NEUTRON ACTIVATION ANALYSIS
WITH $K_0$-STANDARDISATION:
GENERAL FORMALISM
AND PROCEDURE

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Instrumental neutron activation analysis with $k_0$-standardisation is a powerful tool for multi-element analysis at a broad range of trace element concentrations. An overview is given of the basic mechanisms, fundamental equations and general procedure of the method. The different aspects involved in the description of the neutron activation reaction rate are discussed, applying the Hogdahl convention. A general activation-decay formula is derived and its application in NAA demonstrated. Relevant $k_0$-definitions for different activation decay schemes are summarised and upgraded to situations of extremely high flux. The main standardisation techniques for NAA are discussed, emphasising the peculiarities of the $k_0$-standardisation. Some general aspects of the basic equipment and its calibration are discussed, such as the characterisation of the neutron field and the tuning of the spectrometry part. A method for the prediction and optimisation of the analytical performance of INAA is presented.
I. INTRODUCTION

1.1 NAA as an analytical tool

As an analytical tool, Neutron Activation Analysis (NAA) still has its place amongst the most sensitive methods for several trace elements. Due to many years of nuclear research and a continuous improvement of the activation analysis technique at various labs, the theoretical understanding of the method and the determination of the physical parameters involved have become well established. All sources of systematic or random variation are identifiable and predictable down to the limits of detection.

The neutron activation analysis technique is based on a few fundamental facts: the high penetrability of matter by neutrons, the probability for $(n,\gamma)$ reactions on a wide variety of isotopes and the existence of a delayed witness signal of these reactions; i.e. the characteristic radiation emitted in the specific decay of the unstable nuclei which are formed. The rules that govern these processes are known and accurate quantitative information is available in numerous cases.

Consequences of the basic mechanism are that NAA is a bulk analysis method with multi-element capability, that the relation between measured signal and trace element concentration is mostly matrix independent, that matrix preparation can be kept simple and that treatment of the sample after irradiation - like e.g. chemical separation - is possible. Another interesting feature is that NAA is insensitive to some commonly occurring elements like e.g. H, C, N, O, which makes them ideal constituents for matrices. Since the witness signal, i.e. the characteristic $\gamma$-rays, have a high penetrability through matter, the analyst can use extended geometry samples.

The general procedure for Instrumental Neutron Activation Analysis is that the matrix is exposed to an intense neutron flux (like in a nuclear reactor channel) during a well defined time period and is later subjected to gamma spectrometry for identification and concentration evaluation of the activated trace elements. The identification is done primarily by determination of the gamma ray energies and in second place by consideration of the characteristic half-life of the decay chain.
Figure 1.1: Schematic illustration of the physical phenomena involved in Neutron Activation Analysis. A neutron interacts with a target nucleus by non-elastic collision, thus forming a highly excited compound nucleus. The compound nucleus has a short lifetime and can deexcite in different ways which usually involve emission of nuclear particles or gamma rays. Prompt Gamma NAA is based on the in-situ measurement of the latter. In most cases, the new nucleus is radioactive and will further evolve towards stability. Its nuclear decay is often accompanied by the emission of very characteristic gamma rays, which can be considered as a fingerprint. A statistical correlation exists between the number of target nuclei and the amount of gammas in the activation spectrum recorded by a spectrometer.
1.2 Complementary to other methods

Although very sensitive and accurate non-nuclear analytical techniques exist, NAA has several advantages which support its use as a complementary tool.

First of all, a different suite of elements is measurable by using nuclear rather than chemical reactions, and the detection limits are quantitatively different. Equally important, the kinds of errors to which nuclear methods are subject are due to different physical phenomena and are therefore likely to give a different bias in the results. Furthermore, the results are independent of the chemical state of the elements; since NAA is merely based on nuclear processes, it is not influenced by atomic binding. The method is also free from analytical blank and other problems related to dissolution, since little pre-irradiation sample preparation is required. Therefore the instrumental NAA technique - apart from radiochemistry - can be performed already with some basic chemical skills, such as simple weighing and packaging.

Whereas most analytical techniques are available in any institute or industrial plant requiring its results, this is not the case with NAA. It is commonly performed at research reactors paid by the government or university and the irradiations and/or the full analytical analyses have to be made available to the users. This limited accessibility is probably one of the reasons why the excellent properties of the technique are not always fully known and exploited in the chemical world.

1.3 $k_o$-standardisation

An interesting step forward for the NAA technique was the introduction of the $k_o$-standardisation by De Corte (INW, Gent) [DEC87] and Simonits (KFKI, Budapest) [SIM75]. (For an overview of the relevant references concerning the $k_o$-technique, the reader is referred to [DEC94a].)

The burden of choosing the best set of nuclear data amongst the abundant available information was largely lifted by the publication of the so-called $k_o$-factors for the major $\gamma$-lines observed in neutron activation spectra [DEC87] [DEC89] [DEC93] [SIM97] [DEC97]. The $k_o$-numbers - containing information about the molar mass, isotopic abundance, $\gamma$-intensity and ($n_{th}\gamma$) cross section of the considered isotope - are reactor and detector independent. Moreover, they can also be derived directly from NAA experiments. Besides the gain in accuracy and traceability through the use of a homogeneous set of (verifiable) nuclear data, the $k_o$-method eases the way for panoramic element analyses with minimal flux monitoring. These arguments encouraged the IRMM and SCK•CEN to
collaborate on the implementation of the k_0-NAA technique at the BR1 reactor [ROB94] [HAR94].

1.4 Overview of this report

In chapter II we elaborate on the different aspects involved in the determination of the relevant neutron activation reaction rate; the reactor neutron energy spectrum, the activation cross section, the Høgdahl convention, neutron self shielding, competing nuclear reactions, etc.

In chapter III the activation and decay laws are discussed. Original general formulas for activation and decay are presented and their use demonstrated. Their derivation is discussed in detail in appendix A. A classification of the decay types encountered in NAA is shown in appendix B.

In chapter IV the main standardisation methods used in NAA are discussed, with an emphasis on the characteristics of the k_0-standardisation.

In chapter V some aspects of the procedure are considered; the basic set-up, the determination of the neutron field characteristics, the detector calibration (efficiency, dead-time, true coincidence effects) and concentration calculations. Explicit correction formulas for true coincidence loss in the spectrometer are presented in appendix C.

In chapter VI a method for the prediction and optimisation of the analytical performance of INAA is presented.

A list of symbols is given in appendix D.
II. THE NEUTRON ACTIVATION RATE

2.1 Reactor neutron spectrum representation

The reactor neutrons are mainly prompt neutrons from the fission reaction. They are evaporated typically at $10^{15}$s after scission. At this time the fission fragments have reached almost their full acceleration from mutual coulomb repulsion. Consequently the neutrons receive on the average a comparable acceleration, varying slightly from one fissioning system to another. These fast neutrons lose their energy by collisions with surrounding materials and finally become thermalised.

The reactor neutron energy spectrum can be represented in a semi-empirical way as the superposition of three components: the fission neutrons, a thermalised fraction and in between a fraction of partly thermalised neutrons; the so-called epithermal neutrons. Following formal representation could be used:

$$\varphi(E) = \varphi_f(E) + \varphi_e(E) + \varphi_{th}(E)$$

$$= 0.484 \cdot \Phi_f \cdot e^{-E} \cdot \sinh(\sqrt{2.E}) \quad \text{ (E > 10 keV)}$$

$$\frac{\Phi_e(E)}{E^{1+\alpha}} \cdot \left[ \left(1 - \exp\left(\frac{E}{E_c}\right)\right) \cdot \exp\left(\frac{E}{E_d}\right) \right] \quad \text{ (0.1 eV < E < 100 keV)}$$

$$\varphi_{th} \cdot \frac{E}{E_0^2} \cdot \exp\left(-\frac{E}{E_0}\right) \quad \text{ (E < 1 eV)}$$

with $\varphi_f$, $\varphi_e$ and $\varphi_{th}$ respectively the fast, epithermal and thermal neutron flux per energy unit (cm$^{-2}$.s$^{-1}$.eV$^{-1}$), $\Phi_f$ the total fast neutron flux, $\Phi_e$ the epithermal neutron flux, $\Phi_{th}$ the total thermal neutron flux (cm$^{-2}$.s$^{-1}$), $E_c=0.1$ eV, $E_d=300$ keV and $E_0=k.T_0$ (=0.0253 eV at 20°C).

Formula 2.2 is the Watt representation for fission neutrons (assuming isotropic neutron evaporation in the centre of mass system of the accelerated fragment). The thermal component is represented by the well known Maxwell-Boltzmann distribution in formula 2.4. Formula 2.3 describes the typical $1/E^{1+\alpha}$ behaviour of the epithermal neutron component. Two extra factors are added here to provide a smooth connection with the Maxwell-Boltzmann and Watt spectrum. A hypothetical example of the total neutron spectrum is shown in figure 2.1.
2.2 Activation cross section behaviour

The probability of inducing an (n,γ) process is expressed by the corresponding cross section σ [barn = 10^{-24} cm^2]. The (n,γ) cross sections are typically proportional to 1/v (or 1/E^{0.5}), with several resonances superposed on this general behaviour. An example is shown in figure 2.2. The resonances, and also the '1/v'-tail, are described by the Breit-Wigner equation [BRE36]. In most cases the resonances are situated in the epithermal energy region. Only a few (n,γ) reactions of interest in NAA show a significant deviation from the 1/v-dependence in the energy region below 1.5 eV, due to low lying resonances.
Figure 2.2: Activation cross section versus neutron energy $E$ for $^{60}$Co($n,\gamma$)$^{60}$Co

2.3 Reaction rate

The ($n,\gamma$) reaction rate per nucleus of isotopes undergoing a certain neutron flux is given by:

$$R = \int_0^\infty \varphi(E) \cdot \sigma(E) \, dE$$  \hspace{3cm} (2.5)

with $R$ in [s$^{-1}$], $\varphi(E)$ in [cm$^2$.s$^{-1}$.eV$^{-1}$] and $\sigma(E)$ in [cm$^2$]. An equivalent formula can be used when writing the flux and cross section as a function of the neutron velocity $v$:

$$R = \int_0^\infty \varphi(v) \cdot \sigma(v) \, dv$$  \hspace{3cm} (2.6)

with $\varphi(v)$ in [cm$^3$].

So, in principle the reaction rate could be calculated from a numerical integration of the product of the energy/velocity dependent neutron flux and the ($n,\gamma$) cross section. The
impracticality of this procedure has lead to the adoption of conventions or formalisms in order to simplify the calculation of the reaction rate. In this work the Høgdahl convention is adopted. It deals with the contribution of the thermal neutrons and that of the epithermal neutrons separately. Often measurements with Cd-covered samples are used to obtain information on the epithermal part. Before giving an outline of the Høgdahl convention, the concept of the effective Cd cut-off energy is discussed in next paragraph.

2.4 Effective cadmium cut-off energy

When irradiating nuclides under a Cd-cover, the \((n,\gamma)\) reaction rate is drastically reduced in the low energy region, due to the extremely high neutron absorption cross section in Cd. This is mainly caused by the \(^{113}\text{Cd}(n,\gamma)\) resonance at 0.178 eV. For high neutron energies, however, the cross section is 4 orders of magnitude lower. These are excellent qualities for a selective neutron filter. For a monodirectional neutron beam hitting directly on a 1 mm Cd-foil, the transmission function \(T(E)\) can be calculated from:

\[
T(E) = \exp\left[-\sigma_{\text{tot}}(E) \cdot N_{\text{Cd}} \right]
\]

(2.7)

where \(\sigma_{\text{tot}}(E)\) [cm\(^2\)] is the total neutron absorption cross section and \(N_{\text{Cd}}\) [cm\(^{-2}\)] the number of Cd atoms per unit of surface area. The result of such calculations is shown in figure 2.3, together with the used cross section data. The transmission is about zero for \(E < 0.2\) eV and close to one for \(E > 2\) eV.

The transmission curve can almost be idealised as a step function situated at the so-called 'Cd cut-off energy' \(E_{\text{cd}}\); i.e. 0 at \(E < E_{\text{cd}}\) and 1 at \(E > E_{\text{cd}}\). So only epicadmium neutrons are seen and the epicadmium \((n,\gamma)\) reaction rate can be written as:

\[
R_{\text{e}} = \int_{E_{\text{cd}}}^{\infty} \varphi(E) \cdot \sigma(E) \, dE
\]

(2.8)

Goldstein et al [GLS61] recommended a value of \(E_{\text{cd}}=0.55\) eV for nuclides with a \(1/\nu\) cross section behaviour at least up to \(E\sim1.5\) eV, irradiated in the centre of a cylindrical Cd box with 1 mm wall thickness and a height/diameter ratio = 2. The material to be irradiated should be relatively small, in order not to touch the Cd vial walls, where local neutron flux perturbations arise. The neutron flux should be homogeneous and isotropic, with an epithermal fraction following the \(1/E\) law down to \(E\sim0.35\) eV. As shown in [DEC87], this \(E_{\text{cd}}\)-value does not change critically when used in irradiation sites with \(1/E^{1/\nu}\) type of fluxes, nor does the influence of the Maxwellian neutron flux on \(E_{\text{cd}}\) in the case of extreme
thermalisation or of high temperatures $T_n$ present a problem.

Figure 2.3: (upper part) Cd total cross section curve versus $E$
(lower part) actual and idealised Cd transmission functions (see text)
2.5 The Høgdahl convention.

The (extended) Høgdahl convention [HØG65] [DEC87] is based on two principle ingredients: the proportionality of the \((n,\gamma)\) cross section with \(1/v\) up to \(E_{Cd}\) and the \(1/E^{1+\alpha}\) shape of the epithermal neutron spectrum \((E > E_{Cd})\). The contribution of the fission neutrons to the total \((n,\gamma)\) reaction rate is negligible and therefore not considered in the convention.

In view of the equivalence of the reaction rate representations by the formulas 2.5 and 2.6, the total reaction rate can in any case be written as:

\[
R = \int_0^{v_{Cd}} \varphi(v) \sigma(v) \, dv + \int_{E_{Cd}}^\infty \varphi(E) \sigma(E) \, dE
\]

(2.9)

with \(v_{Cd}\) the neutron velocity corresponding to \(E_{Cd}\). When the Høgdahl conditions are met, this can be considerably simplified to:

\[
R = \sigma_0 v_0 \int_0^{v_{Cd}} n(v) \, dv + \Phi_e \cdot (1eV)^\alpha \int_{E_{Cd}}^\infty \sigma(E) / E^{1+\alpha} \, dE
\]

(2.10)

\[
= \Phi_s \cdot \sigma_0 + \Phi_e \cdot I_0(\alpha)
\]

(2.11)

with:

\(\Phi_s = n_s v_0\); the subcadmium (or 'thermal') neutron flux [cm\(^2\).s\(^{-1}\)] and \(n_s = \int_0^{v_{Cd}} n(v) \, dv\) the subcadmium neutron density [cm\(^3\)] \((\varphi(v) = n(v) \cdot v)\). This notation is indifferent of the explicit shape of the neutron energy distribution!

\(\Phi_e = \varphi(1eV) \cdot (1eV) = \varphi(E) \cdot E^{1+\alpha} / (1eV)^\alpha\); the epithermal neutron flux [cm\(^2\).s\(^{-1}\)] with 1 eV an arbitrarily chosen reference energy.

\(\sigma_0\); the \((n,\gamma)\) cross section at a chosen velocity \(v_0 = 2200\) m/s (corresponding to the most probable neutron energy \(E_0\) in the Maxwell-Boltzmann distribution at 20°C; see formula 2.4).

\(I_0(\alpha)\); the resonance integral for a \(1/E^{1+\alpha}\) spectrum [cm\(^2\)]

The calculation of the reaction rate is hereby reduced to the determination of a limited number of parameters. The mechanism is roughly as follows: 1) \(\sigma_0\) and \(I_0\) are determined by a physical method for a common standard reaction, like e.g. \(^{197}\)Au\((n,\gamma)^{198}\)Au; 2) by measuring the reaction rates \(R\) and \(R_e = \Phi_e I_0(\alpha)\) for this monitor (formula 2.11 and 2.8) the flux
parameters $\Phi_s$ and $\Phi_e$ can be deduced; 3) finally $\sigma_0$ and $I_0$ can be determined for other $(n,\gamma)$ reactions from the corresponding $R$ and $R_e$.

### 2.6 The resonance integral and the effective resonance energy

In the literature the evaluated resonance integral $I_0$ in a perfect $1/E$ epithermal neutron spectrum can be found for several nuclides. In most reactor channels a $1/E^{1+\alpha}$ dependence is more valid, in which the effect of $\alpha$ is often not negligible. Instead of evaluating the integral for each neutron field, $I_0(\alpha)$ is calculated relatively from $I_0(\alpha=0)$. This is done by introducing the concept of the effective resonance energy $\bar{E}_r$ [RYV69]. This would be the energy of a hypothetical single resonance which gives the same resonance activation rate $I_0'$ as the actual resonances of the isotope, the $1/v$ part subtracted, i.e. [MOE79]:

$$I_0'(\alpha) = I_0' \cdot (1\text{eV})^{\alpha} \bar{E}_r^{\alpha}$$

with

$$I_0' = I_0 - \int \frac{\sigma_0 \cdot v_0}{v} \frac{dE}{E} = I_0 - 2\sigma_0 \sqrt{\frac{E_0}{E_{Cd}}}$$

and

$$I_0'(\alpha) = I_0(\alpha) - \int \frac{\sigma_0 \cdot v_0}{v} \cdot (1\text{eV})^{\alpha} \frac{dE}{E^{1+\alpha}}$$

$$= I_0(\alpha) - 2\sigma_0 \sqrt{\frac{E_0}{E_{Cd}}} \frac{(1\text{eV})^{\alpha}}{(1+2\alpha)E_{Cd}^{\alpha}}$$

(2.13)

The $\alpha$-dependent resonance integral is finally evaluated from [DEC86]:

$$I(\alpha) = \left( I_0 - 0.429\sigma_0 \right) \frac{\bar{E}_r^{\alpha}}{E_{Cd}} + 0.429\sigma_0 / [(2.\alpha + 1)0.55^{\alpha}] \cdot (1\text{eV})^{\alpha}$$

(2.15)

which is indeed found by combining the formulas 2.12-2.14, on condition that $E_{Cd}=0.55$ eV and $E_0=0.0253$ eV.

The effective resonance energy is dependent on $\alpha$, and therefore on the specific neutron field used. Nevertheless De Corte et al. opted for the use of one fixed, reactor-independent value for each nuclide, calculated through the first order approximation of the Breit-Wigner...
expression for $\bar{E}_r^{\alpha}$, which leads to [MOE79] [DEC86]:

$$\left[ \bar{E}_r(\alpha) \right]^{-\alpha} = \sum_i \frac{w_i E_i^{\alpha}}{\sum w_i} \quad \rightarrow \quad \ln(\bar{E}_r) \approx \frac{\sum_i w_i \ln(E_{r,i})}{\sum w_i}$$  \hspace{1cm} (2.16)

with $i$ the resonance indicator
- $w = (g \cdot \Gamma_\gamma \cdot \Gamma_n / \Gamma) / E_r^2$
- $g =$ statistical weight factor
- $\Gamma_\gamma =$ radiative resonance width
- $\Gamma_n =$ neutron resonance width
- $\Gamma =$ total resonance width

Error propagation calculations predict only a small error induced on the final results of the analytical data. The most sensitive cases are those with low thermal activation contribution and with strong resonances lying far apart on the energy scale. The use of a fixed $\bar{E}_r$ can then, in extreme irradiation conditions, lead to errors of some percent on the analytical result. If this is judged unacceptable, a correction factor can be derived from the second order term in the series expansion of the Breit-Wigner expression (2.16) [JOV84] [DEC86]:

$$\bar{E}_r(\alpha) = \bar{E}_r \cdot e^{p \cdot \alpha}$$  \hspace{1cm} (2.17)

$$p = \frac{\sum_i w_i \left[ \ln \left( \frac{E_{r,i}}{\bar{E}_r} \right) \right]^2}{2 \cdot \sum w_i}$$  \hspace{1cm} (2.18)

Tabulated $p$-values for some relevant cases can be found in [DEC86] [DEC87].

### 2.7 Sample-induced neutron flux deviations

#### 2.7.1 Flux modification in samples

For several reasons, the flux in a set of coirradiated samples can be unequally distributed. Three cases, besides the possible presence of a neutron flux gradient in the irradiation facility, are demonstrated in figure 2.4: neutron self-shielding, neutron flux depression and self-moderation. Also flux hardening and scattering effects can be responsible for flux deviations in the samples.
Figure 2.4 [ERD86] Different cases of neutron flux distortion in and nearby irradiated samples:
1) neutron self-shielding due to high neutron absorption in the sample;
2) neutron flux depression in the vicinity of a highly neutron absorbing medium;
3) self-moderation of epithermal and fast neutrons by scattering on light nuclei, finally adding to the thermal flux component.

 Flux hardening is due to the fact that low-energy neutrons, because of the $1/v$ dependence of the absorption cross section, are in principle easier caught than neutrons of higher energy. Their number is therefore less abundant than predicted by the Maxwellian distribution. In most practical cases, however, this effect is negligible [ERD86].

 Self-moderation means that incoming neutrons can reduce their energy by scattering on the (light) sample atoms. Due to the large energy transfer in collisions with protons, a thermalisation of the epithermal and fast neutron fractions are most likely to occur in the presence of hydrogen. Self-moderation, mainly observed in aqueous solutions, counteracts the flux-hardening. Effects of this nature can be simulated with Monte Carlo computations.

 Neutron self-shielding is a considerable decrease of the neutron flux in the sample due to the absorption of neutrons undergoing nuclear reactions. It is a typically sample-induced flux modification which is nearly irrespective of the irradiation site. The shielding effect is also felt as a flux depression in the vicinity of the sample. (This can be understood by considering the general absorption law for a unidirectional neutron beam traversing the sample, reducing the outcoming flux by an exponential factor.)

 The reaction rate calculated from equation 2.11 has sometimes to be corrected for neutron self-shielding. Correction factors, $G_{lh}$ and $G_{c}$, have to be determined for thermal and epithermal neutrons separately. Evidently, the best way of dealing with the self-shielding is avoiding it; e.g. by using thin wires or foils, by diluting fine powders with inert materials or
by dissolving chemical substances in inert solvents. But, even then one should be able to judge when self-shielding is negligible.

Also neutron scattering, in combination with the absorption processes, can be responsible for a noticeable effect on internal flux. In following sections, thermal neutron self-shielding is considered first in a purely absorbing matrix with simple geometry and next in a mixed scattering and absorbing medium. Epithermal self-shielding is discussed separately.

**2.7.2 Thermal neutron self-shielding in a pure absorber**

The thermal correction factor $G_{\text{th}}$ for a homogeneous and isotropic Maxwellian neutron flux distribution can be calculated in the case of simple geometries, making simplifying assumptions on the neutron field [STE59] [ZWE60] [FLE82] [ERD86] [BLA97]. The first assumption is that the neutrons can be treated as monoenergetic (neutron cross section and geometry become separable) and the second is treating the neutron field as either isotropic or as a parallel beam.

One defines the thermal self-shielding factor as:

$$G_{\text{th}} = \frac{\Phi_{\text{sample,th}}}{\Phi_{\text{th}}}$$  \hspace{1cm} (2.19)

Considering a pure absorber (no scattering), one applies the entities absorption mean free path $l$ and macroscopic absorption cross section $\Sigma_a$ in the sample, defined by:

$$l^{-1} = \sum_i N_i \cdot \bar{\sigma}_{\text{abs},i} = \Sigma_a$$  \hspace{1cm} (2.20)

with: $N_i = \text{the atom density of element } i [\text{cm}^{-3}]$

$$\bar{\sigma}_{\text{abs}} = \frac{\sigma_{0,\text{abs}}}{2} \sqrt{\frac{293.59 \pi}{T_n}} [\text{cm}^2]$$

$\sigma_{0,\text{abs}}$ = absorption cross section of the element at $v_0=2200 \text{m/s}$

Cross section values $\sigma_{0,\text{abs}}$ can be found in e.g. Table VIII.3-1 of [DEC87]. (When lacking information on the neutron temperature $T_n$, a value of 60°C (333.15 K) can be used for the

* If also scattering occurs, then the total cross section has to be applied (see next paragraph).
average absorption cross section to a good approximation.) Nuclides in a homogeneous mixture all undergo the same shielding effect for thermal neutrons (since $\sigma(v) \sim 1/v$). The $G_\text{th}$ value should be calculated from all elements in the mixture which give rise to significant neutron absorption and should then be applied to all $(n,\gamma)$ reactions.

The self-shielding factor for a sphere with radius $r$ [cm] can be calculated from [FLE82]:

$$G_{\text{th, sphere}} = \frac{3}{\xi^3} \left[ \frac{\xi^2}{2} - 1 + (1 + \xi) e^{-\xi} \right]$$

or

$$G_{\text{th, sphere}} = 1 - \frac{9}{8} \cdot \xi$$

(for $\xi < 0.003$) (2.21) (2.22)

with: $\xi = 2V/S \cdot 1^1 = 2/3 \cdot r \cdot \Sigma_a$

$x = 3 \xi$

$V =$ sample volume [cm$^3$]

$S =$ sample surface [cm$^2$]

For symmetry reasons the expression is valid for an isotropic neutron field as well as for parallel neutron beams. (This was not fully realised by Fleming, who inconsistently applied different cross sections for these situations [FLE82].)

For an infinite slab (foil of thickness $t$ [cm]) in an isotropic neutron field:

$$G_{\text{th, foil}} = \frac{1}{\xi} \left[ \frac{1}{2} - 2E_3(\xi) \right]$$

with: $E_3(\xi) = \frac{1}{2} \left[ (1-\xi) e^{-\xi} + \xi^2 E_1(\xi) \right]$

$$-E_1(-\xi) = \int_{\xi}^{\infty} \frac{u}{\xi} du = -\left( 0.577215 + \ln(\xi) + \sum_{n=1}^{\infty} \frac{(-\xi)^n}{n.n!} \right) \cdot$$

or

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

and in a parallel neutron beam, with axis normal to the foil:

$$G_{\text{th, foil}} = \frac{1-e^{-\xi}}{\xi}$$

(2.23) (2.24)

with $\xi = 2V/S \cdot 1^1 = t \cdot \Sigma_a$, as defined above.

