

Neutron activation analysis

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Introduction

Neutron activation analysis (NAA) is a nuclear process used for determining the concentrations of elements in a vast amount of materials. NAA relies on excitation by neutrons so that the treated sample emits gamma-rays. It allows the precise identification and quantification of the elements, above all of the trace elements in the sample. NAA has applications in chemistry but also in other research fields, such as geology, archeology, medicine, environmental monitoring and even in the forensic science.

The method is based on neutron activation and therefore requires a source of neutrons. The sample is bombarded with neutrons, causing the elements to form radioactive isotopes. The radioactive emissions and radioactive decay paths for each element are well known. Using this information, it is possible to study spectra of the emissions of the radioactive sample, and determine the concentrations of the elements within it. A particular advantage of this technique is that it does not destroy the sample, and thus has been used for analysis of works of art and historical artifacts.

Neutron Activation Analysis is very sensitive and is therefore used to analyse for minor elements, which are present in very low concentrations. The method is especially useful for trace element analysis, e.g. in high-purity substances, and is therefore important in semiconductor techniques. It can also be used to detect trace element in water, biological

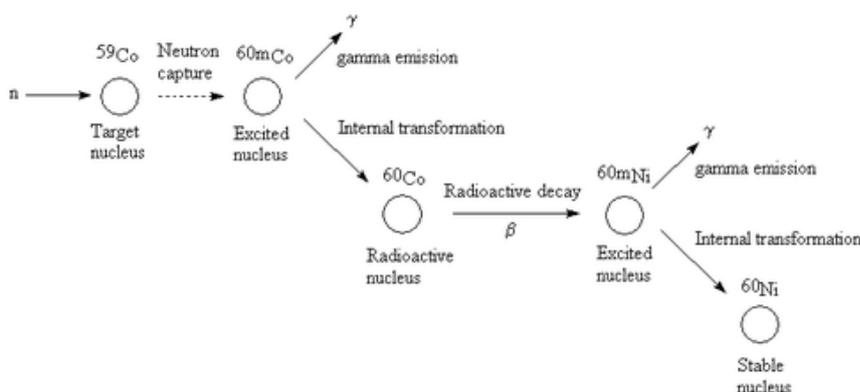
material and minerals. In archaeology, NAA can give useful information about the origin of the findings according to the so-called “fingerprint” of the individual element composition in their raw materials. It is usually used as an important reference for other analysis methods.

NAA can detect up to 74 elements depending on the experimental procedure, with minimum detection limits ranging from 10^{-7} to 10^{-15} g/g, depending on the elements and matrix materials. Some nuclei can capture a number of neutrons and remain relatively stable, not undergoing transmutation or decay for many months or even years. Different nuclei have different cross sections and half-lives, and the intensities of the emitted gamma-rays can also vary – therefore the detection limits are quite variable. Rare earth elements (REE) have very high thermal neutron cross sections and NAA is usually the first choice for the determination of REEs in a trace elements analysis.

With the use of automated sample handling (e.g. using rabbit system), gamma-ray measurement with solid-state detectors, and computerized data processing it is generally possible to simultaneously measure more than thirty elements in most sample types without chemical processing. The application of purely instrumental procedures is commonly called instrumental neutron activation analysis (INAA) and is one of NAA's most important advantages over other analytical techniques, especially in the multi-element analysis. If chemical separations are done to samples after irradiation to remove interferences or to concentrate the radioisotope of interest, the technique is called radiochemical neutron activation analysis (RNAA). The latter technique is performed infrequently due to its high labor cost.

Principle of method

Neutron activation analysis (NAA) is a method for element determination based on the measurement of characteristic gamma energies from artificially produced radionuclides. These radionuclides are formed by bombarding stable elements with neutrons. NAA is performed using a nuclear reactor that produces thermal neutrons. When stable elements are irradiated with thermal neutrons in a reactor, the elements become radioactive due to the neutron capture of the core.



