Neutron Activation Analysis for low background experiments

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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.

The principle is very simple:

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

$$\Big\downarrow$$

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

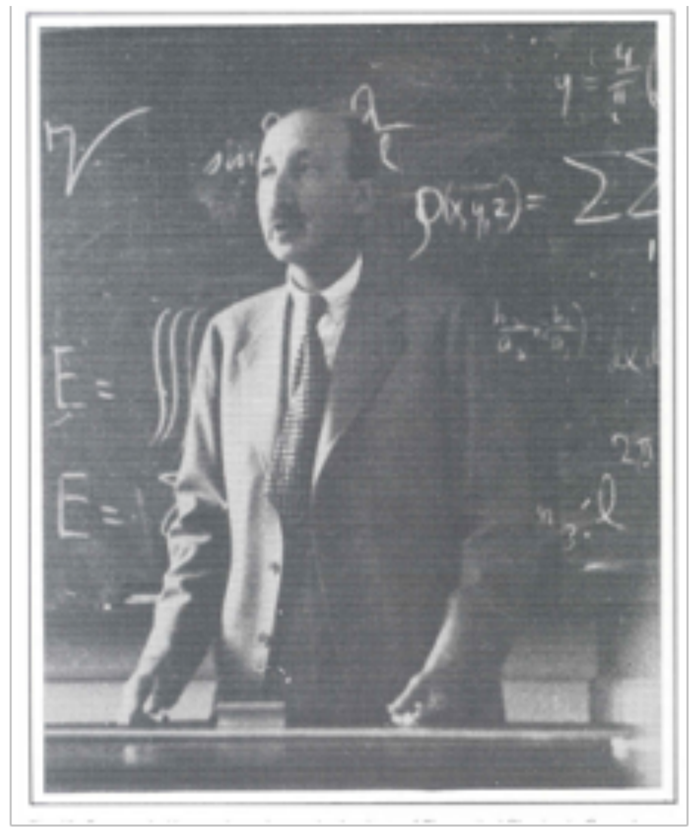
→ to be measured

- Multi-element capability
- Sensitivity for many elements

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}Ra+Be) to measure activated Dy atoms.


Niels Bohr Archive

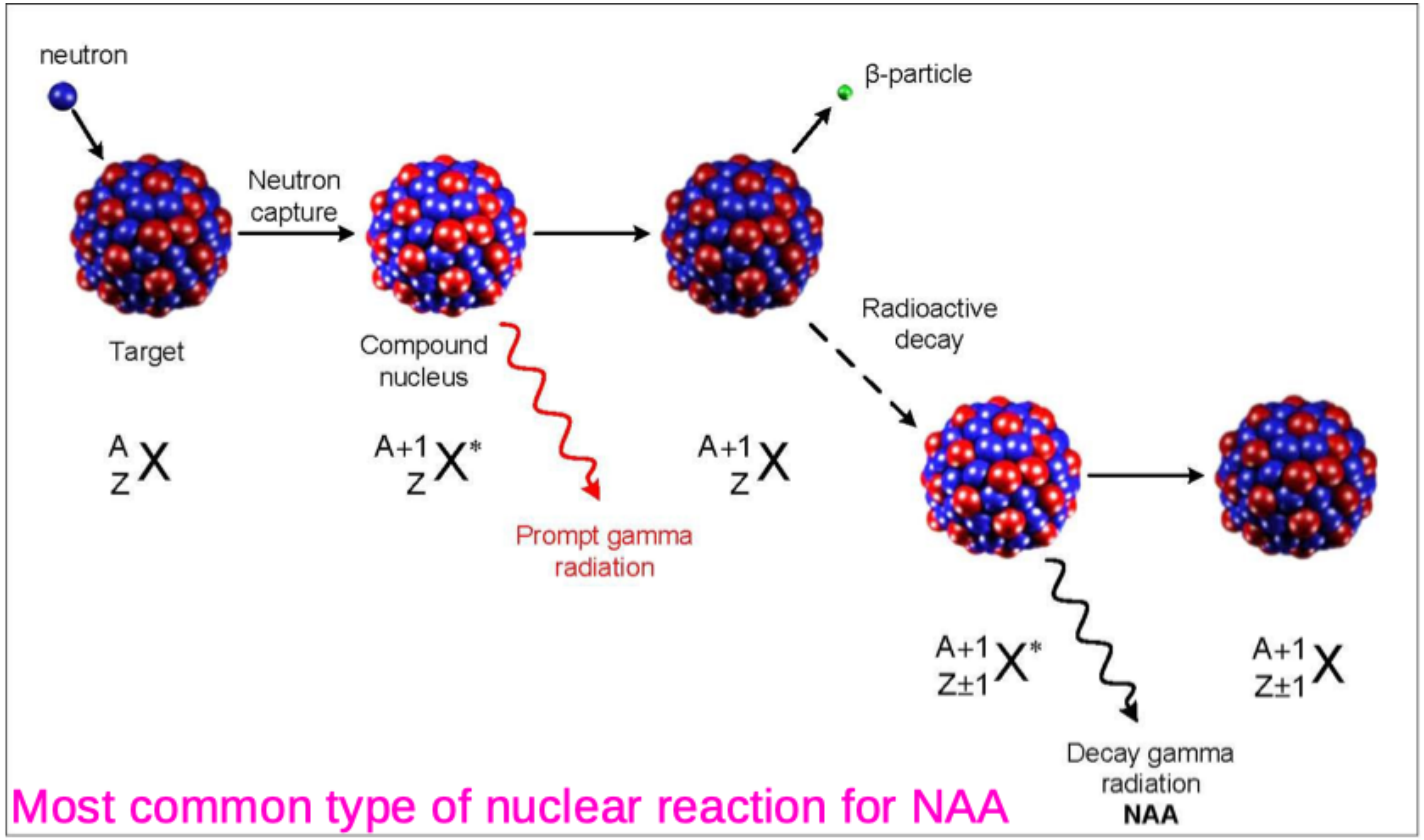


- In the first decade of activation analysis, many worked on the measurement of fundamental data of radionuclides, using GM counters and ionization chambers as major instruments.

- 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

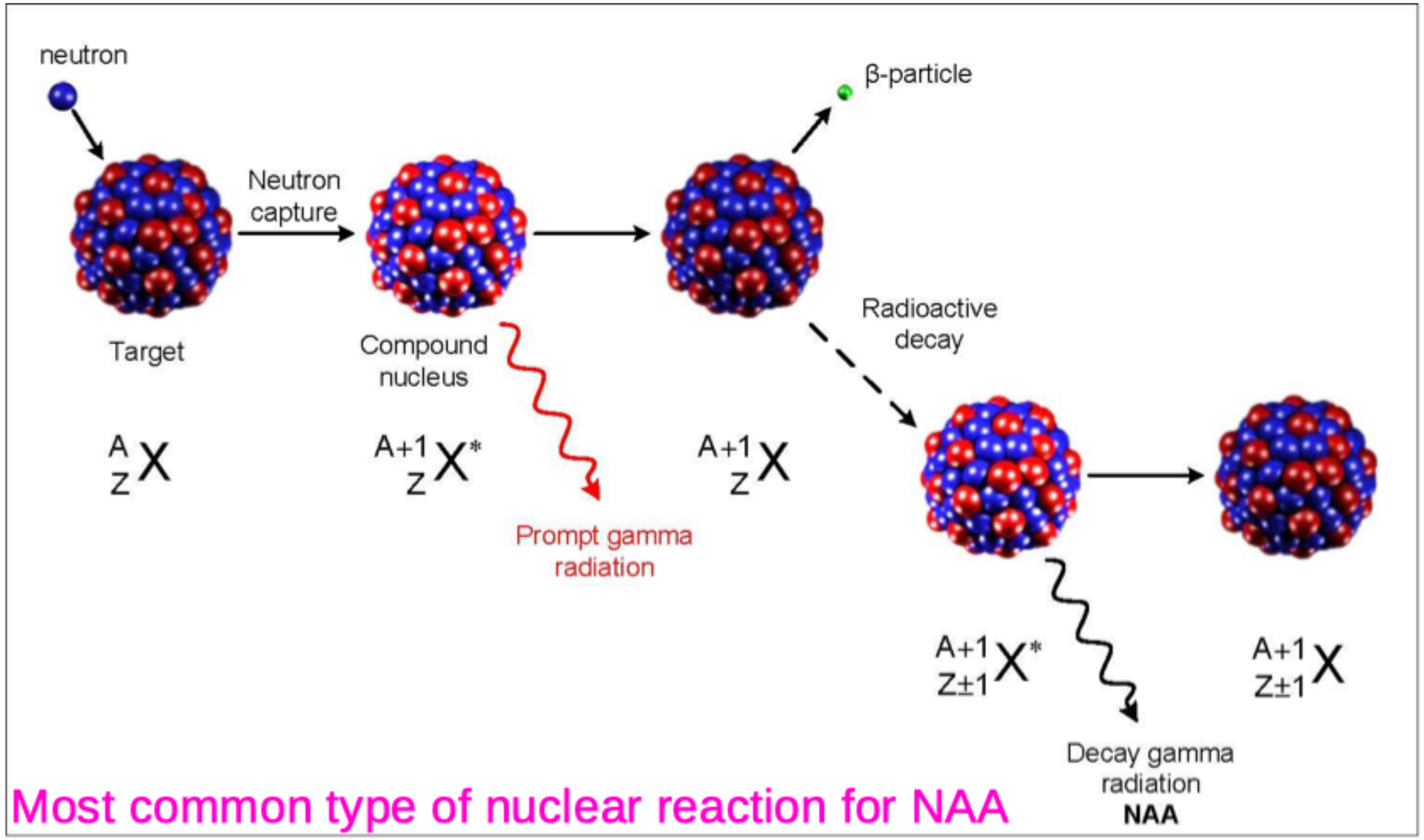


Most common type of nuclear reaction for NAA

- 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



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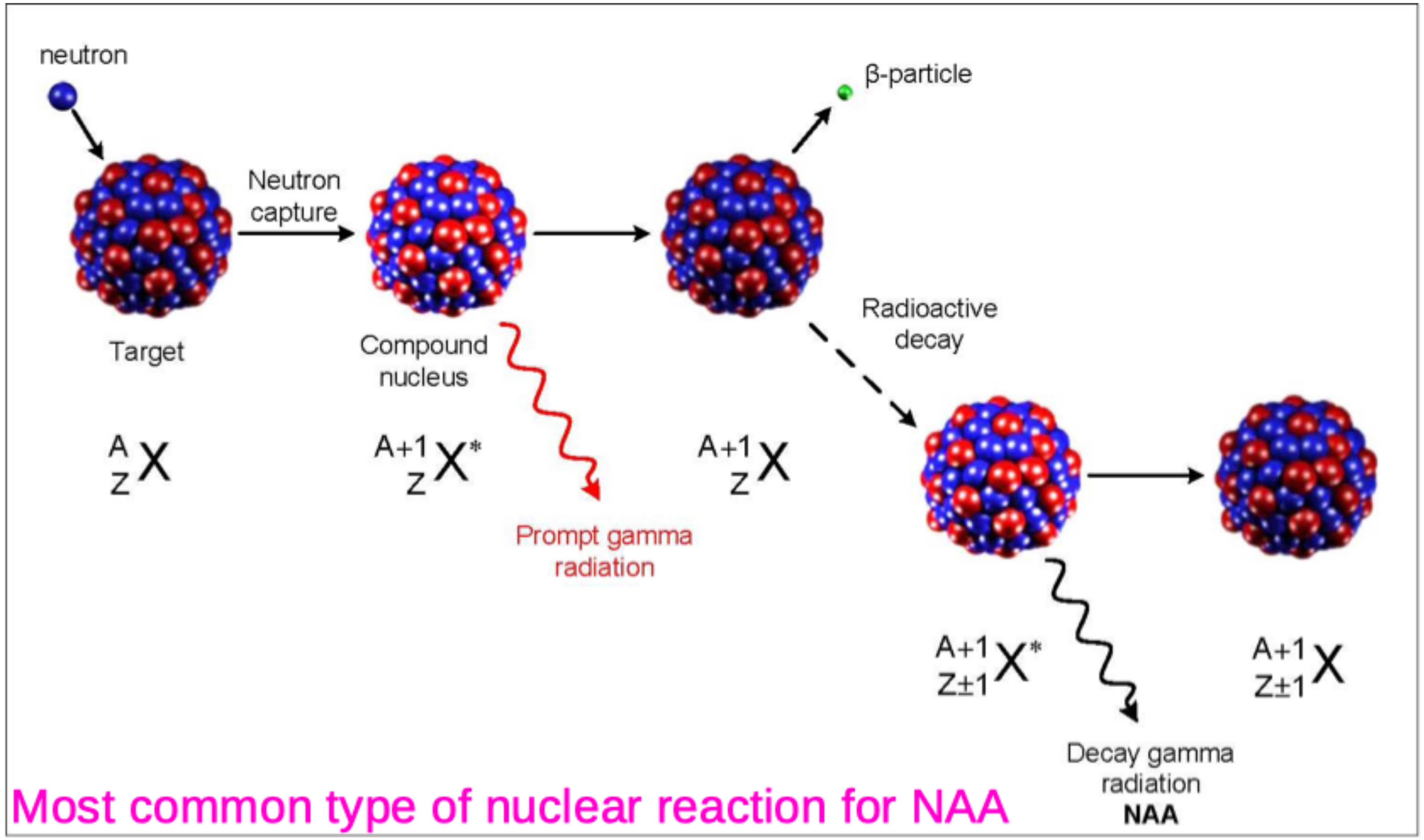
Prompt radiation emitted ~10^{-12} s after neutron capture.

↳

Prompt gamma Analysis (PGA):

measurement of γ rays during de-excitation of the compound nucleus after neutron capture

Basic principles of NAA



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- A bombarding particle is absorbed by an atomic nucleus after a nuclear reaction.
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Commonly employed method in NAA.
It is useful for many types of elements that produce radioactive nuclei.
Measuring time and sensitivity depend on decay half-life.

Delayed Gamma Neutron Activation Analysis (DGNAA):

measurement of γ rays emitted during the decay of the product nucleus after the capture reaction is stopped.

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 (α,n) or (γ,n) reactions, like ^{241}Am(Be), ^{124}Sb(Be), ...
- Spontaneous fission sources, like ^{252}Cf.

