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Nuclear Reactions and Physical Models for Neutron Activation Analysis

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1 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, while up to 60 elements can be determined performing two irradiations and several gamma-spectrum measurements after different decay periods. 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 [1] and reference materials of the International Atomic Energy Agency.

The k_0 standardisation method of NAA (k_0-NAA), a concept launched in 1975, can be interpreted as an absolute standardisation method. It relies k_0 and Q_0 factors and a few other parameters [2], which are composite constants that can be derived from the 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 NAA and their relation to the exact definition from the basic nuclear data,
- identify sources of uncertainties and approximations and their propagation to calculated reaction rates.

The overall objective is to define the basis that will improve the understanding of the definitions and lead eventually to the improvement in the nuclear constants for NAA, as well as the basic nuclear data where accurately measured composite constants for NAA can provide additional constraints for the basic nuclear data evaluation process.

2 Definitions

2.1 Reaction rates

Reaction rate A of particles travelling through a material with nuclei of that material is parameterised by the reaction cross section $\sigma(E)$, which is the property of the material and the neutron flux spectrum $\varphi(E)$, which is related to the density of the particles travelling through the material and their speed

$$\varphi(v) = v \, n(v) \,. \tag{1}$$

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

$$A = K \int_0^\infty \sigma(E)\varphi(E)\, dE \; ; \qquad \varphi(1eV) = 1. \tag{2}$$

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

$$A = K \int_0^\infty \sigma(v)\, v \cdot n(v)\, dv. \tag{3}$$

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

$$A = K \left[\int_0^{E_{cd}} \sigma(E)\varphi(E)\, dE + \int_{E_{cd}}^\infty \sigma(E)\varphi(E)\, dE \right]. \tag{4}$$

The above expressions are *exact*; the problem is that neither the cross sections nor the neutron flux spectrum are known accurately due to the strong dependence of the parameters on the particle energy. For example, to represent the capture cross section of ^{238}U to within 0.1% tolerance, several 100 000 data points are needed.

Without loss of generality, the expression commonly used in NAA for reaction rates is given by:

$$A = \varphi_t\, \sigma_0\, g\, G_t\, _+\, \varphi_f\, I\, G_f \qquad = \qquad \varphi_t\, \sigma_0 \left[g\, G_t + \frac{1}{f}\, Q\, G_f \right], \tag{5}$$

where the symbols have the following meaning:
  φ_t thermal flux,
  φ_f epithermal flux,
  f ratio of thermal to epithermal flux φ_t/φ_f,
  σ_0 thermal cross section at 2200 m/s neutron speed,
  g generalised g-factor that measured the deviation of the thermal cross section from $1/v$ shape,
  I effective resonance integral,
  Q ratio of the resonance integral and the thermal cross section I / σ_0,
  G_t thermal flux depression factor,
  G_f resonance self-shielding factor.

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

In the k_0 standardization method of NAA the measured activities are compared to the activity of some well-defined standard, which is usually gold, because it has well-known cross sections and a gamma ray of accurately-known intensity that is relatively easy to measure. It can be shown that the ratio of the activity of the sample A_a relative to the activity of the standard A_s is related to the ratio of reaction rates, given by the following expression:

$$\frac{A_a}{A_s} = k_{0,a} \frac{G_t\, f\, g_a + G_{f,a}\, Q_a}{G_t\, f\, g_s + G_{f,s}\, Q_s} \tag{6}$$

where

$$k_{0,a} = \frac{M_s \Theta_a \gamma_a \sigma_{0,a}}{M_a \Theta_s \gamma_s \sigma_{0,s}} \qquad (7)$$

and the constants with index a for sample and s for standard are:

M_x — molar mass of sample,
Θ_x — natural atomic abundance,
γ_x — gamma emission probability of the measured gamma ray,
$\sigma_{0,x}$ — thermal capture cross section.

2.2 Thermal cross-section σ_0, g-factor and thermal flux depression factor G_t

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

$$A_t = K \int_0^{v_{cd}} \sigma(v)\, v \cdot n(v)\, dv. \qquad (8)$$

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

$$\sigma(v) = \sigma_0 \frac{v_0}{v} \qquad (9)$$

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_t

$$A_t = K\, \sigma_0 v_0 \int_0^{v_{cd}} n(v)\, dv = K\, \sigma_0 v_0 N_t, \qquad (10)$$

where N_t is the total thermal neutron density. Note that the reaction rate proportional to the total thermal neutron density is independent of the neutron speed distribution $n(v)$.

In the energy domain the equivalent expression for the thermal reaction rate is

$$A_t = K \int_0^{E_{cd}} \sigma(E)\varphi(E)\, dE \qquad (11)$$

Substituting the expression for kinetic energy into equation (9) for a $1/v$ absorber

$$\sigma(E) = \sigma_0 \sqrt{\frac{E_0}{E}} \qquad (12)$$

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 reaction rate 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.

Assuming that the thermal neutron flux has Maxwellian distribution

$$\phi(E) = E\, e^{-E/kT}, \qquad (13)$$

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

$$A_t = K \int_0^{E_{cd}} \sigma(E) E\, e^{-E/kT}\, dE. \tag{14}$$

For a $1/v$ absorber

$$A_t = K\, \sigma_0 \sqrt{E_0} \int_0^{E_{cd}} \sqrt{E}\, e^{-E/kT}\, dE. \tag{15}$$

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

$$\sigma_{th} = \frac{\int \sigma(E)\phi(E)\, dE}{\int \phi(E)\, dE} = \frac{K\, \sigma_0 \sqrt{E_0} \int \sqrt{E}\, e^{-E/kT}\, dE}{K \int E\, e^{-E/kT}\, dE}. \tag{16}$$