* Perform summing up to $n=5$ if $\xi<0.1$, $n=10$ for $0.1<\xi<1$ and $n=\lceil \text{int}(\xi)+5 \rceil$ for $\xi>1$
For an infinite cylinder (wire with radius \( r \) [cm]) in an isotropic neutron field [FLE82]:

\[
G_{\text{th, wire}} = \frac{2 \xi}{3} \left[ 2 \left[ K_1(\xi) I_1(\xi) + K_0(\xi) I_0(\xi) - 1 \right] + \frac{K_1(\xi) I_1(\xi)}{\xi} - K_0(\xi) I_1(\xi) + K_1(\xi) I_0(\xi) \right]
\]

or

\[
G_{\text{th, wire}} \approx 1 - \frac{4 \xi}{3} + \frac{\xi^2}{2} \left( \ln(2/\xi) + 5/4 - 0.577215 \right)
\]

with \( \xi = 2 V/S . l^{-1} = r \cdot \Sigma_a \)

\( K_n(\xi) \) and \( I_n(\xi) \) Bessel functions

For a finite cylinder (short wire or thick foil with radius \( r \) and height \( h \)) in an isotropic neutron field [ERD86]:

\[
G_{\text{th, cyl}} = G_{\text{th, foil}} + \left( \frac{8 \xi^4}{5} \cdot e^{-3.725} + 0.4 \cdot e^{8 \xi} \right) \left( G_{\text{th, sphere}} - G_{\text{th, foil}} \right)
\]

with \( G_{\text{th, sphere}}, G_{\text{th, foil}} \) calculated as defined above, using \( \xi = 2 V/S . l^{-1} = r . h/(r+h) \cdot \Sigma_a \)

### 2.7.3 Self-shielding in a scattering medium

In voluminous and hydrogenous samples one can expect a perturbation of the neutron field due to scattering. Scattering does not only influence the neutron energy distribution but can also alter the internal neutron density. Kitto [KIT87] and Mackey [MAC91] performed Prompt Gamma NAA experiments where 'sensitivity enhancements' were observed when analysing hydrogenous samples. The effects were larger than what could be accounted for by a mere neutron thermalisation. It has been shown through Monte Carlo calculations that in a scattering matrix the mean path length of the neutron in the matrix may increase or decrease because of scattering [COP89], depending on the shape of the body and the neutron field - isotropic, parallel beam or intermediate.

The expressions for neutron self-shielding in previous paragraph ignore the effect of neutron scattering in the absorber. This effect is often small and can be estimated using the expression [STE59]:

\[
G_{\text{th}} = \frac{G_0}{1 - \frac{\Sigma_s}{\Sigma_t}(1-G_0)}
\]

with \( \Sigma_s, \Sigma_t \); total and scattering macroscopic cross section in the medium
$G_0$; a hypothetical self-shielding factor for a non-scattering body with identical
total cross section as the sample ($\Sigma_0 = \Sigma_s + \Sigma_a$)

In the literature some confusion has arisen on the procedure and the interpretation of the
symbols [STU57] [STE59] [ZWE60] [FLE82]. Blaauw [BLA97] summarised the method as
following: first an intermediate self-shielding factor $G_{in}$ must be computed using the total
cross section $\Sigma_0$, as if it were $\Sigma_s$ and the body did not scatter neutrons. Then equation 2.27 is
used to correct for the scattering in the body and to obtain the final self-shielding factor $G_{lh}$.
(This way some discrepancies in [FLE82] are avoided.)

### 2.7.4 Epithermal neutron self-shielding

Calculation of the epithermal neutron self-shielding factor $G_c$ is considerably more difficult.
Since epithermal shielding is mainly caused by high resonance cross sections, it is quite
specific to a particular nuclide. Interference will occur when a nuclide of analytical interest
has a resonance which is partly or completely overlapped by the resonance of a major
absorber.

An overview of calculational methods for resonance self-shielding is given in [DNV92].
Approximate formulas are available in the case of one dominant resonance [CHR58]
[DEC87] and relevant nuclear data can be found in [MUG81] [MUG84]. Trubey et al.
[TRU59] did calculations for a purely absorbing foil. The calculation procedure of Roe
includes Doppler broadening of the resonances [ROE54]. In practice, an experimental
determination of the epithermal self-shielding is often preferred to a theoretical one.

It has been shown [DNV92] that the resonance self-shielding has little effect on the nominal
value of the effective resonance energy, which justifies the use of a fixed value.

### 2.7.5 Self-shielding in typical Au and Zr foils

It is of interest to mention here the $G_{th}$ and $G_c$ values for some monitors frequently applied in
$k_{in}$-NAA. The Au-Al alloys with ~0.1% Au content have $G_{th}=G_c=1$ for both 1 mm diameter
wire and 100 $\mu$m thick foil. For a 0.5% Au content, $G_{th}=1$ but $G_c=0.985$ [HOW62]. The
$^{91}$Zr$(n,\gamma)$ and $^{92}$Zr$(n,\gamma)$ reactions were experimentally examined as a function of the Zr foil
thickness [SIM87]. $G_{th}=1$ up to 500 $\mu$m thickness. $G_c=0.983 (\pm 0.3\%)$ for $^{91}$Zr$(n,\gamma)$ and
0.973 (±0.4%) for $^{92}$Zr$(n,\gamma)$ for the frequently used 125 $\mu$m Zr foils.
2.8 Non 1/v nuclides

The fact that the Høgdahl convention was chosen is related to its simplicity, its accuracy and its applicability to roughly 150 analytically interesting \((n,\gamma)\) reactions. Only in a few cases the convention does not apply, the most important being \(^{151}\text{Eu}(n,\gamma)^{152}\text{Eu}\), \(^{151}\text{Eu}(n,\gamma)^{152}\text{Eu}\), \(^{168}\text{Yb}(n,\gamma)^{169}\text{Yb}\) and \(^{176}\text{Lu}(n,\gamma)^{177}\text{Lu}\). For these reactions, the cross section does not follow the required 1/v behaviour up to \(-1.5\) eV, being the energy at which the transmission of neutrons through a cadmium cover approaches unity (see paragraph 2.4 and 2.5). The simplified expression for the thermal reaction rate is no longer valid (see formula 2.11). Still other reactions show slight deviations from the 1/v behaviour, leading to small errors when applying the Høgdahl convention. Even the \(^{198}\text{Au}\) monitor should be added to this list (0.2% error).

This situation can be resolved by applying the more sophisticated Westcott formalism [WCT55] [WCT62], which was modified to account for the \(1/E^{1/\nu}\) epithermal neutron spectrum shape [DEC94b]. In this formalism the non 1/v cross section dependence is accounted for through the so-called Westcott \(g(T_e)\)-factor. This implies that \(T_e\) should be measured as an additional neutron spectrum parameter [DEC93]. For reactions with a pure 1/v behaviour, a direct relation can be expressed between the equations for the Høgdahl and the Westcott formalism respectively [VHK94]. Alternatively the Stoughton-Halperin convention can be applied [STO59].

2.9 Cd-transmission factor for epithermal neutrons

The non-ideality of the Cd-transmission function can create a deviation of the reaction rate \(R_e\) for Cd-covered nuclides as to the expected value \(G \cdot \Phi_e \cdot I_0(\alpha)\). Yet. the latter expression remains true for the epithermal fraction in an uncovered irradiation! The Cd-transmission factor \(F_{cd}\) for epithermal neutrons can in principle be defined as:

\[
F_{cd} = \frac{(R_e)_{cd}}{[G_e \cdot \Phi_e \cdot I_0(\alpha)]}
\]  

(2.28)

the ratio between the Cd-covered reaction rate \((R_e)_{cd}\) and the (bare) epithermal reaction rate \(R_e\). Usually \(F_{cd}\)-factors do not significantly differ from unity. However, when the resonances of Cd and the Cd-covered isotope partially overlap (e.g. \(^{186}\text{W}(n,\gamma)\)), \(F_{cd}\) can be markedly lower than unity. This is also the case for isotopes with a giant resonance in the 1-10 eV range, which will be partly suppressed by the high energy tailing of the dominant \(^{112}\text{Cd}\) resonance at 0.178 eV (see figure 2.3). Well known cases are \(^{115}\text{In}\) (1.457 eV) and \(^{197}\text{Au}\) (4.906 eV). \(F_{cd}\) can also be higher than one, when resonantly scattered neutrons in the Cd are
resonantly captured in the covered isotope (e.g. $^{65}$Cu : 233 eV resonance, while $^{111}$Cd : 233.4 eV).

Calculated or measured $F_{\text{cd}}$-values can be found in [ELN81] or in tables V.3-3 and VIII.3-1 of [DEC87].

### 2.10 Competing nuclear reactions

Up to now, only the $(n,\gamma)$ reaction is considered for the formation of the unstable isotope $^{A}ZX$, from which the radioactive decay will be monitored:

$$^{A}Z^{-1}X + n \rightarrow ^{A}ZX + \gamma \rightarrow \begin{cases} ^{A}Z_{+1}X \ (\beta^-) \\ ^{A}Z_{X^g} \ (\gamma) \\ ^{A}Z_{-1}X \ (\text{EC}) \\ ^{A}Z_{-1}X \ (\beta^+) \end{cases}$$

However the isotope can also be created by other processes; primary interferences induced by neutrons, like $(n,n')$, $(n,n)$, $(n,2n)$, $(n,p)$, $(n,\alpha)$, $(n,f)$ or secondary reactions induced by $\gamma$s or charged particles available from the $(n,\gamma)$, $(n,p)$ or $(n,\alpha)$ reactions. Fortunately these are threshold reactions, which are only evoked in a fast neutron field. In a research reactor, the fast neutron flux is in general much lower than the thermal neutron flux, and in addition the fast neutron cross sections for these reactions are considerably lower than the thermal $(n,\gamma)$ cross sections. Therefore, the contributions of interfering reactions can only become significant if the concentration of the interfering element in a sample is much higher than that of the element of interest. Evidently, interference of secondary reactions is even more seldom, either because the particles have too low energy or too low intensity.

Some $(n,n')$ and $(n,2n)$ interferences of practical importance are [DEC87] :

- $^{136}\text{Ba}(n,\gamma)^{137m}\text{Ba}$ interfered by $^{137}\text{Ba}(n,n')^{137m}\text{Ba} \quad \text{and} \quad ^{138}\text{Ba}(n,2n)^{137m}\text{Ba}$
- $^{134}\text{Ba}(n,\gamma)^{135m}\text{Ba}$ interfered by $^{135}\text{Ba}(n,n')^{135m}\text{Ba} \quad \text{and} \quad ^{136}\text{Ba}(n,2n)^{135m}\text{Ba}$
- $^{116}\text{Sn}(n,\gamma)^{117m}\text{Sn}$ interfered by $^{117}\text{Sn}(n,n')^{117m}\text{Sn} \quad \text{and} \quad ^{118}\text{Sn}(n,2n)^{117m}\text{Sn}$
- $^{110}\text{Cd}(n,\gamma)^{111m}\text{Cd}$ interfered by $^{111}\text{Cd}(n,n')^{111m}\text{Cd}$
- $^{86}\text{Sr}(n,\gamma)^{87m}\text{Sr}$ interfered by $^{87}\text{Sr}(n,n')^{87m}\text{Sr}$
- $^{76}\text{Se}(n,\gamma)^{77m}\text{Se}$ interfered by $^{77}\text{Se}(n,n')^{77m}\text{Se}$

In cases of high neutron exposure (long irradiation time, high neutron flux), also second order reactions have to be anticipated. Two types occur : those who enhance the presence of a trace
element and those who (seemingly) lower it. Indeed, activation products of a major constituent (having adjacent atomic numbers) may decay to a stable isotope of the trace element, gradually adding to its concentration. On the other hand, 'concentration losses' might occur due to burn-up of the activation product; these are mostly cases of two subsequent \((n,\gamma)\) reactions. The analyst will therefore deduce a smaller concentration of the trace element, since a fraction of the activation product is lost. Obviously this effect can be expected in particular for activation products having a high \((n,\gamma)\) cross section. In figure 2.5 a schematic overview is given of the different types of interferences.

![Figure 2.5: Schematic view of different types of interferences on a simple activation reaction](image)

The effects of ingrowth and burn-up can be calculated from activation formulas (see paragraph 3.4). Also the influence of primary reactions can be determined; theoretically, on condition that the fast neutron flux is known, or experimentally.

Irrespective of whether the fast neutron induced reaction is considered as an interference or on the contrary as a useful activation mechanism, knowledge of the cross section averaged in the fast neutron spectrum is of importance. It is defined as:

\[
\bar{\sigma} = \int_{0}^{\infty} \sigma(E) \cdot \chi(E) \, dE
\]

(2.29)
where $\sigma(E)$ is the activation cross section and $\chi(E)$ the normalised flux density distribution of the fission neutron spectrum. The reaction rate per nucleus is then:

$$R_f = \Phi_f \cdot \bar{\sigma}$$

(2.30)

Averaged cross sections for various reactions in the $^{235}\text{U}(n_{th},f)$ fast neutron spectrum can be found in [CAL74] [IAE90]. Note that recent nuclear data guides often refer to the fast neutron spectrum of $^{252}\text{Cf}(SF)$, which has a slightly different energy distribution and leads to higher cross section averages (see e.g. [BAA89]).

The average cross section value can change in a distorted hard neutron spectrum, which mainly occurs in cases of high thermalisation. Fortunately, under the given circumstances, the threshold reactions will be of little importance in direct competition with a (dominant) thermal activation reaction. The threshold reactions as such should however be studied in undistorted fission neutron spectra, with little or no thermalisation.
2.11 Summary

The reaction rate per nuclide, according to the (extended) Høgdahl convention, is written as:

\[
R = R_s + R_e = G_{th} \cdot \phi_s \cdot \sigma_0 + G_e \cdot \phi_e \cdot I_0(\alpha)
\]  

(2.31)

and for Cd covered activation:

\[
(R_e)_{Cd} = G_e \cdot F_{Cd} \cdot \phi_e \cdot I_0(\alpha)
\]  

(2.32)

The subcadmium reaction rate is then:

\[
R_s = R - R_e = R - (R_e)_{Cd} / F_{Cd}
\]  

(2.33)

Another useful quantity is the experimentally measured Cd-ratio \( R_{Cd} \), being the ratio between the reaction rate of bare and Cd-covered nuclides:

\[
R_{Cd} = \frac{R}{(R_e)_{Cd}} = \frac{G_{th} \cdot \phi_s \cdot \sigma_0 + G_e \cdot \phi_e \cdot I_0(\alpha)}{G_e \cdot F_{Cd} \cdot \phi_e \cdot I_0(\alpha)}
\]  

(2.34)

This quantity is of course strongly related to the ratio of subcadmium ('thermal') and epithermal flux, \( f \), and the ratio of the "cross sections" \( Q_0(\alpha) \):

\[
R_{Cd} \cdot F_{Cd} = \frac{G_{th} \cdot f}{G_e \cdot Q_0(\alpha)} + 1
\]  

(2.35)

with \( f = \phi_s / \phi_e \)

\[
Q_0(\alpha) = I_0(\alpha) / \sigma_0
\]

An alternative way of writing the total reaction rate (formula 2.31) is the following:

\[
R = \phi_e \cdot \sigma_0 \cdot [G_{th} \cdot f + G_e \cdot Q_0(\alpha)]
\]  

(2.36)
III. ACTIVATION AND DECAY LAWS

3.1 Simple case of growth and decay

The most typical activation-decay scheme encountered in NAA is the (n,γ) reaction and a subsequent β-decay of the unstable product, leading to the emission of a characteristic γ-ray:

![Diagram of activation and decay process](image)

The growth and decay of the unstable product (2) is governed by statistical laws. During and after activation, the number of atoms obeys the following differential equations respectively:

\[
\begin{align*}
\text{during:} & \quad \dot{N}_2 = R_1 N_1 - \lambda_2 N_2 \\
\text{after:} & \quad N_2 = -\lambda_2 N_2
\end{align*}
\]

(3.2)

with \( R_1 \) the (n,γ) reaction rate on the nuclei (1) in the neutron field

\( \lambda_2 = \ln(2)/T_{1/2} \) is the decay constant of nucleus (2)

At a certain decay time \( t_d \) after the end of an irradiation with constant neutron flux (and no burn-up), the remaining number of produced product (2) atoms is statistically given by (see appendix A):

\[
N_2(t_d) = \frac{N_1 R_1}{\lambda_2} \cdot [1 - e^{-\lambda_2 t_{\text{irr}}}] \cdot e^{-\lambda_2 t_d} = N_2^\infty \cdot S_2 \cdot D_2
\]

(3.3)

The number of atoms is limited by the competition of the natural decay with the (n,γ) reaction, expressed by the ratio \( N_2^\infty = N_1 R_1 / \lambda_2 \). A high number of atoms can be built up in the case of a low natural decay probability of the unstable product and of a high neutron flux and (n,γ) cross section. The saturation factor \( S_2 = [1 - e^{-\lambda_2 t_{\text{irr}}}] \) demonstrates that the maximum abundance of product (2) is nearly reached after an irradiation time of a few times its typical half-life \( T_{1/2} \). The decay factor \( D_2 = e^{-\lambda_2 t_d} \) describes the typical exponential decay law.
The analyst will monitor the decay of product (2) during a certain time interval \([t_d, t_d+t_m]\) to derive indirectly the concentration of product (1) in the irradiated sample. The (average) number of disintegrated product (2) atoms during the measurement is then:

\[
\Delta N_2 = \int_{t_d}^{t_d+t_m} \lambda_2 \cdot N_2(t) \, dt = N_2(t_d) - N_2(t_d+t_m)
\]

\[= N_2^0 \cdot S_2 \cdot D_2 \cdot [1-e^{-\lambda_2 t_m}]\]  \hspace{1cm} (3.4)

in which the counting factor \(C_2 = [1-e^{-\lambda_2 t_m}]\) is the fraction of the remaining atoms that will be monitored during the measurement.

An alternative way of grouping the different factors is by writing:

\[
\Delta N_2 = (N_1 \cdot R_1 \cdot t_{irr}) \cdot \left[ \frac{1-e^{-\lambda_2 t_{irr}}}{\lambda_2 t_{irr}} \right] \cdot e^{-\lambda_2 t_d} \cdot [1-e^{-\lambda_2 t_m}]\]

\[= \Delta N_1 \cdot E_2 \cdot D_2 \cdot C_2\]  \hspace{1cm} (3.5)

The parameter \(\Delta N = N_1 \cdot R_1 \cdot t_{irr}\) is the total number of converted product (1) atoms by the \((n,\gamma)\) reaction. The factor \(E_2 \approx 1 - \frac{\lambda_2 t_{irr}}{2!} + \frac{(\lambda_2 t_{irr})^2}{3!} \ldots\) represents the fraction of the produced product (2) atoms that will be available after the irradiation for subsequent measurement. It is close to 1 for short irradiation times and converges to zero for long irradiations.

### 3.2 Burn-up

In the case of extremely high neutron fluxes and/or long irradiation times, the element concentrations can diminish considerably because of the large fraction undergoing an activation reaction. The growth and decay formula can be adapted by introducing a modified 'disappearance constant', being the sum of the decay constant and the reaction rate:

\[\Lambda = \lambda + R\]  \hspace{1cm} (3.6)

The formal expression (3.3) can be kept, using the revised factors (see appendix A):

\[N_2^\infty = \frac{\Lambda_1}{\Lambda_2 - \Lambda_1} \cdot N_{1,0}\]

\[S_2 = [e^{-\Lambda_1 t_{irr}} - e^{-\Lambda_2 t_{irr}}]\]  \hspace{1cm} (3.7)

with \(N_{1,0} = N_1(t_{irr}=0)\), the number of product (1) atoms at the beginning of the irradiation.
3.3 Complex activation and decay

The formulas can be extended to cases in which the monitoring element is only produced after several successive decays and/or in which branching occurs in the activation or decay processes. Also reactions on decay products (as e.g. 2\textsuperscript{nd} order interferences from successive neutron capture) can contribute to the production of the monitoring product. For a determination of the general activation and decay formulas, we already refer to appendix A (see also [POM96] [POM97b]).

The natural decay constant of each unstable product (i) in the decay scheme is in principle the sum of probabilities for several decay processes. Whereas the alternative decay modes do not (necessarily) lead to the monitoring product (k), they can be decisive for the disappearance rate of product (i). The decay formulas will therefore refer to the total decay constant \( \Sigma \lambda = \lambda + \lambda' + \ldots \) as well as the specific decay constant \( \lambda^* = \lambda \) of the branch leading to product (k). Equivalently, the product (i) can undergo competing activation reactions, which do not (necessarily) contribute to the production of the monitoring product (k). The total disappearance constant includes all participating reaction rates \( \Sigma R = R + R' + \ldots \), while \( R^* = R \) corresponds to the branch of interest. The total reaction rate is the sum of the (n,\( \gamma \)), (n,p), (n,2n), etc. contributions, excluding the (n,n') reactions (unless these would result in an excited state whose lifetime is not insignificant compared to the 'lifetime' of the ground state nucleus in the neutron field).

The disappearance constant can be generalised to include all participating activation and decay branches:

\[
\Lambda = \Sigma \lambda + \Sigma R
\]  

while the specific disappearance constant corresponding to the branch of interest is denoted:

\[
\Lambda^* = \lambda^* + R^*
\]  

For a simple case of activation and decay, one can write (appendix A):

\[
\Delta N_2 = \frac{N_{1,0} \cdot R^*}{\Lambda_2 - \Lambda_1} \cdot F_2 \cdot [ e^{-\Lambda_1 \cdot t_{\text{irr}}} - e^{-\Lambda_2 \cdot t_{\text{irr}}} ] \cdot e^{-\lambda_2 \cdot t_d} \cdot [ 1 - e^{-\lambda_2 \cdot t_m} ]
\]  

in which the branching factor \( F_2 = \lambda_2^* / \lambda_2 \) represents the part of the decay that is considered. Usually this factor is omitted, since it is incorporated in the gamma intensity (= average number of a certain \( \gamma \)-emission per disintegration)
To find a general solution for any possible nuclear activation-decay scheme, the problem is initially restricted to sequential processes; i.e., no feedback or joining branches (see figure 3.1).

Figure 3.1: Sequential activation and decay series; each product being a decay or activation product of the previous one in the chain.

The general formula for the number of monitored nuclei (k) after production in a constant neutron field through the activation of a stable product (1) and following one specific branch in the decay process, can be written as (see appendix A, formula A.21):

\[
\Delta N_k = N_{1,0} \cdot R_1^* \cdot \sum_{i=2}^{k} \left( \prod_{m=i+1}^{k} \frac{\lambda_m}{\lambda_{m-1}^*} \right) \cdot F_i \cdot D_i \cdot C_i \times \ldots
\]

(3.11)

with \( S_j = \left[ e^{-\Lambda_{j,1}^* t_{irr}} - e^{-\Lambda_{j,1}^* t_{irr}} \right] \) (j>1): the extended saturation factors;

\( D_i = e^{-\lambda_i t_{id}} \), \( C_i = (1-e^{-\lambda_i t_{id}}) \) (i>1): the decay and counting factors;

\( F_i = \frac{\lambda_i^*}{\lambda_i} \): the branching factors.
If the product \((k)\) is created by different branches, their contributions can be summed independently. Even if some branches join again, they can still be treated as separate chains. Beyond the branch point, a factor \(F_j\) is associated to each path, corresponding to its fractional weight and hence also determining its importance to the production of a common member. Finally the solution can be applied to complex networks of products, communicating with each other through nuclear reactions and/or decay (see figure 3.2).

**Figure 3.2**: The activation-decay formulas are applicable to complex networks of interrelated products

When using moderate neutron field intensities and irradiation times, in most cases no burn-up effects or higher order interference reactions have to be considered. Then the more classical formulas can be applied (see appendix A, formula A.27):

\[
\Delta N_k = \Delta N_1^* \cdot \sum_{i=2}^{k} \left( \prod_{n=2}^{k} \frac{\lambda_n^*}{\lambda_n - \lambda_i} \right) \cdot F_i \cdot E_i \cdot D_i \cdot C_i
\]

\[
= N_{1,0} \cdot R_1^* \cdot \frac{k}{i=2} \left( \prod_{n=2}^{k} \frac{\lambda_n^*}{\lambda_n - \lambda_i} \right) \cdot F_i \cdot \frac{S_i}{\lambda_i} \cdot D_i \cdot C_i
\]

(3.12)

with \(\Delta N_1^* = N_{1,0} \cdot R_1^* \cdot t_{irr}\)
In the absence of burn-up and higher order reactions, the contributions of consecutive irradiations are practically independent and can be summed directly.

Explicit expressions of the general activation-decay formulas 3.11 and 3.12 are presented in table A.1 (appendix A) for the cases $k=2$, $3$ and $4$.

### 3.4 Examples of activation and decay schemes

#### 3.4.1 Competing reactions

We consider the most common situation in which the monitoring product B is being populated by reactions on two different stable isotopes, A and A'. Both contributions are summed.

\[
E_i = S_i / (\lambda_i \cdot t_{irr})
\]

\[
S_i = \left( 1 - e^{-\lambda_i \cdot t_{irr}} \right)
\]

$F_i$, $D_i$ and $C_i$ as defined in formula 3.11

\[
\Delta N_B = \Delta N_2(A,B) + \Delta N_2(A',B)
\]

\[
= \left[ \frac{N_A \cdot R_A}{\lambda_B \cdot R_A} + \frac{N_{A'} \cdot R_{A'}}{\lambda_{B'} \cdot R_{A'}} \right] \cdot S_B \cdot D_B \cdot C_B
\]

This could e.g. describe the competition between a simple $(n,\gamma)$ activation with an interfering reaction ($(n,p)$, $(n,\alpha)$,...) leading to the same reaction product.
3.4.2 Branching

Starting from one stable element, the activation can follow different branches, which can join again in a later stage of the decay. We consider a typical situation in which an isomer $B^n$ is populated, which decays back to the monitoring product $B$. This example illustrates the role played by branching factors $F_i$. (Burn-up effects are omitted here.)