  → different energy spectra and rates depending on the involved reaction

Neutron generators:

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

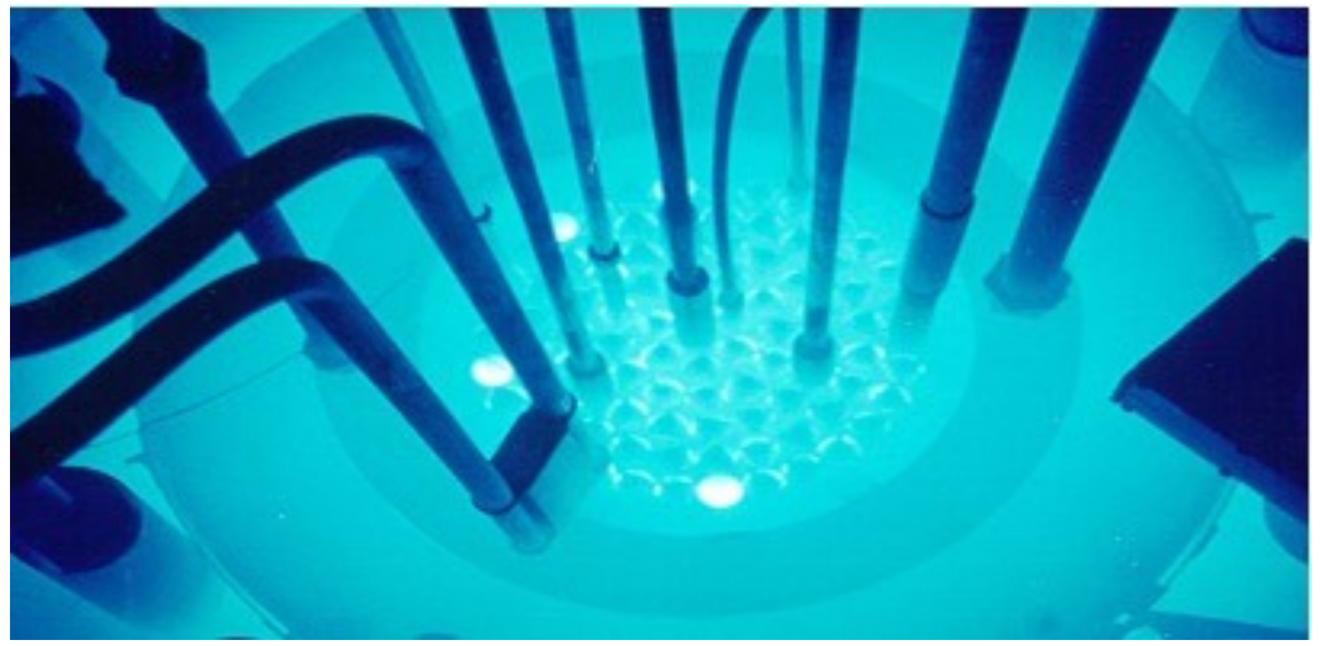
Nuclear research reactors:

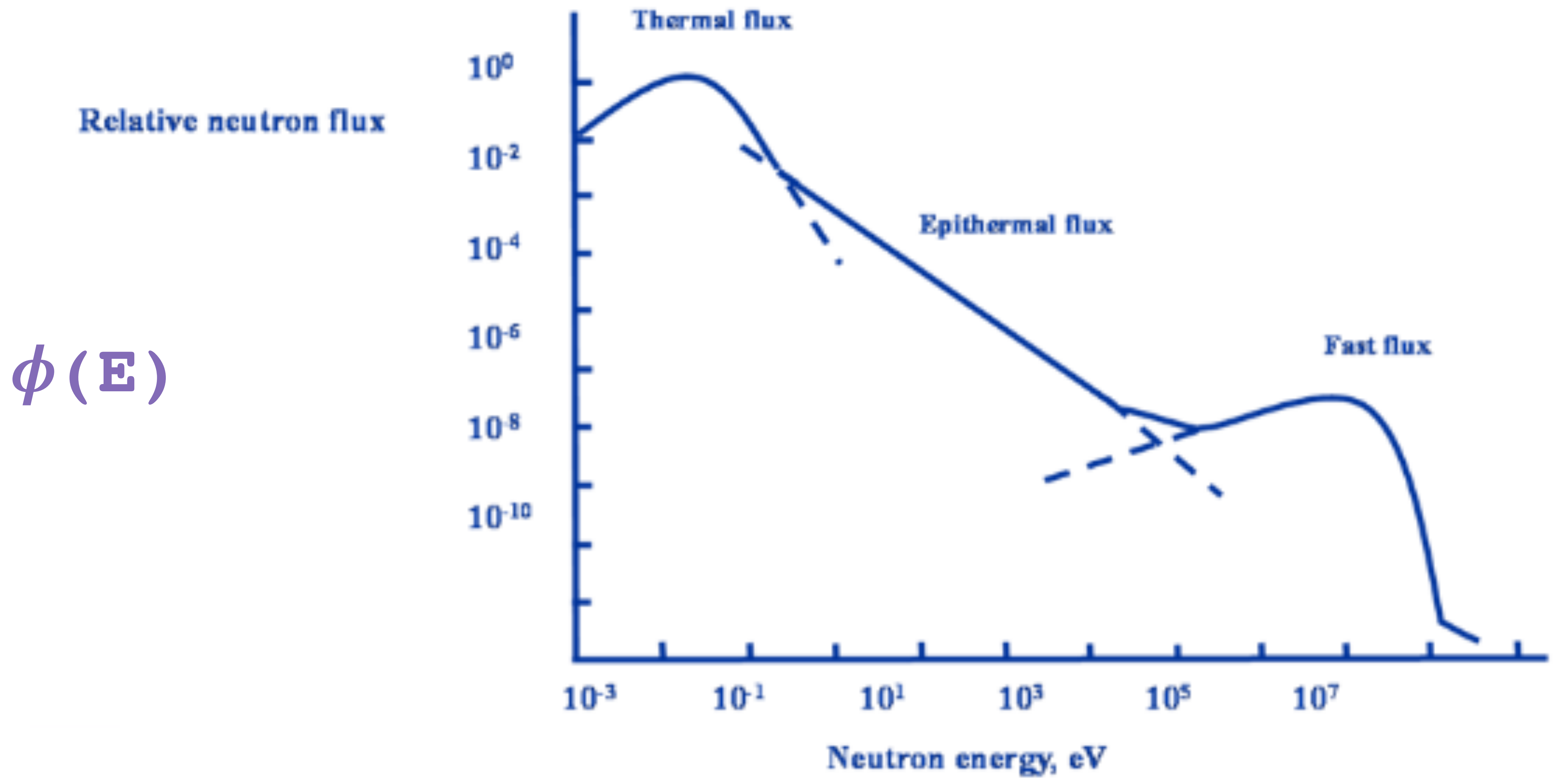
mostly used

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^{-2} s^{-1}** 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





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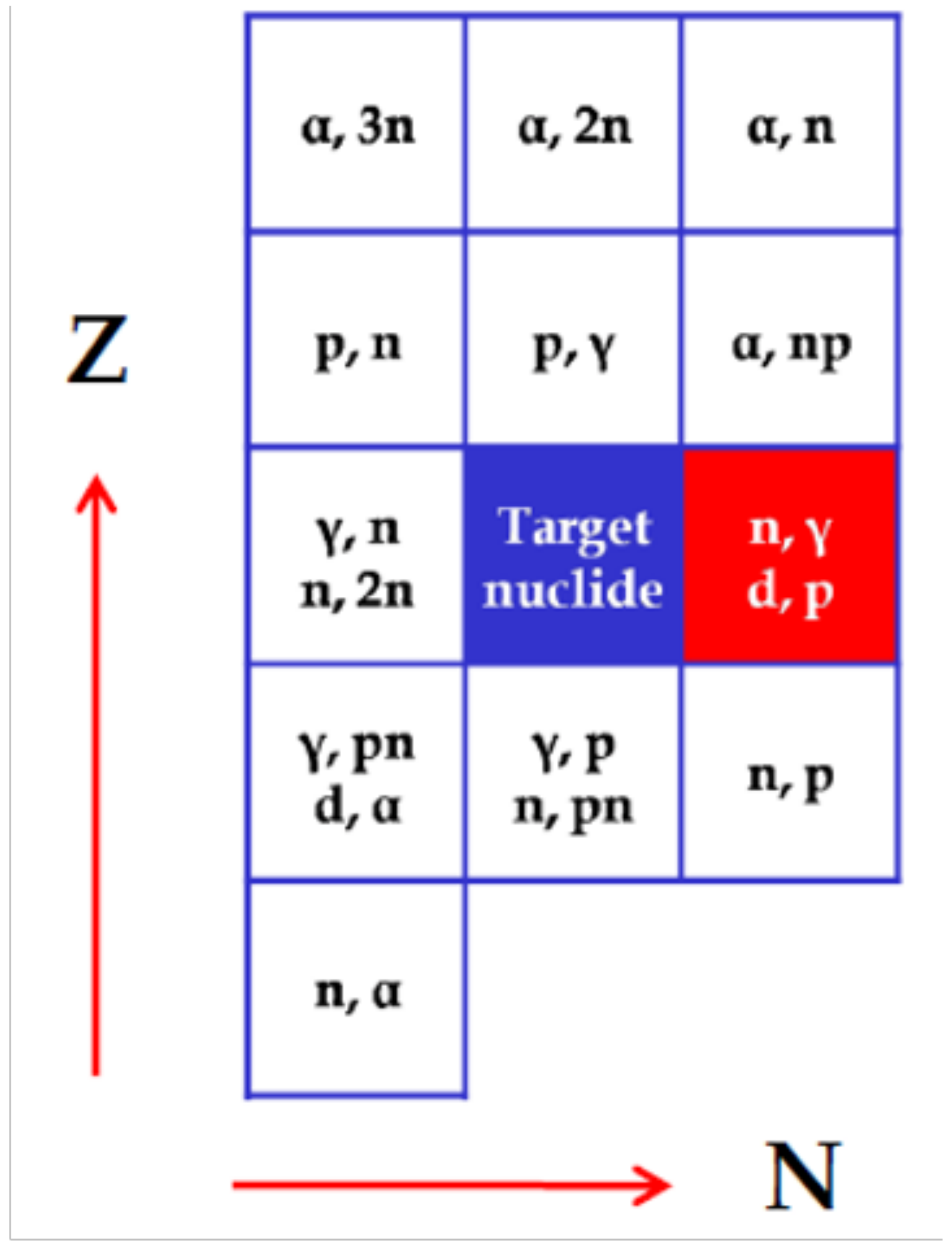
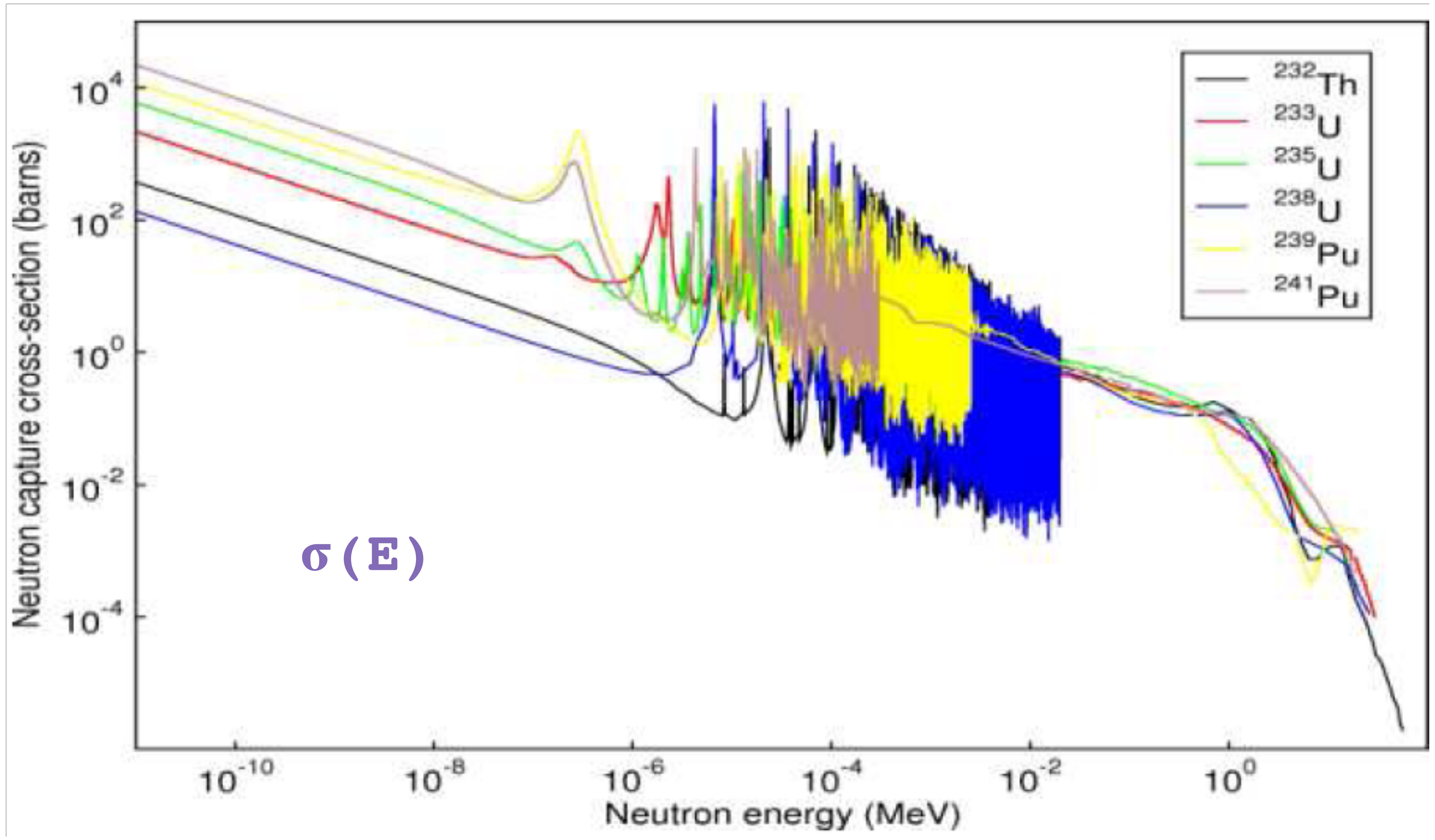
Activation via (n, γ) reactions





Neutron capture cross section vs Energy for major actinides

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 γ-ray counting.

It can be applied to measure natural contaminant (^{232}Th, ^{238}U, ^{40}K) concentrations in detector materials with no long-lived neutron activation products.

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

Key ingredients for NAA

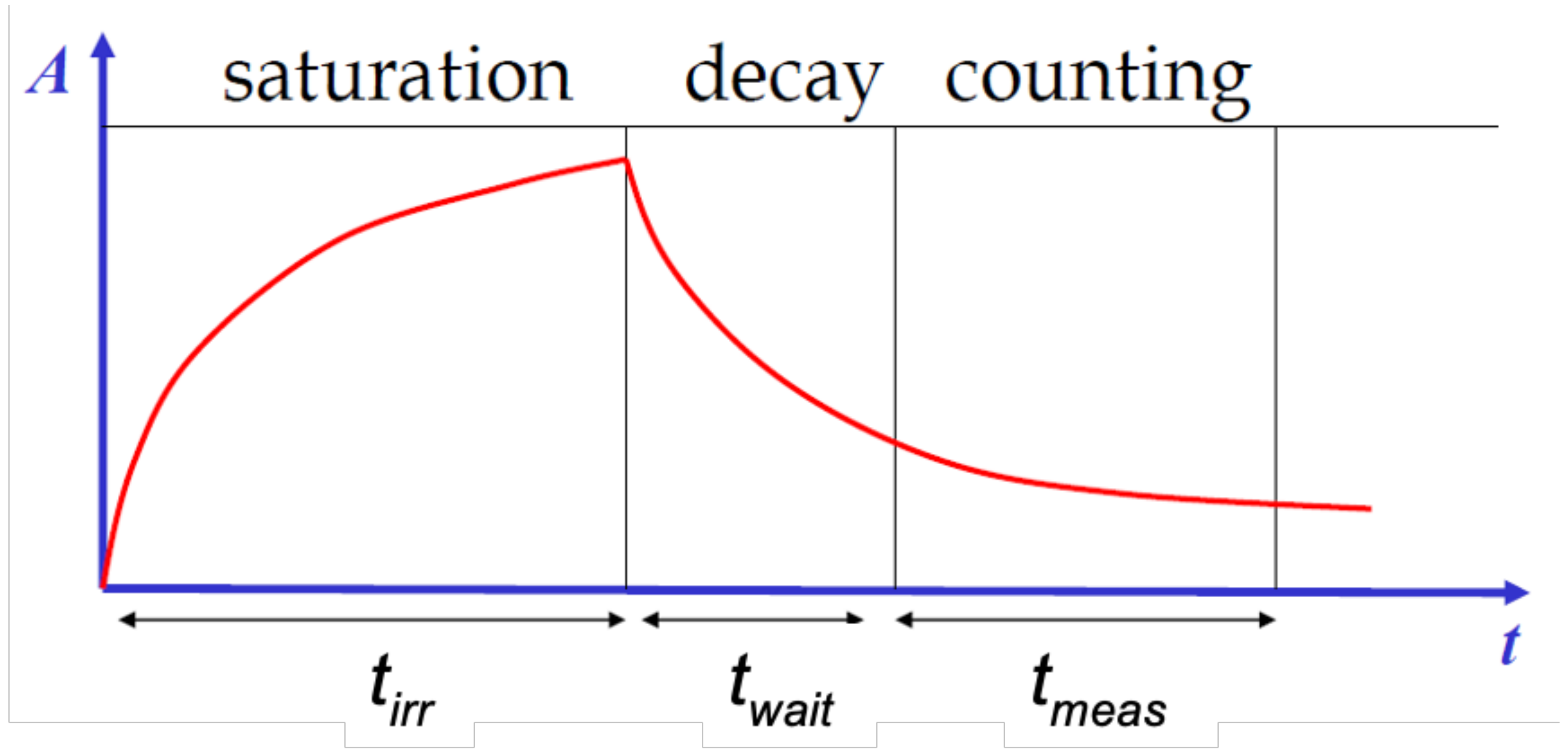
$$ {}^{A}X + n \longrightarrow {}^{A+1}X \xrightarrow[\beta^-]{} {}^{A+1}_{Z+1}Y + \gamma_{\text{cascade}} $$

