

# DETERMINATION OF IN SITU DETECTION EFFICIENCY FOR IM-NAA OF NON-STANDARD GEOMETRICAL SAMPLES

NGUYEN DUY QUANG<sup>(1)</sup>, TRINH VAN CUONG<sup>(1)</sup>, TRAN TUAN ANH<sup>(1)</sup>,  
HO VAN DOANH<sup>(1)</sup>, NGUYEN THI THO<sup>(1)</sup>, HO MANH DUNG<sup>(2)</sup>

<sup>(1)</sup>*Nuclear Research Institute, 01 Nguyen Tu Luc Street., Da Lat, Lam Dong.*

<sup>(2)</sup>*Center For Nuclear Techniques, 217 Nguyen Trai street, District 1, HCM City.*

*Email: duyquang1691@gmail.com*

**Abstract:** The  $k_0$ -based internal mono-standard (IM) method was first proposed for concentration analysis of samples of non-standard geometry in the 2000s. The method has demonstrated several advantages such as elimination of gamma-ray self-attenuation and geometrical effects. On the other hand, the accuracy of the method principally depends on the in situ relative detection efficiency, which requires to be obtained in each measurement. Therefore, the relative detection efficiency is always under consideration for improvement of the analysis results. The present paper describes a simple and automatic procedure for determination of the relative efficiency using one or more activation products emitting gamma rays over a considered range of the spectrum. The procedure can be applied for INAA and PGNAA analysis.

**Keywords:** INAA, PGNAA, internal mono-standard method, relative efficiency, non-standard geometry samples.

## 1. INTRODUCTION

Neutron activation analysis (NAA) is a sensitive multi-element analytical technique used for both qualitative and quantitative analysis of elements in a vast amount of materials. The technique has applications in chemistry, geology, archeology, medicine, environmental monitoring and even in the forensic science [1-4]. However, there are limitations due to sample size for application in bulk analysis, in particular for archaeology and cultural art artifacts, forensic materials as well as geological studies. For examples, large and non-standard geometrical samples give rise to problems of neutron self-shielding, gamma rays attenuation and certain geometrical effects. Therefore, the internal mono-standard analysis method has been proposed to overcome the mentioned difficulties [5]. In this method, the in situ relative detection efficiency is required to be obtained in each measurement and then used for elemental concentration analysis. The in situ relative detection efficiency plays a key role in the analysis as it is valuable to the correction of sample geometry effects [6]. In this study, a computer code for determination of the in situ relative efficiency has been developed. Using Prompt Gamma NAA (PGNAA) and Instrumental NAA (INAA) nuclear data, the software requires only a peak area report file for calculation of relative efficiency and perform further analysis. Results from measurements of standard reference materials have been found to be in good agreement with certified values.

## 2. MATERIAL AND METHOD

In INAA using  $k_0$  approach, consider two arbitrary elements  $x$  and  $y$  presented in an activated sample which emits two series of characteristic gamma rays  $E_{x,i}$  and  $E_{y,j}$  ( $i, j = 1, 2, \dots$ ), respectively. The mass ratio of element  $x$  to  $y$  can be expressed as follow [5]:

$$\frac{m_x}{m_y} = \frac{(SDC(f + Q_0(\alpha)))_y P_{E_{x,i}} \varepsilon_{E_{x,i}} k_{0,E_{y,j}}}{(SDC(f + Q_0(\alpha)))_x P_{E_{y,j}} \varepsilon_{E_{y,j}} k_{0,E_{x,i}}} \quad (1)$$

where  $S$  is the saturation factor,  $D$  is the decay factor,  $C$  is the measurement factor,  $f$  is the ratio of the thermal to epithermal neutron fluxes,  $Q_0(\alpha)$  is the ratio of the resonance integral-to-thermal neutron cross section corrected for the non-ideal epithermal neutron flux distribution ( $\alpha$ ),  $P$  is the peak area and  $\varepsilon$  is the full energy peak detection efficiency. In case of high  $f$ , the value of  $(f + Q_0(\alpha))_y / (f + Q_0(\alpha))_x$  in eq. (1) tends to unity and therefore, eq. (1) can be simplified as:

$$\frac{m_x}{m_y} = \frac{(SDC)_y P_{E_{x,i}} \varepsilon_{E_{x,i}} k_{0,E_{y,j}}}{(SDC)_x P_{E_{y,j}} \varepsilon_{E_{y,j}} k_{0,E_{x,i}}} \quad (2)$$

