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Assessment of Nuclear Characteristics of NAA #1 Irradiation Hole in HANARO Research Reactor for Application of the k_0-NAA Methodology

Jong Hwa Moon, Sun Ha Kim, Yong Sam Chung
Korea Atomic Energy Research Institute
150 Dukjin-dong, Yuseung-gu, Daejeon 305-353, Korea
jhmoon1@kaeri.re.kr

Ho Mahn Dung
Vietnam Atomic Energy Institute
Nuclear Research Institute, 01 Nguyen Tu Luc St., Dalat, Vietnam

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Abstract

Neutron activation analysis based on k_0-standardization method (k_0-NAA) is known as one of the most remarkable progresses of the NAA with advantages of experimental simplicity, high accuracy, excellent flexibility with respect to irradiation and counting conditions, and suitability for computerization. This study was carried out to determine the reactor neutron spectrum parameters, i.e. α and f as the main factors of irradiation quality at NAA #1 irradiation hole on HANARO research reactor, to evaluate peak detection efficiency of the gamma-ray spectrometer for the use in the k_0 experiments and to compare the measured concentration results with the certified values of some SRMs applying the experimentally determined k_0-parameters.

Key Words : k_0-standardization, α and f parameters, SRM analysis, quality control

1. Introduction

Since Hevesy and Levi proposed Neutron Activation Analysis(NAA) as a method for quantitative determination of elemental concentration in 1936, NAA has been developed in the aspects of both instrumentation and technology for a long period of time. Although some other trace analytical techniques have been developed to put them onto a competitive position with NAA, NAA is the best analysis technique for solid samples. NAA can be divided into two categories. One is INAA(Instrumental NAA) without chemical treatment, the other is RNAA(Radiochemical NAA) with chemical separation processes. In the present, INAA is used more generally than RNAA because of it' s simplicity. Quantitative methods for INAA are absolute, relative, single-comparator and k_0-standardization method. Absolute method directly

uses physical nuclear parameters, e.g. isotopic abundance, cross section, gamma-ray branching ratio and atomic mass taken from literature. Uncertainty of these parameters leads to large systematic errors in some cases. In relative method, unknown sample is irradiated with standard sample containing a known amount of interesting element. So various standard sample is always necessary for relative method. In single-comparator method, k-factors should be determined experimentally for all elements[1]. If characteristics of irradiation hole is changed, all k-factor should be re-measured. For the compensation of these disadvantages in the above quantitative methods, the k_0-standardization method of neutron activation analysis (k_0-NAA) was launched in 1975[1]. It is not a theory describing a physical phenomenon but a protocol for calibration procedures. It has been developed as an absolute standardization method, where the unreliable nuclear data are replaced by accurate experimentally determined compound nuclear constants with high accuracy, so called k_0-factor, or as a single comparator standardization which is flexible with respect to varying characteristics of the neutron spectrum and of the detector and the source-detector configuration.

This work intended to evaluate characteristics to the NAA #1 irradiation hole of the HANARO research reactor for application of k_0-NAA method by determination of k_0-parameters and analysis of standard reference materials.

2. Methodology

k_0-factor of analyte a versus monitor m is defined as :

$$k_{0,m}(a) = \frac{M_m \ \gamma_a \ \theta_a \ \sigma_{0,a}}{M_a \ \gamma_m \ \theta_m \ \sigma_{0,m}} \qquad (1)$$

where, M : atomic weight, γ: absolute gamma intensity, θ:isotopic abundance and σ_0:(n,γ) reaction cross-section for 2200 m/sec neutrons.

