



**CENTRE FOR ENERGY RESEARCH** HUNGARIAN ACADEMY OF SCIENCES  
NUCLEAR ANALYSIS AND RADIOGRAPHY DEPARTMENT



# **LABORATORY EXERCISE FOR NEUTRON ACTIVATION ANALYSIS**

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# 1 Introduction to neutron activation analysis (NAA)

Instrumental neutron activation analysis (NAA) is a method for quantitative determination of chemical elements based on the conversion of stable nuclei in the sample to radioactive nuclei by nuclear reactions, followed by the quantitation of these reaction products via their gamma radiations. NAA utilizes the delayed gamma rays from the radioactive daughter nucleus (with short or long half-lives), observed after the irradiation. The selective measurement of the radiation gives quantitative and qualitative information about the produced radioactive atoms.

The NAA is especially capable of the determination of trace elements in  $\mu\text{g/g}$  concentration range or below (e.g. impurities in high-purity materials). The typical limits of detection are less than  $0.01 \mu\text{g}$  for 30-50 elements, depending on the nuclear properties of the elements of interest, the actual measurement conditions, the neutron flux, density and in some cases the matrix composition.

The fuel elements of the active zone in thermal reactors are surrounded by a moderator. During nuclear fission the generated neutrons, created in the fuel rods (the so-called fission neutrons) penetrate the moderator, collide elastically with its nuclei and therefore they slow down gradually. The kinetic energy of these slowed-down neutrons became into thermal equilibrium with the media, therefore they are called thermal neutrons. Their behaviour, in many ways, is similar to the diffusion of monoatomic gases. Neutrons at the irradiation sites of the research reactor have a continuous energy distribution while interacting with the sample. The neutron spectra of the thermal reactor spans over a wide energy range and usually divided into three categories (Figure 1.).

- thermal neutron flux (the energy of thermal neutrons is in equilibrium with the environment) they follow the Maxwell-Boltzmann distribution ( $E < 0.5 \text{ eV}$ )
- epithermal neutron flux ( $0.5 < E < 100 \text{ eV}$ )
- fission fast neutron flux ( $100 \text{ eV} < E < 20 \text{ MeV}$ )

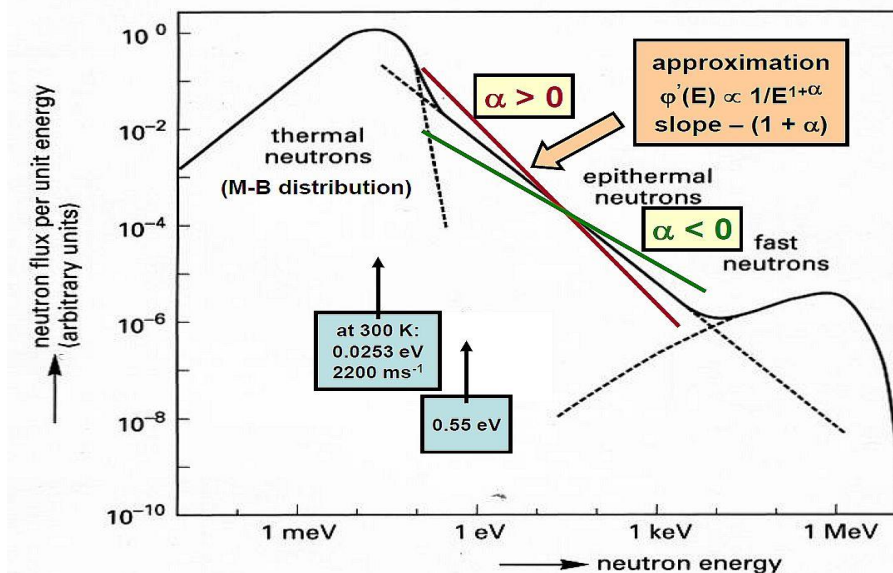


Figure 1. Typical distribution of neutron flux, in a thermal nuclear reactor.

The epithermal and the thermal neutrons usually induce  $(n, \gamma)$  nuclear reactions; the contribution of fission neutrons is negligible in the mentioned reactions. The breakdown of the neutron spectrum to thermal and epithermal ranges has a particular advantage, as in a well moderated reactor the shape of the energy spectra in these ranges always the same: a) The thermal neutron energies follow Maxwellian distribution. b) The epithermal neutron energy

range distribution can be approximated with an  $1/E$  function on log-log scale. The shape of the thermal/epithermal neutron spectra depends on the design and the power of the reactor, the layout of the active zone and the location of the irradiation site. Further advantage is that thermal neutrons can be filtered with cadmium shielding, so it is possible to activate the samples mainly with epithermal neutrons, and to calculate the epithermal activation component

The cross section of the  $(n,\gamma)$  reactions is very low in the fission reactions range, only the thermal and the epithermal ranges are important. However, threshold reactions induced by fast neutrons can also have analytical importance. They can be used for quantitative determination (e.g.  $^{58}\text{Ni} (n, p) ^{58}\text{Co}$ ), and on the other hand, if the resulting isotope of an interfering  $(n, x)$  reaction, where  $x$  particle can be  $p, \gamma, n$ , etc. is the same as the product of the  $(n, \gamma)$  reaction, this interference should be taken into account.

All irradiation channels can be characterized by the thermal and epithermal neutron flux (or their ratio instead, i.e. the  $f$  parameter), the epithermal flux shape factor ( $\alpha$ ), and perhaps with the neutron temperature.

