

LOW RADIOACTIVITY TECHNIQUES 2019 WORKSHOP (LRT 2019)  
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# NEUTRON ACTIVATION ANALYSIS



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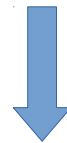
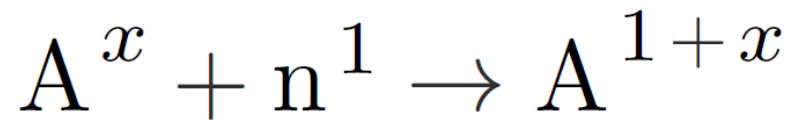


# The technique

Neutron activation analysis (NAA) is a very sensitive method for qualitative and quantitative determination of elements based on the measurement of characteristic radiation from radionuclides formed directly or indirectly by neutron irradiation of the material.

- Multi-element capability
- Sensitivity for many elements

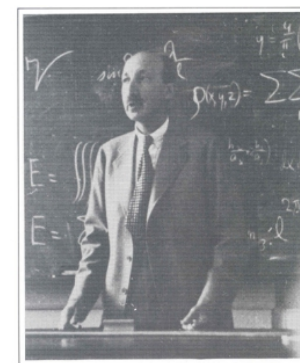
The principle is very simple:



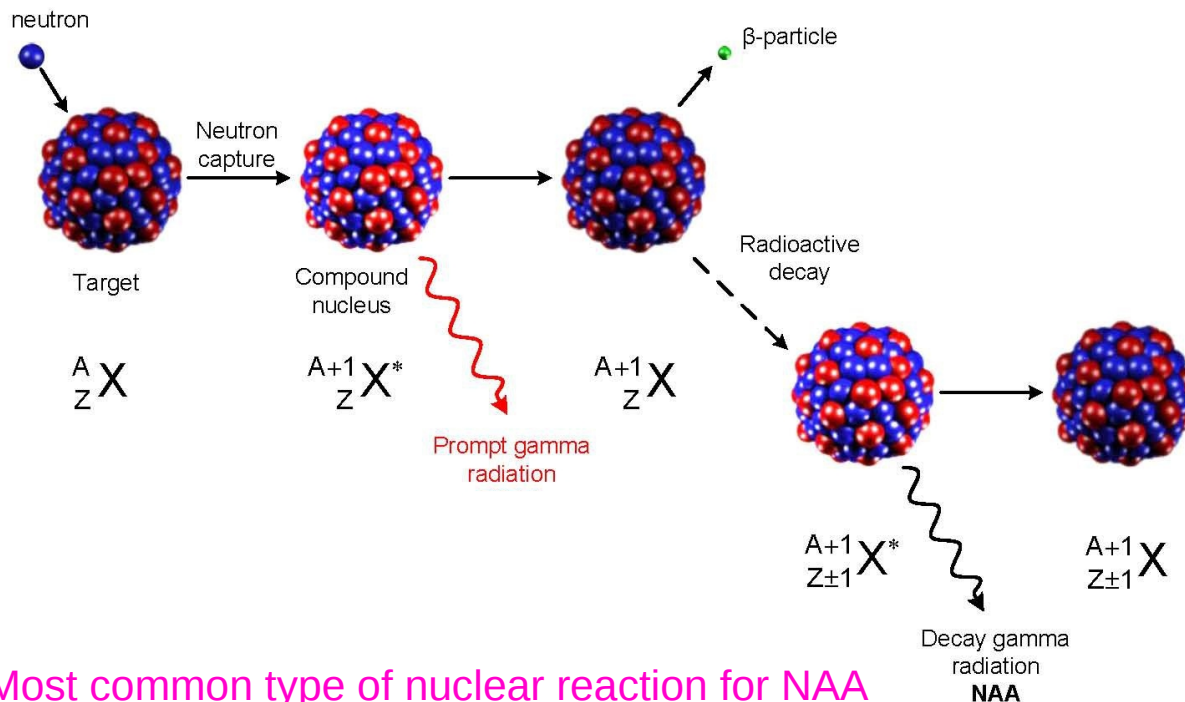
to be measured

# Brief history

- After the discovery of the neutron by Chadwick in 1932, neutron activation was first suggested by G. Hevesy and H. Levi in 1936, using a neutron source ( $^{226}\text{Ra}+\text{Be}$ ) to measure activated Dy atoms.
- In the first decade of activation analysis, many worked on the measurement of fundamental data of radionuclides, using GM counters and ionization chambers as major instruments.
- In the 1940s, research reactors became an available source of neutrons increasing the fluxes at one's disposal of at least six orders of magnitude.
- The availability of scintillation detectors in the 1950s, the development of semiconductor detectors and multichannel analyzers in the 1960s, and the advent of computers and relevant software in the 1970s, made the nuclear technique an important analytical tool for the determination of many elements at trace level.



# Basic principles of NAA



Prompt radiation emitted  $\sim 10^{-14}$  s after neutron capture.

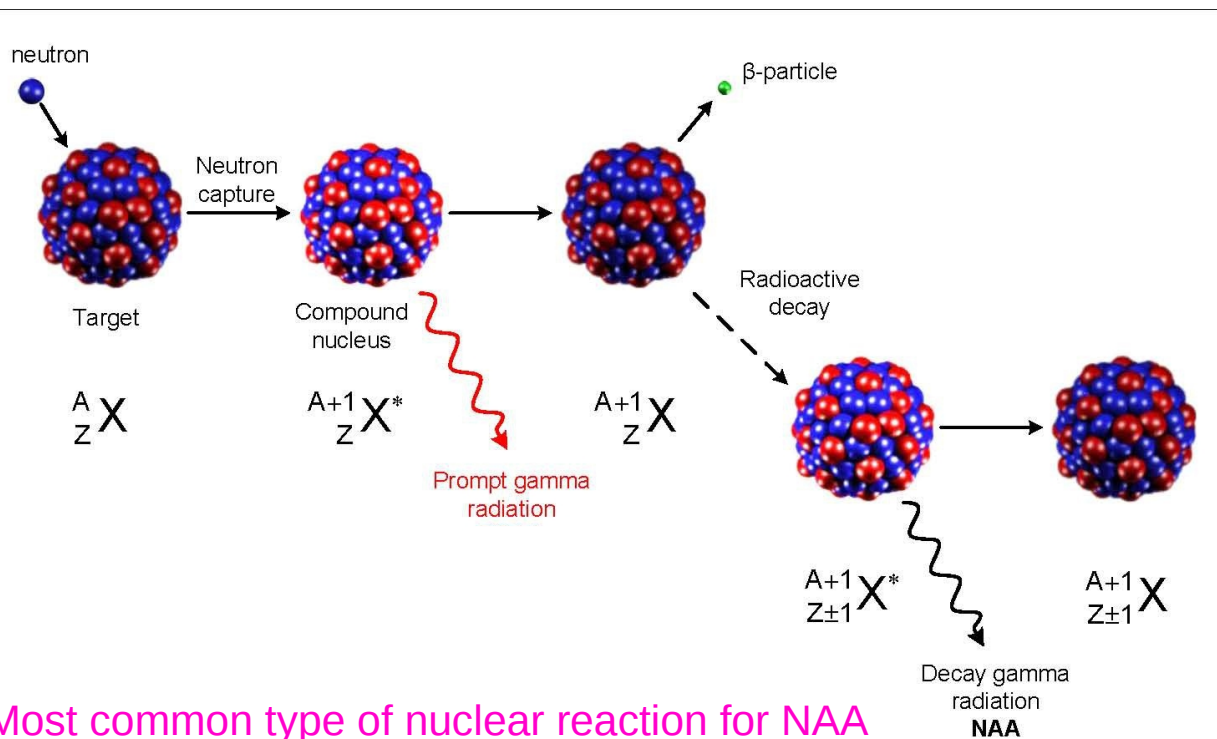
**Prompt-gamma Analysis (PGA):** measurement of gamma-rays during de-excitation of the compound nucleus after neutron capture.