Three key ingredients:

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

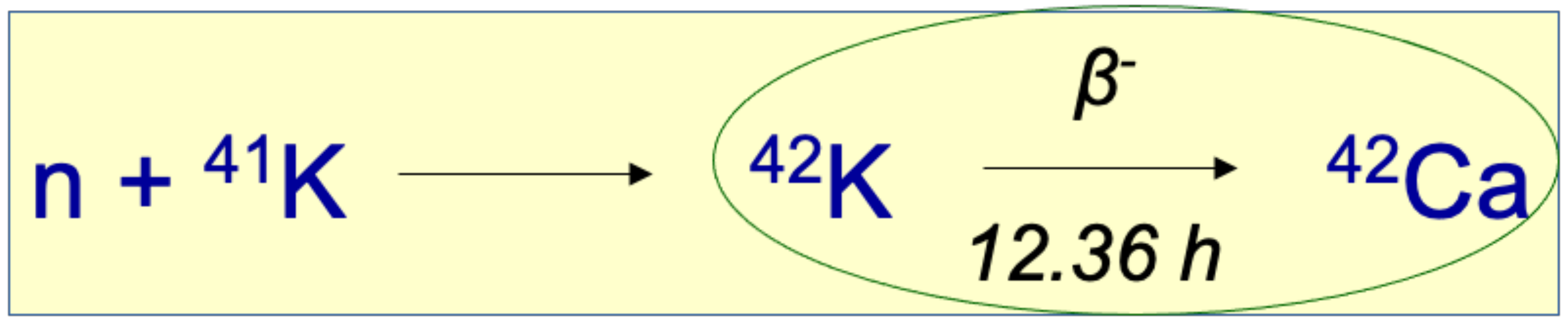
Sensitivity depends on:

- type 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}K, ^{238}U, ^{232}Th

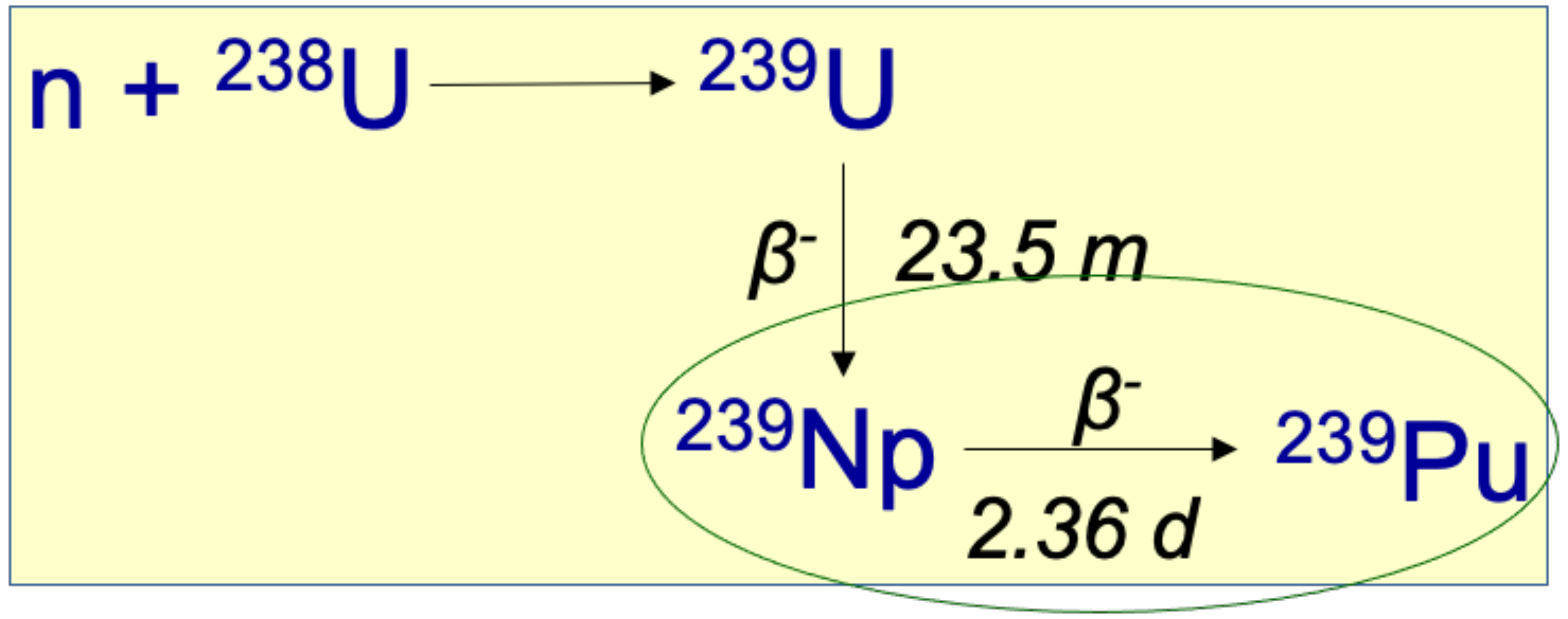


$$n + {}^{41}K \longrightarrow {}^{42}K \xrightarrow[12.36\ h]{\beta^-} {}^{42}Ca$$

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

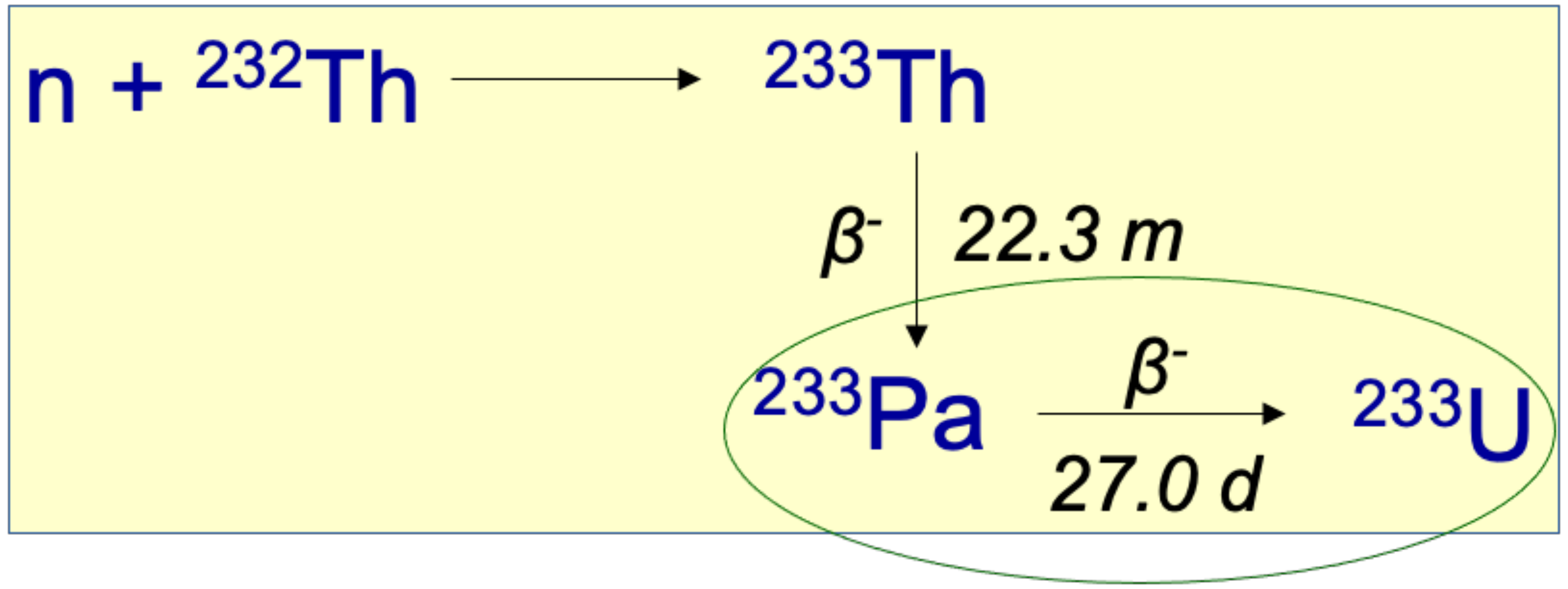
↓

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



$$n + {}^{238}U \longrightarrow {}^{239}U \xrightarrow[23.5\ m]{\beta^-} {}^{239}Np \xrightarrow[2.36\ d]{\beta^-} {}^{239}Pu$$

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.



$$n + {}^{232}Th \longrightarrow {}^{233}Th \xrightarrow[22.3\ m]{\beta^-} {}^{233}Pa \xrightarrow[27.0\ d]{\beta^-} {}^{233}U$$

NAA for ^{40}K

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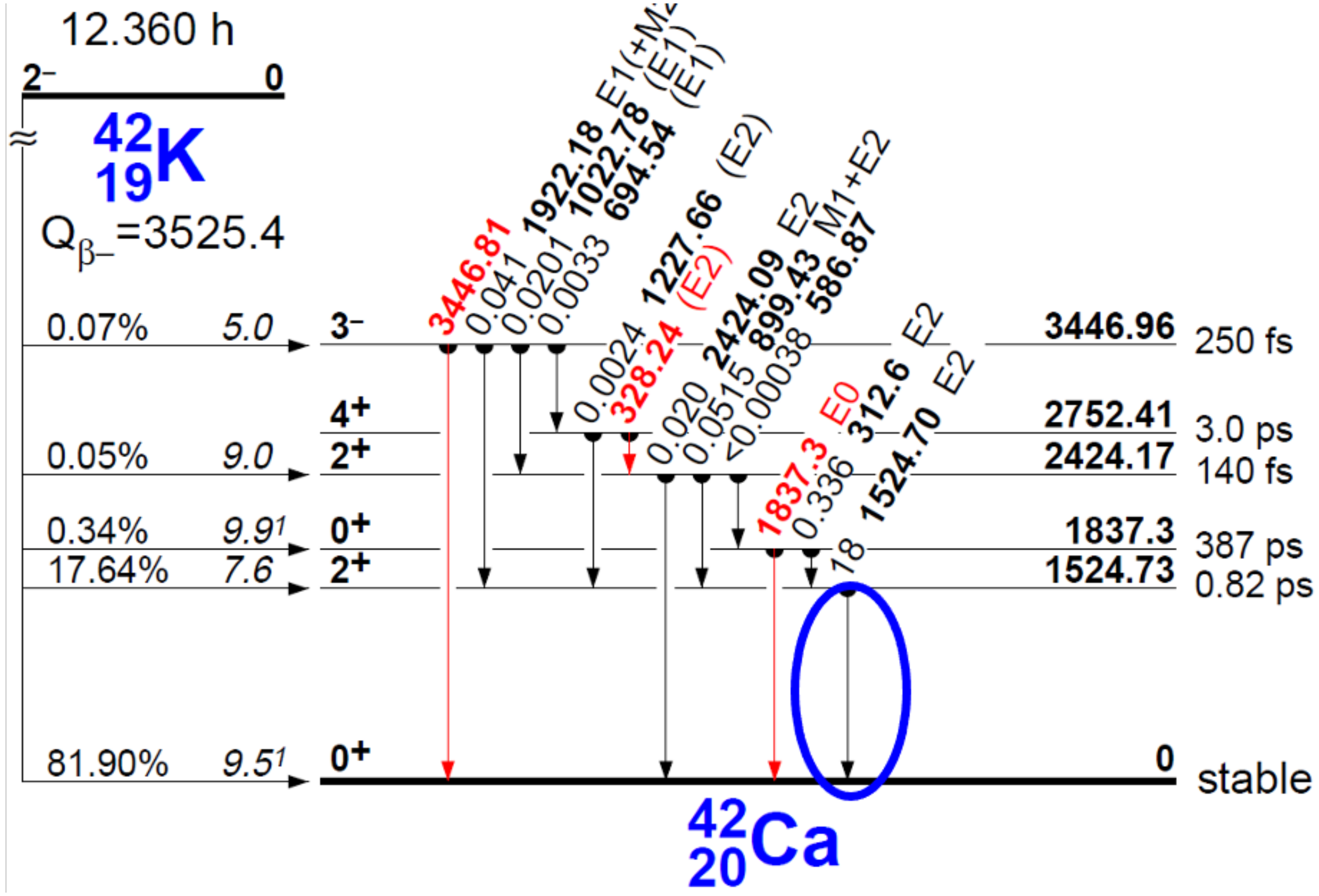
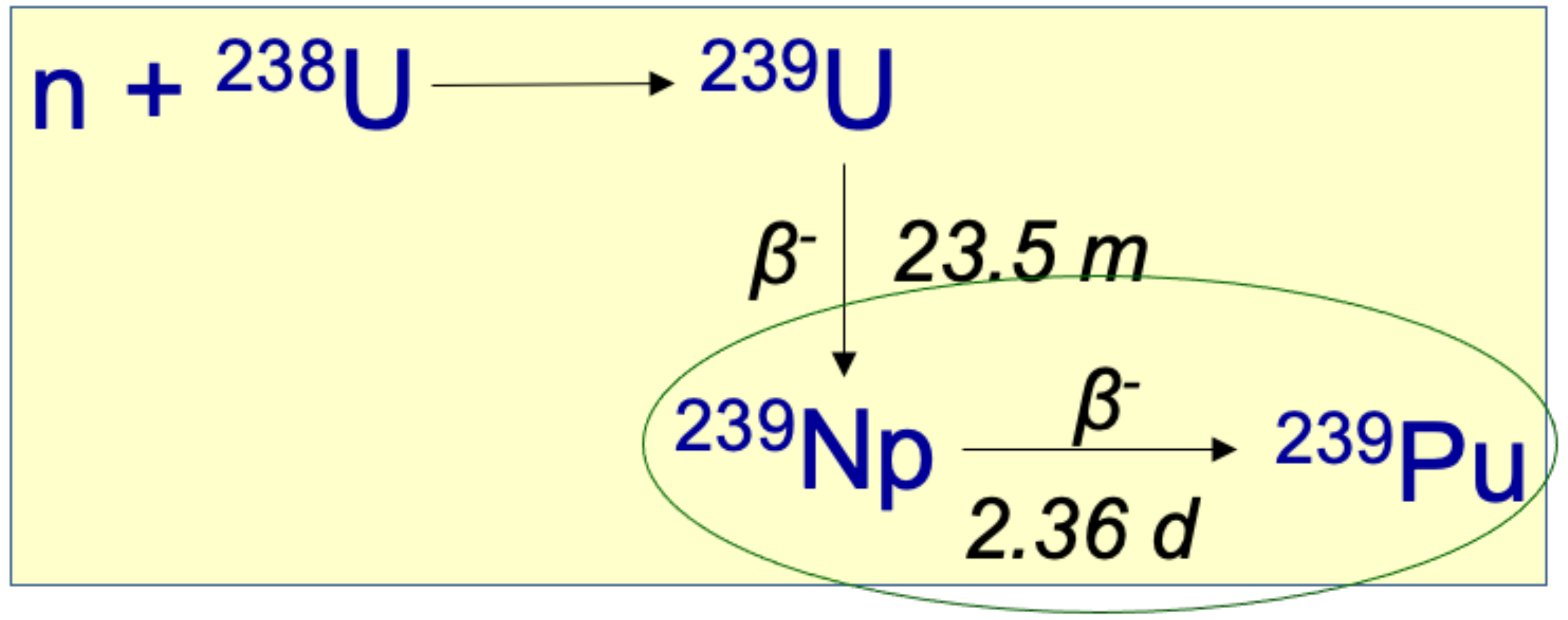