The $k_{0,\,Au}$ factors experimentally determined at the Institute for Nuclear Sciences, Gent, Belgium and the Central Research Institute for Physics, Budapest, Hungary[2], and later with valuable contributions from other laboratories as well, were tabulated and published in literature as a generally useful parameter. Then, the coirradiated sample with a monitor Au, the analyte concentration, ρ_a can be obtained by following expression[3] :

$$\rho_a = \frac{A_{sp,a}}{A_{sp,Au}} \frac{1}{k_{0,Au}(a)} \frac{G_{th,Au} \cdot f + G_{e,Au} \cdot Q_{0,Au}(\alpha)}{G_{th,a} \cdot f + G_{e,a} \cdot Q_{0,a}(\alpha)} \frac{\varepsilon_{p,Au}}{\varepsilon_{p,a}} \qquad (2)$$

where,

$A_{sp,a} = (N_p/t_c)/SDCW$, specific count rate

W : sample weight, gram

N_p : measured gamma net peak area (counts)

t_c : counting time

S : saturation factor, $1- \exp(-\lambda t_i)$

λ : decay constant, $\ln 2/T_{1/2}$

$T_{1/2}$: half life

t_i : irradiation time

D : decay factor, $\exp(-\lambda t_d)$

t_d : dacay time

C : counting factor, $[1- \exp(-\lambda t_c)]/\lambda t_c$

t_c : counting time

$A_{sp,Au} = (N_p/t_c)/SDCW$, specific count rate

w : monitor weight, gram

G_{th} : correction factor for thermal neutron self shielding

G_e : correction factor for epithermal neutron self shielding

$f = \Phi_{th}/\Phi_e$: thermal to epithermal flux ratio

α : parameter for the deviation of the

epithermal neutron distribution form 1/E-law, approximated by $1/E^{1+\alpha}$ dependence. The α value can be positive or negative depending on the reactor condition (e.g. moderator material, geometry of irradiation site, etc.)

$$Q_0(\alpha): I_0(\alpha)/\sigma_0 = \{(Q_0 - 0.429)/\overline{Er}^{\alpha}\} + \{0.429/E_{cd}^{\alpha}(2\alpha+1)\}(1eV)^{\alpha} \quad (3)$$

where, $Q_0 = I_0/\sigma_0$, I_0 : resonance integral, $\overline{Er}$: effective resonance energy E_{cd} : cadmium cut-off energy, 0.55 eV

ε_p : full-energy(photo) peak detection efficiency

Equation (2) indicates that I_0 (or Q_0) must be converted to $I_0(\alpha)$ [or $Q_0(\alpha)$] as expressed by Eq. (3) in the k_0-NAA method. This means that α should be known or experimentally determined. The physical and mathematical basis of the α-determination can be described as follows:

The deviations from the ideal 1/E-law can be approximated by a non-ideal, real epithermal neutron spectrum, expressed by[3,4] :

$$\Phi e(E) = \frac{\Phi e}{E^{1+\alpha}} \quad (4)$$

where, $\Phi e(E)$: epithermal flux per unit of neutron energy interval

Φe : energy independent proportionality constant

= integrated epithermal flux per unit of ln E-interval,

Equation (4) is rearranged as :

$$\Phi e(E)E = \Phi e E^{-\alpha} \quad (5)$$

Thus, when plotting $\Phi e(E)E$ versus logE for some suitable monitors, a straight line will be obtained with slope $-\alpha$.

From Eq. (5), a formula for the α-determination based on "Cd-ratio for multi-monitor" method in which monitors are characterized by the effective resonance energy, $\overline{E_r}$ is derived as follows :

A set of N monitors are irradiated with and without Cd-covers, and the induced activities are measured on a Ge detector. If all the monitors have a $\sigma(v) \propto 1/v$ dependence up to 1.5 eV, the slope of the straight line, $-\alpha$, can be obtained by plotting [3,5] :

$$\log \frac{(\overline{Er_{,i}})^{\alpha}}{[(F_{cd,i} \cdot R_{cd,i} - 1) \cdot Q_{0,i}(\alpha) \cdot (G_{e,i}/G_{th,i}]} \quad (6)$$

versus $\log \overline{Er_{,i}}$

where, i denotes isotope 1, 2, ···, n. Two monitors with three nuclides of ^{197}Au, ^{94}Zr and ^{96}Zr, so called triple-monitor, are an optimal selection for both reliability in result and experimental simplicity. Relevant nuclear data is listed in Table 1. In practice, one can select a number of physically suitable monitors(e.g. metallic or alloyed foils and wires) with $\overline{Er}$ ranging from low to high to check the linearity of the plotting line, thus proving that α is constant over the whole epithermal neutron energy region in the reactor irradiation position under consideration

