NEUTRON ACTIVATION ANALYSIS

1. Introduction [1]

Neutron Activation Analysis (NAA) is a quantitative and qualitative method of high efficiency for the precise determination of a number of main-components and trace elements in different types of samples. NAA, based on the nuclear reaction between neutrons and target nuclei, is a useful method for the simultaneous determination of about 25-30 major, minor and trace elements of geological, environmental, biological samples in ppb-ppm range without or with chemical separation. In NAA, samples are activated by neutrons. During irradiation the naturally occurring stable isotopes of most elements that constitute the rock or mineral samples, biological materials are transformed into radioactive isotopes by neutron capture. Then the activated nucleus decays according to a characteristic half-life; some nuclides emit β particles only, but most nuclides emit gamma-quanta (gamma-photon), too, with specific energies. The quantity of radioactive nuclides is determined by measuring the intensity of the characteristic gamma-ray lines in the spectra. For these measurements a gamma-ray detector and special electronic equipment are necessary. As the irradiated samples contain radionuclides of different half-lives different isotopes can be determined at various time intervals. Although the development of analytical techniques has led to the expansion of new methods (ICP-AAS, ICP-MS, etc.), which can also be widely applied in analytical chemistry, NAA is still competitive in many areas. The indisputable advantage of the method is its sensitivity and accuracy especially in respect of some trace elements. The method is of a multielement character, i.e. it enables the simultaneous determination of many elements without chemical separation. In the case of instrumental determination, the preparation of samples involves only the preparation of representative samples, i.e. pulverization or homogenization in most cases, and this reduces the danger of contamination to a minimum and accelerates the whole analytical process. If the determination of some special elements or groups of elements can be carried out only through chemical separation, it is possible to carry out after irradiation. Thus the pollution caused by the different chemicals will not get activated, the chemical yield can be measured by feeding inactive carriers and the chemical processes can be better controlled. During NAA the neutrons get into interaction with the nucleus, therefore, the chemical composition and crystal structure of the substance under analysis will have an effect on the result only in exceptional cases. The development of the method has contributed to the elaboration of some very simple and accurate methods of

standardization, which lead to a surpassingly accurate analysis. The widespread application of NAA is hindered, however, by some conditions. Among the different fields of application, the Instrumental Neutron Activation Analysis (INAA) following a reactor irradiation is the most competitive. In view of the increasing protest against nuclear energy, a number of research reactors have been shut down; therefore, the possibilities of irradiation are limited in many countries. The equipment needed for the analysis is rather expensive and requires special laboratories and a highly qualified staff.

2. Principles of the NAA method

In the process of NAA the neutrons interact with the stable isotopes of the target element converting them to radioactive ones. The so-called compound nucleus emits gamma rays promptly with extremely short half-lives in the order of ps and these can be measured during irradiation through a technique called prompt gamma activation analysis (PGAA). In most cases, the radioactive isotopes decay and emit beta particles accompanied by gamma quanta of characteristic energies, and the radiation can be used both to identify and accurately quantify the elements of the sample. Subsequent to irradiation, the samples can be measured instrumentally by a high resolution semiconductor detector, or for better sensitivity, chemical separations can also be applied to reduce interferences. The qualitative characteristics are: the energy of the emitted gamma quanta (E_γ) and the half-life of the nuclide ($T_{1/2}$). The quantitative characteristic is: the I_γ intensity, which is the number of gamma quanta of energy E_γ measured per unit time.

1. Step of the analysis: sample preparation means in most cases only pulverising, homogenising, mass determination, packing, as well as the selection of the best analytical process and the preparation of the standards, if any.

2. Step of the analysis: for irradiation one can choose from the various types of neutron sources according to need and availability.

3. Step of the analysis: after the irradiation the analysts face the dilemma whether or not a chemical separation should be carried out for better sensitivity. If it is needed, the measurement shall be made after the separation. If there is no chemical treatment, the measurement is performed after a suitable cooling time (t_c).

4. Step of the analysis: measurement, evaluation and calculation involve taking the gamma spectra and the calculating trace element concentrations of the sample. The most widely used

gamma spectrometers consist of germanium based semiconductor detectors connected to a computer used as a multichannel analyser for spectra evaluation and calculation.

2.1. Irradiation facilities

2.1.1. Neutron sources

Isotopic neutron sources [2]

In the case of the most frequently used isotopic neutron sources an alpha emitting radioactive material is mixed with beryllium and an (α,n) reaction generates the neutrons.

