NEUTRON ACTIVATION ANALYSIS

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Neutron Activation Analysis (NAA) is an experimental technique used to detect and quantify trace elements in various samples. It is renowned for its high accuracy and broad applicability across a wide range of elements. NAA is particularly valuable in fields such as environmental science, geology and geochemistry, materials science, and forensics. The method is based on the capture of neutrons by stable nuclei. This nuclear reaction produces radioactive isotopes that emit characteristic prompt and delayed gamma rays. These emissions are then detected using gamma-ray spectrometers. By analysing the energy of the emitted gamma rays, the identity of the parent nuclide can be determined. The number of gamma rays detected at a certain energy provides information about the concentration of the nuclide in the sample. A particularly powerful variant of this technique is the k_0-standardization method, in which both the sample and a reference monitor are irradiated simultaneously, enabling accurate calibration and comparative analysis. This method allows for the precise quantification of up to 144 radionuclides.

NEVTRONSKA AKTIVACIJSKA ANALIZA

Nevtronska aktivacijska analiza (NAA) je eksperimentalna tehnika, ki se uporablja za odkrivanje in kvantifikacijo elementov v sledovih v različnih vzorcih. Znana je po svoji visoki natančnosti in široki uporabnosti za širok spekter elementov. NAA je še posebej uporabna na področjih, kot so okoljske znanosti, geologija in geokemija, znanost o materialih in forenzika. Metoda temelji na zajetju nevtronov s strani stabilnih jeder. Prek te reakcije nastanejo radioaktivni izotopi, ki oddajajo značilne takojšnje in zapoznele gama žarke. Ti žarki se nato zaznajo z gama spektrometri. Z analizo energije izsevanih gama žarkov je mogoče določiti identiteto matičnega nuklida. Število gama žarkov, zaznanih pri določeni energiji, podaja informacije o koncentraciji nuklida v vzorcu. Posebna različica te tehnike je metoda k_0-standardizacije, pri kateri se vzorec in referenčni monitor obsevata hkrati, kar omogoča natančno kalibracijo in primerjalno analizo. Ta metoda omogoča natančno kvantifikacijo do 144 radionuklidov.

1. Introduction

Neutron Activation Analysis (NAA) is a nuclear analytical technique that takes advantage of the characteristics of nuclear reactions to simultaneously determine the concentrations of specific elements or nuclides in an unknown sample. By analysing the reaction products – either the radiation emitted almost immediately after neutron capture by Prompt Gamma Activation Analysis (PGAA) or the radioactivity induced as the products decay by Neutron Activation Analysis (NAA) – we can identify and quantify the elements present in the sample. In this article, we will focus on the latter. The main characteristics of Neutron Activation Analysis are the ability to detect around 70% of the elements in the periodic table, the possibility of non-destructive analysis, and high accuracy compared to other trace element analysis techniques for multi-element analysis of macroscopic samples (detection limit: 10^{-12} g of element per 1 g of sample).

Due to the inherent sensitivity and high accuracy, Neutron Activation Analysis has extensively been applied to environmental sciences, nutritional studies, health-related studies, geological and geochemical sciences, material sciences, archaeological studies, forensic studies and nuclear data measurements. In addition to Neutron Activation Analysis, there also exist other types of nuclear activation analysis: Charged Particle Activation Analysis (CPAA), which uses energetic charged particles such as protons produced by a cyclotron, and Photon Activation Analysis (PAA), which uses bremsstrahlung photons generated by electrons, accelerated in a linear accelerator or by a cyclotron. However, neutron activation, using high fluxes of mostly thermal neutrons produced by a thermal research reactor, provides the best sensitivities of detection for most elements and is the most developed and widely used form of nuclear activation analysis [1, 2].

2. Nuclear reactions

Nuclear reactions are mainly divided into two types: Direct reactions and reactions via an intermediate nucleus. Direct reactions occur immediately after the projectile enters the nucleus. They are typically denoted as $B + a \rightarrow Y + b$, or, in abbreviated notation, $B(a, b)Y$, where B is the target nucleus, a is the projectile, Y is the resulting nucleus, and b is the emitted particle. Lowercase letters are conventionally used for the projectile and emitted particle, which are usually much lighter than the target and resulting nuclei. Direct reactions occur on a timescale comparable to the projectile's flight time through the nucleus, typically $\sim 10^{-22} - 10^{-21}$ s. Reactions via an intermediate nucleus (denoted by X^*) take place mainly in two steps ($B + a \rightarrow X^* \rightarrow Y + b$) and last as long as the lifetime of the intermediate nucleus, typically $\sim 10^{-16} - 10^{-14}$ s. The intermediate nucleus has a precisely defined energy level. If the energy levels of the nucleus are far apart compared to the energy of the projectile, then the cross section for the reaction is known only in very narrow regions of energy (resonances). In this article, we are going to look only at reactions in which the capture of a neutron in a target B produces an intermediate nucleus X^* in an excited state, which, by emitting prompt gamma photons, passes to the ground state of the same nucleus X; this nucleus then decays further (with a typical half-life of a few seconds to several years) by emitting β particles to an excited intermediate nucleus Y^*, which passes to the ground state Y by emitting one or more delayed photons. Let's have a closer look at this. The target nucleus is denoted as ${}^{\mathrm{A}}_{\mathrm{Z}}\mathrm{B}$ and the intermediate nucleus as ${}^{\mathrm{A+1}}_{\mathrm{Z}}\mathrm{X}^*$. By emitting prompt gamma photons, the nucleus passes to an unstable nucleus denoted as ${}^{\mathrm{A+1}}_{\mathrm{Z}}\mathrm{X}$, which decays mainly through β decay to an excited intermediate nucleus ${}^{\mathrm{A+1}}_{\mathrm{Z+1}}\mathrm{Y}^*$. This nucleus passes to the ground state by releasing delayed gamma photons [1]. As an example of this type of reaction, let us have a look at a neutron capture process in gold (with only one stable isotope ${}^{197}\mathrm{Au}$), as shown in Figure 1.

