Nuclear reactions and physical models for neutron activation analysis

Andrej Trkov · Vladimir Radulović

Abstract Neutron activation analysis, especially in its k_0 standardization is fairly robust down to the level of accuracy of a few percent, but further improvement is riddled with difficulties, i.e. multiple physical effects having opposite influences and introducing bias and uncertainty in the measured results. It is the aim of this paper to give a comprehensive review of the physical models in k_0-NAA, by providing exact definitions of the physical quantities, detailing the procedures used for the determination of the physical constants and by discussing the approximations and sources of uncertainty therein. Furthermore, indications are given on how accurately known k_0-NAA constants can be of value for other applications, namely the measurement and validation of nuclear cross sections.

Keywords Neutron activation analysis · k_0 standardisation · Physical models · Nuclear constants

Introduction

Due to its selectivity and sensitivity, neutron activation analysis (NAA) occupies an important place among the various analytical methods. It has proven to be a powerful non-destructive analytical technique for concentrations at or below the µg/g range. Up to 60 elements can be determined, performing two irradiations and several gamma-spectrum measurements after different decay periods [1]. The main fields of NAA application are analytical chemistry, geology, biology and the life and environmental science. Its accuracy, the virtual absence of matrix effects and the completely different physical basis when compared to other analytical techniques, make it particularly suitable for the certification of candidate reference materials (RMs), providing e.g. the bulk of the literature data on the standard RMs of the National Institute of Standards and Technology [2] and reference materials of the International Atomic Energy Agency.

The k_0 standardisation method of NAA (k_0-NAA), a concept launched in 1975 [3], can be interpreted as an absolute standardisation method. It relies on k_0 and Q_0 factors and a few other parameters, which are composite physical constants that can be derived from basic nuclear data. In practice they are usually determined by direct measurements, partly because equivalent constants derived from the basic data are often discrepant. The purpose of this paper is to:

- define the reaction rate equations as used in k_0-NAA and their relation to the exact definitions from the basic nuclear data,
- identify sources of uncertainties and approximations and their propagation to calculated reaction rates.

The overall objective is to give a detailed description of the process of neutron activation from the basic physics. This will improve the understanding of the definitions of the nuclear constants used in k_0-NAA and lead eventually to the improvement in these nuclear constants, as well as the basic nuclear data, where accurately measured composite constants for k_0-NAA can provide additional constraints for the

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basic nuclear data evaluation process. A better understanding of the physics of neutron activation will also be of benefit to users of the relative and single-comparator methods of NAA because they are often confronted with questions of neutron self-shielding, variations of reaction rates with neutron temperature and changing neutron spectra.

Definitions

Specific activities

When a material is irradiated in a neutron field, some nuclei of the material may capture neutrons to form excited nuclei, which transition promptly to the ground state (or metastable isomeric states) by emitting gamma radiation. The capture product nuclei are often radioactive. Decay by beta particle emission produces nuclei in an excited state, which decay into the ground state (or a metastable isomeric state), again by emitting gamma radiation. Gamma radiation associated with the radioactive decay of a nucleus is actually the radiation of its decay product transitioning to the ground state. Different variants of activation analysis as an analytical technique differ in the radiation that is being measured. Usually these are either prompt gamma rays emitted by the excited capture product or the delayed gamma rays emitted by the excited decay product nuclei.

If irradiations are performed in a neutron field with a significant fraction of high energy neutrons, it is possible that some threshold reactions on other nuclei present in the sample produce the same product nucleus as obtained by capture in the measured nucleus. Furthermore, if fissile material is present in the sample, such material may yield on fission the same nuclei as the capture product nuclei. These are interference reactions and must be taken into account. During the irradiation some of the capture products decay and some may themselves interact with neutrons to form a different nucleus and are lost for the purpose of the measurement. At high neutron flux levels the target nuclei may become depleted, which also affects the production of the capture-product nuclei. The differential equation governing the rate of change of the concentration of the nuclei of interest N_c is given by:

$$\frac{dN_c}{dt} = \phi N_m \sigma_m \gamma_{m,c} + \sum_h \phi N_h \sigma_h \gamma_{h,c} + \lambda_p N_p - \phi N_c \sigma_c$$
$$- \lambda_c N_c \quad (1)$$

where ϕ is the neutron flux, σ are the cross sections, N the nuclei number densities in the sample, λ the decay constants and γ the branching ratios or the fission product yields. The terms are as follows:

dN_c/dt	rate of change of the decaying nucleus c, the activity of which is measured,
$\phi N_m \sigma_m \gamma_{m,c}$	production rate of the decaying nucleus c; this is the reaction rate of nuclide m that is investigated, producing product c, which on decay produces characteristic radiation that is measured; $\gamma_{m,c}$ is the branching ratio (in case of the decay radiation of an isomer). By definition, $\phi N_m \sigma_m \gamma_{m,c}$ is the reaction rate A_m

$$A_m = \phi N_m \sigma_m \gamma_{m,c}. \quad (2)$$

$\phi N_h \sigma_h \gamma_{h,c}$	is the production rate of the decaying nucleus c from (threshold) reactions in admixed constituents h in the sample; $\gamma_{h,c}$ is the branching ratio (in the case of isomer production) or the fission yield (if σ_h is the fission cross section of an admixed fissile constituent),
$\lambda_p N_p$	production of the decaying nucleus c from precursor nucleus p by decay,
$-\phi N_c \sigma_c$	removal of the decaying nucleus c by capture or other reactions,
$-\lambda_c N_c$	removal of the nucleus c by decay.

An equation similar to the above can be written for each type of nucleus (denoted by subscripts c, m, h, p), forming a system of coupled first order linear differential equations that can be solved numerically, or analytically, with some approximations.

The last term in the right-hand side of Eq. (1) is the removal term due to radioactive decay at any time, while the first term on the right-hand side gives the reaction rate for nuclide production. In a "long" irradiation (neglecting all other terms), the nuclide concentration reaches equilibrium and the derivative on the left-hand side is zero. The rate of production of nuclei c then equals the removal rate. For this reason the term $\lambda N_c(t_{irr} \to \infty)$ is sometimes called the specific saturation activity, which is equal to the reaction rate A_m.

Neglecting the second and third term on the right-hand side of Eq. (1) that correspond to contributions of admixed constituents of the sample, the equation is recognised as the Leibnitz equation, which can be solved analytically. Integrating the analytical solution of Eq. (1) over the irradiation time t_{irr}, we obtain the expression for the concentration of nuclide c at the end of irradiation:

$$N_c(t_{irr}) = \frac{N_m^0 \sigma_m \phi \gamma_{m,c} e^{-\sigma_m \phi t_{irr}}}{\lambda_c + (\sigma_c - \sigma_m)\phi} \left[1 - e^{-(\lambda_c + (\sigma_c - \sigma_m)\phi)t_{irr}} \right] \quad (3)$$

If in Equation (1) we also neglect the rate of change of the target nucleus due to capture ($N_m = N_m^0$) and the rate of removal of the capture product due to capture ($\sigma_c = 0$), the commonly used equation is obtained:

$$N_c(t_{irr}) = \frac{N_m^0 \sigma_m \phi \gamma_{m,c}}{\lambda_c} \left[1 - e^{-\lambda_c t_{irr}} \right] \qquad (4)$$

After irradiation the concentration of nuclide c changes due to radioactive decay:

$$N_c(t_{irr} + t_{cool}) = N_c(t_{irr}) e^{-\lambda_c t_{cool}} \qquad (5)$$

The photon emission rate is equal to the product of the decay rate $\lambda_c N_c(t)$ and the gamma-emission probability $P_{\gamma,c}$. If t_{cool} is the cooling time and t_m is the measurement time, the average characteristic γ-photon emission rate R_c over the time period from t_{cool} to $t_{cool} + t_m$ is obtained by integrating Eq. (5):

$$
\begin{aligned}
R_c &= \frac{\lambda_c P_{\gamma,c}}{t_m} \int_{t_{cool}}^{t_{cool}+t_m} N_c(t) dt = \frac{\lambda_c P_{\gamma,c} N_c(t_{irr})}{t_m} \int_{t_{cool}}^{t_{cool}+t_m} e^{-\lambda_c t} dt \\
&= \frac{\lambda_c P_{\gamma,c} N_c(t_{irr})}{t_m} \frac{e^{-\lambda_c t_{cool}}}{\lambda_c} \left[1 - e^{-\lambda_c t_m} \right]
\end{aligned}
$$

$$(6)$$

Substituting $N_c(t_{irr})$ from Eq. (4) we get:

$$R_c = N_m^0 \sigma_m \phi \gamma_{m,c} P_{\gamma,c} \left[1 - e^{-\lambda_c t_{irr}} \right] e^{-\lambda_c t_{cool}} \left[\frac{1 - e^{-\lambda_c t_m}}{\lambda_c t_m} \right]. \qquad (7)$$

In principle the more accurate expression for $N_c(t_{irr})$ [Eq. (3)] could be used in deriving Eq. (7), in practice however, difficulties arise with the capture cross sections of the radioactive nuclei σ_c, which are generally unavailable in the present activation databases, but could become significant in specific cases of long irradiations under high flux conditions. The correction due to the burnup of the investigated nuclei m during the irradiation can generally be neglected, since in routine applications, even at low concentrations, the number of atoms m in the samples is very large compared to the number of transmuted nuclei during the irradiation.