The situation is very simple in case of PGNAA where the correction factors  $S$ ,  $D$  and  $C$  can be eliminated. Though, it should be noted that the  $k_0$  databases for two different techniques are different. Having it in mind, the mass ratio in both INAA and PGNAA can be rewritten as

$$\frac{m_x}{m_y} = \frac{c_{E_{x,i}} \varepsilon_{E_{x,i}}}{c_{E_{y,j}} \varepsilon_{E_{y,j}}} \quad (3)$$

Where  $c$  is the coefficient calculated using  $k_0$  database and experimental data

$$c_{E_{x,i}} = \frac{P_{E_{x,i}}}{(SDC)_x \times (f + Q_0(\alpha))_x \times k_{0,E_{x,i}}} \quad (4)$$

and in some cases can be simplified as

$$c_{E_{x,i}} = \frac{P_{E_{x,i}}}{(SDC)_x \times k_{0,E_{x,i}}} \quad (5)$$

As clearly seen in eq. (3), the relative concentration of element  $x$  to  $y$  can be determined by the ratio of full peak detection efficiencies. This leads to the need of using relative detection efficiency which can be determined straightforwardly from eq. 3 using a fitting procedure. The relation of detection efficiencies is as follow:

$$\varepsilon_{E_{y,j}} = \frac{c_{E_{x,i}} m_y}{c_{E_{y,j}} m_x} \varepsilon_{E_{x,i}} \quad (6)$$

Hence,

$$\ln(\varepsilon_{E_{y,j}}) = \ln\left(\frac{m_y}{m_x}\right) + \ln\left(\frac{c_{E_{x,i}}}{c_{E_{y,j}}}\right) + \ln(\varepsilon_{E_{x,i}}) \quad (7)$$

The efficiencies at different gamma energies of each element are derived from eq. (6)

$$\ln(\varepsilon_{E_{x,i}}) = \ln\left(\frac{c_{E_{x,1}}}{c_{E_{x,i}}}\right) + \ln(\varepsilon_{E_{x,1}}), i = 2, 3, \dots \quad (8)$$

$$\ln(\varepsilon_{E_{y,j}}) = \ln\left(\frac{c_{E_{y,1}}}{c_{E_{y,j}}}\right) + \ln(\varepsilon_{E_{y,1}}), j = 2, 3, \dots \quad (9)$$

Thus, relative efficiency curves in logaric scale constructed individually from each element are expected to be differ by constant factors, say  $t$ . Because of using relative efficiency, an arbitrary positive value can be firstly assigned to one detection efficiency of each element, e.g.  $\text{Arb } \varepsilon_{E_{k,i}} = 10\%$  for any  $k$ -th element where “Arb” indicates the first choice of detection efficiency. The relative detection efficiencies are then corrected by  $t$ -factors:

$$\ln(\text{Rel } \varepsilon_{E_{k,i}}) = \ln(\text{Arb } \varepsilon_{E_{k,i}}) + t_k \quad (10)$$

In general, the expression for relative efficiency curve is

$$\ln(\text{Rel } \varepsilon(E)) = \sum_{i=0}^n a_i (\ln E)^i \quad (11)$$

Where  $a_i$  is the coefficient and  $n$  is the order of the polynomial that can be chosen depending on the energy range of interest. After the relative efficiency calibration curve (11) is constructed, the relative concentrations can be calculated from eq. (3) and converted to absolute concentration using a well-know mass fraction of an element presented in the sample. If concentration of  $m$  elements are required to be analysed there will be  $m+n+1$  parameters needed to be optimized in fitting procedure, including  $a_i, i=0,1,..n$  and  $t_k, k=1,2,..m$ . The iteration loop for determination of all mentioned parameters is presented in Fig. 1.