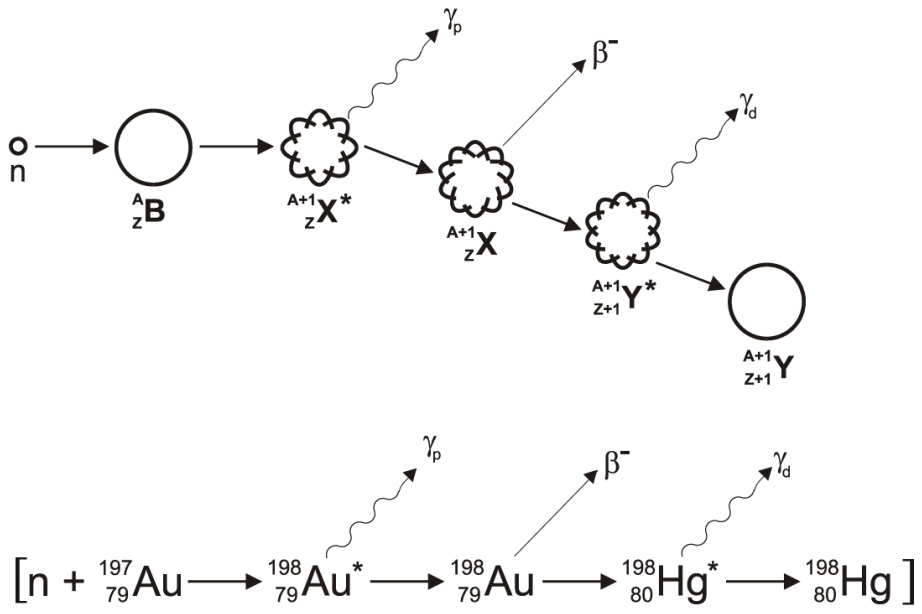

Figure 1. Schematics of a nuclear reaction via an intermediate nucleus. Adapted from [1].

Prompt gamma photons are the primary focus in Prompt Gamma Activation Analysis, while delayed gamma photons are key in Neutron Activation Analysis. These photons, prompt or delayed, have characteristic energy and intensity which are useful for identifying the nucleus and, furthermore, the target nucleus in the sample.

2.1 Reaction rate

In a homogeneous isotropic neutron flux with neutron speeds between v and $v + \mathrm{d}v$ the following holds:

$$R'(v)\mathrm{d}v = N\sigma(v)\phi'(v)\mathrm{d}v. \tag{1}$$

The reaction rate[1] $R'(v)$ (unit $[\mathrm{cm}^{-1}]$) for the (n,γ) reaction can be defined, where the notation indicates that the projectile is a neutron and the emitted particle is a gamma photon. Here, N is the number of irradiated nuclei in the target, while $\sigma(v)$ is the probability of the (n,γ) reaction occurring for neutrons with velocity v. The quantity $\sigma(v)$ is also referred to as the reaction cross section and is given in units of cm^2, with the practical unit being the barn, where $1\ \mathrm{b} = 10^{-24}\ \mathrm{cm}^2$. Finally, $\phi'(v)$ denotes the neutron flux per unit velocity interval at neutron velocity v (unit $[\mathrm{cm}^{-3}]$). Neutron flux can be described as:

$$\phi'(v) = v \cdot n'(v), \tag{2}$$

where $n'(v)$ is neutron abundance per unit of speed interval (unit $[\mathrm{cm}^{-4}\mathrm{s}]$). Kinetic energy of a neutron can be denoted as:

$$E = \frac{m_\mathrm{n} v^2}{2}, \tag{3}$$

where m_n is rest mass of a neutron and v its velocity[2]. For the energy interval $E + \mathrm{d}E$, the equation for the reaction rate can be written as:

$$R(E)\mathrm{d}E = N\sigma(E)\phi(E)\mathrm{d}E. \tag{4}$$

Here, N represents the number of irradiated nuclei in the target, $\sigma(E)$ is the cross section for the (n,γ) reaction occurring with neutrons of energy E, and $\phi(E)$ denotes the neutron flux per unit energy interval at neutron energy E (units $[\mathrm{cm}^{-2}\mathrm{s}^{-1}\ \mathrm{eV}^{-1}]$). The cross section is a property of the material, so: $\sigma(v) = \sigma(E)$. Both equations for neutron flux are describing the same neutron field, therefore $\phi'(v)\mathrm{d}v = \phi(E)\mathrm{d}E$. Using the kinetic energy equation and the relationship between the neutron flux distributions in the energy and velocity scales, the following expression can be derived:

$$\phi(E) = \phi'(v)\frac{\mathrm{d}v}{\mathrm{d}E} = \frac{1}{m_\mathrm{n} v}\phi'(v). \tag{5}$$

Finally, the reaction rate is given by:

$$R'(v)\mathrm{d}v = R(E)\mathrm{d}E. \tag{6}$$

Neutrons in a nuclear reactor cover a wide spectrum of energies. The overall reaction rate R (unit $[\mathrm{s}^{-1}]$) is obtained by integrating over all energies of the spectrum at which neutrons appear:

$$R = N\int_0^\infty \sigma(E)\phi(E)\mathrm{d}E. \tag{7}$$

Specific reaction rate per nuclide in target can be defined as:

$$R_X = \frac{R}{N} = \int_0^\infty \sigma(E)\phi(E)\mathrm{d}E. \tag{8}$$

Cross section values can fluctuate significantly due to resonances, and the neutron flux distribution strongly depends on the irradiation location inside the nuclear reactor. By introducing some generally valid characteristics and so-called formalisms or conventions in describing the reaction rate, actual integrations can be avoided [1, 2].