This produces isotopes through (n, γ) nuclear reactions in accordance with:



The γ energy is specific for the nucleus with a specific decay rate, and can be measured.

If nuclide produced is radioactive, nuclear transformations will follow a 1-order kinetic reaction according to:

$$D_t = D_0 e^{-\lambda t} \quad (2)$$

where

D_0 = disintegration during irradiation termination

D_t = disintegration after a time t

λ = disintegration constant

The disintegration constants are as we know, characteristic for each nuclide. Disintegration, D , is proportional to the number of radionuclides, N , giving:

$$D = \lambda N \quad (3)$$

where λ = disintegration constant, $\ln 2/t_{1/2}$,

$t_{1/2}$ = the physical half-life,

N = number of radionuclides.

Detection of radionuclides

The irradiated material is now radioactive and can be measured using conventional radiochemical methods i.e. a Ge-detector.

A certain amount of irradiated material is measured over a certain time, depending on the amount of radioactive material in the sample. Instrument background and blank samples measured in advance, and energy calibration and efficiency calibration of the respective geometries are added.

Disintegration measured in Becquerel (Bq), is used for quantitative detection. Decay of the radionuclides produced in an (n, γ) reactions by irradiation finally given by:

$$D_T = \sigma \Phi N_T (1 - e^{-\lambda T}) \quad (4)$$

where

N_T = number of stable nuclides that are irradiated,

σ = reaction probability (capture cross, 1barn = 10^{-24} cm²),

Φ = neutron flux (number of neutrons sec⁻¹ cm⁻²) and

T = irradiation time.

After waiting ten from irradiation end disintegration given by:

$$D_t = \sigma \Phi N_T (1 - e^{-\lambda T}) e^{-\lambda t} \quad (5)$$

$$N_T = (m / M) X N_A \quad (6)$$

where

m = the amount of irradiated sample

M = the molar mass of the substance,

X = frequency of the irradiated isotope,

N_A = Avogadro's number

For specific reactions the variables commonly known, the number of nuclei, N_T , which is irradiated, can be calculated. However, as a rule, are factors that capture cross (response probability, σ) of a nuclide and neutron flux in the reactor is somewhat uncertain.

The sensitivity is dependent on the flux at the activating particles (Φ), the reaction probability or cross section of the reaction (σ), irradiation time (T) and the nuclides half-life. Meanwhile, the properties of the radiation emitted by the formed nuclide and efficiency to detect this radiation, determines methods suitable.

Kinetics of activation

In the case of nuclear reactions induced by neutrons the radioactivity of the examined isotope depends on the flux of the neutrons and the cross section of the given nuclear reaction. The cross section and the neutron flux highly depend on the energy of neutrons, and therefore the usual activation equation is:

$$R = N \int_0^{\infty} \sigma(E) \cdot \phi(E) dE \quad (7)$$

Where:

N = number of interacting isotopes

$\sigma(E)$ = cross-section [in cm^2] at neutron energy of E [in eV]

$\phi(E)$ = neutron flux per unit of energy interval [in $\text{cm}^{-2} \text{s}^{-1} \text{eV}^{-1}$]

R = reaction rate

In nuclear reactors the integral in Equation [7] is usually replaced by the sum of two integrals separating the thermal and epithermal regions, the lower limit of the epithermal component of a neutron spectrum most commonly is 0.55 eV:

$$R = N (\phi_{th} \cdot \sigma_{th} + \phi_e \cdot I_o) \quad (8)$$

Where:

σ_{th} = conventional thermal neutron flux [in cm^2]

ϕ_{th} = effective thermal neutron cross-section [in cm^2]

ϕ_e = conventional epithermal neutron flux [in $\text{cm}^{-2} \text{s}^{-1} \text{eV}^{-1}$]

I_o = resonance integral cross section (in epithermal region), for 1/E epithermal spectrum [in cm^2]

The activity (A) of the isotopes depends on time. During irradiation the activity of the radioactive isotope produced grows according to a saturation characteristic governed by a saturation factor $S=1-e^{-\lambda t_i}$. Subsequent to the irradiation the isotope decays according to the exponential law: $D=e^{-\lambda t_d}$.