NAA for ^{238}U



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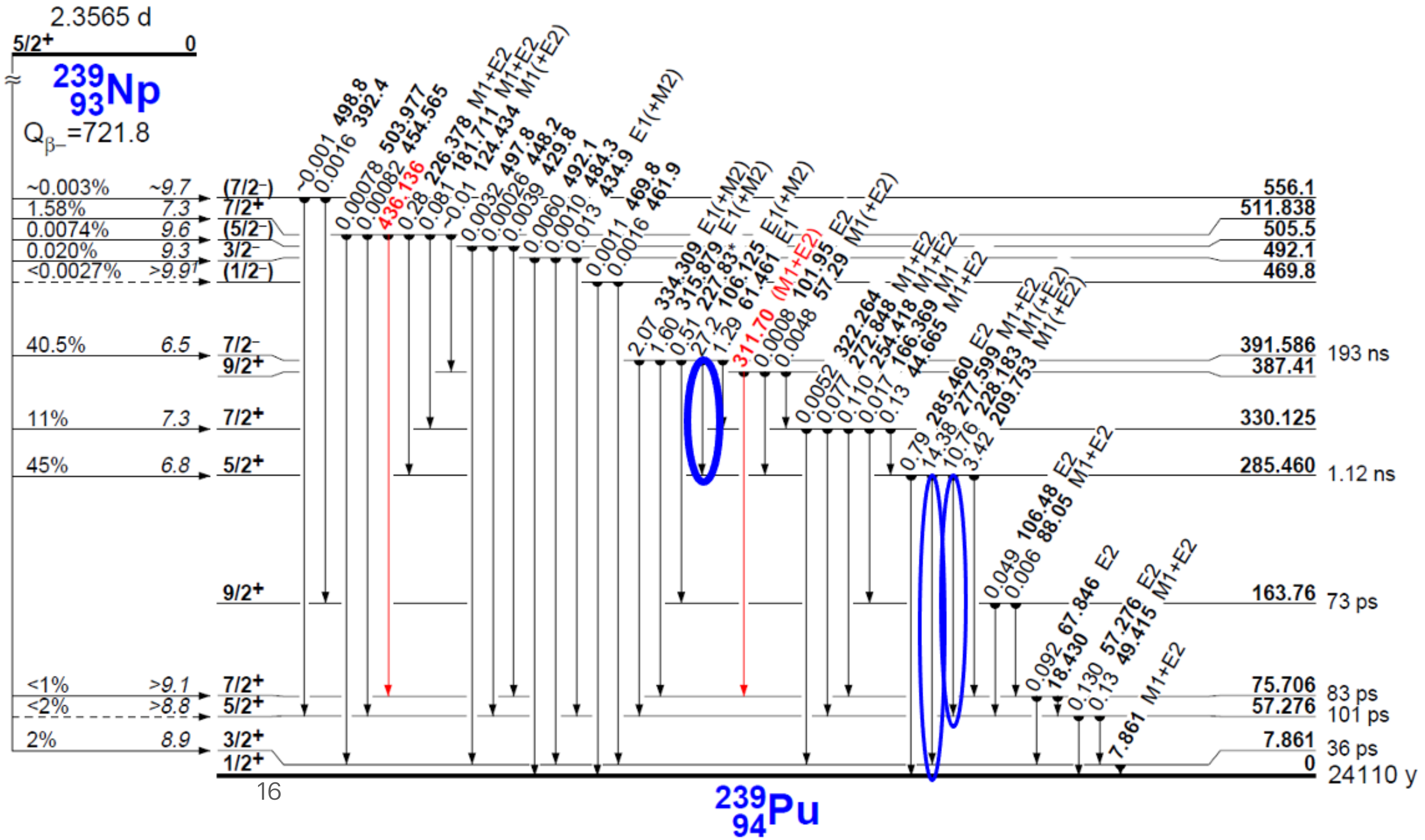
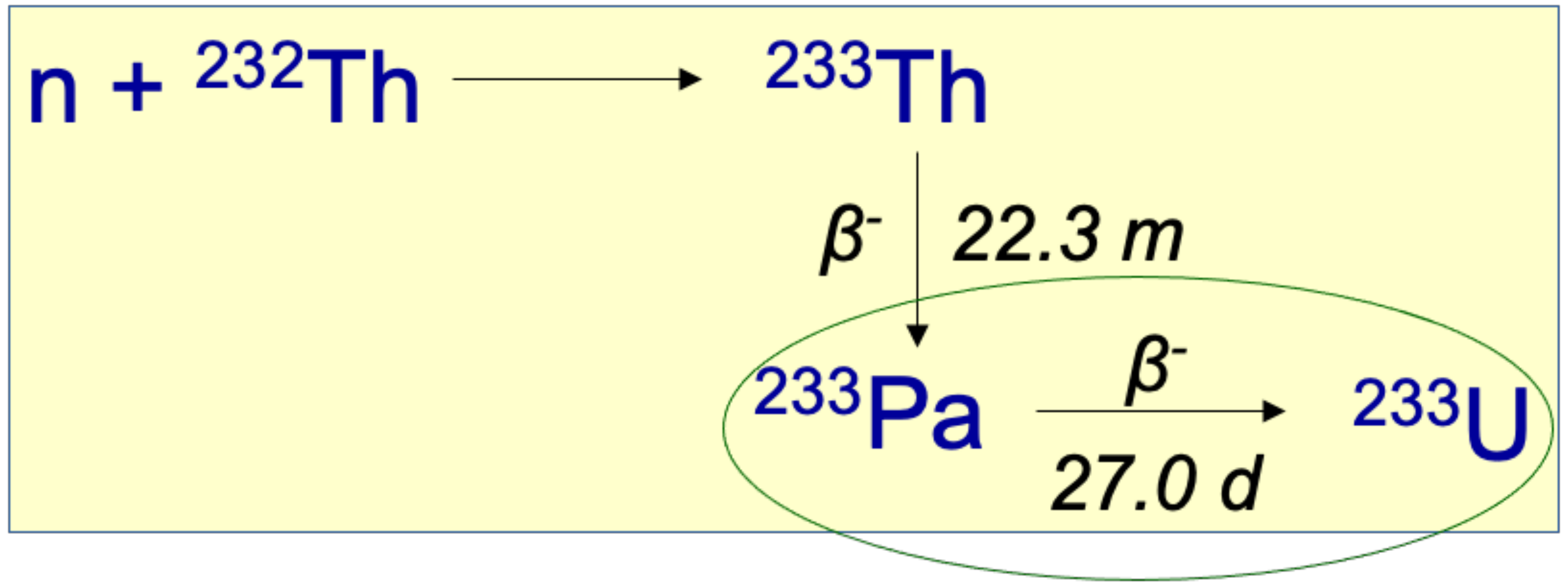
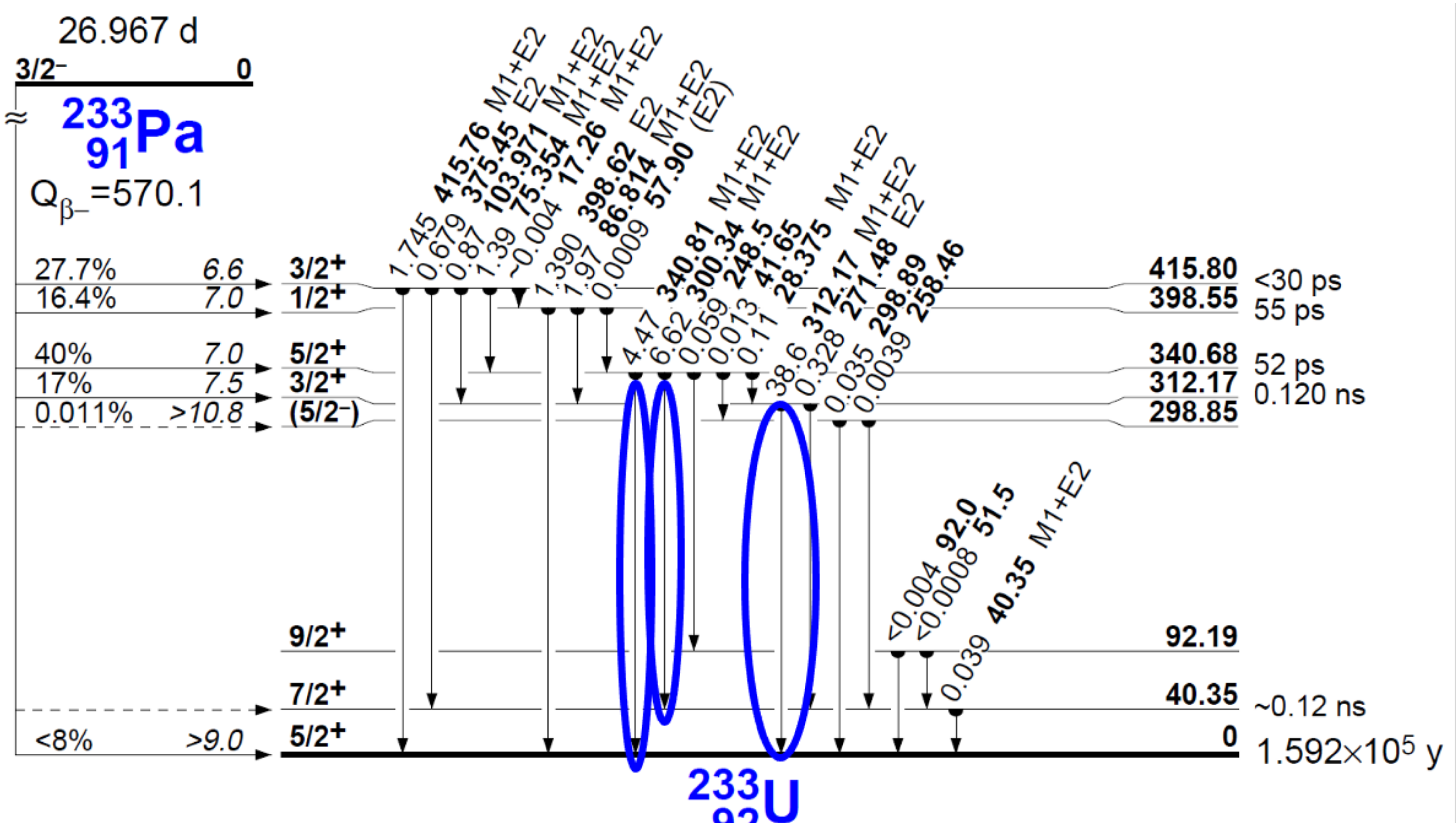


NAA for ^{232}Th



$$\begin{tikzcd} n + {}^{232}\mathrm{Th} \arrow[r] & {}^{233}\mathrm{Th} \arrow[d, "\beta^-"', "22.3\ m"] & \\ & {}^{233}\mathrm{Pa} \arrow[r, "\beta^-", "27.0\ d"'] & {}^{233}\mathrm{U} \end{tikzcd}$$



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 (or long-lived) isotope in the sample:

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

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 each irradiation facility.

$$\sigma_{\mathrm{eff}} = \frac{\int \phi(E)\sigma(E)\mathrm{d}E}{\int \phi(E)\mathrm{d}E}$$

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

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

$$\Phi_{\mathrm{tot}} \equiv \int \phi(E)\mathrm{d}E$$

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]

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:

$$dN = R\,dt - N\lambda\,dt$$

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:

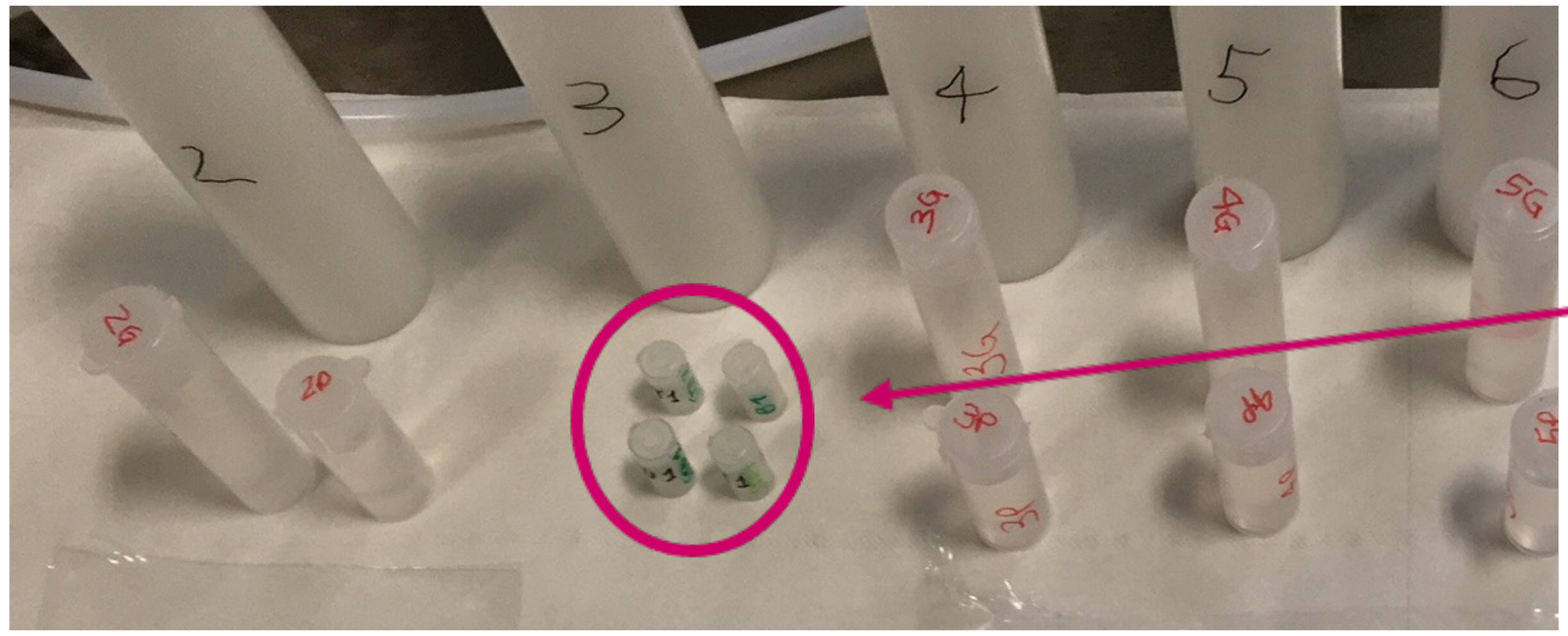
$$n_{\text{dec}} = \frac{R}{\lambda}\left(1 - e^{-\lambda t_{\text{irr}}}\right)e^{-\lambda t_{\text{wait}}}\left(1 - e^{-\lambda t_{\text{meas}}}\right)$$