- A bombarding particle is absorbed by an atomic nucleus after a nuclear reaction.
- A compound nucleus is formed (highly excited, unstable nucleus).
- The compound nucleus de-excites, usually by ejecting a small particle and a product nucleus.



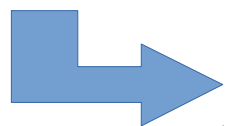
The particle may be an elementary particle (neutron, electron, proton), an alpha particle or a photon. The product nucleus may be stable or radioactive.

# Basic principles of NAA



- A bombarding particle is absorbed by an atomic nucleus after a nuclear reaction.
- A compound nucleus is formed (highly excited, unstable nucleus).
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**Delayed-gamma Neutron Activation Analysis (DGNAA):** measurement of gamma-rays emitted during the decay of the product nucleus after the capture reaction is stopped.



It is the commonly employed method in NAA. It is useful for many types of elements that produce radioactive nuclei. The measuring time and sensitivity depend on decay half-life.

# Types of NAA

There exist many classifications according to the involved chemistry, to the energy of incoming neutrons, to the way the irradiation is performed (e.g. cyclic irradiations).

We consider two broad categories:

## **Destructive or Radiochemical NAA (RNAA):**

A method of NAA in which chemical separations are applied after the irradiation to separate activities of interest from interfering activities.

## **Non-destructive or Instrumental NAA (INAA):**

The most widely applied method of NAA, in which no chemical procedures are applied before or after the irradiation. The selectivity of activities of interest is accomplished by the measurement after different decay times and by the use of special radiation detectors.

# Neutron sources

## Radioisotopic neutron sources:

- Two component neutron source based on ( $\alpha$ ,n) or ( $\gamma$ ,n) reactions, like  $^{241}\text{Am}(\text{Be})$ ,  $^{124}\text{Sb}(\text{Be})$ , ...
- Spontaneous fission sources, like  $^{252}\text{Cf}$ .
  - different energy spectra and rates depending on the involved reaction

## Neutron generators:

- 2.4 MeV neutrons from  $\text{D}(\text{d},\text{n})^3\text{He}$
- 14 MeV neutrons  $\text{D}(\text{t},\text{n})^4\text{He}$

## Spallation neutron sources:

Heavy elements such as W, Pb, U irradiated with high-energy protons or other particles are spalled into two or more fragments and many neutrons are released.

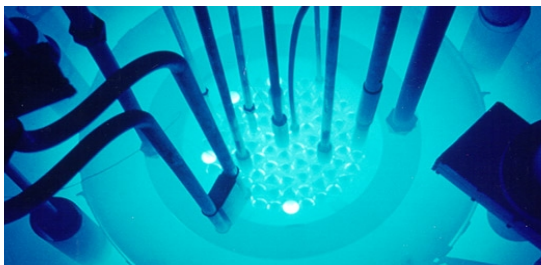
## Nuclear research reactors:

mostly used

# Nuclear research reactors

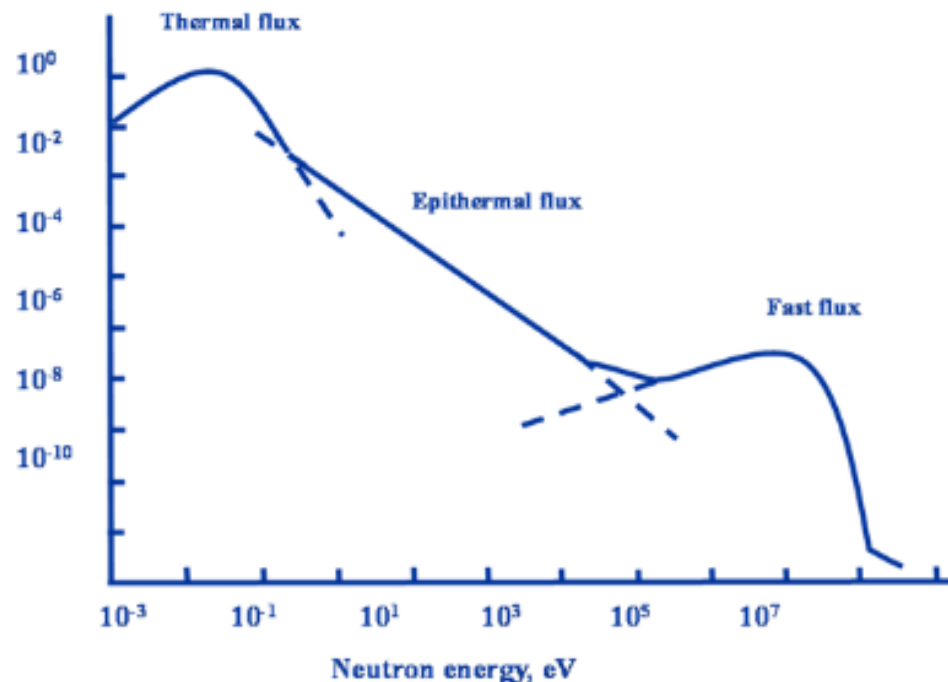
Owing to the high neutron flux, nuclear research reactors operating in the power region of 20 kW -10 MW, with maximum thermal neutron fluxes of  $10^{11} - 10^{14}$  **neutrons cm<sup>-2</sup> s<sup>-1</sup>** are the most efficient neutron sources for high sensitivity activation analysis induced by epithermal and thermal neutrons.

