Neutron Activation Analysis in Life Sciences

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Neutron Activation Analysis (NAA) is an analytical techniqe based on inducing artificial radioactivity in sample, by irradiating in the flux of neutrons, and measuring the characteristic gamma radiation emited by radionuclides. The basis of determination of element content in sample are comparsative measurements relative to Certified Reference Material (CRM) wich one is irradiated with the sample. The neutron capture process is an inelastic collision of a neutron with the nucleus, resulting that the nucleus enters an excited state and then emits two types of gamma radiation: prompt (when tne nucleus is deexcitating) and delayed (from decaying nucleus). In this report two types of NAA: Instrumental NAA and Cyclic NAA will be described.

1 Introduction

Background The history of NAA starts in 1930's with experiments of George de Hevesy and his asistant Hilde Levi. They were using neutron source from pulverized berylium in an agate mortar and mixing it in a glass ampule with ^{222}Rn from solution of radium salt[1]. To measure induced radioactivity they were using Geiger counter. The Neutron Activation term was suggested in 1949[2]. In the same year it was suggested to use uranium pile as a high flux neutron source. Nowadays nuclear reactors with high flux of neutrons (e.g. 10^{16} n/cm^2/s on the surface of the moderator in the IBR-2M research reactor) are main neutron sources for NAA. For the measurement of gamma radiation High Purity Germanium (HPGe) detectors are used. This type of detector provides the best energy resolution of the gamma spectra with Full Width at Half Maximim (FWHM) about 2 keV for 1332.5 keV gamma energy.

Neutrons spectrum and interaction of neutron with nuclei In the energy spectrum of neutron flux from nuclear reactor We can duistinguish three regions of energies.

1. **Fast neutrons**-the energy of those neutrons ranges from 100 keV to 25 MeV. In the reactor (except FBR type reactors), fast neutrons have to be moderated (slowed down) by the collisions with moderator to obtain higher fission reaction efficiency.
2. **Epithermal neutrons**-by this term, we call neutrons with energies from 0.5 eV to 100 keV.
3. **Thermal neutrons**-These are neutrons which have Maxwellian energy distribution and average velocity v_0 = 2200 m/s at 20 Celsius degrees wich is equivalent to energy 0.025 eV.

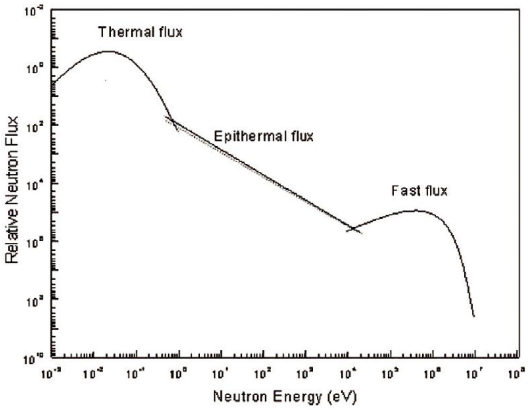
A typical spectrum of neutrons can be plotted as a function of neutron flux depending on their enegy.

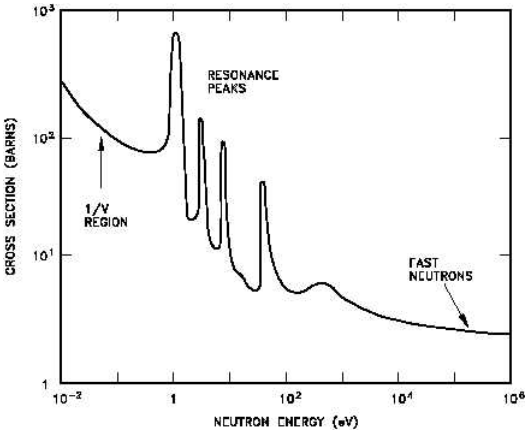
The most important nuclear reaction for NAA is neutron-gamma (n,γ) reaction. The cross section (probability that an interaction of neutron with nuclei will occur expressed in Barns) for this reaction is the highest for thermal neutrons. Cross section is inversely proportional to the neutron velocity for the thermal neutrons. For epithermal neutrons the cross section may be higher than for thermal, when discrete energy of neutrons is in resonance region[3].