Isotopic neutron sources:

α-emitter	Half life	Neutrons 1/(sCi) emitted	Average neutron energy [MeV]
^{227}Ac	22 y	1.5×10^7	4
^{226}Ra	1620 y	1.3×10^7	3.6
^{239}Pu	2.4×10^4 y	1.4×10^7	4.5
^{210}Po	138 d	2.5×10^6	4.3

The spontaneous fission of some artificially produced transuranium isotopes can be applied as a small neutron source. E.g. ^{252}Cf (half-life 2.6y) undergoes fission, producing 3.76 neutrons of 1.5 MeV per event. One milligram of ^{252}Cf emits 2.28×10^9 neutrons per second. The major advantage is that the isotopic neutron sources can be made portable and generate a stable neutron flux. But, as the neutron flux is rather low in comparison to a nuclear reactor their use in NAA is limited to the determination of elements of high activation cross section which are present in major concentrations.

2.1.2. Neutron generators

These neutron sources are accelerators where a convenient target material is bombarded by accelerated charged particles and the neutrons are produced in a nuclear reaction. In the most frequently used and commercially available neutron generators, deuterons are accelerated and the target material is tritium. The nuclear reaction carried out is ^{3}H (d,n) ^{4}He. The energy of the produced monoenergetic neutrons is 14 MeV. The typical neutron yields of about 10^{11} neutrons 1/(smA) means a neutron flux of approximately 10^9 neutrons 1/(cm^{2}s). Due to the emitted fast neutrons, in NAA the neutron generators are used for the determination of

elements of high cross section in this energy region. Examples of elements of geochemical interest determined by the fast neutrons of generators [3]:

Magnesium:	^{26}Mg (n,a) ^{23}Ne	$T_{1/2} = 37.6$ s
Aluminium:	^{27}Al (n,p) ^{27}Mg	$T_{1/2} = 9.5$ min
Silicon:	^{28}Si (n,p) ^{28}Al	$T_{1/2} = 2.3$ min
Titanium:	^{46}Ti (n,p) ^{46m}Sc	$T_{1/2} = 18.7$ s
Iron:	^{56}Fe (n,p) ^{56}Mn	$T_{1/2} = 2.58$ h
Zirconium:	^{90}Zr (n,2n) ^{89m}Zr	$T_{1/2} = 4.2$ min
Nickel:	^{60}Ni (n,p) ^{60m}Co	$T_{1/2} = 10.5$ min

2.1.3. Nuclear reactors

Owing to the high neutron flux, experimental nuclear reactors operating in the maximum thermal power region of 100 kW - 10 MW with a maximum thermal neutron flux of 10^{12}-10^{14} neutrons $1/(cm^2 s)$ are the most efficient neutron sources for high sensitivity activation analysis induced by epithermal and thermal neutrons. The reason for the high sensitivity is that the cross section of neutron activation is high in the thermal region for the majority of the elements. There is a wide distribution of neutron energy in a reactor and, therefore, interfering reactions must be considered. In order to take these reactions into account, the neutron spectrum in the channels of irradiation should be known exactly. E.g. if thermal neutron irradiations are required, the most thermalized channels should be chosen.

2.2. Kinetics of activation [2]

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:

$$R = N \int_0^\infty \sigma(E)\phi(E)dE \qquad (1)$$

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 $1/(cm^2 \, s \, eV)$]

R: reaction rate

In nuclear reactors the integral in Equation [1] 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:

$$R = N \, (\phi_{th} \cdot \sigma_{th} + \phi_e \cdot I_0) \tag{2}$$

ϕ_{th}: conventional thermal neutron flux [in $1/(cm^2 s)$]

σ_{th}: effective thermal neutron cross-section [in cm^2]

ϕ_e: conventional epithermal neutron flux [in $1/(cm^2 seV)$]]

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

$$A = (\phi_{th}\sigma_{th} + \phi_e I_0) \frac{m \, f_i N_{Av}}{A_{rel}} SD \tag{3}$$

N_{Av} : 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

$$N_P = A * f_\gamma * \varepsilon_\gamma * t_m \tag{4}$$

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, t_m is the measuring time.

2.3. Choosing the appropriate procedure [4]

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.

2.3.1. 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_o/σ_{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 interferences 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}Al(n,γ)^{28}Al and ^{28}Si(n,p)^{28}Al. The (n,γ) reactions are initiated mainly by thermal neutrons, while for (n,p), (n,α) 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.

2.3.2. 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 bellow 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.

2.3.3. 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 [5]. 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.

2.4. Methods of standardization

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 standardisation procedure.

2.4.1. Absolute method

Since the theory of NAA is well founded, an "absolute" standardisation procedure can be applied. The quantitative measurement can be effected by determining the neutron flux and counting the absolute gamma rays. The direct calculation of concentration is made by applying nuclear constants according to Eq. 3., 4. According to Girardi's investigation [6], systematic errors up to tens of percent may be the consequences of the uncertainties of nuclear data taken from literature, especially those on decay schemes and activation cross-section. Although recently the conditions have much improved, the factor of uncertainty is still considerable compared to the relative methods. Irrespective of this, the ability to estimate the quantity of an element in an unknown sample is a very important feature of NAA.