For the determination of the parameter f, the ratio of the thermal to epithermal neutron flux, Cd-ratio method can be used[3,5] :

$$f = (R_{cd}F_{cd} - 1)\, Q_0(\alpha)(G_e/G_{th}) \quad (7)$$

where, F_{Cd} : cadmium transmission factor for epithermal neutrons,

R_{Cd} : cadmium ratio.

The monitor used is an element with well-known Q_0 and $\overline{Er}$ values (Au is suitable for this requirements), which is irradiated subsequently with and without Cd-cover.

Table 1. Relevant Nuclear Data for Use in α-determination by Triple-monitor Method[5]

Monitor	$\overline{Er}$, eV	Q_0	half-life	Gamma Energy (keV)	$k_{0,Au}$
$^{197}Au(n,\gamma)^{198}Au$	5.65	15.71	2.695 d	411.8	1 (F_{cd} = 0.991)
$^{96}Zr(n,\gamma)^{97}Zr/^{97m}Nb$	338	248	16.9 h	743.3	1.30E-05
$^{94}Zr(n,\gamma)^{95}Zr$	6260	5	64.02 d	724.2 756.7	9.32E-05 1.15E-04

3. Experimental

3.1. Efficiency Calibration of Gamma-ray Spectrometer

Gamma-ray spectrometer, HpGe detector(EG & G ORTEC, GEM35185) and an 8192 MCA, was used for this study. Eq. (2) implies that the full-energy peak detection efficiency(ε_p) of gamma-ray spectrometer used must be determined. The calibration of the gamma-ray spectrometer according to the k_0-NAA method has been defined as having three main problems. The first one is the determination of gamma energy peak detection efficiency using gamma-ray standard sources and the second is the correction for true-coincidence effects. The last is the correction for practical sample geometric conditions. The correction of true-coincidence effects and sample geometry was not yet done in this work due to the lack of proper k_0-software program. Fig. 1 shows the peak detection efficiency curve for three measurement positions. Distance of source-end cap of detector at position 3, 5 and 7 were 8.4 cm, 13.8 cm and 19.2 cm, respectively. In order to fit the experimental points, a fourth degree polynomial method was used.