[1] Levi H.: Semicentennial Lecture. 7th International Conference Modern Trends in Activation Analysis 23th June 1986, Copenhagen, Denmark.

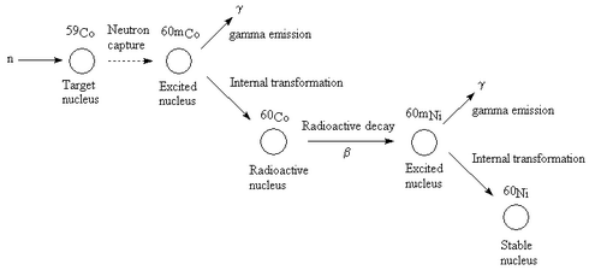
[2] Boyd G. E.: Method of Activation Analysis. Anal. Chem. 21 (1949), p. 335–347.

[3] http://www.naa-online.net/theory/equations/





It is possible to proceed irradiation only in resonance energies by using cadmium screen. Cadmium cuts off thermal neutrons and only epithermal and fast neutrons are present. The E_{Cd} = 0.55 eV value is called Cd cut off energy. The principle of neutron activation is shown on a picture below.



The stable nucleus after capture of neutron can be converted into unstable. When the nucleus captures neutron it forms compound nuclei which is in excited state. This nuclei need to deexcitate by emmiting prompt gamma ray in the time about 10^{-14} s. The next step is a radioactive decay of the nucleus formed. The neutron-rich nucleus can undergo β^- decay to a stable nuclei. When nucleus decays e.g. emmiting electron (β^- particle) there also might be emmited delayed gamma rays. They are emmited by an excited daughter isotope formed by radioactive decay of target nuclei. The delayed gamma rays are used most in NAA but it s also possible to measure prompt gamma rays, in that case we call it Prompt-Gamma Neutron Activation Analysis (PGNAA). In some cases neutron capture by atomic nuclei can result in conversion of one stable nucleus into another one, also stable.

2 Types of NAA

Instrumental Neutron Activation Analysis (INAA) INAA is a non destructive method consisting irradiation of samples and measurement of induced radioactivity. This is also the most frequently used type of NAA. It can be used for determination of trace and ultratrace amounts of elements in samples. Because it is non destructive, INAA can be used for analysis of valuable samples (e.g. archeological or pieces of art). A typical sample mass ranges from 300 mg to 1000 mg. It is depends on concentration of an element of interest and composition of sample matrix. Preparation of the sample and analytical process is as follows: first the sample must to be dried and homogenized. The sample drying can be processed in conventional dryer or by a freeze-drying. The dry sample is then weighted and compressed by a hydraulic press to the form of a pastille. This sample geometry is a standard in Sector of Neutron Activation Analysis and Applied Research (Frank Laboratory of Neutron Physics). In most cases from each sample two pastilles are prepared from each sample - for short and long irradiation. For short irradiation (lasting minutes) samples are packed into plastic bags and polyethylene vials. Because this package is sensitive for radiation and thermal damage, for long irradiation (hours) samples are packed in aluminium foil and aluminium containeers. Then samples are transported to irradiation channel by pneumatic transport system. After irradiation samples are waiting for decrease of activity (to

reduce background and dead time of counting) and then are measured. In the same way Certified Reference Material (CRM) is prepared and being measured. In the INAA total time of analysis is given by a formula:

$$T = T_i + T_d + T_c \tag{1}$$

Where T_i is time of irradiation, T_d is time of activity decreasing and T_c is the counting time. The number of nuclei decaying during measurement time can be described as follows:

$$N(t_i, t_d, t_c) = R{\cdot}\, N_0{\cdot}\, (1{-}e^{-\lambda\cdot t_i}){\cdot}\, e^{-\lambda\cdot t_d}{\cdot}\, \frac{(1-e^{-\lambda\cdot t_c})}{\lambda\cdot t_c} \tag{2}$$