[1] The apostrophe $'$ does not indicate derivation; it simply marks velocity-dependent quantities to distinguish them from energy-dependent quantities.

[2] We are dealing mostly with thermal neutrons that are in thermal equilibrium with the environment (their speeds around 2200 m/s). For epithermal or even for fast neutrons with approx. 2 MeV kinetic energy, relativistic effects are still negligible; therefore, the classical approximation is used.

2.2 Cross section function

For most nuclides relevant in Neutron Activation Analysis at the neutron energy range below 1.5 eV (thermal neutrons have energies approx. 0.025 eV), the cross section dependence $\sigma(v) \propto 1/v$ or $\sigma(E) \propto \sqrt{1/E}$ applies. Reference velocity v_0 or energy E_0 can be chosen. Then the dependence of the cross section on neutron velocity or energy can be written as:

$$\sigma = \sigma_0 \frac{v_0}{v} = \sigma_0 \sqrt{E_0/E}. \tag{9}$$

At higher energies, some resonances emerge. A resonance is an energy interval with very high probability of neutron capture. In Figure 2, a schematic representation of the cross section function for the reaction (n, γ), as a function of neutron energy is shown.

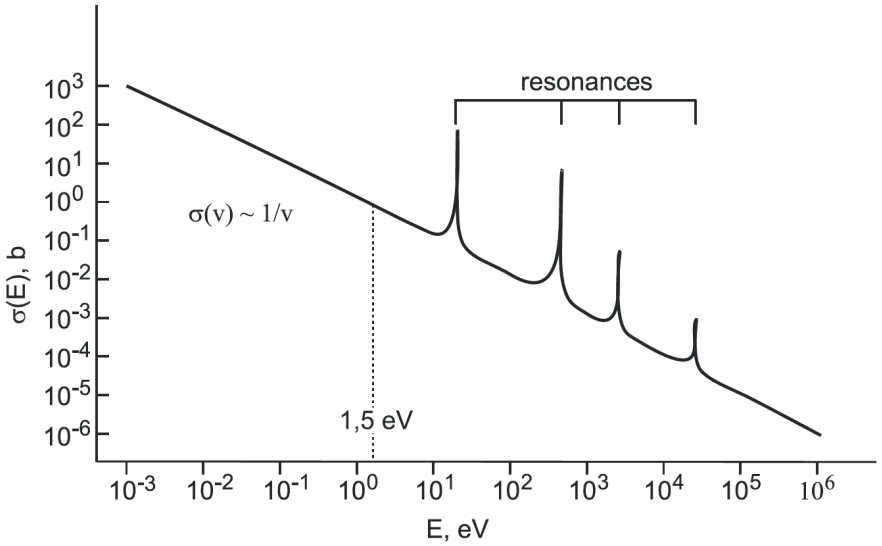

Figure 2. Cross section as a function of neutron energy. Adapted from [1].

2.3 Neutron flux function

Neutron flux distribution for a typical research reactor can be characterized in three major regions:

1. **The fission region, or fast-neutron region,** has a maximum (most probable energy) at ~ 0.7 MeV. Due to the relatively small cross section for (n, γ) reactions around this energy, the contribution of fast neutrons to reaction rate is in most cases negligible.

2. Neutron flux in **the epithermal region** can theoretically be described as $\phi(E) \propto 1/E$. This assumption is valid only for an infinitely large and homogeneous moderator with a homogeneous distribution of neutron sources and negligible absorption of neutrons in the moderator... In real conditions, a deviation is expected from ideal conditions, so the above expression must be replaced with the appropriate dependence $\phi(E) \propto 1/E^{1+\alpha}$, where α, in the range $-1 < \alpha < 1$, is a correction factor that can be determined using nuclides with widely different resonance energies, which are highly sensitive to variations in the neutron spectrum shape.

3. **Thermal neutrons, or the slow neutron region,** are in thermal equilibrium with the moderator. Therefore, their distribution can be described as a Maxwell-Boltzmann distribution. At standard conditions, $T = 293$ K, the maximum of this distribution is located at $E_0 = 0.025$ eV or $v_0 = 2200$ m/s. At these conditions, the thermal cross section for the (n, γ) reaction can be defined as $\sigma_0 = \sigma(v_0)$.

In Figure 3, a neutron-flux spectrum is presented with the three main regions indicated.

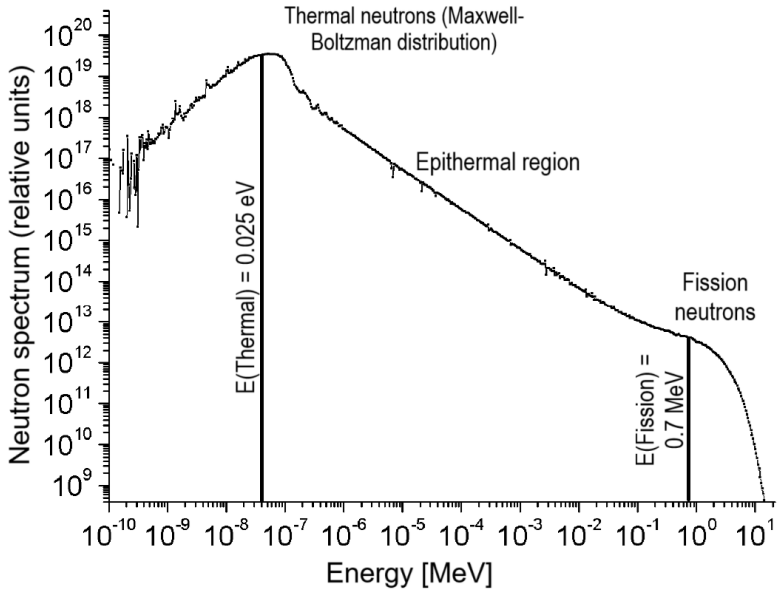

Figure 3. Neutron spectrum in TRIGA Mark II research reactor fuel at Jožef Stefan Institute. Adapted from [3].