## 2 Characteristics of NAA

- High sensitivity for minor and trace elements in a wide range of matrices
- Multi-elemental and mostly non-destructive determination
- Small sample amount is enough for analysis
- Significant matrix independence
- Bulk analysis
- External contamination does not disturb or can be eliminated
- Standardisation is relatively simple
- It can be considered as a reference method in metrology

The NAA is especially capable for trace element determination (e.g. impurities in high purity materials) in ppm and ppt concentration range. The limit of detection is less than 0.01  $\mu\text{g}$  for 60-70 elements, depending on the nuclear properties of the elements of interest, the measurement conditions, and the neutron flux density and in some cases the matrix composition.

Using one or two activation cycles and subsequent gamma spectrometry measurements often allows 30 to 40 elements to be determined in favourable matrices (multi-elemental or panoramic analysis). By this way, theoretically it is possible to measure about 2/3 of the chemical elements. The uncertainties of measurements are between 1-10%, depending on the sample composition and measurement conditions.

For NAA measurements a few milligrams of samples are sufficient. This allows that several samples can be packed together enabling the simultaneous irradiation of these samples under the same irradiation conditions. This feature is extremely important in comparative inter-laboratory studies.

An advantage of the instrumental approach over radiochemical NAA, is that only little sample preparation or treatment is needed (e.g., homogenisation, eliminating surface contamination or pre-concentration). In most cases non-destructive measurements of the induced radioactivity can be carried out selectively with high resolution HPGe-based gamma spectroscopic technique. Identification based on nuclear characteristics is of high reliability. The mentioned advantages together give the possibility to solve analytical challenges (i.e. rare earth elements analysis in geological samples) which hardly can be carried out by other means. The chemical state of the element does not influence the analytical results.

In cases of special needs, the selectivity and the precision can be increased using chemical processes (preconcentration, radiochemical separation, pre-irradiation separation).

It is very important part of INAA is the planning of the irradiation and measurement conditions. Unknown samples may contain unexpected, highly activated components. Therefore, before irradiation, its irradiation parameters/conditions must be planned. The weight of the sample prepared for irradiation should also be estimated, in order to reach suitable activity levels, since highly activated samples can be dangerous, and working over a given radiation dose rate is not permitted. Time parameters are chosen based on calculations and earlier experiences, regarding the temperature and irradiation conditions at the channel. The optimisation of irradiation, cooling and measuring times should be done together, regarding the number of radionuclides formed, which influence the selectivity of the measurement and the sensitivity of the analysis by increasing the background and spectral/irradiation interferences.

Like any other analytical method, classical NAA has its own methodological and technical limits. Because of their disadvantageous nuclear properties some elements cannot or can only be detected with poor sensitivity, e.g. H, B, C, N, O, P (light elements), or Pb, Bi and Tl. These elements (e.g. O, Pb) can be analysed well with special measurement set-ups or other activation techniques like PGAA (e.g., H and B). However, matrices composed of the above listed elements are very advantageous for measuring other elements.

### 3 Standardisation methods of NAA

In the case of instrumental neutron activation analysis the irradiation of the samples are not followed by chemical or physical separation, but the masses of the analytes are determined by mathematical interpretation of the (energy-dispersive) experimental data. There are several methods for quantitative data evaluation – calculating the concentration – in NAA multi element analysis, depending on the standardization conventions.

#### 3.1. Absolute standardisation

One of the experimentally simplest ways to obtain the mass of the element of interest with NAA is based on the following equation:

$$m = \frac{M}{N_A \Theta \varepsilon_p \gamma (\Phi_{th} \sigma_{th} + \Phi_e I_0)} \cdot \frac{N_p / t_m}{SDC}, \quad (1)$$

where  $m$  is the mass of the element,  $M$  is the atomic weight,  $N_p$  is the net peak area,  $N_A$  is the Avogadro number,  $\Theta$  is the isotopic abundance,  $\varepsilon_p$  is the full-energy peak detection efficiency,  $\gamma$  is the absolute intensity of the gamma-line with energy  $E_\gamma$ .  $\Phi_{th}$  is the thermal neutron flux,  $\Phi_e$  is the epithermal neutron flux,  $\sigma_{th}$  is the thermal neutron capture cross section (at 2200 m/s neutron velocity).  $I_0$  is the resonance integral (integral cross-section for epithermal neutrons),  $S = 1 - \exp(-\lambda t_i)$  is the saturation factor,  $D = \exp(-\lambda t_d)$  is the decay factor, and  $C = [1 - \exp(-\lambda t_m)] / [\lambda t_m]$  is the counting factor,  $\lambda$  is the decay constant:  $\lambda = \ln 2 / T_{1/2}$ , where  $T_{1/2}$  is the half-life,  $t_i$  is the irradiation time,  $t_m$  measuring time, and  $t_d$  is the cooling time.

High precision experimental determination of  $\varepsilon_p$ , the absolute detection efficiency is an important prerequisite to the accurate analysis. The  $M$ ,  $N_A$ ,  $\Theta$ ,  $\gamma$  and  $\lambda$  constants are usually known with adequate accuracy and precision (uncertainty < 1%), and are tabulated in open nuclear databases. The inaccuracies of the activation cross sections ( $\sigma$ ,  $I_0$ ) and some decay constants can be problematic. The uncertainty of experimental neutron field parameters' ( $\Phi_{th}$

and  $\Phi_e$ ) determination can be up to 5-20%. A disadvantage is that it can only be applied for the given measurement set-up.