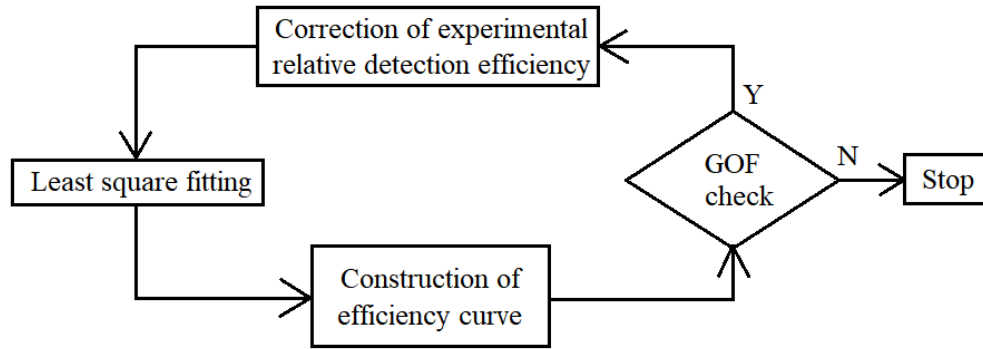


Fig.1 Iteration for optimization of fitting parameters

The loop starts with a reference efficiency curve which is then used for the correction of experimental relative detection efficiency at different energies of all elements, i.e. calculation of all characteristic factors  $t$  in eq. 9 (see Fig. 2). In the next step, least square fitting is performed to construct a new efficiency curve. Goodness of fit (GOF) in the fitting step is used for stop condition. The loop is forced to stop whenever the GOF starts to increase. On the other hand, it will stop if the number of loop is large enough and the GOF is almost saturated. A typical curve corresponding to the detector used for spectrum acquisition may be chosen as the original reference efficiency curve. It has been found that employment of different original reference efficiency curves gives a very small divergence on final analysis results.

For evaluation of the method performance  $u_{score}$  test was implemented.  $u_{score}$  factor was calculated as follow:

$$u_{score} = \frac{|m_x - m_y|}{\sqrt{\sigma_{m_x}^2 + \sigma_{m_y}^2}} \quad (12)$$

In this study, the limiting value for  $u_{score}$  has been set to 2.58 for level of probability at 99% to determine if a result passes the evaluation. The  $u_{score}$  values less than 1.96 means that the result probably does not differ significantly from the certified value while  $u_{score}$  less than 1.64 that means the result does not differ significantly from the certified value.