We recognise the term $N_m^0 \sigma_m \phi \gamma_{m,c}$ in Eq. (7) as the reaction rate A_m in Eq. (2). The characteristic γ-photon emission rate R_c is thus related to the reaction rate A_m of the measured nuclide given by Eq. (2), which is implicit in the term $N_c(t_{irr})$. The gamma photon emission rates are determined from the measured characteristic photon peak areas, after taking into account the detection efficiency and photon coincidences. The subject of detection efficiency is however beyond the scope of the present discussion. The remainder of this paper is devoted to the topic of reaction rate calculation and to associated nuclear constants.

Reaction rates

The reaction rate A of particles travelling through a material is parametrised by the reaction cross section $\sigma(v)$, which is a property of the material and the neutron spectrum $\varphi(v)$, which is related to the density of the particles travelling through the material $n(v)$ and their speed v:

$$\varphi(v) = v n(v). \qquad (8)$$

Expressed in terms of the kinetic energy E of the incident particles, which is related to the speed v by the relation $E = (1/2) m v^2$ (where m is the particle mass), the reaction rate is:

$$A = K \int_0^\infty \sigma(E) \varphi(E) dE; \quad \varphi(1\,\text{eV}) = 1. \qquad (9)$$

The normalisation of $\varphi(E)$ is quite arbitrary and is chosen for convenience. The constant K ensures that the integral of $\varphi(E)$ over the entire energy range results in the total neutron flux:

$$K \int_0^\infty \varphi(E) dE = \phi. \qquad (10)$$

In terms of neutron speed the equivalent expression for the reaction rate can be written as:

$$A = \int_0^\infty \sigma(v) v n(v) dv. \qquad (11)$$

The integral can be split into the thermal part up to energy E_{Cd} (corresponding to the neutron speed v_{Cd}) and the epithermal part:

$$A = K \left[\int_0^{E_{Cd}} \sigma(E) \varphi(E) dE + \int_{E_{Cd}}^\infty \sigma(E) \varphi(E) dE \right]. \qquad (12)$$

We denote the neutron spectrum in the range up to E_{Cd} as the thermal spectrum component: $\varphi_{th}(E) = \varphi(E), E < E_{Cd}$, and the neutron spectrum above E_{Cd} as the epithermal spectrum component: $\varphi_{epi}(E) = \varphi(E), E > E_{Cd}$. The epithermal spectrum component can be further decomposed into the resonance part $\varphi_r(E)$ and the suitably normalised fast (fission) spectrum contribution $\varphi_h(E)$ for convenience:

$$\varphi_{epi}(E) = \varphi_r(E) + h \varphi_h(E); \quad E > E_{Cd} \qquad (13)$$

Precise modelling of the fission spectrum contribution does not have a significant influence on calculated reaction rates in well-thermalised spectra; it might improve the modelling of reaction rates in irradiation facilities with a strong epithermal neutron spectrum component, but it is crucial for threshold reactions. The reaction rate equation becomes:

$$
\begin{aligned}
A = K \Bigg[&\int_0^{E_{Cd}} \sigma(E) \varphi_{th}(E) dE + \int_{E_{Cd}}^\infty \sigma(E) \varphi_r(E) dE \\
&+ h \int_{E_{Cd}}^\infty \sigma(E) \varphi_h(E) dE \Bigg].
\end{aligned}
\qquad (14)
$$

The above expressions are exact; the problem is that neither the cross sections nor the neutron spectrum are known

accurately enough due to the strong dependence of the parameters on neutron energy. For example, to represent the capture cross section of ^{238}U to within 0.1 % tolerance, several 100,000 data points are needed. Such detailed representation is necessary to ensure proper account of the Doppler broadening effect due to temperature and for the estimation of the self-shielding effects.

Without loss of generality, the integral Eq. (14) can be cast into the expression commonly used in k_0-NAA by a suitable definition of constants:

$$A = \phi_{th}\sigma_0 g G_{th} + \phi_{epi}(IG_{epi} + Jh)$$
$$= \phi_{th}\sigma_0\left[gG_{th} + \frac{1}{f}(QG_{epi} + Hh)\right], \tag{15}$$

where the symbols have the following meaning: ϕ_{th} is the thermal flux, defined as $K\sqrt{\pi}/2\int_0^{E_{Cd}}\varphi(E)dE$; ϕ_{epi} is the epithermal flux scaling factor K, equal to the flux at 1 eV [1]; f is the ratio between the thermal and the epithermal flux, equal to $\sqrt{\pi}/2\int_0^{E_{Cd}}\varphi(E)dE$ due to our choice of epithermal spectrum normalisation to 1 at 1 eV; σ_0 is the reaction cross section at a neutron speed of 2,200 m/s; g is the generalized Westcott g-factor, which measures the deviation of the thermal cross section from $1/v$ behaviour; I is the effective resonance integral; J is the effective fission spectrum integral; Q is the ratio between the resonance integral, and the 2,200 m/s cross section, I/σ_0; H is the ratio between the fission integral and the 2,200 m/s cross section J/σ_0; h is the fission spectrum factor; G_{th} is the thermal flux depression factor; G_{epi} is the resonance self-shielding factor.

The last term in Eq. (15), containing H and h and representing the fission neutron contribution to the reaction rate, has always been neglected in k_0-NAA. Indeed, this term is negligible in well-thermalised neutron spectra, but may affect the constants, as discussed in the "Fission spectrum contribution to reaction rate" section.

The applicability and the accuracy of the above expression [Eq. (15)] depend on the approximations involved in determining the constants. Correspondence and definitions of individual terms are discussed in the sections that follow.

To avoid the need to determine the neutron flux, the k_0 standardization method of NAA relies on the measurement of the ratio of specific activities (and reaction rates) of the measured nuclide and some well-defined standard. The commonly applied standard is gold, because it has well-known cross sections and an associated gamma ray of accurately-known emission probability that is relatively easy to measure. The ratio of the specific activity of the

sample A_a relative to the specific activity of the standard A_s is related to the ratio of reaction rates, given by the following expression:

$$\frac{A_a}{A_s} = k_{0,a}\frac{G_{th}fg_a + G_{epi,a}Q_a + H_a h}{G_{th}fg_s + G_{epi,s}Q_s + H_s h}, \tag{16}$$

where

$$k_{0,a} = \frac{M_s\Theta_a P_{\gamma,a}\sigma_{0,a}}{M_a\Theta_s P_{\gamma,s}\sigma_{0,s}} \tag{17}$$

and the constants (index $x = a$ denotes the samples and $x = s$ the standard) are: M_x molar mass of sample; Θ_x natural atomic abundance; $P_{\gamma,x}$ gamma emission probability of the measured gamma ray; $\sigma_{0,x}$ thermal capture cross section.

Thermal cross section σ_0, g-factor and thermal flux depression factor G_{th}

The contribution of thermal neutrons to the reaction rate, expressed in the neutron speed domain is given by:

$$A_{th} = \int_0^{v_{Cd}}\sigma(v)vn(v)dv. \tag{18}$$

For a $1/v$ absorber the cross section is:

$$\sigma(v) = \sigma_0\frac{v_0}{v}, \tag{19}$$

where the symbols are: v_0 thermal neutron speed, 2200 m/s by definition; σ_0 cross section at neutron speed v_0. Substituting into the equation for A_{th}

$$A_{th} = \sigma_0 v_0\int_0^{v_{Cd}}n(v)dv = \sigma_0 v_0 N_{th}, \tag{20}$$

where N_{th} is the total thermal neutron density (i.e. total number of neutrons per unit volume). Note that the reaction rate is independent of the neutron speed distribution $n(v)$. In the energy domain the equivalent expression for the thermal reaction rate is:

$$A_{th} = K\int_0^{E_{Cd}}\sigma(E)\varphi_{th}(E)dE. \tag{21}$$

Substituting the expression for kinetic energy into Eq. (19) for a $1/v$ absorber we obtain

$$\sigma(E) = \sigma_0\sqrt{\frac{E_0}{E}}, \tag{22}$$

where E_0 is the energy of thermal neutrons corresponding to v_0 and is equal to 0.0253 eV. Simplification of the integral for the reaction rate in Eq. (21) in the energy domain is not possible. The reaction rate is proportional to the total thermal neutron density, but not to the total thermal neutron flux.

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[1] In energy bin (group) representation, $K = \phi_{1\,eV}/\ln(E_2/E_1)$, where $\phi_{1\,eV}$ is the group flux in the energy bin around 1 eV and E_1 and E_2 are the corresponding energy bin boundaries.