Neutron energy distribution in a light-water moderated research reactor



Relative neutron flux

$\phi(E)$

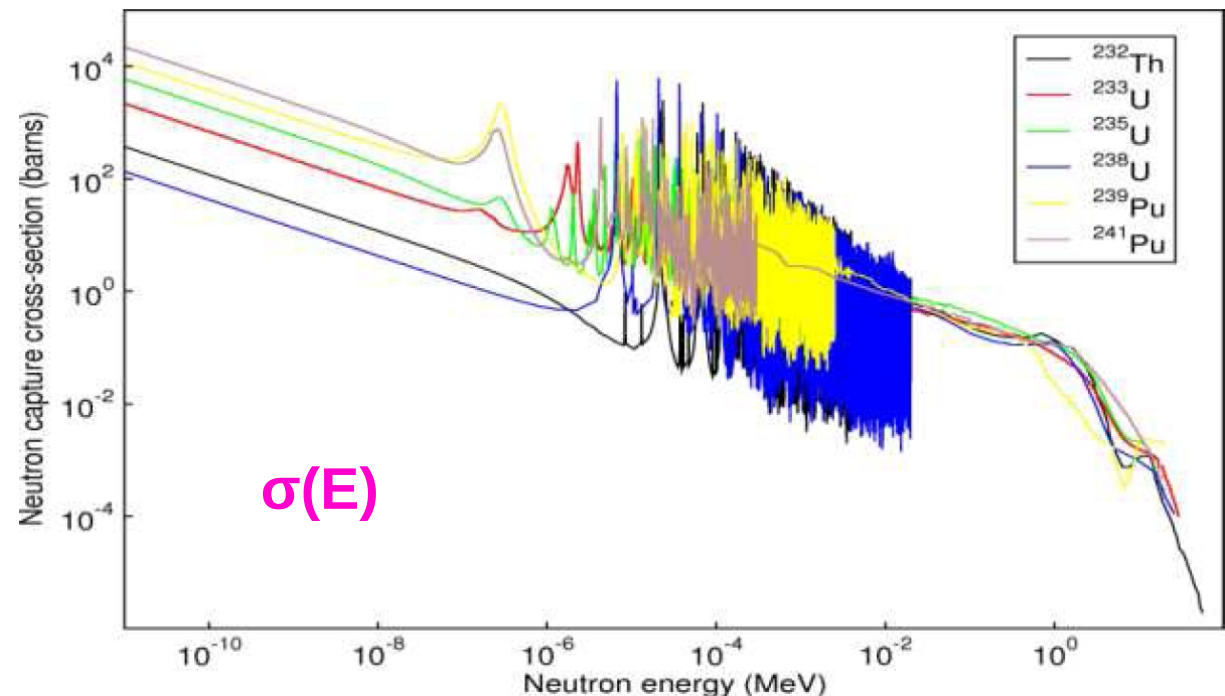


# Nuclear research reactors

Owing to the high neutron flux, nuclear research reactors operating in the power region of 20 kW -10 MW, with maximum thermal neutron fluxes of  $10^{11} - 10^{14}$  neutrons  $\text{cm}^{-2} \text{s}^{-1}$  are the most efficient neutron sources for high sensitivity activation analysis induced by epithermal and thermal neutrons.

## Activation via (n, $\gamma$ ) reactions

	$\alpha, 3n$	$\alpha, 2n$	$\alpha, n$
	$p, n$	$p, \gamma$	$\alpha, np$
$Z$	$\gamma, n$ $n, 2n$	Target nuclide	$n, \gamma$ $d, p$
	$\gamma, pn$ $d, \alpha$	$\gamma, p$ $n, pn$	$n, p$
	$n, \alpha$		
			$N$



Neutron capture cross section vs Energy for major actinides

# Activation rate

The number of radioisotopes that each second are created by neutron-induced reactions (the *activation rate*  $R$ ) is related to the amount ( $N$ ) of the original, stable isotope in the sample:

$$R = \mathcal{N} \int \phi(E) \sigma(E) dE$$

Usually one defines an *effective cross section*, which gives the mean value of the cross section weighted for the neutron energy distribution: it is different in the various irradiation facilities.

$$\sigma_{\text{eff}} = \frac{\int \phi(E) \sigma(E) dE}{\int \phi(E) dE}$$

The activation rate is then simply related to the integral neutron flux:

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

$$\Phi_{\text{tot}} \equiv \int \phi(E) dE$$

Monte Carlo simulations like MCNP may be used for the numerical calculation of the effective cross section [e.g. D.Chiesa et al., Ann. Nucl. Energy 85 (2015) 925]

# Typical applications of NAA

- **Archeology:** amber, bone, ceramics, coins, glasses, jewellery, metal artefacts and sculptures, mortars, paintings, pigments, pottery, raw materials, soils and clays, stone artefacts and sculptures, ...
- **Biomedicine:** animal and human tissues activable tracers, bile, blood and blood components, bone, brain cell components and other tissues, breast tissue, cancerous tissues, ...
- **Environmental:** aerosols, atmospheric particulates (size fractionated), dust, fossil fuels and their ashes, soils, sediments, tobacco and tobacco smoke, surface and ground waters, volcanic gases, ...
- **Forensics:** bomb debris, bullet lead, explosives detection, glass fragments, paint, hair, ...
- **Geology and geochemistry:** asbestos, crude oils, kerosene, petroleum, rocks, sediments, soils, ...
- **Industrial products**

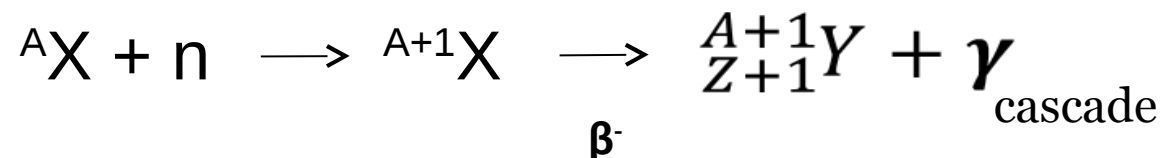
# Application to low background experiments

NAA can achieve substantially greater sensitivity than direct  $\gamma$ -ray counting. It can be applied to measure natural contaminant ( $^{232}\text{Th}$ ,  $^{238}\text{U}$ ,  $^{40}\text{K}$ ) concentrations in detector materials with no long-lived neutron activation products.



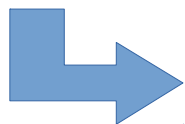
- For natural decay chains ( $^{232}\text{Th}$ ,  $^{238}\text{U}$ ) it is complementary to  $\gamma$ -ray counting, since it measures only parent nuclide concentrations (as ICP-MS) → no infos on secular equilibrium breaks.
- For  $^{40}\text{K}$ , NAA reaches far greater sensitivities than all other techniques (ICP-MS has low sensitivity to  $^{40}\text{K}$  because of interferences, mainly  $^{40}\text{Ar}$ ).