Where

t_i = time of irradiation;

t_d = time of decay;

λ = decay constant

$$A = \left(\phi_{th} \cdot \sigma_{th} + \phi_e \cdot I_o \right) \frac{m \cdot f_i \cdot N_{Av}}{A_{rel}} S \cdot D \quad (9)$$

N_A = Avogadro number

f_i = isotopic abundance

m = the mass of the irradiated element

A_{rel} = atomic mass of target element

The intensity of the measured gamma line is proportional to the activity. The measured parameter is the total energy peak area (N_P) at a particular energy given by

$$N_P = A f_\gamma \epsilon_\gamma t_m \quad (10)$$

The efficiency (ϵ_γ) of a semiconductor detector varies with gamma energy. The emission probability of a gamma photon at a given energy is the f_γ , where t_m is the measuring time.

Choosing the appropriate procedure

When solving an analytical problem by means of activation analysis, or any other method, the analyst must select an appropriate procedure. In attempting an optimisation, one must consider a number of aspects. A set of experimental parameters must be chosen for adjustment, the others being fixed by practical considerations.

A number of elements have more than one isotope which can be activated by neutrons. Each activation product has its own cross-section, isotopic abundance and decay scheme. The first decision is to choose the most selective nuclear reaction in order to optimise the procedure.

Irradiation conditions

The incident flux of the irradiating particles directly affects the level of radioactivity produced, generally the neutron self absorption is negligible.

In a nuclear reactor the neutron flux cannot be freely changed, but there are some possibilities to choose. The effective cross-section of a nucleus depends on the energy of the bombarding particles. Some reactions, “threshold reactions”, do not occur below certain energy. Some interferences can be avoided by proper selection of the energy range. In nuclear reactors there are several irradiation channels with different neutron energy spectra.

The use of a thermal neutron filter is an important option of selection. This type of analysis is called Epithermal Neutron Activation Analysis (ENAA), where Cd or B is used as a filter. ENAA is advantageous in cases when the nuclide has a high I_0/s_{th} ratio. Some elements can be determined with higher sensitivity by ENAA, e.g. As, Br, Rb, Sr, Mo, Sb, Ba, Ta and U.

Some interference can also be avoided by this way. Sometimes, the same radionuclide can be produced from two different elements, e.g. ^{28}Al which is produced from $^{27}\text{Al}(n,g)^{28}\text{Al}$ and $^{28}\text{Si}(n,p)^{28}\text{Al}$. The (n,g) reactions are initiated mainly by thermal neutrons, while for (n,p), (n,a) reactions, fast neutrons are required. In this case, the samples can be activated twice, with and without cadmium filter, in order to determine both Al and Si in the sample.

Measurement of radioactivity

Generally, the activation product emits more than one gamma quanta, each of different energy and emission probability. To choose the proper analytical gamma line(s) the gamma abundance, the efficiency and the possible interferences must be considered, in exceptional cases self absorption can be the main problem. Sometimes, it is also possible to use more than one gamma line in order to improve the accuracy and the reliability of the measurement.

The region of gamma ray spectrum below 150 keV is generally quite complex, and it is frequently advisable to count the samples with a Low-Energy Photon Detector (LEPD). In geological samples, the use of alternate gamma lines in the low energy region is more effective in the case of Ba, Nd, Sm, Tb, Hf, Th and U, while the determination of Gd, Ho, and Tm can be successfully realized only by measuring the photons at low energies.

Measuring geometry: the efficiency of the measurement depends on the solid angle presented by the detector to the sample. Therefore, the detection efficiency is highly affected by the shape of the sample and its distance from the detector. The counting rate can also be changed in this way.

In the case of shortage of samples (analysis of meteorites, special minerals etc.), very low concentrations in biological samples the use of a well-type detector is desirable.