Where R is a reaction rate per nucleus and N_0 is a concentration of target nuclei. The specific activity A_{sp} of irradiated sample is given by equations:

$$A_{sp} = \frac{N_A{\cdot}\,\theta{\cdot}\,\gamma}{M}{\cdot}\,[G_{th}{\cdot}\,\phi_{th}{\cdot}\,\sigma_0 + G_e{\cdot}\,\phi_e{\cdot}\, I_0(\alpha)]{\cdot}\,\varepsilon \tag{3}$$

and for epithermal neutron activation analysis (ENAA)

$$(A_{sp})_{Cd} = \frac{N_A{\cdot}\,\theta{\cdot}\,\gamma}{M}{\cdot}\, G_e{\cdot}\,\phi_e{\cdot}\, I_0(\alpha){\cdot}\,\varepsilon{\cdot}\, F_{Cd} \tag{4}$$

Where N_A is Avogadro number, θ is a isotopic abundance, γ is gamma ray emmision probability, M is a mass of sample, G_e and G_{th} are correction factors for epithermal and thermal neutron self shielding, ϕ_{th} and ϕ_e are thermal and epithermal eutron flux, σ_0 is an neutron capture effective cross section, $I_0(\alpha)$ is the resonance integral for a $\frac{1}{E^{1+\alpha}}$ epithermal spectrum, F_{Cd} is cadmium cut out and ε is photopeak efficiency.

Cyclic Neutron Activation Analysis CNAA is a modification of NAA which allows reduce the detection limits for determination of ultratrace elements in a sample. It can be also helpful, when element of interest is interfering with some other products of activation in INAA. In the CNAA we are using short-lived isotopes (with half-lifes usually less than 1 min). The sample is irradiated repeatedly (n = 4 or more) and the spectra are summed. This is the way to optimize counting statistics and reduce detection limits. Because activity of background isotopes is accumulating, in some cases series of fresh samples is irradiated. This method is called Pseudo-Cyclic NAA (PCNAA)[4]. The time of analysis in CNAA can be described as:

$$T = T_i + T_d + T_c + T_w \tag{5}$$

Where T_w is the time of waiting between irradiations. For the first irradiation the detector response D_1 will be equal to:

$$D_1 = \frac{N_0{\cdot}\,\sigma{\cdot}\,\phi{\cdot}\,\gamma{\cdot}\,\varepsilon}{\lambda}{\cdot}\,(1-e^{-\lambda t_i}){\cdot}\, e^{-\lambda t_d}{\cdot}\,(1-e^{-\lambda t_c}) \tag{6}$$

And for n-th cycle the detector responde will be given by a formula:

$$D_n = D_1{\cdot}\,(1{+}e^{-\lambda T}{+}e^{-2\lambda T}{+}e^{-3\lambda T}{+}...{+}e^{(n-1)\lambda T}) \tag{7}$$

The cumulative detector response D_C for sample ($_SD_C$) and for background ($_BD_C$) after all cycles will be given by:

$$D_C = \sum_{i=1}^{n} D_i \tag{8}$$

And the detection limit in CNAA will be calculated as:

$$L_d = \frac{3\sqrt{{}_BD_C}}{\frac{{}_SD_C}{m}} = \frac{3m\sqrt{{}_BD_C}}{{}_SD_C} \tag{9}$$

Where $\frac{{}_SD_C}{m}$ is a number of counts for a mass unit of element. The CNAA also be useful in determination of half-life time of activated radionuclides. After all spectra are collectedn D_C will be linear function of N. Than slope and intercept can be calculated by following equation:

$$a = \frac{D_1}{1-e^{-\lambda T}} \tag{10}$$

$$b = \frac{D_1 e^{-\lambda T}}{(1-e^{-\lambda T})^2} \tag{11}$$

And then, the half-life of an element will be given by a formula:

$$t_{1/2} = \frac{T\ln 2}{\ln(1-\frac{a}{b})} \tag{12}$$

[4]Hou, Xiaolin. Cyclic activation analysis.Encyclopedia of Analytical Chemistry (2000).