Assuming that the thermal neutron spectrum has Maxwellian distribution:

$$\varphi_{th}(E) = E e^{-E/kT}, \tag{23}$$

where k is the Boltzman constant and T is the temperature, the thermal reaction rate is given by:

$$A_{th} = K \int_0^{E_{Cd}} \sigma(E) E e^{-E/kT} dE. \tag{24}$$

For a $1/v$ absorber

$$A_{th} = K \sigma_0 \sqrt{E_0} \int_0^{E_{Cd}} \sqrt{E} e^{-E/kT} dE. \tag{25}$$

The average thermal cross section σ_{th} is defined by:

$$\sigma_{th} = \frac{\int \sigma(E) \varphi_{th}(E) dE}{\int \varphi_{th}(E) dE} = \frac{K \sigma_0 \sqrt{E_0} \int \sqrt{E} e^{-E/kT} dE}{K \int E e^{-E/kT} dE}. \tag{26}$$

Extending the integration limits from 0 to ∞ (possible by the fact that the exponential factors decrease rapidly above E_{Cd}), recognising the integral in the numerator as the gamma function $\Gamma(3/2)$ and using the relation between the energy and the temperature $E_0 = kT_0$, the average thermal cross section σ_{th} is related to the thermal cross section σ_0 by the relation:

$$\sigma_{th} = \frac{K \sigma_0 (kT)^{3/2} \sqrt{kT_0} \sqrt{\pi}}{2 K (kT)^2} = \frac{\sqrt{\pi}}{2} \sigma_0 \sqrt{\frac{T_0}{T}}. \tag{27}$$

Note that this relation is strictly valid only for a pure $1/v$ absorber in a Maxwellian spectrum. In practice, the cross sections may deviate from the $1/v$ behaviour and the spectrum may be distorted (depending on the irradiation facility). Westcott attempted to correct for the nonideal cross section behaviour by introducing the Westcott g-factor [4, 5], but still assumed that the spectrum was of Maxwellian shape. He even took the trouble to extract the $1/v$ part of the cross section contribution from the resonance range above the energy E_{Cd}. At the time when the Westcott formalism was developed, the knowledge of cross section shapes was lacking and determining the spectral shape was based more on intuition and educated guessing than anything else. Computational power posed additional limitations, which favoured analytical approaches. With many of these constrains relaxed, it is possible to introduce an alternative definition of the generalised g-factor, which can be used to calculate reaction rates without loss of generality and is applicable to non-$1/v$ absorbers as well as spectra which deviate from the Maxwellian shape. The drawback of using the more elaborate Westcott formalism was also noted by other authors [6]. Comparing Eqs. (14) and (15) see that:

$$\phi_{th} \sigma_0 g G_{th} = K \int_0^{E_{Cd}} \sigma(E) \varphi_{th}(E) dE. \tag{28}$$

Arbitrarily we define:

$$\phi_{th} = K \frac{\sqrt{\pi}}{2} \int_0^{E_{Cd}} \varphi_{th}(E) dE \tag{29}$$

Neglecting the thermal flux depression factor G_{th} for the time being (assuming it is equal to 1), the definition of the generalised g-factor follows:

$$g = \frac{\int_0^{E_{Cd}} \sigma(E) \varphi_{th}(E) dE}{\sigma_0 \frac{\sqrt{\pi}}{2} \int_0^{E_{Cd}} \varphi_{th}(E) dE} = \frac{2}{\sqrt{\pi}} \frac{\sigma_{th}}{\sigma_0}. \tag{30}$$

Substituting the integrals with the expression for σ_{th} it is easily seen that for a $1/v$ absorber in a Maxwellian spectrum the above definition gives the well-known Westcott g-factor relation:

$$g = \sqrt{\frac{T_0}{T}} g_0, \tag{31}$$

where g_0 is the value of the g-factor for a Maxwellian spectrum at room temperature. In addition to the applicability to arbitrary spectra, the main difference in the generalised definition of the g-factor is the upper integration limit E_{Cd}, commonly taken as 0.55 eV. Normally this does not affect the value of the g-factors in Maxwellian spectra because the Maxwellian distribution function falls off very rapidly above 0.55 eV and its contribution to the integral is very small. The generalised g-factor can be calculated easily from the cross sections, which are available for practically all nuclides of interest. The value of the calculated g-factor does not depend on the absolute magnitude of the cross sections, which may have significant systematic errors, but only on the shape. Introduction of the generalised definition of the g-factor extends the applicability of the methods which rely on simple expressions for reaction rates such as given in Eq. (15), to irradiation facilities with spectra that deviate significantly from the Maxwellian shape in the thermal region.

The thermal neutron flux depression factor G_{th} is often referred to as the "thermal self-shielding factor", but the term is misleading, because it implies primary dependence on the measured nuclide in the sample. This is indeed the case with resonance absorption in the epithermal range range, but not in the thermal range, where neutron transport effects play a dominant role. The thermal neutron flux depression factor is therefore determined by the macroscopic cross sections of the sample material as a whole. It can be calculated by a direct transport calculation or from parameterised expressions, which are discussed in more detail in the literature [7–9].

For reference, the thermal flux depression factor formulae are given. For slabs, the factor is given by:

$$G_{th,slab} = \frac{1}{2\xi}\left[1 - \exp(-\xi) + \xi\exp(-\xi) - \xi^2\int_\xi^\infty \frac{e^{-u}}{u}du\right],$$

(32)

$$\int_\xi^\infty \frac{e^{-u}}{u}du \approx -\left[C + \ln\xi + \sum_{n=1}^p \frac{1}{n}\frac{(-\xi)^n}{n!}\right]$$

(33)

$$\xi = \frac{l}{2}\sum_k \Sigma_k,$$

(34)

where the summation over k represents the summation over the nuclides present in the sample, Σ_k are the macroscopic cross sections of the nuclides, C is the Euler constant = 0.577215, p is the number of terms in the series; the terms can be summed until the relative contribution of the last term is sufficiently small, e.g. 10^{-6}, and l is the mean chord length in the sample. For wires (infinite cylinders), a rough approximation for the thermal flux depression factor is:

$$G_{th,wire} = 1 - \frac{4}{3}\xi.$$

(35)

For spheres, defining $y = 3\xi/2$

$$G_{th,sphere} = \begin{cases} 1 - \frac{9}{8}\xi, & \xi \le 0.003 \\ \frac{3}{4y^3}\left[y^2 - \frac{1}{2} + \left(\frac{1}{2} + y\right)e^{-2y}\right], & \xi \ge 0.003. \end{cases}$$

(36)

In addition, the original derivation of the equation for slabs has been reviewed and a correction has been introduced [9]:

$$G_{th}^* = \frac{G_{th}}{1 - W\frac{\Sigma_s}{\Sigma_t}(1 - G_{th})},$$

(37)

where Σ_s and Σ_t are the macroscopic scattering and total cross sections, respectively, and the parameter W represents an arbitrary weight (ideally equal to 1) and is used to improve the agreement of the expression with results from more detailed calculations of the thermal flux depression factors.

Resonance integral I, cadmium transmission factor F_{Cd} and Q value

The reference resonance integral I_0 is usually defined by the product of the cross section and a pure $1/E$ spectrum, integrated between some chosen cadmium cutoff energy E_{Cd} and an arbitrarily chosen upper limit E_3:

$$I_0 = \int_{E_{Cd}}^{E_3} \sigma(E)\psi(E)dE; \quad \psi(E) = \frac{1}{E}.$$

(38)

Similarly, the reference Q_0 value is given by:

$$Q_0 = \frac{I_0}{\sigma_0}.$$

(39)

This definition is rather artificial because such a spectrum with sharp cutoff energies cannot be produced experimentally. Measurements are usually done in thermal reactor spectra, which approximately follow the $1/E$ behaviour in the epithermal energy range. If the irradiation position is separated from the fission source (usually the reactor core) by a relatively thick moderator material region, relatively few fission neutrons reach the irradiation position directly, so the fission peak in the spectrum is small. The fission spectrum falls off rather rapidly above the peak, so the energy around 2 MeV is the natural upper cutoff energy. At the low energy end, thermal neutrons can be filtered by a strong absorber like cadmium, which has a huge resonance at 0.178 eV and relatively weak resonances at higher energies. A 1 mm cadmium filter effectively removes most neutrons below 0.55 eV. The total and absorption cross sections of cadmium are shown in Fig. 1. The resonance integral can be approximated by the reaction rate I_{Cd} measured under a cadmium filter.
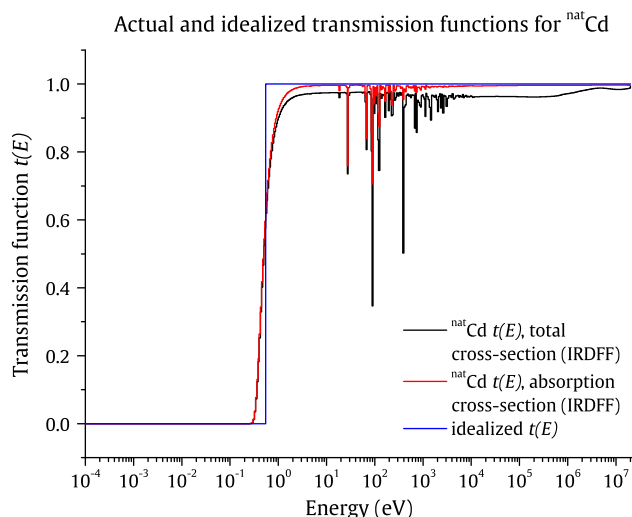
Introducing the cadmium transmission function $t(E)$, a more precise definition of the measured resonance integral under cadmium cover I_{Cd} in a real spectrum $\varphi^*(E)$ is obtained:

$$I_{Cd} = \int_0^\infty t(E)\sigma(E)\varphi^*(E)dE.$$

(40)