# Key ingredients for NAA



Three key ingredients:

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

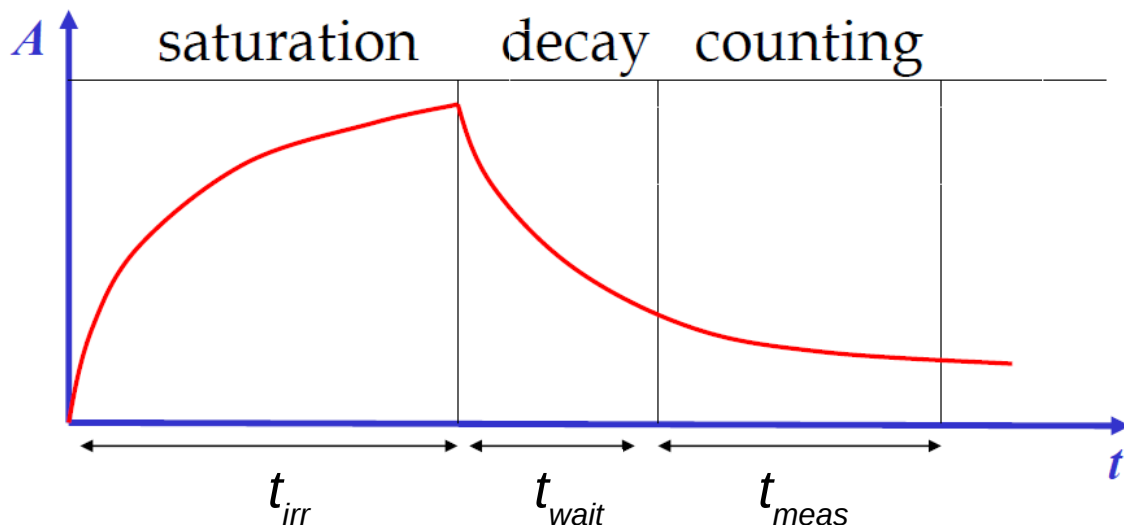


Sensitivity depends on:

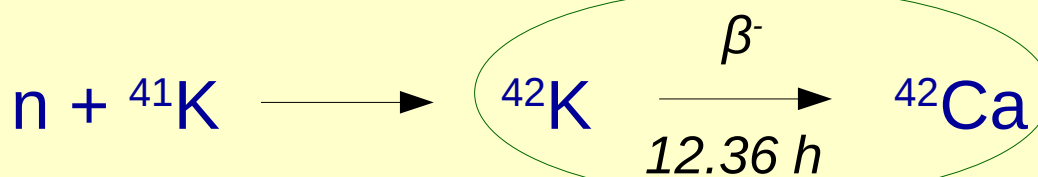
- type of material (short-lived activation products)
- neutron exposure time
- interferences in the matrix
- background in the region of the gamma emission



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



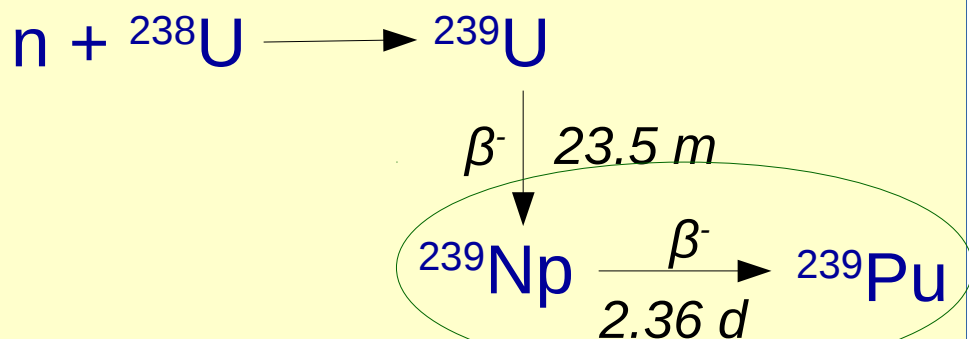
# NAA for $^{40}\text{K}$ , $^{232}\text{Th}$ , $^{238}\text{U}$



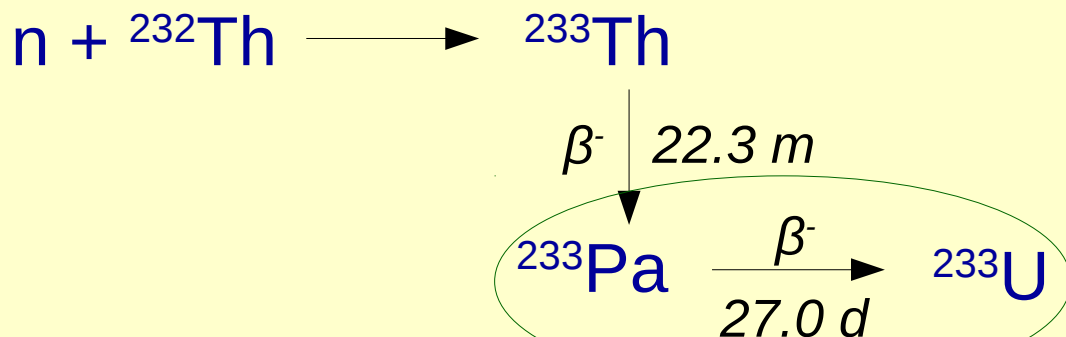
- $^{41}\text{K}$  isotopic abundance is 6.7%
- $^{40}\text{K}$  isotopic abundance is 0.01%



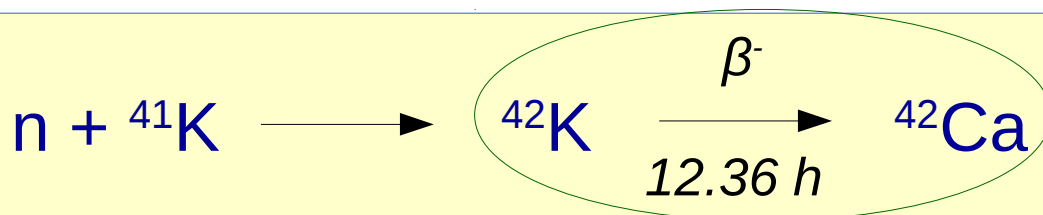
$^{40}\text{K}$  contamination is calculated from  $^{41}\text{K}$  one



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  $^{42}\text{K}$ .