3. Høgdahl convention and Cadmium ratio

As mentioned earlier, calculating the reaction rate analytically can be quite challenging. To address this, certain approximations are often introduced. One of these approximations is called the Høgdahl convention. Cadmium, known for its high absorption of thermal neutrons, is commonly used as a neutron filter during the irradiation process. Samples are frequently irradiated while wrapped in a cadmium foil, ensuring that only epithermal neutrons can contribute to the reaction rate in the sample. Figure 4 shows the total cross section of cadmium (including contributions from scattering, capture, fission, etc.) as well as the transmissivity of a 1 mm thick cadmium foil, both as functions of neutron energy [2].

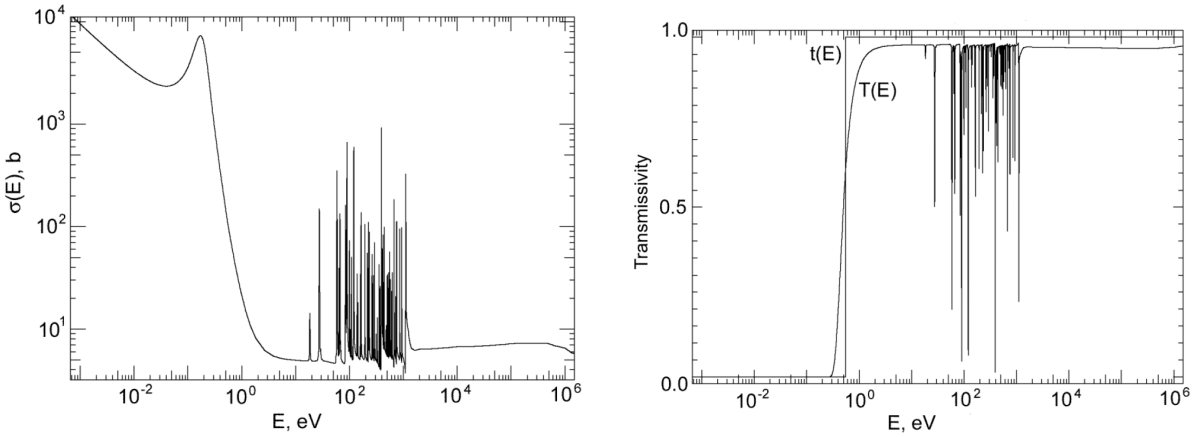

Figure 4. Total cross section for cadmium on left and transmissivity for 1 mm thick cadmium foil on right. Adapted from [1].

The function $T(E)$ represents the actual transmissivity, while $t(E)$ is its step-function approximation. The point at which $t(E)$ abruptly rises to 1 is known as the *cadmium edge*, and its corresponding energy is $E_{\mathrm{Cd}} = 0.55\,\mathrm{eV}$ [2]. Following the Høgdahl convention, the reaction rate can

now be split into two different integrals, one for thermal neutrons (below cadmium edge) and one for epithermal neutrons (above cadmium edge):

$$R_X = \int_0^{v_{\mathrm{Cd}}} \sigma(v)\phi'(v)\mathrm{d}v + \int_{E_{\mathrm{Cd}}}^{E_2} \sigma(E)\phi(E)\mathrm{d}E = R_{X,\mathrm{th}} + R_{X,\mathrm{e}}. \tag{10}$$

Here E_2 is set at 2 MeV, because the share of fast neutrons with energies over 2 MeV is orders of magnitude lower than the share of thermal or epithermal neutrons. Combining Equation (9) for the thermal cross sections and Equation (2) for the neutron flux with the thermal part of the integral for the reaction rate $R_{X,\mathrm{th}}$, gives:

$$R_{X,\mathrm{th}} = \int_0^{v_{\mathrm{Cd}}} \sigma_0 \frac{v_0}{v} \cdot v \cdot n'(v)\mathrm{d}v = \sigma_0 v_0 \int_0^{v_{\mathrm{Cd}}} n'(v)\mathrm{d}v = \sigma_0 v_0 n_{\mathrm{th}}, \tag{11}$$

where n_{th} is an atomic density of thermal neutrons (unit [cm^{-3}]). This equation shows that for cross sections that follow the $1/v$ law, reaction rate in the thermal region (below the cadmium edge) is independent of the neutron flux spectrum.

Cross sections of many elements have some resonances in epithermal regions. These resonances are contributing to the reaction rate, so they need to be included in calculations. At this point, resonance integral $I_0(\alpha)$ (units [cm^2]) for $1/E^{1+\alpha}$ spectrum dependency in epithermal region is introduced as:

$$I_0(\alpha) = \int_{E_{\mathrm{Cd}}}^{E_2} \frac{\sigma(E)}{E^{1+\alpha}}\mathrm{d}E. \tag{12}$$

For $\alpha = 0$, the resonance integral follows the theoretical ($\phi_{\mathrm{e}} \propto 1/E$) function between the cadmium edge and the fast neutrons, and it can be denoted simply as $I_0 = I_0(\alpha = 0)$. The relation between I_0 and $I_0(\alpha)$ can be written as:

$$I_0(\alpha) = (I_0 - 0.429\sigma_0) \cdot (\overline{E}_{\mathrm{r}})^{-\alpha} + \sigma_0 \cdot C_\alpha, \tag{13}$$

introducing two parameters as:

$$C_\alpha = \frac{0.429}{(2\alpha + 1)(E_{\mathrm{Cd}})^\alpha}, \qquad 2\sqrt{\frac{E_0}{E_{\mathrm{Cd}}}} \approx 0.429, \tag{14}$$

where $E_0 = 0.025$ eV, $E_{\mathrm{Cd}} = 0.55$ eV and $\overline{E}_{\mathrm{r}}$ is the *effective resonance energy* defined as the energy of a single hypothetical resonance that produces the same reaction rate as all the resonances combined.