### 3.2. Relative standardisation

In the relative standardization method, a chemical standard (index  $s$ ) with known mass ( $m_s$ ) of the element to be determined co-irradiated with the sample, and both of them are consequently measured in the same geometrical conditions with respect to the HPGe detector. The weight to be determined  $m_x$  is obtained as:

$$m_x = \frac{\left[ \frac{N_p/t_m}{D \cdot C} \right]_{sample}}{\left[ \frac{N_p/t_m}{D \cdot C} \right]_{standard}} \cdot m_s, \quad (2)$$

where

$S_x = S_s$ ,  $A_p = N_p/t_m$  is the count rate

$A_{sp} = \frac{N_p/t_m}{S \cdot D \cdot C \cdot m}$  is the specific count rate of the element.

For evaluation the same analytical line of the nuclei is applied. The advantage is that the characterization of the neutron field and use of nuclear constants ( $\Phi_{th}$ ,  $\Phi_{epi}$ ,  $\sigma$ ,  $I_0$ ,...  $\varepsilon_p$ ) are not necessary at all, as the method is based on direct comparison. Although 1% uncertainty can be achieved this way, it is very laborious for routine multi-element determinations.

### 3.3. Comparator standardisation

Only one carefully chosen comparator standard is co-irradiated with the sample, and all elements are analysed relative to one comparator. The experimental determination of the so-called  **$k_c$  factors** is necessary for all investigated elements. Mostly high purity Au-, Ir-, Co-, Zn-, Cu-, Ni- or Fe-foils are used, depending on activation time. The analysed samples are activated together with the comparators and the quantitative analysis can be done with the known  $k_c$  factors. The  $k_c$  factor is constant, if the measurement conditions are always the same (e.g. when setting up a new detector,  $k_c$  factors must be re-determined) and if the neutron spectrum and the thermal/epithermal neutron flux ratio in the reactor does not change.

### 3.4. The theory of $k_0$ -method

As the neutron channels of the Budapest Research Reactor at BNC are well thermalized and have a high neutron flux ( $\Phi_s > 10^{13}$  n/cm<sup>2</sup>s), we implemented the  **$k_0$ -method** that has been developed in a collaboration between the Budapest NAA Laboratory and the University of Gent (Simonits et al. 1976, 1982; De Corte 1987; De Corte Simonits 2003).

Assuming that the sample is point-like (i.e. the neutron attenuation and the gamma absorption are negligible), the epithermal flux distribution (1/E-law) is ideal, and the sample-detector distance is large ( $d=100$ -250 mm, so the real coincidence effect is negligible), the  **$k_0$ -factor** can be defined, as follows:

$$k_0 = \frac{M^* \cdot \theta \cdot \gamma \cdot \sigma_0}{M \cdot \theta^* \cdot \gamma^* \cdot \sigma_0^*} \quad (3)$$

Here the  $*$  refers to the comparator element. The  **$k_0$ -factor** is an experimentally determined composite nuclear constant which gives the ratio of the specific activities ( $A_{sp}$ ) of two elements during irradiation in pure thermal flux ( $\Phi_e = 0$ ).

$$A_{sp} = \frac{N_p / t_m}{S \cdot D \cdot C \cdot w}, \quad (4)$$

where  $w$  is the mass of the sample (g).

The  $k_0$  data are nowadays available in the literature, therefore it is enough to determine the thermal/epithermal flux ratio of the irradiation channel  $f = \Phi_{th} / \Phi_{epi}$  and the detector's efficiency-energy curve for data evaluation. This way the so-called literature  $k_0$ -factors can be converted to our given system using the typical  $f$  and  $\varepsilon_p$  parameters, as follows:

$$k_{anal} = \frac{A_{sp}}{A_{sp}^*} = k_0 \cdot \frac{f + Q_0}{f + Q_0^*} \cdot \frac{\varepsilon_p}{\varepsilon_p^*} \quad (5)$$

The reference  $k_0$ - factors are usually given for the Au comparator, because it only has one stable isotope and one characteristic gamma line, and the nuclear data of the (n, $\gamma$ ) nuclear reaction are well known. However, all isotopes can be used as comparators, if their  $k_{0,Au}(komp)$  factors are known exactly or determined earlier:

$$k_{0,komp}(x) = \frac{k_{0,Au}(x)}{k_{0,Au}(komp)}. \quad (6)$$

The concentration of the unknown element  $c_x$  in a sample of  $w$  weight can be calculated as follows:

$$c_x(ppm) = \frac{\left[ \frac{N_{p,x}}{t_m \cdot S \cdot D \cdot C \cdot w} \right]}{A_{sp,Au}} \cdot \frac{1}{k_{0,Au}(x)} \cdot \frac{f + Q_{0,Au}(\alpha)}{f + Q_{0,x}(\alpha)} \cdot \frac{\varepsilon_{p,Au}}{\varepsilon_{p,x}}, \quad (7)$$

where  $\alpha$  is the epithermal shape-factor and  $Q_0$  is the resonance integral-to-thermal cross-section ratio.

Any (n, $\gamma$ ) reaction can be applied for analysis, if the  $k_{0,Au}(x)$  factors,  $Q_0$  and the half-lives are accurately known. The  $f$  flux ratio (thermal/epithermal), the epithermal shape-factor ( $\alpha$ ) and the exact energy calibration of the detector's efficiency at the time of the activation has to be determined experimentally with great care. Additionally, corrections must be applied in order to take into account the effects of the non-ideal irradiation conditions.