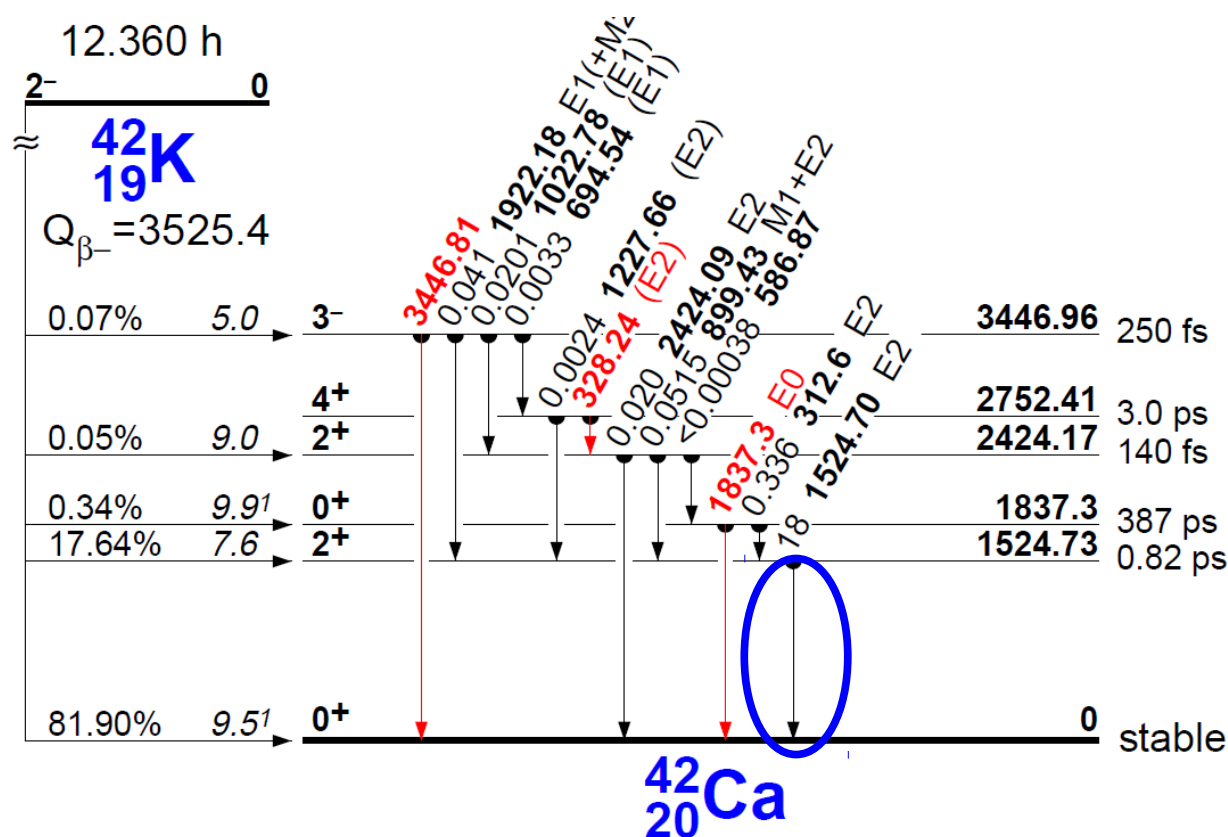
# NAA for $^{40}\text{K}$



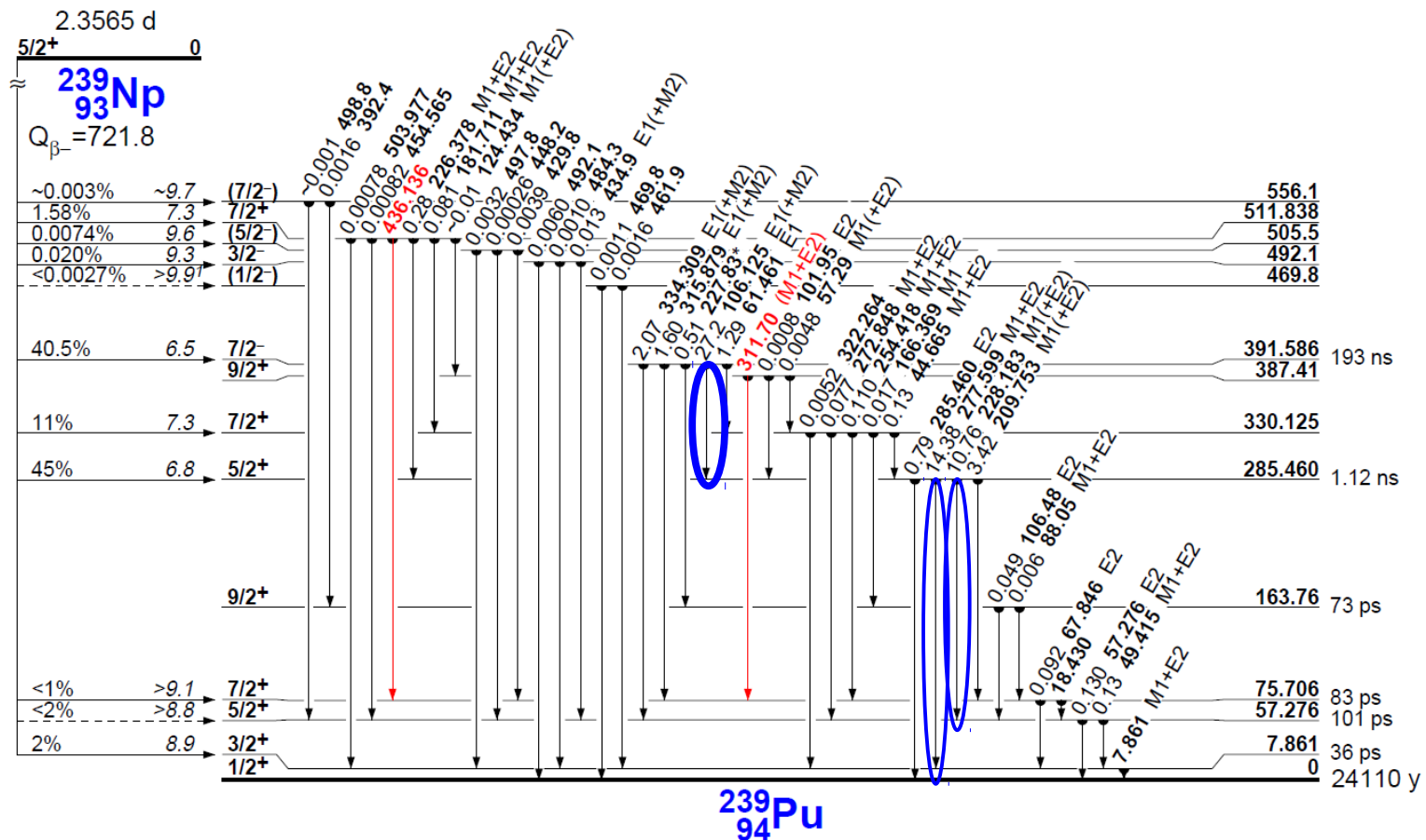
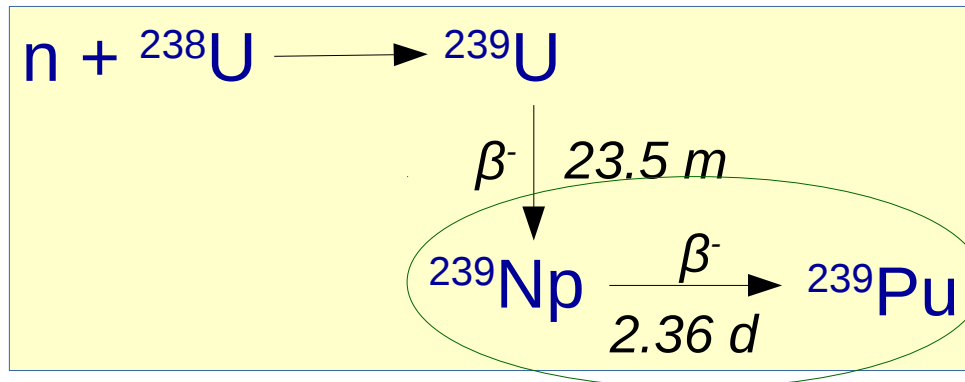
- $^{41}\text{K}$  isotopic abundance is 6.7%
- $^{40}\text{K}$  isotopic abundance is 0.01%