with

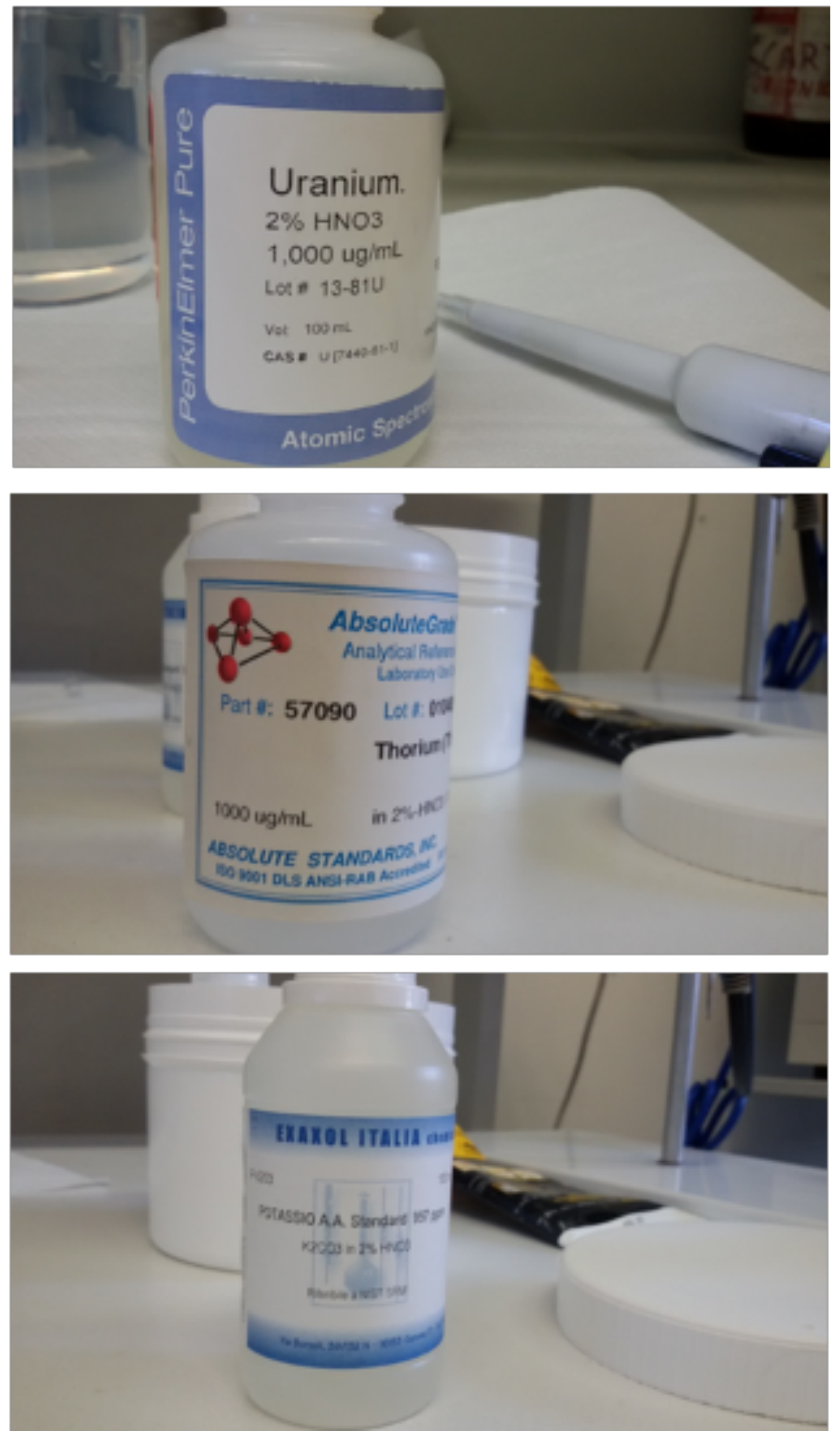
$$R = \mathcal{N}\sigma_{eff}\Phi_{TOT}$$

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



The element standards are irradiated together with the samples 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.

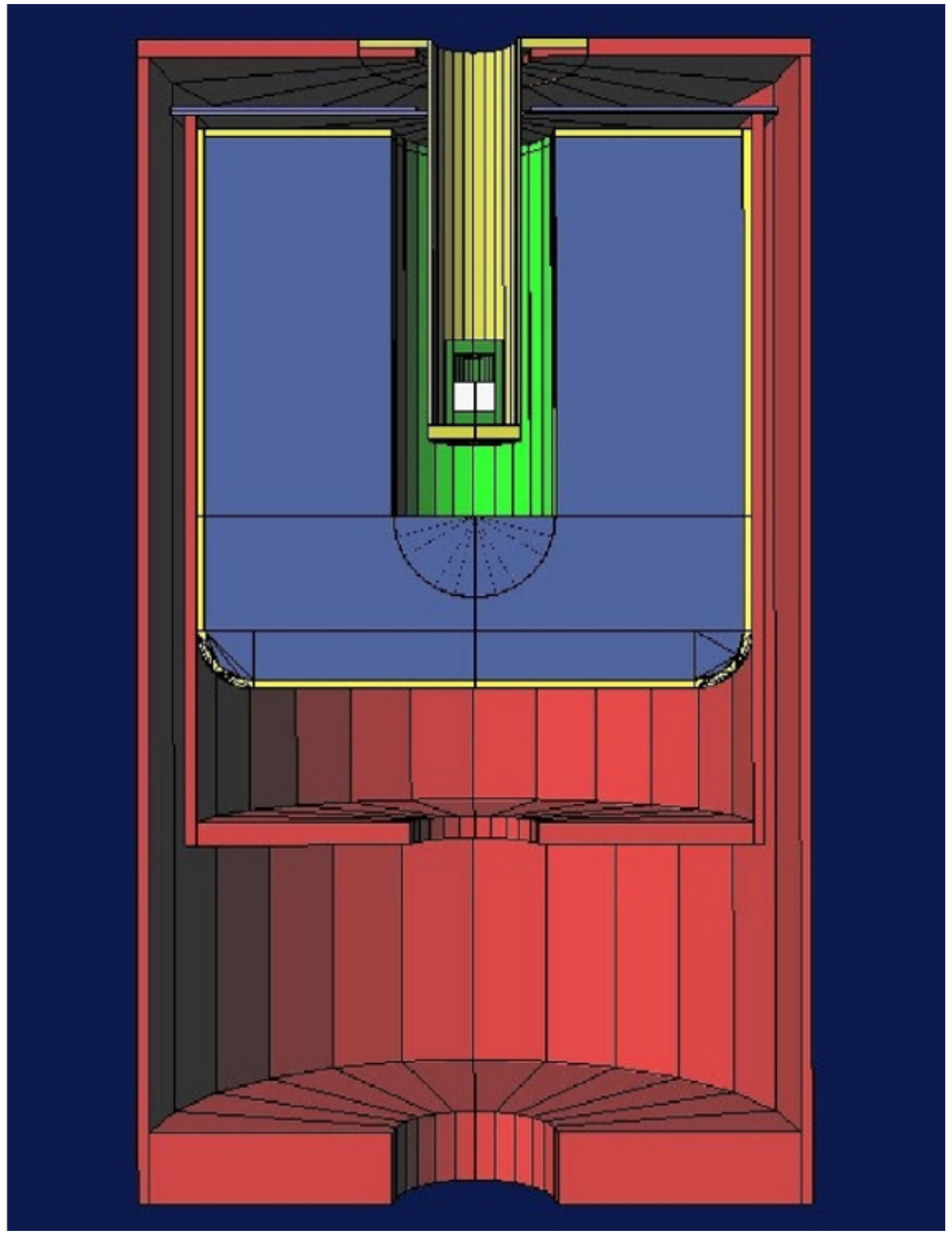
HPGe measurement efficiency

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):

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

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)

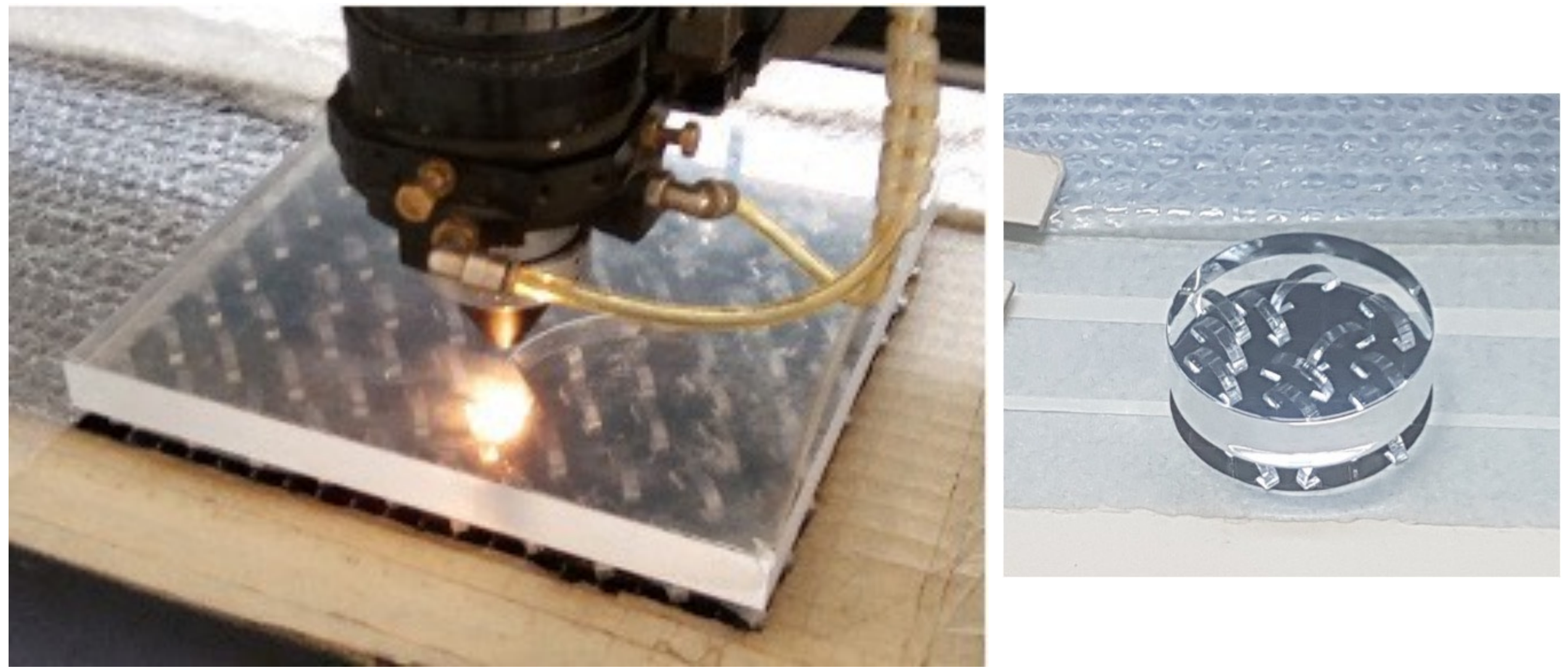
  ↳ in ultra-trace measurements, extreme care is needed to avoid adding unwanted contaminants during this step

- **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:

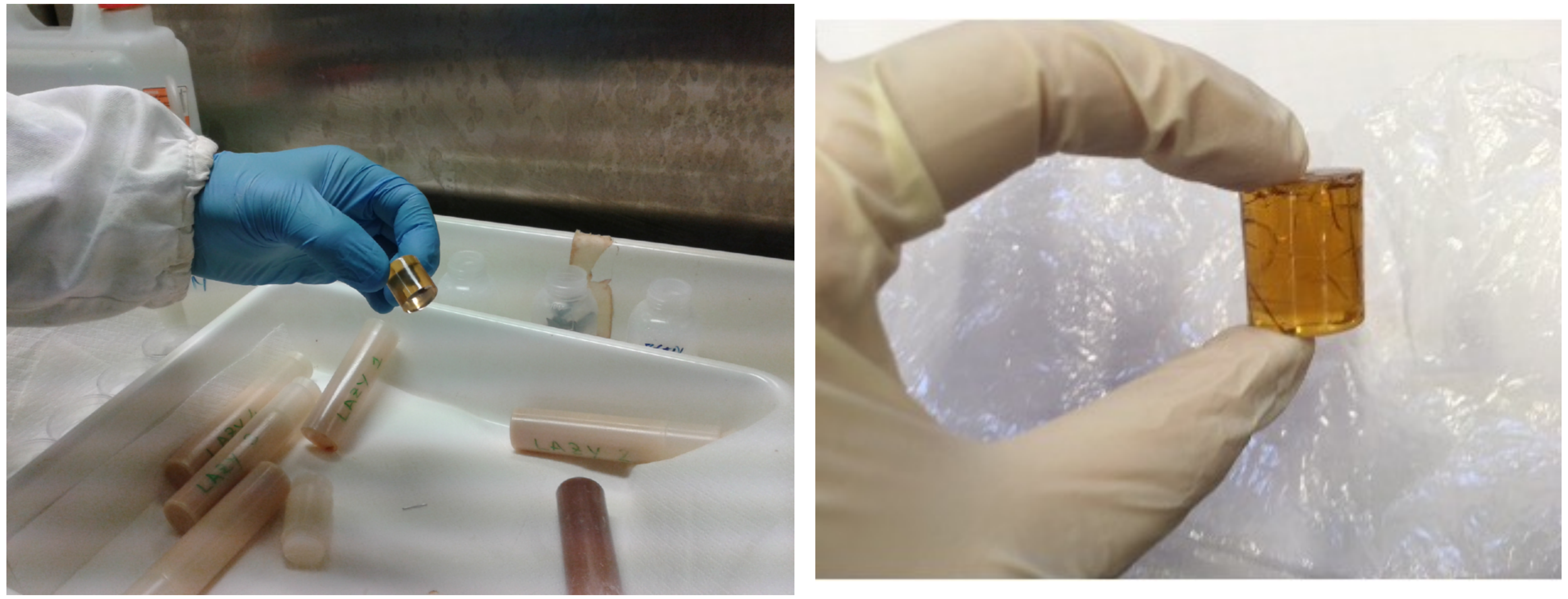
Clean room class 1000 with MilliQ water system

Acrylic samples

LAB samples

Practical NAA

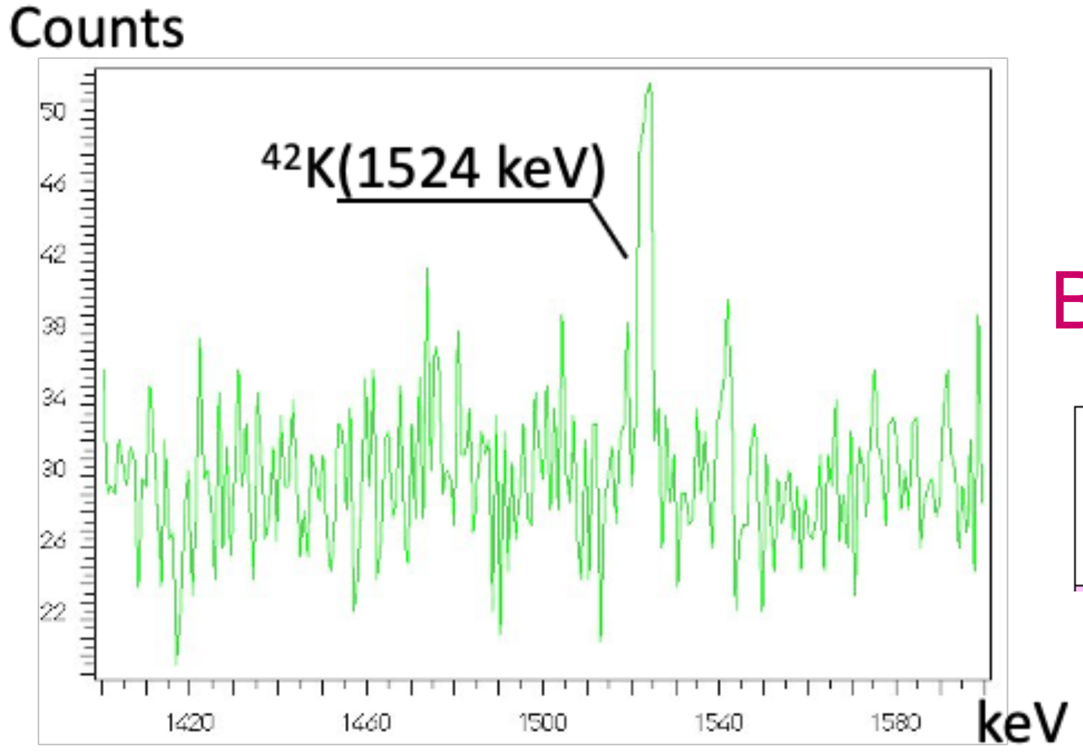
Neutron irradiation



Radiolysis during neutron irradiation must be taken into account!