There are several ways (e.g. Cd ratio method) to determine the  $f = \Phi_{th}/\Phi_e$  flux ratio. One of the simplest methods is to irradiate a thin Zr foil (so-called flux monitor) together with the samples. Zirconium has favourable features for using as a multi-isotopic flux monitor, because of its two isotopes can be characterized by very different  $Q_0$  values, and they are known to high precision:  $^{94}\text{Zr}(n,\gamma)^{95}\text{Zr}$   $Q_0=5.31$  and  $^{96}\text{Zr}(n,\gamma)^{97}\text{Zr}$   $Q_0=251.6$ . The measured gamma-lines have high energies (gamma-absorption is negligible), and are free of true coincidences. Measuring the radiation of the Zr foil and with the exactly known  $k_{0,Au}(^{95}\text{Zr}, ^{97}\text{Zr})$  values, the actual  $f$  flux ratio can be expressed as:

$$f = \frac{\frac{k_{0,Au(1)}}{k_{0,Au(2)}} \cdot \frac{\varepsilon_{p,1}}{\varepsilon_{p,2}} \cdot Q_{0,1}(\alpha) - \frac{A_{sp,1}}{A_{sp,2}} \cdot Q_{0,2}(\alpha)}{\frac{A_{sp,1}}{A_{sp,2}} \cdot \frac{k_{0,Au(1)}}{k_{0,Au(2)}} \cdot \frac{\varepsilon_{p,1}}{\varepsilon_{p,2}}}, \quad (8)$$

where  $^{(1)} ^{95}\text{Zr}$  (724.2+756.7 keV),  $^{(2)} ^{97}\text{Zr}$  (743.3 keV)

## 4 The role of the $\alpha$ parameter

The  $1/E$  distribution for the epithermal neutron spectrum is only valid under certain conditions. The  $1/E^{1+\alpha}$  function gives a better approximation to the real epithermal neutron flux, where  $\alpha$  is the **epithermal shape factor**. Corrections are developed in order to measure the bias from ideal case, as in most  $(n, \gamma)$  reactions there are more than 100 resonances.

**The calculation of  $I_0(\alpha)$  and  $Q_0(\alpha)$  is based on** (as  $I_0$  and  $Q_0 = \frac{I_0}{\sigma_{th}}$  are available in tables) the  $E_r$  effective resonance energy values, which were introduced at reaction rate calculations (Ryves, 1969).

$$Q_0(\alpha) = \frac{Q_0 - 0.429}{E_r^\alpha} + \frac{0.429}{(2\alpha + 1)(0.55)^\alpha} \quad (9)$$

The value of  $\alpha$  is generally zero or negative in light water moderated reactors, at the poorly thermalized channels close to the zone. In other types of reactors (e.g. graphite, heavy water moderated) the value of  $\alpha$  can be up to +0.2. In low-power reactors the parameters of irradiation channels do not vary for longer periods of time, but the ones with higher power (more intensive fuel-burn-up) they change more significantly because of the frequent core reconfigurations.

Three different methods are developed for simultaneous determination of the thermal/epithermal flux ratio and  $\alpha$ : irradiation only with Cd-cover, with and without Cd-cover and without Cd-cover. The latter, without cover version uses the Bare Triple Monitor method with  $^{94}\text{Zr}$ ,  $^{96}\text{Zr}$  and  $^{197}\text{Au}$  isotopes.

## 5 Analytical applications

- NAA is frequently used to certify the concentrations of elements in standard reference materials of environmental, biomedical and geological origin
- In the field of **nuclear energy production**, the corrosion products of structural materials in the primary coolant of nuclear power plants were determined.
- Adsorption-desorption processes on structural materials of nuclear power plants can be investigated using radiotracer technique. The extent of the adsorption of the metal ions of corrosion (Cr, Fe and Co) and some fission products (Cs, Ce, I) on the surfaces of structural materials (stainless steel and Zr1%Nb alloys) were studied.
- **In the field of environmental chemistry** NAA is suitable for analysing chemical properties of industrial aerosols.
- The associations between the **environmental hazards, nutrition related diseases** and essential micro and macro elements can also be investigated with this method.
- **Selective irradiation** has important role in instrumental activation analysis, which enables the determination of many elements with high precision and sensitivity within short turn-around time. Boron filter ( $\text{B}_4\text{C}$ ) has been constructed and used for epithermal neutron activation analysis of biological, geological and fiberglass samples. Using a boron shield the NAA method can be used to samples with unfavourable matrices (e.g. Na, Ca, Sc, P) and when the induced activities of major components are high.
- Monitoring water chemistry parameters is required for the safe operation of the research reactor. The activity concentrations of characteristic fission and corrosion products in the primary cooling water and the concentrations of different impurity

components in various water systems and in the fuel storage ponds of the Budapest Research Reactor (BRR) are measured.

- In the research field of nuclear waste treatment and disposal, the radionuclide  $^{135}\text{Cs}$ , which is one of the difficult to measure nuclides, was determined in nuclear waste samples. The method based on the selective separation of Cs and the detection of  $^{135}\text{Cs}$  by two independent measuring methods, i.e. NAA and ICP-MS.
- **In geological samples** rare earth elements are determined and meteorites can be studied as well.

## 6 NAA at the Budapest Research Reactor (BRR)

The Budapest Research Reactor is a light-water moderated and cooled tank-type reactor. The thermal power of the reactor is 10 MW, whereas the thermal neutron flux in the core can reach  $2.2 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$ . There is a possibility of short, and long term irradiation of samples for instrumental neutron activation measurements.