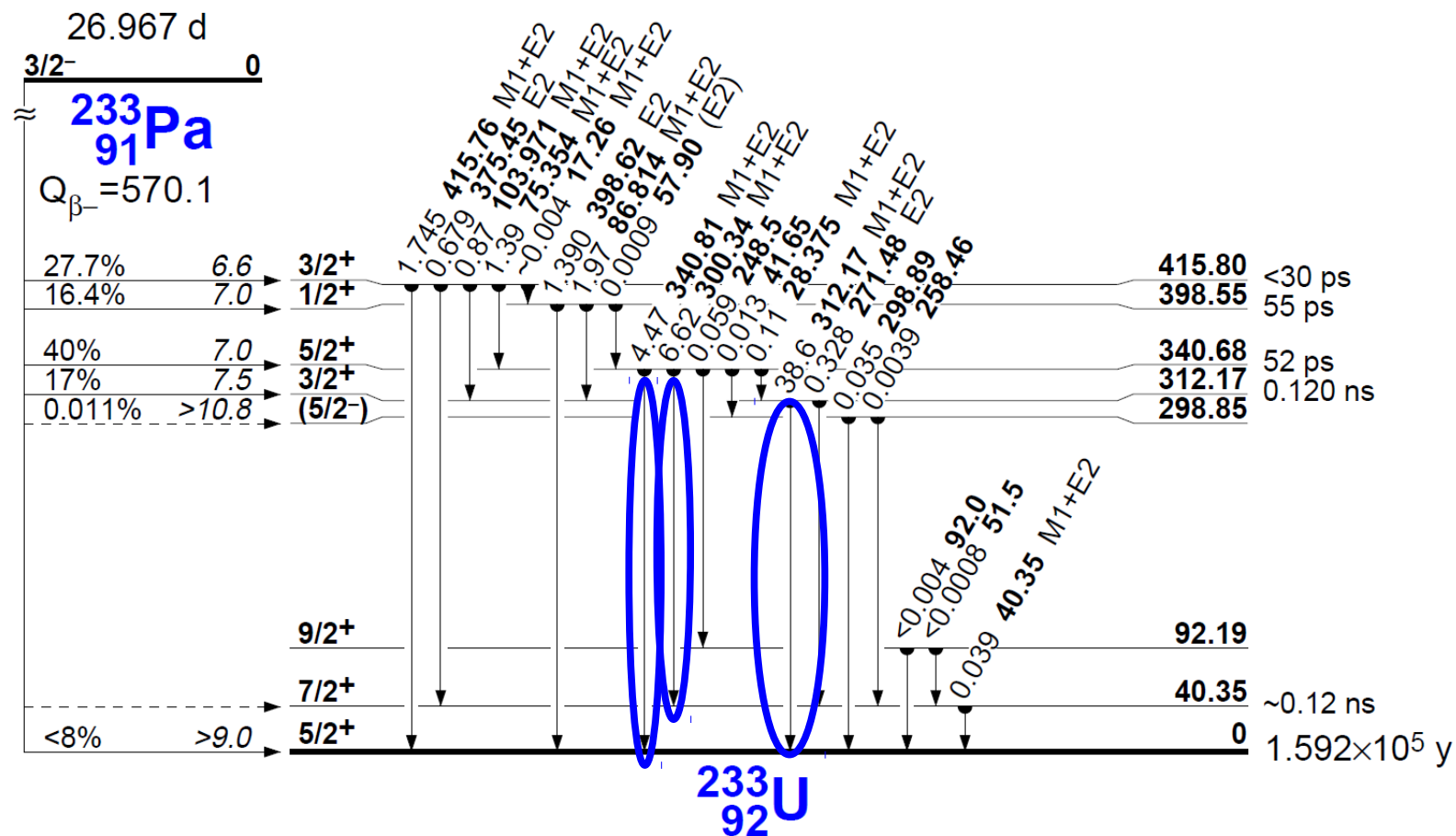
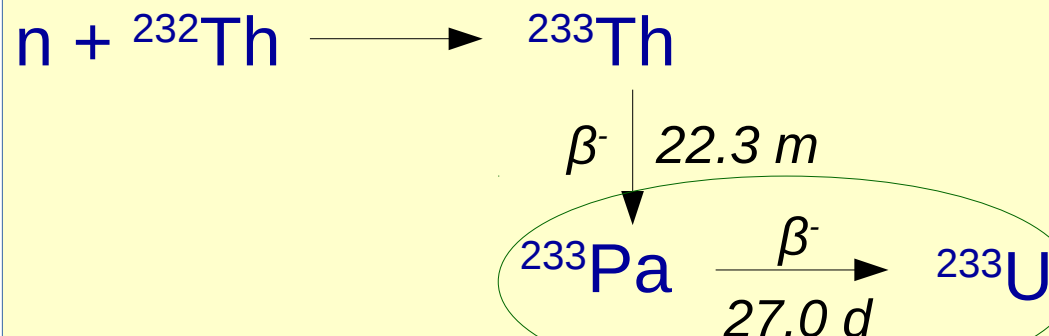
$^{40}\text{K}$  contamination is calculated from  $^{41}\text{K}$  one



# NAA for $^{238}\text{U}$



# NAA for $^{232}\text{Th}$



# Concentration of trace elements evaluation

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

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

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

$$N(t_{irr}) = \frac{R}{\lambda} (1 - e^{-\lambda t_{irr}})$$

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 :

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

Two HPGe detectors at the  
Radioactivity Laboratories  
of INFN Milano-Bicocca



GeGEM  $\epsilon_{rel}$  30%



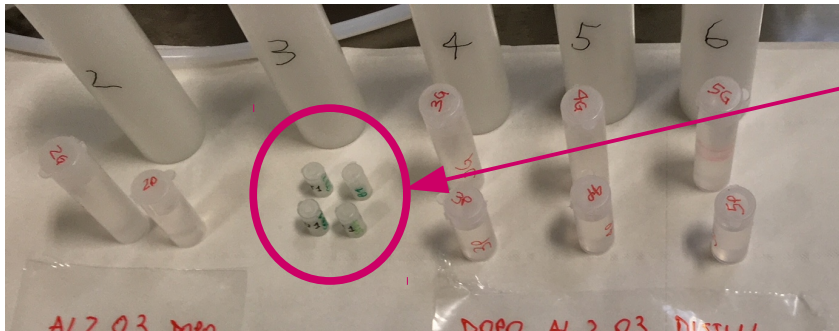
BeGE detector  $\epsilon_{rel}$  50%

# The relative method – irradiation standards

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

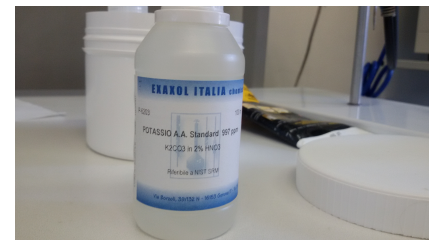
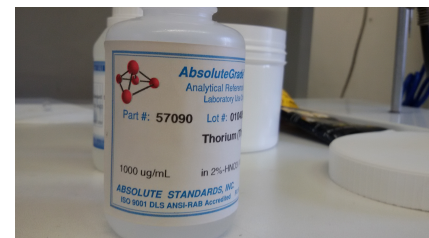
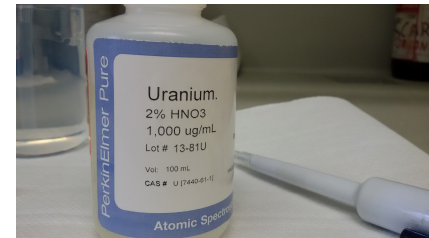
$$n_{dec} = \frac{R}{\lambda} \left( 1 - e^{-\lambda t_{irr}} \right) e^{-\lambda t_{wait}} \left( 1 - e^{-\lambda t_{meas}} \right) \quad \text{with} \quad R = N \sigma_{eff} \Phi_{TOT}$$

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



The irradiation standards are irradiated together with the sample in the same irradiation channels.