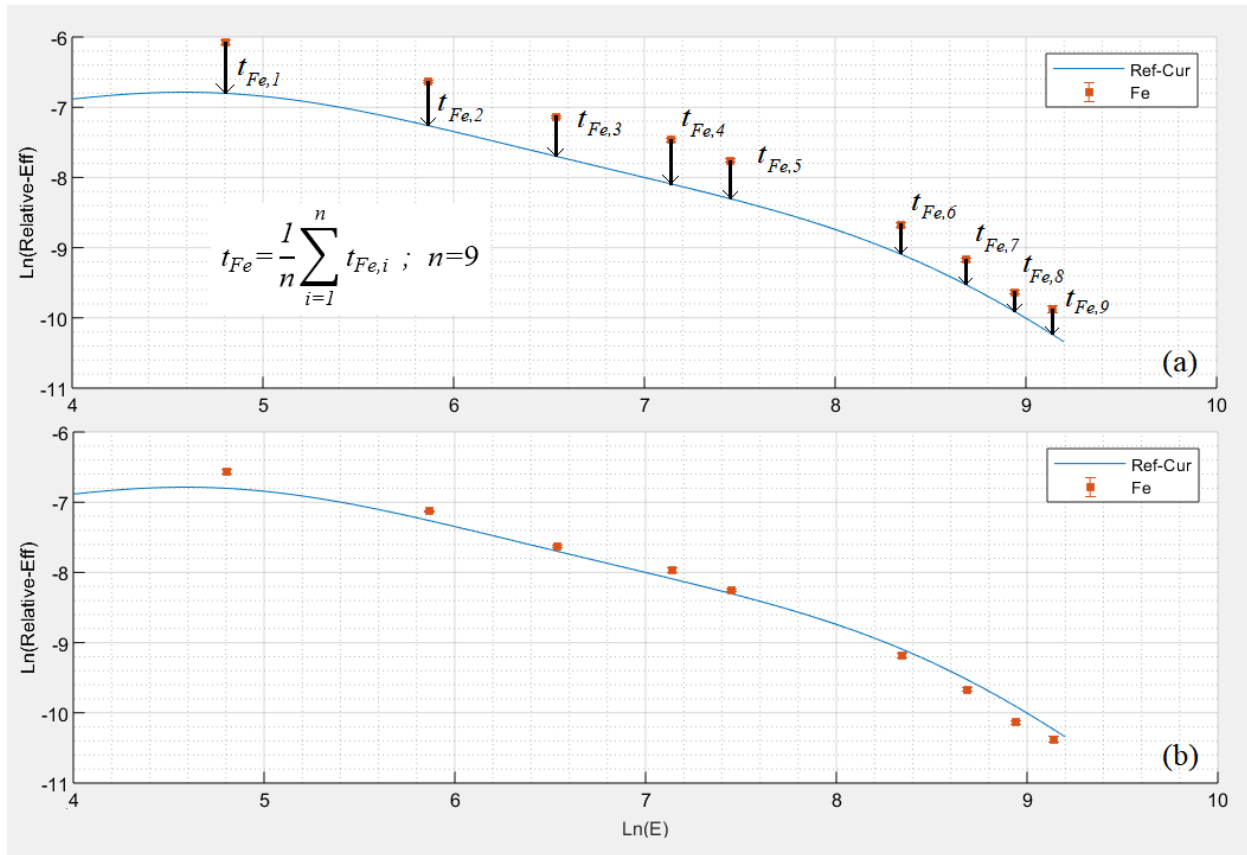


Fig.2 Illustration of relative efficiency correction for iron by  $t_{Fe}$ -factor.  
(a) before correction, (b) after correction

### 3. EXPERIMENTAL

Standard reference materials, BIR-1 and SMELS-III, were used for quality verification of the element concentration for PGNAA and INAA, respectively. BIR-1 sample had been irradiated and analyzed by KFKI lab using  $k_0$  approach. The acquired spectrum was re-used to construct a relative efficiency curve for internal monostandard analysis. In case of INAA, the SMELS III sample was sealed in polyethylene bag and irradiated for 09 hours at vertical channel No.13-2 of Dalat research reactor. The ratio  $f$  between thermal and epithermal neutron flux is 37.3 and epithermal neutron spectrum factor  $\alpha$  is 0.073 [7]. The measurement was carried out for about ~18 hours after ~5 days of decay. To assess feasibility of the method, analysis of large samples has been attempted. Two NIST-679 samples of different sizes and weights were prepared and irradiated. The small one (103.25mg) was analyzed by  $k_0$  approach while the large (1.365g) were studied by IM-method using both optimized and non-optimized efficiency curves. Gamma spectrum was acquired by a HPGe detector. The detector solution is 1.90 keV for 1332.5 keV ( $^{60}\text{Co}$ ).

### 4. RESULTS AND DISCUSSION

In situ relative efficiency for each samples has been constructed using the mentioned fitting procedure. Fig. 3 indicates the improvement of efficiency curves before and after fitting step. As