The reaction rate for the thermal and epithermal parts can now be written as:

$$R_X = \sigma_0 v_0 n_{\mathrm{th}} + \phi_{\mathrm{e}} I_0(\alpha). \tag{15}$$

3.1 Cadmium ratio

Finally, a cadmium ratio can be defined as the ratio of the reaction rate in the full spectrum to the reaction rate in the epithermal spectrum:

$$R_{\mathrm{Cd}} = \frac{R_X}{R_{X,\mathrm{e}}} = \frac{\sigma_0 v_0 n_{\mathrm{th}} + \phi_{\mathrm{e}} I_0(\alpha)}{\phi_{\mathrm{e}} I_0(\alpha)} = 1 + \left(\frac{f}{Q_0(\alpha)}\right). \tag{16}$$

Here $f = \frac{\phi_{\mathrm{th}}}{\phi_{\mathrm{e}}}$ is the ratio of the thermal flux to the epithermal flux for the irradiation channel and $Q_0(\alpha) = \frac{I_0(\alpha)}{\sigma_0}$ is the ratio of the resonance integral to the thermal cross section. Similarly to Equation (13), $Q_0 = Q_0(\alpha = 0)$, therefore $Q_0 = \frac{I_0}{\sigma_0}$ and:

$$Q_0(\alpha) = (Q_0 - 0.429) \cdot (\overline{E}_{\mathrm{r}})^{-\alpha} + C_\alpha. \tag{17}$$

Values of Q_0 are tabulated in the literature (experimentally determined or theoretically calculated). In practical work tabulated data are replaced with those corrected for the appropriate deviation of the dependence of $\phi(E)$ on the parameter α.

4. Measurements, relative method and k_0 method

In the case of Neutron Activation Analysis, the irradiation takes place in a nearly isotropic field of neutrons in an irradiation channel inside a research reactor. After the irradiation, the sample is transferred to a low background counting facility, where the gamma radiation is collected by a spectrometer (usually High-purity Germanium; HPGe). The electronic pulses from the gamma spectrometer are sorted by their amplitudes into channels of a multichannel analyser (MCA). Figure 5 shows the change in relative activity as a function of time throughout the entire NAA process. During the irradiation time, the activity exponentially approaches saturation. After the end of the irradiation it starts to drop exponentially, but since the activity also decreases exponentially during the measurement time, fewer photons are detected compared to the case of constant activity, and this is corrected by the integral of the exponential function over the measurement time (red area under the curve). The saturation, the decay, and the counting correction factors are introduced as:

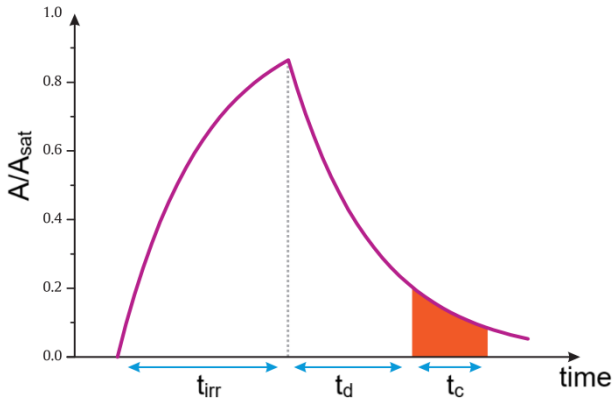

Figure 5. Schematic illustration of the irradiation time, decay time, and counting time. Adapted from [4].

$$S = 1 - e^{-\lambda t_{\mathrm{irr}}}, \qquad D = e^{-\lambda t_{\mathrm{d}}}, \qquad C = \frac{1 - e^{-\lambda t_{\mathrm{c}}}}{\lambda t_{\mathrm{c}}}, \tag{18}$$

where t_{irr}, t_{d} and t_{c} are the irradiation, the decay (cooling), and the counting times, respectively, and λ is the decay constant of the specified nuclide of interest [5]. The decay constant can also be denoted as $\lambda = \frac{\ln(2)}{t_{1/2}}$, where $t_{1/2}$ is the nuclide half-life.