### 6.1. Short-term irradiation at the BRR with fast rabbit system

There are 40 vertical irradiation channels in the research reactor, and one of them is equipped with short time irradiation possibility directly from the laboratory. The rabbit system ensures that the irradiated sample goes from the reactor zone to the gamma spectrometer in the shortest time possible. With the present parameters of the research reactor (zone design, reactor power, neutron flux parameters: thermal, epithermal, fast) irradiations up to 5 minutes can be carried out while cooling the carrier capsule with  $\text{CO}_2$  gas stream.

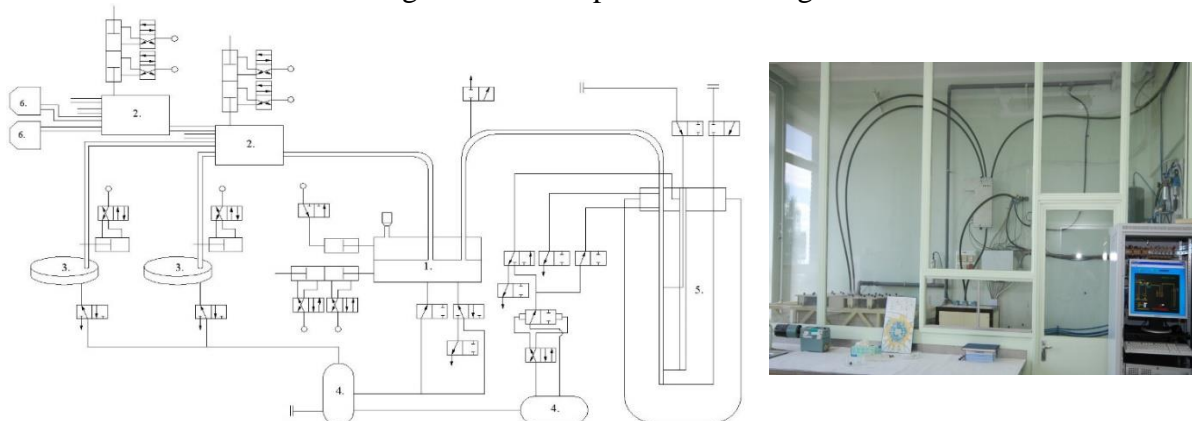


Figure 2. The block scheme and photo of the fast rabbit system at the BRR. 1. Sender/Receiver Station, 2. Router, 3. Delay Stacker, 4. Air tank, 5. Reactor vessel, 6. Drop Out Station.

Operation of the fast rabbit system:

- Few tens of mg of the samples are weighted into high purity polyethylene capsules or prepared in pellet form of 6 mm diameter using manual hydraulic press and Whatmann 41 filter paper for packing, and placed to the loading station in a small polyethylene (PE) capsule (8 mm x 5 mm), and in an inner and outer capsule (1.). In the same irradiation capsule, but separate holder an element comparator of known weight (e.g. Zr, Au, Cu) is co-activated.
- The sample from here gets to the irradiation channel of the reactor with compressed air.
- The arrival of the sample to the end position in the channel is detected by a sensor that activates the pre-set countdown counter for irradiation time.



- At the end of the irradiation compressed air brings back the capsule to the sample loading station (1.).
- From here, depending on its induced radioactivity the capsule goes either to one of the sample handling glove boxes (6) or one of the delay stacker for decay (3) using compressed air.

An irradiation sheet is electronically stored reporting irradiation conditions, person responsible for irradiation, sample identifier, sample weight, typical nuclides created in the sample, estimated activity, irradiation time, exact date and time of irradiation. Neutron flux parameters have been measured with the "Bare Triple-Monitor".

## 6.2. Long-term irradiation at the BRR

Long-term irradiation (typically 1–24 h) is done separately, in the No. 17 rotating, well-thermalized channel located in the Be reflector (thermal neutron flux density is  $1.86 \times 10^{13} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ ; Figure 3a). Samples, in dried and powdered form (50–200 mg), are sealed in high-purity quartz ampoules (Figure 3b). A set of 6–8 quartz ampoules are wrapped together using aluminium foils (Figure 3c), as well as monitor foils of Au, Zr or Ni. Samples are irradiated in hermetically closed Al carriers. After irradiation and a typical decay time of 3–4 days, the quartz vials are unpacked and surface cleaned. Each sample is counted for two or three times. First measurement takes place at about 4–5 days after irradiation (for 10–15 minutes), when the elements As, Br, Ca, K, La, Na, Sb, U can be determined. The second, optional measurement takes place 7–14 days later (for 1–2 h), if the detection limits are needed to be improved, i.e. during this period the  $^{24}\text{Na}$ ,  $^{42}\text{K}$  isotopes decay out. After a cooling period of 15–30 days (when the  $^{82}\text{Br}$ ,  $^{140}\text{La}$  isotope decayed out), the samples can be counted for a third time for 2–6 hours at appropriate distance, when typically Ba, Ce, Co, Cr, Cs, Eu, Fe, Rb, Sb, Sc, Ta, Tb, Yb, Zn, Zr elements are analysed.

