NAA
NEUTRON ACTIVATION ANALYSIS
(ANALISI PER ATTIVAZIONE NEUTRONICA)

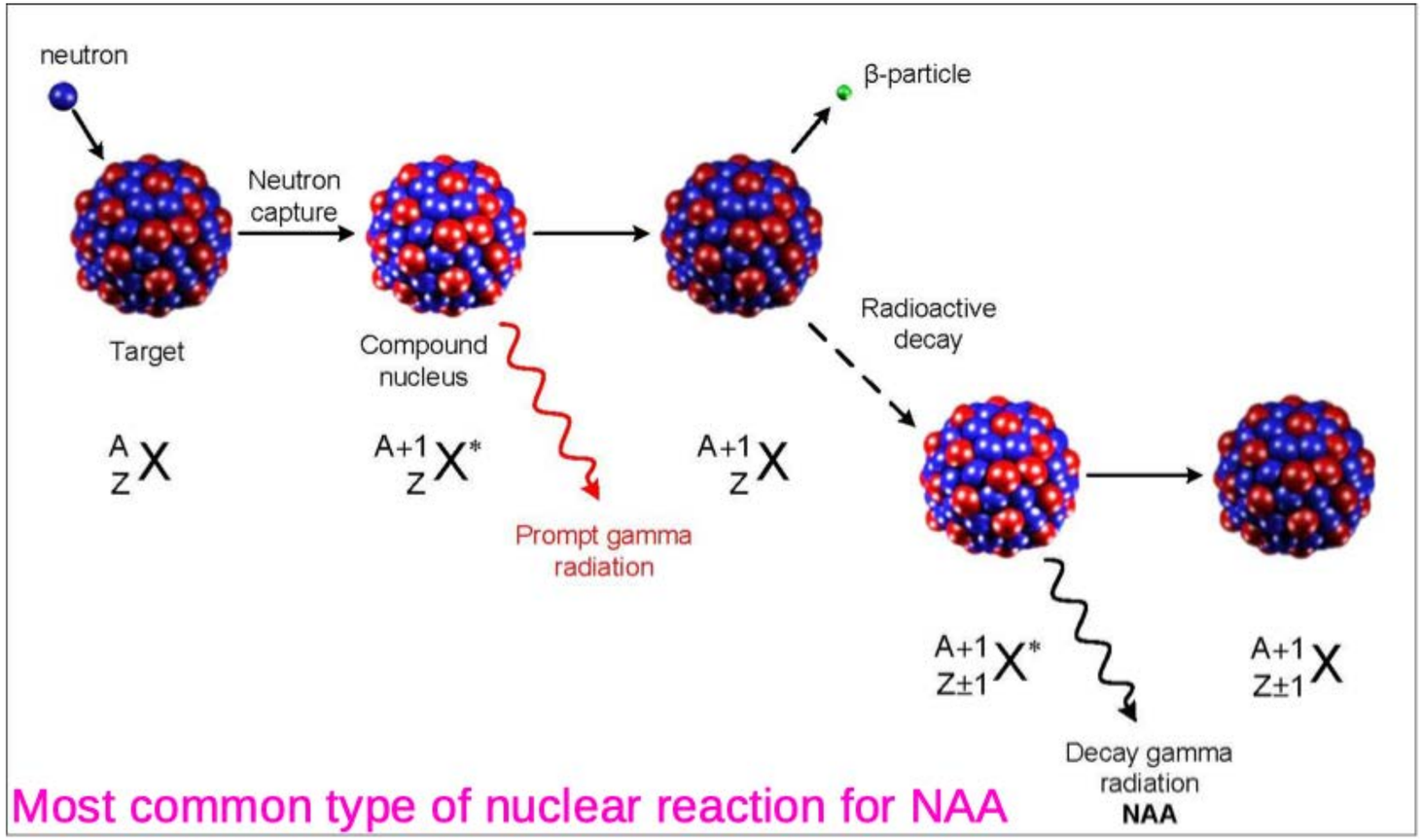
La tecnica

$$\mathrm{A}^{x} + \mathrm{n}^{1} \rightarrow \mathrm{A}^{1+x}$$

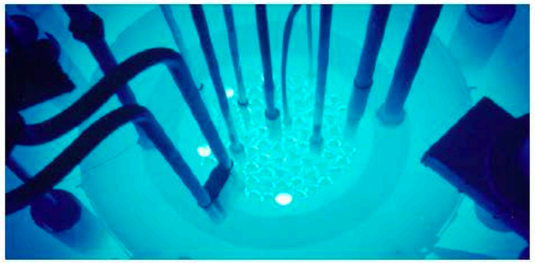
$$\mathrm{A}^{1+x} \rightarrow \mathrm{B} + \text{radiation}$$