Extending the integration limits from 0 to ∞, 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 cross section is

$$\sigma_{th} = \frac{K\, \sigma_0 (kT)^{3/2} \sqrt{kT_0} \sqrt{\pi}/2}{K\, (kT)^2} = \frac{\sqrt{\pi}}{2} \sigma_0 \sqrt{\frac{T_0}{T}}. \tag{17}$$

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 non-ideal cross section behaviour by introducing the Westcott g-factor, but still assumed that the spectrum was Maxwellian. 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. Comparing equations (4) and (5) see that:

$$\varphi_t\, \sigma_0 g\, G_t = K \int_0^{E_{cd}} \sigma(E)\varphi(E)\, dE. \tag{18}$$

Arbitrarily we define

$$\varphi_t = K\, \frac{\sqrt{\pi}}{2} \int_0^{E_{cd}} \varphi(E)\, dE. \tag{19}$$

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

$$g = \frac{\int_0^{E_{cd}} \sigma(E)\ \varphi(E)\ dE}{\sigma_0\ \dfrac{\sqrt{\pi}}{2} \int_0^{E_{cd}} \varphi(E)\ dE} = \frac{2}{\sqrt{\pi}}\ \frac{\sigma_{th}}{\sigma_0}. \tag{20}$$

Substituting the integrals with the expression for σ_t 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

$$g_w = \sqrt{\frac{T_0}{T}} \, . \tag{21}$$

The upper integration limit of E_{cd} is normally not a problem because the Maxwellian distribution function falls off very rapidly and the contribution to the integral above 0.5 eV is very small.

The generalised g-factor can be calculated easily from the cross sections, which are readily 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.

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 equation (5), to irradiation facilities with spectra that deviate significantly from the Maxwellian shape in the thermal region.

The thermal neutron flux depression factor G_t 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, 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 [3,4]

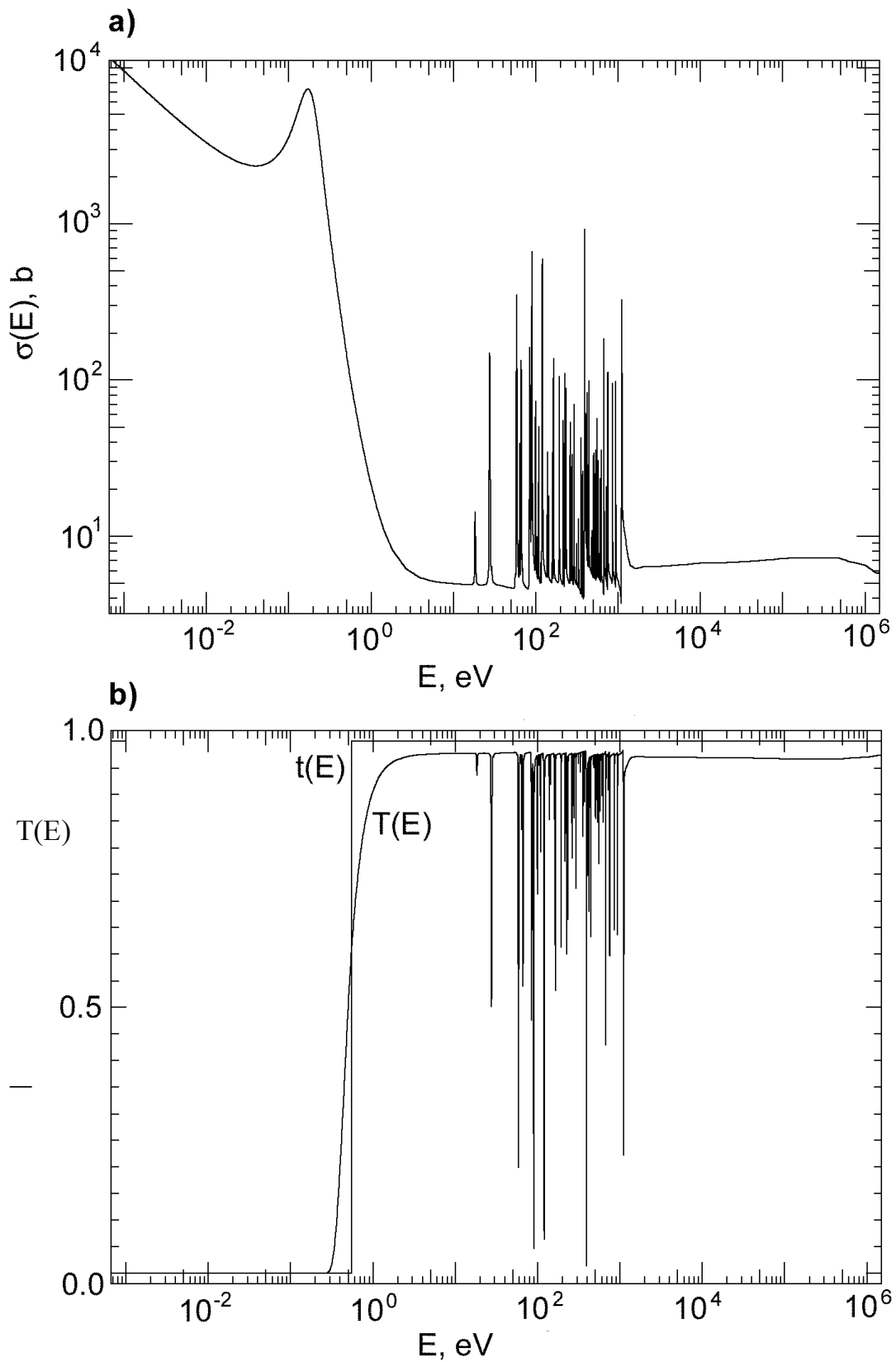### 2.3   Resonance integral I, cadmium transmission factor F_{cd} and Q value

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_c and an arbitrarily chosen upper limit E_3:

$$I_0 = \int_{E_{cd}}^{E_3} \sigma(E) \psi(E) \, dE \quad ; \quad \psi(E) = \frac{1}{E} \, . \tag{22}$$

Similarly, the reference Q_0 value is given by:

$$Q_0 = \frac{I_0}{\sigma_0} \tag{23}$$

This definition is rather artificial because such a spectrum with sharp cutoff energies cannot be produced experimentally. Measurements are usually done in well-thermalised reactor spectra, which approximately follow the 1/E behaviour in the epithermal energy range. If the irradiation channel is separated from the fission source 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 cutoff energy, which is effectively introduced by a suitable definition of the weighting function $\phi(E)$. At the low energy end, thermal neutrons are usually filtered by a strong absorber like cadmium, which has a huge resonance at 0.178 eV and relatively weak resonances at higher energies. The total cross section of cadmium is shown in Figure 1 part a).

