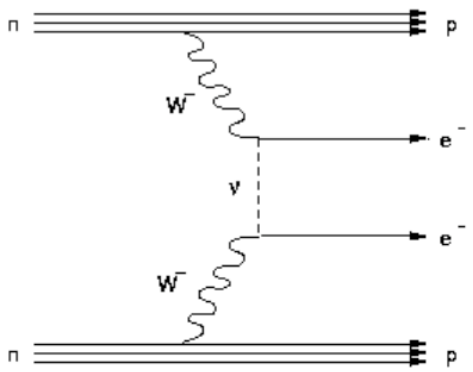
($T^{2\nu}_{1/2} \approx 10^{18}$-$10^{21}$ y)

0νββ:

Ettore Majorana(1937)



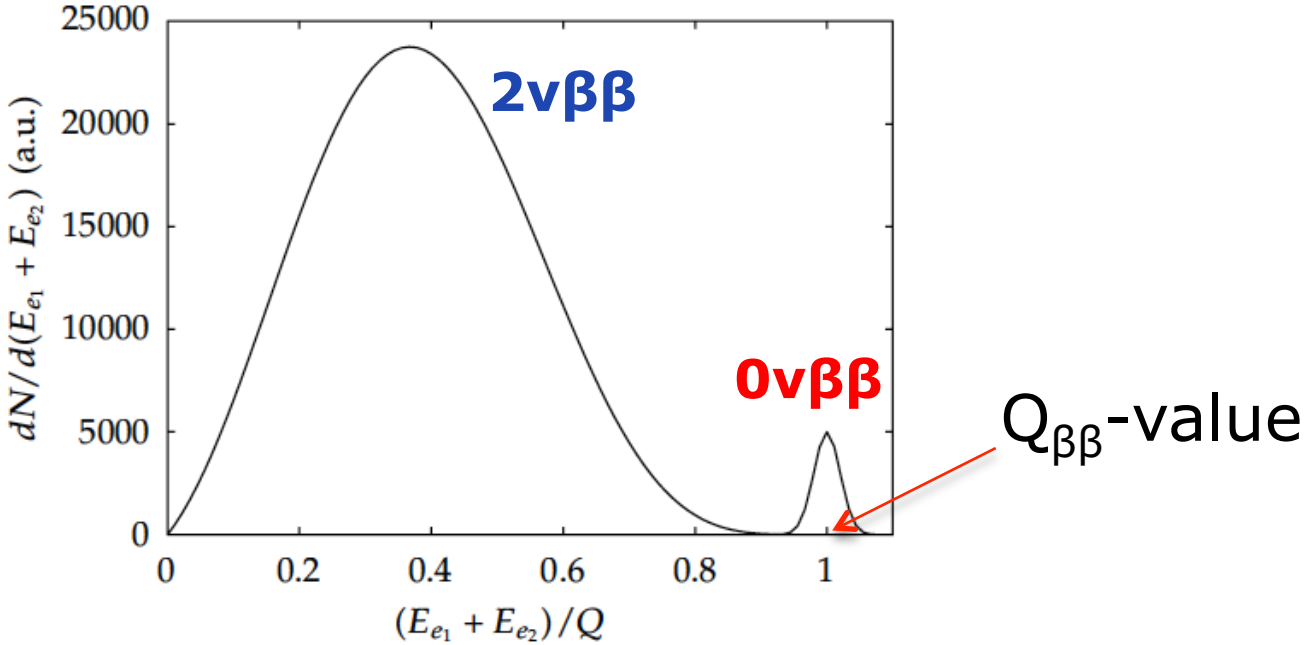
$$ {}^{A}_{Z}X \xrightarrow{\beta^-\beta^-} {}^{A}_{Z+2}Y + 2e $$



$\Delta L = 2$

Physics beyond Standard Model
neutrino=antineutrino

($T^{0\nu}_{1/2} \geq 10^{24}$ y)



$$\left(T_{0\nu}^{1/2}\right)^{-1} = G_{0\nu}(Q,Z)\cdot\left|M_{0\nu}\right|^2\cdot\left\langle m_{\beta\beta}\right\rangle^2$$

- Majorana nature of neutrino
- Information about neutrino mass

$$m_{\beta\beta} = \left|\sum_i m_{\nu_i} U_{ei}^2\right|$$

Effective Majorana mass