2.9. Neutron activation analysis of archaeological artifacts

Example 1: Medieval Silver Coins

- Turnosgroschen, Tours
- Großpfennig, Bonn
- Matapan / Grosso, Venedig
- Denar, Aachen
- Sterling, Jüllich
- Denar, Osnabrück
- Brakteat, Demmin
- Denar, Lodz
- Denar, Heinsberg
- Brakteat, Stralsund
- Denar, Brabant
Origin of silver coins
Accelerator based neutron source

Neutrons can be produced by charged particle nuclear reactions: (p,n), (a,n), (g,n) at a wide range of energies (white neutron source).

Reaction $^7\text{Li}(p,n)$ produces non-thermal neutron distribution.
Neutron activation with accelerators

\[ _{109}^{109}\text{Ag}(n,\gamma)^{110}\text{Ag} \]
activity measurement:
\[ _{110}^{110}\text{Ag}(\beta^{-})^{110}\text{Cd} \]
\((t_{1/2}=250\ \text{d})\)

Determination
of neutron flux

\[ _{197}^{197}\text{Au}(n,\gamma)^{198}\text{Au} \]
activity measurement
\[ _{198}^{198}\text{Au}(\beta^{-})^{198}\text{Cd} \]
\((t_{1/2}=2.7\ \text{d})\)

Additional measurement of Cu and Au content in coin!

Stable Silver isotope \(^{109}\text{Ag}\)
Stable Gold isotope \(^{197}\text{Au}\)

Neutron source:
\[ ^{7}\text{Li}(p,n)^{7}\text{Be} \]
Quasi-Maxwell-Distribution:

\[ kT = 25 \text{ keV} \]
\[ E_{\text{max}} = 110 \text{ keV} \]

Much higher than thermal reactor neutrons, \( kT=26 \text{ meV} \); the activation is not as efficient since the cross section is much lower (1/\( v \) law) – but well known! A thermalization of neutrons could be achieved by mounting paraffin blocks or some other thermalizing material with a high neutron scattering cross section.
Detection of characteristic $\gamma$-radiation

2 Ge-Clover-detectors, with irradiated probe wedged in between
Detection efficiency at 1115 keV:

single crystal:
\[
\eta_{\text{tot}} = 11 \%
\]
\[
\eta_{\text{peak}} = 1.1 \%
\]

detector array:
\[
\eta_{\text{peak}} = 15 \%
\]
Characteristic $\gamma$ spectrum after neutron activation
Activity of Au and Ag contents

\[ ^{109}\text{Ag}(n,\gamma)^{110}\text{Ag} \quad T_{1/2}(^{110}\text{Ag})=250 \text{ d}; \]
\[ \lambda_{\text{Ag}}=1.16\cdot10^{-4} \text{ 1/h} \]
\[ E_\gamma=658 \text{ keV} \]

\[ ^{197}\text{Au}(n,\gamma)^{198}\text{Ag} \quad T_{1/2}(^{198}\text{Ag})=2.7 \text{ d}; \]
\[ \lambda_{\text{Au}}=1.07\cdot10^{-2} \text{ 1/h} \]
\[ E_\gamma=412 \text{ keV} \]

Activity after 2 hours of irradiation with \(10^{10}\) n/cm\(^2\)s with
\(\sigma_{\text{Au}}=3\text{mb}\) and \(\sigma_{\text{Ag}}=2\text{mb}\)

\[
\frac{A_{\text{Au}}(t)}{A_{\text{Ag}}(t)} = \frac{P_{\text{Au}} \cdot (1 - e^{-\lambda_{\text{Au}} \cdot t})}{P_{\text{Ag}} \cdot (1 - e^{-\lambda_{\text{Ag}} \cdot t})} = \frac{\sigma_{\text{Au}} \cdot N_{\text{Au}} \cdot (1 - e^{-\lambda_{\text{Au}} \cdot t})}{\sigma_{\text{Ag}} \cdot N_{\text{Ag}} \cdot (1 - e^{-\lambda_{\text{Ag}} \cdot t})}
\]

\[
\frac{I_{\text{Au}}(t)}{I_{\text{Ag}}(t)} = \frac{\eta(412\text{keV}) \cdot A_{\text{Au}}(t)}{\eta(658\text{keV}) \cdot A_{\text{Ag}}(t)}
\]
Efficiency and Count Rate

\[ \eta_{Au} = 0.5\% = 0.005 \]

\[ \eta_{Ag} = 0.2\% = 0.002 \]

\[ I_{ag} = 6 \cdot 10^5 \]

\[ I_{au} = 1 \cdot 10^5 \]

\[
\frac{N_{Ag}}{N_{Au}} = \frac{\sigma_{Au} \cdot (1 - e^{-\lambda_{Au} \cdot t}) \cdot I_{Ag} \cdot \eta_{Au}}{\sigma_{Ag} \cdot (1 - e^{-\lambda_{Ag} \cdot t}) \cdot I_{Au} \cdot \eta_{Ag}} = \frac{1.91 \cdot 10^{-25}}{9.28 \cdot 10^{-29}} \approx 2 \cdot 10^3
\]
Results for single coin measurements