Figure 1:   **a) Total cross section of cadmium.**
                 b) Cadmium transmission function for a 1mm thick cadmium cover.

Introducing the cadmium transmission function $t(E)$, a more general definition of the measured resonance integral under cadmium cover I_{cd} in a real spectrum $\phi^*(E)$ is obtained:

$$I_{cd} = \int_0^\infty t(E)\sigma(E)\phi^*(E)\,dE .$$

(24)

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:

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

(25)

A more realistic form of the cadmium transmission function is:

$$t(E) = e^{N_{cd}\,d\,\sigma_{cd}(E)}$$

(26)

where d is the cadmium cover thickness, σ_{cd} is the cadmium cross section and N_{cd} is the number density of cadmium atoms in the cover. It is calculated as:

$$N_{cd} = \frac{\rho_{cd}N_A}{M_{cd}} ,$$

(27)

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 the 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 dimension 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. Note that this is the first approximation introduced so far.

Resonance integral defined by equation (23) is a measurable quantity. This is to be compared with the required form evident from equations (4) and (5). The cadmium transmission factor F_{cd} is introduced to compensate for the difference:

$$I = \int_{E_{cd}}^{E_3} \sigma(E)\phi(E)\,dE = \frac{1}{F_{cd}}\int_0^\infty t(E)\sigma(E)\phi(E)\,dE .$$

(28)

From this it follows that:

$$F_{cd} = \frac{\displaystyle\int_0^\infty t(E)\sigma(E)\phi(E)\,dE}{\displaystyle\int_{E_{cd}}^{E_3} \sigma(E)\phi(E)\,dE} .$$

(29)

Deviation of F_{cd} from unity arises from the cadmium transmission function and possibly from the difference in the upper integration limit. The contribution of the later is negligible 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 equation (29), 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. It 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 NAA databases very few nuclides have F_{cd} factors that deviate from one, and even those have to be considered with care. Commonly adopted value for [186]W is 0.908 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 [8]. Direct calculation using cross sections to simulate the transmission of neutrons through 1 mm cadmium layer results in a cadmium transmission factor that differs from one 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 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 equation (23):

$$Q = \frac{I}{\sigma_0}$$ (30)

The reference Q_0 for an ideal $1/E$ spectrum is already defined by equation (23). Relation between the reference Q_0 and the general Q is discussed in Section 2.5. Some comparisons between measured values and those calculated using cross sections from evaluated nuclear data files are given in Section 3.2.

2.4 Resonance self-shielding factor G_f

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 $\phi^*(E)$ is expressed in terms of the spectrum unperturbed by the resonance absorber $\phi(E)$ by the expression:

$$\phi^*(E) = \frac{\sigma_0 + \lambda \sigma_p(E)}{\sigma_0 + \lambda \sigma_a(E) + \sigma_s(E)} \phi(E)$$ (31)

where:

    σ_0 Bondarenko background cross section, which measures the effective dilution of the resonance absorber,

    σ_a absorption cross section of the resonance absorber,

    σ_s scattering cross section of the resonance absorber,

σ_{p} potential scattering cross section of the resonance absorber,

λ Goldstein - Cohen parameter - a "measure" of the resonance width,

$\phi(E)$ smooth spectrum (unperturbed by the resonances).

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

Resonance theory is based on the assumption that that the absorber atom is surrounded by a moderator of approximately constant cross section, represented 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:

$$\sigma_0 = \frac{1}{N_a} \sum_i N_i \lambda_i \sigma_i \tag{32}$$

where
    N_a absorber atom number density,
    N_i number density of the i-th moderator nucleus,
    σ_i cross section of the i-th moderator nucleus,
    λ_i 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 [5].

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 on in an infinite medium. In reactor physics this is called the equivalence theorem. 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:

$$\sigma_0 = \frac{1}{N_a} \left[\Sigma_e + \sum_i N_i \lambda_i \sigma_i \right] \tag{33}$$

The escape cross section is given by the simple expression:

$$\Sigma_e = \frac{a}{l} \tag{34}$$

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

The mean chord length for a convex volume is given by

$$l = \frac{4V}{S} \tag{35}$$

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

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

$$G_f = \frac{\int_{E_{cd}}^{E_3} \sigma(E) \phi^*(E)\, dE}{\int_{E_{cd}}^{E_3} \sigma(E) \phi(E)\, dE} \tag{36}$$

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_0. The user can then calculate the relevant value of σ_0 from equations (33-34) and retrieve the required G_f by interpolation. The main approximations in this approach are those inherent in the IR resonance approximation and the assumption that G_f factors are not sensitive to small deviations in the weighting spectrum $\phi(E)$, which is usually assumed to be of the $1/E$ form.