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.



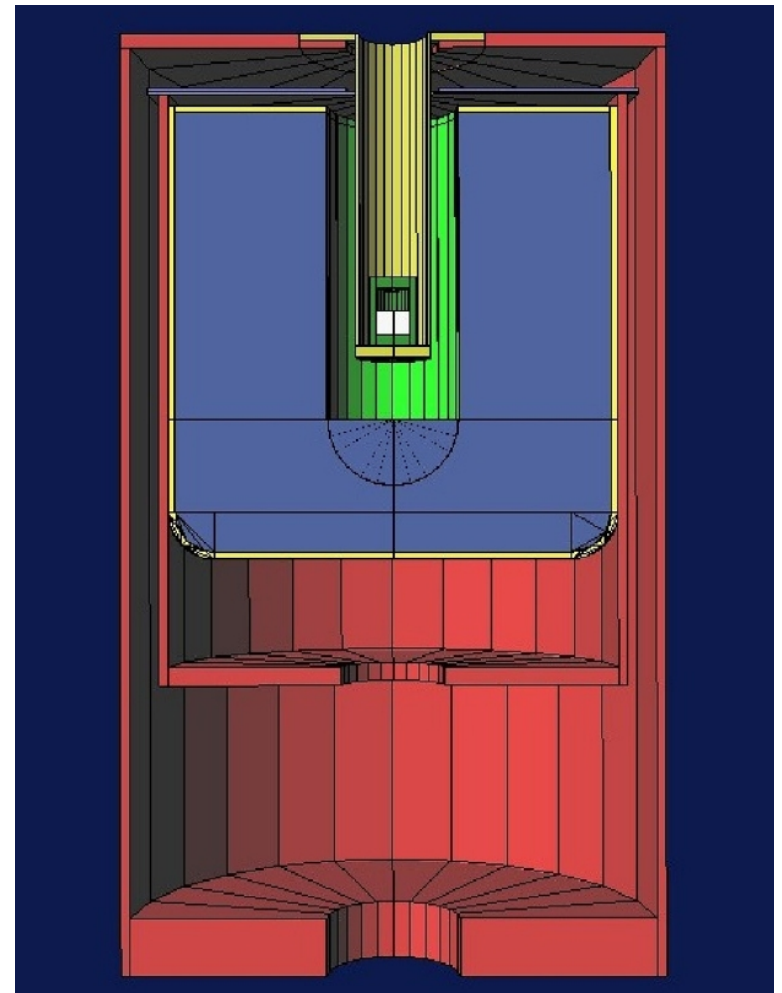
# HPGe measurement efficiency

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):

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

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.



# NAA procedure

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

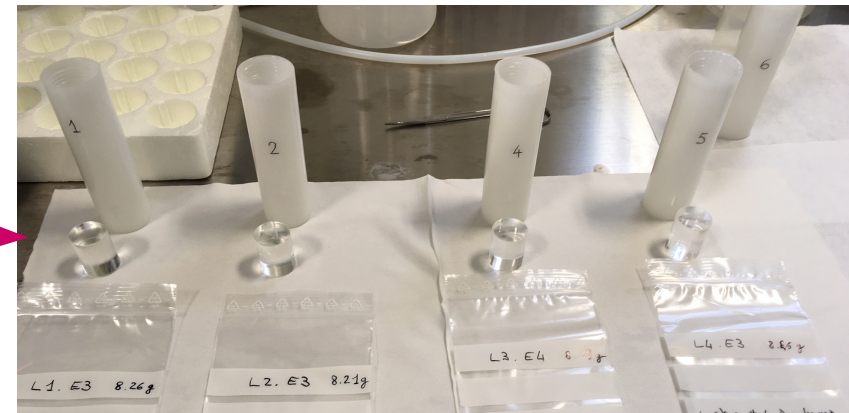
- **Sample preparation**

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



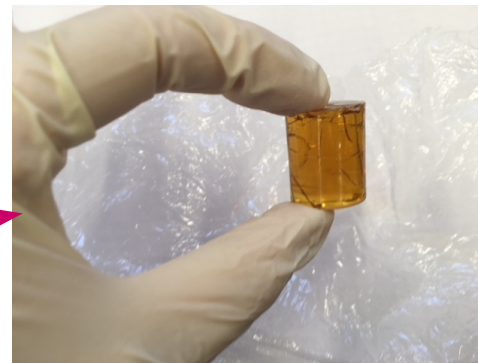
in ultra-trace measurements, extreme care is needed to avoid adding unwanted contaminants during this step

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



Clean room preparation of samples at Milano-Bicocca

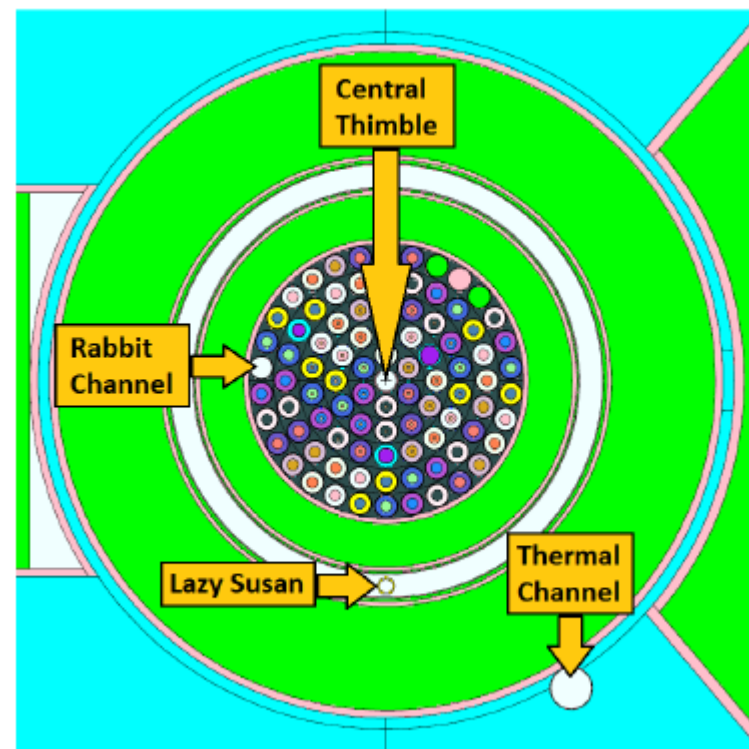
Radiolysis during neutron irradiation must be taken into account!