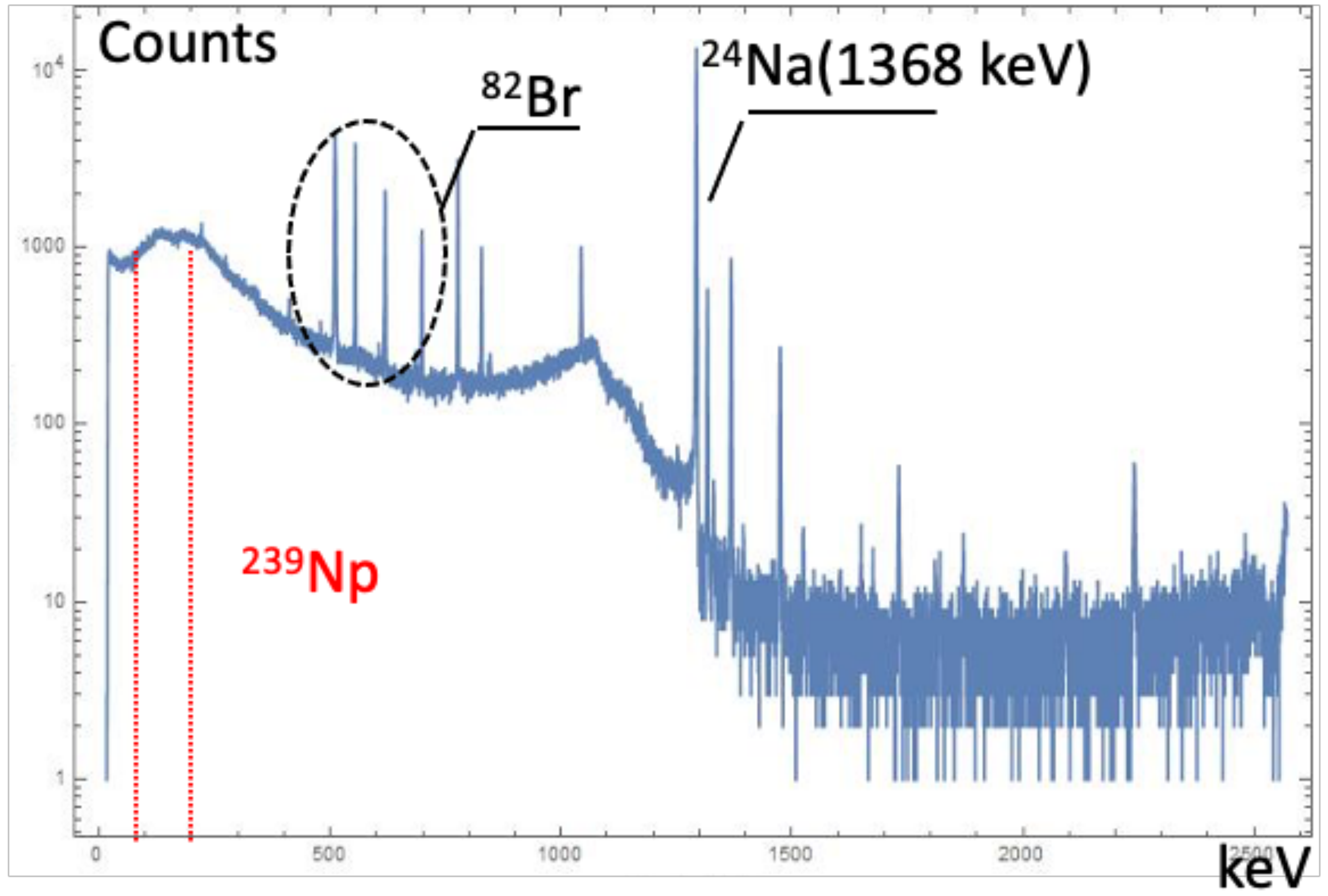
Practical NAA

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



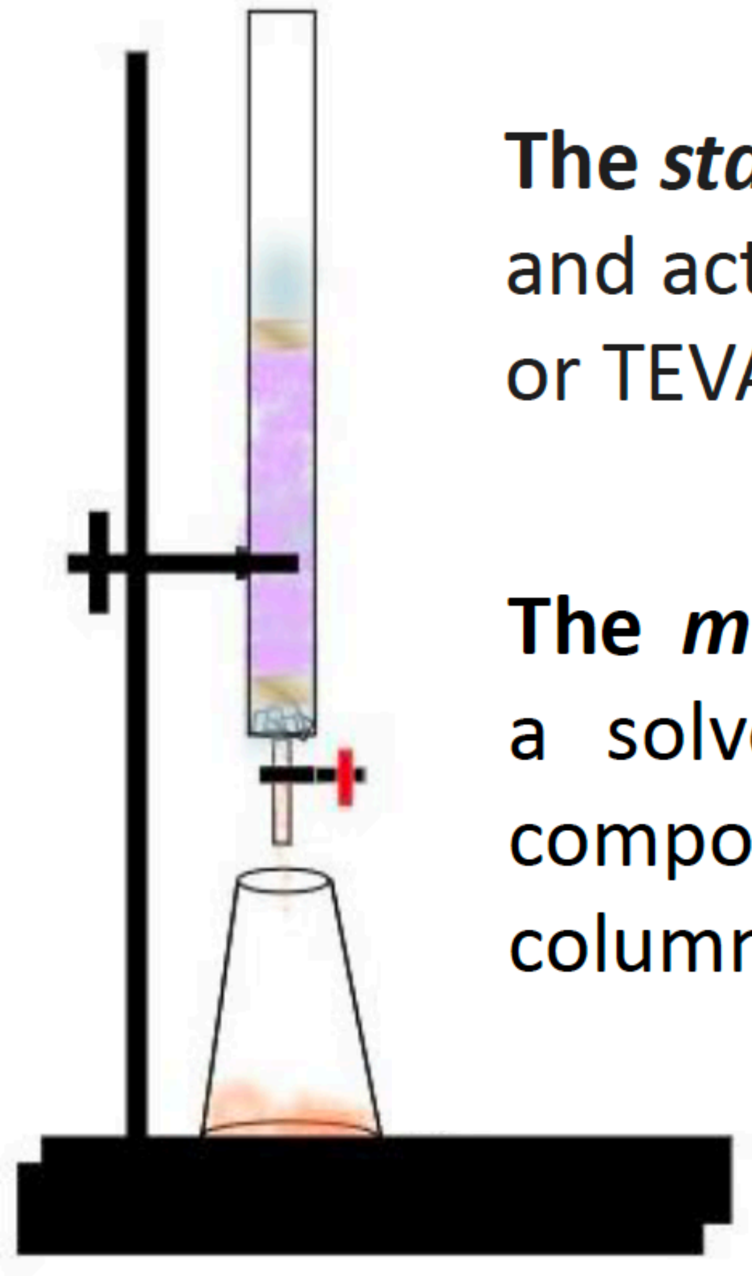
→ Effect of interferences in the sample matrix

Practical NAA

Radiochemical separation

Extraction Chromatography

Column Chromatography



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

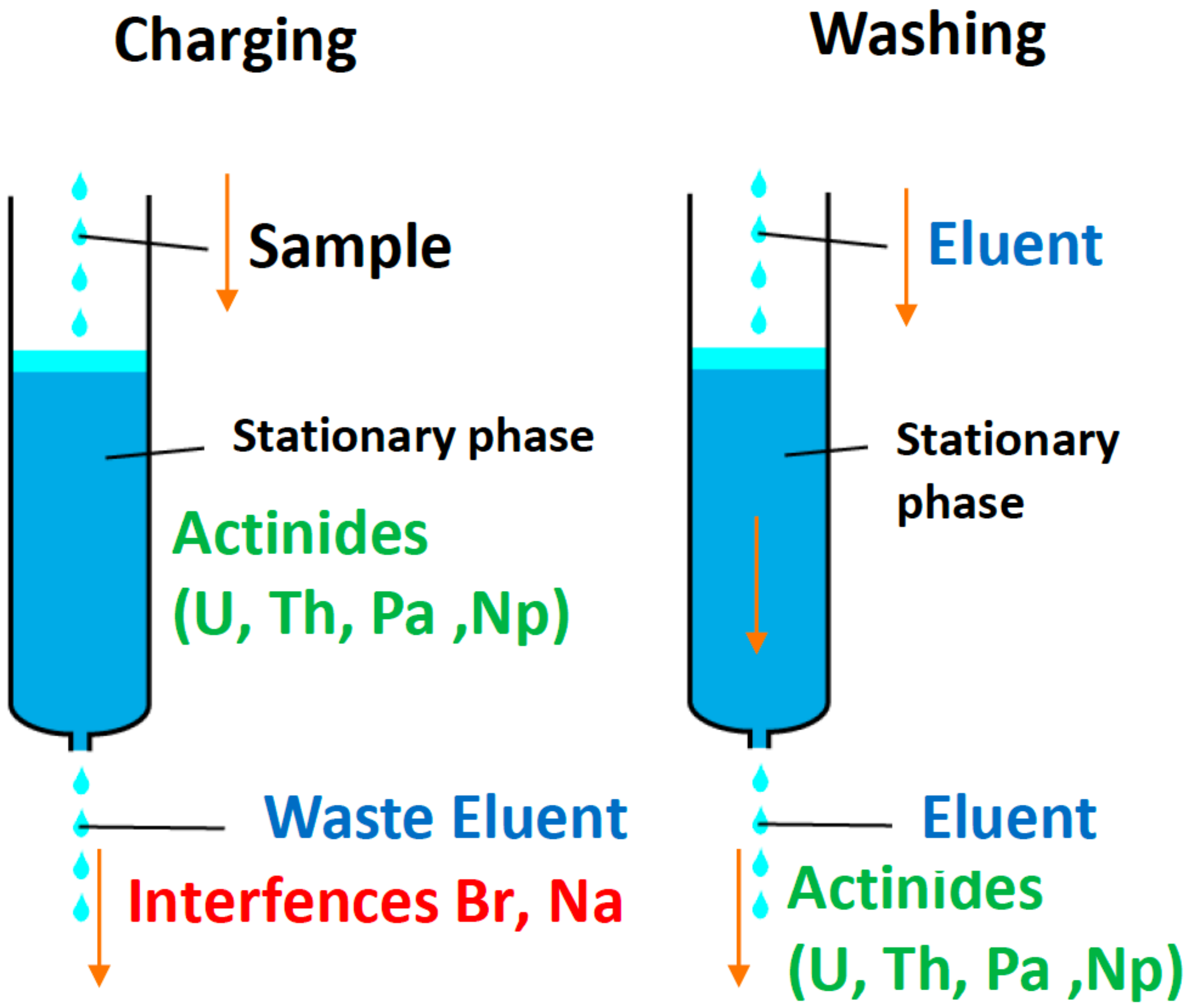
The *mobile phase* or *eluent* is a solvent used to move the compounds through the column.

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



Charging

Sample

Stationary phase

Actinides (U, Th, Pa ,Np)

Waste Eluent

Interfences Br, Na

Washing

Eluent

Stationary phase

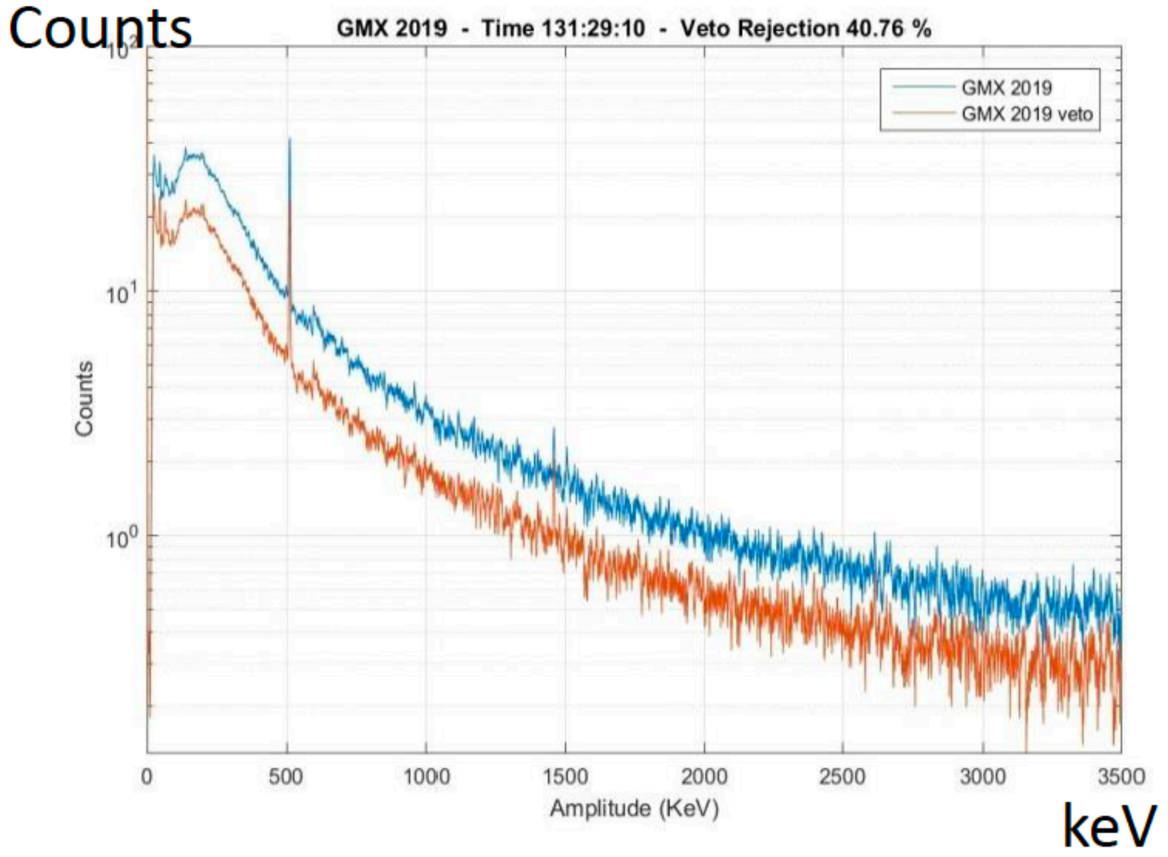
Eluent

Actinides (U, Th, Pa ,Np)