2.5   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

$$\phi(E) = \frac{1}{E^{1+\alpha}} \quad, \tag{37}$$

where α is a constant, and assuming that resonances can be represented by the single-level Breit-Wigner formula, an analytical expression is available for the dependence of the Q value on α in terms of the reference Q_0 value in a pure $1/E$ spectrum:

$$Q(\alpha) = \frac{Q_0 - 0.429}{(E_r)^\alpha} + \frac{0.429}{(2\alpha + 1)(0.55)^\alpha} \tag{38}$$

To verify the validity of the approximation for $Q(\alpha)$, exact values were calculated directly from the cross sections based on Equations (28) and (20) for a set of α values in the range between –0.1 and +0.1, and using idealised cadmium transmission function with cutoff at 0.55 eV. By inverting equation (38) an expression for E_r can be obtained:

$$E_r(\alpha) = \left\{ \frac{Q_0\, 0.429}{Q(\alpha) - \dfrac{0.429}{(2\alpha + 1)(0.55)^\alpha}} \right\}^{1/\alpha} \tag{39}$$

The average E_r is define by the integral

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

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 by the average E_r) for different nuclides is shown in Figure 2. The calculated average effective resonance energy E_r also differs quite significantly from the values usually adopted for NAA, which were derived from the available resonance parameters. The comparison is shown in Table 1. In the case of ^{94}Zr the difference exceeds a factor of two.

Table 1: Comparison of Effective Resonance Energies E_r for Neutron Activation Analysis

E_r nuclide	Kayzero [eV]	This work [eV]	Dif. [%]
Mn-55	468.0	488.1	4.3
Co-59	136.0	122.4	-10
Zn-64	2560.0	4268.2	67
Zr-94	6260.0	15401.0	146
Zr-96	338.0	387.2	15
Mo-98	241.0	319.5	33
Mo-100	672.0	899.5	34
Au-197	5.7	5.7	0
Th-232	54.4	74.4	37
U-238	16.9	18.2	7.7

A similar analysis was performed for $Q(\alpha)$. Exact values calculated by direct integration of equations (22) and (23) were compared to the approximate ones based on equation (38), using Q_0 and average E_r calculated as described before. For easier comparison between different nuclides all values were normalised with the corresponding Q_0 value. The comparison is shown in Figure 3. 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 equation (38) does not introduce a large error into the calculated $Q(\alpha)$. The differences are larger for nuclides with a higher effective resonance energies E_r and may exceed 3% in some cases. It is interesting to note that equation (38) always leads to the underprediction of $Q(\alpha)$.
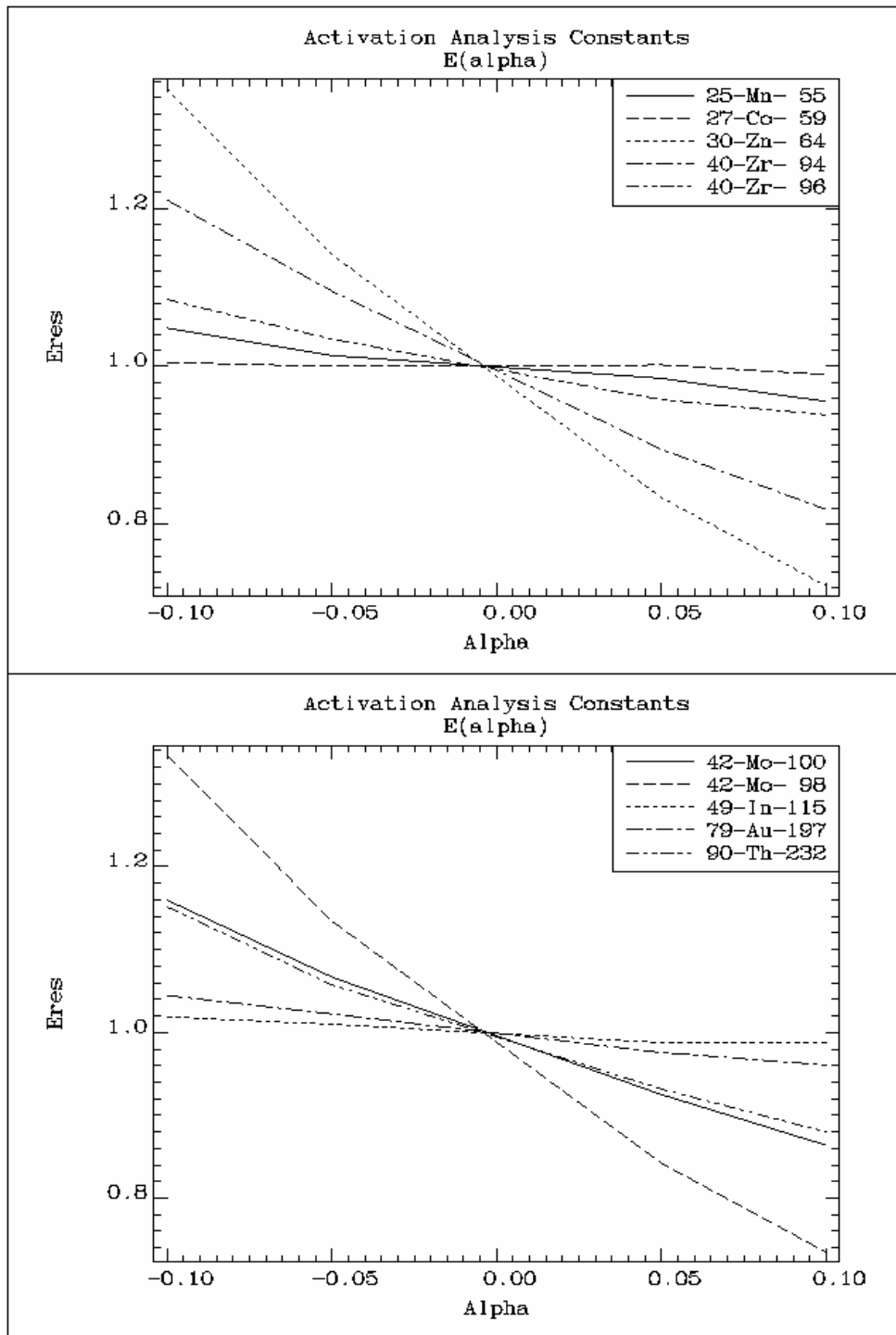
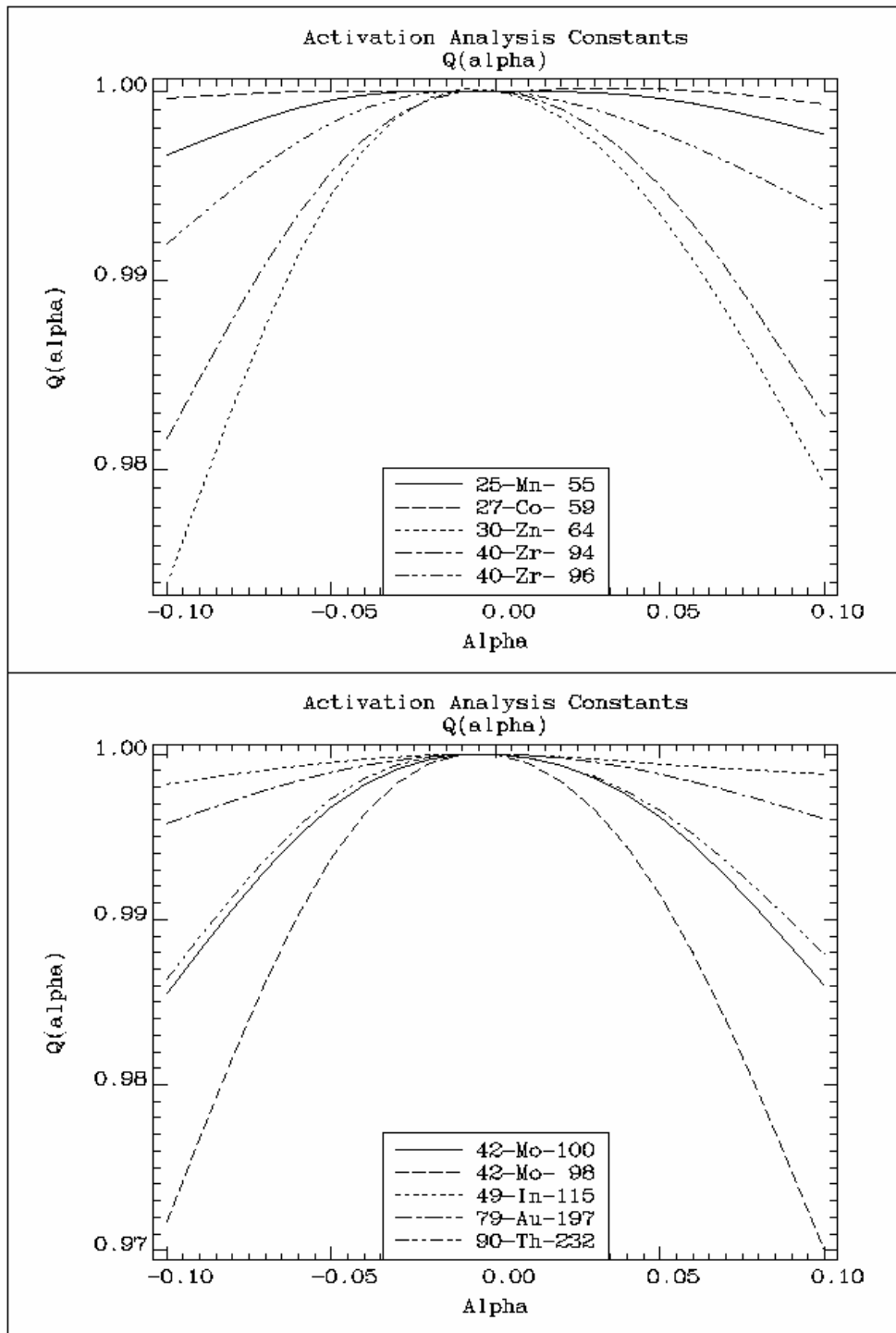**Figure 2: Variations of E_r with α for different nuclides.**