to be measured

Principio base di NAA

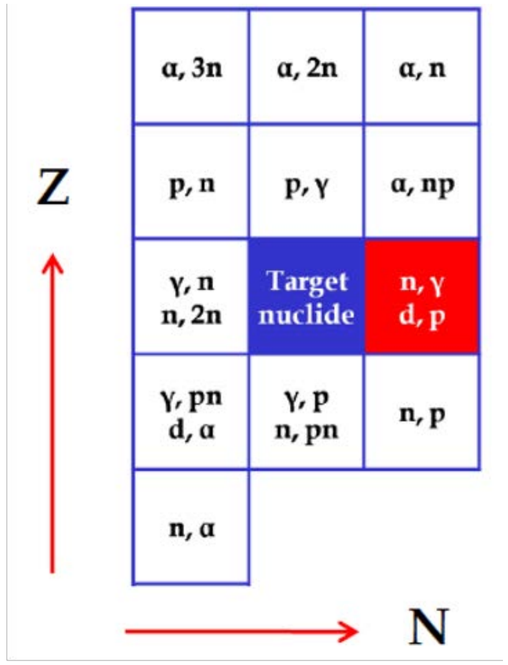


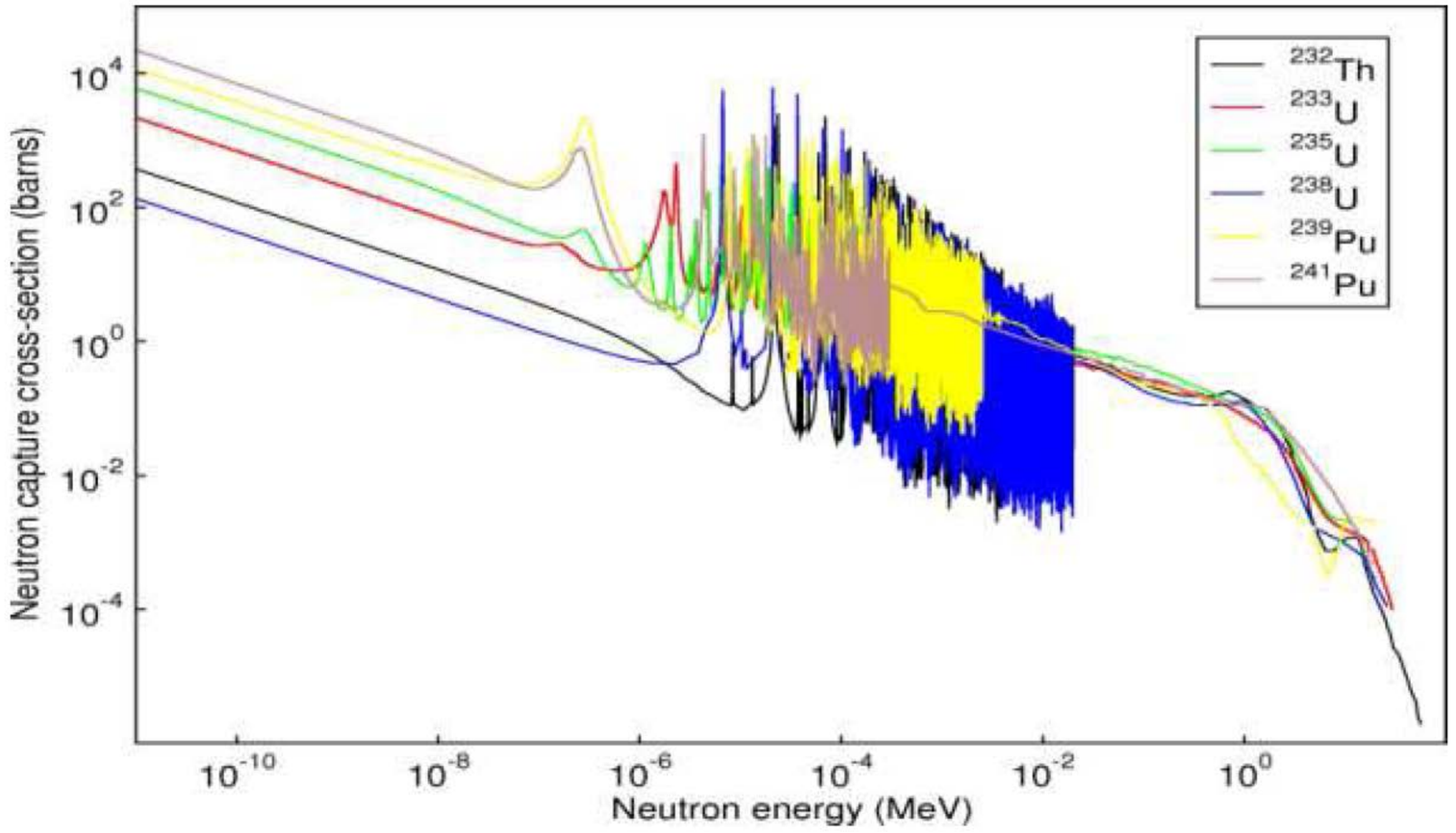
Reattori nucleari



Reattori nucleari

Attivazione tramite reazioni (n,γ)





Ingredienti chiave per NAA

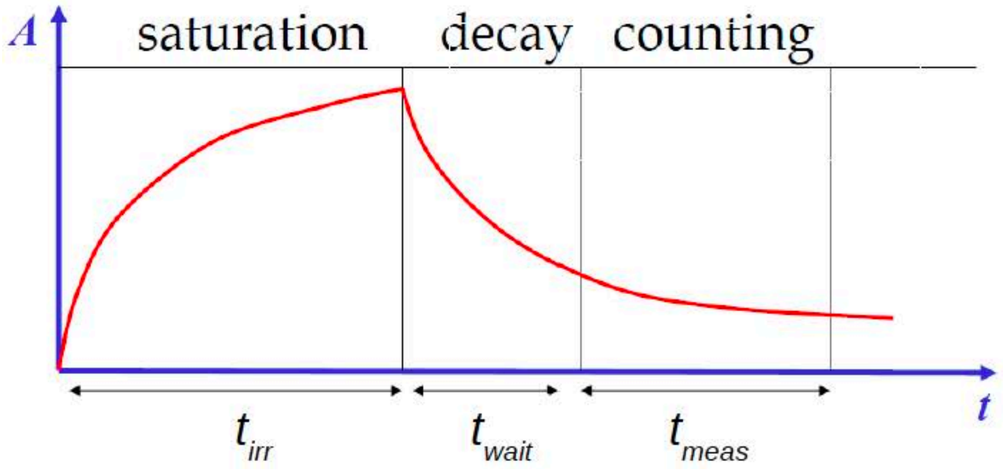
$$^{A}X + n \longrightarrow {}^{A+1}X \xrightarrow{\beta^-} {}^{A+1}_{Z+1}Y + \gamma_{cascade}$$

Three key ingredients:

- High neutron flux
- High enough neutron capture cross section
- “Convenient” daughter nucleus (γ emission, half-life time)

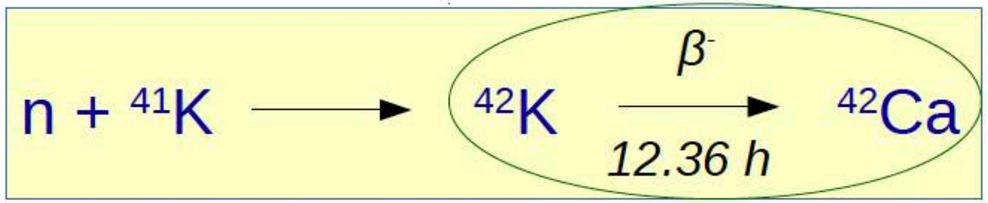
Sensitivity depends on:

- type pf material (short-lived activation products)
- neutron exposure time
- interferences in the matrix
- background in the region of the gamma emission



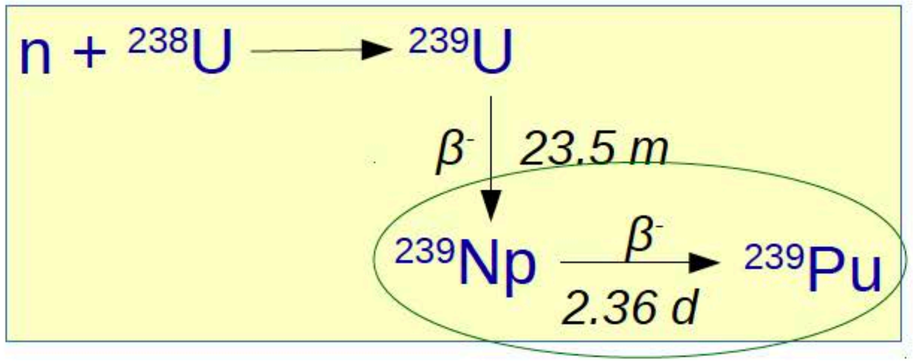
- care in the sample preparation is extremely important!
- the radiopurity of the sample container is also of concern!

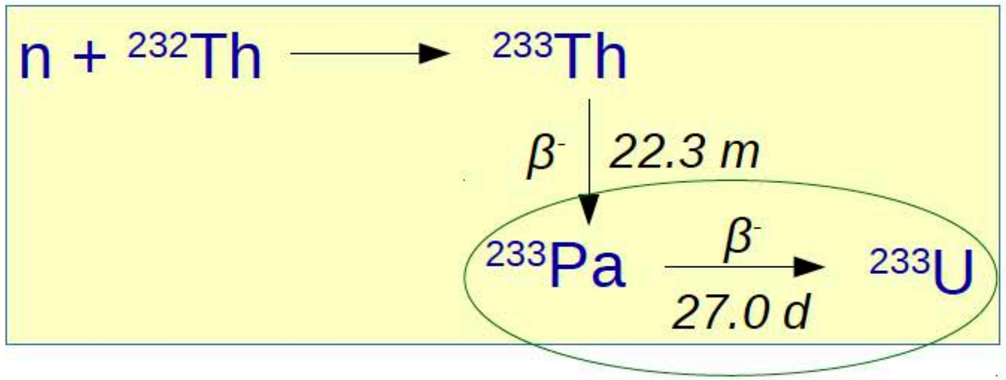
NAA per contaminanti naturali



- ^{41}K isotopic abundance is 6.7%
- ^{40}K isotopic abundance is 0.01%

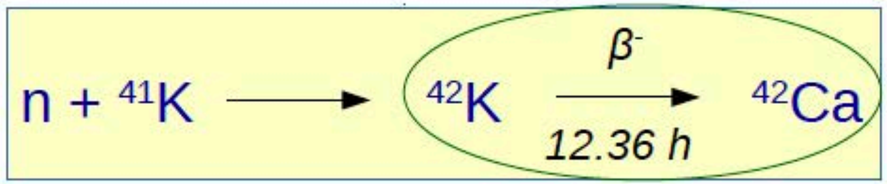
^{40}K contamination is calculated from ^{41}K one