Practical NAA

Coincidence measurements

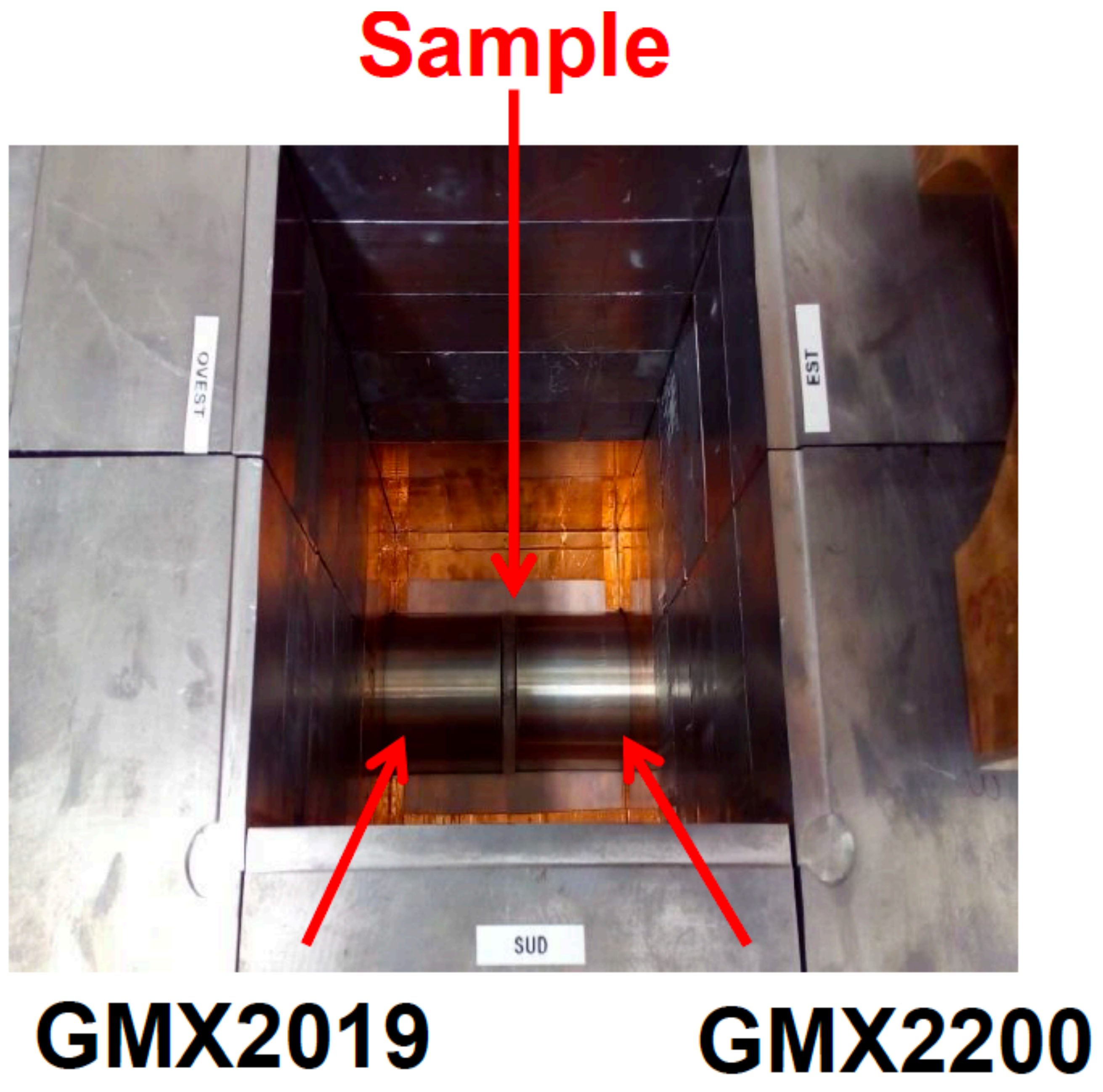
Ge-Ge HPGe: Background reduction



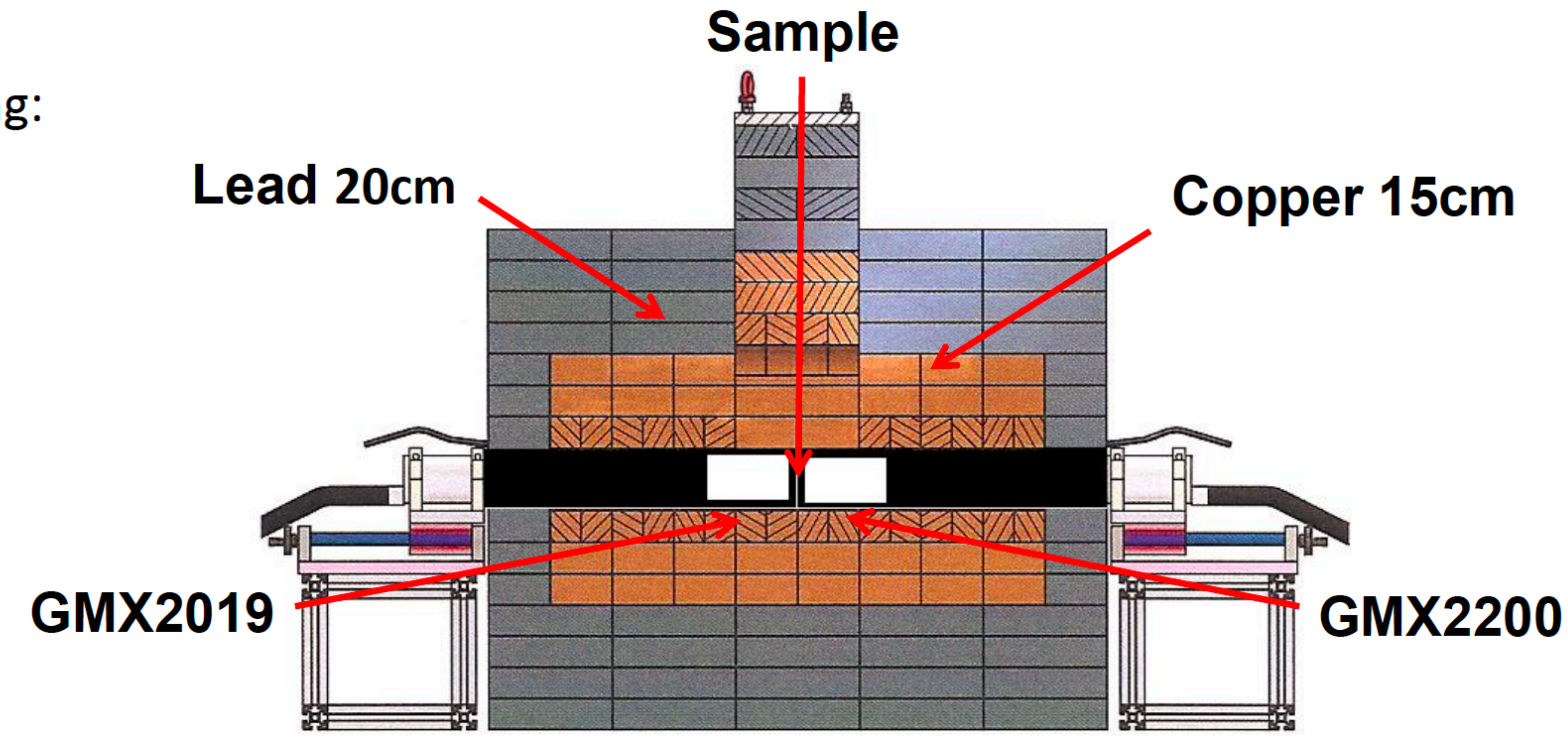
Plastic scintillator veto

Anticoincidence technique

Background suppression **~40%**



Shielding:



2x GMX detectors:

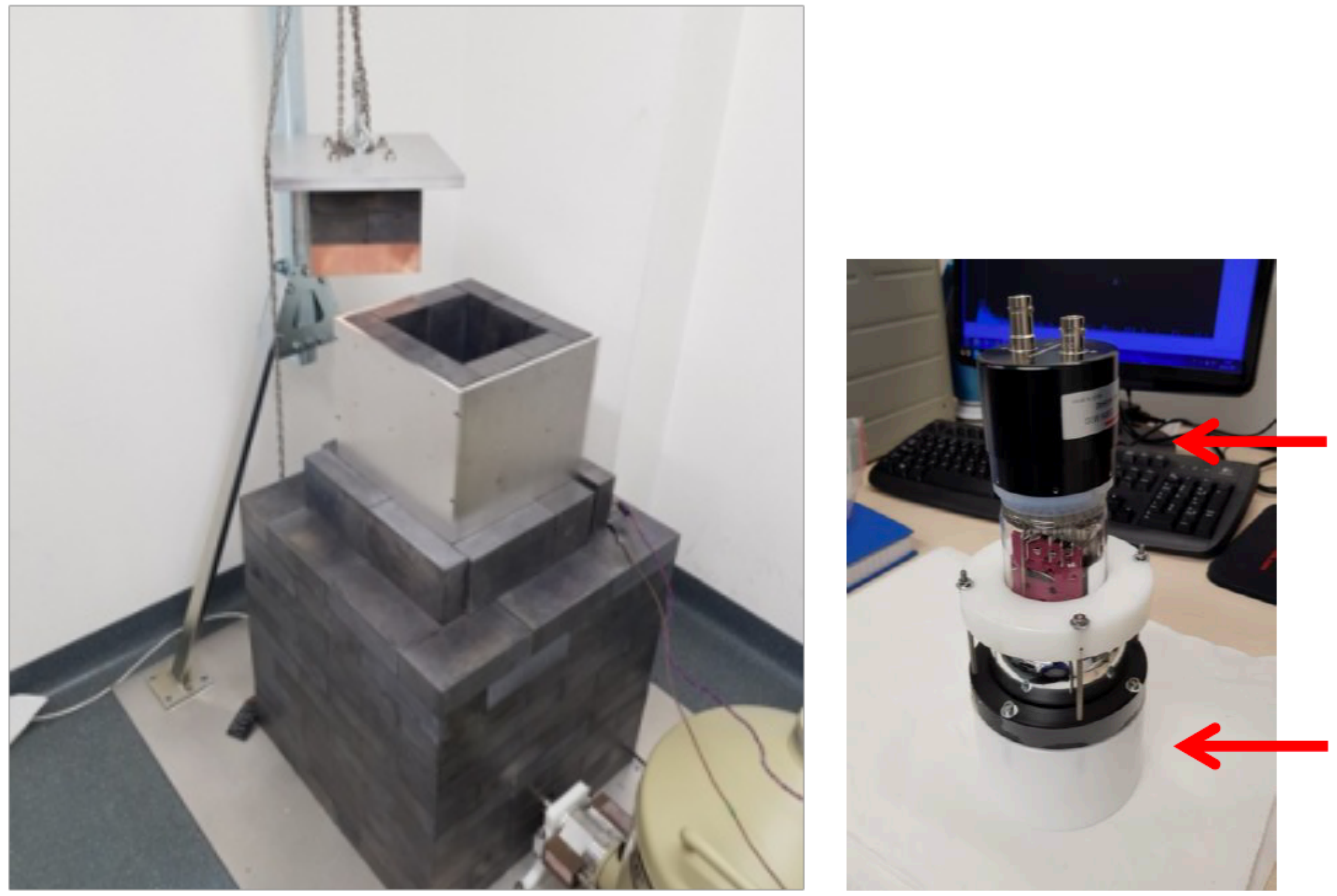
- Coaxial detector (n-type)
- Relative efficiency: 100%
- Ultra Low Background configuration
- Low Threshold (20 keV)
- Muon veto