Figure 3: Comparison of exact and approximate *Q(α)* values for different nuclides.

2.6 Neutron Spectrum

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. 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_t, the epithermal region ψ_e and the fission spectrum ψ_f defined by:

$$\begin{aligned}
\psi_t &= C_t\, E\left[e^{-E/kT} + C_{t1}e^{-E/kT_1} + C_{t2}e^{-E/kT_2}\right] \\
\psi_e &= E^{-1-\alpha_0 - \alpha_1 \log E - \alpha_2 (\log E)^2} \\
\psi_f &= C_f\, e^{-E/W_a}\, \sinh\left(\sqrt{EW_b}\right) \quad \text{or} \\
&= C_f\sqrt{E}\, e^{-E/E_T}
\end{aligned} \tag{40}$$

where:
- k is the Boltzman constant,
- α_j are the constants that determine deviation from the $1/E$ spectrum in the epithermal range,
- W_a, W_b are the parameters of the Watt fission spectrum,
- T is the temperature,
- C_t, C_f are continuity constants such that $\psi_t(E_t) = \psi_e(E_t)$ and $\psi_f(E_f) = \psi_e(E_f)$, respectively,
- E_t, E_f are breakpoints between thermal, epithermal and the fast spectrum range.

The full function ψ representing the spectrum is defined by:

$$\psi = K_t\,\psi_t + K_e\,\psi_e + K_f\,\psi_f \quad , \tag{41}$$

where
$$K_e = 1 \quad \text{for} \quad E_t < E < E_f$$
$$\quad\quad 0 \quad \text{otherwise}$$

$$K_t = 1 + O_t - K_e$$
$$K_f = 1 + O_f - K_e.$$

Parameters O_t 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:
- Thermal region is a superposition of three Maxwellian functions at different temperatures, which allows one to model distortions in the spectrum at low energies.
- The α- parameter that measured the deviation from the $1/E$ shape is allowed to be energy-dependent.
- Fast fission spectrum can be the Maxwellian or the Watt function.

