Applied Radiation and Isotopes 68 (2010) 592–595

Contents lists available at ScienceDirect

Applied Radiation and Isotopes

journal homepage: www.elsevier.com/locate/apradiso

Determination of the neutron spectrum shape parameter α in k_0 NAA methodology using covariance analysis

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ARTICLE INFO

Keywords:
k_0 method
Neutron
Activation
Covariance
Uncertainty

ABSTRACT

The k_0 method for quantitative reactor neutron activation analysis (NAA) has been applied in several laboratories for the determination of multi-elemental concentrations in different materials. The general formula that yields the concentration value can be divided in two parts: one involving detection parameters and the other involving irradiation parameters. A rigorous uncertainty calculation must take into account the correlations between each of these parameters. The Nuclear Metrology Laboratory at IPEN has a research program intended to develop a methodology applying covariance analysis in order to obtain the overall uncertainty in the concentrations of different elements in a given sample, and the correlation between each pair of them. The present paper concentrates in the determination of the neutron spectrum shape factor α by two methods: *Cd-covered* and *Cd-ratio*, using experimental data obtained in the IEA-R1 research reactor. The final values for α were: (0.001 ± 0.018) and (0.001 ± 0.019) for the *Cd-covered* and *Cd-ratio* methods, respectively, in good agreement with each other.

1. Introduction

One of the most widely used methods for measuring multi-element concentrations in different samples is the neutron activation analysis (NAA) (see for instance De Corte, 2000; De Corte and Simonits, 2003). This method can be applied in two different ways: comparing the result with element standards irradiated together with the sample of interest, or by means of the k_0 method, as described by De Corte (2000). In the latter case, the sample is irradiated together with a comparator (usually Au) and from the ratio between the sample and comparator activities, the element concentrations can be derived.

The k_0 method can only be applied if the neutron spectrum shape characteristics are known. In this context, the neutron spectrum shape parameter α plays an important role in NAA methodology. Ideally, the epithermal neutron spectrum is described as a $1/E$ function, where E is the neutron energy. In practice, distortions can change this behavior but the spectrum can still be described approximately by $1/E^{1+\alpha}$ where α is the spectrum shape parameter. If the neutron spectrum is shifted to higher energies then α is negative and inversely if the neutrons tend to be more thermalized then α becomes positive (De Corte et al., 1984).

The α parameter determination is based on the response of selected activation nuclei having resonance peaks for neutron capture at different neutron energies in the epithermal region. Three methods have been described in the literature, namely: *Cd-covered multi-monitor*, *Cd-ratio multi-monitor* and *Bare-irradiation* methods (De Corte, 1987; Dung and Sasajima, 2003). The first two require a smaller number of flux monitors and less effort to obtain the result, whereas the third one requires twice as many monitors. However, the latter method is based on a smaller number of parameters and, in principle, can achieve a lower uncertainty. The present paper is focused on the covariance analysis of *Cd-covered* and *Cd-ratio* methods.

2. Methodology

2.1. Determination of neutron spectrum shape parameter α

2.1.1. Cd-covered multi-monitor method

In this technique (De Corte, 1984; De Corte, 1987; Dung and Sasajima, 2003) a set of monitors is irradiated under a cadmium cover and the radionuclide activities are measured with an efficiency calibrated HPGe gamma-ray spectrometer. If the neutron capture cross sections of the monitors behave according to $1/v$ law in the thermal region, then α can be obtained from the slope of the curve $Y_i = a + \alpha X_i$ where:

$$X_i = \ln \overline{E}_{r,i} \tag{1}$$

and

$$Y_i = \ln \frac{(\overline{E}_{r,i})^{-\alpha} (A_{sp,i})_{Cd}}{k_{0,Au}(i) \cdot \varepsilon_{p,i} \cdot F_{Cd,i} \cdot Q_{0,i}(\alpha) \cdot G_{e,i}} \tag{2}$$

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doi:10.1016/j.apradiso.2009.09.065

In these expressions, index i refers to the i-th target nucleus and: $\overline{E}_{r,i}$ is the average resonance energy; $(A_{sp,i})_{Cd}$ is the total absorption gamma-ray peak area of the reaction product, corrected for saturation, decay time, cascade summing, geometry, measuring time and mass; $k_{0,Au}(i)$ is the k_0 factor for the monitor with respect to Au; $\varepsilon_{p,i}$ is the HPGe peak efficiency for the monitor gamma-ray energy; $F_{Cd,i}$ is the Cd transmission factor for epithermal neutrons; $Q_{0,i}$ (α) is the ratio between the resonance integral and thermal cross section of the target nucleus as a function of α and $G_{e,i}$ is the self-shielding correction factor for epithermal neutrons.