Silver
Copper
Gold

#12 shows mint deviations in Co, Ag, & Au content
### Comparison with official mint statements

**Previous Results**

1. **part 16. century**
   - Weight: 1.30g
   - Ag content: 889/1000
   - Ag weight: 1.16g

2. **part 16. century**
   - Weight: 0.92g
   - Ag content: 977/1000
   - Ag weight: 0.90g

**Present Results**

1. **part 16. century**
   - Weight: 1.33g
   - Ag content: 972/1000
   - Ag weight: 1.14g

Großpfennig, Bonn
Example 2: Qumran Pottery Provenance

All clay sources on earth have a unique geochemical history, but show a slightly different impurity composition. Based on the analysis of these impurities the pottery can be traced to the site where it has been manufactured. Similarly, other artifacts made from pumice, obsidian glass, amber, basalt and sporadically flint can be traced to a distinctive source.

Analysis of Qumran Pottery should establish the origin of the dead sea scroll containers and yield information on the cultural connection with other groups and villages.
The Qumran Scrolls
Qumran site and samples

Analysis of Qumran Pottery should establish the origin of dead sea scroll containers and yield information on the cultural connection with other groups and villages.

Is there a difference between pottery found in the caves and at the Qumran site? Was the pottery made locally or was it imported?
Taking & Preparing a Sample

A pottery sample is taken by grinding off 100 mg of ceramic resulting into a powder. This is then mixed with pure cellulose (50 mg) (as a binder) and pressed into a pellet of uniform size and thickness. The pellets—representing sherds or complete vessels—are wrapped in pure aluminum and set on edge into an aluminum capsule which is sent to a nuclear reactor where it is submitted to a neutron flux. Two or more samples of a standard of known chemical composition are added to the rest of the pellets.
Neutron activation with reactors
Activation procedure with thermal neutrons in reactor

Probe is positioned into neutron line
Gamma-ray spectrum showing several short-lived elements measured in a sample of pottery irradiated for 5 seconds, decayed for 25 minutes, and counted for 12 minutes with an HPGGe detector.
Long-lived Isotopes

Gamma-ray spectrum from 50 to 800 keV showing medium- and long-lived elements measured in a sample of pottery irradiated for 24 hours, decayed for 9 days, and counted for 30 minutes on a HPGe detector.
High energy $\gamma$-radiation

Gamma-ray spectrum from 800 to 1600 keV showing medium- and long-lived elements measured in a sample of pottery irradiated for 24 hours, decayed for 9 days, and counted for 30 minutes on a HPGe detector.
Gamma-ray Counts to Calculate Element Concentration

To calculate the concentration (i.e., ppm of element) in the unknown sample it is irradiated together with a comparator standard containing a known amount of the element of interest. If the unknown sample and the comparator standard are both measured on the same detector, one usually corrects the measured counts (or activity) for both samples back to the end of irradiation using the half-life of the measured isotope. The equation used to calculate the mass of an element in the unknown sample relative to the comparator standard is

\[
\frac{A_{\text{sam}}}{A_{\text{std}}} = \frac{m_{\text{sam}}}{m_{\text{std}}} \left( e^{-\lambda t} \right)_{\text{sam}} \left( e^{-\lambda t} \right)_{\text{std}}
\]

where \( A \) = activity of the sample (sam) and standard (std), \( m \) = mass of the element, \( \lambda \) = decay constant for the isotope and \( t \) = decay time. For short irradiations, the irradiation, decay and counting times are the same for all samples and standards such that the time dependent factors cancel. Thus the above equation simplifies into

\[
c_{\text{sam}} = c_{\text{std}} \frac{W_{\text{std}}}{W_{\text{sam}}} \frac{A_{\text{sam}}}{A_{\text{std}}}
\]

where \( c \) = concentration of the element and \( W \) = weight of the sample and standard.