A Monte Carlo simulation of the whole core with irradiation channels of the TRIGA Mark-II reactor in Ljubljana is presented to illustrate the features of the analytical function. The calculated spectrum was binned on a fine energy mesh and is shown in Figure 4 as squares. The statistical uncertainty error bars were suppressed for clarity. Fitting of the parameters was done with the GRUPINT code as follows:

Fit-0: represents the initial guess with α=0, the thermal energy breakpoint at E_t=0.2 eV, thermal Maxwellian spectrum at T=300K and a small contribution (3.6%) of a secondary Maxwellian spectrum at T_1=640K. The fast energy breakpoint is E_f=2 MeV.

Fit-1: is the result of fitting the alpha parameter, allowing α to vary linearly (α_0=0.0495, α_1=-0.0179).

Fit-2: includes fitting of the thermal spectrum parameters (E_t=0.2199 eV, C_{t1}=0.0359, O_t=0.8418).

Fit-3: optimises fast spectrum parameters, but the changes to the spectrum are small (E_f=18.1 MeV).
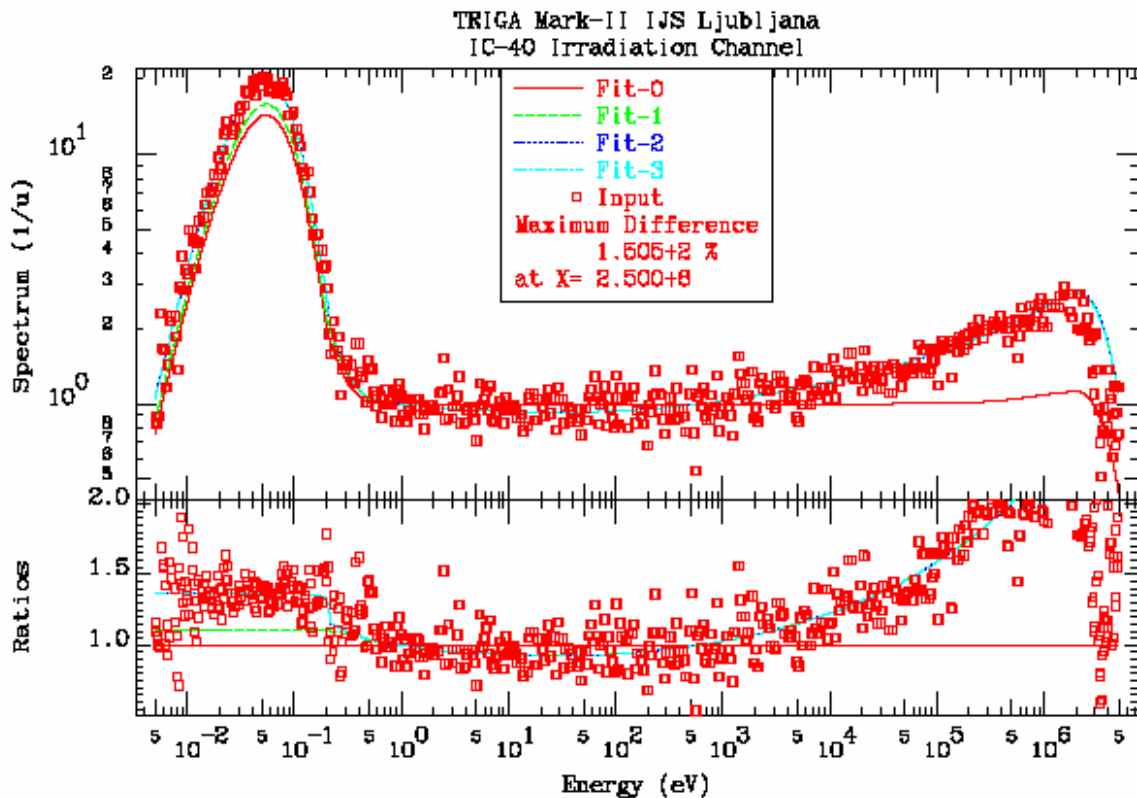

Figure 4: Calculated spectrum fitted with analytical spectrum function.

The exercise demonstrates the potential of the analytic function to represent the real spectra in irradiation facilities for the use in spectrum unfolding procedures, smoothing of the calculated spectra, etc.

3 Experimental Measurements

3.1 k₀ measurements, thermal capture cross section and gamma emission probability

From equations (6) and (7) 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):

$$k_{0,a} = \frac{M_s \Theta_a P_{\gamma,a} \sigma_{0,a}}{M_a \Theta_s P_{\gamma,s} \sigma_{0,s}} = \frac{A_a}{A_s} \cdot \frac{G_t \ f \ g_s \ + \ G_{f,s} \ Q_s}{G_t \ f \ g_a \ + \ G_{f,a} \ Q_a} \ . \tag{42}$$

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 resulting from the decaying nucleus and the capture cross section

$$\frac{\sigma_{\gamma,a}}{\sigma_{\gamma,s}} = \frac{P_{\gamma,a} \sigma_{0,a}}{P_{\gamma,s} \sigma_{0,s}} = k_{0,a} \frac{M_a \Theta_s}{M_s \Theta_a} \ . \tag{43}$$

Partial gamma production cross sections have not been used for the determination of the thermal cross sections, except in a few cases where the experimentalists explicitly reported the derived cross section values in the publication [6]. An 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 k₀ values) and directly-measured gamma emission probabilities were analysed simultaneously by a generalised least squares procedure, taking correlations into account whenever possible [7]. This method yields a self-consistent set of cross sections, gamma emission probabilities, their uncertainties and correlations.