Practical NAA

Coincidence measurements

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

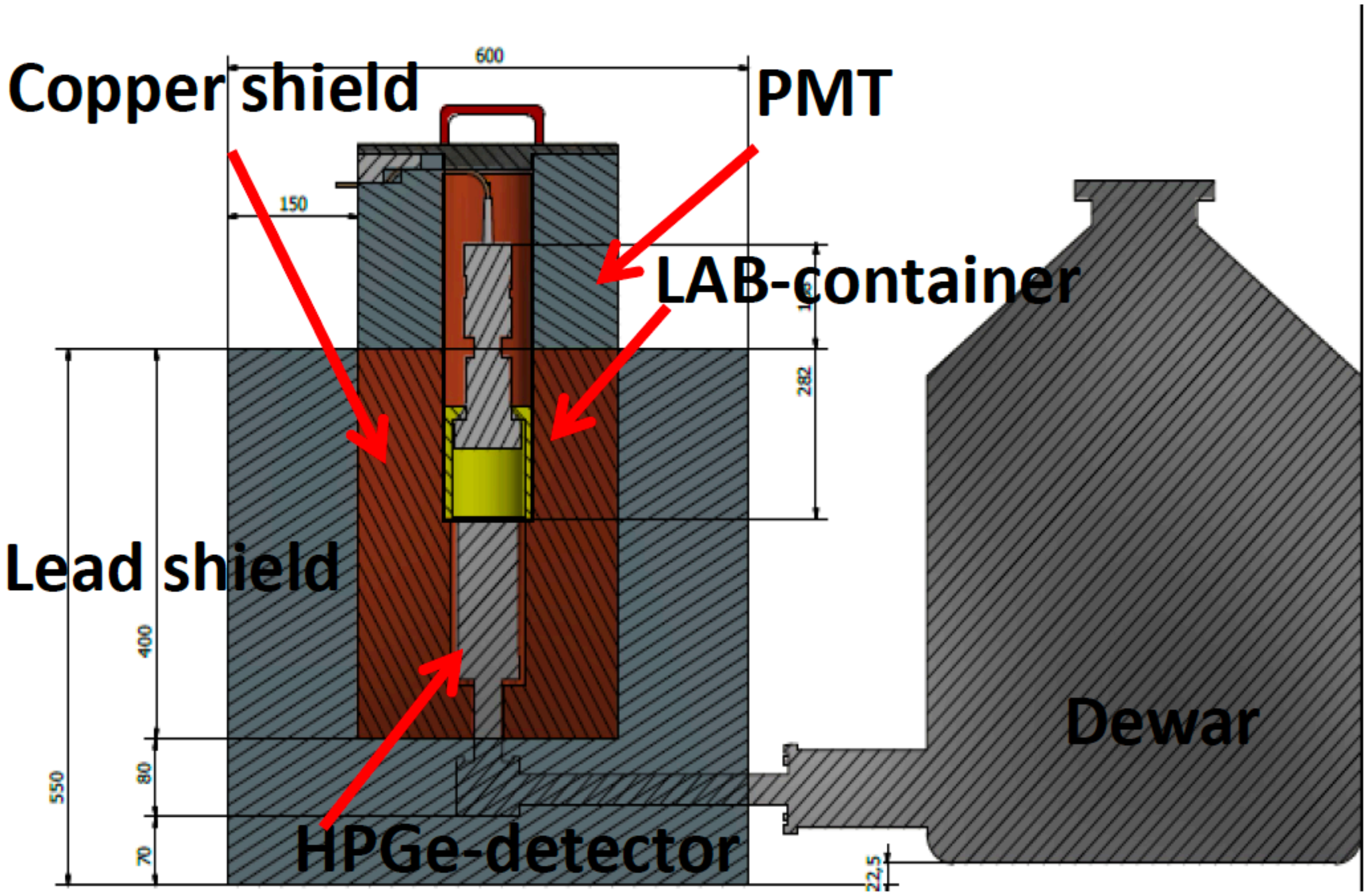
β-ϒ coincidence detector

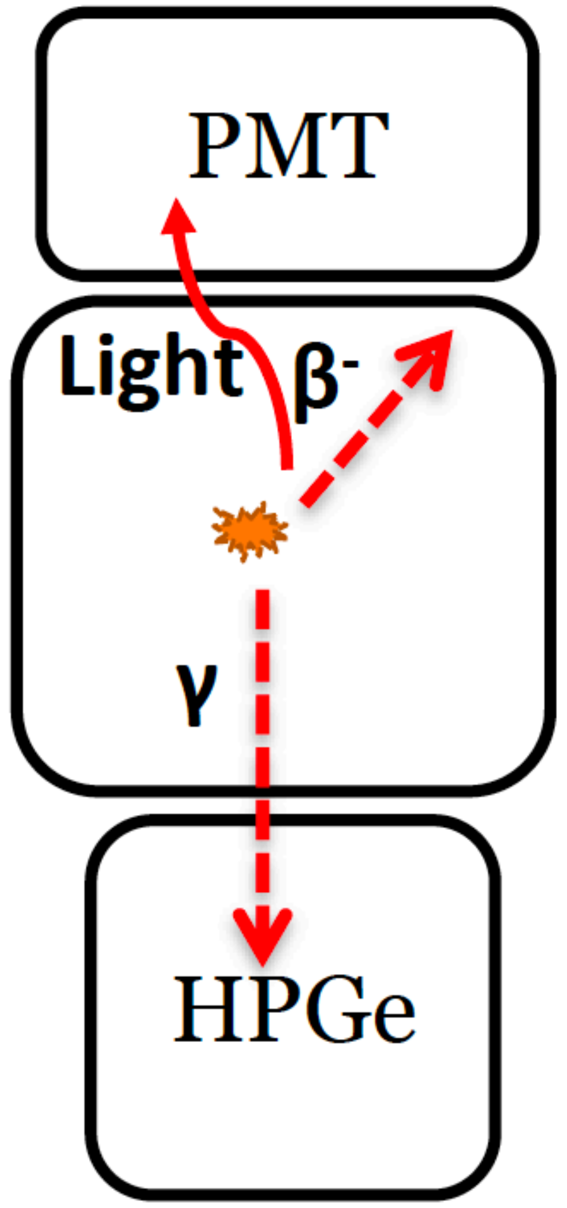


PMT

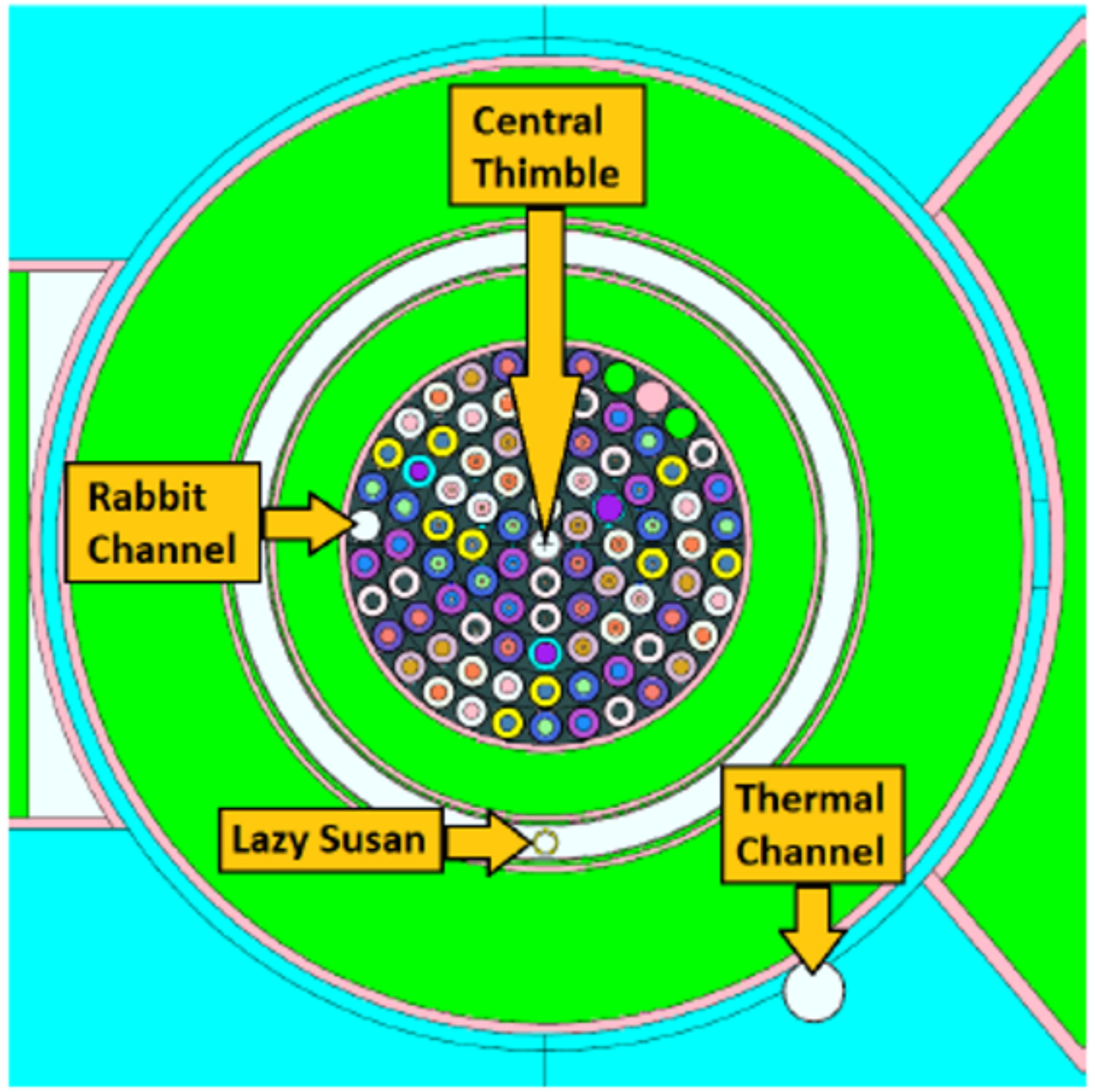
Liquid Scintillator Container

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

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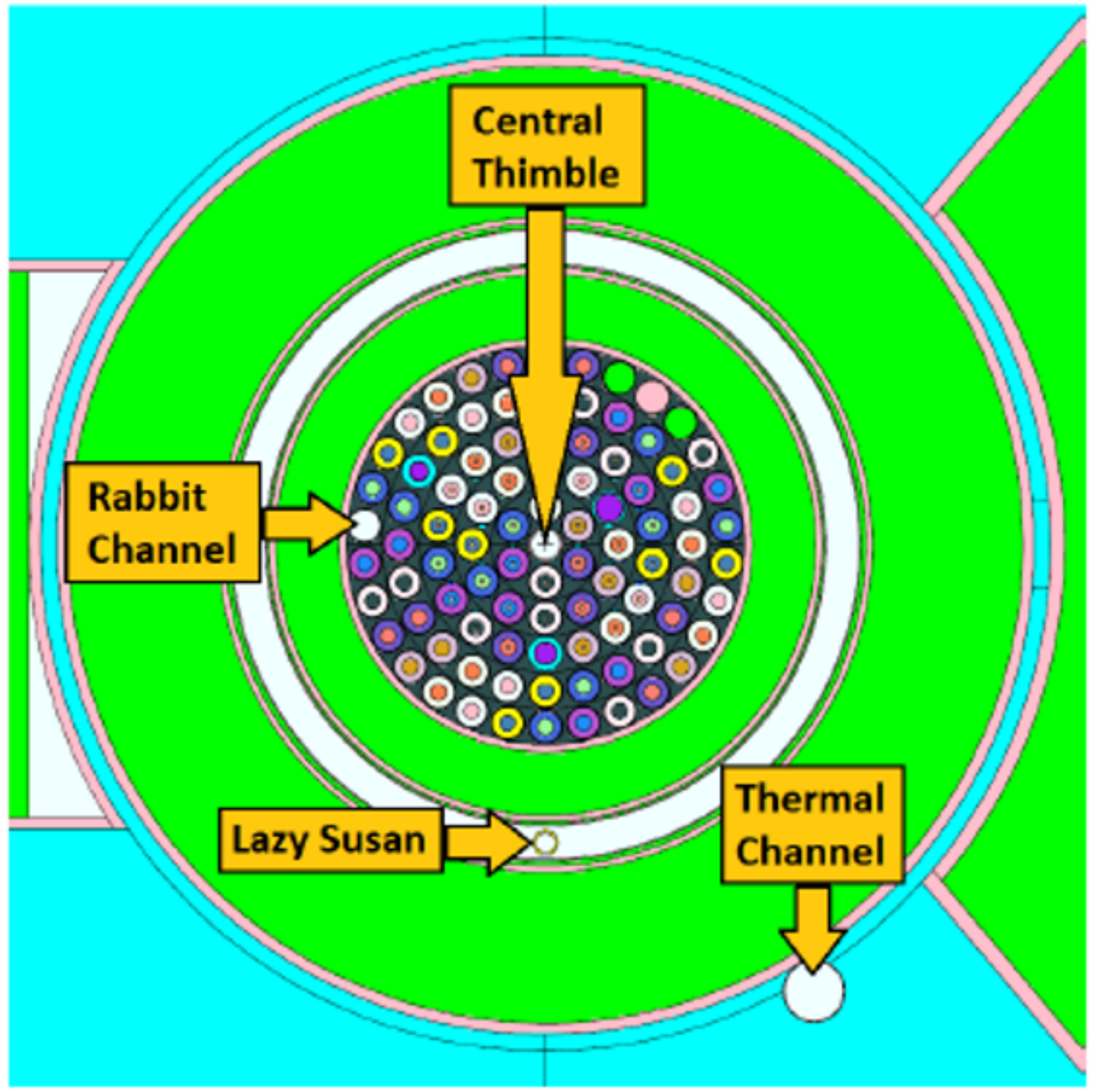

Neutron irradiation:

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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**

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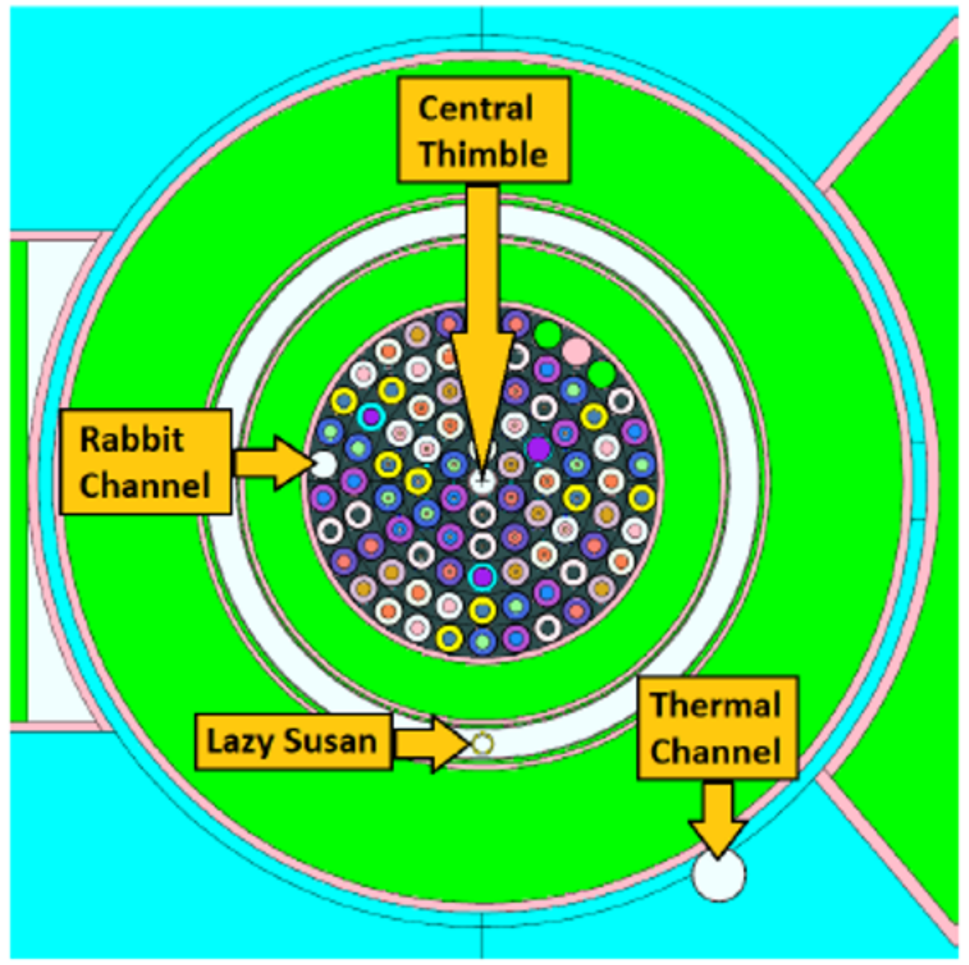

Neutron irradiation:

TRIGA Mark II
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RNAA: in this case ^{233}Pa was chemically separated using an Actinide Resin

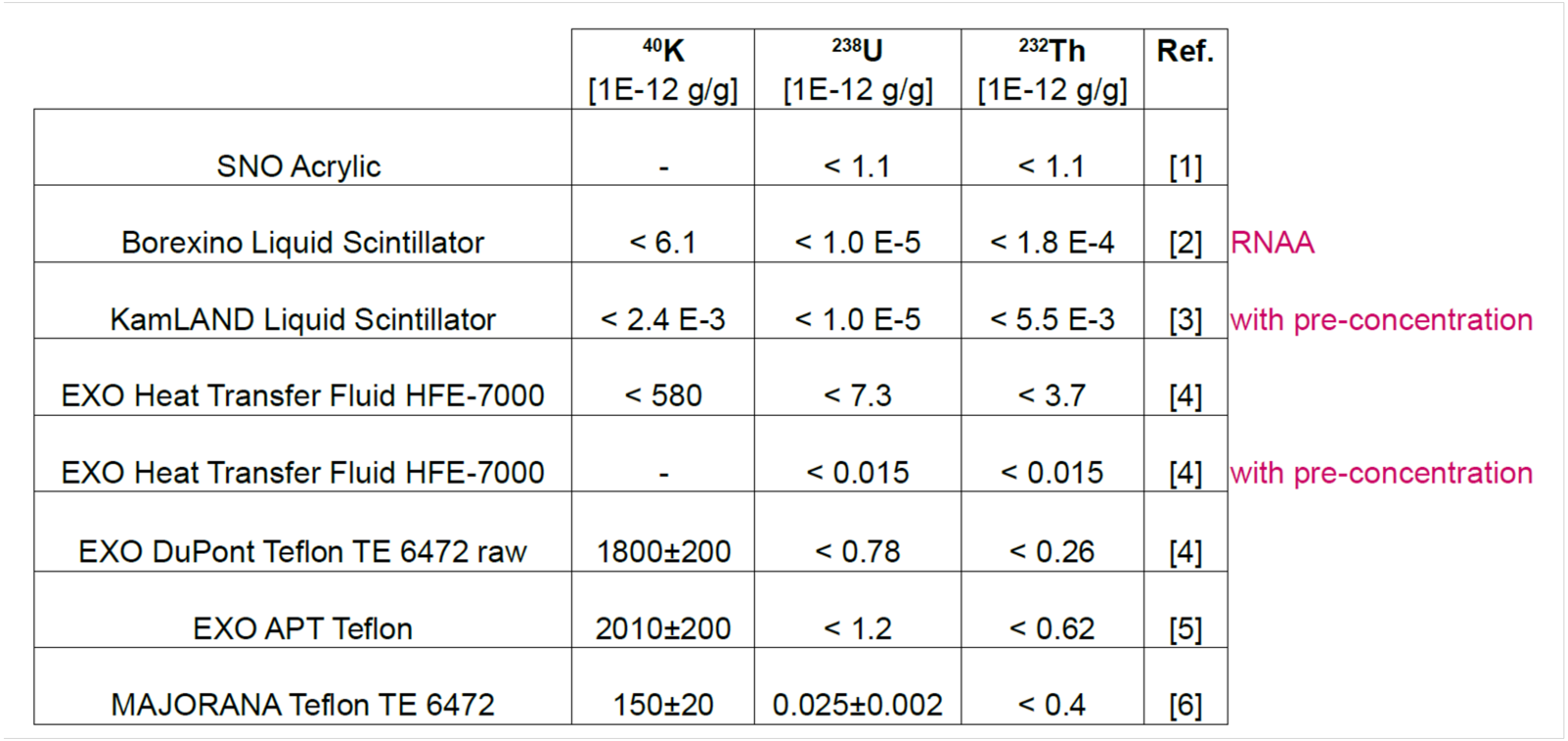
Sample preparation and HPGe measurement at Milano-Bicocca:

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

@ 90% C.L.	^{232}**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



	^{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

Summary

- 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.