![Diagram of branching process]

\[
\begin{align*}
\Lambda_1 &= R_{A^n_1} + R_{A^n_2}, \quad \Lambda_1^* = R_{A^n_1} \\
\Lambda_2 &= \Lambda_2^* = \lambda_B \\
\Lambda_3 &= \lambda_{n^m}, \quad \Lambda_3^* = F_2 \lambda_{n^m} \\
\Lambda_4 &= \Lambda_4^* = \lambda_{n} 
\end{align*}
\]

The table provides the branching factors for each branch:

<table>
<thead>
<tr>
<th>branch $AB$</th>
<th>branch $AB^nB$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Lambda_1 = R_{A^n_1} + R_{A^n_2}, \quad \Lambda_1^* = R_{A^n_1}$</td>
<td>$\Lambda_1 = R_{A^n_1} + R_{A^n_2}, \quad \Lambda_1^* = R_{A^n_1}$</td>
</tr>
<tr>
<td>$\Lambda_2 = \Lambda_2^* = \lambda_B$</td>
<td>$\Lambda_2 = \lambda_{n^m}, \quad \Lambda_2^* = F_2 \lambda_{n^m}$</td>
</tr>
<tr>
<td>$\Lambda_3 = \Lambda_3^* = \lambda_{n}$</td>
<td>$\Lambda_3 = \Lambda_3^* = \lambda_{n}$</td>
</tr>
</tbody>
</table>

\[
\Delta N_B = \Delta N_2(A,B) + \Delta N_3(A,B^n,B) \\
= [N_A R_{AB}] \cdot \frac{S_B}{\lambda_B} \cdot D_B \cdot C_B \\
+ [N_A R_{AB^n}] \cdot \left[ \frac{\lambda_B}{\lambda_{B^n}} \cdot \frac{S_B}{\lambda_{B^n}} \cdot F_2 \cdot D_{B^n} \cdot C_{B^n} + \frac{F_2 \lambda_{B^n}}{\lambda_{B^n} \lambda_B} \cdot \frac{S_B}{\lambda_B} \cdot D_B \cdot C_B \right]
\]

In case the isomer has a short half-life ($\lambda_{B^n} \gg \lambda_B$), this formula soon ($D_{B^n} \approx 0$) reduces to

\[
\Delta N_B \approx N_A \cdot (R_{AB} + F_2 \cdot R_{AB^n}) \cdot \frac{S_B}{\lambda_B} \cdot D_B \cdot C_B
\]
3.4.3 Backward branching or looping

A special case of branching has been left out of consideration up to now; the case in which the abundance of the initial product is fed by a reaction on one of its daughter products. So, as matter 'flows' from one 'compartment' to another, there is also a feedback mechanism populating the first. This backward branching can in principle still be treated in forward direction, by infinite looping. In practice, summations will be limited according to the requested mathematical precision.

\[ \Delta N_k = \Delta N_k(A,...,k) + \Delta N_{k+n}(A,...,B,...,A,...,k) + \Delta N_{k+2n}(A,...,B,...,A,...,B,...,A,...,k) + ... \]
\[ = \sum_{i=0}^{\infty} \Delta_{k+i,n}(A,[...,B,...,A]\times i,...,k) \]

Whereas such situations are commonly found in the description of biological or chemical systems, they rarely turn up in some chain of activation reactions. An example can be found in the activation of gold:

\[ ^{197}\text{Au} \rightarrow ^{198}\text{Au} \rightarrow ^{196}\text{Pt} \rightarrow \rightarrow ^{197}\text{Pt} \rightarrow ^{197}\text{Au} \]

\[ ^{197}\text{Pt} \rightarrow ^{197}\text{Pt} \rightarrow ^{197}\text{Pt} \rightarrow ^{197}\text{Au} \]
3.4.4 Burn-up of daughter product

The impact by burn-up of any of the products on the abundance of the monitoring product follows directly from the general formula 3.11. As an example, we consider the burn-up of the daughter products in a mother-daughter decay. The burn-up and transformation of other products is considered as being negligible.

\[ A_* = R_A \]

\[ A_* = \lambda_B \]

\[ A_* = \lambda_C \]

\[ \Lambda_1 = \lambda_a \]

\[ \Lambda_2 = \lambda_a + \lambda_i \]

\[ \Lambda_3 = R_x \]

\[ \Lambda_4 = \lambda_c \]

\[ \Lambda_5 = \lambda_c + \lambda_i \]

\[ \Delta N_C = N_{A,0} \cdot R_A \cdot \left[ \frac{S_B}{\lambda_B} \left( \frac{\lambda_C}{\lambda_C - \lambda_B} \right) \right] \cdot D_{B,C_B} \]

\[ + N_{A,0} \cdot R_A \cdot \left[ \frac{S_B \cdot \lambda_C - S_C \cdot \lambda_B}{\lambda_C \cdot (\lambda_C - \lambda_B)} - \frac{S_B}{\lambda_C - \lambda_B} \right] \cdot D_{C,C_C} \]

3.4.5 Successive neutron capture

Besides the stable elements, also the activation products can undergo nuclear reactions. Sometimes two consecutive neutron captures are the easiest way to produce some product C by neutron activation. We consider a double activation. The possible natural decay of the intermediate product (\(\lambda_B > 0\)) is also taken into account ('decay-away').

\[ \Lambda_1 = \lambda_a \]

\[ \Lambda_2 = \lambda_a \cdot \lambda_B \]

\[ \Lambda_3 = \lambda_c \]

\[ \Lambda_4 = \lambda_c + \lambda_i \]

\[ \Lambda_5 = \lambda_i \]
\[ \Delta N_C = \Delta N_3(A,B,C) \]
\[ = N_{A,0} R_A R_B \left[ \frac{S_B}{(R_B + \lambda_B R_A)} \left( \frac{1}{\lambda_C - R_B - \lambda_B} \right) + \frac{S_C}{(R_B + \lambda_B - \lambda_C)} \right] D_C C_C \]

When saturation is reached (no burn-up of A), one gets:

\[ \Delta N_C = \frac{N_{A,0} R_A R_B}{(R_B + \lambda_B R_A)} D_C C_C \]

Since the abundances are proportional to \( R_A, R_B \), or \( \Phi^2 \), the interference of these 2\textsuperscript{nd} order reactions to a competing 1\textsuperscript{st} order activation will increase proportionally with the neutron flux \( \Phi \). Generally, a \( n^\text{th} \) order activation reaction is proportional to \( \Phi^n \). Evidently, such transformations by successive neutron capture have some relevance to the theories regarding stellar nucleosynthesis.

### 3.4.6 Fission products

Neutron activation analysis can be interfered by neutron induced fission reactions on traces of fissile material. Indeed, a large variety of nuclei (>1000) are directly or indirectly produced in fission. The high neutron excess in the 'primary fission fragments' cause immediate neutron evaporation. The resulting 'primary fission products' then move further towards stability by successive \( \beta^- \)-decay. So, in general the decay schemes run in parallel along the lines of fixed mass number, with little mutual interference. In each mass chain, the main primary yield \( Y(Z|M) \) is concentrated in three to four isotopes. Their interdependence is determined by:

\[
\begin{align*}
\dot{N}_1 &= -R_f N_1 \\
\dot{N}_2 &= +R_f N_1 Y(M).Y(Z_2|M) - \Lambda_2 N_2 \\
\dot{N}_i &= +R_f N_1 Y(M).Y(Z_i|M) - \Lambda_i N_i + \lambda^*_i N_{i-1} (i \geq 3)
\end{align*}
\]

with \( R_f \) the fission reaction rate, \( Y(M) \) the relative yield for products with mass \( M \) and \( Y(Z|M) \) the conditional isotopic yield. The product disintegrations are calculated from:

\[ \Delta N_k = N_{1}.R_f.Y(M) \left[ Y(Z_k|M) \cdot \Delta_2(1,k) + Y(Z_{k-1}|M) \cdot \Delta_3(1,k-1,k) + \ldots + Y(Z_2|M) \cdot \Delta_k(1,2,\ldots,k) \right] \]

\[ = N_{1}.R_f.Y(M) \cdot \sum_{i=2}^{k} Y(Z_i|M) \cdot \Delta_{k-i+2}(1,i\rightarrow k) \]

with \( \Delta_i \) = the general activation-decay formula \((3.11)\) with the factor ' \( N_{1,0}.R_f^* \) ' set equal to 1.
The relative yield of the different 'primary fission products' can be calculated with the \( Z_{P} \) or \( A_{P} \)-model of Wahl [WAH88,89]; this is a parametrisation of the charge and mass distributions for several fission processes. In principle, using this model, the identification of the fissioning system together with the determination of the fission yield of one isotope should be sufficient for a full characterisation of all other fission yields.

### 3.5 Consecutive Irradiations

We consider the case of two consecutive irradiations of the same sample. In absence of burn-up, both contributions are independent and can be summed directly. In case the burn-up of product (1) has to be considered, the initial abundance \( N_{1,0} \) of the stable isotope is reduced at the start of the second irradiation cycle, with a factor \( \exp(-R_{1}t_{irr}^{(1)}) \). Summing (in absence of the burn-up of daughter nuclei) is then performed like this:

\[
\Delta N_2 = \left( N_{1,0}^{(1)} \cdot \frac{R_{1}^{*(1)}}{\lambda_{2-R_{1}^{(1)}}} \right) \cdot \left[ e^{-R_{1}t_{irr}^{(1)}} - e^{-\lambda_{2}t_{d}^{(1)}} \right] \cdot e^{-\lambda_{2}t_{d}^{(1)}} \cdot C_{2}
\]

\[
+ \left( N_{1,0}^{(1)} \cdot e^{-R_{1}t_{irr}^{(1)}} \cdot \frac{R_{1}^{*(2)}}{\lambda_{2-R_{1}^{(2)}}} \right) \cdot \left[ e^{-R_{1}t_{irr}^{(2)}} - e^{-\lambda_{2}t_{d}^{(2)}} \right] \cdot e^{-\lambda_{2}t_{d}^{(2)}} \cdot C_{2}
\]

In the common case of equal neutron flux in both irradiation periods, the reaction rates will also be equal, \( R_{1}^{(1)} = R_{1}^{(2)} = R_{1} \).

The situation becomes more complicated when higher-order reactions and burn-up of daughter products have to be accounted for. Indeed, the contribution from a particular irradiation is no longer unaffected by the next irradiation(s). One could use following formalism to ensure a principally correct evaluation after \( n \) irradiation periods:

\[
\Delta N_{k}^{(n)} = N_{1}^{(n-1)} \cdot \Delta_{k}^{(1,...,k)}
\]

\[
+ N_{2}^{(n-1)} \cdot \Delta_{k-1}^{(2,...,k)}
\]

\[
+ ...
\]

\[
+ N_{k}^{(n-1)} \cdot \Delta_{1}^{(k)}
\]

\[ (3.13) \]
with: \( N_i^{(n-1)} \); the abundance of product i at the beginning of irradiation (n); this is after (n-1) irradiations and possibly as many cooling periods (see formula (A.13) or (A.19))

\[ \Delta_i \quad \text{the general activation and decay formula (A.20) of order i (without the condition of stability of the initial nuclei), in which the factor 'N_{i,0}' is set equal to 1} \]

### 3.6 Variable neutron flux

Up to now, constant reaction rates have been assumed. The activation formulas for a variable neutron flux, and reaction rate, are quite more complicated. The growth of the activation product in a variable flux is in principle calculated from:

\[
N_{2, \text{ irr}} = e^{-\int_{0}^{t_{\text{irr}}} A_{2} \, dt} \left( N_{1}(t) \cdot R_{1}(t) \cdot e^{\int_{0}^{t} A_{2} \, dt} \right.
\]

with \( N_{1}(t) = N_{1,0} \cdot e^{-\int_{0}^{t} A_{1}(t) \, dt} \)

Consider for example an exponential start and stop of the reactor neutron flux, i.e.:

\([t_a, t_b] : R_{1}^{*} = R_{1} \cdot [1 - e^{-(t-t_0)/\tau_a}] \]

\([t_1, t] : R_{1}^{*} \approx R_{1} \cdot e^{-(t-t_1)/\tau_b} \quad (t_1-t_0 >> \tau_a) \]

The number of product (1) atoms at a time \( t \) after the irradiation is then:

\[
N_{1}(t) = N_{1,0} \cdot e^{-R_{1} \cdot [(t_1+\tau_b)-(t_0+\tau_a)]} \cdot e^{-R_{1} \cdot [(t-t_0)/\tau_a] + \tau_b \cdot e^{-(t_1-t_0)/\tau_b}}
\]

\( \approx N_{1,0} \cdot e^{-R_{1} \cdot [(t_1+\tau_b)-(t_0+\tau_a)]} \quad (t_1-t_0 >> \tau_a \cdot t-t_1 >> \tau_b) \)

As an approximation, one could assume a constant neutron flux with start time at \( t_a+\tau_a \) and stop time \( t_1+\tau_b \). The abundance of the daughter decay product (2) is calculated from:

\[
N_{2}(t) = N_{1,0} \cdot R_{1} \cdot \left[ \frac{1 - e^{-\lambda_2 \cdot (t-t_0)}}{\lambda_2} \right] \cdot e^{-\lambda_2 \cdot (t-t_1)} + N_{1,0} \cdot R_{1} \cdot \left[ \frac{e^{-\lambda_2 \cdot (t-t_0)} - e^{-(t_1-t_0)/\tau_a}}{\lambda_2 \cdot 1/\tau_a} \right] \cdot e^{-t_0/\tau_a} \cdot e^{-\lambda_2 \cdot (t-t_1)} + N_{1,0} \cdot R_{1} \cdot \left[ \frac{e^{-\lambda_2 \cdot (t-t_1)} - e^{-(t_1-t_1)/\tau_b}}{\lambda_2 \cdot 1/\tau_b} \right] \cdot e^{-t_1/\tau_b}
\]
From a numerical test it seems that the above mentioned approximation is still satisfactory for long lived activation products. For short lived products ($\tau_s < t_m$), only the end of the irradiation is of relevance. The exponential tail of the neutron flux can create serious deviations from the expected abundances in a steady regime.

### 3.7 In-beam measurements

The activity of the decay products can in principle also be monitored during the activation at an external neutron beam of the reactor. If $t_0 = 0$ corresponds to the beginning of the activation, a measurement during a time interval $[t_1, t_2]$ yields following integrated activity:

$$\Delta N_k = \sum_{i=2}^{k-1} \prod_{n=2}^{k-1} \Lambda_n \cdot N_{1.0} \cdot R_1^* \cdot \lambda_k^* \cdot \left( \frac{e^{-\Lambda_1 t_2} - e^{-\Lambda_1 t_1}}{\Lambda_1} \right) \cdot \left( \frac{e^{-\Lambda_i t_2} - e^{-\Lambda_i t_1}}{\Lambda_i} \right)$$

(3.15)

and in the limit of low burn-up:

$$\Delta N_k = N_{1.0} \cdot R_1^* \cdot \sum_{i=2}^{k-1} \prod_{n=2}^{k-1} \frac{\lambda_n^*}{\lambda_n - \lambda_i} \cdot F_i \cdot \left( (t_2 - t_1) - \frac{e^{-\lambda_i t_2} - e^{-\lambda_i t_1}}{\lambda_i} \right)$$

(3.16)

These expressions are readily obtained from:

$$\Delta N_k = \int_{t_1}^{t_2} \lambda_k^* \cdot N_k(t) \, dt$$

with $N_k(t)$ represented by formula A.6 and A.24 respectively.

Consider now the most simple case of activation:

$$\Delta N_2 = N_{1.0} \cdot R_1^* \cdot \left( (t_2 - t_1) - \frac{e^{-\lambda_2 t_1} - e^{-\lambda_2 t_2}}{\lambda_2} \right)$$

(3.17)

Short lived products can easily be measured at saturation. In competition with one classical measurement, after an irradiation in the reactor core (assuming here that $t_n = t_m = t_{core} = T_{1/2}$) one gets then:

$$\frac{(\Delta N_2)^{beam}}{(\Delta N_2)^{core}} \approx \frac{(N_{1.0} \cdot R_1^* \cdot t_m)^{beam}}{(N_{1.0} \cdot R_1^*/(8\lambda_2))^{core}} = \frac{8 \cdot (\Phi \cdot t_m)^{beam}}{\Phi_{core} \cdot t_2}$$

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In-beam measurements will yield at least the same amount of gamma-emissions when:

\[(t_{irr})_{beam} > \tau_2 \cdot \left( \frac{\Phi_{core}}{8 \cdot \Phi_{beam}} \right)\]

In competition with cyclic in-core irradiations (assuming here that \(t_d < t_{irr} = t_m\) and \(t_{irr} + t_d + t_m \approx 2 \cdot \tau_2\)), the (continuous) in-beam measurements (with \((t_{irr})_{beam} = (t_m + t_d + t_m)_{core}\)) become more efficient when:

\[(t_d)_{cyclic} > \tau_2 \cdot \ln\left( \frac{\Phi_{core}}{8 \cdot \Phi_{beam}} \right), \quad \text{since} \quad \frac{(\Delta N_2)_{beam}}{(\Delta N_2)_{core}} \approx \frac{(R^*_1)_{beam} \cdot 2 \cdot \tau_2}{(R^*_1 \cdot D_2)_{core}} \frac{4 \cdot \lambda_2}{\lambda_2}\]

Therefore, in-beam measurements can be a useful alternative if the analyst has no rabbit system at his disposal for fast sample transport between irradiation and measurement site. The method is also advantageous in case the irradiation or decay time of the classical NAA is not accurately defined \((\Delta t_{irr} \cdot \Delta t_d \sim \tau_2\)), causing a large uncertainty in the activation and decay formulas. Such uncertainties are possible with short rabbit measurements.

3.8 Classification of analytical reactions

Whereas the general activation and decay formulas are valid for any hypothetical decay scheme, only a limited number of decay types do actually occur in NAA. De Corte classified 8 major different decay schemes and in addition 9 derived schemes, which are simplifications of the former [DEC87] [DEC89]. An overview is given in appendix B, together with some relevant parameters (defined elsewhere in this paper). Whereas the original formulas appearing in the definitions are only valid in the low burn-up approximation, they have been upgraded to a more general level by Pommé et al. (this work and [POM96] [POM97b]).
IV. STANDARDISATION METHODS

4.1 Absolute standardisation

In this context, the expression 'standardisation' has to be interpreted in the sense of 'calibration of NAA'; i.e. finding the correlation between the concentration of an analyte and the corresponding 'intensity' of the witness signal in the activation spectra.

The concentration \( \rho \) of an analyte (1) in the sample can be derived from the area of the full energy peak \( N_p \) corresponding to a characteristic gamma from a decay product (k). The average amount of counts in the photon peak can be calculated from:

\[
N_p = \frac{N_{A}}{M} \cdot \frac{W \cdot \rho \cdot \theta}{R_f} \cdot \Delta_k \cdot \gamma_k \cdot \varepsilon_p
\]  

(4.1)

with

\[
N_{I,0} = \frac{N_A \cdot W \cdot \rho \cdot \theta}{M}, \text{ the initial number of nuclei (from one isotope of the analytical element of interest, leading to the observed activation reaction), with:}
\]

- \( N_A \), the Avogadro number \((6.2022 \times 10^{23}/\text{mol})\)
- \( W \), the sample mass \([\text{g}]\)
- \( \rho \), the element concentration \([\text{g/g}]\) \((\rho = w_s/W)\)
- \( \theta \), the isotopic fraction
- \( M \), the molar mass of the analyte \([\text{g/mol}]\)

\( R_f = \Phi_f \cdot \sigma_0 \left[ G_{th,f} + G_e \cdot Q_0(\alpha) \right] \), the reaction rate per nucleus (formula 2.36)

\( \Delta_k = \frac{AN_k}{N_{I,0} R_f} \), the number of decaying product (k) nuclei per unit of \( N_{I,0} \cdot R_f \) during a measurement period \( t_m \), started at a time \( t_r \) after an irradiation at constant neutron flux during a time \( t_{irr} \) (see also the formulas 3.11 and 3.12)

\( \gamma_k \), the absolute gamma intensity in the decay of the monitored product (k)

\( \varepsilon_p \), the full-energy peak detection efficiency for the sample-detector geometry (including attenuation and true coincidence effects)
The concentration of the analyte in the sample is then:

\[
\rho(\mu g/g) = N_p \cdot \left[ \Delta_k \cdot \frac{N_A \cdot W \cdot \theta \cdot \gamma_k}{M} \cdot \epsilon_p \cdot \Phi_e \cdot \sigma_0 \cdot \left( G_{th,f} + G_e \cdot Q_0(\alpha) \right) \right]^{-1} \cdot 10^6
\]

(4.2)

Whereas the calculation of the concentration is in principle perfectly feasible from this expression, the poor knowledge of some nuclear parameters can lead to systematic errors up to 20% [SIM92]. Indeed, the values for \( \sigma_0 \) (and \( Q_0 \)), \( \gamma \) and \( \theta \) can be found in literature, but due to their combined uncertainties, they lead to a deterioration of the accuracy and traceability of the analytical results. Besides that, the accurate determination of the neutron field characteristics, the detector efficiency, neutron self shielding factors, ... require quite some effort from the analyst.

4.2 Relative standardisation

In the relative standardisation method, a chemical standard with known content (mass \( w_s \)) of the element of interest is coirradiated with the sample and both are subsequently counted in the same geometrical configuration. The concentration of the analyte in the sample can then be derived relatively from the result for the standard at the same gamma energy:

\[
\rho(\mu g/g) = \frac{w_s}{W} \cdot \frac{(N_p/\Delta_k)_s}{(N_p/\Delta_k)_a} \cdot \frac{[G_{th,f} + G_e \cdot Q_0(\alpha)]_s}{[G_{th,f} + G_e \cdot Q_0(\alpha)]_a} \cdot \left( \frac{\epsilon_p}_s \right) \cdot \left( \frac{\epsilon_p}_a \right) \cdot 10^6
\]

(4.3)

In ideal cases, the sample and standard have the same geometrical properties and equivalent compositions (+ invariable isotopic abundance). Then the comparison can be performed with identical efficiency and neutron flux gradient (i.e. \( \epsilon_p = \epsilon_p \cdot G_{th,c} = G_{th,c} \cdot G_{th,c} = G_{th,c} \)), leading to this simple expression:

\[
\rho(\mu g/g) = \frac{w_s}{W} \cdot \frac{(N_p/\Delta_k)_s}{(N_p/\Delta_k)_a} \cdot 10^6
\]

(4.4)

The potential advantages of the relative standardisation are its simplicity and accuracy. The analyst can avoid the determination of the reaction rates and the detection efficiency (including true coincidence effects). The accuracy, possibly of the order of 1-2%, is of course limited by the accuracy on \( w_s \). The main disadvantage is its limited use in routine multi-element analysis, where preparation, counting and spectrum evaluation of the standards are time consuming; not to mention the nearly inevitable cases in which an unexpected element turns up for which no standard was coirradiated.
4.3 Single-comparator standardisation

Routine analysis can benefit from a reduction of the number of coirradiated standards to only one, which acts as a comparator for all other elements. The corresponding comparator factors $k_n(s)$ are determined experimentally by coirradiating a standard $(s)$ with the comparator standard $(c)$ [GIR65]:

$$k_c(s) = \frac{A_{sp,s}}{A_{sp,c}} \quad (4.5)$$

with $A_{sp} = \frac{N_p}{w \cdot \Delta_k}$, the specific count rate $[s^{-1} \cdot g^{-1}]$ (4.6)

The concentration of each analyte can then be obtained from coirradiation of sample $(a)$ and single-comparator $(c)$:

$$\rho(\mu g/g) = \left[ \frac{N_p}{w \cdot \Delta_k} \right]_a \cdot \frac{1}{A_{sp,c} \cdot k_c(s)} \cdot 10^6 \quad (4.7)$$

This method allows a fast and rather accurate analysis, under certain experimental conditions (see e.g. [DEC87] [SIM92]). The k-factors are however 'local', since they depend on the used neutron field characteristics, the detection geometry, the sample and standard geometry and composition,... Any change in the set-up calls for a redetermination of the conversion factors.

4.4 $k_0$-standardisation

The $k_0$-methodology combines the accuracy of the relative and single-comparator method with the flexibility and generality of the absolute calibration. For each gamma line of interest to NAA, one can consider the constant:

$$k_a = \left[ \frac{N_A \cdot \gamma \cdot \sigma_0}{M} \right] \quad (4.8)$$

occurring in the concentration formula (4.2). Unlike the k-factors of Girardi, this entity is independent of the experimental conditions. The so-called $k_0$-factors can be calculated as the ratio of this constant with the analogue for a comparator gamma [SIM75]:

$$k_{0,c}(a) = \frac{M_c \cdot \theta_c \cdot \gamma_c \cdot \sigma_{0,c}}{M} = \frac{k_a}{k_c} \quad (4.9)$$
in which the 411.8 keV gamma line in the decay of $^{198}$Au, through the $^{197}$Au(n,γ)$^{198}$Au reaction, is most commonly chosen as a reference, and:

$$k_{Au} = \frac{6.022 \times 10^{23} \cdot 1.9556\% \cdot 98.65 \times 10^{-24}}{196.9665} = 0.2882$$  \hfill (4.10)

The $k_0$-standardisation can now be seen as a single-comparator method, in which the analyte concentration is obtained from:

$$\rho(\mu g/g) = \left[ \frac{N_p}{W \cdot \Delta k} \right]_{Au} \cdot \frac{1}{A_{sp,Au} \cdot k_{0,Au}(a)} \cdot \frac{[G_{th,f} + G_{e,Q_0(\alpha)]_{Au}}}{[G_{th,f} + G_{e,Q_0(\alpha)]}_{a}} \cdot \frac{(\epsilon_p)_{Au}}{(\epsilon_p)_{a}} \cdot 10^6$$  \hfill (4.11)

and for epicadmium irradiations (ENAA):

$$\rho(\mu g/g) = \left[ \frac{N_p}{W \cdot \Delta k} \right]_{Cd,a} \cdot \frac{1}{(A_{sp})_{Cd,Au} \cdot k_{0,Au}(a)} \cdot \frac{[F_{Cd,G,C,Q_0(\alpha)]_{Au}}}{[F_{Cd,G,C,Q_0(\alpha)]}_{a}} \cdot \frac{(\epsilon_p)_{Au}}{(\epsilon_p)_{a}} \cdot 10^6$$  \hfill (4.12)

The analyst can opt for another monitor than Au. When the Au based $k_0$-factor of the monitor has been determined, alternative $k_0$-factors can be calculated for each analyte, with the monitor acting as the new comparator:

$$k_{0,m}(a) = k_{a} \cdot k_{Au} \cdot k_{m} = k_{0,Au(a)} \cdot k_{0,Au(m)}$$  \hfill (4.13)

Again, compared to the absolute standardisation, uncertainties on nuclear constants are reduced by using one - experimentally verifiable - composite parameter. Indeed, $k_0$ can be obtained directly from experiment, through a Cd-difference measurement; i.e. by irradiating standard and comparator with and without Cd-cover:

$$k_{0,c(s)} = \left[ \frac{A_{sp} \cdot (A_{sp})_{Cd} / F_{Cd}}{A_{sp} \cdot (A_{sp})_{Cd} / F_{Cd}} \right]_{c(s)} \cdot \frac{G_{th,c}}{G_{th,s}} \cdot \frac{\epsilon_{p,c}}{\epsilon_{p,s}}$$  \hfill (4.14)

since  

$$[A_{sp} \cdot (A_{sp})_{Cd} / F_{Cd}]_x = k_x \cdot G_{th,x} \cdot \Phi_s \cdot \epsilon_{p,x}$$

Whereas the Cd-difference method is generally applicable, the $k_0$-factor can also be derived from the bare irradiations on condition that the $f$ and $Q_0(\alpha)$ parameters are sufficiently well known:

$$k_{0,c(s)} = \frac{A_{sp,s}}{A_{sp,c}} \cdot \frac{[G_{th,f} + G_{e,Q_0(\alpha)]}_c}{[G_{th,f} + G_{e,Q_0(\alpha)]}_s} \cdot \frac{\epsilon_{p,c}}{\epsilon_{p,s}}$$  \hfill (4.15)
Most $k_0$-factors have been determined at INW (Gent) and KFKI (Budapest); always with Au as comparator [DEC87] [DEC89] [DEC93].