3.2 Q₀ measurements by the cadmium ratio method

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

$$R_{cd} = \frac{A}{A_{cd}} = \frac{\phi_t \sigma_0 \ g \ G_t + \phi_f I \ G_f}{\phi_f I_{cd} \ G_f} = \frac{\phi_t \sigma_0 \ g \ G_t + \phi_f I \ G_f}{\phi_f I \ F_{cd} \ G_f} \tag{44}$$

from which it follows that

$$R_{cd} = \left[1 + g \frac{f}{Q} \frac{G_t}{G_f} \right] \frac{1}{F_{cd}} \quad ; \quad Q = \frac{g \ f}{\left(R_{cd} F_{cd} - 1 \right)} \frac{G_t}{G_f} \ . \tag{45}$$

The reference Q_0 can be obtained through relation derived from equation (38):

$$Q_0 = \left[Q + \frac{0.429}{(2\alpha + 1)(0.55)^\alpha} \right] (E_r)^\alpha + 0.429 \tag{46}$$

The only assumption in this definition is that parameters F_{cd} and G_f are approximately independent of α and that equation (38) adequately describes the dependence of Q on α.

It is important to consider error propagation, which originates from the uncertainty Δf in the measured value of f and ΔR_{cd} in the measured cadmium ratio.

$$\Delta Q = \frac{g}{R_{cd}F_{cd}-1}\left[\Delta f + \frac{F_{cd}\Delta R_{cd}}{R_{cd}F_{cd}-1}\right]\frac{G}{G} \tag{47}$$

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. Label EAF-99 refers to the European Activation Library, RNAL to the Reference Neutron Activation Library, JENDL/D-99 to the Japanese activation library and FENDL/A-2 to the FENDL-2 activation library. The Nudat results were retrieved from the IAEA web page "http://www-nds.iaea.org/". The corresponding values commonly applied in NAA are labelled Kayzero. The results are compared in Table 2. The column "+/- %" gives the specified uncertainty while the columns labelled "Dif [%]" give the percent difference from the Nudat values.

Comparison of the Q_0 values shows that the Kayzero data for important monitor reactions agree very well with the Nudat values, except for zirconium. There is also good agreement with the values derived from evaluated data files. Particularly, excluding [55]Mn and [94]Zr, the EAF-99 values of Q_0 are practically always within the experimental uncertainty of the Nudat values.

Table 2: Comparison of Q_0 nuclear constants for neutron activation analysis.

	Kayzero	+/- %	Nudat	+/- %	EAF-99	Dif. [%]	RNAL	Dif. [%]	JENDL/D99	Dif. [%]	FENDL	Dif. [%]
Mn-55	1.053	2.6	1.053	3.7	0.845	-19.7	1.110	5.5	0.845	-19.7	1.110	5.5
Co-59	1.993	2.7	1.990	2.9	1.930	-3.1	1.893	-4.9	1.934	-2.8	1.925	-3.3
Zn-64	1.908	4.9	1.908	7.0	1.933	1.3	1.923	0.8	-		1.922	0.7
Zn-68	3.190	1.4	-		3.632		3.634		-		-	
Zr-94	5.306	3.3	4.609	9.6	6.743	31.6	6.747	46.4	-		6.743	46.3
Zr-96	251.6	0.97	231.4	10.5	242.1	4.4	-		-		242.1	4.6
Mo-98	53.10	6.3	53.08	9.4	54.01	1.7	54.06	1.9	-		54.01	1.8
Mo-100	18.84	4.3	18.84	5.6	19.65	4.1	19.46	3.3	-		19.40	3.0
Au-197	15.71	1.8	15.71	1.9	15.48	-1.5	15.46	-1.6	15.45	-1.6	15.44	-1.8
Th-232	11.53	3.6	11.5	4.3	11.1	-4.1	-		10.9	-5.4	10.9	-5.5
U-238	103.4	1.3	103.4	1.8	100.0	-3.4	-		99.6	-3.6	99.2	-4.0

3.3 Determination of spectral parameters

The spectral parameters in NAA are mainly the spectral ratio f and the spectrum slope parameter α. Equivalent spectral parameters implied by equation (40) are the energy breakpoint E_t between the thermal and the epithermal spectrum and the α_j 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 NAA are not very sensitive to the other parameters that appear in equation (40).

The spectral ratio f is usually 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:

$$H_{(j)}(\alpha) = \left\{ \frac{G_e}{G_t} \left(R_{cd(j)} - 1 \right) Q_{(j)} \left(\overline{E}_{r(j)} \right)^{\alpha} \right\}^{-1} \tag{48}$$

Alternatively, the spectral parameters can be determined directly by minimising χ^2, which is defined as the sum of the squares of the relative differences between the measured and calculated cadmium ratios or specific activities. Reaction rate ratios can be calculated with GRUPINT from energy-dependent cross sections and the parameterised neutron spectrum. GRUPINT then performs χ^2- minimisation by a systematic variation of the spectral parameters. An example is described in the next section.

4   Examples of Application

4.1   Determination of spectral parameters

To determine nuclear constants for NAA of zirconium, experimental data from earlier measurements by De Corte et al [9] on the Thetis reactor at Gent were analysed. Measured cadmium ratios for monitors ^{55}Mn, ^{59}Co, ^{64}Zn, ^{98}Mo, ^{100}Mo, ^{197}Au, ^{232}Th and ^{238}U were available. The nuclear constants were calculated from the pointwise cross section data with GRUPINT. Spectral parameters E_f=1 MeV, α_1=α_2 =0 were fixed while parameters α and E_t were varied by the code until χ^2 was minimised. The residues from the fitting procedure are shown in Table 3. Their magnitude is comparable to the uncertainty in the Q_0 values, what strongly supports the self-consistency of the data and the fitting procedure.

Table 3: Residues from fitting spectral parameters to measured cadmium ratios.