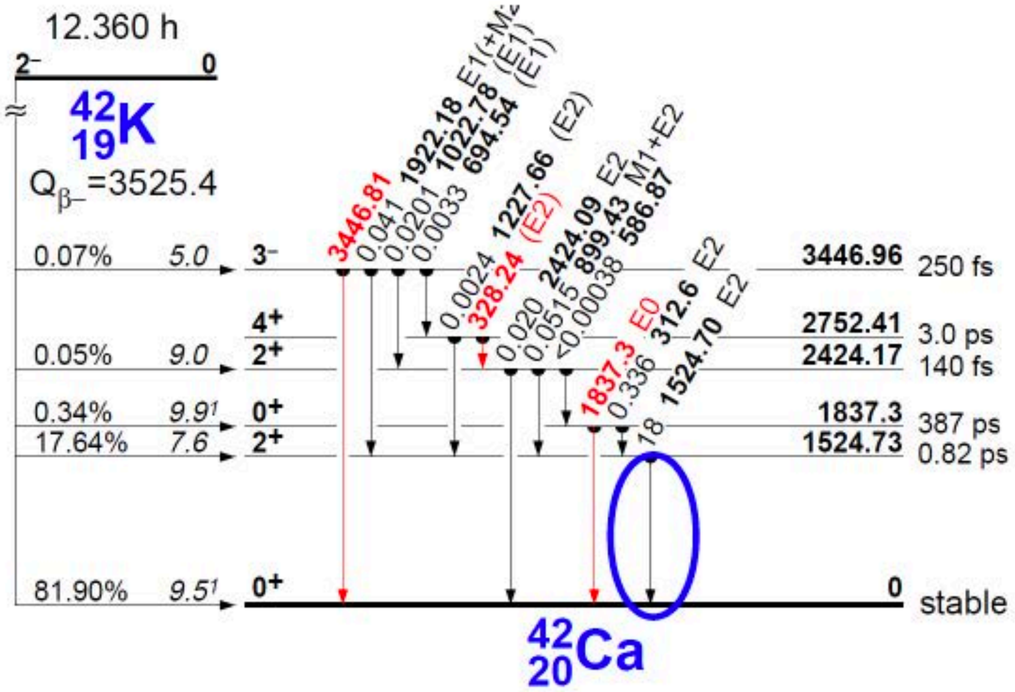
The material of the sample container should not form long-lived radioisotopes during neutron irradiation: too long cooling times after the irradiation may prevent measuring shorter living nuclides, like ^{42}K.

NAA per 40K

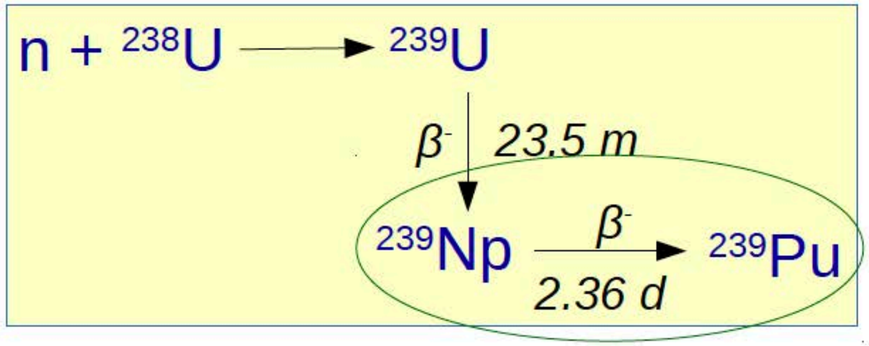


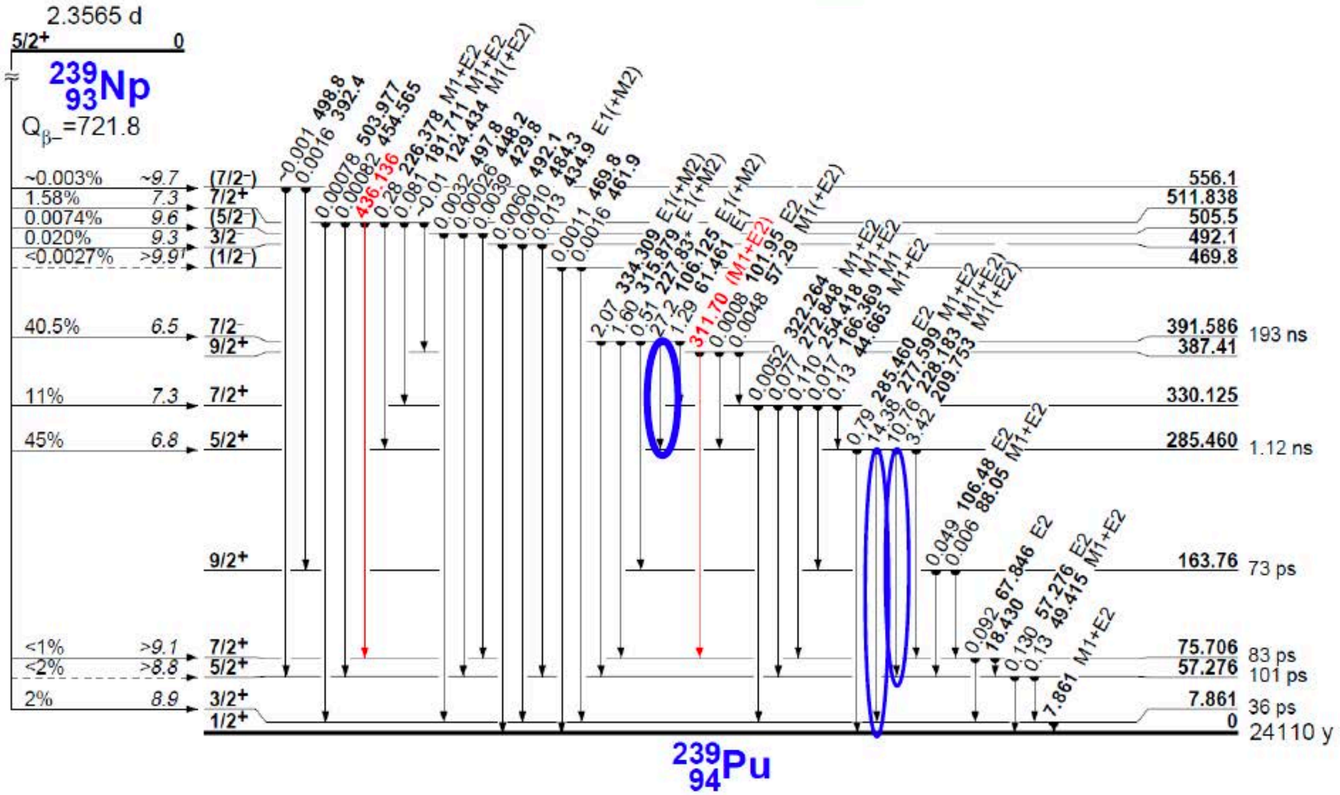
- ^{41}K isotopic abundance is 6.7%
- ^{40}K isotopic abundance is 0.01%