The $k_0$-standardisation has some aspects in common with the absolute standardisation. The general applicability of the $k_0$-factor is paid by the necessity of an additional, accurate determination of the detection efficiency ($\varepsilon_p$) and the neutron field characteristics ($f$ and $\alpha$). Yet, the analyst gains an accurate tool for panoramic analysis of trace constituents (even unexpected ones), yielding concentrations - or at least upper limits - for about 60 elements.

### 4.5 $k_0$-factors for complex decay

In more complex decay schemes, the explicit expression for the $k_0$-factor changes slightly, however not fundamentally. An overview is shown in appendix C (see also [POM96]). The thermal activation cross section is in some cases replaced by the sum of two or three contributing cross sections. The atomic mass and isotopic abundance part remains unchanged. The gamma intensity always corresponds to the monitoring decay product. A remarkable fact is that the authors have decided to remove (some of) the branching factors (partly) from the decay formulas and to include them into the $k_0$-factor (see e.g. [DEC87]). The reason can be found in the philosophy of the use of $k_0$ itself; a reduction of the build up of uncertainties on the different nuclear constants. On the other hand, this makes the definition of the $k_0$-factor less transparent, since now reference has to be made to a table of definitions for the different types of decay. The formulas 4.11-4.15 are still valid, if one remembers to use $\Delta_k/(F_2.F_3...)$ instead of $\Delta_k$ (see appendix C).

### 4.6 $k_0$ for threshold reactions

The specific count rate for decay products from threshold reactions in the fast neutron spectrum is given by (see also formula 2.30):

$$ (A_{sp})_{fast} = \frac{N_A \theta \cdot \gamma \cdot \bar{\sigma}}{M} \cdot \Phi_f \cdot \varepsilon_p $$

(4.16)

As pointed out in [LIN81] [LIN89], the concept of $k_0$-factors can be extended to the case of threshold reactions:

$$ k_{0,Au}^{fast}(a) = \frac{M_c}{M} \cdot \frac{\theta}{\theta_c} \cdot \frac{\gamma}{\gamma_c} \cdot \frac{\bar{\sigma}}{\bar{\sigma}_{0,c}} $$

(4.17)
The fast neutron flux can be obtained from the coirradiation of a conventional monitor (like Au) and a fast neutron monitor (e.g. $^{54}$Fe(n,p)$^{54}$Mn):

$$\Phi_f = \Phi_S \cdot \frac{(A_{sp})_{Mn}}{(A_{sp})_{Au} \cdot k_{0,Au}(Fe)} \cdot \frac{f + Q_{0,Au}(\alpha)}{f} \cdot \frac{\varepsilon_{p,Mn}}{\varepsilon_{p,Au}}$$  (4.18)

as an alternative to the direct method, through:

$$\Phi_f = \frac{A_{sp} \cdot M}{N_A \cdot \theta \cdot \gamma \cdot \bar{\sigma} \cdot \varepsilon_p}$$  (4.19)

In a well characterised neutron field ($\Phi_s$, $\Phi_f$, $f$, $\alpha$), the expression 4.18 can (after rearrangement) also be used for the experimental determination of the $k_{0,\text{fast}}$-factors. This way the sometimes large uncertainty on the literature $\bar{\sigma}$-values [CAL74] can be avoided.

We can now consider the situation in which the activation reaction $l(n,\gamma)3$ is interfered by a threshold reaction $2(n,x)3$. The contribution of the interference reaction will seemingly increase the concentration of element 1, which is of analytical interest. For each ppm of element 2, one has to correct for an apparent concentration of element 1 given by:

$$\text{"p}(l)\)(ppm) = (1\text{ppm}) \cdot \frac{(A_{sp,3})_{\text{fast}}}{(A_{sp,3})_{n,\gamma}}$$

$$= (1\text{ppm}) \cdot \frac{\theta_2,\bar{\sigma}_2,M_1}{\theta_1,\sigma_{0,1},M_2} \cdot \frac{f}{f + Q_{0,1}(\alpha)} \cdot \frac{\Phi_f}{\Phi_S}$$  (4.20)

or equivalently:

$$\text{"p}(l)\)(ppm) = (1\text{ppm}) \cdot \frac{k_{0,Au}(2)}{k_{0,Au}(1)} \cdot \frac{f}{f + Q_{0,1}(\alpha)} \cdot \frac{\Phi_f}{\Phi_S}$$  (4.21)

Quite similar expressions can be formulated for other kind of reactions like e.g. fission [LIN81] [LIN89] [KUP92] or prompt gamma cold neutron activation (PGCNA) [LND92] [ROS92].
4.7 $k_0$ and the Westcott formalism

From its definition, it is clear that the $k_0$-factor is a nuclear constant, independent of any convention or formalism. This means that the $k_0$-factors for '1/ν-reactions' - obtained in the framework of the Høgdahl convention - can be introduced unaltered in the expression for the concentration calculation written in the Westcott formalism. The only basic difference with respect to the formula 4.11 is the part describing the following ratio [DEC94b] [VHK94]:

$$\frac{[G_{th}.f + G_e.Q_0(\alpha)]_{Au}}{[G_{th}.f + G_e.Q_0(\alpha)]_{a}} \rightarrow \frac{[G_{th}.g(T_n) + G_r . n(\alpha) . \sqrt{T_n/T_0} . s_0(\alpha)]_{Au}}{[G_{th}.g(T_n) + G_r . n(\alpha) . \sqrt{T_n/T_0} . s_0(\alpha)]_{a}}$$

(4.22)

with: $G_{th}$, $G_r$, self shielding corrections factors for Maxwell-Boltzmann neutrons and resonance neutrons respectively;

$$r(\alpha) . \sqrt{T_n/T_0}$$,

the modified spectral index; a measure for the epithermal to total neutron density ratio;

$$s_0(\alpha) = \frac{2}{\sqrt{\pi}} . \frac{l_0'(\alpha)}{\sigma_0}$$,

the modified reduced resonance integral to 2200 m/s (n,γ) cross section ratio;

$$g(T_n) = \frac{\sigma(T_n)}{\sigma_0} = \frac{1}{\sigma_0} \int_0^{\infty} \frac{\sigma(v).v}{v_0} . n(v) \, dv = 1$$,\n
with $\int_0^{\infty} n(v) \, dv = 1$, with $\int_0^{\infty} n(v) \, dv = 1$.

the Westcott factor, describing the cross section departure from the 1/ν law (at thermal energies) at a neutron temperature $T_n$, and $n(v)$ is the normalised Maxwell-Boltzmann neutron density per unit of velocity interval. In any case, $g(T_n)=1$ for ideal 1/ν cross sections.

One should be aware that the epithermal self-shielding factors $G_e$ cannot be adopted automatically, since the cut-off energy is taken at $E=\mu kT$ in the Westcott and Stoughton-Halperin conventions, instead of $E=E_{cd}$ [VUK92].
V. PROCEDURE

5.1 Set-up

The neutron activation technique requires two main facilities; an intense neutron source and a γ-spectrometry set-up. We use neutron fields in the research reactor BR1 of the SCK at Mol (typical neutron flux parameters in e.g. irradiation channel Y4: $\Phi_{n} = 3.85 \times 10^{14}$ s$^{-1}$cm$^{-2}$, $f = 35.8$, $\alpha = 0.061$ [ROB95]). For the γ-spectrometry HPGe detectors with well defined properties are used (40% relative efficiency). System dead-time and pulse pileup losses are corrected for by an LFC-module ('Loss Free Counting'). For the γ-spectrum deconvolution, we have the programs 'PC-HYPERMET' and 'SAMPO90' at our disposal. The commercially available software 'SOLCOI®' and 'KAYZERO®' is applied for the calculation of the detector efficiencies and the trace concentrations respectively [VSL92]. Detector efficiency determinations are based on the semi-empirical method of Moens et al. [MOE81a,82,83]. Concentrations are calculated following the $k_{r}$-methodology [DEC87]. A more detailed description of the current set-up of IRMM and SCK and on calibration results can be found in [ROB95] [POM98] or updated internal reports of either institute.

5.2 Neutron flux characterisation

5.2.1 Cd-ratio method

The Cd-ratio method is an adequate technique for a priori neutron field monitoring, when the latter is known to be stable as a function of time. A set of $N$ monitor pairs is irradiated, one half with Cd-cover and the other without. Their activities are subsequently measured on a spectrometer. If all monitors are of the '1/v'-type, one can derive $f$ and $\alpha$ when plotting the straight line:

$$y_i = \log \left( \frac{(E_{r,i})^{-\alpha}}{f_i} \right) \quad \text{versus} \quad x_i = \log(E_{r,i})$$

with:

$$f_i = (F_{Cd,i} \cdot R_{Cd,i} - 1) \cdot Q(\alpha) \cdot \frac{G_{Cd,i}}{G_{th,i}}$$

(i=1,...,N)

$f_i$: the subcadmium-to-epithermal flux ratio measured with monitor $i$
The parameter $\alpha$ is found as the slope ($-\alpha$) and the flux ratio $f$ is found as the intercept $1/f$ at $E_r=0$. At least two monitors are required. In view of the $\alpha$-dependence of $Q_0(\alpha)$, an iterative fitting procedure has to be applied. An unweighted least squares fit of the slope is equivalent with solving the equation:

$$\alpha + \frac{\sum_{i=1}^{N} (x_i - \langle x \rangle) \cdot (y_i - \langle y \rangle)}{\sum_{i=1}^{N} (x_i - \langle x \rangle)^2} = 0$$  \hspace{1cm} (5.2)$$

In practice a weighted fit is to be preferred, since e.g. the experimental accuracy on $(R_{Cd}^{-1})$ will be relatively low for monitors with a very high $Q_0$-value.

The Cd-ratio method is the only one which is not leading to a vicious circle in the experimental $\alpha$ and $k_0$-determination (except when $k_0$ is derived from the Cd-subtraction method), since the knowledge of $k_0$ is not required for calculating $\alpha$.

### 5.2.2 Bare multi-monitor method

The bare multi-monitor method is essential for in-situ neutron flux characterisation for conventional NAA. A set of monitors is irradiated in (nearly) the same conditions as the sample and subsequently measured on the detector. If the monitors fulfil the Høgdahl conditions, then ($-\alpha$) can be obtained as the slope of the straight line when plotting [DEC87] :

$$\log \left( \frac{(E_r;\alpha)^{-\alpha} \cdot A_1}{\log(E_r;\alpha)} \right) \text{ versus } \log(E_r;\alpha)$$  \hspace{1cm} (5.3)

with:

$$A_i = \frac{A_{sp,i}}{k_0(\alpha)^\varepsilon_p,i} - \frac{A_{sp,1}}{k_0(\alpha)^\varepsilon_p,1} \cdot \frac{Q_{0,1}(\alpha) \cdot G_{e,i}}{G_{th,i}} \cdot \frac{Q_{0,1}(\alpha) \cdot G_{e,1}}{G_{th,1}} \hspace{1cm} (i=2,...,N)$$

and where the monitor 1 acts as 'reference'. The procedure for the $\alpha$-determination is analogous as in previous section.

The flux ratio $f$ can be calculated from two different monitors :

$$f = \frac{G_{e,1} \cdot \frac{k_0(1)}{k_0(2)} \cdot \frac{\varepsilon_p,1}{\varepsilon_p,2} \cdot Q_{0,1}(\alpha) \cdot \frac{A_{sp,1}}{A_{sp,2}} \cdot \frac{Q_{0,2}(\alpha)}{Q_{0,2}(\alpha)}}{G_{th,2} \cdot \frac{A_{sp,1}}{A_{sp,2}} \cdot \frac{\varepsilon_p,1}{\varepsilon_p,2} \cdot \frac{k_0(1)}{k_0(2)}} - \frac{G_{e,2} \cdot \frac{A_{sp,1}}{A_{sp,2}} \cdot \frac{Q_{0,1}(\alpha)}{Q_{0,1}(\alpha)}}{G_{th,1} \cdot \frac{A_{sp,1}}{A_{sp,2}} \cdot \frac{\varepsilon_p,1}{\varepsilon_p,2} \cdot \frac{k_0(1)}{k_0(2)}}$$  \hspace{1cm} (5.4)
For a full characterisation of the thermal and epithermal neutron field a minimum of three monitors is required. The ideal triple set would have following properties: one reaction is dominantly induced by thermal neutrons, while two others are dominantly induced by the epithermal fraction; one with a low effective resonance energy for a good f-determination with low $\alpha$-influence and one with a high effective resonance energy for the $\alpha$-determination.

The *bare triple-monitor method* is of great importance for routine flux monitoring, particularly with $^{197}$Au and $^{94}$Zr-$^{96}$Zr as monitors. Some interesting aspects of these particular monitors can be derived from table 5.1. The zirconium offers two well suited reactions for the f-determination; one with a low $Q_0$ and another with an extremely high $Q_0$. The gold value is intermediate. Equally important, there is a wide spread on the effective resonance energy, which facilitates the $\alpha$-determination. On the other hand, the effect of the high energy resonance for $^{96}$Zr$(n,\gamma)$ is partly masked by the relatively large thermal neutron contribution. So, any inaccuracy on the result for the thermal neutron flux will have its repercussion on the determination of the f- and $\alpha$-values.

**Table 5.1 : Some relevant parameters of the reactions used in the Au-Zr bare triple-monitor method for the neutron field characterisation.**

<table>
<thead>
<tr>
<th>monitor</th>
<th>$Q_0$</th>
<th>$E_r$ (eV)</th>
<th>$E_1$ (keV)</th>
<th>$T_{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{197}$Au$(n,\gamma)^{198}$Au</td>
<td>15.71</td>
<td>5.65</td>
<td>411.8</td>
<td>2.695 d</td>
</tr>
<tr>
<td>$^{94}$Zr$(n,\gamma)^{95}$Zr</td>
<td>5.05</td>
<td>6260</td>
<td>724.2, 756.7</td>
<td>64.03 d</td>
</tr>
<tr>
<td>$^{96}$Zr$(n,\gamma)^{97}$Zr$^{72m}$Nb</td>
<td>248</td>
<td>338</td>
<td>743.3</td>
<td>16.74 h</td>
</tr>
</tbody>
</table>

Zr and Au reference materials are readily available in a convenient shape. The monitors have convenient half-lives, allowing the completion of the analysis within the first days after the irradiation, on the basis of three short measurements. Usually the Au and Zr monitors are measured on the first day after the irradiation, at the 'reference' position of the detector (ca. 30cm). Since the measurement of $^{95}$Zr often requires an excessively long counting time, the Zr is remeasured in a close-by geometry after about 3 days, when the disturbing $^{97}$Zr$^{72m}$Nb-activity is much reduced. The gamma-lines involved require no true coincidence corrections. It is sufficient to have an accurate detection efficiency value for the reference position. The efficiency for the 743.3 keV line of $^{97}$Zr at the close-in geometry is as good as equal to that of the combination of the 724.2 and 756.7 keV lines of $^{97}$Zr$^{72m}$Nb. By comparing the activity of the latter at both measurement positions, one can easily derive the detection
efficiency for the 743.3 keV line of $^{95}$Zr in the lower position relative to the reference position.

In general the error propagation factors and the resulting uncertainties on $\alpha$ for the "bare multi-monitor method" are larger than for the "Cd-covered" and the "Cd-ratio" measurements. This is not surprising, considering the fact that the latter techniques allow an easy elimination of the thermal neutron contribution. Nevertheless the reached accuracy is sufficient in view of the large error reduction factor towards the analytical result. In recent years evidence is gathering that the Au-Zr bare triple monitor method provides results which distinctly deviate from those of the Cd-ratio method. Preliminary reevaluations of the Zr $k_e$-factors show significant deviations from the currently used values [SIM97].

The $f$ and $\alpha$-determination is done in a quite similar fashion in the Westcott convention (including non-$1/v$-nuclides), only with slightly different reaction rate representations [DEC94b]. For high neutron flux regimes, a method has been devised to determine the gold burnup correction factor prior to any flux characterisation, based on the spectrometry of $^{199}$Au decay gammas [POM97d].

5.2.3 In-situ Cd-covered method

This method is essential for the $\alpha$-determination in epicadmium NAA. A set of at least two monitors is irradiated under Cd-cover and subsequently measured on a calibrated detector. For '1/v-nuclei', the $\alpha$-value is found as the slope ($-\alpha$) of:

$$\log \left[ \left( \frac{E_{r,i}}{T_i} \right)^{\alpha} \cdot T_i \right] \quad \text{versus} \quad \log(E_{r,i})$$

with:

$$T_i = \frac{A_{sp,i}^{Cd}}{k_{0,Au} \cdot \varepsilon_{p,i} \cdot F_{Cd,i} \cdot Q_{0,i}(\alpha) \cdot G_{e,i}}$$

5.3 Detector calibration

5.3.1 Detection efficiency of the spectrometer

High purity germanium detectors are recommendable tools for the spectrometry part of NAA. They combine excellent resolution properties with a reasonable detection efficiency. The detection efficiency - defined as the ratio between the full peak count rate and the photon emission rate at the corresponding energy - is specific for each 'detector - source - geometry' combination. In practice the absolute efficiency is determined by measuring the peak count
rate of a reference source with known activity and at the same geometrical conditions as the samples for which the calibration is performed.

This practice of detector calibration is the most straightforward and practical one when measurements are restricted to a limited number of geometries. On the other hand, when applying a multitude of samples with different sizes, shapes, constituents and placed at various sample-detector positions, the whole procedure of preparing and measuring carefully calibrated sources would become quite cumbersome and time consuming. Additional problems can be caused by true coincidence effects; i.e. the simultaneous detection of two or more photons produced coincidentally in the same nuclear decay process. These effects are particularly important in closely geometries with high efficiency detectors.

An alternative procedure - based on calculation - is foreseen to tackle these problems. We have opted for the semi-empirical technique developed by Moens et al. [MOE81a,83], which is applied in the commercially available software SOLCOI* [VSL92]. The program allows efficiency and true coincidence calculations for cylindrical samples placed in the centre of axis of a coaxial detector. The sample radius should not exceed that of the Ge-crystal. An accurate knowledge on the geometrical aspects of the crystal and its housing is required. Also the sample dimensions and composition, as well as the thickness and composition of all absorbers between emitter and detector should be known. The method is applicable to detectors with or without p-core.

5.3.2 Mathematical procedure for cylindrical sources

In order to have a valid 'full energy' event, the photon emitted from the source should hit the active zone of the detector and deposit all of its energy by one or more interactions in the crystal. The photon should therefore not undergo any energy degradation or absorption in the source or in whichever material between source and active detector zone. Also partial energy depositions, poor charge collection and coincidences with other detector pulses lead to invalid signals.

Direct calculations of the full peak efficiency $\varepsilon_p$ at a certain photon energy $E_y$ lead to complex computations. Moens et al. have opted for an indirect approach, by calculating the total efficiency $\varepsilon_t$. The semi-empirical determination of the efficiency is still based on one reference measurement; this is the full peak efficiency $\varepsilon_{p,ref}$ versus $E_y$ for point sources positioned at a reference position (typically 30 cm away from the detector cap). The efficiency at energy $E_r$ for any other geometrical situation of interest is then obtained from:

$$\varepsilon_{p,geo} = \frac{(p/t)_geo}{(p/t)_ref} \cdot \frac{\varepsilon_{t,geo}}{\varepsilon_{t,ref}} \cdot \varepsilon_{p,ref} \quad (5.6)$$
in which \( p/t \) is an intrinsic peak-to-total ratio, characteristic of the detector, at energy \( E_r \). This is not the typical peak-to-total ratio \( P/T \) obtained in experimental situations, which is affected by surrounding materials, like the lead shielding, detector-can, Ge dead layer, etc. and is therefore dependent on sample and counting geometry. The intrinsic peak-to-total at a certain energy relates to the bare detector only. In first approximation, it can be assumed constant for different sample geometries and distances.

The calculations now mainly concentrate on the total efficiency, which is directly proportional to the 'effective solid angle'. This parameter incorporates three components; a true geometrical solid angle \( \Omega \), a directionally dependent photon attenuation factor \( F_{\text{att}} \) for attenuation outside the active detector zone and an efficiency factor \( F_{\text{eff}} \) expressing the probability for energy deposition in the sensitive crystal. The effective solid angle should be calculated for each point of the source and integrated:

\[
\Omega = \int_{\text{source}} \Omega \cdot F_{\text{att}} \cdot F_{\text{eff}} \, dv
\]  

(5.7)

The authors stress the importance of treating the three factors in the same integrand, instead of separating them into individually evaluated factors. The calculation of the multiple integral is not straightforward. A procedure has been developed explicitly for cylindrically shaped samples and coaxial detectors [MOE81a,82,83]. This method has been extended to sample sizes exceeding the crystal diameter (e.g. Marinelli beakers) [MIH93] [DEC94b,c] [VUK97] [JOV97] [TKW97].

From ample experimental verification on different detectors and source geometries it has become clear that the ratio of the efficiencies is very well reproduced by the corresponding ratio of the effective solid angles. The assumption of an invariant intrinsic peak-to-total characteristic seems to be justified. The calculated efficiencies have an accuracy within 3%, on the condition that all geometrical aspects of the detector-source combination are accurately known [MOE81a,82,83]. Evidently the method is applicable also to disks and point sources, being simplifications of the more general cylindrical source shapes.

5.3.3 Detector calibration and fine-tuning

Activation spectra are usually stored in 8K channels, with a typical energy calibration of 0.4 keV/channel. Thus, an energy range between 0 and 3.2 MeV is covered. This is only useful if the efficiency curve can be determined for the full extent of the experimental scope. The semi-empirical method used here requires one experimental determination of the detection efficiency as a function of the energy; preferably for a point source at a relatively large distance from the detector (~30 cm); the so-called 'reference position'.
This is done with calibration sources of well known activity and half-life; e.g. $^{241}$Am, $^{133}$Ba, $^{109}$Cd, $^{57}$Co (in the low energy region), $^{60}$Co, $^{137}$Cs, $^{88}$Y, $^{54}$Mn, $^{22}$Na, $^{152}$Eu (in a medium energy range) and $^{226}$Ra in equilibrium with its decay products (in a wide range from low to high energy). These are long-lived products, which are commercially available as point source (e.g. from PTB). They sufficiently cover an energy range roughly between 55 keV and 2.45 MeV. A polynomial fit is performed to describe the behaviour of (the logarithm of) the efficiency as a function of (the logarithm of) the energy. Often the low energy range is fit quasi-independently from the medium and high energy range. To cover even higher energies one can consider the use of home-made secondary multi-gamma sources such as $^{72}$Ga, $^{182}$Ta, $^{24}$Na and $^{56}$Co, emitting gammas below as well as above the 2.45 MeV.

Relative to the efficiency in reference conditions, we can calculate the efficiencies for other geometries. As one gets closer to the detector, small geometry deviations result in appreciable changes in efficiency. The calculations become then susceptible to inaccuracies in the parametrisation of the whole configuration. It turns out that two critical detector parameters are usually not accurately controlled by the manufacturer: the vacuum gap between the crystal and its housing and the thickness of the dead layer (outer n' contact layer of a p-type crystal). Fortunately these parameters can be 'fine-tuned' by searching an optimum harmony between calculations and experimental results from a series of measurements with calibrated point sources at different distances.

It should be stressed that detector and sample holder are considered as a unity in the calculations. When changing to a different sample holder, one has to consider whether a new efficiency determination at reference position is required or whether a mathematical trick can be applied to reinterpret the previously performed calibration.

Still two major problems have to be tackled on the detector side: true coincidence effects and spectrometer pulse loss (system dead-time and pulse pileup). Both subjects are discussed next.

* Suppose one is changing to a holder with a thinner base. In this case no new calibration measurements are required. The initial calibration is equivalent with hypothetical measurements on the new sample holder with sources having an extra absorbing layer at the bottom, i.e. corresponding with the difference in thickness of the two holders.
5.4 True coincidence effects

5.4.1 True coincidence effects on detection efficiency

The observed γ-rays are often part of a complex cascade of deexcitation processes particular of unstable nuclei. Instead of being the sole witnesses of a nuclear transition, they can be accompanied by other γ-rays or charged particles. With increasing efficiency of the detection system, the simultaneous detection of two phenomena belonging to the same decay becomes more probable. The spectrometer is not able to discriminate between both if the lifetime of the intermediate levels in the nuclear decay are shorter than the resolving time of the spectrometer. The corresponding full or partial energy releases in the sensitive crystal are combined to a single pulse. Contrary to 'random coincidences', the occurrence of such 'true coincidences' is independent of the total count rate registered by the detection system. It is merely related to the high detection efficiency (and solid angle) and limited resolving time of the spectrometer set-up.

True coincidences create undesired deviations on the full peak detection efficiency for closeby sample-detector geometries. Consider a hypothetical energy level scheme in figure 5.1. If the gamma transition B is detected (fully or partially) together with gamma transition C, a pulse count is lost in the spectrum at energy $E_c$. In the terminology of Debertin and Helmer, this is a case of 'summing-out' [DEB88]. In case both B and C are fully detected simultaneously, there will be summing out in the $E_B$ and $E_C$ peaks together with a 'summing-in' in the $E_A$ peak ($E_A = E_B + E_C$).

![Figure 5.1](image.png)

*Figure 5.1: Hypothetical decay scheme, in which gamma transition A connects the same energy levels as the consecutive transitions B and C.*

The magnitude of these effects on the $E_A$ peak area often amounts to several percent. This can be ignored in the case of NAA with relative standardisation (when using identical geometries for standard and sample), but has to be computed when applying absolute or
k_0 standardisation. The full energy peak area N_{p,A} of transition A is corrected with a factor "COI":

\[
\frac{N_{p,A}^{(\text{correct})}}{N_{p,A}^{(\text{observed})}} = \text{COI}
\]

(5.8)

with: \( \text{COI} = (1-L[A]) \cdot (1+S[A]) \) and \( L[A] \) and \( S[A] \) respectively the total probabilities for summing-out and summing-in of the A-peak.

Summing out events do not only arise from the simultaneous detection of several \( \gamma \)-rays, but also from beta particles and their associated bremsstrahlung, annihilation radiation from positron decay and X-rays emitted after (i) IC ; internal conversion of a gamma transition and (ii) EC ; electron capture of an orbital electron. Electron vacancies may give rise to phenomena other than X-ray emission; ejection of Auger electrons and Coster-Kronig transitions [DEB88].

A hypothetical decay scheme is shown in figure 5.2, demonstrating different processes liable of causing summing-out effects on a gamma-transition A. The calculation of correction factors involves peak and total detection efficiencies, transition energies and intensities, branching ratios, X-ray energies and intensities, internal conversion coefficients and electron capture probabilities. Rigorous calculations would include angular correlations between consecutively emitted gammas [AND72,73]. In practice, the modest gain in accuracy doesn't outweigh the increased complexity of the formalism [MOE81b.82.83] [DEB79] [MCA75].