Target	Product	R_{Cd} (ref)	Dif. [%]
Mn-55	Mn-56	203.2	-5.4
Co-59	Co-60	114.7	-2.7
Zn-64	Zn-65	131.1	1.7
Mo-100	Mo-101	14.62	-2
Mo-98	Mo-99	5.433	1.3
Au-197	Au-198	12.71	-0.2
Th-232	Th-233	19.43	6.1
U-238	U-239	2.914	2.9

The results of the fitting procedure are as follows:

0.0757   Fitted α parameter (this work).
0.071   Value by the authors in the original analysis.

159.9   Fitted sub-cadmium to epi-cadmium spectrum ratio of 159.9.
159.9±5.2   Average spectral ratio obtained from measured cadmium ratios of the monitors using constants generated by GRUPINT. The uncertainty is the standard deviation,
162   Value of the spectral ratio from the original analysis.

The fitted parameters α and f compare well with the values from the original analysis by the authors.

4.2 Q_0 values of the zirconium isotopes

The average cadmium ratio given below is calculated from five measurements and the quoted uncertainty is the standard deviation. Together with the fitted spectral ratio f and its uncertainty (defined in the previous section for the Thetis reactor), the Q values calculated from equation (38) are:

$$R_{cd\,(meas.)}(^{94}Zr) = 57.16 \pm 0.81 \qquad Q_{(meas.)}(^{94}Zr) = 2.827 \pm 0.093$$
$$R_{cd\,(meas.)}(^{96}Zr) = 2.006 \pm 0.023 \qquad Q_{(meas.)}(^{96}Zr) = 157.8 \pm 5.2$$

Calculating Q with GRUPINT for the same spectral parameters gives the following values:

$$Q_{(calc.)}(^{94}Zr) = 3.468$$
$$Q_{(calc.)}(^{96}Zr) = 154.6$$

Assuming that equation (38) is approximately valid, the error in Q is propagated to Q_0 through the relation:

$$\Delta Q_0 = E^{\alpha}\,\Delta Q \qquad\qquad (49)$$

Therefore, corrected Q_0 values are obtained by adding $E^{\alpha}\Delta Q$ to the calculated ones:

$$Q_{0\,(calc.)}(^{94}Zr) = 6.743 \qquad Q_{0\,(corr.)}(^{94}Zr) = 5.50 \pm 0.19$$
$$Q_{0\,(calc.)}(^{96}Zr) = 242.1 \qquad Q_{0\,(corr.)}(^{96}Zr) = 247.2 \pm 8.1$$

The corrected estimate of Q_0 for ^{96}Zr is slightly higher than obtained from the original analysis, but well within the uncertainty interval. The results indicate that the Nudat value is low and that the assigned uncertainty is underestimated. The corresponding Q_0 for ^{94}Zr resulting from this analysis is slightly lower compared to the original one, but the estimated uncertainty is significantly larger, primarily due to the contribution of the uncertainty in the spectral ratio f. Due to the large uncertainty assigned to Q_0 in Nudat the values are consistent.

4.3 Sensitivity of the results on other spectral parameters

Higher order terms describing the epithermal and fast energy range of the spectrum were not included in the fitting procedure, because the monitors are fairly insensitive to these parts of the spectrum. A manual variation of parameters was performed. The influence on the corrected Q_0 is shown in Table 4. The choice of parameters is weakly supported by a small decrease in the residuals in the fitting procedure. Generally the effects are stronger for ^{94}Zr, which has a very high effective resonance energy, but it is within or close to the estimated uncertainty of the reference values, which were calculated with nominal values of the additional spectral parameters.

Table 4: Sensitivity of Q_0 to perturbations in selected spectral parameters.

	Ref	α_1 +.002	α_2 -.0001	E_f 0.5MeV
40-Zr- 94	5.50	5.70	5.32	5.23

40-Zr- 96	247.2	245.0	249.0	248.8

The results shown above serve mainly to illustrate the procedures and should not be interpreted as the final analysis of the Q_0 values of the zirconium isotopes.

References

[1]   E.S. Gladney et al.: "Standard Reference Materials: Compilation of Elemental Concentration Data for NBS Chemical, Biological, Geological and Environmental SRMs", NBS Special Publication 260-111, NIST, Gaithersburg (1987), MD.

[2]   A. Simonits: J. Radioanal. Nucl. Chem. **24** (1975) 31.

[3]   J. Salgado, I.F. Gonçalves, E. Martinho: Development of a Unique Curve for Thermal Neutron Self-Shielding Factor in Spherical Scattering Materials, Nucl. Sci. Eng. 148, 426-428 (2004).

[4]   M. Blaauw: The Derivation and Proper Use of Stewart's Formula for Thermal Neutron Self-Shielding in Scattering Media, Nucl. Sci. Eng., 124, 431 (1996).

[5]   F. Leszczynski, D. Lopez Aldama, A. Trkov: WIMS-D Library Update, International Atomic Energy Agency, draft document, August 2003, http://www-nds.iaea.org/wimsd/libraries.htm.

[6]   F. De Corte and A. Simonits: ko-Measurements and related nuclear data compilation for (n, γ) reactor neutron activation analysis, J. Radioanal. Nucl. Chem., 133 (1989) 43-130.

[7]   A. Trkov, G. L. Molnár, Zs. Révay, S. F. Mughabghab, R. B. Firestone, V. G. Pronyaev, A. L. Nichols, M. C. Moxon: Revisiting the U-238 Thermal Capture Cross Section and Gamma-ray Emission Probabilities from Np-239 Decay, Nucl. Sci. Eng., to be published, June 2005.

[8]   A. Simonits, F. De Corte, T. El Nimr, L. Moens, J. Hoste: Comparative study of measured and critically evaluated resonance integral to thermal cross-section ratios, Part II, J. Radioanal. Nucl. Chem. Articles, 81 (1984) 397.

[9]   F. De Corte, private communication.