^{40}K contamination is calculated from ^{41}K one

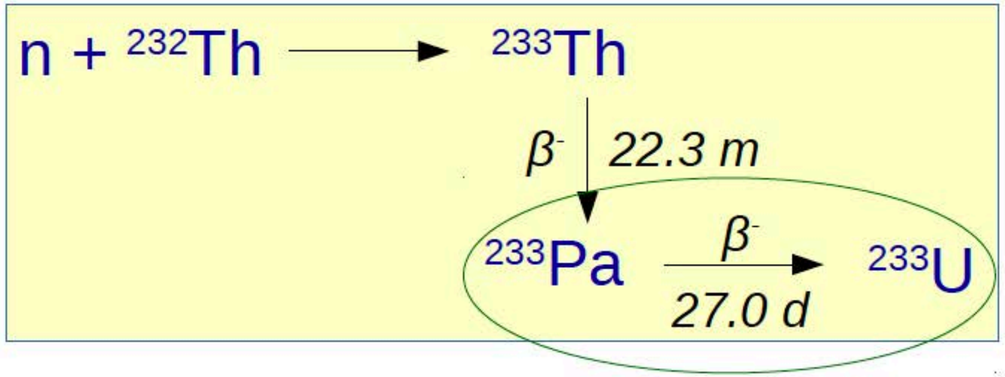


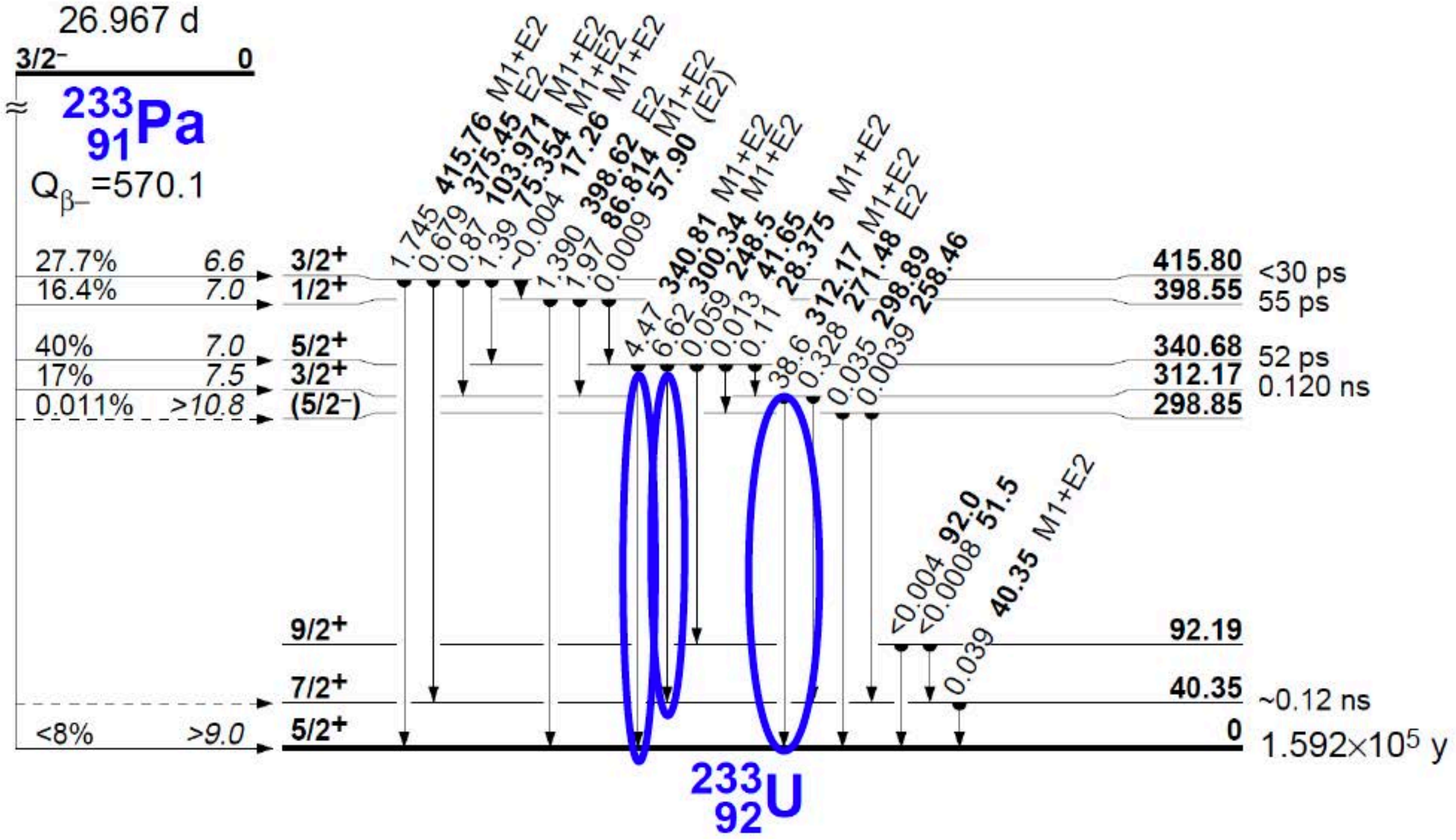
NAA per 238U


n + 238U
239U
β-
23.5 m
239Np
β-
2.36 d
239Pu


2.3565 d
5/2+
0
239 93Np
Q β−=721.8
239 94Pu
24110 y
556.1
511.838
505.5
492.1
469.8
391.586
387.41
193 ns
330.125
285.460
1.12 ns
163.76
73 ps
75.706
83 ps
57.276
101 ps
7.861
36 ps
0
(7/2−)
7/2+
(5/2−)
3/2−
(1/2−)
7/2−
9/2+
7/2+
5/2+
9/2+
7/2+
5/2+
3/2+
1/2+
~0.003%
1.58%
0.0074%
0.020%
<0.0027%
40.5%
11%
45%
<1%
<2%
2%

NAA per 232Th





Concentration of trace elements

During the irradiation, the time evolution of the production of the activated isotope (with *decay constant* λ) in the irradiated sample is:

$$dN = Rdt - N\lambda dt$$

At the end of the irradiation, the number of activated nuclei is:

$$N(t_{irr}) = \frac{R}{\lambda}\left(1 - e^{-\lambda t_{irr}}\right) \stackrel{\text{def}}{=} N_0$$

The amount (N) of the original, stable isotope in the sample is then calculated via the counts measured with HPGe detectors in the gamma peaks following the decays of the activated isotope:

$$n_{\text{dec}} = \frac{R}{\lambda}\left(1 - e^{-\lambda t_{\text{irr}}}\right)e^{-\lambda t_{\text{wait}}}\left(1 - e^{-\lambda t_{\text{meas}}}\right)$$