The above equation reduces to the previous idealised one if the range of integration is limited from E_{Cd} to E_3, the spectrum is pure $1/E$, and $t(E)$ is an idealised Heaviside function:
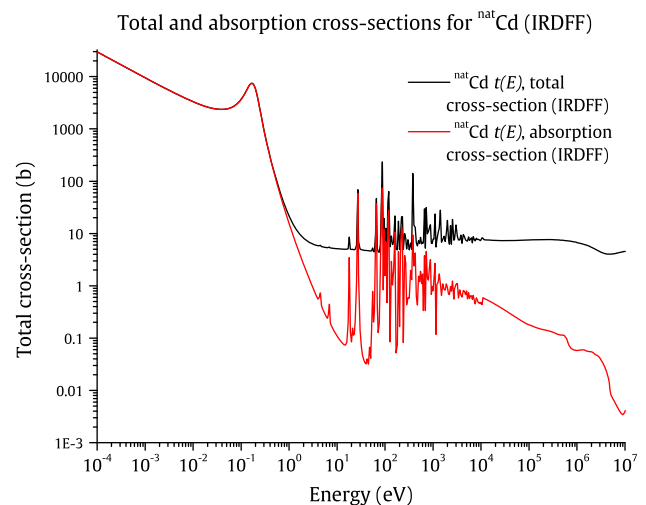
Fig. 1 Total and absorption cross sections of natural cadmium

Actual and idealized transmission functions for ^{nat}Cd

Fig. 2 Actual and idealized cadmium transmission functions for a 1-mm thick cadmium cover

$$t(E) = \begin{cases} 0 & \text{for } E < E_{Cd} \\ 1 & \text{for } E \geq E_{Cd} \end{cases} \quad (41)$$

A more realistic form of the cadmium transmission function is obtained by assuming exponential attenuation of neutrons through cadmium:

$$t(E) = e^{N_{Cd} d \sigma_{Cd}(E)}, \quad (42)$$

where d is the cadmium cover thickness, $\sigma_{Cd}(E)$ is the cadmium cross section and N_{Cd} is the number density of cadmium atoms in the cover, given as:

$$N_{Cd} = \frac{\rho_{Cd} N_A}{M_{Cd}}, \quad (43)$$

where ρ_{Cd} is the density of cadmium, N_A the Avogadro number and M_{Cd} the molar mass of cadmium.

In a collimated narrow neutron beam incident on a small target, any reaction on cadmium would remove a neutron from its path. Using the total cross section for σ_{Cd} the cadmium transmission function would be valid exactly. In practice, the beam profile and target dimensions are finite; the neutron field may be isotropic, in which case there is a high probability that scattered neutrons would also reach the target. In such cases only the absorption reaction really removes the neutrons so it may be more appropriate to define σ_{Cd} as the absorption cross section. In reality the truth is somewhere in between. Figure 2 displays the cadmium transmission functions obtained from the total and absorption cross-sections and the idealized cadmium transmission function. The problem is schematically presented in Fig. 3. Note that the form of the cadmium transmission function is the first approximation in the definitions introduced so far.

The resonance integral defined by Eq. (40) is a measurable quantity. This is to be compared with the required form evident from Eqs. (14) and (15). The cadmium transmission factor F_{Cd} is introduced to compensate for the non-ideal shape of the cadmium filter transmission function, assuming the spectrum closely follows the $1/E$ behaviour and ignoring (or subtracting out) the high energy contribution of the fission spectrum:

$$I = \int_{E_{Cd}}^{E_3} \sigma(E)\varphi(E)dE = \frac{1}{F_{Cd}} \int_0^\infty t(E)\sigma(E)\varphi(E)dE. \quad (44)$$

From this it follows that:

$$F_{Cd} = \frac{\int_0^\infty t(E)\sigma(E)\varphi(E)dE}{\int_{E_{Cd}}^{E_3} \sigma(E)\varphi(E)dE}. \quad (45)$$

Deviation of F_{Cd} from unity arises from the cadmium transmission function and from the difference in the upper integration limit. The contribution of the latter is small in the case of $1/E$ spectrum with a small component of the fission neutrons in the spectrum. This is usually the case for irradiation facilities behind a reflector. Cadmium transmission factor values can be calculated from the cross sections by direct integration according to Eq. (45), assuming a $1/E$ spectrum and choosing appropriate integration limits in the numerator and the denominator ($E_3 = 2$ MeV, say); the lower integration limit E_{Cd} is chosen to approximately match the effective cutoff of the cadmium cover, which depends on the cadmium thickness. The value 0.55 eV is usually adopted for a cadmium thickness of 1 mm.

Irradiation channels inside (or near) the reactor core may exhibit spectra with a significant contribution of fission neutrons. In such cases the neutron spectrum characterisation has to be done very carefully and the cadmium transmission factor calculated directly from the cross sections and the actual spectrum of the irradiation facility.

In k_0-NAA databases very few nuclides contain F_{Cd} factors that deviate from unity, and even those have to be considered with care. For example, the commonly adopted value for ^{186}W is 0.908 [10] and yields measured Q_0 values which disagree by nearly 10 % from those calculated from the energy-dependent cross sections in evaluated nuclear data files [11]. Direct calculations, using cross sections to simulate the transmission of neutrons through a 1 mm cadmium layer, result in a cadmium transmission factor that differs from unity by about 1 %. Furthermore, the measured value of 0.908 is not given with the associated uncertainty. From the original paper on the measurement the uncertainty is likely to be high and the quoted measured F_{Cd} is probably incorrect.

With the resonance integral uniquely defined, the Q value for a general neutron spectrum can also be defined in a way analogous to Eq. (39):

Fig. 3 Limiting cases for irradiations using cadmium filters: narrow collimated neutron beam, isotropic neutron field
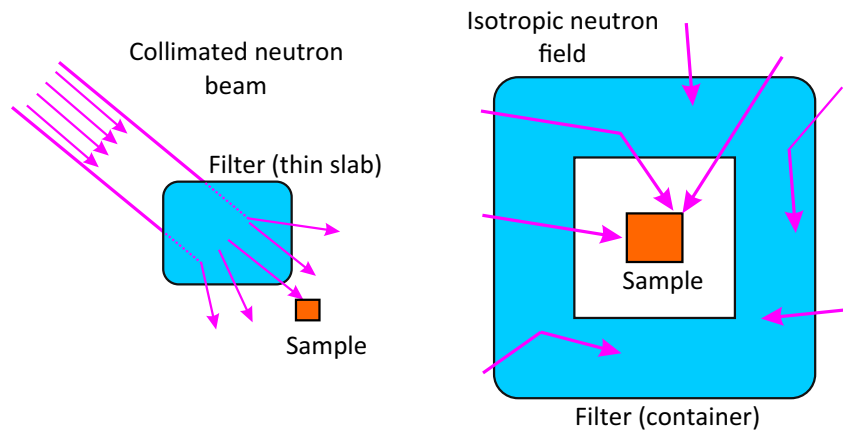
$$Q = \frac{I}{\sigma_0}. \tag{46}$$

The reference Q_0 for an ideal $1/E$ spectrum is already defined by Eq. (39). The relation between the reference Q_0 and the general Q is discussed in the "Effective resonance energy E_r" section. Some comparisons between measured values and those calculated using cross sections from evaluated nuclear data files are given in the "Q_0 measurements by the cadmium ratio method" section.

Resonance self-shielding factor G_{epi}

In the absence of strong absorbers the neutron spectrum as a function of energy is a smooth function. When resonance absorbers are present in significant quantities, the resonances tend to create dips in the spectrum shape. This phenomenon is well known in reactor physics and has been dealt with extensively in the so-called resonance theory. In the intermediate resonance approximation (IR) the real spectrum $\varphi^*(E)$ is expressed in terms of the spectrum unperturbed by the resonance absorber $\varphi(E)$ by the expression:

$$\varphi^*(E) = \frac{\sigma_b + \lambda \sigma_p(E)}{\sigma_b + \lambda \sigma_a(E) + \sigma_s(E)} \varphi(E), \tag{47}$$

where σ_b is the Bondarenko background cross section, which measures the effective dilution of the resonance absorber; σ_a is the absorption cross section of the resonance absorber, σ_s is the scattering cross section of the resonance absorber; σ_p is the potential scattering cross section of the resonance absorber; λ is the Goldstein–Cohen parameter—a "measure" of the resonance width, and $\varphi(E)$ is the smooth spectrum (unperturbed by the resonances).