# Examples of achievable sensitivities with NAA

## Neutron irradiation:

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



## Sample preparation and HPGe measurements at Milano-Bicocca



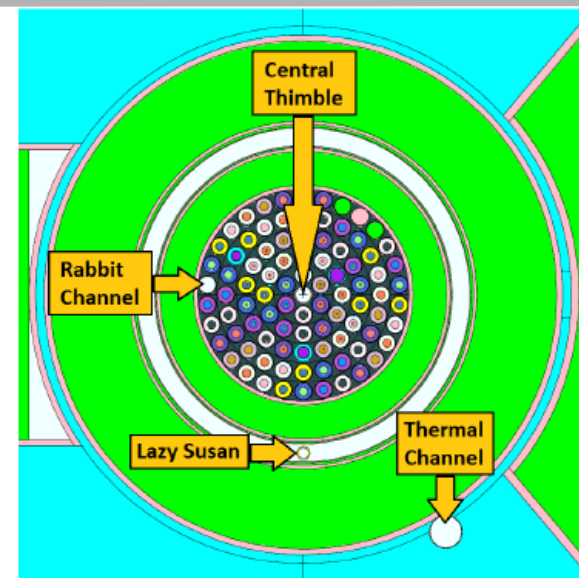
### 2x GMX detector

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

# Examples of achievable sensitivities with NAA

## Neutron irradiation:

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



## Sample preparation and HPGe measurements at Milano-Bicocca

$^{238}\text{U}$  → 0.012 mBq/kg – 1 ppt

$^{232}\text{Th}$  → 0.004 mBq/kg – 1 ppt

$^{40}\text{K}$  → 0.27 mBq/kg – 1 ppt

## Sensitivity achieved on **Acrylic** @ INFN Milano-Bicocca PRELIMINARY RESULT

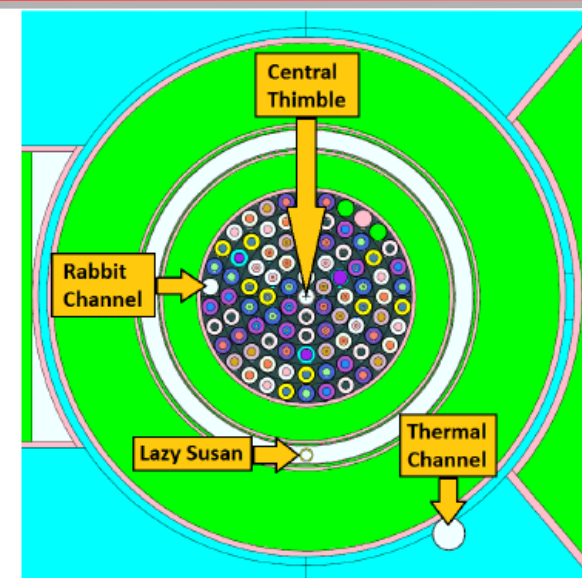
	$^{40}\text{K}$ [1E-12 g/g]	$^{238}\text{U}$ [1E-12 g/g]	$^{232}\text{Th}$ [1E-12 g/g]
Acrylic sample (8.2 g)	< 0.016	< 0.3	< 0.5

@ 90% C.L.

# Examples of achievable sensitivities with NAA

## Neutron irradiation:

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



Sample preparation  
and  
HPGe measurements  
at  
Milano-Bicocca

RNAA: in this case  $^{233}\text{Pa}$  was chemically  
separated using an Actinide Resin

Sensitivity achieved on **Copper** @ INFN Milano-Bicocca  
using RNAA:

@ 90% C.L.

$^{238}\text{U}$	→	0.012 mBq/kg – 1 ppt
$^{232}\text{Th}$	→	0.004 mBq/kg – 1 ppt
$^{40}\text{K}$	→	0.27 mBq/kg – 1 ppt

	$^{232}\text{Th}$ [1E-12 g/g]
Copper sample (199 g)	< 0.5

M.Clemenza et al., LRT 2010, AIP Conf. Proc. 1338 (2011) 37

# Examples of achievable sensitivities with NAA

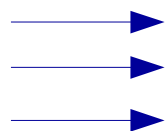
	<sup>40</sup> K [1E-12 g/g]	<sup>238</sup> U [1E-12 g/g]	<sup>232</sup> Th [1E-12 g/g]	Ref.
SNO Acrylic	-	< 1.1	< 1.1	[1]
Borexino Liquid Scintillator	< 6.1	< 1.0 E-5	< 1.8 E-4	[2]
KamLAND Liquid Scintillator	< 2.4 E-3	< 1.0 E-5	< 5.5 E-3	[3]
EXO Heat Transfer Fluid HFE-7000	< 580	< 7.3	< 3.7	[4]
EXO Heat Transfer Fluid HFE-7000	-	< 0.015	< 0.015	[4]
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]

RNAA

with pre-concentration

with pre-concentration

and many other  
materials in  
these papers

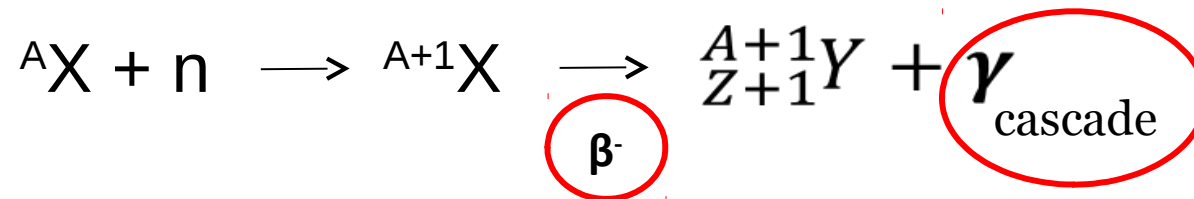


- [1] J. Boger et al., Nucl. Instr. and Meth. A 449 (2000) 172
- [2] R.v. Hentig et al., Nucl. Phys. B (Proc. Suppl.) 78 (1999) 115
- [3] Z. Djurcic et al., Nucl. Instr. and Meth. A 507 (2003) 680
- [4] D.S. Leonard et al., Nucl. Instr. and Meth. A 591 (2008) 490
- [5] D.S. Leonard et al., Nucl. Instr.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

# How to improve sensitivities?

HPGe background and, more severely, interfering isotopes in the matrix that are activated during the neutron irradiation (examples are  $^{24}\text{Na}$  and  $^{82}\text{Br}$ ) may spoil the achievable sensitivity because of the Compton tails of the main peaks.

One possibility to reduce that is to profit from **decay coincidences**.



**$\beta$ - $\gamma$**  coincidence detector



See M. Nastasi's talk later today

INFN Milano-Bicocca  
Radioactivity Laboratory

# Conclusions

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NAA is a very powerful analytical technique complementary to other assay methods for material selection and screening in low background experiments.

Trace elements analysis requires careful preparation of the irradiation campaign and of the test samples in order to reach sub-ppt sensitivities.

Chemical treatments and/or coincidence spectroscopy may help increasing the achievable sensitivities.