HPGe detectors at the Radioactivity Laboratories of Milano-Bicocca

GeGEM detector ε_{rel}30%

BeGE detector ε_{rel}50%

The relative method - irradiation standards

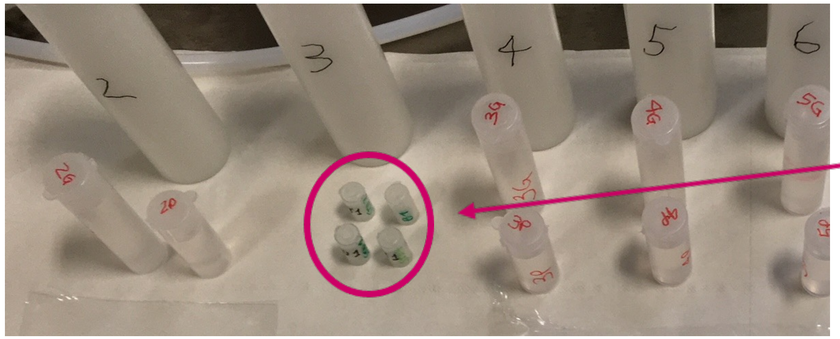
To calculate the amount (N) of the original, stable isotope in the sample we should know precisely Φ_{TOT} and σ_{eff} in every position of the reactor and for every irradiation campaign:

$$n_{dec} = \frac{R}{\lambda}\left(1 - e^{-\lambda t_{irr}}\right)e^{-\lambda t_{wait}}\left(1 - e^{-\lambda t_{meas}}\right)$$

with $R = \mathcal{N}\sigma_{eff}\Phi_{TOT}$

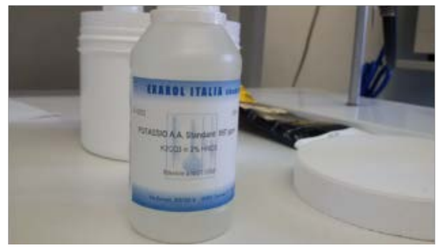
To avoid this, one usually uses irradiation standards, containing the same elements to be traced in the sample with a known amount.

N is thus obtained by comparing n_{dec} for standards and sample



When multi-element searches are performed, e.g. in environmental samples, the k_0-comparator method (non-relative method) is used to reduce the number of irradiation standards.

The element standards are irradiated together with the samples in the same irradiation channels



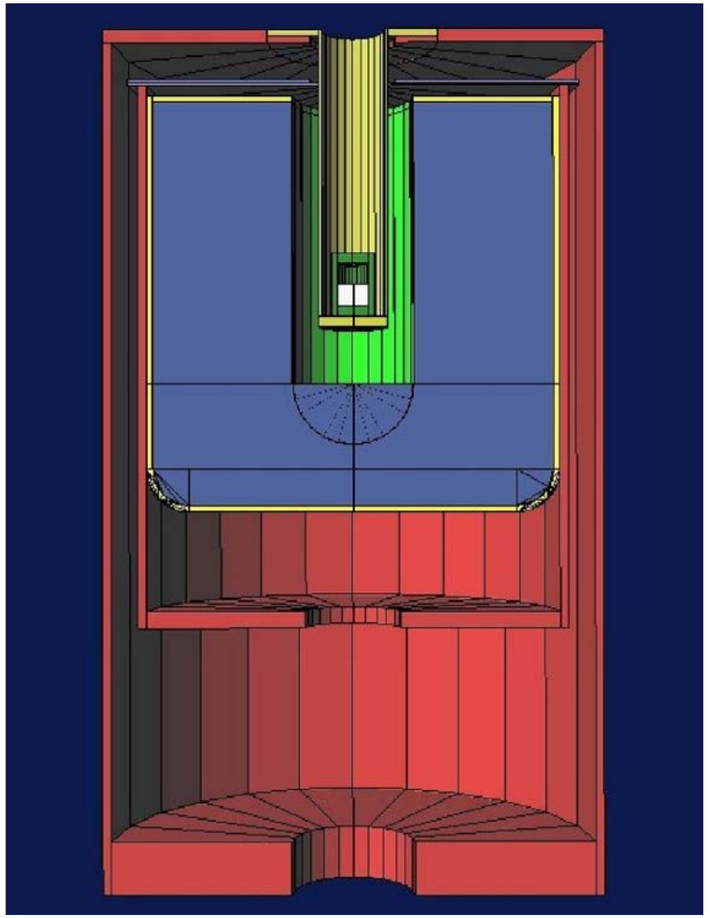
HPGe measurement efficiency

To evaluate n_{dec} from gamma-ray spectroscopy with HPGe detectors, the detection efficiency must be known.

This is best achieved through MonteCarlo simulations of each experimental configuration (sample-HPGe):

$$n_{\mathrm{dec}} = \frac{C_{\mathrm{meas}}}{C_{\mathrm{sim}}} n_{\mathrm{sim}}$$

where C_{meas} and C_{sim} are the gamma-ray peaks' counts for the measured and simulated spectra with n_{sim} simulated decays for each isotope of interest.



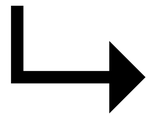
Example of a reconstructed experimental configuration with a GEANT4 MonteCarlo simulation.

A.Borio di Tigliole et al. Prog. Nucl. Energy 70 (2014) 249

Practical NAA

A neutron activation campaign may involve some or all of the following steps:

- **Sample preparation**
  → cut to fit in irradiation container, cleaning, packing (eventual pre-treatment)



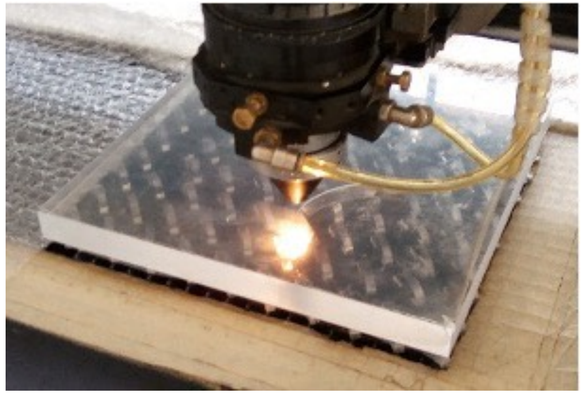
in ultra-trace measurements, extreme care is needed to avoid adding unwanted contaminants during this step

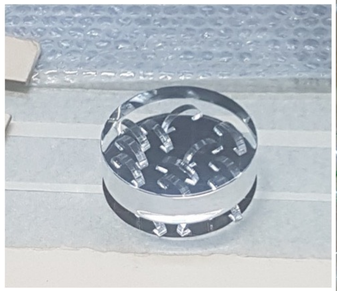
- **Irradiation / Activation at the nuclear reactor**
- **Radiochemical separation (only in RNAA)**
- **Activity measurements by HPGe detectors**
- **Elemental concentration calculation**

Practical NAA

Sample preparation

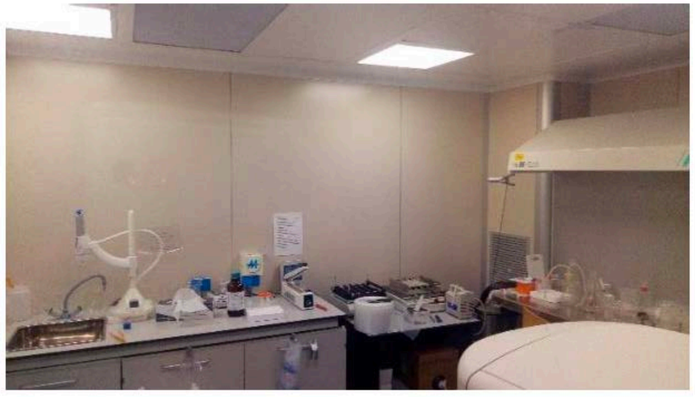
Preparation of standards inside quartz vials (for high neutron fluxes)