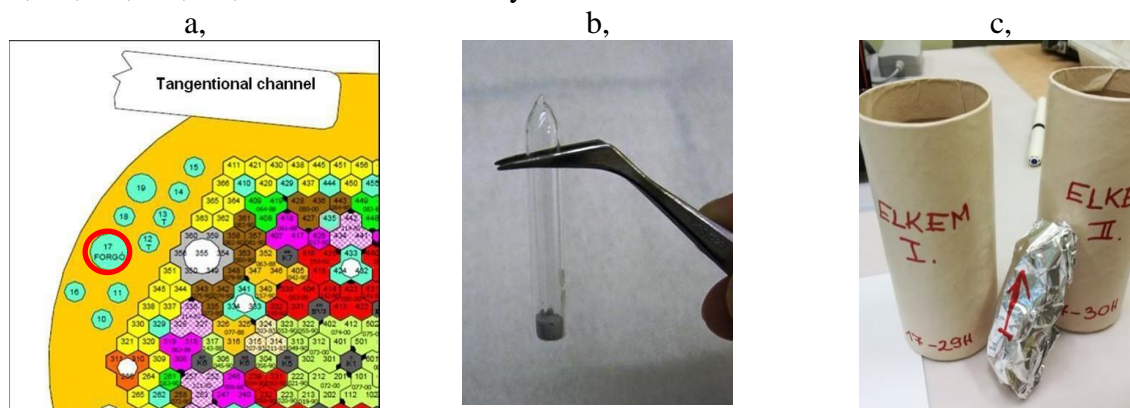


Figure 3. a, The N<sup>o</sup>. 17 rotating, well-thermalized channel in the Be reflector of the BRR, used for long-term irradiation. b, High purity quartz ampoules containing powdered rock samples. c, Set of 6–8 quartz ampoules are wrapped together using aluminium foils.

Protocol during long-term irradiation NAA:

- 50–150 mg of the powdered, well homogenised, and dried samples are sealed in a surface cleaned high purity quartz ampoules (6 cm long, 6 mm Ø, Heraeus Suprasil ®). A set of 6–8 quartz ampoules are wrapped together with monitor foils of Au, Zr or Ni/Fe ("Bare Triple-Monitor"). Samples are irradiated in hermetically closed aluminium container.
- The container containing the samples is manually placed in the 2nd position of the well thermalized, rotating vertical channel of the BRR.
- After the requested irradiation time, the container put out and moved to the hot cell, where the aluminium container is opened up.

- From here, after 3-4 days cooling time, the samples are carried up to the laboratory to be cleaned from alumina foils and surfaced cleaned with acid.

The irradiation parameters are recorded in report sheet containing person responsible for irradiation, exact irradiation time, start and finish, typical nuclides created in the sample, estimated and measured activity after irradiation. Neutron flux parameters have been measured with the "Bare Triple-Monitor".

## 7 Gamma-spectroscopic measurement

After short- and or long-term irradiation of the sample, the decay gamma measurements are following the same procedure. Few year ago the hardware and software of the NAA laboratory at BNC had been upgraded (Szentmiklósi et al 2016.). The gamma-rays emitted from the samples are counted in low-level counting chambers (to reduce the external background), with a carefully calibrated p-type Ortec HPGe detector, having an energy resolution of 1.75 keV and a relative efficiency of 55 %, in a 50-3300 keV energy range. The detector is connected to a dual-input ORTEC DSPEC 502 spectrometer, and operated by the ORTEC Maestro 7 software. The spectra are recorded with 2×16 k channel and zero-dead time (ZDT) option. The immediate result of a gamma spectroscopy measurement is the raw spectrum, in which full energy peaks appear corresponding to gamma photons of different energies. Channel numbers on the gamma spectra's horizontal axis can be calibrated in gamma energy (keV) based on known energy gamma lines of standard radioactive isotopes. Gamma spectrometers usually have very good linearity, which makes the so-called two-point calibration possible, in combination with the nonlinearity. The radioactive nuclei (chemical elements) can qualitatively be identified by their peak positions (energies) of the measured gamma peaks, while the quantity, i.e. the concentration of isotopes (elements) can be derived from their background corrected net peak areas.

The corrected and uncorrected halves of the spectra are stored in a single SPC file. For spectrum evaluation HyperLab 2013.1 software is used. For identification of radioactive isotopes and for calculation of the element concentrations, KayZero for Windows 3.06 program (De Corte et al. 2001) is applied, which is able to take into account the thermal-epithermal neutron flux ratio ( $f$ ), alpha ( $\alpha$ ), and  $F_c$  calculation factors. KayZero calculates concentrations using the  $k_0$ -standardization method, according to De Corte and Simonits (2003).

### 7.1. Calibration of the gamma spectrometer

The calibration of the gamma spectrometer is based on the determination of three fundamental parameters: *detection efficiency*, *channel-energy calibration with nonlinearity* and *the energy resolution*. For determining these parameters certified gamma-sources are used, whose energy and activity data are known to a high precision and its gamma-lines are distributed evenly in the measured energy range (50-3300 keV). The detection-efficiency is determined with the lines of  $^{241}\text{Am}$ ,  $^{133}\text{Ba}$ ,  $^{60}\text{Co}$ ,  $^{137}\text{Cs}$ ,  $^{152}\text{Eu}$ ,  $^{226}\text{Ra}$  sealed radioactive point sources and with additional radioisotopes produced in research reactor or accelerator, like  $^{51}\text{Cr}$ ,  $^{56}\text{Co}$ ,  $^{65}\text{Zn}$ ,  $^{198}\text{Au}$ ,  $^{110\text{m}}\text{Ag}$ ,  $^{75}\text{Se}$ . Calculations are carried out with the EFFICIENCY, NONLINEARITY and RESOLUTION ANALYSIS modules of HyperLab program.