4.1 Relative method

There are mainly two types of Neutron Activation Analysis. The first, simpler, is called the *relative method* because it uses standards. Suppose that along with the original sample a similar sample with a known concentration of the element of interest is being co-irradiated, which we take as a standard. Consider a sample of mass m in which the concentration of the element of interest is c. The element may be composed of several stable isotope types i; their abundances are given by θ_i. During the irradiation each one of the isotope types may be transformed into different radionuclides. Let us consider reactions on only one isotope with abundance θ. The radionuclide created from this isotope during irradiation emits gamma rays at a certain energy with probability (intensity) P_γ. After a decay time t_{d} following the irradiation, the count rate of these particular gamma rays is measured for a counting time t_{c}. The detection efficiency for the particular gamma rays is ϵ. The number of registered gamma rays N_p divided by the counting time t_{c} is given by the following expression:

$$\frac{N_p}{t_{\mathrm{c}}} = \frac{m}{M} R_X \theta c S D C P_\gamma \epsilon, \tag{19}$$

where R_X is the reaction rate per nucleus and M [g/mol] is the molar mass of the element of interest, S, D, and C are the saturation, the decay, and the counting factors. A similar equation holds for the standard as well:

$$\frac{N_{p,\mathrm{s}}}{t_{\mathrm{c,s}}} = \frac{m_{\mathrm{s}}}{M} R_X \theta c_{\mathrm{s}} S D_{\mathrm{s}} C_{\mathrm{s}} P_\gamma \epsilon, \tag{20}$$

where the index s stands for the standard. Note that the mass of the standard, the concentration of the element of interest in the standard, the decay and counting times for the standard are different from those for the sample, but the irradiation time remains the same. The detection efficiency ϵ remains the same (because the same energy of gamma photons is measured), but only if both samples are measured using the same detector and in the same position (distance) from the detector (to preserve the same solid angle). If we now divide equations for the sample and the standard, we obtain the following expression:

$$\frac{N_p/t_\mathrm{c}}{N_{p,\mathrm{s}}/t_{\mathrm{c,s}}} = \frac{mc}{m_\mathrm{s}c_\mathrm{s}}\frac{D}{D_\mathrm{s}}\frac{C}{C_\mathrm{s}}. \tag{21}$$

Furthermore, if the equation above is rearranged, concentrations of the element of interest can be denoted:

$$c = c_\mathrm{s}\frac{N_p/t_\mathrm{c}}{N_{p,\mathrm{s}}/t_{\mathrm{c,s}}}\frac{m_\mathrm{s}}{m}\frac{D_\mathrm{s}}{D}\frac{C_\mathrm{s}}{C}. \tag{22}$$

We have obtained a relation between the concentrations of the element of interest in the sample and the standard, which does not involve quantities pertaining to the neutron spectrum (i.e. the reaction rate R_X) or the detection system (i.e. the detection efficiency). Moreover, the isotopic abundance of the particular isotope on which the observed nuclear reaction takes place and the gamma ray emission probability cancel out. This is highly advantageous, since every one of these quantities contributes to the overall uncertainty in the measurement [4].

4.2 k_0 method

The main disadvantage of the relative method is that, in addition to the sample, a standard for each nuclide of interest in the sample must be irradiated, which also creates the problem of having to know in advance which elements we are looking for in the sample and providing suitable standards. Here the k_0 standardization comes into play. The k_0 method is a highly successful standardization method developed in 1975 by Simonits et al. and assumes the validity of the Høgdahl convention. This method is regarded as a „quasi-absolute“ technique, usually using the composite nuclear constants k_0 and Q_0. These constants are generally applicable and relatively independent of the irradiation and counting devices, and minor corrections can be taken into account by introducing additional parameters. After the careful calibration of the irradiation and counting facilities, the k_0 method makes the use of elemental standards unnecessary. Masses of the components are determined relative to the flux monitor that is irradiated with the sample because the thermal flux may change from irradiation to irradiation, but the flux monitor can be the same for all nuclides of interest. Thus, multi-element analysis could be performed with the same amount of work as was previously needed for single-element analysis [1].

A composite nuclear constant, the k_0 factor, was introduced in the standardization of NAA as:

$$k_{0,\mathrm{c}}(\mathrm{x}) = \frac{M_\mathrm{c}\theta_\mathrm{x}P_{\gamma,\mathrm{x}}\sigma_{0,\mathrm{x}}}{M_\mathrm{x}\theta_\mathrm{c}P_{\gamma,\mathrm{c}}\sigma_{0,\mathrm{c}}}, \tag{23}$$

where x denotes the investigated element, and c the comparator. From the definition of the k_0 factor, we see that it is independent of the irradiation and measurement conditions. For a selected nuclide, the k_0 factor can be calculated from data given in the literature or determined experimentally. For the latter, the k_0 factor can be expressed in another way:

$$k_{0,\mathrm{c}}(\mathrm{x}) = \frac{\left(\frac{N_p}{m\epsilon SDCt_\mathrm{c}}\right)_\mathrm{x} - \left(\frac{N_p}{m\epsilon SDCt_\mathrm{c}}\right)_{\mathrm{Cd},x}}{\left(\frac{N_p}{m\epsilon SDCt_\mathrm{c}}\right)_\mathrm{c} - \left(\frac{N_p}{m\epsilon SDCt_\mathrm{c}}\right)_{\mathrm{Cd,c}}}. \tag{24}$$

This expression does not contain physical constants, but experimental data only: peak areas, counting times, other time-related quantities, counting efficiency and sample masses. The terms with the Cd subscript subtract the epithermal contribution from the specific activity measured without a cadmium cover; thus the k_0 factor is the ratio of specific activities calculated for thermal activation. The k_0 value can thus be thought of as the number of gamma rays emitted per unit mass of the element, activated in the thermal neutron flux, relative to a similar quantity of the flux monitor. In Section 3.1 it was mentioned that Q_0 values can also be determined experimentally. Here an example is shown of determining the Q_0 value using the cadmium ratio method, discussed in Equation (16):

$$Q_0 = \frac{f}{\left(\frac{N_p}{mSDCt_c}\right) / \left(\frac{N_p}{mSDCt_c}\right)_{\mathrm{Cd}} - 1}. \tag{25}$$

Here f is predetermined during the calibration of the irradiation channel, and in the denominator the ratio of the specific activities measured without and with a cadmium cover can be seen. Since the same gamma line is measured in both cases, because of the same nuclide of interest, the efficiency cancels from the ratio [5].