Laser cutting of acrylic samples

Clean room preparation of samples:



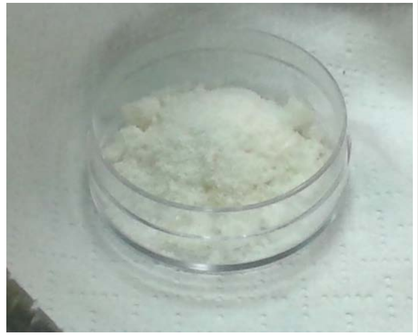
Clean room class 1000 with MilliQ water system

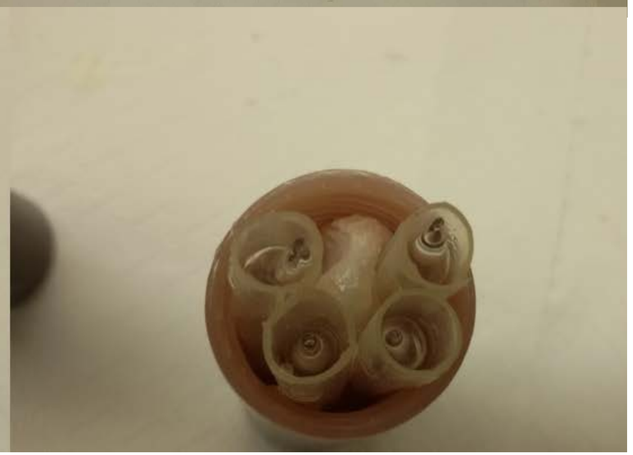
Acrylic samples

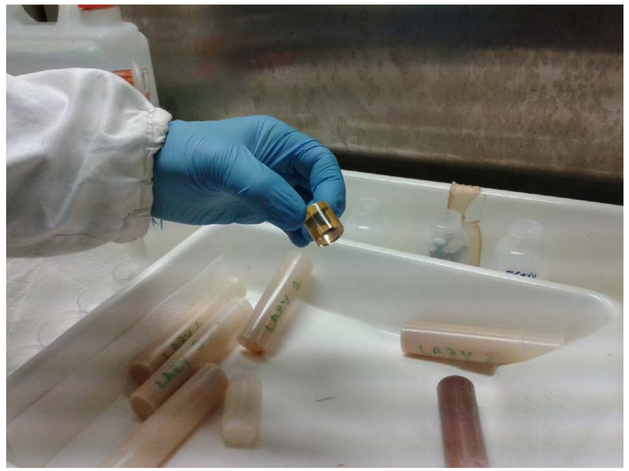
LAB samples

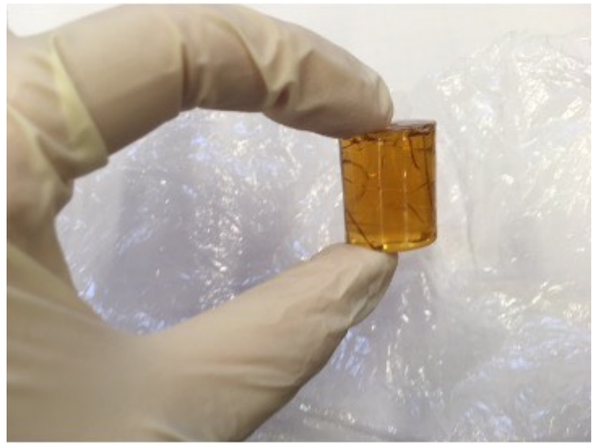
Practical NAA

Neutron irradiation





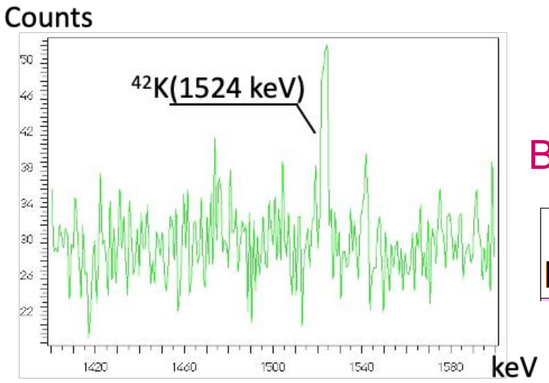




Radiolysis during neutron irradiation must be taken into account!

Practical NAA

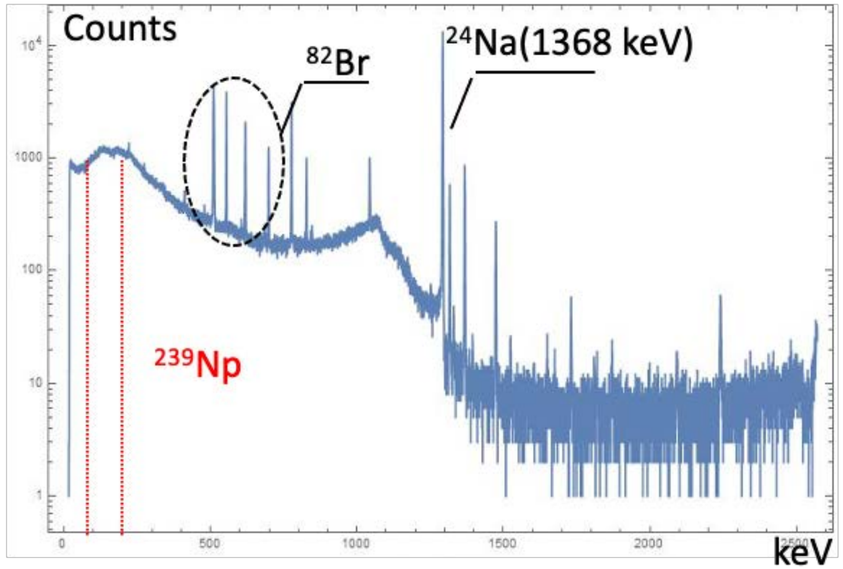
Measurements after irradiation



Before and after sample grating

	^{40}K – pre [1E-12 g/g]	^{40}K – post [1E-12 g/g]
PANEL 1 (step2) – sample E3	0.37 ± 0.05	< 0.16

→ A surface contamination may appear also with NAA



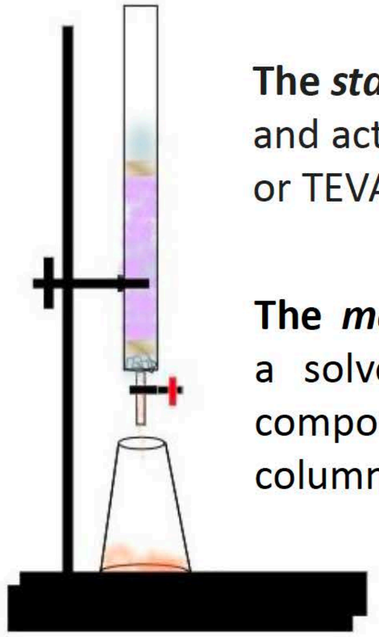
→ Effect of interferences in the sample matrix

Practical NAA

Radiochemical separation

Extraction Chromatography

Column Chromatography



The ***stationary phase***: column and actinide absorb resin (TRU or TEVA)

