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NEUTRON ACTIVATION ANALYSIS

Monica Sisti
Università and INFN
Milano-Bicocca
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:

\[ A^x + n^1 \rightarrow A^{1+x} \]

\[ A^{1+x} \rightarrow B + \text{radiation} \]

- Multi-element capability
- Sensitivity for many elements
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.

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**

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.

Most common type of nuclear reaction for 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.
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).

- The compound nucleus de-excites, usually by ejecting a small particle and a product nucleus.

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 (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
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
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.

Activation via $(n, \gamma)$ reactions

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:

$$R = N \int \phi(E)\sigma(E)\,dE$$

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:

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

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

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**
NAA can achieve substantially greater sensitivity than direct γ-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 γ-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

\[ ^A X + n \rightarrow ^{A+1} X \rightarrow ^{A+1}_{Z+1} Y + \gamma \text{ cascade} \]

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, $^{232}$Th, $^{238}$U

- $^{41}$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 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 $^{238}\text{U}$

$n + ^{238}\text{U} \rightarrow ^{239}\text{U}$

$^{239}\text{Np} \xrightarrow{\beta^-} ^{239}\text{Pu}$

$^{239}\text{Np}$

$Q_{\beta^-} = 721.8$ MeV

$2.3565 \text{ d}$

$5/2^+$

$9/2^+$
NAA for $^{232}\text{Th}$

$\text{n} + ^{232}\text{Th} \rightarrow ^{233}\text{Th}$

$^\beta^- \ 22.3 \text{ m}$

$^\beta^- \ 27.0 \text{ d}$

$^{233}\text{Pa} \rightarrow ^{233}\text{U}$

$^{233}\text{Pa}$

$Q_{\beta^-} = 570.1$

$26.967 \text{ d}$

$^{233}\text{U}$

$1.592 \times 10^5 \text{ y}$
During the irradiation, the time evolution of the production of the activated isotope (with decay constant $\lambda$) in the irradiated sample is:

$$dN = Rd\tau - N\lambda d\tau$$

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

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

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:

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

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

GeGEM $\varepsilon_{rel} 30\%$

BeGE detector $\varepsilon_{rel} 50\%$
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.

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 Monte Carlo simulations of each experimental configuration (sample-HPGe):

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

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

Example of a reconstructed experimental configuration with a GEANT4 Monte Carlo simulation.
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**

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**

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}\text{U}$</td>
<td>0.012 mBq/kg – 1 ppt</td>
</tr>
<tr>
<td>$^{232}\text{Th}$</td>
<td>0.004 mBq/kg – 1 ppt</td>
</tr>
<tr>
<td>$^{40}\text{K}$</td>
<td>0.27 mBq/kg – 1 ppt</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Concentration [1E-12 g/g]</th>
<th>Sensitivity [1E-12 g/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{40}\text{K}$</td>
<td>0.016</td>
<td>&lt; 0.016</td>
</tr>
<tr>
<td>$^{238}\text{U}$</td>
<td>0.3</td>
<td>&lt; 0.3</td>
</tr>
<tr>
<td>$^{232}\text{Th}$</td>
<td>0.5</td>
<td>&lt; 0.5</td>
</tr>
</tbody>
</table>

Acrylic sample (8.2 g) @ 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 $^{233}$Pa was chemically separated using an Actinide Resin

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

$^{232}$Th @ 90% C.L.

$[1E-12 \text{ g/g}]$

Copper sample (199 g) < 0.5

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$^{238}$U → 0.012 mBq/kg – 1 ppt
$^{232}$Th → 0.004 mBq/kg – 1 ppt
$^{40}$K → 0.27 mBq/kg – 1 ppt
Examples of achievable sensitivities with NAA

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

and many other materials in these papers

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.

$$^{A}X + n \rightarrow ^{A+1}X \rightarrow ^{A+1}_{Z+1}Y + \gamma_{\text{cascade}}$$

$\beta$-$\gamma$ coincidence detector

See M. Nastasi's talk later today
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.