The k_0 factor can also be determined without the use of cadmium foils, once the irradiation channel is well calibrated, and if the Q_0 value is also known:

$$k_{0,\mathrm{c}}(\mathrm{x}) = \frac{\left(\frac{N_p}{m\epsilon SDCt_c}\right)_{\mathrm{x}}}{\left(\frac{N_p}{m\epsilon SDCt_c}\right)_{\mathrm{c}}} \frac{1 + \frac{Q_{0,\mathrm{c}}}{f}}{1 + \frac{Q_{0,\mathrm{x}}}{f}}. \tag{26}$$

The most common comparator is gold (^{197}Au (n,γ) ^{198}Au), it has been widely used as a flux monitor, because it has only one stable isotope ($\theta = 1$) and its nuclear data [6, 7] are known with high accuracy:

$$\sigma_0 = 98.65 \pm 0.09 \text{ b } (\pm 0.09\%), \qquad I_0 = 1550 \pm 28 \text{ b } (\pm 1.8\%), \qquad \theta = 1. \tag{27}$$

From these data, the Q_0 value for gold can be calculated: $Q_0 = 15.71 \pm 0.28$ ($\pm 1.8\%$). The definition of the k_0 factor is of course not limited to gold; it can be extended to any provided comparator, if $k_{0,\mathrm{Au}}(\mathrm{c})$ is known, by a simple transformation:

$$k_{0,\mathrm{c}}(\mathrm{x}) = \frac{k_{0,\mathrm{Au}}(\mathrm{x})}{k_{0,\mathrm{Au}}(\mathrm{c})}. \tag{28}$$

In this convention, $k_{0,\mathrm{Au}}(\mathrm{Au}) = 1$.

When k_0 NAA is performed, the irradiation and counting facilities must first be calibrated, which means determining ϕ_{th}, f, α and ϵ. The masses of the elements in the sample can then be determined using this equation:

$$m_{\mathrm{x}} = \frac{\left(\frac{N_p}{\epsilon SDCt_c}\right)_{\mathrm{x}}}{\left(\frac{N_p}{m\epsilon SDCt_c}\right)_{\mathrm{c}}} \frac{1}{k_{0,\mathrm{c}}(\mathrm{x})} \frac{1 + \frac{Q_{0,\mathrm{c}}(\alpha)}{f}}{1 + \frac{Q_{0,\mathrm{x}}(\alpha)}{f}}, \tag{29}$$

where the index x refers to the unknown nuclide and c to the comparator.

4.2.1 Neutron self-shielding

For a complete description of the reaction (n,γ) in the Høgdahl convention, we must introduce additional correction factors to describe the actual neutron flux rate in the irradiated sample [1].

G_{th} is *thermal neutron self-shielding*. This is the factor of reduction of the neutron flux due to absorption of thermal neutrons within the sample. It depends on the density of the nuclei and the cross sections. It is calculated by transport calculations from the cross sections, taking into account the shape of the sample (foil, sphere, cylinder, etc.).

G_{e} is *epithermal neutron self-shielding* and depends on the density of nuclei and the resonance parameters of the nuclides present in the sample. Its calculation is more complicated due to the high resonance cross sections that are characteristic of individual nuclides and the possible overlaps of resonances of different nuclides.

The thermal and epithermal self-shielding factors, G_{th} and G_{e}, are equal to unity under ideal conditions and are very close to unity for most activation reactions in most samples, such as biological materials, and can therefore be ignored. But the self-shielding effect is important for samples containing large amounts of nuclides with high neutron capture cross sections and for thick samples. Historically, the calculation of G_{th} and G_{e} was extremely difficult, and it was recommended to dilute the samples in a fluid that does not significantly interact with neutrons to avoid self-shielding or to use the same geometry for both the sample and the comparator if solid samples are used. With the self-shielding correction factors, the above equation becomes:

$$m_{\mathrm{x}} = \frac{\left(\frac{N_p}{\epsilon S D C t_{\mathrm{c}}}\right)_{\mathrm{x}}}{\left(\frac{N_p}{m \epsilon S D C t_{\mathrm{c}}}\right)_{\mathrm{c}}} \frac{1}{k_{0,\mathrm{c}}(\mathrm{x})} \frac{G_{\mathrm{th,c}} f + G_{\mathrm{e,c}} Q_{0,\mathrm{c}}(\alpha)}{G_{\mathrm{th,x}} f + G_{\mathrm{e,x}} Q_{0,\mathrm{x}}(\alpha)}. \tag{30}$$

The cross sections of certain nuclides (like ^{176}Lu and ^{151}Eu) do not strictly follow the $1/v$ law due to low-energy resonances. These nuclides will be activated somewhat differently, depending on the temperatures of the irradiation channels. In some cases, these reactions are replaced by others that follow the $1/v$ law (e.g. ^{174}Yb (n,γ) ^{175}Yb) or correction factors are determined for the irradiation channel experimentally [1, 5].

4.2.2 A practical example of a comparison of results of k_0-INAA

Jožef Stefan Institute (JSI) was invited to participate in the certification process for the determination of mass fractions for major and trace elements in three coal materials: ERM®-EF411 (hard coal), ERM®-EF412 (brown coal) and ERM®-EF413 (furnace coke) organized by the European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, Belgium [8]. The JSI used the k_0-INAA[3] technique for the studies of coal samples and reported mass fractions for As, Co, Cr, Mn, Sb, Se, V, Zn, Ca, Mg, Na, K and Cl. An example of a comparison of the results of the k_0-INAA with certified values is presented below for ERM®-EF412 (Figures 6 and 7). For evaluation of the results, the E_{n}-score [9] was used, defined as follows:

$$E_{\mathrm{n}} = \frac{x_{\mathrm{lab}} - x_{\mathrm{ref}}}{\sqrt{(U_{\mathrm{lab}})^2 + (U_{\mathrm{ref}})^2}}, \tag{31}$$

where:

- x_{ref} - certified value given by IRMM,
- U_{ref} - expanded uncertainty of certified value x_{ref} with a coverage factor $k = 2$ (the 95 % confidence interval),
- x_{lab} - reported laboratory value,

[3] INAA — Instrumental Neutron Activation Analysis, when NAA is conducted directly on irradiated samples, in comparison to RNAA — Radiochemical Neutron Activation Analysis, where irradiated samples are subjected to chemical separation to remove interfering species or to concentrate the radioisotope of interest.