2.4.2 Classic relative method

The method is based on the simultaneous irradiation of the sample with standards of known quantities of the elements in question in identical positions, followed by measuring the induced intensities of both the standard and the sample in a well-known geometrical position. A relative standardisation can be performed by means of individual monoelement standards, or by using synthetic or natural multielement standards. The calculation of the unknown quantity (m) is made according to Eq.5.

$$m = \frac{I}{I_{st}},$$

$$I_{st} = \frac{N_{p,st}}{S_{st} D_{st} C_{st} m_{st}},$$

$$I = \frac{N_p}{SDC} \tag{5}$$

(st) refers to the standard. 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 are commercial multielement Standards Reference Materials (SRM) available. They aim at improving the accuracy of the measurements and allowing a proper quality assurance in the laboratories.

2.5. Measurement and evaluation [6]

The modern gamma measuring systems consist of a gamma detector, usually a HPGe type and sometimes NaI(Tl) scintillation crystals. The detectors are connected to a multichannel analyzer (MCA) by an appropriate electronic system (preamplifier, spectroscopy amplifier, etc.). Nowadays, the MCAs are computer based systems with the ability of an automatic spectrum evaluation. The most important parameters of the detectors are the efficiency and resolution. The efficiency of the NaI(Tl) detectors is quite high, but their resolution is poor comparing to the semiconductor germanium detectors. The typical resolution of a 3x3" NaI(Tl) detector at 1333 keV energy is 90 keV and the same for a HPGe detector with a 30% relative efficiency (related to a 3x3" NaI(Tl) in similar circumstances) is 1.9-2.2 keV.

2.5.1. Analysis of the gamma spectra

The usual objective of the measurements by gamma ray spectrometers is the determination of the number and energy of the photons emitted by the source. The peak location and the peak area in the spectra have to be determined. The peak location is a measure of the gamma energy, while the peak area is proportional to the photon emission rate. For the energy measurement the pulse height scale must be calibrated with standard sources emitting photons of known energies. In order to calculate the activities, the full-energy-peak efficiencies of the source- detector system have to be determined by using sources of known activities. For the determination of the peak areas the background under the peak interval has to be subtracted. The net count (N_p) results from $N_P = N_{int} - N_B$, (N_{int} integral under the peak and N_B refers to the background). 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 analysed.

2.5.2. Counting statistics

The nuclear decay processes occur at random, and follow a Poisson distribution, where the standard deviation (s) equals to $N^{1/2}$ (N is the observed number of events). In gamma spectrometry, the peak area is the measured parameter. The standard deviation is: $\sigma=(N+2N_B)^{1/2}$ where the confidence level is 68%. The counting statistic is only one of the possible sources of errors in NAA, the overall value depending on a number of different factors (e.g. sample preparation, weighing, and uncertainty of standardisation).

3. Equipment and materials

- Sample for analysis (chosen by the students: hair sample, soil or steel)
- Standard solutions (Ca, Mn, Na standard solutions)
- Analytical balance
- Micropipette
- Reactor for irradiation
- HPGe detector, spectrometer

4. Procedure

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 - nuclear reaction - analytical gamma line - 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 using analytical balance
    - prepare standards using micropipettes
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. Determine the elemental concentrations and their uncertainties using standard method (Eq. 4.).

5. Data processing – uncertainty estimation

Thermal neutron flux (at 10kW): $2,4 \cdot 10^{11}$ neutron/cm^{2}sec, measurable intensities at the chosen gamma line: 10 counts/sec.

Element	Nuclear reaction	σ (barn)	Isotopic abundance (%)	$T_{1/2}$	Gamma energy (keV)	Gamma abundance (%)	Efficiency* (%)
Na	$^{23}Na(n,\gamma)^{24}Na$	0.513	100	14.959 h	1368.6	100	
Mg	$^{26}Mg(n,\gamma)^{27}Mg$	0.0372	11.01	9.458 m	843.8 1014.4	71.4 28.6	
Al	$^{27}Al(n,\gamma)^{28}Al$	0.226	100	2.24 m	1778.9	100	
Cl	$^{37}Cl(n,\gamma)^{38}Cl$	0.423	24.23	37.21 m	1642.4	32.5	
Ca	$^{48}Ca(n,\gamma)^{49}Ca$	1.12	0.187	8.719 m	3084.4	91.7	
Mn	$^{55}Mn(n,\gamma)^{56}Mn$	13.2	100	2.578 h	846.8 1810.7	98.9 27.2	

* Efficiencies of the HPGe detector at measuring position.

6. Knowledge check

1. What is the difference between absolute and relative methods?

2. How can we determine e.g. Ca in lead (why it is difficult)?

3. How can we measure Al in soil?

7. References

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