2007 International Nuclear Atlantic Conference - INAC 2007
Santos, SP, Brazil, September 30 to October 5, 2007
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: 978-85-99141-02-1

COVARIANCE ANALYSIS OF DETECTION PROCESSES IN k_0 NAA METHODOLOGY

Vanderlei Cardoso, Mauro S. Dias, Ana Maria G. Figueiredo, Marina F. Koskinas

Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242, Cidade Universitária
05508-000 São Paulo, SP
vcardoso@usp.br
msdias@ipen.br
anamaria@ipen.br
koskinas@ipen.br

ABSTRACT

The use of k_0 for quantitative reactor neutron-activation analysis (NAA) is a well known method for 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. The rigorous uncertainty calculation must take into account the correlations between each of these parameters. The present work describes a methodology applying covariance analysis to obtain the overall uncertainty in the concentrations of different elements in a given sample and the correlation between each pair of them. This first paper concentrates in the detection process parameters using experimental data obtained in the IEA-R1 research reactor.

1. INTRODUCTION

The Neutron Activation Analysis (NAA), one of the most important methods in radiochemistry, is based on the activity value of a radionuclide produced by a nuclear reaction[1-9]. This activity is directly related to the corresponding element concentration present in the sample and is usually determined by gamma-ray spectrometry.

One of the NAA methodologies applied all over the world is known as k_0 method. In this technique, the element concentration is determined from the ratio between the activities of radionuclides obtained from each element of interest and a single comparator, usually gold, irradiated together with this element. The advantage of this method is to avoid the need of multiple standards to cover all elements of interest.

The factor k_0 is defined by the following relationship:

$$\left(k_{0,Au}\right)_a = \frac{M_{Au}\Theta_a\sigma_{0,a}\gamma_a}{M_A\Theta_{Au}\sigma_{0,Au}\gamma_{Au}} \qquad (1)$$

Where: M_x, Θ_x, σ_x e γ_x correspond to atomic mass, isotopic abundance, thermal neutron cross section and the gamma-ray emission probability per decay. As can be seen, for each gamma line there will be a specific k_0 value. The k_0 values have been determined for a large number of elements and can be found in the literature [2,3].

The element concentration is given by the following equation:

$$c_a = \frac{\left(\frac{N_p / t_m}{WDC}\right)_a}{\left(\frac{N_p / t_m}{WDC}\right)_{Au}} \times \frac{\varepsilon_{p,Au}}{\varepsilon_{p,a}} \times \frac{1}{(k_{0,Au})_a} \times \frac{f_i + Q_{0,Au}(\alpha)}{f_i + Q_{0,,a}(\alpha)} \times \frac{S_{Au}}{S_a} \qquad (2)$$

The first two factors are related to detection parameters involved in activity determination by gamma-ray spectrometry, including both the radionuclide of interest and comparator. The third factor is k_0 and the last factors are related to parameters involved with neutron field characteristics, decay constant and irradiation time.

The parameters in equation (2) are:

N_p total energy absorption peak from the considered gamma line (corrected for dead time, geometrical factors, summing effects etc);
t_m measuring time;
S $1-\exp(-\lambda t_{irr})$, saturation factor (t_{irr}: irradiation time);
D $\exp(-\lambda t_d)$, decay correction between irradiation and counting (t_d: decay time);
C $[1-\exp(-\lambda t_m)]/\lambda t_m$, decay correction within counting time (t_m: measuring time);
W sample or comparator mass;
λ decay constant;
f epithermal to thermal neutron flux ratio;
$\varepsilon_{p,x}$ total absorption peak efficiency obtained from gamma-ray activity standards;
$Q_0 = I_0 / \sigma_0$, where σ_0 (n, γ) is the thermal neutron cross section (at 2200 m s^{-1}) and I_0 is the resonance integral;
α parameter related to epithermal neutron energy distribution, given approximately by $1/E^{1+\alpha}$;
"a" e "Au" subscripts refer to sample and gold, respectively.

A few papers can be found in the literature concerning uncertainty determination in the k_0 method [5-9]. However, these works do not perform complete statistical treatment, taking into account the complexity of correlations among the parameters in equation (2). The main goal of the present work was to perform a rigorous statistical treatment of uncertainties related to parameters from equation (2) related to gamma-ray spectrometry.