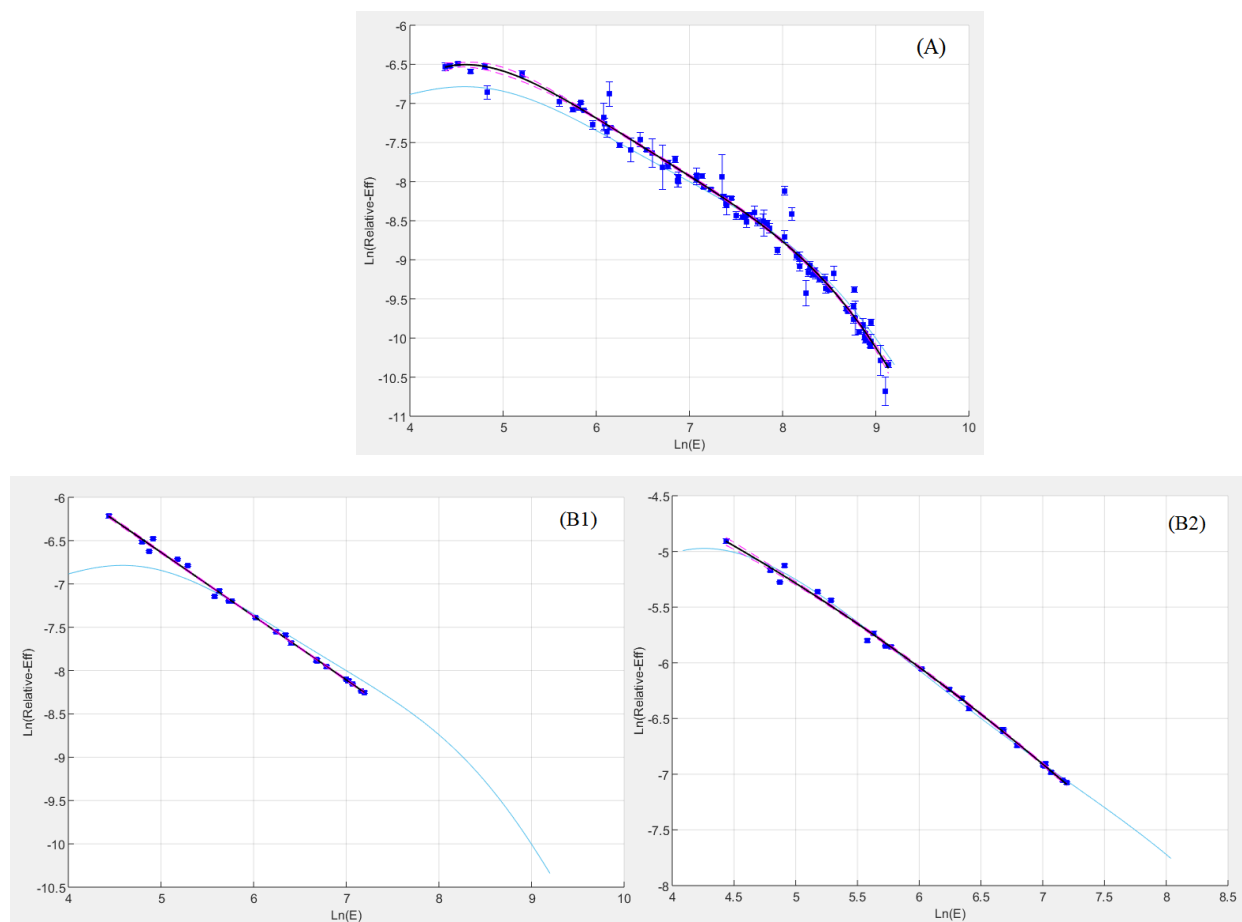


Fig. 3 Construction of in situ relative efficiencies.(A) BIR-1 sample, original curve 1, (B1) SMELIS-III sample, original curve 1, (B2) SMEIS-III sample, original curve 2.

for BIR-1 sample, the efficiency curve demonstrates a small change at high energy region while in the low energy region the divergence becomes large. To assess feasibility of the procedure, two different original efficiencies curve were used in the study of SMELIS-III sample. As clearly seen, the obtained relative efficiency curves are very similar, showing the differ from each other by nearly a constant factor of about 1.3 in logarithm of relative efficiency.

Analysis of element concentration in the samples has been implemented using corresponding efficiency curve. Table 1 shows the mass fraction of 15 elements in BIR-1 sample. A majority of IM's element concentration has been found in good agreement with certified values, excluding results for Cr, Mn and Co. However,  $k_0$  approach shows a very similar pattern in case of Cr and Co when the results are about 2 times greater than the certified values. The situation becomes better when using IM's method in INAA study of SMELIS-III sample (see Table. 2). Despite of using different original efficiency curves, the results are convergent and very close to assigned values.

Study of samples of different sizes and weights has been attempted. Table 3 compares mass fraction of 10 elements present in NIST-679 samples with certified and informative values.

As clearly seen, the difference in sample size and weight gives rise to some variation in obtained relative concentration of Cr, Zn, Rb, Ce to Fe. If the optimized efficiency curve is employed it can help to correct the results for Ce. However, the difference in sample size and weight gives insignificant change in relative efficiency curve. Therefore, it is desired for further verification of the method using large samples of various shape and size.