**Figure 5.2 : Hypothetical decay scheme, in which gamma transition A is preceded and followed by other transitions, resp. B and C, and where 'summing out' can be expected due to X-rays from EC and IC processes.**
5.4.2 $\gamma$-$\gamma$ coincidence summing

Consider again the case presented in figure 5.1. Per disintegration, one has to determine the relative probability of simultaneous full detection of B and C transitions, compared to the single A transition. The relative contribution of $\gamma$-$\gamma$ coincidence summing is given by:

\[ S(A=B+C) = \frac{\gamma_B \cdot a_C \cdot c_C}{\gamma_A} \cdot \frac{\epsilon_{p,B} \cdot \epsilon_{p,C}}{\epsilon_{p,A}} \]  

with: $\gamma =$ absolute gamma intensity; $a =$ branching ratio; $c = (1+\alpha_i)^{-1}$ and $\alpha_i =$ total internal conversion coefficient; $\epsilon_p =$ full-energy peak efficiency.

Triple coincidences are treated similarly, i.e. by multiplying expression (5.9) with an additional factor $a_x \cdot c_x \cdot \epsilon_{p,x}$ [DEC87].

The independent contribution of different cascades yielding the same total energy $E_A$ are summed:

\[ S(A) = S(A=B+C) + S(A=D+E+F) + ... \]  

The sum pulses coming from B+C, etc. are subject to the same true-coincidence losses as A itself.

5.4.3 $\gamma$-$\gamma$ and $\gamma$-KX(IC) coincidence loss

Coincidence loss by $\gamma$-KX(IC) processes are treated simultaneously with $\gamma$-$\gamma$ coincidences, since both originate from the same energy transitions. Gamma-rays are regarded as analytically important if their energy is higher than $\sim 100$ keV, mainly because of the low detection efficiency and high Compton continuum of typical Ge detectors at lower energies. The presence of attenuating materials also implies that only photons of sufficient energy (>50-60 keV) can cause a significant coincidence effect. Therefore only KX-rays are considered here, even though the principle has been extended to LX-rays for applications with low-energy photon detectors (LEPD) [CMF93] [DEC92].
Consider the simple case of a transition A followed by a transition B, with a total conversion probability of \( \alpha = \alpha_{K\alpha_1} + \alpha_{K\alpha_2} + \ldots \) \((\alpha = N_{\text{electron}}/N_{\gamma\text{amma}})\). The probability for summing-out of a measured transition A with the gamma B or a \( K\alpha_1 \) or \( K\alpha_2 \) X-ray from conversion of transition B, represented by \( L(A-B) \), \( L[A-K_{\alpha_1}(B)] \) and \( L[A-K_{\alpha_2}(B)] \) respectively, are calculated from:

\[
L(A-B) = a_B \cdot c_B \cdot e_{i,B} \tag{5.11}
\]

where
- \( a_B \) is the probability A is followed by transition B,
- \( c_B = 1/(1 + \alpha_{t,B}) \) is the probability gamma-ray B is emitted,
- \( e_{i,B} \) is the probability partial or full energy detection.

\[
L[A-K_{\alpha_1}(B)] = a_B \cdot c_B \cdot \alpha_{K,B} \cdot \omega_k \cdot k_{\alpha_1} \cdot e_{i,K_{\alpha_1}} \tag{5.12}
\]

where
- \( a_B \) is the probability A is followed by transition B,
- \( c_B \) is the probability K-electron is emitted,
- \( \omega_k \) is the probability KX-ray is emitted (fluorescence yield),
- \( k_{\alpha_1} \) is the probability KX-ray is \( K\alpha_1 \) (rel. emission rate),
- \( e_{i,K_{\alpha_1}} \) is the probability partial or full energy detection.

and so on for \( L[A-K_{\alpha_2}(B)] \), etc.

The contributions of \( \gamma-\gamma \) and \( \gamma-KX \) coincidences to the pulse loss of A are summed:

\[
L(A) = L[A-B/KX(B)] = L(A-B) + L[A-K_{\alpha_1}(B)] + L[A-K_{\alpha_2}(B)] + \ldots
\]

\[
= a_B \cdot c_B \cdot (e_{i,B} + \alpha_{K,B} \cdot \omega_k \cdot \sum_i k_i \cdot e_{i,K_i}) \tag{5.13}
\]

with \( i = \alpha_1, \alpha_2, \ldots \).

The above reasoning for a simple cascade of two transitions can 'easily' be extended to more complex schemes. As an example, consider a series B-C-A. Introducing the notation:

\[
\Sigma_y = e_{i,y} + \alpha_{K,y} \cdot \omega_k \cdot \sum_i k_i \cdot e_{i,K_i} \quad (y = B, C, \ldots) \tag{5.14}
\]

one can write the probability \( L(A) \) as follows [MOE81b] [DEC87]:

\[
L(A) = L[B/KX(B) - C/KX(C) - A]
\]

\[
= \frac{\gamma_B}{\gamma_A} a_c a_A c_A \Sigma_B + \frac{\gamma_C}{\gamma_A} a_A c_A \Sigma_C - \frac{\gamma_B}{\gamma_A} a_c a_A c_A \Sigma_B c_B \Sigma_C \tag{5.15}
\]

55
The first term takes care of the coincidence loss of a measured transition A with a (partly) detected transition B (involving cascade via intermediate transition C); the second term involves loss of A due to transition C; the third term is a correction for the double counting of events in which transitions B and C are detected simultaneously.

In practice, the contribution of cascades of more than five transitions turns out to be negligible. In appendix C, expressions are given for summing-out of A in series of five transitions (for each possible position of A in the series). In practice, the first terms of expressions C.1-C.5 are dominant, while the others can be left out of consideration because they contain multiplications of two or more detection efficiencies (in most cases $\varepsilon_1 \varepsilon_2 << 0.04$). These expressions can also be applied to less complex series, by omitting unnecessary terms (see appendix C). A table of relevant cascades and nuclear data for analytically important isotopes is presented in [DEC87].

If transition A is part of several cascades, one calculates the total probability for coincidence loss by summing the individual contributions. In many cases, some 'sub-cascades' (including A) are common to the different cascading series and a proper subtraction is needed so as to count their contribution only once. Occasionally, this procedure leads to the necessity of adding again extra terms to compensate for unwanted subtractions [MOE81b] [DEC87].

Consider e.g. following cascades: B-A-C-D, E-A-C-D, B-A-F, and E-A-F. To count each branch only once, one should write:

\[
L(A) = L(B-A-C-D) + L(E-A-C-D) + L(B-A-F) + L(E-A-F) \\
- L(A-C-D) - L(A-F) - L(B-A) - L(E-A)
\]

\[5.16\]

### 5.4.4 $\gamma$-KX(EC) coincidence loss

When using regular Ge-detector set-ups (threshold 50-60 keV), the $\gamma$-KX(EC) coincidence loss is only significant for few analytically interesting radionuclides ($Z>70$). Explicit treatment for $^{175}$Hf and $^{185}$Os can be found in [DEC87]. Again, a more general formalism has been developed for LEPD's, including LX-rays [CMF93] [DEC92].

The principle of $\gamma$-KX(EC) coincidence loss correction will be demonstrated here with one example; i.e. the situation presented in figure 5.2. The formulas are similar to the ones in appendix C. Omitting higher order terms in $\varepsilon_1$, one gets:

 indication of KX-ray contribution from internal conversion omitted for convenience here
\[
L(A) = L(X_{ECI}-B-A-C) + L(X_{ECII}-A-C) - L(A-C)
\]
\[
\approx PP_{IA} \cdot \Sigma_{ECI} + \frac{\gamma_{B}}{\gamma_{A}} \cdot a_{A} \cdot c_{A} + a_{C} \cdot c_{C} + PP_{IIA} \cdot \Sigma_{ECII}
\]

with :
\[
PP_{IA} = \frac{a_{B} \cdot \epsilon_{I}}{(\epsilon_{II} + a_{B} \cdot \epsilon_{I})} = \text{probability that } A \text{ is preceded by } EC,I
\]
\[
PP_{IIA} = \frac{\epsilon_{II}}{(\epsilon_{II} + a_{B} \cdot \epsilon_{I})} = \text{probability that } A \text{ is preceded by } EC,II
\]
\[
\epsilon_{I}, \epsilon_{II} = \text{electron capture branching ratios}
\]
\[
\Sigma_{EC,I} = P_{K,1} \cdot \omega_{K} \cdot \sum_{i} k_{i} \cdot \epsilon_{i,ki} \quad (i=\alpha_{1}, \alpha_{2}, ...)
\]
\[
P_{K,1} = \text{probability that } EC,I \text{ is } K \text{ electron capture}
\]

5.4.5 Delayed \( \gamma-\gamma \) coincidence

The calculation of true coincidence effects gets slightly more complicated when the resolving time of the spectrometer is comparable to the lifetime \( T_{1/2} \) of intermediate nuclear levels involved in the cascade. The expressions above, leading to the coincidence correction factor \( COI \), implicitly assume no appreciable time delay between cascade transitions. Yet, in some cases an alternative factor \( COI' \) has to be determined, corresponding to the situation in which a nuclear level (and subsequent sub-cascade) 'survives' the detection of previous transitions. The consequences of time delay depend on the type of coincidence effect.

Considering coincidence loss of the type \( A-B \), a full-energy pulse of \( A \) will only be obtained if the time delay \( T_{d} \) is larger than the pulse peaking time \( T_{p} (=2.3 \tau) \) of the shaping amplifier of the spectrometer. This corresponds to a probability of :

\[
P(T_{d}>T_{p}) = \exp[ - \left( \frac{T_{p} \cdot \ln2)}{T_{1/2}} \right] \]

and the complementary probability \( P(T_{d}<T_{p}) = 1-P(T_{d}>T_{p}) \).

The coincidence correction for \( A \) can then be calculated as :

\[
COI'' = P(T_{d}<T_{p}) \cdot COI + P(T_{d}>T_{p}) \cdot COI'
\]

In the case of coincidence loss of the type \( B-A \), a clean full-energy pulse of \( A \) can only be obtained after the full processing of the preceding signal of \( B \), i.e. after the 'dead-time' \( DT \). The latter corresponds either with the end of the trailing edge of the pulse shape (fast ADC) or the transfer of ADC output to MCA. The probability is :

\[
P(T_{d}>DT) = \exp[ - \left( DT \cdot \ln2) / T_{1/2} \right] \]

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with DT possibly depending on the signal caused by B, in particular when using a Wilkinson type ADC.

**Perfect coincidence summing A=B+C** will occur only when the time delay between detection of B and C is very small compared to $T_p$, say e.g. 0.01 $T_p$. Otherwise appreciable tailing can be expected at the low-energy wing of the sum peak A.

### 5.4.6 Peak-to-total ratio

The calculation of coincidence loss requires knowledge on the detection efficiency, which can be obtained from the full peak efficiency as:

$$
\epsilon_T = \frac{\epsilon_p}{P/T}
$$

with $P/T$ = the peak-to-total ratio.

$P/T$ is experimentally determined by use of coincidence-free, preferably mono-energetic, gamma-emitters. Use can be made of $^{241}$Am (59.5 keV), $^{109}$Cd (88.1 keV), $^{57}$Co (122.1 keV), $^{203}$Hg (297.2 keV), $^{51}$Cr (320 keV), $^{137}$Cs (661.6 keV), $^{65}$Zn (1115.5 keV),... The peak-to-total ratio depends on several parameters, such as the photon energy, the source-detector separation, the source geometry and composition and the presence of absorbing and scattering materials (e.g. the lead shielding). A typical $P/T(E_y)$ curve has a similar shape as the peak efficiency curve, with a maximum situated at roughly 150 keV. In practice, point sources are often used for the determination of $P/T$ at different source-detector distances and the same result is then also applied to other source geometries. Whereas this is not an excellent approximation for voluminous or dense sources, there is a strong error propagation reduction towards the analytical result, considering the moderate impact of true coincidence loss corrections.

The spectra used for the $P/T$-determinations should be corrected for background counts and the Compton continuum has to be extrapolated below the ADC discriminator, down to 0 keV. One should also subtract counts originating from emission other than the considered gamma-line; e.g. the 511 keV $\beta^+$ annihilation radiation for $^{65}$Zn, the $^{203}$Hg X-rays and the $^{57}$Co 136.5 keV gamma-ray. This can be done iteratively, by deducing their corresponding $P/T$-values from a polynomial fit to the provisional $P/T$-value of the considered $\gamma$-lines. In a few steps, one can identify the portion of continuum counts belonging either to the selected $\gamma$-peak or to the disturbing radiation [DEC-87].

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5.5 Spectrometer pulse loss compensation

5.5.1 Loss-Free Counting

With increasing activity of the samples a higher number of event signals are lost for measurement: i) the spectrometer is more often 'busy' processing accepted electronic pulses and hence unavailable for new input, ii) more pulse pileup occurs as the probability for random coincidence increases. Since the analytical result is directly influenced by pulse loss, a precise correction in any circumstance is mandatory.

Traditional built-in live-time correction systems are unable to adequately compensate for pulse loss at high counting rates. They are of little or no use in real-time situations and for the measurement of products with short half-lives. Fixed dead-time correction systems offer a solution for measurements at varying counting rates, at the cost of a deliberately rejected fraction of the input. Pulser techniques can compensate for pileup effects but are generally inadequate in situations with variable dead-time and clumsy in low count rate regimes, where they generate extra dead-time in the system. The latter is even left unnoticed by the pulser technique itself if the test pulses cannot interfere with each other, e.g. by applying a fixed pulser frequency.

Alternatively, the problem can be addressed with "Loss-Free Counting" or LFC techniques. These are statistical methods compensating any pulse loss by adding 'n' counts instead of '1' to the spectrum. LFC techniques differ in the way the weighting factor 'n' is determined and their ability to rapidly adjust its value under varying counting regimes. One of these techniques is the "Virtual Pulse Generator" or VPG method presented by Westphal [WPH82]. Instead of introducing actual test pulses into the preamplifier, the status of the analyser is inspected by means of a correlative test of the baseline of the shaping amplifier and the 'busy' output of the pulse height analyser. Such tests, the success of which is the prerequisite for pileup-free counting, are initiated periodically by a high-frequency digital clock, supplying an 'up-to-date' real-time correction factor within milliseconds and without interfering with the actual data taking.

The VPG concept is illustrated in figure 5.3. The Pulse Evolution Time (PET) is defined as the time between the point that the pulse rises above the baseline noise and the point where it 'reaches' its peak (=when the trailing edge is discerned). For a successful test it is required that the amplifier base line remains steady for one PET and that the analyser is 'not busy' at the end of the PET. Each system 'busy' signal is extended with one PET, simulating the time it would take to detect a true, pileup-free test pulse. The subsequent trials may overlap for better statistical precision, since no physical pulser signal is used. The weighting factor 'n'.
being the ratio of total trials to successful trials, is applied to the events processed during the next inspection period. The duration of an inspection period is determined by the test frequency (5 MHz for a ND599 unit), a preset value of positive trials (256 [WPH82]) and the instantaneous weighting factor n (i.e. period=n×51.2 μs).

In practice, the LFC module is fine-tuned by adjusting the PET. Its operation can be verified by checking the count rate stability from a fixed weak source, when an interfering strong source is moved closer to the detector. The maximum count rate at which the LFC can still properly compensate for pulse loss depends on the shaping time of the amplifier; an optimum has to be chosen between fast timing and energy resolution. To reduce the 'noise' level in the spectra, it is recommendable to opt for a shaping detector with built-in pileup rejection.

5.5.2 Statistical variance of counting

Whereas Poisson statistics play a fundamental role when counting large numbers of nuclear disintegrations, one cannot expect the LFC corrected activation spectra to obey Poisson statistics. In fact this shouldn't be taken for granted in any type of experimental counting, since the statistics of detection does not necessarily follow the statistics of emission [ICR94] [POM97c,e]. A Poisson process is fully characterised by the typical exponentially varying

![Diagram](image-url)
time interval distribution of consecutive events. Significant non-random event losses due to pileup and dead-time distort the time distribution of detected radioactivity events, hence induce deviations from Poisson statistics. The Loss-Free Counting method introduces additional distortions, by clustering artificial counts to real events [POM97e].

The effects on counting uncertainty depends on the type of count loss. In the literature, one distinguishes between 'extending' and 'non-extending' dead-time, depending on whether or not the 'dead-time' of the system is prolonged by a new pulse arriving during an ongoing dead-time period. In common circumstances, the counting uncertainty can be calculated respectively from [ICR94] [MUL73] [MUL74] [LIB76]:

\[
\frac{\sigma e}{\sqrt{N}} \approx \frac{1}{1 + R_0 \cdot \tau}
\]

and

\[
\frac{\sigma ne}{\sqrt{N}} \approx \sqrt{1 - 2. R_0 \cdot \tau \cdot e^{-R_0 \cdot \tau}}
\]

with \(R_0\) the incoming count rate, \(\tau\) the (fixed) dead-time and \(N\) the number of counted events.

Such 'Müller distributions' have a variance-to-mean ratio less than one, whereas this is one for Poisson distributions. The validity of 'Müller statistics' has been experimentally verified in numerous types of measurements [JOR78]. These formulas pertain to the integrated counts of the full spectrum of events being processed by the system (and contributing to the dead-time). When observing a smaller fraction (like e.g. one peak in a \(\gamma\)-spectrum), the count scatter converges towards Poisson behaviour. Indeed, the corresponding time interval distributions are flatter and therefore less influenced by time distortions at low time intervals [POM97e].

Traditionally, the \(\gamma\)-spectrometer is considered as a "system with non-extending dead-time", i.e. the dead-time is not extended by events falling within the dead-time. The condition of non-extending dead-time is valid in the case that the ADC is the major source of system dead-time. Nowadays, ultra-fast ADC's are available which introduce no significant system dead-time to the spectrometry system (e.g. 800 ns Fixed Dead-Time ADC). The bottleneck has shifted towards the shaping amplifier: if the time constant of the amplifier is shortened to provide a rapid baseline restoration for high count rate work, the signal quality degrades by allowing too much noise through the filters. (Typical time constants used are 2-4 \(\mu\)s.) Consequently the contribution of pileup to the system 'dead-time' becomes increasingly important and requires specific statistical treatment. Whereas pulse pileup is loss of the extending type, it is not equivalent to extending dead-time [POM97e]. When considering energy-selective spectrometry or data taking with a built-in pileup rejecter, the pileup leads to the loss of at least two signals: the first as well as the second pulse. This peculiarity of pulse
loss by pileup is not included in the Müller statistics (formula 5.22). It turns out that pileup leads to a higher count scatter than dead-time [POM97c,e].

Computer simulations show that the LFC technique is able to reproduce the average incoming count rate, irrespective of the type and amount of event loss [POM97c,e]. It is unable to reproduce the original time interval distribution, hence presents a problem of statistical control. It was argued that the standard deviation of Loss-Free Counting can be calculated from [WPH79]:

\[
\left( \frac{dN_{LFC}}{N_{LFC}} \right)^2 = \left( \frac{dN}{N} \right)^2 + \frac{1}{N} \left( \frac{dn}{<n>} \right)^2 \Rightarrow \left( \frac{dN_{LFC}}{N_{LFC}} \right) = \frac{1}{\sqrt{N}} \times \sqrt{1 + \frac{1}{N} \left( \frac{dn}{<n>} \right)^2}
\] (5.24)

Formula 5.24 is based on a statistical law for the variance of the product of two independent variables, in this case the average weighting factor \(<n>\) and the number of processed events \(N\). This expression conceals some simplifications [POM97e]: (1) the implicit assumption of a Poisson distribution for \(N\), which is not rigorous in extreme counting conditions; (2) strictly speaking, the applied sum rule for variances is only to be applied to independent variables that are gaussian distributed. In contrast, the applied weighting factor \(n\) has a discrete distribution and is dependent on the amount of processed counts in the previous VPG inspection period; (3) it is assumed that a fresh, independent \(n\)-value is generated for each incoming event, whereas the same \(n\)-value can be used for several (tens) of events (depending on the settings of the virtual pulser).

Instead of a product of two 'independent' variables, \(N_{LFC}=<n> \cdot N\), one should be describing the sum of a variable number of grouped \(n\)-values, \(N_{LFC} = \sum_{i} n_i \cdot N_i\), the weighting factor of each group depending on the number of events in the previous one(s). Such rigorous treatment is not trivial [POM97e]. Up to now, no overall statistical control of Loss-Free Counting has been achieved.

Not unexpectedly, the formula 5.24 underestimates the true experimental LFC uncertainty at extremely high count rates, as the latter is not exactly proportional to the square root of the number of processed events [POM97e] [HEY97]. Nevertheless formula 5.24 is a useful approximation at practical conditions of analysis, able to account for the observed variability between duplicate countings at low or moderate count rates [HEY97].

The interpretation of LFC-spectra requires an adaptation of the existing spectrum deconvolution software and the routine for the determination of detection limits.
5.6 Analysis Software

5.6.1 Spectrum deconvolution

The interpretation of activation spectra is probably best performed with specialised software. Manual inspection methods still work adequately in the case of well separated peaks on flat continua, but modern computer routines can perform a full spectrum analysis much faster, including complex background subtraction, multiplet fitting, automatic peak width fitting, etc. It is nevertheless recommendable to verify automatic spectrum deconvolutions visually and where necessary repeat the analysis locally, possibly by fixing some parameters.

The recently growing popularity of the Loss-Free Counting technique with dual spectra is putting a new demand on the contemporary software. Instead of the typical 8K spectrum, one gets a 16K tandem spectrum, consisting of a pulse loss corrected part (8K) and an uncorrected part (8K). A correct use of the LFC technique implies a full analysis of both parts. Since the classical peak search routines assume spectra of Poisson nature, their criteria might be triggered too soon in the vicinity of highly staggering LFC corrected channel counts. One can avoid defining new peak search criteria for LFC spectra by copying the peak locations found in the uncorrected spectrum. In Poisson statistics, the reciprocal channel counts are used as weighting factors for least squares fitting. The appropriate weighting factors for LFC spectra can be derived by combining both spectrum parts, e.g. by assuming the same relative error. Only at this stage, the total peak areas can be fitted from the corrected spectrum and the corresponding uncertainties derived from the uncorrected spectrum. As peak widths tend to increase in high counting rate situations, errors can be avoided by applying automatic peak width fitting. Complications arise in multiplets with individual peaks detected at different counting rate regimes.

Currently one commercially available package has been adapted to cope with LFC tandem spectra [FAZ97].

5.6.2 Concentration calculations

The $k_0$-methodology can be applied to convert the $\gamma$-peak areas into concentrations. To reduce possible human errors in the interpretation stage, the software should use all available information to check the validity of the assumptions made and to reduce the chances on interfering effects. Before assigning a certain $\gamma$-peak to some element, the program could assist in verifying whether complementary $\gamma$-lines are also present in the activation spectrum. In case of doubt about the origin of a certain $\gamma$-peak, the software can already exclude certain hypotheses on the basis of the available information. Knowing the concentration of some elements, the rate of their corresponding nuclear reactions can be calculated and hence also
the interference caused on the detection of neighbouring elements (see paragraph 2.20). At least this could be done for the main matrix components, if necessary by feeding the main matrix composition directly to the program. The software could also provide restrictions on the analytical result in the absence of complete analytical determination of the sample, e.g. by pointing to the fact that a certain fraction of the measured signal could be coming from an unverified interfering reaction or that some uncertainty exists on the self-shielding factor due to insufficient information on the sample composition.

It can be argued that, in principle, NAA can only be safely operated when full analytical characterisation is reached down to trace level. This explains the plea for a holistic approach of spectrometry in INAA [BLA93]. In fact, the ultimate software should provide total integration of all operations involved, making use of all available information. One could imagine an 'intelligent' program steering the irradiations, sample changer, data acquisition as well as the subsequent analysis steps. Such 'master' program could adjust its time schedule while processing and interpreting all incoming data.

Analysis software for $k_0$-INAA is commercially available (KAYZERO* [VSL92]), with a complete library of $k_0$-factors and other parameters valid in the Høgdahl convention. Good connectivity is provided with spectrum deconvolution software and a program for the calculation of the detection efficiency. Concentration results can be viewed individually or statistically integrated over the different $\gamma$-lines and/or samples. As yet, the Westcott convention is not implemented, nor are the formulas for multiple irradiations, burn-up and self-shielding. There is also no support for the calculation of possible interference effects, nor does the software generate warning messages for them.
VI. PERFORMANCE OPTIMISATION

6.1 Need for a priori information

Almost regardless of the application field, there exists a problem of a priori determination and optimisation of the analytical performance of INAA. Evidently, the performance is strongly related to the characteristics of the applied neutron field and the gamma spectrometer. However, the main difficulty with INAA is that the quality of the results strongly depends on the matrix activities at measuring time. The procedure often has to be adjusted to the type of sample analysed.

The goal of optimisation is to give a set of parameters - such as activation time, decay time, measuring time, sample weight, sample-detector distance, etc. - that yields good analysis performance at a reasonable cost of effort, time and money. Particularly in the case of multi-element analysis one needs some computational assistance to make an adequate choice. The problem has been addressed by several authors, using methods with varying applicability and complexity [BUR90]. We have opted for a simple but efficient method, which is fully integrated in a spreadsheet [POM97a].

6.2 Procedure

Obviously a direct computation of the optimum solution for the optimisation of NAA is far from being straightforward. The complexity of the equations involved grows rapidly as the number of adjustable parameters is increased, in particular if a multi-element determination is attempted.

A realistic approach probably has to follow a few logical steps: i) computer simulation of the activation and consequent spectrometry of the sample, ii) computation of the analytical response from the spectra and finally iii) search of the best parameter values (requiring the repetition of the first two steps). Contrary to the solution of complex systems of equations, this approach is rather easy, assuming that the analyst can rely on a complete library of nuclear constants, reactor and detector parameters, etc. Most of the required information is normally present in each NAA-lab. In our case, we have based our calculations on the data published by De Corte et al. in the framework of the $k_{eq}$-method. All necessary parameters and formulas have been introduced in a spreadsheet file on PC (Quattro Pro 5.00).
6.3 Simulation of gamma-spectra

A first step to make is the simulation of the hypothetical activation and subsequent spectrometry of the sample. It merely suffices to calculate three essential types of parameters: (i) the full energy peak area, (ii) the 'noise' counts underneath the peak (Compton continuum, background activity, spectral interferences) and (iii) the total count rate. They will provide information respectively on (i) detection limits, (ii) obtained statistical accuracy on the peak area and hence the concentrations, (iii) system dead-time.

The full energy peak area $N_p$ is calculated directly from the concentration formula (4.2). The corresponding total area of low energy counts from incomplete energy depositions (mainly Compton interactions) is calculated from $N_p(T/P - 1)$, with $P/T$ the peak-to-total ratio at the energy $E_r$.