The intermediate resonance approximation is an improvement to the narrow resonance (NR) approximation ($\lambda = 1$, implying that the resonances are so narrow that any scattering event will decrease neutron energy sufficiently to fall outside the resonance) and the wide resonance (WR) approximation ($\lambda = 0$, assuming that energy loss in a scattering event is small compared to the resonance width).

Resonance theory is based on the assumption that the absorber atom is surrounded by a moderator of approximately constant cross section, presented by the Bondarenko background cross section, which effectively measures the dilution of the absorber and is defined as the macroscopic potential cross section of the moderator per absorber atom:

$$\sigma_b = \frac{1}{N_a} \sum_i N_i \lambda_i \sigma_i, \tag{48}$$

where N_a is the absorber atom number density; N_i is the number density of the ith moderator nucleus; σ_i is the cross section of the ith moderator nucleus; λ_i is a parameter related to the Goldstein–Cohen parameter that measures the moderator effectiveness. By definition it is equal to 1 for hydrogen. Further details can be found in the documentation of the WIMS-D Library Update Project [12].

The above derivation is applicable to infinite homogeneous media, but irradiated samples are of finite dimensions. In the surrounding medium (analogous to a moderator without strong resonance absorbers) the spectrum is relatively smooth. The neutrons enter the sample (containing a resonant absorber), but their depth of penetration at resonance energies is limited due to the absorption in the resonances. The process is therefore similar to the one in an infinite medium. In reactor physics this is called the equivalence theorem. The equation for the Bondarenko background cross section is modified to include the so-called escape cross section Σ_e, which accounts for the finite dimensions of the sample:

$$\sigma_b = \frac{1}{N_a} \left[\Sigma_e + \sum_i N_i \lambda_i \sigma_i \right] \tag{49}$$

The escape cross section is given by the simple expression:

$$\Sigma_e = \frac{a}{l}, \tag{50}$$

where a is the Bell factor (usually assumed constant with value 1.16); l is the mean chord length.

The mean chord length for a convex volume is approximately given by:

$$l = \frac{4V}{S}, \tag{51}$$

where V is the volume and S is the surface area.

The epithermal self-shielding factor describing the effects of resonance absorption can be defined by:

$$G_{epi} = \frac{\int_{E_{Cd}}^{E_3} \sigma(E)\varphi^*(E)dE}{\int_{E_{Cd}}^{E_3} \sigma(E)\varphi(E)dE}, \tag{52}$$

with the weighting spectrum $\varphi^*(E)$ defined by Eq. (47). A practical procedure is to generate a library of self-shielding factors for all nuclides of interest, and particularly the main likely constituents of sample materials with significant absorption properties, tabulated as a function of the Bondarenko background cross section σ_b. This operation can be performed e.g. by using the MATSSF code [13], readily available from the IAEA website (http://www-nds.iaea.org/naa/matssf/). The user can then calculate the relevant value of σ_b from Eqs. (49) and (50), and retrieve the required G_{epi} by interpolation. The main approximations in this approach are those inherent in the IR resonance approximation and the assumption that G_{epi} factors are not sensitive to small deviations in the weighting spectrum $\varphi(E)$, which is usually assumed to be of the $1/E$ form. Also, the interference between resonances is neglected in cases where the sample contains several strong resonance absorbers present in significant quantities.

Effective resonance energy E_r

The resonance integral and the Q value depend on the shape of the neutron spectrum in the epithermal range. Assuming that the spectrum deviates only slightly from the $1/E$ behaviour such that it can be represented by:

$$\varphi(E) = \frac{1}{E^{1+\alpha}}, \tag{53}$$

where α is a constant. To relate the $Q(\alpha)$ in terms of the reference Q_0 value corresponding to $\alpha = 0$ in a pure $1/E$ spectrum, a semi-empirical relation is usually applied [14, 15]:

$$Q(\alpha) = \frac{Q_0 - 2\sqrt{E_0/E_{Cd}}}{(E_r/1\,\mathrm{eV})^\alpha} + \frac{2\sqrt{E_0/E_{Cd}}}{(2\alpha + 1)(E_{Cd}/1\,\mathrm{eV})^\alpha} \tag{54}$$

The numerical value of $2\sqrt{E_0/E_{Cd}} \approx 0.429$ is often seen in the equations in the literature. The relation is based on

the assumption that resonances can be represented by the single-level Breit–Wigner formula. An *effective* resonance energy E_r is defined as a weighted average of the true resonance energies, where the contributions of the particular resonances to the resonance integral are used as weights. Replacing the resonances by a single resonance at E_r of width such that it reproduces the true resonance integral, an analytical expression for the integral for any value of α can be derived. Rearranging the expressions, Eq. (54) is obtained.

To verify the validity of the approximation for $Q(\alpha)$, exact values were calculated directly from the cross sections based on Eqs. (44), (45) and (46) for a set of α values in the range between -0.1 and $+0.1$, and using an idealised cadmium transmission function with cutoff at 0.55 eV. By inverting Equation (54) an expression for E_r can be obtained:
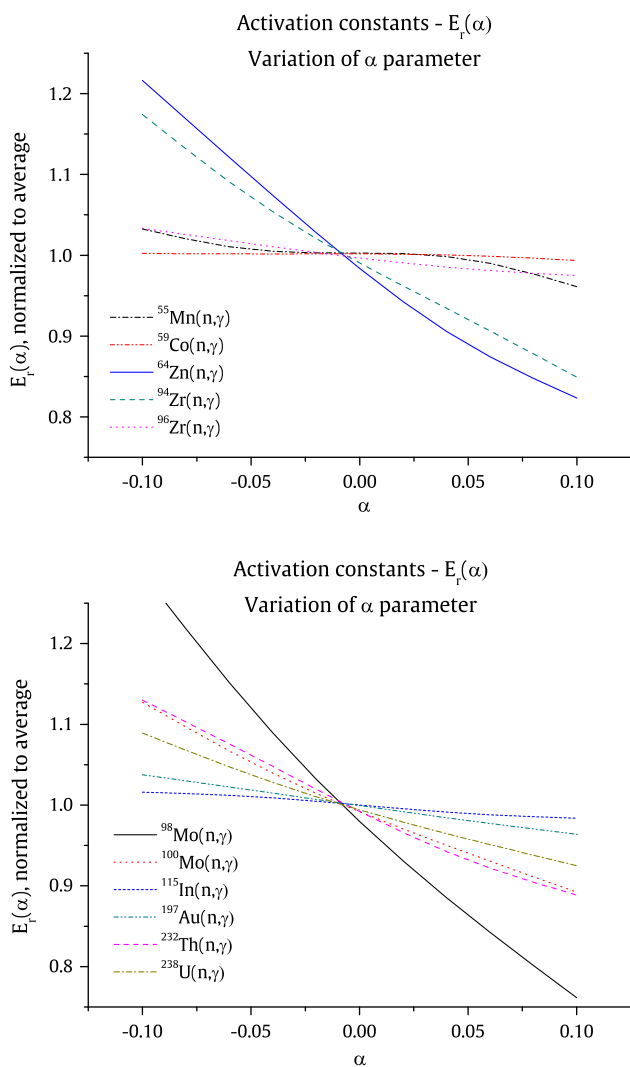
$$E_r(\alpha) = \left[\frac{Q_0 - 0.429}{Q(\alpha) - \frac{0.429}{(2\alpha+1)(0.55)^\alpha}}\right]^{1/\alpha} \tag{55}$$

The average E_r is defined by the integral:

$$E_r = \frac{1}{\alpha_{hi} - \alpha_{lo}} \int_{\alpha_{lo}}^{\alpha_{hi}} E_r(\alpha)d\alpha \tag{56}$$

and the integration limits α_{hi} and α_{lo} are chosen $+0.1$ and -0.1, respectively. The calculated $E_r(\alpha)$ for different values of α were found to vary by up to 30 % from the average value E_r. The α-dependent $E_r(\alpha)$, (normalised with respect to the average E_r) for different nuclides is shown in Fig. 4. The average effective resonance energies E_r calculated from modern differential cross section data also differ quite significantly from the values in the database usually adopted for k_0-NAA, which were derived from the available resonance parameters [16]. The comparison is shown in Table 1; the values from the k_0-NAA database are labeled "Kayzero". In the case of ^{94}Zr the difference exceeds a factor of two.

A similar analysis was performed for $Q(\alpha)$. Exact values calculated by direct integration of Eqs. (38) and (39) were compared to the approximate ones based on Eq. (54), using Q_0 and average E_r calculated as described before. For easier comparison between different nuclides all values were normalised with respect to the corresponding Q_0 value. The comparison is shown in Fig. 5. Fortunately it turns out that the dependence of $Q(\alpha)$ on E_r is rather weak. Although the α-dependence of E_r is quite strong, the use of the average value in conjunction with Eq. (54) does not introduce a large error into the calculated $Q(\alpha)$. The differences are larger for nuclides with higher effective resonance energies E_r and may exceed 3 % in some cases. It is interesting to note that Eq. (54) always leads to the underprediction of $Q(\alpha)$. It has been shown that improved

Activation constants - $E_r(\alpha)$
Variation of α parameter

Activation constants - $E_r(\alpha)$
Variation of α parameter

Fig. 4 Comparison of effective resonance energies E_r for neutron activation analysis

$Q(\alpha)$ values can be obtained if one uses E_r values calculated from modern differential cross section data and if the variation of E_r with α is taken into account. Compilation of E_r values from basic nuclear data libraries is work in progress and is beyond the scope of the present discussion.