Other types of NAA

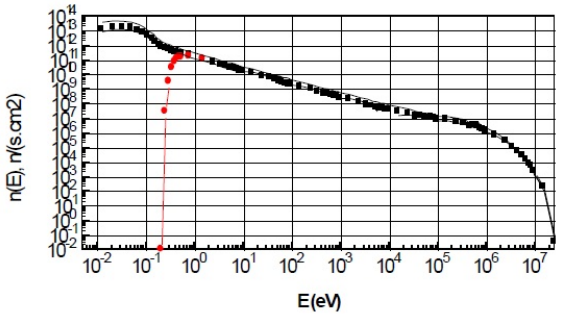
1. RNAA-Radiochemical Neutron Activation Analysis
2. MNAA-Molecular Neutron Activation Analysis
3. PGNAA-Prompt Gamma Neutron Activation Analysis
4. TNAA-Thermal Neutron Activation Analysis
5. FNAA-Fast Neutron Activation Analysis
6. ENAA-Epithermal Neutron Activation Analysis

3 Experimental setup

IBR-2M Fast Pulsed Reactor The IBR-2M is a pulsed reactor[5]. The main difference between IBR-2M and other reactors, is a fact, that reactivity in IBR-2M is mechanically modulated by movable reflector. The reflector has two parts: main and auxiliary, rotating in opposite directions with different velocities. A power pulse is generated when both reflectors coincide near the reactor core. The reactor parameters are presented in table below.

Average power	2 MW
Fuel	PuO_2
Number of assemblies	69
Maximum burnup, %	9
Pulse repetition rate, Hz	5; 10
Pulse half-width, μs:	
fast neutrons	240
thermal neutrons	340
Rotation rate, rev/min:	
main reflector (MMR)	600
auxiliary reflector (AMR)	300
MMR and AMR material	nickel + steel
MR service life, hours	55000
Background, %	7.5
Thermal neutron flux density from the surface of the moderator:	
time average	10^{13} n/cm^2/s
burst maximum	10^{13} n/cm^2/s

For NAA two irradiation channels are being used. Channel 1 has a cadmium screen for thermal neutrons cut out and channel 2 has a full spectrum of neutrons. Red line on a plot below shows spectrum of neutrons in channel 1 and the black line in channel 2. The temperatures in irradiation channels are 70 degrees for channel 1 and 60 degrees for channel 2, at 1.5 MW of reactor power, so this is the reason, why for long irradiation time, the samples must be packed in aluminium foil. The second reason is radiation damage of the package.



HPGe detectors The High Purity Germanium (HPGE) detectors are example of semiconductor radiation detectors. These detectors have good resolution, with FWHM about 2 keV for 1332.5 keV gamma energy and their efficiency, relative to NaI

[5]Frontasyeva, M. V., and S. S. Pavlov. Analytical investigations at the IBR-2 reactor in Dubna."JINR Preprint E14-2000-177. Dubna 15 (2000).

standard detector, is close to 30%. HPGe detectors are operating in liquid nitrogen temperature (77 K) to reduce noise and electrons leakage to the conductivity band of germanium. HPGe experimental set-up contains of: the high voltage is applied to the crystal to ensure fast migration of electrons and holes. Signal induced by gamma ray (e.g. by photoelectric effect) goes to the preamplifier and next to the amplifier. From there, signal is directed to ADC unit (Analog Digital Converter) and finally to MCA (Multi Channel Analyzer). ADC, HV supplier and Amplifier are devices in NIM or CAMAC standard. The spectra are being collecting and analyzed using GENIE 2k software.

4 Applications of NAA

As a non-destructive, multielement analytical technique, NAA has a lot of applications in several scientific fields.

Enviromental sciences The neutron activation analysis is very useful method for studying enviroment pollutions. For example, analysis of mosses samples can be wery good enviroment monitoring method. Moss collects atmospheric deposition of pollutants (e.g. heavy metals) very efficiently. Also, mosses doesn't have roots, so there is no uptake of elements from soil (only from atmospheric deposition).