3.2. Determination of Cd-ratio and *f*-Parameter

The "Cd-ratio for triple-monitor" method and

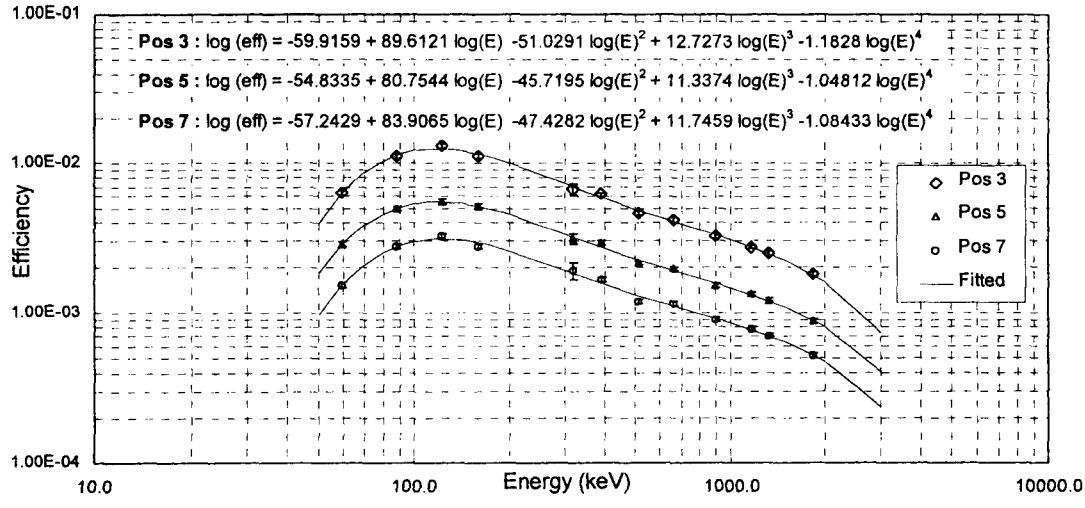

Fig. 1. Efficiency Curve of the HPGe Detector(EG & G ORTEC, GEM35185) for Three Measurement Positions

Table 2. Experimental Values of Cd-ratio, α and f Parameters for Irradiation Hole(NAA#1) Applying Triple-monitor Method

Monitor	Cd-ratio				Mean ± SD*
	Set #1	Set #2	Set #3	Set #4	
$^{197}Au(n,\gamma)^{198}Au$	83.03	88.38	76.31	79.96	81.92 ± 5.11
$^{96}Zr(n,\gamma)^{97}Zr/^{97m}Nb$	11.04	11.03	10.99	10.60	10.94 ± 0.23
$^{94}Zr(n,\gamma)^{95}Zr$	533	588	496	550	542 ± 38
α	0.122	0.127	0.126	0.133	0.127 ± 0.005
f	1032	1105	938	984	1014 ± 71

* indicates standard deviation

Cd-ratio method were respectively applied to determine α and f parameters for NAA #1 irradiation hole of HANARO research reactor. Four sets of monitors consisting of pieces of Zr sheet (99.7329%, thickness 0.125 mm), Au-Al wire(Au 0.1124%, dia. 0.508 mm), and pure cadmium cover(thickness 1.0 mm), were applied. Each monitor set was irradiated for 10 minutes. The calibrated gamma-ray spectrometer and GammaVision 5.1 software[6] were used for gamma-ray measurement and analysis of collected spectra.

3.3. Standard Reference Materials for Method Validation

In order to validate k_0-NAA method in our system, four kinds of NIST Standard Reference Materials(SRMs), NIST SRM 1633a(Coal Fly Ash), 1577b(Bovine Liver), 2704(Buffalo River Sediment) and 2709(SanJoaquin Soil) were prepared and analyzed with experimentally determined k_0-parameters. The samples with the weight of 150 ~ 200 mg for the elemental analysis using medium and long half-life nuclides were irradiated at NAA #1 hole for 30 minutes. For the elemental analysis using short half-life nuclides, NIST SRM 1633a and 1577b samples with the weight of 10 ~ 30 mg were irradiated for 1 minute. After the proper cooling time, gamma-rays from each sample were measured and the elemental concentrations were calculated by k_0-NAA method.

4. Results and Discussion

4.1. The Values of α and f Parameters

Calibration of the reactor neutron spectrum parameters related to k_0-NAA at the NAA #1 irradiation hole in HANARO research reactor was carried out by the "Cd-ratio for triple-monitor"

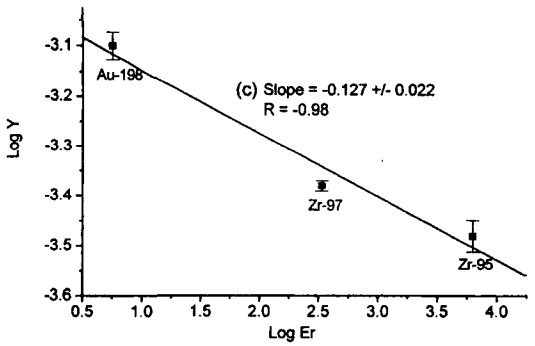

Fig. 2. The Result of α-determination by "Cd-ratio triple-monitor" Method. ($Y = (\overline{E\gamma_i})^{-\alpha} / [(F_{cd,i} \cdot R_{cd,i} - 1) \cdot Q_{0,i}(\alpha) \cdot (G_{e,i}/G_{th,i})]$)