Since Y_i depends on the shape parameter α, an iterative procedure becomes necessary in order to obtain a final value for α. From Eqs. (1) and (2) correlation between factors involving $Q_{0,i}$ and $\overline{E}_{r,i}$ can be observed because both parameters depend on the same α parameter. This effect occurs for the same Y_i value and also for different pairs of Y_i. There is another correlation between efficiencies for different gamma lines from the same monitor and for each pair of monitors because all of them were taken from the same calibration curve. An additional correlation exists between X_i and Y_i, because both depend on the same value of $\overline{E}_{r,i}$.

2.1.2. Cd-ratio multi-monitor method

This technique is similar to the previous one (De Corte, 1984; De Corte, 1987; Dung and Sasajima, 2003), except that two set of monitors are prepared. One is irradiated with a cadmium cover and the other without. The cadmium ratios ($R_{Cd,i}$) are calculated and the value of α can be obtained from the curve $Y_i = a + \alpha X_i$ where, X_i is the same as in the previous case and:

$$Y_i = \log \frac{(\overline{E}_{r,i})^{-\alpha} \cdot G_{th,i}}{(F_{Cd,i} \cdot R_{Cd,i} - 1) \cdot Q_{0,i}(\alpha) \cdot G_{e,i}} \quad (3)$$

In this expression $G_{th,i}$ is the self-shielding correction factor for thermal neutrons.

The correlations observed in the previous case also occur in Eq. (3) except for the case of HPGe efficiency values which are not present because they cancel out when the cadmium ratios are evaluated.

In expressions (2) and (3), the values of the average resonance energy, Q_0 and k_0 were taken from Kolotov and De Corte (2002). The values of G_{th} and G_e were calculated on basis of expressions given by Martinho et al. (2003, 2004), respectively, using gamma-ray width (Γ_γ) and neutron width (Γ_n) taken from Cullen (2007).

2.2. Covariance analysis

From the series expansion of the function $Y = Y(a_1, a_2, a_3, \ldots, a_n)$, it can be shown that (Smith, 1991):

$$\sigma_Y^2 \cong \sum_{\nu=1}^{n} \frac{\partial Y}{\partial a_\nu} \sum_{\lambda=1}^{n} \frac{\partial Y}{\partial a_\lambda} \langle (a_\nu - a_{0,\nu})(a_\lambda - a_{0,\lambda}) \rangle \quad (4)$$

The partial derivatives in (4) are calculated at $a = a_0$, where a_0 is the expectancy value of a. The parameter $\langle (a_\nu - a_{0,\nu})(a_\lambda - a_{0,\lambda}) \rangle$ is called *covariance* of a_ν with respect to a_λ and usually has a nonzero value. When a_ν is independent of a_λ the covariance is zero. The variance of a_ν corresponds to the covariance of a_ν with itself:

$$\sigma_\nu^2 = \mathrm{cov}(a_\nu, a_\nu) = \langle (a_\nu - a_{0,\nu})(a_\nu - a_{0,\nu}) \rangle = \mathrm{var}(a_\nu) \quad (5)$$

The expression for the covariance of Y becomes:

$$\sigma_Y^2 \cong \sum_{\nu=1}^{n} \left. \frac{\partial Y}{\partial a_\nu} \right|_{a=a_0} \sum_{\lambda=1}^{n} \left. \frac{\partial Y}{\partial a_\lambda} \right|_{a=a_0} \mathrm{cov}(a_\nu, a_\lambda) \quad (6)$$

Table 1
Parameters of function Y and their derivatives.

Variable	Parameter	Derivative Eq. (2)	Derivative Eq. (3)
a_1	$\overline{E}_{r,i}$	$-\frac{\alpha}{\overline{E}_{r,i}}$	$-\frac{\alpha}{\overline{E}_{r,i}}$
a_2	$(A_{sp,i})_{Cd}$	$1/(A_{sp})_{Cd}$	
a_3	$k_{0,Au}(i)$	$-\frac{1}{k_{0,Au(i)}}$	
a_4	$\varepsilon_{p,i}$	$-\frac{1}{\varepsilon_{p,i}}$	
a_5	$F_{Cd,i}$	$-\frac{1}{F_{Cd,i}}$	$-\frac{R_{Cd,i}}{F_{Cd,i}R_{Cd,i}-1}$
a_6	$Q_{0,i}$ (α)	$-\frac{1}{Q_{0,i}(\alpha)}$	$-\frac{1}{Q_{0,i}(\alpha)}$
a_7	$G_{e,i}$	$-\frac{1}{G_{e,i}}$	$-\frac{1}{G_{e,i}}$
a_8	$G_{th,i}$		$\frac{1}{G_{th,i}}$
A_9	$R_{Cd,i}$		$-\frac{F_{Cd}}{F_{Cd}R_{Cd}-1}$

Using matrix notation, the covariance becomes $V_{\nu,\lambda} = \mathrm{cov}(a_\nu, a_\lambda)$, and the vector for the partial derivatives, $G = \partial Y/\partial a_\nu|_{a=a_0}$. Function G can be understood as the gradient of $Y(a)$ calculated at point a_0. In this notation, Eq. (6) can be rewritten as:

$$V_{\nu,\lambda} = G^t V G \quad (7)$$

In order to get vector G, all variables from function Y should be considered and the corresponding derivatives are shown in Table 1.