#### *Detection efficiency*

One of the most important parameters of  $\gamma$ -detectors is the **absolute full-energy peak efficiency** ( $\varepsilon_p(E_\gamma)$ ). Its value gives the proportion how much a gamma-radiation with  $E_\gamma$  energy emitted by the source contributes to the corresponding measured full-energy peak in the spectrum. It can be described by a 6-8 degree polynomial on a log-log scale (Figure 4.). The

absolute full-energy peak efficiency of a given detector depends on the source-detector distance, the shape and extent of the source and its  $\gamma$ -ray energy.

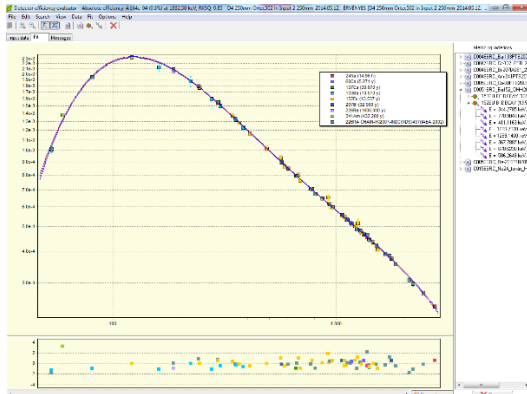


Figure 4. The absolute efficiency curve of the NAL NAA D4 measuring system for point-source geometry (2014)

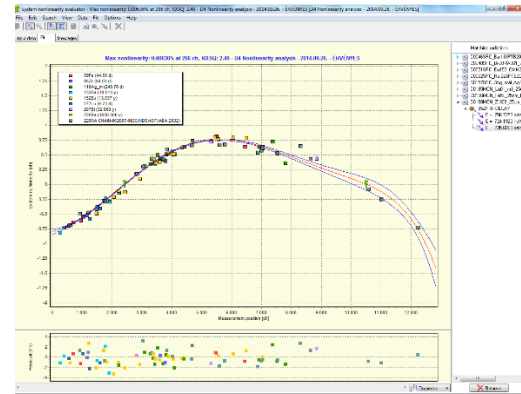


Figure 5. The nonlinearity of the NAL NAA D4 measuring system (2014)

### Nonlinearity

The partial processes of the detection and the signal processing are fundamentally linear in nature, thus the channel number of the spectrum is proportional with the energy. In practice this is not completely true. The linearity of the energy determination can be improved further during the spectrum evaluation by correcting it with its experimentally determined small deviation from linearity, which is caused by the electronics and hence are constant over a period for a given set-up. The systematic, thousandths-level deviation is the so-called **differential nonlinearity**. The nonlinearity calibration is determined from the same set of data as the efficiency, when peaks of well-known energies are measured, and the differences of positions and literature data are fitted with a polynomial. Energies measured in the analysis are then corrected with this function (Figure 5.).

### Energy resolution

In gamma-spectroscopy the **energy resolution of the detector** has a key role. Its characterised by the *FWHM*: (*full width at half maximum*), which is for the  $^{60}\text{Co}$  peak at 1332.5 keV about 1.8 keV (Figure 6.). The spectrometer's resolution is determined by the electronics and the detector together, and can be given as the square sum of the 3 terms as a function of energy. These are the contributions from the electronics, the statistical fluctuation of charge production and the effects of the imperfect charge collection of the detector, respectively.

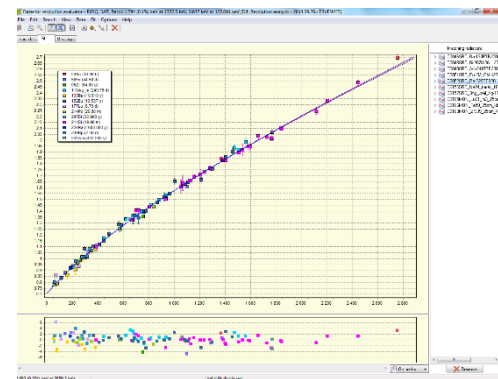


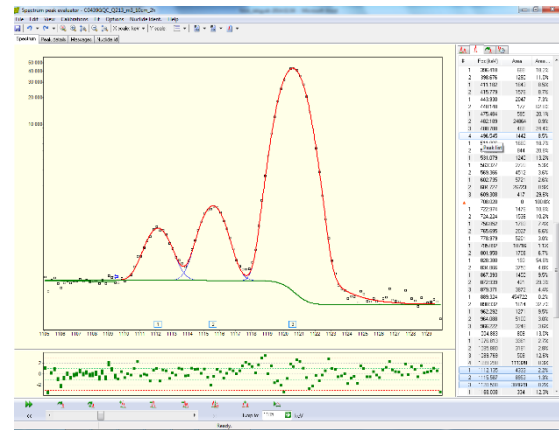
Figure 6. The energy resolution of the NAL NAA D4 measuring system (2014)

## 7.2. Evaluating gamma spectra, calculating the concentration

The analytical information of the spectra is in the full energy peak positions and their area. The goal of the spectrum evaluation is the most precise determination of these parameter couples for every peak.

For spectrum evaluation the *HyperLab* program is used. First of all a low and a high energy intense peak of a known nuclide is chosen, to calibrate the energy axis and peak-widths. After the program runs through the spectrum, identifies the peaks significantly above the background, determines the optimal limits of the regions and fits the model function in each region. From these, peak positions, peak areas and their uncertainties can be determined. After the **automatic fit**, results shall be revised regarding to the  $\chi^2$  values and the residuum. Where it is necessary, peaks should be added or removed, region boundaries or the model functions have to be modified in order to make the fit better.