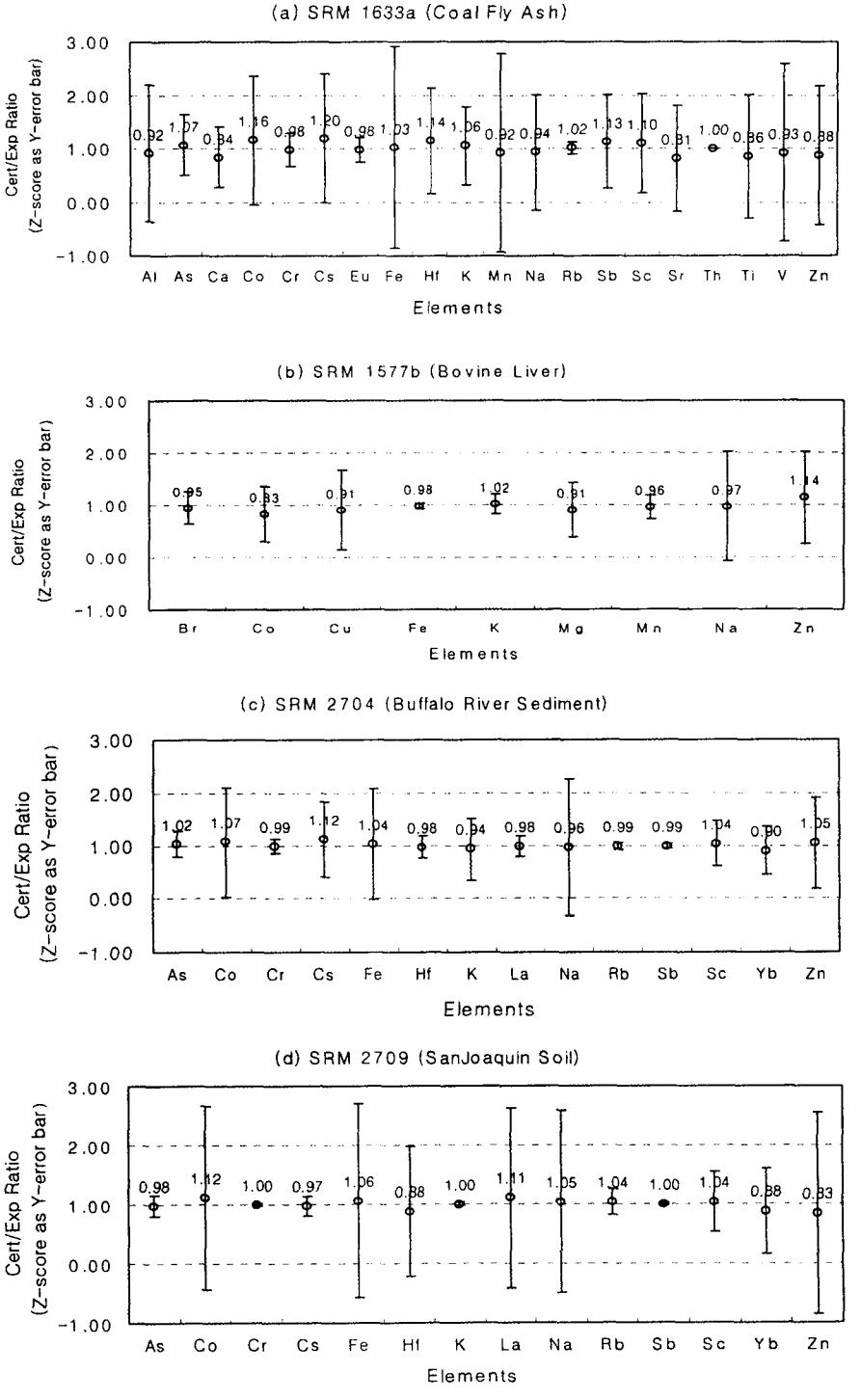

Fig. 3. Comparison of Experimental Results with Certified Values for NIST SRMs

method. Because neutrons of NAA #1 irradiation hole are well thermalized, there are only small fraction of epithermal neutrons in comparison with thermal neutrons ($R_{Cd,Au} \fallingdotseq 82$). In this case, the activities induced by epithermal neutrons in (n,γ) reactions are very low and then overlapped by the statistical fluctuations of the ones induced by thermal neutrons. Therefore, it is advised to use of the Cd-ratio methods for both determination of α and f parameters, which gives the most reliable results if a proper choice of monitors is made. Table 2 shows the Cd-ratio determined by three nuclides of ^{198}Au, $^{97}Zr/^{97m}Nb$ & ^{95}Zr for four sets of monitor and the values of α and f parameters calculated from Eq. (6) and Eq. (7). Furthermore, Fig. 2 shows the value of α parameter determined considering the experimental variation and fitting line with a good correlation coefficient of 0.98.

4.2. The Analytical Results of SRMs

Analysis of the SRMs applying a k_0-NAA procedure with the determined neutron spectrum parameters (i.e. α and f parameters) along with $A_{sp,Au}$ (specific count rate for ^{198}Au) and the detector efficiency values was carried out. Comparison between experimental results and certified values was done in terms of the ratio of the experiment to certified values. For the accuracy evaluation, Z-score values is used frequently. Z-score is defined by :

$$\text{Z-score} = | Value_{cert.} - Value_{exp.} | / \{(Unc_{cert.})^2 + Unc_{exp.})^2\}^{1/2} \quad (8)$$

where, $Value_{cert.}$: certified value,
$Value_{exp.}$: experimental value,
$Unc_{cert.}$: uncertainty in the certified value
$Unc_{exp.}$: uncertainty in the experimental value

The analytical results of 4 SRMs in various elemental composition are presented in Fig. 3 with Z-score plotted as Y-error bar. The analytical results can be briefly summarized as follows :