2. THEORY

Detection Function

The part of equation (2) related to detection processes can be given by a *detection function Z*, defined by the following relationship:

$$Z = \left(\frac{N_p \lambda t_m}{W(e^{-\lambda td})(1-e^{-\lambda tm})}\right)_a \left(\frac{W(e^{-\lambda td})(1-e^{-\lambda tm})}{N_p \lambda t_m}\right)_{Au} \frac{\varepsilon_{p,Au}}{\varepsilon_{p,a}} \qquad (3)$$

This function involves several parameters and the uncertainty and correlation between each pair of them must be considered. On the other hand, some of these parameters are determined by means of other parameters not explicitly shown in equation (3). For instance, the detection efficiency ε is obtained by least square fitting of additional gamma-ray spectrometric measurements performed with standard radionuclides. This fitting involves other uncertainty sources together with their correlations.

The present work makes use of an analytical procedure which includes the uncertainties in the parameters of equation (3) and covariance matrix methodology. This procedure allows rigorous analysis of complex correlations among these parameters and their uncertainties.

Variance

A function Z of several random variables: $y_1, y_2, ..., y_n$ is considered. From series expansion it can be shown that Z can be given by:

$$\sigma_z^2 \cong \sum_{\nu=1}^{n} \frac{\partial z}{\partial y_\nu} \sum_{\lambda=1}^{n} \frac{\partial z}{\partial y_\lambda} \left\langle \left(y_\nu - y_{0,\nu}\right)\left(y_\lambda - y_{0,\lambda}\right) \right\rangle \tag{4}$$

The partial derivatives in (4) must be calculated at $y = y_0$, where y_0 is the expectancy value of y. The parameter $\left\langle \left(y_\nu - y_{0,\nu}\right)\left(y_\lambda - y_{0,\lambda}\right) \right\rangle$ is called *covariance* of y_ν with respect to y_λ and usually has non zero value. When y_ν is independent of y_λ the covariance is zero. The variance of y_ν can be understood as the covariance of y_ν with itself:

$$\sigma_\nu^2 = \mathrm{cov}(y_\nu, y_\nu) = \left\langle \left(y_\nu - y_{0,\nu}\right)\left(y_\nu - y_{0,\nu}\right) \right\rangle = \mathrm{var}(y_\nu)$$

Therefore, the covariance can be given by:

$$\sigma_z^2 \cong \sum_{\nu=1}^{n} \left.\frac{\partial z}{\partial y_\nu}\right|_{y=y_0} \sum_{\lambda=1}^{n} \left.\frac{\partial z}{\partial y_\lambda}\right|_{y=y_0} \mathrm{cov}(y_\nu, y_\lambda) \tag{5}$$

Using matrix notation for the covariance:

$$V_{\nu,\lambda} = \mathrm{cov}(y_\nu, y_\lambda),$$

and the following vector for the partial derivatives:

$$G = \left.\frac{\partial z}{\partial y_\nu}\right|_{y=y_0}$$

Function G can be understood as the gradient of Z(y) calculated at point y_0. In this notation, equation (5) can be rewritten as:

$$V_{\nu,\lambda} = G^t \, V \, G \tag{6}$$

In order to get vector G, all variables from detection function Z were considered and the corresponding derivatives.

3. EXPERIMENTAL

A sample with 16.6 mg of certificated material type AGV-1 has been irradiated at position 24A, near the core of the IEA-R1 nuclear research reactor, together with 7.44 mg of 0.1% gold-aluminum alloy for 1.0 h, irradiation time. The decay times were approximately 7.4 and 2.2 days for the certificated material and gold, respectively.

Both samples were measured in a HPGe gamma-ray spectrometer, previously calibrated with standard sources of ^{88}Y, ^{57}Co, ^{139}Ce, ^{137}Cs, ^{54}Mn, ^{60}Co and ^{152}Eu. Nineteen efficiency calibration points were obtained from 88 to 1408 keV. Two elements were selected in the present paper to apply the covariance methodology, namely Sc and La. These elements produce gamma-ray emitting radionuclides ^{46}Sc and ^{140}La, respectively, by neutron capture reactions.

4. RESULTS AND DISCUSSION

A third degree polynomial in log-log scale was used for fitting the total absorption peak efficiency as a function of the gamma-ray energy, applying covariance matrix methodology[10,11]. Code Alpino[12] was used for calculating all parameters necessary for the activity determination, namely: net peak area, decay, dead time, geometrical factor, attenuation factor and efficiency, for each gamma line from the irradiated certificated material and gold. Table 2 shows the efficiency parameters and the corresponding covariance matrix.