Fission spectrum contribution to reaction rate

The k_0 standardization of NAA relies on measurements of specific activities of radionuclides produced by radiative capture reactions, which in the majority of cases have a very low cross section at higher neutron energies. Moreover, the irradiation facilities used for k_0-NAA typically have a very well thermalized neutron spectrum, where even the contribution to the reaction rates from the resonance energy region is small compared to the main contribution from the thermal region. For typical k_0-NAA facilities, the fission spectrum contribution is altogether neglected.

Table 1 Comparison of effective resonance energies E_r for neutron activation analysis

| Nuclide	E_r (eV) (Kayzero)	E_r (eV) (This work)	Relative difference (%)
^{55}Mn	468.0	393.5	−16
^{59}Co	136.0	123.3	−9
^{64}Zn	2560.0	2785.5	9
^{94}Zr	6260.0	13142.3	110
^{96}Zr	338.0	346.0	2
^{98}Mo	241.0	319.8	33
^{100}Mo	672.0	881.8	31
^{115}In	1.6	1.5	−6
^{197}Au	5.7	5.7	0
^{232}Th	54.4	72.6	33
^{238}U	16.9	18.2	8

However, generalizing the equations used in k_0-NAA by the introduction of new terms describing the fission spectrum contribution has several benefits. Firstly, in cases where the reaction cross sections exhibit a very long $1/v$ dependence it enables to separate the fission spectrum contribution from the measured resonance integal. One such case is the ^{27}Al(n, γ) reaction. The Q_0 factor for this reaction has been determined from cadmium ratio measurements in two irradiation channels of the JSI TRIGA Mark II reactor with different spectral characteristics—the Central Channel in the reactor core, with a strong fission spectrum component and the IC40 irradiation channel in the graphite reflector surrounding the reactor core, with a significantly smaller fission spectrum component [17]. For the Central Channel it has been shown that the correction to Q_0 due to the fission spectrum contribution is about 8 %.

Secondly, the benefit of the generalization is that it enables the implementation of this analytical method at irradiation facilities with a strong fission spectrum component and it allows for the extension of the method to threshold nuclear reactions with an alternative definition of the k_0 factors, although this possibility has not been explored in detail.

The mathematical definition of the fission spectrum integral is:

$$\begin{aligned}
J &= \int_{E_{Cd}}^{\infty} \sigma(E)\varphi_h(E)dE \\
&= \frac{1}{h}\int_{E_{Cd}}^{\infty} \sigma(E)[\varphi_r(E) + h\varphi_h(E)]dE \\
&\quad - \frac{1}{h}\int_{E_{Cd}}^{\infty} \sigma(E)\varphi_r(E)dE,
\end{aligned} \tag{57}$$

where the fission spectrum fraction h depends on the spectrum normalisation. Once the fission spectrum shape is
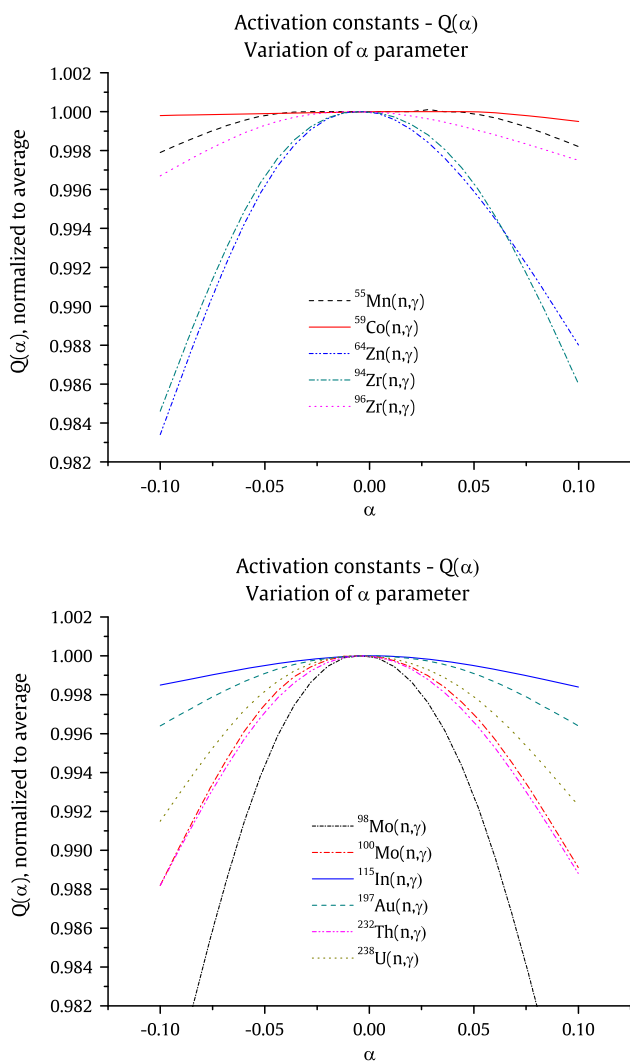
Fig. 5 Comparison of exact and approximate $Q(\alpha)$ values for different nuclides

defined, the fission spectrum integrals can readily be calculated from the cross sections. The fraction h itself can then be determined through measurements of threshold reaction rates. By determining the parameters f, α and h the neutron spectrum is fully characterized.

An alternative definition for the k_0 factor, analogous to Eq. (16) can be written for threshold reactions:

$$\frac{A_a}{A_s} = k_{0,a} \frac{I_a + J_a h}{G_{th} f g_s + G_{epi,s} Q_s + H_s h},$$ (58)

where

$$k_{0,a} = \frac{M_s \Theta_a \gamma_a}{M_a \Theta_s \gamma_s \sigma_{0,s}},$$ (59)

and the constants have their usual meaning. Note that in the above expression there is no thermal component. There might be a small contribution to the resonance integral for reactions with threshold below the upper cutoff energy for

the resonance integral. Note also that the k_0 factor is defined without the cross section in the numerator, because it is zero for threshold reactions.

The quantities in the denominator of the expression for k_0 refer to the standard and are well known. The largest uncertainty probably originates from the gamma emission probability of the threshold reaction product. However, if threshold reactions are only needed to determine interference lines in the spectra, their uncertainties are less important.

Neutron spectrum

The neutron spectrum in thermal reactors is determined by the fission neutron source, the slowing-down process at intermediate energies, and the thermal region where neutrons are in equilibrium with the surrounding crystal lattice. It is useful to define an analytical function that is representative of the general features of the spectrum. A typical light water reactor spectrum, which can be used as a weighting function for averaging cross sections and calculating reaction rates is approximated by the thermal Maxwellian part ψ_{th}, the epithermal region ψ_{epi} and the fission spectrum ψ_f defined by:

$$\psi_{th} = C_{th} E^l \left[e^{-E/kT} + C_{t1} e^{-E/kT_1} + C_{t2} e^{-E/kT_2} \right]$$

$$\psi_{epi} = E^{-\left[1 + \alpha_0 + \alpha_1 \log(E) + \alpha_2 (\log(E))^2\right]}$$

$$\psi_f = \begin{cases} C_f & e^{-E/W_a} \sinh\left(\sqrt{EW_b}\right) \frac{1}{E^{m_0 + m_1 E}} \quad \text{or} \\ C_f & \sqrt{E} e^{-E/E_f} \frac{1}{E^{m_0 + m_1 E}} \end{cases},$$ (60)

where k is the Boltzmann constant; α_i are the constants that determine the deviation from $1/E$ behaviour in the epithermal range; W_a, W_b are the constants of the Watt fission spectrum; T is the temperature; E_{th}, E_f are breakpoints between thermal, epithermal and fast spectrum ranges; C_{th}, C_f are continuity constants such that $\psi_{th}(E_{th}) = \psi_{epi}(E_{th})$ and $\psi_f(E_f) = \psi_{epi}(E_f)$, respectively; m is the fast neutron slowing-down factor (equals 0 for no slowing-down and 1 for fast neutron sources surrounded by a moderator). It may vary linearly with energy, in which case the coefficients m_0 and m_1 are defined.

The full function ψ representing the spectrum is defined by:

$$\psi = K_{th} \psi_{th} + K_{epi} \psi_{epi} + K_f \psi_f,$$ (61)

where:

$$K_{epi} = \begin{cases} 1 & \text{for} \quad E_{th} < E < E_f \\ 0 & \text{otherwise} \end{cases}$$ (62)

$$K_{th} = 1 + O_{th} - K_{epi}$$ (63)

$$K_f = 1 + O_f - K_{epi}.$$ (64)

The parameters O_{th} and O_f can be chosen arbitrarily to define overlap for a smooth transition between different regions (0 for no overlap, about 1 for a moderate overlap, typically). The weighting function thus defined gives the spectrum shape with the required characteristics and a smooth transition between the thermal, epithermal and the fast energy range. It is equal to 1 at energy 1 eV.