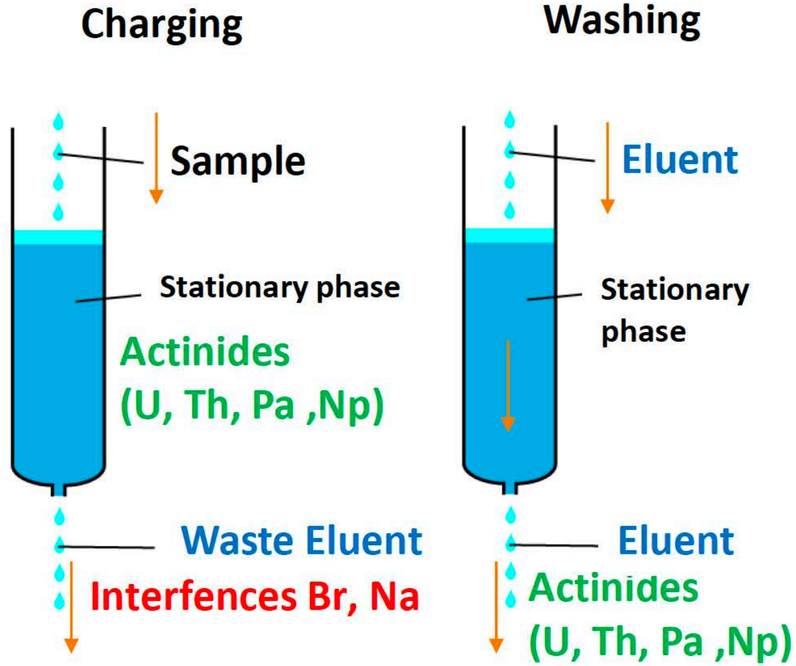
The ***mobile phase*** or *eluent* is a solvent used to move the compounds through the column.

Ideally the column chromatography **selectively absorbs actinide activities** (U, Th, Pa ,Np) while allowing interferences (Br, Na) pass through

$$^{238}_{92}U + n \xrightarrow{\beta^-} {}^{239}_{93}Np + \gamma$$

$$^{232}_{90}Th + n \xrightarrow{\beta^-} {}^{233}_{91}Pa + \gamma$$

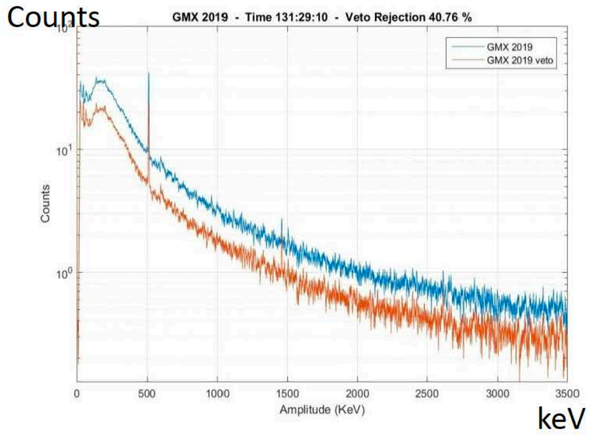
After irradiation



Practical NAA

Coincidence measurements

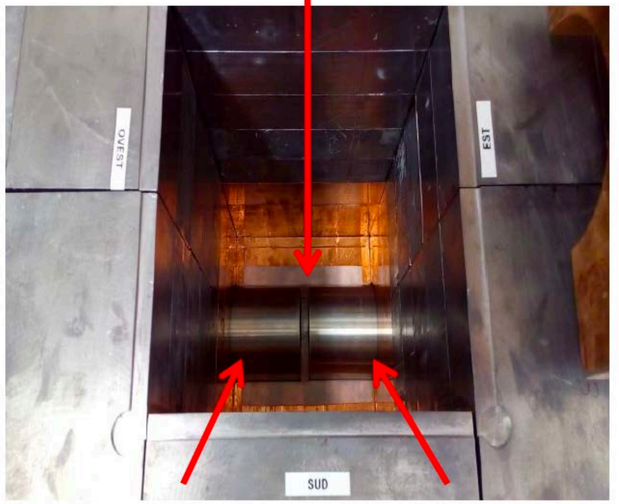
Ge-Ge HPGe: Background reduction



Plastic scintillator veto

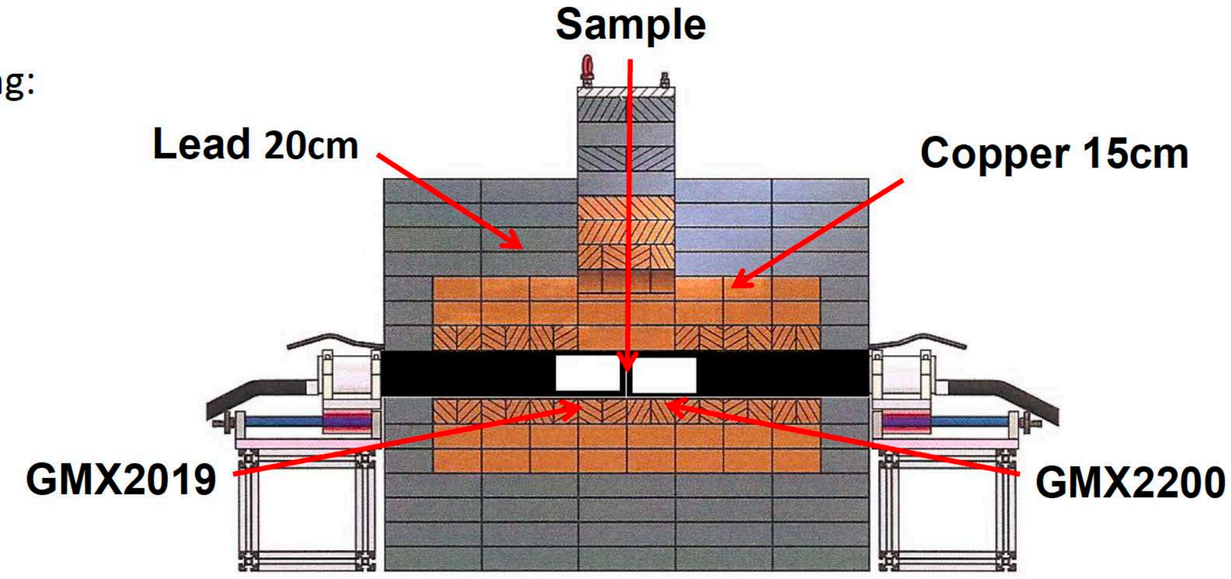
Anticoincidence technique

Background suppression **~40%**



GMX2019 **GMX2200**

Shielding:



2x GMX detectors:

- Coaxial detector (n-type)
- Relative efficiency: 100%
- Ultra Low Background configuration
- Low Threshold (20 keV)
- Muon veto