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

Fitting parameters	Value	Covariance Matrix
$\mathbf{a_0}$	−2.451E+01	3.529E+00
$\mathbf{a_1}$	1.186E+01	−1.850E+00 9.716E−01
$\mathbf{a_2}$	−2.099E+00	3.183E−01 −1.675E−01 2.893E−02
$\mathbf{a_3}$	1.137E−01	−1.800E−02 9.491E−03 −1.642E−03 9.344E−05

Table 3 shows the partial errors considered in the detection process, in percent, for each gamma-ray energy. As can be seen the main contribution comes from the detection efficiency. The row below the element gives the correlation factor between each pair of partial errors. In the case of efficiency the correlations were obtained from the least square fitting applied to the interpolated energies.

Table 4 shows the correlation matrix of function ***Z***, calculated on the basis of all partial errors involved for each gamma-ray energy.

Table 3 – Partial errors involved in the detection process.

Element	Energy (keV)	Peak Area	Half-life	Mass	Decay time	Efficiency
Scandium	889.3 1120.5	0.25 0.29	0.05	0.10	0.0035	1.20 1.26
Correlation Factor		0	1	1	1	0.637
Lanthanum	328.8 487.0 815.8	0.57 0.32 0.96	0.02	0.10	0.06	1.74 1.59 1.31
Correlation Factor		0	1	1	1	1 0.819 1 0.329 0.766 1

Table 4 – Correlation matrix of function *Z*.

	E (keV)	Z	Total Uncertainty (%)	Correlation Matrix				
Scandium	889.3	5.40E-04	2.5	1000				
	1120.5	5.38E-04	3.2	637	1000			
Lanthanum	328.8	1.842E-03	2.1	229	-94	1000		
	487.0	4.21E-03	2.0	651	12	819	1000	
	815.8	2.378E-03	2.6	980	474	329	766	1000

5. CONCLUSION

A complete analysis of uncertainties in k_0 method must take into account all correlations involved in the methodology. The present paper performed this treatment considering the partial errors in the detection process. Further improvements are foreseen which will include other factors, such as cascade summing corrections, geometrical factors for finite sources etc. Major studies to be performed will involve irradiation parameters.

6. REFERENCES

2. F. De Corte. "k_0 and Comparator NAA: Influences and Interactions". J. Radioanal. Nucl. Chem., 245/1 (2000) 157-161.

3. V.P. Kolotov, F. De Corte. “Compilation of k_0 and Related Data for Neutron-Activation Analysis (NAA) in the Form of an Electronic Database”. Pure and Appl. Chem., 76 (2004), 1921-1925.
4. F. De Corte, A. Simonits. “Recommended Nuclear Data for use in the k_0 Standardization of Neutron Activation Analysis”. Atomic Data and Nuclear Data Tables 85 (2003) 47-67.
5. F. De Corte, A. Simonits, A. DE Wispelaere, J.Hoste. “Accuracy and Applicability of the k_0 – Standardization Method”. J. radioanal. Nucl. Chem. 113/1 (1987) 145-161.
6. J. Kragten. “Calculating Standard Deviations and Confidence Intervals with a Universally Applicable Spreadsheet Technique”. Analyst, 119 (1994) 2161.
7. F. De Corte. “The Standardization of Standardless NAA”. J. Radioanal. Nucl. Chem. 248 (2001) 13-20.
8. P. Robouch, G. Arana, M. Eguskiza, S. Pomme, N. Etxebarria. “Uncertainty Budget for k_0-NAA”, J. Radioanal. Nucl. Chem., 245/1 (2000) 195-197.
9. J. Kucera, P. Bode, V. Stepanek. “The 1993 ISO Guide to the Expression of Uncertainty in Measurement Applied to NAA”. J. Radioanal Nucl. Chem., 245/1 (2000) 115-122.
10. D. L. SMITH, “Probability, Statistics and Data Uncertainties in Nuclear Science and Technology”. Illinois-ANS (1991).
11. M.S. Dias, V. Cardoso, V.R. Vanin, M. F. Koskinas, “Combination of nonlinear function and mixing method for fitting HPGe efficiency curve in the 59-2754 keV energy range”. Applied Radiation and Isotopes, v. 60, n. 5, (2004) 683-687.
12. M.S. Dias, “Alpino – code for calculating efficiency and activity of HPGe gamma-ray spectrometers”, Nuclear Metrology Laboratory, IPEN, Internal Report, 2002.