2.3. Determination of the gamma-ray detection efficiency curve

The HPGe gamma-ray efficiency curve has been determined by means of ^{60}Co, ^{133}Ba, ^{137}Cs and ^{152}Eu standard sources supplied by the IAEA (International Atomic Energy Agency), in the energy range from 244 and 1408 keV. The distance from the radioactive source to HPGe detector frontface was approximately 17.9 cm for reducing cascade summing corrections. A sigmoidal step function has been applied to the gamma-ray peak in order to subtract the source background, as described by Dias et al. (2004).

The detector efficiency curve as a function of the gamma-ray energy has been fitted by means of a third degree polynomial in log–log scale, applying covariance matrix methodology (Smith, 1991). All partial errors involved in each calibration energy as well as their correlations have been considered, namely: peak area statistics, standard activity value, decay correction, geometric correction, dead time, cascade summing correction and gamma emission probability per decay.

2.4. Irradiation process

The selected targets were ^{197}Au (0.10% Al alloy), ^{94}Zr, ^{64}Zn, ^{45}Sc and ^{139}La (0.47% Al alloy), activated by (n,γ) reaction. The samples were encapsulated in aluminum and the masses ranged from around 5 (^{94}Zr) to 250 (^{64}Zn) mg.

Two irradiations were performed in sequence using two set of samples: one with and the other without Cd cover. The irradiation times were 1 and 2 h, respectively, in a 1.6×10^{13} cm^{-2} s^{-1} thermal neutron flux. The gamma spectrometry was carried out after at least one day and the measurement times ranged from 10^3 to 2×10^5 s.

3. Results

3.1. HPGe efficiency curve

Table 2 shows the parameters and corresponding covariance matrix of the polynomial fit in log–log scale, between the HPGe peak efficiency as a function of the gamma-ray energy. The uncertainty in the interpolated values resulted between 0.36 and 0.79%. Fig. 1 shows the behavior of the efficiency curve. The error bars are too small to be visible.

Table 2
Efficiency parameters and corresponding covariance matrix of the polynomial fitting.

Fitting parameters	Value	Covariance matrix
a_0	−5.984024	1.07091E+01
a_1	1.901061	−5.07090E+00 2.40317E+00
a_2	−0.5163550	7.96689E−01 −3.77881E−01 5.94691E−02
a_3	0.03019941	−4.15337E−02 1.97163E−02 −3.10543E−03 1.62296E−04
χ^2	1.25	

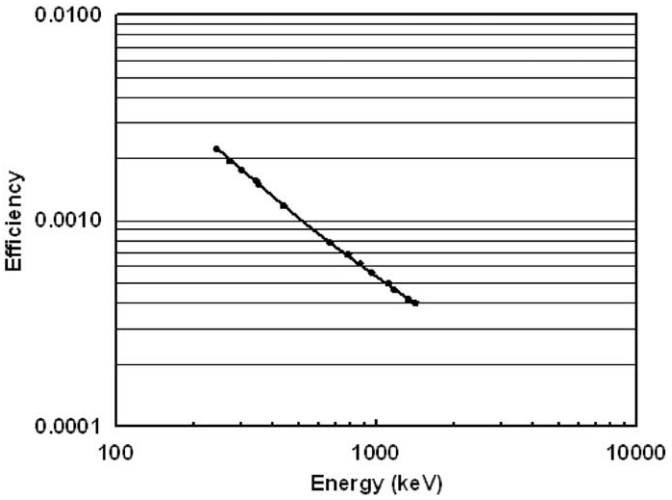

Fig. 1. Behavior of the HPGe peak efficiency curve in log–log scale.

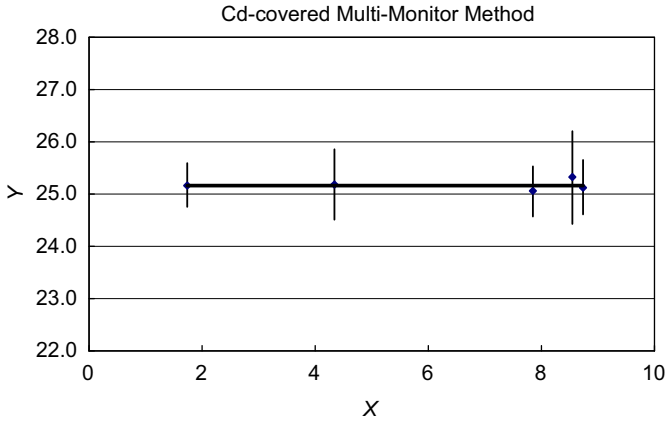

Fig. 2. Behavior of parameter Y as a function of X for the *Cd-covered multi-monitor method*.