Practical NAA

Coincidence measurements

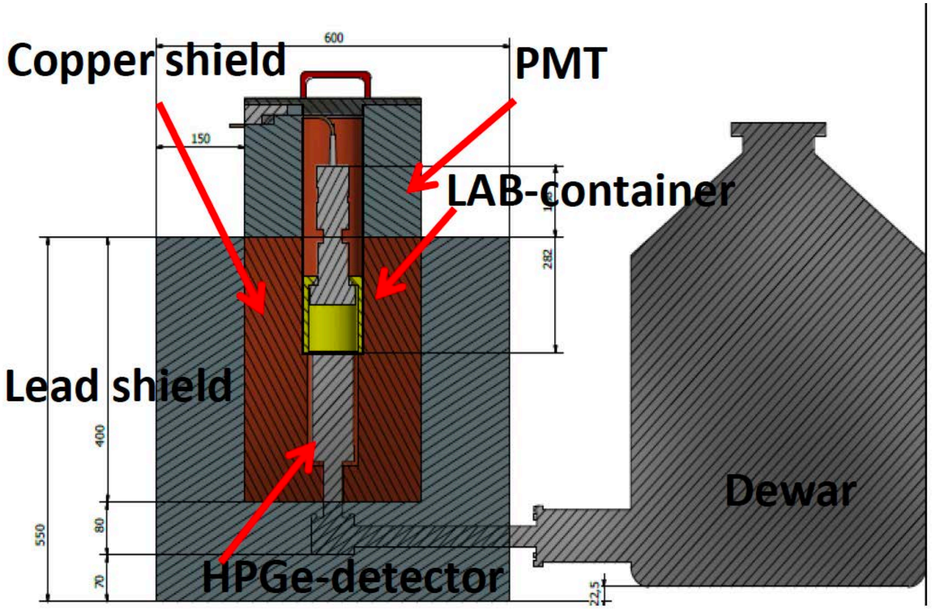
$$^{A}X + n \longrightarrow {}^{A+1}X \xrightarrow{\beta^-} {}^{A+1}_{Z+1}Y + \gamma_{cascade}$$

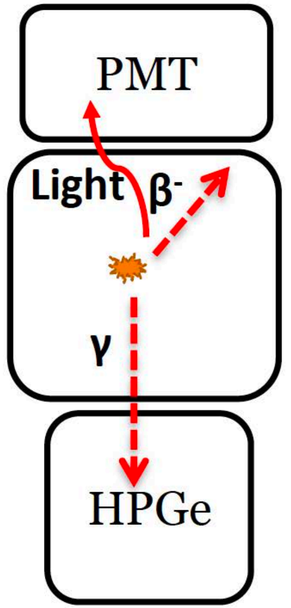
β-ϒ coincidence detector

PMT

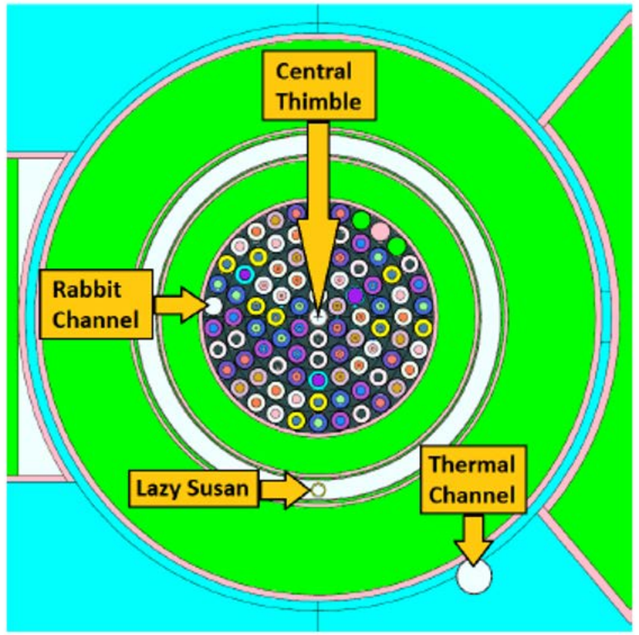
Liquid Scintillator Container

GeSparK: β-γ detector





Examples of achievable sensitivities with NAA



Neutron irradiation:

TRIGA Mark II research reactor (250 kW) - Pavia, Italy

^{238}U → 0.012 mBq/kg – 1 ppt

^{232}Th → 0.004 mBq/kg – 1 ppt

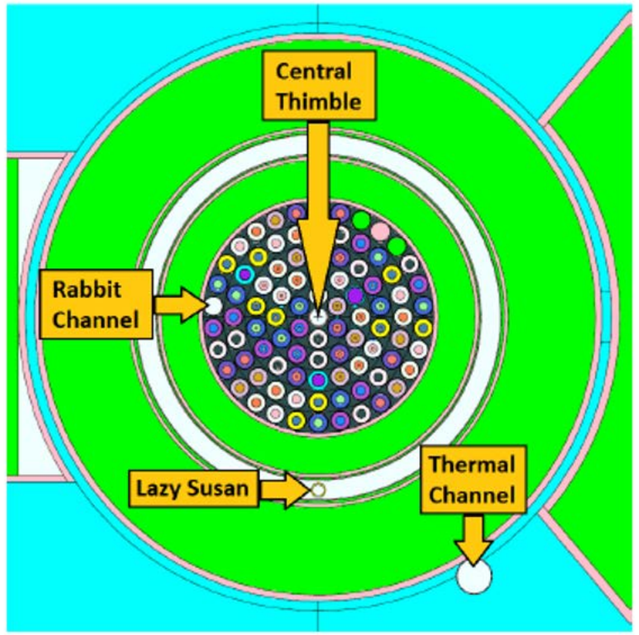
^{40}K → 0.27 mBq/kg – 1 ppt

Sample preparation and HPGe measurement at Milano-Bicocca:

Acrylic sample of 6 g

CONCENTRATIONS		
$[^{40}K]$ $(10^{-12}$ g/g)	$[^{238}U]$ $(10^{-12}$ g/g)	$[^{232}Th]$ $(10^{-12}$ g/g)
0.09 ± 0.02	< 0.17	< 0.13

Examples of achievable sensitivities with NAA



Neutron irradiation:

TRIGA Mark II research reactor (250 kW) - Pavia, Italy

Sample preparation and HPGe measurement at Milano-Bicocca:

LAB sample

Detector	LAB Sample	Sample mass	^{238}U [g/g]	^{232}Th [g/g]
β-ϒ detector	Distillated	22g	**<6·1E-14**	**<3·1E-13**

Limit for the sentivity Limit @ 90% C.L.

Sample **mass is limited** at few tens of grams

Presence of interferences **^{82}Br** and **^{24}Na**

Examples of achievable sensitivities with NAA

	^{40}K [1E-12 g/g]	^{238}U [1E-12 g/g]	^{232}Th [1E-12 g/g]	Ref.	
SNO Acrylic	-	< 1.1	< 1.1	[1]	
Borexino Liquid Scintillator	< 6.1	< 1.0 E-5	< 1.8 E-4	[2]	RNAA
KamLAND Liquid Scintillator	< 2.4 E-3	< 1.0 E-5	< 5.5 E-3	[3]	with pre-concentration
EXO Heat Transfer Fluid HFE-7000	< 580	< 7.3	< 3.7	[4]	
EXO Heat Transfer Fluid HFE-7000	-	< 0.015	< 0.015	[4]	with pre-concentration
EXO DuPont Teflon TE 6472 raw	1800±200	< 0.78	< 0.26	[4]	
EXO APT Teflon	2010±200	< 1.2	< 0.62	[5]	
MAJORANA Teflon TE 6472	150±20	0.025±0.002	< 0.4	[6]	

and many other materials in these papers →

[1] J. Boger et al., Nucl. Instr. and Meth. A 449 (2000) 172
[2] R.v. Hentig et al., Nucl. Phys. B (Proc. Suppl.) 78 (1999) 115
[3] Z. Djurcic et al., Nucl. Instr. and Meth. A 507 (2003) 680
[4] D.S. Leonard et al., Nucl. Instr. and Meth. A 591 (2008) 490
[5] D.S. Leonard et al., Nucl. Instr. and Meth. A 871 (2017) 169
[6] N. Abgrall et al., Nucl. Instr. and Meth. A 828 (2016) 22