Additional counts are registered from ambient radiation; the true background events. The continuum part is roughly exponentially distributed as a function of the energy (or ADC channel). By fitting a straight line $(a'+b'.ch)$ to the logarithm of the counts found in a typical background spectrum (measurement time $T_m$), one can easily calculate a good estimate of the background in a typical NAA spectrum from $(t_m/T_m).10^{(a'.k.ch)}$, on condition of identical pulse amplification $(a=E/ch)$.

A third factor of importance is the possible spectral interference by one or more neighbouring $\gamma$-lines. When both $\gamma$-energies match perfectly, no distinction is possible and the total interfering peak area can be seen as additional 'noise'. (Correction is possible by determining the activity of the interfering nucleus from another $\gamma$-line in the spectrum.) As the interference peaks move further away on the energy scale, the chance grows that the spectrum deconvolution software arrives at determining the peak areas separately. The accuracy of the result depends on the spectrometer resolution and the (relative) peak heights involved. One of the many possible ways of treating the interferences is by adding to the noise an extra term $\Sigma N_{pi}.exp[-(E_{i}E_{r})^{2}/(w^{2}/(N_{p}/N_{pi}+N_{pi}/N_{p}))]$ (width parameter $w$~FWHM($E_{r}$)). It varies from zero to $\Sigma N_{pi}$, with increasing proximity and height difference of the peaks.
At last one should consider the number of channels that are involved in the characterisation of the \( \gamma \)-peak and its corresponding noise. We have chosen a range of \( n=3 \) times the FWHM, i.e. \( n_{\text{ch}} = n \cdot \text{FWHM}(ch) = 3 \cdot \text{FWHM}(E_{\gamma})/a \). It should also be realised that a fraction of the incoming counts are lost due to system dead-time. The 'noise' events associated with each peak are finally calculated from:

\[
B = n_{\text{ch}} \cdot \bar{b}(ch) \approx n_{\text{ch}} \cdot \left\{ \sum_{E>E_{\gamma}+w} \frac{N_p(T/P-1)}{(E-w)/a} + 10(a^i+b^i\cdot ch) \cdot \frac{I_m}{T_m} \right\} \cdot <\text{LT}> + ...
\]

\[\ldots + \sum_{E_{\gamma}-n.w}^{E_{\gamma}+n.w} \sum_{\text{interf. peaks}} N_{p,i} \cdot \exp \left[ \frac{-(E_i-E_{\gamma})^2}{N_{p,i}/N_{p} \cdot w^2} \right] \cdot <\text{LT}>\]

(6.1)

with \( <\text{LT}> \) the average live-time of the spectrometer during the hypothetical measurement.

The rectangular representation of the (Compton) continuum is of course very crude, and by far inferior to more refined models of spectrum simulation [ZIK78] [GUI82] [HSI87] [AMU87]. Yet, this is not a crucial issue if the composition of the sample - in particular the concentrations of easily activatable isotopes - is only known to the level of an order of magnitude. The advantage of the used representation is that the continuum part can easily be calculated in the spreadsheet, when the \( \gamma \)-lines are ordered by energy. The contribution of the peaks can be accumulated, when moving from high to low energy. It is quite essential that one has a list of all (major) \( \gamma \)-lines occurring in NAA, and not only those of particular analytical interest for the matrix at hand. Only then the (average) spectrometer live-time is fully accountable for:

\[
<\text{LT}> = 1 - <\text{DT}> = e^{-N_{\text{tot}}/N_{\text{char}}}
\]

(6.2)

with:

\[
N_{\text{tot}} = \sum_{\text{peaks}} N_p(E_{\gamma}) / (P/T)(E_{\gamma})
\]

\[
N_{\text{char}} = -N_{\text{tot}}/\ln(\text{LT}) \quad ; \text{characteristic count rate at which LT}=e^{-1}.
\]

It should be realised that any performance evaluation should always be based on the truly registered peak area \( N_p <\text{LT}> \) and not on the pulse loss corrected value \( N_p \). Also the use of e.g. a loss free counting module does not alter the sensitivity or accuracy of the method. The use of an average \( <\text{LT}> \)-value can be deceiving in situations with rapidly changing count rates. This can e.g. be avoided by using measurement times \( t_m \) which are not exceedingly longer than the cooling times \( t_d \).
6.4 Analytical response function

As soon as the problem of spectrum simulation is taken care of, the analytical performance corresponding with each spectrum can be evaluated. Optimisation is supposed to lead to an optimum quality of analytical performance. A delicate issue is the choice of the response function of the analytical system; some numerical quantity that expresses the success of the applied procedure. It determines what aspect of the analytical performance is optimised. A variety of response functions have already been proposed in literature (see references in [BUR90] [POM97a]): measurement precision, detection limit, analysis time, the peak to baseline ratio, activity of analyte, difference between analyte and matrix activity, cost of analysis, number of elements simultaneously detectable, information content, information profitability, ...

The detection limit - the minimum peak area at which an observable net signal would be detected within a certain confidence level (1-β) and with built-in protection level (1-α) against falsely mistaking a null observation for a real signal - is calculated from [CUR68]:

\[
L_D = k^2 + 2 \cdot k \cdot \sqrt{2 \cdot n \cdot h \cdot b}
\]

with: \(k = k_a = k_β\); statistical factor corresponding with confidence levels 1-α and 1-β
\(h = \text{FWHM(ch)}\); peak width in #channels

The corresponding detection limit on concentration follows directly from formula 1, by replacing \(N_p\) with \(L_D/<\text{LT}>\).

Often the analyst is interested in the minimum concentrations that allow a sufficient detection accuracy. The accuracy on the peak area, considering also the surrounding 'noise' signals, is ruled by Poisson statistics; \(σ_p = \sqrt{N_p \cdot <\text{LT}> + 2 \cdot B}\). For an a priori required accuracy of \(x = σ_p/(N_p \cdot <\text{LT}>),\) the minimum peak area is calculated from:

\[
(N_p \cdot <\text{LT}>)_{\text{min}} = \frac{1 + \sqrt{1 + 8 \cdot x^2 \cdot B}}{2 \cdot x^2}
\]

More than is the case with the calculation of detection limits, the peak area counts can here be affected by the 'noise' coming from other γ-rays of the same nuclear decay, all adding to \(B\). One then needs an iterative procedure in which the calculated minimum concentrations are systematically introduced into the spectrum simulation.

An optimisation on the detection limits or accuracy alone, give no guarantee on the efficiency of the applied procedure. Particularly for multi-element determination, efficiency demands that the number and duration of irradiations and countings are restricted to a minimum. An
interesting set of comprehensive response functions has been derived from information theory by Obrusnik and Eckschlager [OBR87]. The information content quantifies the knowledge gained on the sample composition after carrying out the determination, compared to the a priori state. The information profitability includes further considerations, such as cost. This function is quite complete, but on the other hand, the multitude of parameters might obscure the transparency of the response function and bring about some initialisation and fine tuning work.

In view of our specific application, a simple alternative is suggested. The response function is a number moving from 0 to 1 with increasing appreciation of the performance. It is merely based on the expected concentrations of the analytes and the corresponding attainable detection limits; this to avoid iterative procedures for accuracy predictions. For each analyte and hypothetical measurement, the individual response is calculated from:

$$ R = \left[ 1 + \exp \left( \frac{y \cdot DL + \sigma_y + r}{w + \sigma_y} \right) \right]^{-1} \quad (6.5) $$

with:
- $y = -\log(\rho)$; negative logarithm of the expected analyte concentration $\rho$
- $\sigma_y$; uncertainty on $y$ ($\sigma_y=1$ is equivalent with 1 order of magnitude on $\rho$)
- $DL = -\log(L_D)$; negative logarithm of detection limit in simulated spectrum
- $r$; extra range on $y$ (-0-3)
- $w$; extra width parameter for response distribution (-0.2-1)

The behaviour of this function is rather transparent. The response is low as long as the detection limit is insufficient. It starts to rise smoothly when the detection limit approaches the expected concentration. When the sensitivity beats the (pessimistic estimate of the) analyte concentration by a few orders of magnitude ($DL>y+\sigma_y+r$), the response is converging to one. Further optimisation moves are less and less rewarded. The range parameter $r$ allows the analyst to aim at an even lower concentration than the expected one. It can also be interpreted as a trick to optimise on the statistical accuracy, rather than just detection limits. Indeed, supposing e.g. $r=2$ is used, one aims at $y$-peak areas which are 100 times bigger than $L_D$; and by consequence also of a higher statistical accuracy. The total width parameter $w+\sigma_y$ determines the zone in which significant optimisation can be performed: i.e. the range of concentrations in which $R$ moves away from 0 or 1. The uncertainty $\sigma_y$ will normally not exceed 2. At this large width the response becomes almost linear in $y$ along a wide concentration range. The extra width parameter $w$ (-0.5) is included, to ensure that the response function doesn't transform into a step function in cases of an extremely low $\sigma_y$ value.
The average response over the different elements gives an appreciation of the overall multi-element analysis performance. When several measurements are performed on the sample, the maximum response is selected for each analyte separately. The importance of some analytes can be enhanced by increasing their relative weight $w_i$ in the average:

$$<R> = \frac{\sum w_i \cdot \max(R_j)}{\sum w_i} \tag{6.6}$$

A separate response could be reserved for elements which can absolutely not be analysed at the required sensitivity. This condition can be tested only roughly, by determining the best thinkable performance of the available NAA infrastructure. This would be the hypothetical situation of (i) a trace free matrix; the $\gamma$-peak is only interfered by ambient activity, (ii) most extreme activation and decay timing (S.D.C $\rightarrow \max$) [POM97a]; gives an upper limit for $\Delta_k$ in cases with as well as without burn-up effects, (iii) best spectrometry conditions; highest detector efficiency $\epsilon_p$.

The lowest 'measurable' concentration at a specific irradiation site and corresponding spectrometry set-up is estimated from:

$$\rho_{\text{min}} = \left[ k^2 + 2.6 \cdot \sqrt{\frac{2 \cdot n_{\text{ch}} \cdot T_m}{T_m} \cdot 10^{(a + b \cdot \text{ch})}} \right] \cdot \left[ \Delta_k^{\max} \cdot k_o \cdot W \cdot \epsilon_p^{\max} \cdot \Phi_e \cdot [f + Q_0(\alpha)]^{-1} \right] \tag{6.7}$$

with the symbols as defined in previous formulas. A few measures are taken in order not to drift too far off from reality; the use of realistic timing parameters, the inclusion of a typical ambient background activity and some moderation on the sample weight (since the low 'noise' condition encourages large samples ($\rho \sim W^{-1}$), only limited by a deterioration of the efficiency for voluminous sources).

In order to evaluate whether the required sensitivity is in reach of the NAA procedure, one can use a criterion based on the response formula (6.5), replacing $DL$ by $DL_{\max} = -\log(\rho_{\text{min}})$. Detectability is then ruled by a membership function, which is a commonly used concept in fuzzy set theory [KER92]. When including this limit response value $R_{i,\max}$ as an extra factor into the statistical weight $w_i$ of each element, one can automatically restrict the average response evaluation (formula 6.6) to the 'detectable' elements. The complementary value $1 - R_{i,\max}$ can then be applied as a filter for the 'non-detectable' elements. Their average 'score' can e.g. be evaluated from:

$$<S> = \frac{\sum (1 - R_{i,\max}) \cdot w_i \cdot \max(0, \frac{DL_{\max} - DL_i}{10})}{\sum (1 - R_{i,\max}) \cdot w_i} \tag{6.8}$$
6.5 Parameter search

The third and final step in the procedure is the search in parameter hyperspace for the optimum analytical response. By variation of the different degrees of freedom, the spectrum and response have to be calculated repeatedly. Different strategies have already been reported: by manual inspection on printed lists of responses or interactive computer graphics, by automatic search through a simplex search algorithm or the method of steepest descent (see references in [BUR90] [POM97a]).

The visualisation on interactive computer graphics has appealing features, but is limited on the amount of free parameters that can be inspected simultaneously. Since irradiation and cooling time are two of the most decisive parameters, they could be used on the x- and y-axis, while the other 'hidden' parameters (sample weight, efficiency,...) are automatically adapted in the background. The automatic search algorithms try to move towards the global optimum point on the response surface, by using a limited number of iterations. Constraints are enforced by assigning an unfavourable response to all points outside the permitted region of parameter space.

Nevertheless, in general the NAA response function is not ideally suited for these search methods, which in fact perform well on smoothly varying, unbounded, continuous surfaces. Considerations on the peculiarities of the response function [POM97a] demonstrate that a multitude of restrictions and discontinuities in the degrees of freedom destroy the smoothness of the analytical response surface. The automatic search tends to get trapped in local minima, boundaries imposed by local constraints or be fouled by discontinuously varying parameters. Finally one arrives at repeating the optimisation at different starting points to remedy these shortcomings.

One could rephrase the subject of optimisation as the 'generation' of conditions which give a good chance of reaching a sufficient analytical performance, preferably in comfortable conditions concerning cost, time, effort and ruggedness. The ruggedness represents the degree to which a procedure can depart from the optimum and still produce satisfactory results [CUR68]. After all, is the optimisation problem really a matter of finding the ultimate conditions? If so, it requires procedures for perfect spectrum simulation and a perfect knowledge of the matrix composition. Surely as some uncertainty on the sample content arises, one could end up at chasing a shadow; a theoretical construct in need of a posteriori information.

This - less ambitious - attitude towards the optimisation problem probably corresponds better with routine analysis problems. It can also free us from devising intricate schemes for
automated search algorithms. Indeed, it turns out that searching is easily performed by hand in a spreadsheet program [POM97a].

Modern spreadsheets have some useful features, such as their surveyability of abundant data and on-line interaction ability. Reference can be made to the possibility of orderly displaying all necessary search and response parameters in one sheet and the fact that calculations are performed so efficiently that immediately after changing one parameter the resulting effect is displayed. They allow testing various hypothetical irradiations (short-long, different irradiation channel) and subsequent measurements simultaneously. The redundant hypotheses are 'switched off' manually. Further optimisation is possible through parameters for detector and geometry choice, sample weight and of course the timing parameters. The automatically generated time schedule can be checked for its convenience (which is one of the shortcomings of automated searches) and also aspects of ruggedness can be tested.

One finally arrives at an application that provides the analyst with a priori performance evaluations within negligible calculation time. It allows him, by varying the ample experimental conditions, to search an optimum for the elements of interest. The advance predictions also allow a better service towards customers, who appreciate upfront information on detection limits and prices. The method is nevertheless limited in two ways: in the limit of unknown sample composition due to the lack on information on 'noise' and 'dead-time' and in the limit of overdetermination where the approximative γ-spectrum simulations allow no ultimate precision.
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APPENDIX A:
GENERAL ACTIVATION AND DECAY FORMULAS

A.1 Activation

The NAA technique gives information about the abundance of element (1) through the activation of one of its (stable) isotopes and the detection of gamma-emission during the disintegration of an product (k) in the decay chain. The abundances of the relevant decay products during activation is governed by the following set of differential equations:

\[
\begin{align*}
\dot{N}_1 &= -\Lambda_1 N_1 \\
\dot{N}_i &= -\Lambda_1 N_i + \Lambda_i^* N_{i-1} \quad (i \geq 2)
\end{align*}
\]

(A.1)

with \( \Lambda = \Sigma R + \Sigma \lambda \) the general disappearance constant of a product in the neutron field

\( \Lambda^* = R^* + \lambda^* \) the disappearance constant corresponding to the activation and decay branch of interest

In order not to complicate the formulas, only one activation branch is considered at a time. The generalisation to production by different activation reactions and decay branches will be found by simply summing over all branches. Therefore, as initial conditions \( (t_{irr}=0) \), it is assumed that \( N_{1,0}=N_1(t_{irr}=0) \) and \( N_{2,0}=\ldots=N_{k,0}=0 \). Also only fixed production rates are considered, implying a constant neutron field intensity.

For the solution, the following shape can be suggested:

\[
N_{k,irr} = N_k(t_{irr}) = \sum_{i=1}^{k} A_{k,i} \cdot e^{-\Lambda_i t_{irr}}
\]

(A.2)

Indeed, the validity is readily checked for \( k=1 \) and \( k=2 \), and for a general case \( (k) \) one finds:

\[
N_{k,irr} = e^{-\Lambda_k t} \cdot \left[ C + \int e^{\Lambda_k t} \cdot (\Lambda_i^* N_{k-1}) \, dt \right]
\]

\[
= \left( N_{k,0} - \sum_{i=1}^{k-1} A_{k,i} \right) \cdot e^{-\Lambda_k t_{irr}} + \sum_{i=1}^{k-1} \left( A_{k-1,i} \cdot \frac{\Lambda_i^*}{\Lambda_k - \Lambda_i} \right) \cdot e^{-\Lambda_i t_{irr}}
\]

(A.3)
This confirms the assumption on the explicit shape of the solution, and provides a recursive definition of the factors $A_{k,i}$:

$$
\begin{align*}
A_{k,i} &= \left( \prod_{r=i+1}^{k} \frac{A_{r-1}^*}{A_{r-1}^* - \Lambda_1} \right) \cdot A_{i,i} \\
A_{k,k} &= N_{k,0} - \sum_{i=1}^{k-1} A_{k,i}
\end{align*}
\quad (A.4)
$$

One can verify that the diagonal elements $A_n (i=1,2,...,k-1)$ can be written as:

$$A_{i,i} = \prod_{n=1}^{i-1} \frac{\Lambda_n^*}{\Lambda_n^* - \Lambda_1} \cdot N_{1,0} \quad (A.5)$$

The applicability can be extended to the general case (k), using the formulas A.4 and A.5:

$$
\begin{align*}
A_{k,k} &= 0 \quad - \sum_{i=1}^{k-1} \left( \prod_{r=i+1}^{k} \frac{\Lambda_r - \Lambda_1}{\Lambda_r - \Lambda_1} \right) \cdot \left( \prod_{n=1}^{i-1} \frac{\Lambda_n^*}{\Lambda_n^* - \Lambda_1} \right) \cdot N_{1,0} \\
&= \left( \prod_{n=1}^{k-1} \Lambda_n^* \right) \cdot N_{1,0} \cdot \sum_{i=1}^{k-1} \left( \prod_{m=1}^{i-1} \frac{1}{\Lambda_m - \Lambda_1} \right) \\
&= N_{1,0} \cdot \prod_{n=1}^{k-1} \frac{\Lambda_n^*}{\Lambda_n^* - \Lambda_k}
\end{align*}
$$

Finally, from the formulas A.2, A.4 and A.5, we reach the general activation formula (including burn-up), as was previously also presented by Rubinson [RUB49]:

$$
N_{k,irr} = \sum_{i=1}^{k} \frac{\prod_{n=1}^{i-1} \Lambda_n^*}{\prod_{m=1}^{i} \left( \Lambda_m - \Lambda_1 \right)} \cdot N_{1,0} \cdot e^{\Lambda_1 \cdot t_{irr}} \quad (A.6)
$$

When starting from a stable product (1), one can simplify by putting : $\Lambda_1^* = \lambda_1 = 0$, $\Lambda_1^* = R_1^*$ and $\Lambda_1 = R_1$. 

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A.2 Radioactive decay

After the irradiation period, the product abundances are determined only by the radioactive decay processes:

\[
\begin{align*}
\dot{N}_1 &= -\lambda_1 N_1 \\
\dot{N}_i &= -\lambda_i N_i + \lambda^*_i N_{i-1} \quad (i \geq 2)
\end{align*}
\] (A.7)

At any time \( t \) after the irradiation, the abundances \( N_i(t) \) are described by an expression of the type:

\[
N_i(t) = \sum_{j=1}^{k} B_{k,j} \cdot e^{-\lambda_i t}
\] (A.8)

with:

\[
\begin{align*}
B_{k,i} &= B_{i,i} \cdot \prod_{n=i+1}^{k} \frac{\lambda^*_n}{\lambda_{n-1}} \\
B_{k,k} &= N_{k,\text{irr}} - \sum_{i=1}^{k-1} B_{k,i}
\end{align*}
\] (A.9)

The initial conditions (\( t=0 \)) correspond with the situation at the end of the irradiation. This gives the relation between the \( B_{k,i} \) factors and the \( A_{k,i} \) factors describing the activation (formula A.2):

\[
N_{k,\text{irr}} = \sum_{i=1}^{k} B_{k,i} = \sum_{i=1}^{k} A_{k,i} \cdot e^{-\lambda_i t_{\text{irr}}}
\] (A.10)

and consequently:

\[
B_{i,i} = A_{i,i} \cdot e^{-\lambda_i t_{\text{irr}}} + \sum_{j=1}^{i} \left[ \prod_{r=j}^{i} \frac{\lambda^*_r}{\lambda_{r-1} \cdot \lambda_j} \right] \cdot A_{j,j} \cdot e^{-\lambda_j t_{\text{irr}}} - \sum_{j=1}^{i} \left[ \prod_{r=j}^{i} \frac{\lambda^*_r}{\lambda_{r-1} \cdot \lambda_j} \right] \cdot B_{j,j}
\]

\[
= \sum_{j=1}^{i} \left[ \prod_{r=1}^{i-j} \frac{\lambda^*_s}{\lambda_{s+1-r} \cdot \lambda_j} \right] \cdot \left[ \prod_{i-j \leq r \leq j} \frac{\lambda^*_r}{\lambda_{r+1} \cdot \lambda_j} - \prod_{i-j \leq r \leq j} \frac{\lambda^*_r}{\lambda_{r+1} \cdot \lambda_j} \right] \cdot A_{j,j} \cdot e^{-\lambda_j t_{\text{irr}}}
\] (A.11)
The analyst will finally monitor the gamma emission by a number $\Delta N_k$ of decaying product (k) nuclei during a time interval $[t_d,t_d+t_m]$ after irradiation, calculated through:

$$
\Delta N_k = \int_{t_d}^{t_d+t_m} \lambda_k^* \cdot N_k(t) \, dt = \sum_{i=1}^{k} \frac{\lambda_k^*}{\lambda_i} \cdot B_{k,i} \cdot e^{-\lambda_i t_d} \cdot \left( 1 - e^{-\lambda_i t_m} \right)
$$

(A.12)

The post-irradiation abundances can then be represented by:

$$
N_k(t_d) = N_{1,0} \cdot \sum_{i=1}^{k} \left( \prod_{m=i+1}^{k} \frac{\lambda_{m-1}}{\lambda_{m-\lambda_i}} \right) \cdot e^{-\lambda_i t_d} \times
\prod_{j=1}^{i} \left[ \sum_{r=1}^{i-j} \left( \prod_{s=j+1-r}^{i-s} - \frac{\lambda_s}{\lambda_{s-\lambda_i}} \right) \cdot \left( \prod_{t=j}^{i} \frac{\Lambda_j^*}{\Lambda_{t+1}-\Lambda_j} - \frac{\lambda_t^*}{\lambda_{t+1}-\lambda_j} \right) \right] \cdot \left( \prod_{n=j}^{i} \frac{\Lambda_n^*}{\Lambda_{n+1}-\Lambda_j} \right) \cdot e^{-\lambda_j t_{irr}}
$$

(A.13)

The number of disintegrations during a measurement period follows from an integration of the activity:

$$
\Delta N_k = \int_{t_d}^{t_d+t_m} \lambda_k^* \cdot N_k(t) \, dt = \sum_{i=1}^{k} \frac{\lambda_k^*}{\lambda_i} \cdot B_{k,i} \cdot e^{-\lambda_i t_d} \cdot \left( 1 - e^{-\lambda_i t_m} \right)
$$

(A.14)

This leads to the following explicit solution:

$$
\Delta N_k = N_{1,0} \cdot \sum_{i=1}^{k} \left( \prod_{m=i+1}^{k} \frac{\lambda_{m-1}}{\lambda_{m-\lambda_i}} \right) \cdot \frac{\lambda_k^*}{\lambda_i} \cdot e^{-\lambda_i t_d} \cdot \left( 1 - e^{-\lambda_i t_m} \right) \times \ldots
\prod_{j=1}^{i} \left[ \sum_{r=1}^{i-j} \left( \prod_{s=j+1-r}^{i-s} - \frac{\lambda_s}{\lambda_{s-\lambda_i}} \right) \cdot \left( \prod_{t=j}^{i} \frac{\Lambda_j^*}{\Lambda_{t+1}-\Lambda_j} - \frac{\lambda_t^*}{\lambda_{t+1}-\lambda_j} \right) \right] \cdot \left( \prod_{n=j}^{i} \frac{\Lambda_n^*}{\Lambda_{n+1}-\Lambda_j} \right) \cdot e^{-\lambda_j t_{irr}}
$$

(A.15)

If product (1) is stable, the summation can be started at $i=2$, since $B_{k,i}=0$ ($k>1, \lambda_i=0$). Also the counting factor is zero for the stable isotope (1).
A.3 Alternative expressions

In formula A.15 one easily finds the typical decay and counting factors, respectively

\[ D_j = e^{-\lambda_i t_d} \quad \text{and} \quad C_j = (1-e^{-\lambda_i t_m}) \]

The expressions A.6 and A.15 can be rearranged to show also the typical saturation factors \((1-e^{-\lambda_i t_{irr}})\). Indeed, assuming that \(N_{k,0}=0 \quad (k>1)\), it follows directly from the formulas A.2 and A.5:

\[
N_{k,irr} = N_{k,irr} - N_{k,0} = \sum_{i=1}^{k} A_{k,i} \cdot e^{-\lambda_i t_{irr}} - \sum_{i=1}^{k} A_{k,i} \cdot (1-e^{-\lambda_i t_{irr}})
\]

\[ (A.16) \]

Evidently, the saturation factor has no relevant meaning for the stable product (1), which does not build up but on the contrary burns up in the neutron field. A more appealing description of the activation is then \((k>1):\)

\[
N_{k,irr} = \sum_{i=2}^{k} A_{k,i} \cdot (e^{-\lambda_{1,i} t_{irr}} - e^{-\lambda_{1,irr}}) + \left[ \sum_{i=1}^{k} A_{k,i} \right] \cdot e^{-\lambda_{1,irr}}
\]

\[ (A.17) \]

in which the last term is zero and the extended saturation factors \(S_i = (e^{-\lambda_{1,i} t_{irr}} - e^{-\lambda_{1,irr}})\) converge to the classical ones with decreasing burn-up. The general activation formula (A.6) can now be rewritten as:

\[
N_{k,irr} = \sum_{i=2}^{k} \frac{A_{n,i}}{\prod_{m=2}^{k} \left( \Lambda_{m-i} \right)} \cdot N_{1,0} \cdot A_{1,i} \cdot \left( e^{-\lambda_{1,i} t_{irr}} - e^{-\lambda_{1,irr}} \right)
\]

\[ (k>1) \]

\[ (A.18) \]