Biology and medicine For understanding of trace elements behavior in organism many tpyes of samples can be analysed (e.g. urine, blood or nails). Some of elements, can be also analysed using In-Vivo NAA (e.g. total body nitrogen (TBN)).

History and archeology Because NAA is non-destructive method (except RNAA) i can be used to perform analysis of elemental composition of archeological samples like jewelery or pottery. The knowledge of elemental compositions of archeological samples can explain what kind of materials, pepole living before us used.

Nutritational science The NAA is frequently used for determination trace amounts of essential and toxic elements in food. For example, it is possible to determine iodine in food. The iodine is a highly volatile element and in standard chemical determination, it is very difficult to keep good chemical yield. In the INAA analysis, all iodine is kept in the sample.

CRMs preparation NAA is very important for preparation and homogenity testing of the Certified Reference Materials (CRMs). CRMs are essetnial for ensure quality of measurement in all fields of instrumental analysis, chemistry or radiochemistry. Also in NAA CRMs are used for concentration calculating and laboratory procedures quality assurance.

5 The practice-determination of selenium in legumes samples using instrumental and cyclic NAA

Role of selenium Selenium is one of most important trace element. This element is a component of selenocysteine and selenomethionine. In humans, selenium is a cofactor of of antioxidant enzymes such as glutathione peroxidases (GPx) and thioredoxin reductases (TrxR). It is also very important for thyroid function, as a cofactor of thyroid hormone deiodinases. Some reports suggest, that selenium may inhibit the Hashimoto's disease. Selenium can also reduce the effects of mercury toxicity (The mechanism of mercury toxicity is based on inhibition of selenoenzymes) and aflatoxins (which are strong cancorogens). Selenium can also stimulating immune resistance (suplementing Se in diet increase number of T cells and auxiliary T cells). Low levels of selenium in the organism, can be associated with many diseases (e.g. Friedreich's ataxia, cirrhosis of the liver and pancreas, cardiac and hepatic degeneration, cardiovascular disease, cataract, erythrocyte dysfunction, sudden infant death syndrome or Crohn's disease). On the other hand, excess of this element can cause many syndromes, like for example heart diseases, carcinomas, rash, redness, vomiting, diarrhea or pulmonary edema. The typical disease associated with excess of selenim is se-

lenosis with following syndromes: headache, loss of hair, oss of nails, skin rash, garlic odour on the breath, discoloration of teeth, numbness, paralysis and hemiplegia. Selenium may be intaked by digestive and respiratory system. Also, selenium chlorides may enter through the skin.

Determiantion of selenium using NAA Because selenium occurs in very low concentration (average 0.09 mg/kg in the earth crust), the neutron activation is very good method to determining this element amount in a sample and two types of NAA may be applied. First method is standard INAA with measurements of activity of long-lived ^{75}Se ($t_{1/2} = 120$ d) isotope from ^{74}Se (n, γ) ^{75}Se reaction. ^{75}Se undergoes electron capture and gamma rays with energy 265 keV are emited. In this case, total time of experiment is quite long and there is possibility of interference with ^{203}Hg. The alternate approach is cyclic neutron activation analysis using ^{76}Se (n, γ) ^{77m}Se reaction. The half-life of ^{77m}Se is 17.5 s and gamma rays energy is 162 keV. In CNAA there is a potential interference with ^{116m2}In, but indium rarely occurs in biological matrices. The advantages of CNAA are reduction of detection limit, better precision and accurancy and short total experiment time[6]. The sample preparation and measurement are standard and were described in section 2.

Results Results of determination Se in irradiated samples will be aviable after long and short irradiation. Obtained results will be published, and in case of any questions please contact with me via email adress tmrozek@o2.pl

6 acknowledgments

In this place, I would like to thank my supervisor, head of NAA section - Marina Vladimirovnna Frontasyeva and all members of Her team. I can recommend this laboratory as one of the best place to learn about applications of nuclear methods in life sciences.

[6]Zhang, H., et al. Ćyclic neutron activation analysis for determination of selenium in food samples using 77mSe."Journal of radioanalytical and nuclear chemistry 281.1 (2009): 23-26.