Special features of the function are:

- the thermal region is a superposition of three Maxwellian functions at different temperatures, which allows the modelling of distortions in the spectrum at low energies,
- the α parameter that measures the deviation from the $1/E$ shape is allowed to be energy-dependent,
- the fast fission spectrum can be described by a Maxwellian or a Watt function, with a correction to account for fast neutron slowing-down.

Determination of parameters

Parameters determined from evaluated cross section data

As already mentioned, some of the parameters are difficult to determine experimentally. Having precise definitions of the constants from first principles allows us to calculate them from the basic nuclear data (particularly the energy-dependent cross sections in evaluated nuclear data files) at least in cases when the parameters do not depend on the absolute accuracy of the cross section values but mainly on the shape in a particular energy range. The parameters are given in the following subsections.

Generalized Westcott g-factor

The generalized Westcott g-factor is defined by Eq. (30) and is usually very close to one. It is very difficult to design an experiment for a direct measurement of the g-factor that would be more accurate than the value calculated from cross section data, except perhaps in cases where the g-factor differs significantly from one. The ratio of the g-factors of the measured material to the standard can be determined from the measurements of the k_0 factors in a thermal and a cold neutron beam (see the "Cadmium transmission factor F_{Cd}" section), knowing that at lower neutron energies the deviations of the cross sections from the $1/v$ behaviour are smaller. The precondition for such measurement is good knowledge of the shape of the spectra. Generally it is preferable to use measurements of this kind for the validation of the g-factors calculated from the cross sections rather than their direct determination.

Cadmium transmission factor F_{Cd}

The cadmium transmission factor F_{Cd} defined by Eq. (45) accounts for the difference between the idealised and the measurable resonance integral, taking explicitly into account the interference between the absorber and the cadmium resonances. It would be possible to choose a definition of the resonance integral that would more closely match the measured one, but this would only obscure its subsequent application in the calculation of reaction rates. Defining the cadmium transmission factor to correct for the difference between the measured and the idealised resonance integral in a $1/E$ spectrum between 0.55 eV and 2 MeV is a practical convenience.

Thermal flux depression factor G_{th}, epithermal self-shielding factor G_{epi}

Contrary to the other constants listed in the "Determination of parameters" section, the thermal "self-shielding" (or flux depression) factor G_{th} is not a property of the measured nuclei but of the matrix in which they are embedded. The presence of strong absorbers may cause flux depression (and hence a decrease in the reaction rate), while abundance of organic materials may actually increase the thermal flux locally due to internal moderation. Empirical expressions for the calculation of G_{th} are described in the literature [7] and discussed briefly in the "Thermal cross section σ_0, g-factor and thermal flux depression factor G_{th}" section.

The epithermal self-shielding factor G_{epi} accounts for detailed changes in the spectrum due to resonance absorption. The theoretical approach defined by Eqs. (47), (48), (49), (50), (51) and (52) is well established in reactor physics and gives good results even for absorbers in relatively high concentrations. There is no reason to question its applicability in k_0-NAA, where the levels of self-shielding are usually lower. Accurate direct measurements were reported for some monitor materials by irradiating samples of various thicknesses and extrapolating to zero, but such a procedure is not practical for general implementation to all materials that may occur in real samples; it may serve well for the validation of the resonance self-shielding factors calculated from the cross sections.

For practical purposes, both G_{th} and G_{epi} can be easily calculated with the MATSSF code mentioned above. The user is required to input the sample chemical composition, density and geometrical data. Only cylidrical geometry is considered. The code has been validated against

experimental measurements for moderate levels of self-shielding [18].

Effective resonance energy E_r

The effective resonance energy in its original form was based on the validity of the single-level Breit–Wigner formula for the resonance cross section representation, which is known to be poor. Interpreting expression (54) for $Q(\alpha)$ as a semi-empirical relation, calculating $Q(\alpha)$ directly from the cross sections and using E_r as a fitting parameter in the empirical relation is a far more accurate and satisfactory procedure than any attempt to measure E_r experimentally.

Fission spectrum averaged cross-secion σ_h

The fission spectrum averaged cross-secion can approximately be determined from measurements in a pure fission spectrum (e.g. behind a fission plate), but such estimates are valid only for threshold reactions above the resonance cutoff energy and do not take the distortions of the spectrum (e.g. slowing-down, oxygen resonances, etc.) into account. Calculated cross sections from the differential data and the actual shape of the spectrum are generally more accurate and reliable.
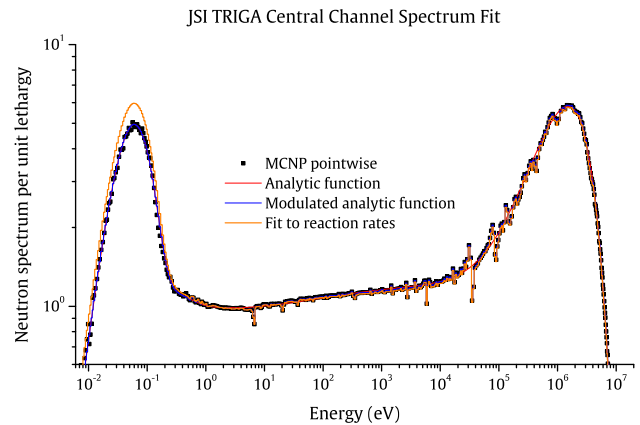
Parameters of the analytical spectrum function

If no additional information is available, the user can assume that the spectrum is purely Maxwellian with strength defined by factor f at thermal energies and deviates by a fraction α from $1/E$ in the resonance range up to 2 MeV, say. This is consistent with the traditional approach in k_0-NAA.

Rapid advances in computational power made possible the development of detailed full-core models (including irradiation facilities), with which the neutron spectrum can be calculated. A Monte Carlo simulation of the spectrum in the central channel of the TRIGA Mark-II reactor in Ljubljana is presented in Fig. 6, labelled "MCNP pointwise". Note the structure in the spectrum below the fission peak, which is due to the oxygen resonances.

The calculated spectrum was fitted with parameter α having a slight quadratic dependence on $\log(E)$, thermal spectrum given by parameter f with small contributions of two secondary Maxwellians at 850 and 1,800 K to fit the shape at around 0.2 eV.

The analytic function fit reproduces very well the overall shape of the spectrum, but not the fine details. To remedy this we define a modulating function as the ratio of the calculated spectrum and the analytic function. Obviously,

Fig. 6 JSI TRIGA central channel spectrum fitting: neutron spectrum calculated with a Monte Carlo calculation, fitted analytical spectrum function, modulated analytical spectrum funcion, fit to reaction rates

scaling the analytic function with the modulating function reproduces exactly the calculated spectrum. Modulation of the analytic fitting function may be suppressed in the regions where the detailed shape of the calculated spectrum is unreliable (for example, below 0.4 eV and above 4 MeV).

If for some reason we need to change slightly the fitting function parameters, the overall characteristics of the spectrum change, but the detailed shape defined by the modulating function is preserved. The curve in Fig. 6 labelled "Fit to reaction rates" was obtained by allowing parameters f, α and m to vary so as to better reproduce the measured reaction rates of dosimetry monitors.

Experimental measurements

k_0 measurements, thermal capture cross section and gamma emission probability

From Eqs. (16) and (17) it follows that the k_0 factor can be determined from the measured ratio of activities of the nuclide of interest (subscript a) and the standard (subscript s):

$$k_{0,a} = \frac{M_s \Theta_a P_{\gamma,a} \sigma_{0,a}}{M_a \Theta_s P_{\gamma,s} \sigma_{0,s}} = \frac{A_a}{A_s} \frac{G_{th} f g_s + G_{epi,s} Q_s + H_s h}{G_{th} f g_a + G_{epi,a} Q_a + H_a h}. \quad (65)$$

The accuracy of the measured k_0 factor depends on the neutron spectrum in which the measurement is done. If the epithermal spectrum contribution is small, the f factor is large, making the contributions of the Q and H terms negligible. The only parameter influencing the result in addition to the measured ratio of specific activities is the ratio of the g-factors of the measured nuclide and the standard.