Fig 3(a) shows the analytical results of NIST SRM 1633a(Coal Fly Ash). 20 elements were determined. The ratio of certified to experiment value was in the range of 0.81(Sr) ~ 1.20(Cs) and the highest Z-score was 1.89(Fe). Fig 3(b) shows the analytical results of NIST SRM 1577b(Bovine Liver). 9 elements were determined. The ratio of certified to experiment value was in the range of 0.83(Co) ~ 1.14(Zn) and the highest Z-score was 1.04(Na). Fig 3(c) shows the analytical results of NIST SRM 2704(Buffalo River Sediment). 15 elements were determined excluding short-lived nuclides. The ratio of certified to experiment value was in the range of 0.90(Yb) ~ 1.12(Cs) and the highest Z-score was 1.30(Na). Finally, Fig 3(d) shows the analytical results of NIST SRM 2709(SanJoaquin Soil). 15 elements were determined excluding short-lived nuclides. The ratio of certified to experiment value was in the range of 0.83(Zn) ~ 1.12(Co) and the highest Z-score was 1.71(Zn).

From the certified/experiment ratio and Z-score, accuracy of the elements, Co, Zn and Fe, was lower than the other elements for the application of k_0-NAA.

5. Conclusions

The assessment of nuclear characteristics to the NAA #1 irradiation hole of the HANARO research reactor for application of k_0-NAA method was carried out including determination of neutron spectrum parameters, i.e. α and f-factor by the "Cd-ratio for triple-monitor" method using Au & Zr monitors, the calibration of a gamma-ray spectrometer using the HPGe detector(EG & G ORTEC, GEM35185), and the analysis of various SRMs applying the experimentally determined k_0-

parameters to compare the measured concentration results with the certified values. The experimental results revealed that the k_0-NAA method is applicable on NAA #1 of HANARO research reactor.

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