- U_{lab} - expanded uncertainty of reported laboratory value x_{lab} with a coverage factor $k = 2$.

A criterion for satisfactory laboratory results is $|E_{\mathrm{n}}| < 1$.

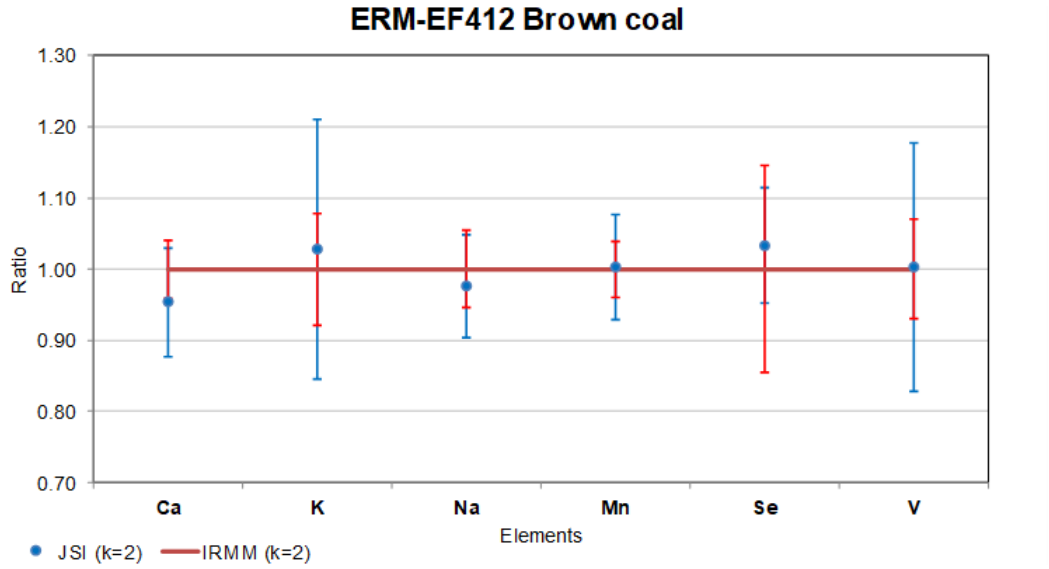

Figure 6. Ratio of results of the k_0-INAA and certified value of ERM®-EF412 (brown coal). Adapted from [10].

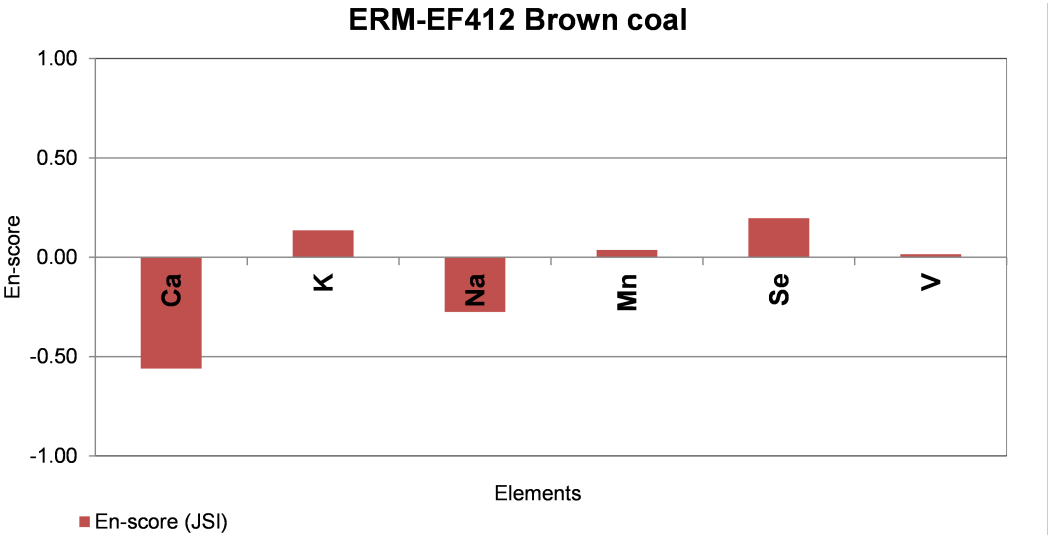

Figure 7. Evaluation of results of the k_0-INAA and certified value of ERM®-EF412 using E_n-score. Adapted from [10].

5. Conclusions

Neutron Activation Analysis is a useful experimental technique for very precise determinations of element concentrations in unknown samples. The physical processes of neutron capture, cross sections, irradiation, reaction rates, neutron fluxes and detection of gamma rays have been studied. It is especially worth highlighting the standardization method k_0, which has proved highly successful for standardizing Neutron Activation Analysis. The k_0 method has been introduced at many NAA laboratories worldwide, providing highly reliable analytical results. Today, in the so-called k_0 nuclear database, there are data for 144 radionuclides, from which we can determine the concentrations of 68 elements in an unknown sample.

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