Table 2 Comparison of Q_0 nuclear constants for neutron activation analysis

Nuclide	Mughabghab	± (%)	Diff. (%)	Kayzero	± (%)	JENDL-4.0	Diff. (%)	ENDF/B-VII.1	Diff. (%)
^{55}Mn	1.003	3.8	−4.7	1.053	3.0	0.995	−5.5	0.995	−5.5
^{59}Co	1.990	2.7	−0.5	2.0	3.0	2.015	0.7	2.016	0.8
^{64}Zn	1.734	5.1	−9.1	1.908	5.0	1.780	−6.7	1.772	−7.1
^{94}Zr	5.668	5.0	6.7	5.31	3.3	5.607	5.6	6.358	19.7
^{96}Zr	230.6	4.8	−8.4	251.6	1.0	208.1	−17	221.0	−12
^{98}Mo	51.54	6.4	−2.9	53.1	6.3	52.21	−1.7	50.17	−5.5
^{100}Mo	18.894	4.3	0.5	18.8	4.0	20.372	8.4	19.247	2.4
^{115}In	16.33	3.8	−2.8	16.8	1.9	15.89	−5.4	15.88	−5.5
^{197}Au	15.71	1.8	0.0	15.71	1.8	15.89	1.2	15.89	1.2
^{232}Th	11.33	1.8	−1.4	11.5	3.6	11.47	−0.3	11.46	−0.4
^{238}U	103.4	1.3	0.0	103.4	1.3	102.6	−0.7	102.5	−0.8

The measured k_0 factor is proportional to the ratio of the partial gamma production cross sections σ_γ, defined by the product of the gamma emission probability P_γ and the capture cross section σ_0:

$$\frac{\sigma_{\gamma,a}}{\sigma_{\gamma,s}} = \frac{P_{\gamma,a}\sigma_{0,a}}{P_{\gamma,s}\sigma_{0,s}} = k_{0,a}\frac{M_a\Theta_s}{M_s\Theta_a}. \tag{66}$$

Partial gamma production cross sections can be used in combination with other experiments to determine the thermal cross section and the gamma emission probabilities. This possibility was generally not exploited, except in a few cases where the experimentalists explicitly reported the derived cross section values in the publication [19]. A more rigorous effort in this direction was made in the re-evaluation of the thermal capture cross section of ^{238}U, where all available measurements of the cross sections, partial cross sections (including k_0 values) and directly-measured gamma emission probabilities were analysed simultaneously by a generalised least squares procedure, taking correlations into account whenever possible [20]. This method yields a self-consistent set of cross sections, gamma emission probabilities, their uncertainties and correlations.

Q_0 measurements by the cadmium ratio method

The cadmium ratio is defined by the ratio of bare and cadmium covered reaction rates:

$$R_{Cd} = \frac{A}{A_{Cd}} = \frac{\phi_{th}\sigma_0 g G_{th} + \phi_{epi}(IG_{epi} + Jh)}{\phi_{epi}(I_{Cd}G_{epi} + Jh)}, \tag{67}$$

from which it follows that:

$$R_{Cd} = \frac{fgG_{th} + QG_{epi} + Hh}{QG_{epi}F_{Cd} + Hh};$$
$$Q = \left[\frac{gf}{R_{Cd}F_{Cd} - 1}\right]\frac{G_{th}}{G_{epi}} - \frac{(R_{Cd} - 1)Hh}{(R_{Cd}F_{Cd} - 1)G_{epi}}. \tag{68}$$

The first term in the expression for Q is well known in the literature on neutron activation analysis. The second term represents the correction for the fission spectrum contribution and vanishes if either the fission spectrum integral or the fission spectrum contribution tends to zero.

The reference Q_0 value be obtained through relation derived from Eq. (54):

$$Q_0 = \left[Q - \frac{0.429}{(2\alpha + 1)(0.55)^\alpha}\right](E_r)^\alpha + 0.429 \tag{69}$$

The only assumption in this definition is that parameters F_{Cd} and G_{epi} are approximately independent of α and that Eq. (54) adequately describes the dependence of Q on α.

It is important to consider error propagation, which originates from the uncertainty Δ_f in the measured value of f, $\Delta_{R_{Cd}}$, in the measured cadmium ratio, $\Delta_{F_{Cd}}$, in the cadmium transmission factor, Δ_h in the fission spectrum contribution and Δ_H in the fission spectrum integral. Note however, that the problem is ill-posed when the measured cadmium ratio is close to one, that is, when the contribution of thermal neutrons to the reaction rate is neglibible.

$$\Delta_Q^2 = \left|\frac{\partial Q}{\partial f}\right|^2\Delta_f^2 + \left|\frac{\partial Q}{\partial R_{Cd}}\right|^2\Delta_{R_{Cd}}^2 + \left|\frac{\partial Q}{\partial F_{Cd}}\right|^2\Delta_{F_{Cd}}^2 + \left|\frac{\partial Q}{\partial h}\right|^2\Delta_h^2$$
$$+ \left|\frac{\partial Q}{\partial H}\right|^2\Delta_H^2 \tag{70}$$

Different sets of evaluated nuclear data files were processed to obtain constants for a number of nuclides that are commonly used as monitors to determine the spectral parameters. Q_0 values were obtained from evaluated nuclear data from the JENDL-4.0 [21] and ENDF/B-VII.1 [22] libraries. The values were compared to the values in the Atlas of Neutron Resonances by Mughabghab [23] and the values from the Kayzero database, applied in k_0-NAA

[24], which are here taken as reference. The results are compared in Table 2. The columns "± (%)" gives the specified uncertainty while the columns labelled "Diff. (%)" give the percent difference from the Kayzero values.

Comparison of the Q_0 values shows that the data from the Atlas of neutron resonances by Mughabghab agrees within the quoted uncertainties with the Kayzero data for important monitor reactions, except for ^{96}Zr. The agreement between the values derived from the evaluated data libraries JENDL-4.0 and ENDF/B-VII.1 and in the Kayzero database is poorer; the values are in agreement within the quoted uncertainties in the Kayzero database for roughly half of the considered reactions.

Determination of spectral parameters

The spectral parameters in k_0-NAA are mainly the spectral ratio f and the spectrum slope parameter α. Equivalent spectral parameters implied by Eq. (60) are the energy breakpoint E_{th} between the thermal and the epithermal spectrum and the α_i parameters. Note that α is allowed to be energy-dependent, parameterised by second-order polynomial coefficients α_0, α_1 and α_2 in $\log(E)$ domain. Normally the nuclear constants for k_0-NAA are not very sensitive to the other parameters that appear in Eq. (60).

Traditionally, the spectral ratio f is determined from the cadmium ratio of the gold standard, but measured cadmium ratios of other nuclides may be used as well. Similarly, the α parameter (assumed constant) can be determined from a linear fit in the log–log scale of H_j as a function of α for several monitor nuclides j, where H_j is given by:

$$H_j(\alpha) = \left[\frac{G_{epi}}{G_{th}} \left(R_{Cd,j} - 1 \right) Q_j \left(E_{r,j} \right)^\alpha \right]. \tag{71}$$

The fission spectrum fraction can be determined from reaction rates sensitive to the fission spectrum using Eq. (16). The obvious candidates are threshold reactions that also have well-defined constants for the capture process, which may serve as a secondary standard. The expression for the fission fraction is:

$$h = \frac{G_{th} \left[g_a k_0 - g_s \frac{A_a}{A_s} \right] + G_{epi,a} Q_a k_0 - G_{epi,s} Q_s \frac{A_a}{A_s}}{H_s \frac{A_a}{A_s} - H_a k_0}. \tag{72}$$

The expression for the threshold k_0 factor defined by Eq. (59) is applicable and the standard in this case is a capture reaction for one of the isotopes of the same element. The above expression becomes much clearer if we note that for a threshold reaction g_a is zero by definition, Q_a is (close to) zero and A_a/A_s and H_s are usually small:

$$h = \frac{A_a}{A_s} \frac{G_{th} f g_s + G_{epi,s} Q_s}{H_a k_0}. \tag{73}$$

Note that Eq. (73) is given for clarity only. In practical calculations there is little penalty for using the full expression of Eq. (72).

Alternatively, the spectral parameters can be determined directly by minimising χ^2, defined as the sum of the squares of the relative differences between the measured and calculated reaction rate ratios or specific activities. Reaction rate ratios can be calculated from energy-dependent cross sections and the parameterised neutron spectrum, such as discussed in the "Neutron spectrum" section. Work is currently in progress through a Co-ordinated Research Project of the International Atomic Energy Agency. The main advantage of this approach is greater flexibility in the treatment of specific features of the neutron spectrum in some particular irradiation facility, but the pre-requisite for a broader application of the method is improved reliability of differential cross section data, gamma emission probabilities and better consistency with currently used integral data.

Conclusions

Nuclear constants used in k_0-NAA are derived from the basic nuclear data from first principles. Except for the details, most of the ideas are known, but they are scattered in various textbooks and articles; they are collected in the present paper for convenience and future reference.

Detailed analysis of underlying equations explains why the relatively simple approach of the k_0-NAA is so successful, like the accuracy of the description of the neutron spectrum using the spectral factor f and the shape factor α along with the concept of the effective resonance energy.

The fission spectrum parametrization with the factor h and an alternative definition of the k_0 factor allow for generalization of the mehod to systems with a strong fission spectrum component and threshold nuclear reactions.

Rigorous definitions of constants for k_0-NAA allows for cross-checking with differential data. Accurately measured integral constants for k_0-NAA can provide additional constraints in the process of cross section evaluation and their validation, which is beneficial to the whole nuclear community.

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