Figure 7 shows a fit of a region from a geological sample by the *HyperLab 2013* program. The step function is clearly visible under the asymmetric peaks with the so-called ‘tail’ on the right hand side. The fitting is finished after the **nonlinearity and efficiency** is loaded. The former is transformed to zero value at the energy calibration base points. The last task is the creation of a **peak list (PTF)** file, which contains peak positions, their energies, half-width values, area, their uncertainties and the  $\chi^2$  values of the fits in a tabulated form.



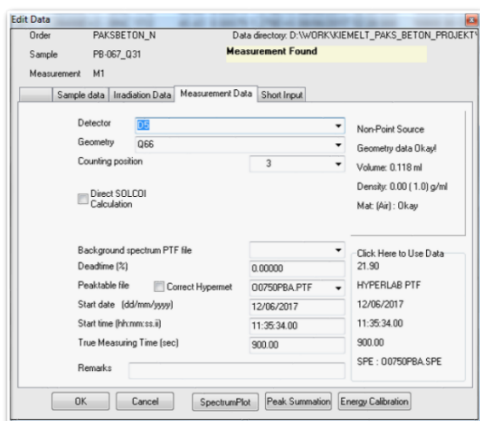


Figure 8. KayZero for Windows 3.06 reading in the .ptf files of peak lists.

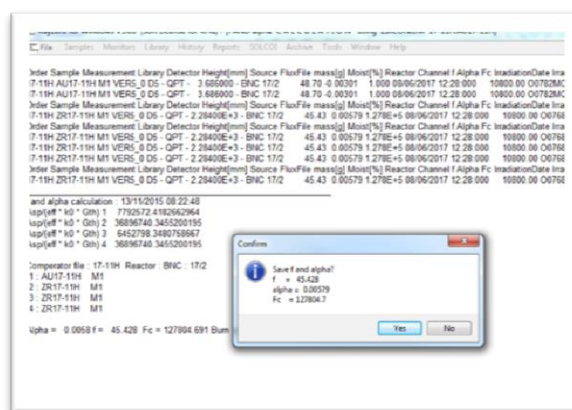


Figure 9. KayZero for Windows 3.06 program calculating  $f$  and  $\alpha$  parameters with the Bare-Triple Monitor Method.

## 8 The laboratory exercise

During the laboratory exercise, geological standards and reference materials are prepared by the participants into high-purity quartz ampules for long-term irradiation the sample preparation room, using METTLER TOLEDO XPE micro balance. A Bare-Triple monitor set is also prepared by them, and packed together for co-irradiation. One sample will be also prepared for short-term irradiation and irradiation will be demonstrated in the rabbit-system laboratory. Unpacking of long-term irradiated sample pack can be experienced behind lead shielding by the participants (for safety reasons on inactive samples). Previously irradiated geological standard and monitors will be measured in the one of the low-level counting chambers of the NAA laboratory. The collected spectra will be fitted with HyperLab 2013 software, and afterwards concentrations will be calculated with the Kayzero for Windows program. The results can be compared to the certificate of the measured sample.

### *Workflow of the laboratory exercise:*

1. Sample preparation: weighting the powdered standard geological samples into quartz ampules and also making pastilles out of them.
2. Visiting the fast rabbit system lab, and theoretically irradiating the prepared sample. In the same lab wrapping out (inactive) quartz ampules from aluminium foil and surface cleaning of quartz.
3. Previously activated samples are placed in a low-level counting chamber for recording gamma spectrum.
4. Fitting the collected spectra with HyperLab program. Energy calibration, and generating of the peak list file.
5. Elemental concentrations are to be calculated with the Kayzero for Windows program. Loading in the sample parameters and peak list file, and recalculated with previously collected spectra from the same sample.
6. Comparison of results with reference data.

## 9 Literature

De Corte F, van Sluijs R, Simonits A et al.: Installation and calibration of Kayzero-assisted NAA in three Central European countries via a Copernicus project Appl. Radiat Isot 55, 347–354. (2001)

- De Corte F., Simonits A., Recommended nuclear data for use in the  $k_0$  standardization of neutron activation analysis. Atomic Data and Nuclear Data Tables 85, 47 (2003).
- De Corte F.: The  $k_0$ -standardization method. Habilitation thesis, Rijksuniversiteit Gent, Gent 1987. [http://www.kayzero.com/k0naa/k0naaorg/Links\\_files/The%20ko-Standardization%20Method.pdf](http://www.kayzero.com/k0naa/k0naaorg/Links_files/The%20ko-Standardization%20Method.pdf)
- Ryves, T. B., 1969, Metrologia 5, 119 (1969).
- Simonits, A., De Corte, F., Hoste, J., Zirconium as a multi-isotopic flux ratio monitor and a single comparator in reactor-neutron activation analysis. J. Radioanal. Chem. 31, 467 (1976).
- Simonits, A., De Corte, F., Moens, L., Hoste, J., Status and recent developments in the  $k_0$ -standardization method. J. Radioanal. Chem. 72, 209 (1982).
- Szentmiklósi, L., Párkányi, D., & Sziklai-László, I. (2016). Upgrade of the Budapest neutron activation analysis laboratory. Journal of Radioanalytical and Nuclear Chemistry, 309(1), 91–99.