To achieve also the introduction of the extended saturation factors in the activation-decay formulas, one can deduce from the previous formulas A.8, A.9, A.15 and the general appearance of formula A.11 (for \(i>1\)) that:

\[
B_{k,i} = \sum_{j=1}^{i} X_{i,j} \cdot e^{-\lambda_{j} t_{irr}} = \sum_{j=2}^{i} X_{i,j} \cdot \left[ e^{-\lambda_{1,i} t_{irr}} - e^{-\lambda_{1,irr}} \right] + \left[ \sum_{j=1}^{i} X_{i,j} \right] \cdot e^{-\lambda_{1,irr}}
\]

in which the last term is zero, because it contains following general structure:

\[
\sum_{j=1}^{k} X_{i,j} = \sum_{n=2}^{i} \left( F_n \right) \left[ \sum_{m=1}^{n} A_{n,m} \right] = 0
\]
By combining the expressions for $B_{ki}$, $B_{i}$, and $A_{i}$, the alternative expression for the post-irradiation abundances is reached:

$$N_k(t_d) = N_{1,0} \cdot \left\{ a_{k,1} \cdot e^{-\Lambda_1 \cdot t_{irr}} \cdot D_1 + \Lambda_1^* \cdot \sum_{i=2}^{k} a_{k,i} \cdot D_i \cdot \left( \sum_{j=2}^{k} b_{i,j} \cdot \frac{S_j}{\lambda_j \cdot \lambda_1} \right) \right\} \quad (A.19)$$

with:

$$a_{k,i} = \left( \prod_{m=i+1}^{k} \frac{\lambda_m^*}{\lambda_m \cdot \lambda_i} \right)$$

$$b_{i,j} = \left[ \sum_{r=1}^{j-1} \left( \prod_{s=i+1-r}^{i} \frac{\lambda_s^*}{\lambda_s \cdot \lambda_i} \right) \cdot \left( \prod_{t=j}^{i} \frac{\Lambda_t^*}{\Lambda_{t+1} - \Lambda_j} - \prod_{t=j}^{i} \frac{\lambda_t^*}{\lambda_{t+1} - \lambda_j} \right) \right] \cdot \left( \prod_{n=2}^{i+1} \frac{\Lambda_n^*}{\lambda_n - \lambda_1} \right)$$

The number of disintegrations during a measurement period follows from:

$$\Delta N_k = N_{1,0} \cdot \left\{ a_{k,1} \cdot e^{-\Lambda_1 \cdot t_{irr}} \cdot F_1 \cdot D_1 \cdot C_1 + \Lambda_1^* \cdot \sum_{i=2}^{k} a_{k,i} \cdot F_i \cdot D_i \cdot C_i \cdot \left( \sum_{j=2}^{k} b_{i,j} \cdot \frac{S_j}{\lambda_j \cdot \lambda_1} \right) \right\} \quad (A.20)$$

In the typical case in which the starting product (1) is stable, the first term disappears ($B_{k,1} \sim \lambda_1^* = 0$) and $\Lambda_1^*$ can be replaced by $R_1^*$. One gets explicitly:

$$\Delta N_k = N_{1,0} \cdot R_1^* \cdot \sum_{i=2}^{k} \left( \prod_{m=i+1}^{k} \frac{\lambda_m^*}{\lambda_m \cdot \lambda_i} \right) \cdot \frac{\lambda_k^*}{\lambda_1} \cdot e^{-\lambda_1 \cdot t_d} \cdot (1 - e^{-\lambda_1 \cdot t_{irr}}) \times ... \quad (A.21)$$

$$\times \left[ \sum_{j=2}^{k} \left( \prod_{s=i+1-j}^{i} \frac{\lambda_s^*}{\lambda_s \cdot \lambda_i} \right) \cdot \left( \prod_{t=j}^{i} \frac{\Lambda_t^*}{\Lambda_{t+1} - \Lambda_j} - \prod_{t=j}^{i} \frac{\lambda_t^*}{\lambda_{t+1} - \lambda_j} \right) \right] \cdot \left( \prod_{n=2}^{i+1} \frac{\Lambda_n^*}{\lambda_n - \lambda_1} \right) \cdot \left( \frac{e^{-\Lambda_1 \cdot t_{irr}} - e^{-\Lambda_j \cdot t_{irr}}}{\lambda_j - \lambda_1} \right)$$

This is the general activation and decay formula, starting from a stable isotope. In case of competing reactions contributing to the yield of product (k), the corresponding activation and decay formulas should be summed to calculate the true abundance.

Note that A.21 could also be found by introducing A.18 in the expression for $B_{k,k}$ (formula A.9), since one obtains similar relationships as the ones obtained in A.10 and A.11. To arrive at the post-irradiation product abundances, it merely suffices to replace the factors $[A_{j,j} \cdot e^{\Lambda_j \cdot t_{irr}}]$ by $[-A_{j,j} \cdot (e^{-\Lambda_1 \cdot t_{irr}} - e^{-\Lambda_j \cdot t_{irr}})]$ in the formulas A.11 and A.15 (for $k>1$) and to exclude $j=1$ from the summations.
A.4 Activation without burn-up

In the case of rather low or moderate neutron fluxes, the burn-up of the (stable) analyte or its decay products is negligible ($R_{i, t_{ir}} < \ll 1$ and $R_0 < \ll \lambda_i$ ($i > 1$)). The relevant differential equations can be reduced to:

\[
\begin{align*}
\dot{N}_1 &= -\lambda_1 N_1 \approx -R_1 N_{1,0} \\
\dot{N}_2 &= -\lambda_2 N_2 + \lambda_1^* N_{1,0} \\
\dot{N}_i &= -\lambda_i N_i + \lambda_{i-1}^* N_{i-1} \quad (i \geq 3)
\end{align*}
\]  

(A.22)

Often in these situations also higher order activation can be neglected. Then the specific disappearance constants can be replaced by the specific decay constants:

\[
\begin{align*}
\dot{N}_1 &= -R_1 N_{1,0} \\
\dot{N}_2 &= -\lambda_2 N_2 + R_1^* N_{1,0} \\
\dot{N}_i &= -\lambda_i N_i + \lambda_{i-1}^* N_{i-1} \quad (i \geq 3)
\end{align*}
\]  

(A.23)

Concentrating on the case expressed in A.23 (no burn-up, no high order activation), one can suggest a solution of the type:

\[
N_{k,\text{irr}} = \sum_{i=2}^{k} C_{k,i} \cdot \left( \frac{1 - e^{-\lambda_i t_{irr}}}{\lambda_i} \right) \quad (k \geq 2)
\]  

(A.24)

Using the same procedure as for the more general activation formulas (see A.3), one finds that ($N_{k,0} = 0$, $k > 1$):

\[
\begin{align*}
C_{k,i} &= C_{i,i} \cdot \prod_{n=i+1}^{k} \frac{\lambda_{n-1}^*}{\lambda_n - \lambda_i} \quad (k \geq 3, \ i = 2, \ldots, k-1) \\
C_{k,k} &= N_{1,0} \cdot R_1^* \cdot \prod_{n=2}^{k-1} \frac{\lambda_n^*}{\lambda_n - \lambda_k} \quad (k \geq 2)
\end{align*}
\]  

(A.25)

and for the subsequent decay, expression A.8 is still valid, with $[N_i(0) = N_{k,irr}]$:

\[
B_{k,i} = C_{k,i} \cdot \left( \frac{1 - e^{-\lambda_i t}}{\lambda_i} \right)
\]  

(A.26)
So, considering also formula A.12, one automatically arrives at the solution:

\[
\Delta N_k = N_{1,0} \cdot R_1^* \cdot \sum_{i=2}^{k} \left( \prod_{m=2}^{i} \frac{\lambda_m^*}{\lambda_m} \right) \cdot \frac{\lambda_i^*}{\lambda_i} \cdot \left( \frac{1-e^{-\lambda_i^* t_{irr}}}{\lambda_i} \right) \cdot e^{-\lambda_i^* t_d} \cdot (1-e^{-\lambda_i^* t_m})
\]

(A.27)

A.5 Explicit expressions

To get a better idea of the composition of the general expressions, the explicit versions of the formulas (A.13) and (A.27) for k=2, 3 and 4 are presented in table A.1. Following symbols are used:

\[
\begin{align*}
N_i^\infty &= \frac{N_{1,0} \cdot \Lambda_i^*}{\Lambda_i - \Lambda_1} \quad \text{or} \quad \frac{N_{1,0} \cdot R_1^*}{\lambda_i} \\
F_i &= \frac{\lambda_i^*}{\lambda_i} \quad \text{or} \quad \frac{\lambda_i^*}{\lambda_i} \\
S_i &= (e^{-\Lambda_1 t_{irr}} - e^{-\Lambda_i t_{irr}}) \quad \text{or} \quad (1-e^{-\lambda_i t_{irr}}) \\
D_i &= e^{-\lambda_i t_d} \quad \text{or} \quad e^{-\lambda_i t_d} \\
C_i &= (1-e^{-\lambda_i t_m}) \quad \text{or} \quad (1-e^{-\lambda_i t_m})
\end{align*}
\]

(A.28)

It is easily verified that formula (A.13) leads directly to (A.27) in the limit of no burn-up and no successive neutron captures, considering:

\[
\begin{align*}
\Lambda_i^*(*) &= \Lambda_i^* (i > 1, R_1 << \lambda_i) \\
\frac{\Lambda_i^*}{\Lambda_j - \Lambda_k} &= \frac{\lambda_i^*}{\lambda_j - \lambda_k} \\
S_i &= (e^{-\Lambda_1 t_{irr}} - e^{-\Lambda_i t_{irr}}) \rightarrow (1-e^{-\lambda_i t_{irr}}) (R_1 << 1/t_{irr}) \\
N_i^\infty &= \frac{N_{1,0} \cdot \Lambda_i^*}{\Lambda_i - \Lambda_1} \rightarrow \frac{N_{1,0} \cdot R_1^*}{\lambda_i}
\end{align*}
\]

(A.29)

One can also verify the compactness of expression (A.15) by comparing with the famous Rubinson formulas [RUB49]. (The corresponding Rubinson solution contains 4, 10 and 20 terms for k=2, 3 and 4 respectively.)
Table A.1: Explicit shape of the activation and decay formulas (3.11/A.13) (left) and (3.12/A.27) (right) for $k=2,3$ and 4. (see text)

<table>
<thead>
<tr>
<th>$k=2$</th>
<th>$\Delta N_2 = N_2^\infty \cdot F_2 \cdot S_2 \cdot D_2 \cdot C_2$</th>
<th>$\Delta N_2 = N_2^\infty \cdot F_2 \cdot S_2 \cdot D_2 \cdot C_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta N_3 = [N_2^\infty \cdot S_2] \cdot \left( \begin{array}{c} \lambda_3 \lambda_2 \ \frac{\lambda_2 \lambda_3}{\lambda_3^2} \end{array} \right) \cdot F_2 \cdot D_2 \cdot C_2$</td>
<td>$\Delta N_3 = N_2^\infty \cdot \left( \frac{\lambda_3}{\lambda_2} \right) \cdot F_2 \cdot S_2 \cdot D_2 \cdot C_2$</td>
</tr>
<tr>
<td></td>
<td>$+ [N_3^\infty \cdot S_3] \cdot \left( \frac{\Lambda_3^<em>}{\Lambda_2^</em>} \lambda_3 \right) \cdot F_3 \cdot D_3 \cdot C_3$</td>
<td>$+ N_3^\infty \cdot \left( \frac{\lambda_3^*}{\lambda_2} \right) \cdot F_3 \cdot S_3 \cdot D_3 \cdot C_3$</td>
</tr>
<tr>
<td></td>
<td>$+ [N_2^\infty \cdot S_2] \cdot \left[ \begin{array}{c} \left( \frac{\Lambda_2^<em>}{\Lambda_3^</em>} \right) - \left( \frac{\lambda_3^*}{\lambda_2} \right) \end{array} \right] \cdot F_3 \cdot D_3 \cdot C_3$</td>
<td></td>
</tr>
<tr>
<td>$k=3$</td>
<td>$\Delta N_4 = [N_2^\infty \cdot S_2] \cdot \left( \begin{array}{c} \lambda_3^* \lambda_2^* \ \frac{\lambda_2^* \lambda_3^<em>}{\lambda_3^</em>} \end{array} \right) \cdot F_2 \cdot D_2 \cdot C_2$</td>
<td>$\Delta N_4 = N_2^\infty \cdot \left( \frac{\lambda_3^*}{\lambda_2} \right) \cdot F_2 \cdot S_2 \cdot D_2 \cdot C_2$</td>
</tr>
<tr>
<td></td>
<td>$+ [N_3^\infty \cdot S_3] \cdot \left( \frac{\Lambda_2^<em>}{\Lambda_3^</em>} \right) \cdot \left( \frac{\lambda_3^*}{\lambda_2} \right) \cdot F_3 \cdot D_3 \cdot C_3$</td>
<td>$+ N_3^\infty \cdot \left( \frac{\lambda_3^*}{\lambda_2} \right) \cdot F_3 \cdot S_3 \cdot D_3 \cdot C_3$</td>
</tr>
<tr>
<td></td>
<td>$+ [N_4^\infty \cdot S_4] \cdot \left( \frac{\Lambda_2^<em>}{\Lambda_3^</em>} \right) \cdot \left( \frac{\lambda_3^*}{\lambda_2} \right) \cdot F_4 \cdot D_4 \cdot C_4$</td>
<td>$+ N_4^\infty \cdot \left( \frac{\lambda_3^*}{\lambda_2} \right) \cdot F_4 \cdot S_4 \cdot D_4 \cdot C_4$</td>
</tr>
<tr>
<td></td>
<td>$+ [N_2^\infty \cdot S_2] \cdot \left[ \begin{array}{c} \left( \frac{\Lambda_2^<em>}{\Lambda_3^</em>} \right) - \left( \frac{\lambda_3^*}{\lambda_2} \right) \end{array} \right] \cdot F_3 \cdot D_3 \cdot C_3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$+ [N_3^\infty \cdot S_3] \cdot \left[ \begin{array}{c} \left( \frac{\Lambda_2^<em>}{\Lambda_3^</em>} \right) - \left( \frac{\lambda_3^*}{\lambda_2} \right) \end{array} \right] \cdot F_4 \cdot D_4 \cdot C_4$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$+ [N_2^\infty \cdot S_2] \cdot \left{ \begin{array}{c} \left( \frac{\Lambda_2^<em>}{\Lambda_3^</em>} \right) \cdot \left( \frac{\lambda_3^<em>}{\lambda_2} \right) + \left( \frac{\lambda_3^</em>}{\lambda_2} \right) \end{array} \right} \cdot F_4 \cdot D_4 \cdot C_4$</td>
<td></td>
</tr>
</tbody>
</table>
A.6 Avoiding singularities

The activation and decay formulae have to be adapted in cases where some products have equal disappearance and/or decay rates, since the computation leads to singularities. Suppose we have a cluster of \((n+1)\) products with equal disappearance rates \(\Lambda_p \approx \Lambda_q \approx \ldots \approx \Lambda_z\), and \(m=k-(n+1)\) products with different \(\Lambda\)'s. The activation formula (A.18) is now calculated by replacing \(\sum_{j=p,q,...,z} A_{k,j} e^{-\Lambda_j t_{irr}}\) by:

\[
A'_{k,p} = \left[ \sum_{i=0}^{n} H'_{k,p} \cdot \left( \frac{t_i}{t_{irr}} \right) \right] \cdot e^{-\Lambda_p t_{irr}}
\]  \hspace{1cm} (A.30)

with:

\[
A'_{k,p} = N_{1,0} \cdot \frac{\prod_{i=1}^{k-1} \Lambda_i^*}{\prod_{i=p,q,...,z} (\Lambda_i - \Lambda_p)}
\]  \hspace{1cm} (A.31)

\[
H'_{k,p} = (-1)^{n-i} \cdot \left( \sum_{i=0}^{n-i} \sum_{n_1=0}^{n-i} \ldots \sum_{n_{m-1}=0}^{n-i-n_{1}-\ldots-n_{m-2}} \prod_{j=1}^{k} (\Lambda_j - \Lambda_p)^{-n[j]} \right)
\]  \hspace{1cm} (A.32)

and:

\[
n_m = n - i - \left( \sum_{s=1}^{m-1} n_s \right)
\]

\([n[j]]\): the index \([j]\) corresponds with the position of the product \(j\) in the list of \(m\) products for which \(\Lambda_j \neq \Lambda_p\)

or alternatively:

\[
H'_{k,p} = (-1)^{n-i} \sum_{j=p,q,...,z} \frac{\left(\Lambda_j - \Lambda_p\right)^{-n[i]+m-1}}{\prod_{l=1}^{k} (\Lambda_l - \Lambda_p)^{-l}(\Lambda_l - \Lambda_p)^{-1}}
\]  \hspace{1cm} (A.33)

The latter expression for \(H'_{k,p}\) is quite compact for high values of \((n-i)\), but needs further reduction in the case that additional clusters appear amongst the \(m\) products, in order to avoid

\[
H_{k,p}^{n+i} = 1; \quad H_{k,p}^{n+i} = -\Sigma(\Lambda_j - \Lambda_p)^i
\]

\(m=1\):

\(H_{k,p}^{k-1} = (\Lambda_i - \Lambda_p)^{k-2} \cdot (-1)^{k-2} \cdot (\Lambda_j - \Lambda_p)^i\)

\(m=0\):

\(H_{k,p}^{k-1} = 1; \quad H_{k,p}^{k-2} = \ldots = H_{k,p}^{k-2} = 0\)
singularities. Expression (A.32) can get rather lengthy, but always remains directly valid for the computation of $H_{k,p}^{n,i}$.

Introducing again the extended saturation factors, one finally gets the following activation formula for an arbitrary amount of clusters:

$$N_{k,irr} = \sum_{i=2}^{k} -A_{k,i} \cdot S_i + \sum_{\text{clusters}} \left[ -H_{k,p}^{n,0} \cdot S_p + \sum_{j=1}^{\text{clusters}} H_{k,p}^{n,i} \cdot \sum_{l=1}^{t_{irr}} \cdot e^{-A_p \cdot t_{irr}} \right] \cdot A_{k,p}$$

(A.34)

In the subsequent decay, also clusters of decay rates are theoretically possible. Suppose e.g. there are clusters of $u+1$ (nearly) identical decay rates ($\lambda_a \approx ... \approx \lambda_y \approx \lambda_z$). The following expression, which is an alternative for formula A.21, takes care of all clusters in activation and/or decay:

$$\Delta N_k = \sum_{i=2}^{k} N_{i,irr} \cdot \left[ \sum_{j=1}^{\text{clusters}} M_{k,ij}^{0,0} \cdot D_j \cdot C_j + \sum_{\text{clusters}} \left[ M_{k,ij}^{[u],f} \cdot \left( \frac{t_{irr}}{|t|} \cdot e^{-\lambda_z \cdot t_{irr}} - \frac{(\lambda_z \cdot t_{irr})^{f}}{|f|} \cdot e^{-\lambda_z \cdot (t_{irr} + t_{im})} \right) \right] \right]$$

(A.35)

with:

$$M_{k,ij}^{0,0} = \left( \prod_{s=i}^{k} \frac{\lambda_s^*}{\lambda_s - \lambda_j} \right) \cdot F_j$$

$$M_{k,ij}^{[u],f} = \left( \prod_{s=1}^{[u]} \frac{\lambda_s^*}{\lambda_s - \lambda_j} \right) \cdot \left( \prod_{s=1}^{[u]} F_s \right) \cdot h_{k,i,z}^{[u],f}$$

(A.36)

$$h_{k,i,z}^{[u],f} = 1 + \sum_{t=1}^{[u]-f} \left( \sum_{n_1=0}^{t-n_1} \ldots \sum_{n_{k-[u]}=0}^{t-n_{k-[u]}} \prod_{s=1}^{[u]} \frac{\lambda_s}{\lambda_s - \lambda_j} \right) \cdot n_{[u]}$$

(A.37)

$$n_{k-i-[u]} = \prod_{g=1}^{(k-i-[u])-1} n_g$$

; $[s] =$ the position of product $s$ in the series

$[u]=0$ for $i \in [z,k]$ ; $[u]=1$ for $i \in [y,z]$ ; $[u]=u$ for $i \in [2,a]$  

The structure of $h_{k,i,a}^{[u],f}$ is comparable with that of $H_{k,p}^{n,i}$ (see expressions A.32 and A.33). $N_{i,irr}$ is calculated from expression A.34.
APPENDIX B:
CLASSIFICATION OF DECAY TYPES

The classification of decay types is based on the work of De Corte et al. [DEC87] [DEC89]. In table B.1, a representation of the decay scheme is shown, together with some parameters relevant to the $k_0$-NAA:

$k_s$; compound nuclear constant typical for a specific gamma associated with a specific activation scheme. It is an essential part of the $k_0$-number, since $k_{0c}(\alpha) = k_s/k_c$ (see paragraph 4.4)

$Q_0 = I_0/\sigma_0$ is a measure for the ratio between the epithermal to thermal activation cross section contribution (see paragraph 2.11)

$\Lambda_k$; decay probability factor for the considered scheme (see appendix A, section III and paragraph 4.1); i.e. average number of product ($k$) disintegrations during the measurement period, per product ($l$) nucleus and at unity reaction rate.

In some situations, activation takes place through two or three isomers. Unavoidably, the ratio of their respective reaction rates ends up in the decay formula (see type IV to VIII). It is calculated from (Hogdahl convention):

$$\frac{R_{1m}^m}{R_{1l}^l} = \frac{\sigma_{0l}^m}{\sigma_{0l}^l} \cdot \frac{G_{1l}f + G_{c}Q_{0l}^m(\alpha)}{G_{1l}f + G_{c}Q_{0l}^l(\alpha)} = \frac{k_{0l}^m}{k_{0l}^l} \cdot \frac{G_{1l}f + G_{c}Q_{0l}^m(\alpha)}{G_{1l}f + G_{c}Q_{0l}^l(\alpha)}$$

involving thermal cross section data, or alternatively $k_0$-factors (see [DEC89]).
### Table B.1: Activation-decay types and relevant expressions for the parameters involved in the \( k_0 \)-method.

<table>
<thead>
<tr>
<th>type</th>
<th>scheme</th>
<th>( k_a )</th>
<th>( Q_0 )</th>
<th>( \Delta_k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td><img src="image" alt="Diagram" /></td>
<td>( \frac{N_A \cdot \sigma_0 \cdot \gamma_2}{M} )</td>
<td>( \frac{l_0}{\sigma_0} )</td>
<td>( \Delta_2(1,2) )</td>
</tr>
<tr>
<td>II/a</td>
<td><img src="image" alt="Diagram" /></td>
<td>( \frac{N_A \cdot \sigma_0 \cdot F_2 \cdot \gamma_3}{M} )</td>
<td>( \frac{l_0}{\sigma_0} )</td>
<td>( \frac{1}{f_2} \cdot \Delta_3(1,2,3) )</td>
</tr>
<tr>
<td>II/b</td>
<td>( \lambda_2 \gg \lambda_3 ) and ( \Lambda_2 \gg \Lambda_3 ) ( D_2 = 0 )</td>
<td>-</td>
<td>-</td>
<td>( \approx \left( \frac{\lambda_2}{\Lambda_2 - \Lambda_3} \right) \cdot \frac{S_3 \cdot D_3 \cdot C_3}{\Lambda_3 - \Lambda_1} )</td>
</tr>
<tr>
<td>II/c</td>
<td>( \lambda_3 &gt; \lambda_2 ) ( D_3 = 0 )</td>
<td>-</td>
<td>-</td>
<td>( \approx \left( \frac{\lambda_3}{\Lambda_3 - \Lambda_2} \right) \cdot \frac{S_2 \cdot D_2 \cdot C_2}{\Lambda_2 - \Lambda_1} )</td>
</tr>
<tr>
<td>II/d</td>
<td><img src="image" alt="Diagram" /></td>
<td>-</td>
<td>-</td>
<td>( \frac{1}{f_2} \cdot \left[ \Delta_3(1,2,3) + \frac{\gamma_2}{\gamma_3} \cdot \Delta_2(1,2) \right] )</td>
</tr>
<tr>
<td>type</td>
<td>scheme</td>
<td>$k_a$</td>
<td>$Q_0$</td>
<td>$\Delta_k$</td>
</tr>
<tr>
<td>-------</td>
<td>--------</td>
<td>------</td>
<td>------</td>
<td>-----------</td>
</tr>
<tr>
<td>III/a</td>
<td></td>
<td>$\frac{N_A \cdot \sigma_0 \cdot F_2 \cdot F_3 \cdot \gamma_4}{M}$</td>
<td>$\frac{l_0}{\sigma_0}$</td>
<td>$\frac{1}{F_2 \cdot F_3} \cdot [\Delta_3(1,2,4) + \Delta_4(1,2,3,4)]$</td>
</tr>
<tr>
<td>III/b</td>
<td>$F_{24}=0$</td>
<td>&quot;</td>
<td>&quot;</td>
<td>$\frac{1}{F_2 \cdot F_3} \cdot \Delta_4(1,2,3,4)$</td>
</tr>
<tr>
<td>III/c</td>
<td>$F_2 + F_{24}=1$, $F_3=1$</td>
<td>$\frac{N_A \cdot \theta \cdot \sigma_0 \cdot \gamma_4}{M}$</td>
<td>&quot;</td>
<td>$\Delta_3(1,2,4) + \Delta_4(1,2,3,4) \approx \frac{F_{24} + F_2}{F_{24}} \cdot \Delta_3(1,2,4)$</td>
</tr>
</tbody>
</table>