3.2. Shape parameter α

Fig. 2 shows the behavior of Y as a function of X for the *Cd-covered multi-monitor method*. The curve is almost flat with all error bar crossing the fitting line, except for ^{46}Sc, which is slightly above the others. The resulting value for α was (0.001 ± 0.018). Fig. 3 shows the behavior of Y as a function of X for the *Cd-ratio multi-monitor method*. The same behavior as in Fig. 2 is observed. Again ^{46}Sc data point is located above the others. The reason for this peculiar behavior is being investigated. The resulting value for α in the latter method was (0.001 ± 0.019), in excellent agreement with the first method.

Table 3 shows the main partial errors involved in the α parameter determination for each monitor in both methods. As can be seen the main contribution comes from Q_0, k_0 and detection efficiency. Tables 4 and 5 show the Y values obtained

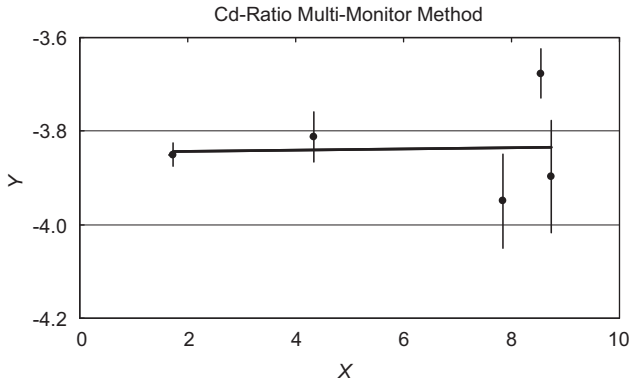

Fig. 3. Behavior of parameter Y as a function of X for the *Cd-ratio multi-monitor method*.

Table 3
Main partial errors involved in function Y (in percent).

Monitor	Energy (keV)	Peak area	Q_0	k_0	R_{Cd}	HPGe efficiency
^{198}Au	411.8	0.85	1.8	0	0.39	0.46
^{140}La	1596.2	1.09	1.3	1.1	0.44	0.44
^{46}Sc	1120.5	0.78	1.4	1.2	0.36	0.79
^{95}Zr	724.2	0.97	3.1	1.3	0.26	0.42
^{65}Zn	1115.5	0.72	2.5	0.4	0.34	0.36

Table 4
Covariance matrix of function Y obtained by the *Cd-ratio multi-monitor* method.

Monitor	X	Y	U_Y (%)	Correlation matrix				
^{198}Au	1.732	−3.851	0.64	1000				
^{95}Zr	8.742	−3.898	3.13	0	1000			
^{65}Zn	7.848	−3.950	2.60	11	0	1000		
^{140}La	8.543	−3.676	1.36	4	0	10	1000	
^{46}Sc	4.3307	−3.8118	1.41	0	0	1	0	1000

Table 5
Covariance matrix of function Y obtained by the *Cd-covered multi-monitor* method.

Monitor	X	Y	U_Y (%)	Correlation matrix				
^{198}Au	1.732	25.173	1.63	1000				
^{95}Zr	8.742	25.130	2.06	144	1000			
^{65}Zn	7.848	25.057	1.92	146	76	1000		
^{140}La	8.543	25.317	3.48	211	113	118	1000	
^{46}Sc	4.331	25.181	2.65	276	148	146	216	1000

from Eqs. (2) and (3), together with their overall uncertainties and corresponding correlation matrixes. For the *Cd-ratio* method the correlation matrix is almost diagonal because several factors involved in the activity determination cancel out. These factors include: detection efficiency, geometry, gamma-ray attenuation and gamma-ray probability per decay.

4. Conclusion

A rigorous uncertainty analysis of k_0 method must consider all correlations involved in the procedure followed in order to obtain the element concentration. The present paper performed this treatment, taking into account all partial errors involved in the determination of neutron spectrum shape parameter α as well as their correlations, by means of two methods, namely: *Cd-covered multi-monitor method* and *Cd-ratio multi-monitor method*. The values of α obtained by these two methods were (0.001 ± 0.018) and (0.001 ± 0.019), respectively, showing a very good agreement. All partial errors involved in the α parameter determination were considered, for each monitor in both methods. The main contribution to the overall uncertainty comes from Q_0, k_0 and detection efficiency.

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