Experimental parameters

By optimising the irradiation, decay and measuring times a lot of elements can be determined with higher sensitivity. A number of interferences can be avoided in this way, too.

For elements with short half lives the shortest irradiation and cooling times are determined by the technical limitations. In this case some special methods are required, e.g. the process of cyclic activation. In this method the samples are repeatedly irradiated and counted, and then, the spectra are summed. The transfer, irradiation and counting times, as well as the number of cycles should be optimised.

The radioactive isotopes of long half lives produced after irradiating the elements for long time (e.g. eight hours) in a thermal channel of the reactor are measured several times. The cooling times are one week and one month or longer in special cases. By this way, usually 25-30 elements can be determined in different types of samples.

Methods of standardisation

The two features of neutron induced reaction - high penetrability for neutrons and gamma radiation - ensure that its standardisation is potentially easy and accurate. As the signal to concentration ratio is nearly matrix independent, the sample preparation is rather easy; therefore, the risk of systematic or random errors is reduced.

The analytical procedure can be made faster and more economical by simplifying the standardization procedure.

Instrumental nøytronaktiveringsanalyse (INAA)

Instrumental nøytronaktiveringsanalyse (INAA) using Ge-detector is a useful tool when it comes to determining a large number of elements in water, soil and vegetation. In fresh water INAA capable to decide about 30 elements at the concentration levels of 1 g/L or lower. INAA may also be useful in studies going on state forms of trace elements, especially in fresh water, if first using fractionation techniques.

Due to factors such as the reaction probability of a nuclide and neutron flux in the reactor will be uncertain; one should compare a sample with an unknown amount of a standard with known amount.

Samples and appropriate standards must be irradiated simultaneously. When the ratio of the amount of trace element, m_p , of the sample and sample disintegration, D_p , be identical to the ratio between the standard's trace element amount, m_s , and disintegration, D_s , and the concentration of the element in the sample can be calculated:

$$m_p / D_p = m_s / D_s \quad (11)$$

$$m_p = D_p \times (m_s / D_s) \quad (12)$$

The accuracy of the relative method depends on the standard preparation procedure (e.g. non stoichiometry of the standard compound, dilution and micropipetting uncertainties).

The disadvantage of the classic relative method lies in the multielement application. The procedure of the standard preparation and counting is rather laborious, and this is coupled with the occasional loss of information if an unexpected element appears for which no standard has been irradiated. The use of home-made multielement standards can be an answer to these problems, but this raises the question of homogeneity and stability. There is commercial multi-element Standards Reference Materials (SRM) available. They aim at improving the accuracy of the measurements and allowing a proper quality assurance in the laboratories.

INAA does not discriminate between different physico-chemical states of the elements, but gives the total concentration in the sample. That is, elements present in the sample ions, colloids and particles will all be included in the analysis.

The peak area can also be calculated by computer programs which fit an analytical function to the peak. The shape is described basically by a Gaussian function, modified by suitable auxiliary functions. Thus all the peaks including also the multiplets can be automatically analyzed.

Procedure in short

1. Before starting the irradiation the following have to be answered:
 - How can we determine Ca, Na, Cl in the samples in the presence of interfering components (e.g. Mg, Al, Si):
 - Choose the proper
 - i. nuclear reaction
 - ii. analytical gamma line
 - iii. irradiation, decay and measuring times,
 - Calculate the quantity of the elements to be used for standardization.
2. Sample preparation:
 - weigh the samples into polyethylene bags/vials using analytical balance
 - prepare standards using micropipettes/analytical balance
 - dry solutions/samples totally before heat sealing vials/bags
 - pack samples in compartments set by reactor
3. Irradiation of the samples using pneumatic system of the reactor
4. Measure the gamma-spectra, evaluate the spectra (determine the peak areas at the given gamma-lines)
5. Identify the isotopes in the spectra using gamma library.
6. Determine the elemental concentrations and their uncertainties using standard method.