$\lambda_3 \gg \lambda_2, \lambda_4$ and $R_3 \ll \lambda_3$

$D_3=0$
<table>
<thead>
<tr>
<th>type</th>
<th>scheme</th>
<th>$k_s$</th>
<th>$Q_0$</th>
<th>$\Delta_k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV/a</td>
<td>$\lambda_2 \gg \lambda_3$ and $R_2 \ll \lambda_2$</td>
<td>$\frac{N_A \sigma_0^m \sigma_0^g \gamma_3}{M}$</td>
<td>$\frac{i_0^g}{\sigma_0}$</td>
<td>$\Delta_2(1,3) + \frac{R_1^m}{R_1} \cdot \Delta_3(1,2,3)$</td>
</tr>
<tr>
<td>IV/b</td>
<td>$\lambda_2 \gg \lambda_3$ and $R_2 \ll \lambda_2$</td>
<td>$\frac{N_A \sigma_0^m \sigma_0^g \gamma_3}{M}$</td>
<td>$\frac{F_2 \sigma_0^m + i_0^g}{F_2 \sigma_0^m + \sigma_0^g}$</td>
<td>$\frac{R_2^8 \Delta_2(1,3) + R_1^m \Delta_3(1,2,3)}{R_1^8 + F_2 R_1^m}$</td>
</tr>
<tr>
<td>IV/c</td>
<td>$\lambda_3 &gt; \lambda_2$</td>
<td>$\frac{N_A \sigma_0^m \sigma_0^g \gamma_3}{M}$</td>
<td>$\frac{i_0^g}{\sigma_0}$</td>
<td>$\frac{1}{F_2} \cdot \left[ \frac{R_1^g}{R_1} \cdot \Delta_2(1,3) + \Delta_3(1,2,3) \right]$</td>
</tr>
<tr>
<td>IV/d</td>
<td>$\lambda_2 \gg \lambda_3$ and $R_2 \ll \lambda_2$</td>
<td>$\frac{N_A \sigma_0^m \sigma_0^g \gamma_3}{M}$</td>
<td>$\frac{i_0^g}{\sigma_0}$</td>
<td>$\Delta_2(1,3) + \frac{R_1^m}{R_1} \cdot \left[ \Delta_3(1,2,3) + \frac{12}{73} \Delta_2(1,2) \right]$</td>
</tr>
<tr>
<td>type</td>
<td>scheme</td>
<td>$k_a$</td>
<td>$Q_0$</td>
<td>$\Delta_k$</td>
</tr>
<tr>
<td>------</td>
<td>--------</td>
<td>------</td>
<td>------</td>
<td>---------</td>
</tr>
<tr>
<td>V/a</td>
<td><img src="image" alt="Scheme V/a" /></td>
<td>$\frac{N_A 0 \sigma^m_0 F_3 \gamma_4}{M}$</td>
<td>$\frac{\Gamma_0^m}{\sigma_0^m}$</td>
<td>$\frac{1}{F_3} \left[ \Delta_3(1,3,4) + \frac{R_1^m}{R_1^e} \Delta_4(1,2,3,4) \right]$</td>
</tr>
<tr>
<td>V/b</td>
<td>$\lambda_2 &gt; \lambda_4$ and $R_2 &lt;&lt; \lambda_2$</td>
<td>$\frac{N_A 0 \left( \Gamma_2^m \sigma_0^m + \sigma_0^m \right) \Gamma_3 \gamma_3}{M}$</td>
<td>$\frac{\Gamma_2^m}{\sigma_0^m + \sigma_0^m}$</td>
<td>$\frac{R_1^m \Delta_3(1,3,4) + R_1^m \Delta_4(1,2,3,4)}{F_3 \left( R_1^e + F_2 R_1^m \right)} \approx \frac{S_4 D_4 C_4}{\Lambda_4 \Lambda_1}$</td>
</tr>
<tr>
<td></td>
<td>$\lambda_3 &gt; \lambda_4$ and $R_3 &lt;&lt; \lambda_3$</td>
<td>$\lambda_2 = \lambda_3 = 0$</td>
<td>$\lambda_2 &gt; \lambda_3$ and $R_2 &lt;&lt; \lambda_2$</td>
<td>$\lambda_4 &gt; \lambda_3$</td>
</tr>
<tr>
<td>type</td>
<td>scheme</td>
<td>$k_n$</td>
<td>$Q_0$</td>
<td>$\Delta_k$</td>
</tr>
<tr>
<td>------</td>
<td>--------</td>
<td>------</td>
<td>------</td>
<td>---------</td>
</tr>
<tr>
<td>VI</td>
<td>$\sigma^m_0 I_0$</td>
<td>$\lambda_2$</td>
<td>$F_2 I_0$</td>
<td>$\lambda_4 / \lambda_2$</td>
</tr>
<tr>
<td></td>
<td>$\sigma^m_0 I_0$</td>
<td>$\lambda_3$</td>
<td>$F_3 I_0$</td>
<td>$\lambda_4 / \lambda_3$</td>
</tr>
<tr>
<td></td>
<td>$\sigma^m_0 I_0$</td>
<td>$\lambda_4$</td>
<td>$F_4 I_0$</td>
<td>$\lambda_4$</td>
</tr>
</tbody>
</table>

$^{124}\text{Sb from } ^{123}\text{Sb}(n,\gamma)$

$\lambda_2 >> \lambda_4$ and $R_2 << \lambda_2$

$\lambda_3 >> \lambda_4$ and $R_3 << \lambda_3$

$F_2 = 1$, $D_2 = D_1 = 0$

(after long decay time)
<table>
<thead>
<tr>
<th>type</th>
<th>scheme</th>
<th>$k_s$</th>
<th>$Q_0$</th>
<th>$\Delta_k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VII/a</td>
<td><img src="image" alt="Diagram" /></td>
<td>$\frac{N_A \sigma_0^g F_3 \gamma_4}{M}$</td>
<td>$\frac{k_0^p}{\sigma_0^p}$</td>
<td>$\frac{1}{F_3} \left[ \Delta_3(1,3,4) + \frac{R_{1}^m}{R_{1}} \Delta_3(1,2,4) + \Delta_4(1,2,3,4) \right]$</td>
</tr>
<tr>
<td>VII/b</td>
<td>$F_3 = 0$</td>
<td>&quot;</td>
<td>&quot;</td>
<td>$\frac{1}{F_3} \left[ \Delta_3(1,3,4) + \frac{R_{1}^m}{R_{1}} \Delta_3(1,2,4) \right]$</td>
</tr>
<tr>
<td>VIII</td>
<td><img src="image" alt="Diagram" /></td>
<td>$\frac{N_A \sigma_0^g F_3 \gamma_4}{M}$</td>
<td>$\frac{k_0^p}{\sigma_0^p}$</td>
<td>$\frac{1}{F_3 F_4} \cdot [\Delta_3(1,3,5) + \Delta_4(1,3,4,5)]$ + $\frac{1}{F_3 F_4} \cdot \frac{R_{1}^m}{R_{1}} \cdot [\Delta_3(1,2,5) + \Delta_4(1,2,4,5)]$</td>
</tr>
</tbody>
</table>
APPENDIX C:
TRUE COINCIDENCE PULSE LOSS

Expressions for the calculation of true coincidence pulse loss for a transition A in five-component decay cascades (see also paragraph 5.4). The formulas for simpler cascades can be derived by dropping irrelevant terms.

definitions:
\[ \Sigma_y = \varepsilon_{i_{y}} + \alpha_{K,y} \cdot \omega_{K} \cdot \sum_{i} k_{i} \cdot \varepsilon_{i_{K,y}} \quad (y=\text{B,C,D,E} : i=K_{a1}, K_{a2}, \text{etc.}) \]
\[ \varepsilon_{i_{y}} , \varepsilon_{i_{K,y}} = \text{total detection efficiency of gamma and KX-ray} \]
\[ \alpha_{K,y} = \text{internal conversion coefficient} \]
\[ c_{y}=1/(1+\alpha_{i_{y}}) = \text{probability gamma-ray is emitted (opposed to conversion)} \]
\[ \omega_{K} = \text{fluorescence yield} \]
\[ k_{a1} = \text{relative emission rate} \]
\[ a_{y} = \text{branching ratio} \]
\[ \gamma_{y} = \text{absolute gamma-intensity} \]

A-B-C-D-E \hspace{1cm} (C.1)

\[
L[ A - B/KX(B) - C/KX(C) - D/KX(D) - E/KX(E) ] \\
= \{ a_{B} \Sigma_{B} + a_{I_{B}} a_{C} c_{C} \Sigma_{C} + a_{B} a_{C} a_{D} c_{D} \Sigma_{D} + a_{B} a_{C} a_{D} a_{E} c_{E} \Sigma_{E} \} \\
- \{ a_{B} a_{C} c_{C} \Sigma_{C} + a_{B} a_{C} a_{D} a_{E} c_{E} \Sigma_{E} + a_{B} a_{C} a_{D} a_{E} c_{E} \Sigma_{E} \} \\
+ \{ a_{B} a_{C} c_{C} \Sigma_{C} + a_{B} a_{C} a_{D} a_{E} c_{E} \Sigma_{E} + a_{B} a_{C} a_{D} a_{E} c_{E} \Sigma_{E} \} \\
- \{ a_{B} a_{C} c_{C} \Sigma_{C} + a_{B} a_{C} a_{D} a_{E} c_{E} \Sigma_{E} \} \\
\]

A-B : \hspace{1cm} a_{C}=a_{D}=a_{E}=0 \\
A-B-C : \hspace{1cm} a_{D}=a_{E}=0 \\
A-B-C-D : \hspace{1cm} a_{E}=0 

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\[ L[ B/KX(B) - A - C/KX(C) - D/KX(D) - E/KX(E) ] \]

\[ = \{ \frac{\gamma_B}{\gamma_A} a_A c_A \Sigma_B + \frac{\gamma_C}{\gamma_A} a_A c_A \Sigma_C + a_d c_d \Sigma_d + a_c a_e c_e \Sigma_e \} \]

\[ - \{ \frac{\gamma_B}{\gamma_A} a_A c_A \Sigma_B a_c c_c \Sigma_c + \frac{\gamma_B}{\gamma_A} a_A c_A \Sigma_B a_d c_d \Sigma_d + \frac{\gamma_B}{\gamma_A} a_A c_A \Sigma_B a_d c_d \Sigma_d + \frac{\gamma_B}{\gamma_A} a_A c_A \Sigma_B a_c c_c \Sigma_c \Sigma_d a_e c_e \Sigma_e + \]

\[ a_c c_c a_d c_d \Sigma_d + a_c c_c \Sigma_c a_d a_e c_e \Sigma_e \} \]

\[ + \{ \frac{\gamma_B}{\gamma_A} a_A c_A \Sigma_B a_c c_c \Sigma_c a_d c_d \Sigma_d + \frac{\gamma_B}{\gamma_A} a_A c_A \Sigma_B a_c c_c \Sigma_c a_d c_d \Sigma_d + \frac{\gamma_B}{\gamma_A} a_A c_A \Sigma_B a_c c_c \Sigma_c a_d c_d \Sigma_d a_e c_e \Sigma_e \} \]

\[ - \{ \frac{\gamma_B}{\gamma_A} a_A c_A \Sigma_B a_c c_c \Sigma_c a_d c_d \Sigma_d a_e c_e \Sigma_e \} \]

\[ \text{B-A : } a_c = a_d = a_e = 0 \]
\[ \text{B-A-C : } a_d = a_e = 0 \]
\[ \text{B-A-C-D : } a_e = 0 \]

\[ L[ B/KX(B) - C/KX(C) - A - D/KX(D) - E/KX(E) ] \]

\[ = \{ \frac{\gamma_B}{\gamma_A} a_A c_A \Sigma_B + \frac{\gamma_C}{\gamma_A} a_A c_A \Sigma_C + a_d c_d \Sigma_d + a_c a_e c_e \Sigma_e \} \]

\[ - \{ \frac{\gamma_B}{\gamma_A} a_A c_A \Sigma_B a_c c_c \Sigma_c + \frac{\gamma_B}{\gamma_A} a_A c_A \Sigma_B a_d c_d \Sigma_d + \frac{\gamma_B}{\gamma_A} a_A c_A \Sigma_B a_d c_d \Sigma_d + \frac{\gamma_B}{\gamma_A} a_A c_A \Sigma_B a_c c_c \Sigma_c \Sigma_d a_e c_e \Sigma_e + \]

\[ \frac{\gamma_C}{\gamma_A} a_A c_A \Sigma_C a_d c_d \Sigma_d + \frac{\gamma_C}{\gamma_A} a_A c_A \Sigma_C a_d c_d \Sigma_d + a_d a_e c_e \Sigma_e \} \]

\[ + \{ \frac{\gamma_B}{\gamma_A} a_A c_A \Sigma_B a_c c_c \Sigma_c a_d c_d \Sigma_d + \frac{\gamma_B}{\gamma_A} a_A c_A \Sigma_B a_c c_c \Sigma_c a_d c_d \Sigma_d + \frac{\gamma_B}{\gamma_A} a_A c_A \Sigma_B a_c c_c \Sigma_c a_d c_d \Sigma_d a_e c_e \Sigma_e + \]

\[ \frac{\gamma_B}{\gamma_A} a_A c_A \Sigma_B a_c c_c \Sigma_c a_d c_d \Sigma_d a_e c_e \Sigma_e \} \]

\[ - \{ \frac{\gamma_B}{\gamma_A} a_A c_A \Sigma_B a_c c_c \Sigma_c a_d c_d \Sigma_d a_e c_e \Sigma_e \} \]

\[ \text{B-C-A : } a_d = a_e = 0 \]
\[ \text{B-C-A-D : } a_e = 0 \]
\[ L[ B/KX(B) - C/KX(C) - D/KX(D) - A - E/KX(E) ] \]

\[ = \left\{ \frac{\gamma_B}{\gamma_A} a_c a_d a_a c_a \Sigma_B + \frac{\gamma_C}{\gamma_A} a_d a_a c_a \Sigma_C + \frac{\gamma_D}{\gamma_A} a_a c_a \Sigma_D + a_e c_e \Sigma_E \right\} \]

\[ - \left\{ \frac{\gamma_B}{\gamma_A} a_c a_d a_a c_a \Sigma_B c_c \Sigma_C + \frac{\gamma_B}{\gamma_A} a_c a_d a_a c_a \Sigma_D \Sigma_D + \frac{\gamma_B}{\gamma_A} a_c a_d a_a c_a \Sigma_B a_e c_e \Sigma_E \right. \]

\[ + \frac{\gamma_C}{\gamma_A} a_d a_a c_a \Sigma_C \Sigma_D + \frac{\gamma_C}{\gamma_A} a_d a_a c_a \Sigma_D a_e c_e \Sigma_E \}

\[ + \left\{ \frac{\gamma_B}{\gamma_A} a_c a_d a_a c_a \Sigma_B c_c \Sigma_C c_D \Sigma_D a_e c_e \Sigma_E + \frac{\gamma_C}{\gamma_A} a_d a_a c_a \Sigma_C \Sigma_D a_e c_e \Sigma_E \right\} \]

\[ - \left\{ \frac{\gamma_B}{\gamma_A} a_c a_d a_a c_a \Sigma_B \Sigma_C \Sigma_D a_e c_e \Sigma_E \right\} \]

B-C-D-A: \hspace{1cm} a_e = 0

\[ L[ B/KX(B) - C/KX(C) - D/KX(D) - E/KX(E) - A ] \]

\[ = \left\{ \frac{\gamma_B}{\gamma_A} a_c a_d a_e a_a c_a \Sigma_B + \frac{\gamma_C}{\gamma_A} a_d a_e a_a c_a \Sigma_C + \frac{\gamma_D}{\gamma_A} a_e a_a c_a \Sigma_D + \frac{\gamma_E}{\gamma_A} a_a c_a \Sigma_E \right\} \]

\[ - \left\{ \frac{\gamma_B}{\gamma_A} a_c a_d a_e a_a c_a \Sigma_B c_c \Sigma_C + \frac{\gamma_B}{\gamma_A} a_c a_d a_e a_a c_a \Sigma_D \Sigma_D + \frac{\gamma_B}{\gamma_A} a_c a_d a_e a_a c_a \Sigma_B c_e \Sigma_E \right. \]

\[ + \frac{\gamma_C}{\gamma_A} a_d a_e a_a c_a \Sigma_C c_D \Sigma_D + \frac{\gamma_C}{\gamma_A} a_d a_e a_a c_a \Sigma_D c_e \Sigma_E \}

\[ + \left\{ \frac{\gamma_B}{\gamma_A} a_c a_d a_e a_a c_a \Sigma_B c_c \Sigma_C c_D \Sigma_D a_e c_e \Sigma_E + \frac{\gamma_C}{\gamma_A} a_d a_e a_a c_a \Sigma_C \Sigma_D a_e c_e \Sigma_E \right\} \]

\[ - \left\{ \frac{\gamma_B}{\gamma_A} a_c a_d a_e a_a c_a \Sigma_B \Sigma_C \Sigma_D a_e c_e \Sigma_E \right\} \]
APPENDIX D:
LIST OF SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>parameter describing shape of epithermal neutron spectrum ((-1/E^{1/2}))</td>
</tr>
<tr>
<td>( \alpha_{K,B} )</td>
<td>internal conversion coefficient of transition B with emission of K electron</td>
</tr>
<tr>
<td>( \alpha_{t,B} )</td>
<td>total internal conversion coefficient of transition B</td>
</tr>
<tr>
<td>( a_B )</td>
<td>branching ratio for transition B</td>
</tr>
<tr>
<td>( A_{sp} )</td>
<td>specific count rate ([s^{-1}g^{-1}])</td>
</tr>
<tr>
<td>( c_B )</td>
<td>probability gamma-ray of transition B is emitted (opposed to IC)</td>
</tr>
<tr>
<td>( C_i )</td>
<td>counting factor of isotope i in an activation-decay scheme</td>
</tr>
<tr>
<td>COI</td>
<td>correction factor for true coincidence effects</td>
</tr>
<tr>
<td>( \Delta N_k )</td>
<td>[dimensionless] number of decaying 'product k' nuclei during measurement time per unit of ( N_{1,p}R_1 ) (=initial 'product 1' atoms ( \times ) reaction rate)</td>
</tr>
<tr>
<td>( D_i )</td>
<td>decay factor of isotope i in an activation-decay scheme</td>
</tr>
<tr>
<td>DT</td>
<td>dead-time (of spectrometer)</td>
</tr>
<tr>
<td>( \varepsilon_p )</td>
<td>full energy peak detection efficiency (including gamma attenuation, true coincidence corrections, etc.)</td>
</tr>
<tr>
<td>( \varepsilon_t )</td>
<td>total detection efficiency (including partial gamma detection)</td>
</tr>
<tr>
<td>( E_2 )</td>
<td>fraction of produced 'irradiation product 2' nuclei available for subsequent measurement</td>
</tr>
<tr>
<td>( E_o )</td>
<td>most probable energy [keV] of thermal neutrons at neutron temperature ( T_o )</td>
</tr>
<tr>
<td>EC</td>
<td>electron capture</td>
</tr>
<tr>
<td>( E_{Cd} )</td>
<td>cadmium cut-off energy (neutron energy where the step function for neutron transmission through a hypothetical ideal Cd filter is located)</td>
</tr>
<tr>
<td>( E_n(x) )</td>
<td>exponential integral of the ( n^{th} ) order</td>
</tr>
<tr>
<td>ENAA</td>
<td>Epicadmium Neutron Activation Analysis</td>
</tr>
<tr>
<td>( E_r )</td>
<td>individual resonance energy [eV]</td>
</tr>
<tr>
<td>( \bar{E}_r )</td>
<td>effective resonance energy [eV] (hypothetical single resonance which gives the same resonance activation rate as the actual resonances of the isotope together, the ( 1/v ) part subtracted)</td>
</tr>
<tr>
<td>( \varphi(E) )</td>
<td>neutron flux per unit of energy ([n.cm^{-2}.s^{-1}.eV^{-1}])</td>
</tr>
<tr>
<td>( f )</td>
<td>subcadmium to epithermal neutron flux ratio</td>
</tr>
<tr>
<td>( \Phi_e )</td>
<td>total epithermal neutron flux ([n.cm^{-2}.s^{-1}])</td>
</tr>
<tr>
<td>( \Phi_f )</td>
<td>total fast neutron flux ([n.cm^{-2}.s^{-1}]) (unmoderated fission neutrons)</td>
</tr>
<tr>
<td>( \Phi_s )</td>
<td>total subcadmium neutron flux ([n.cm^{-2}.s^{-1}]) ('slow' or 'thermal' neutrons not passing 1mm cadmium foil)</td>
</tr>
</tbody>
</table>

• no completeness of list intended
\[ \Phi_{\text{th}} \]  
total thermal neutron flux \([\text{n.cm}^{-2}\cdot\text{s}^{-1}]\) (fully moderated neutrons)

\[ F_i \]  
branching factor for isotope \(i\) in an activation-decay chain

\[ F_{\text{cd}} \]  
cadmium transmission factor for epithermal neutrons

\[ F_{\text{att}} \]  
correction factor for gamma-attenuation

\[ F_{\text{eff}} \]  
probability of gamma-ray depositing energy in detector crystal when entering at
a certain location and following a certain direction

\( \Gamma \)  
total resonance width

\( \Gamma_r \)  
radiative resonance width

\( \Gamma_n \)  
neutron resonance width

\( \gamma \)  
absolute gamma-intensity

\( g(T_n) \)  
Westcott factor

\( G_{\text{th}}, G_e \)  
thermal and epithermal neutron self-shielding factor in a medium

\( G, \)  
self-shielding correction for resonance neutrons

\( h \)  
FWHM peak width in \#channels

\( I_0 \)  
'resonance integral' for a \(1/E\) epithermal neutron spectrum \([\text{cm}^2]\)

\( I_0' \)  
'reduced' resonance integral for a \(1/E\) epithermal neutron spectrum \([\text{cm}^2]\)

\( I_0(\alpha) \)  
'resonance integral' for a \(1/E^{1/\alpha}\) epithermal neutron spectrum \([\text{cm}^2]\)

\( I_0'(\alpha) \)  
reduced resonance integral for a \(1/E^{1/\alpha}\) epithermal neutron spectrum \([\text{cm}^2]\)

\( 1 \)  
absorption mean free path \([\text{cm}^2]\)

\( \Lambda_i \)  
disappearance constant of element \(i\) in an activation-decay scheme, sum of
decay constant and reaction rate per nucleus \([\text{s}^{-1}]\)

\( L(A) \)  
summing-out probability of nuclear transition \(A\)

\( L_D \)  
detection limit

\( \text{LT} \)  
life-time (of spectrometer)

\( M \)  
molar mass \([\text{g/mol}]\)
n number of FWHM of peak taken for calculation of detection limit
n (momentary) LFC correction factor for pulse loss
<n> average LFC correction factor for pulse loss
N number of counted events
N\text{\textsubscript{A}} Avogadro number
NAA neutron activation analysis
N\text{\textsubscript{LFC}} number of counted events with LFC-technique
N\text{\textsubscript{p}} pulse loss corrected full-energy peak area in activation spectrum
P/T peak-to-total ratio
\(\theta\) (fractional) isotopic abundance
Q\text{\textsubscript{0}} ratio of resonance integral for \(1/E\) epithermal neutron spectrum, \(I_0\), and the thermal neutron cross section, \(\sigma_0\), at \(\nu_0 = 2200\) m/s
Q\text{\textsubscript{0}}(\alpha) ratio of resonance integral for \(1/E^{1+}\alpha\) epithermal neutron spectrum, \(I_0(\alpha)\), and the thermal neutron cross section, \(\sigma_0\), at \(\nu_0 = 2200\) m/s
\(p\) correction factor for the epithermal flux shape dependence of the effective resonance energy
\(P_{K,I}\) probability that EC\text{\textsubscript{I}} is K electron capture
\(\text{PP}_{I\text{\textsubscript{A}}}\) proability that transition A is preceded by EC\text{\textsubscript{I}} (opposed to EC\text{\textsubscript{II}} etc.)
\(\rho\) concentration [g/g] of element in sample
r(\alpha)\sqrt{T_0/T_0} modified spectral index (measure for epithermal-to-total neutron density ratio)
R response function, quantification of analytical performance
R (total) reaction rate per nucleus [s\textsuperscript{-1}]
R\text{\textsubscript{Cd}} cadmium ratio, ratio of reaction rate of bare and Cd-covered nuclides
R\text{\textsubscript{e}} reaction rate per nucleus induced with subcadmium neutrons [s\textsuperscript{-1}]
R\text{\textsubscript{e}} reaction rate per nucleus induced with epithermal neutrons [s\textsuperscript{-1}]
(R\text{\textsubscript{c}})\text{\textsubscript{Cd}} reaction rate per nucleus for a Cd-covered irradiation
R\text{\textsubscript{f}} reaction rate per nucleus induced with fast neutrons [s\textsuperscript{-1}]
R\text{\textsubscript{f}} fission reaction rate [s\textsuperscript{-1}]
\(\bar{\sigma}\) average reaction cross section for an unmoderated \(^{235}\text{U}\) fission neutron spectrum [cm\textsuperscript{2}]
\(\sigma_0\) \((n,\gamma)\) cross section [cm\textsuperscript{2}] at neutron velocity \(\nu_0 = 2200\) m/s (or energy \(E_0\))
\(\sigma_0\text{\textsubscript{abs}}\) absorption cross section at \(\nu_0 = 2200\) m/s [cm\textsuperscript{2}]
\(\bar{\sigma}\text{\textsubscript{abs}}\) average absorption cross section assuming Maxwell distribution of neutron density \(n(\nu)\) [cm\textsuperscript{2}]
\(\sigma_e\) standard deviation of counting with extending dead-time
\(\sigma_{\text{nc}}\) standard deviation of counting with non-extending dead-time
\(\sigma(E)\), \(\sigma(\nu)\) reaction cross section as a function of energy and velocity respectively [cm\textsuperscript{2}]

\(1\) barn = \(10^{-24}\) cm\textsuperscript{2}
\( s_0(\alpha) \) modified reduced resonance integral to 2200 m/s cross section ratio
\( \Sigma_a \) macroscopic absorption cross section \([\text{cm}^2]\) \(^*\) (weighted sum of contribution of all elements in medium)
\( \Sigma_n \) \~ probability of detecting transition B or X-ray after IC(B)
\( \Sigma_{EC} \) \~ probability of detecting KX-ray after EC
\( \Sigma_s \) macroscopic scattering cross section \([\text{cm}^2]\)
\( \Sigma_t \) total macroscopic cross section \([\text{cm}^2]\) \* (scattering + absorption)
\( S \) sample surface \([\text{cm}^2]\)
\( S_i \) sample surface \([\text{cm}^2]\)
\( S(A) \) summing-in probability of transition A
\( \tau \) non-extending or extending dead-time of counter [s]
\( \tau \) amplifier shaping time constant [s]
\( t_d \) decay time [s] (between end of irradiation and beginning of measurement)
\( t_{irr} \) irradiation time [s]
\( t_m \) measuring time [s]
\( t(E) \) transmission function for 'ideal' thermal neutron filter
\( T_n \) 293.59K neutron temperature
\( T(E) \) transmission function of neutrons hitting on a 1 mm cadmium foil
\( T_d \) time delay between the detection (or emission) of two transitions from a nuclear cascade [s]
\( T_n \) neutron temperature [K]
\( T_p \) peaking time of shaping amplifier pulse [s]
\( V \) sample volume \([\text{cm}^3]\)
\( v_0 \) 2200 m/s neutron velocity
\( v_{Cd} \) cadmium cut-off velocity (neutron velocity where the step function for neutron transmission through a hypothetical ideal Cd filter is located)
\( \omega_K \) K-fluorescence yield
\( w \) weight of resonance in calculation of effective resonance energy
\( w \) mass of the element [g]
\( w_s \) mass of element in standard [g]
\( W \) mass of the sample [g]
\( \Omega \) solid angle
\( \Omega_e \) 'effective' solid angle (involving probability of partial or full detection)
\( \xi \) sample size/thickness in units of neutron mean free path

\* 1 barn = \(10^{-24}\) cm\(^2\)
Acknowledgements

The authors thank the management of SCK•CEN and IRMM for their continuing interest in this joint $k_0$-NAA project. They are also indebted to experienced members of the $k_0$ community, F. De Corte, A. Simonits, A. de Wispelaere, R. Van Sluijs and others, for their valuable advice and spiritual support.
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