Table 1. Concentration found in BIR-1 sample

No.	El	Certified values		k <sub>0</sub> -approach (KFKI)		IM-approach			Note
		Conc.	+/-	Conc.	%Unc.	Conc.	+/-	U-score	
1	Na	1.82	0.045	1.82	1.9	1.82	0.06	0.00	Oxide - %
2	Mg	9.7	0.079	10	5.	9.4	0.6	0.50	Oxide - %
3	Al*	<b>15.5</b>	<b>0.15</b>	<b>15.0</b>	<b>2.6</b>	<b>15.5</b>	<b>0.9</b>	<b>0.00</b>	<b>Oxide - %</b>
4	Si	47.96	0.19	48	1.4	45.37	1.47	1.75	Oxide - %
5	Ca	13.3	0.12	12.8	3.0	12.5	0.4	1.92	Oxide - %
6	Sc	44	1	56	2.7	49.7	3.4	1.61	El - ppm
7	Ti	0.96	0.01	1.01	2.6	0.98	0.03	0.63	Oxide - %
8	V	310	11	401	3.5	336	40	0.63	El - ppm
9	Cr	370	8	516	5.	626	47	5.37	El - ppm
10	Mn	0.175	0.003	0.175	2.4	0.203	0.010	2.68	Oxide - %
11	Fe	11.3	0.12	11.2	2.4	11.5	0.4	0.48	Oxide - %
12	Co	52	2	104	4.0	116	8	7.76	El - ppm
13	Ni	170	6	180	7.	200	37	0.80	El - ppm
14	Sm	1.1	-	0.80	3.6	0.78	0.04	-	El - ppm
15	Gd	1.8	0.4	1.6	5.	1.82	0.11	0.05	El - ppm

Table 2. Concentration found in SMELTS III sample (unit: ppm)

No.	El.	Assigned values		k <sub>0</sub> -approach		IM-approach, original curve 2			IM-approach, original curve 1		
		Conc.	+/-	Conc.	+/-	Conc.	+/-	U-score	Conc.	+/-	U-score
1	Sc	1.140	0.031	1.21	0.01	1.136	0.039	0.08	1.15	0.039	0.2
2	Cr	86.7	2.6	90.01	3.79	83.5	2.9	0.82	88.8	3	0.53
3	Fe*	<b>8200</b>	<b>190</b>	<b>8655</b>	<b>357</b>	<b>8200</b>	<b>190</b>	-	<b>8200</b>	<b>190</b>	-
4	Co	24.3	0.33	25.45	1.04	23.9	0.8	0.46	23.9	0.8	0.46
5	Zn	618	11	660	27	608	21	0.42	610	21	0.34
6	Se	131	6	144	6	133.5	4.9	0.32	143	5	1.54
7	Sr	8150	200	8891	374	7767	272	1.13	8132	286	0.05
8	Cs	20.80	0.34	22.53	0.92	19.5	0.7	1.67	20.1	0.8	0.81
9	Tm	23.3	0.7	25	1	24.6	1.2	0.94	26.2	1.3	1.96
10	Yb	20.7	0.5	22.5	0.9	22.5	0.8	1.91	24.1	0.8	3.6
11	Au	0.901	0.016	-	-	0.832	0.028	2.14	0.879	0.03	0.65

Table 3. Concentration found in NIST-569 samples (unit: Fe-wt%, others-ppm)

No.	El.	Datasheet Value's		k <sub>0</sub> -approach, Small sample		IM approach Original efficiency, Large sample		IM-approach Optimized efficiency, Large sample		u-score
		Abs. Conc.	+/-	Abs. Conc.	+/-	Abs. Conc.	+/-	Abs. Conc.	+/-	
1	Sc	22.5	-	22.4	0.5	23.3	0.6	23.4	0.7	-
2	Cr	109.7	4.9	120.2	5.5	107.5	2.7	106.7	3.3	0.51
3	Fe*	<b>9.05</b>	<b>0.21</b>	<b>8.95</b>	<b>2.2</b>	<b>9.05</b>	<b>0.21</b>	<b>9.05</b>	<b>0.21</b>	-
4	Co	26	-	24.9	0.8	26.3	0.6	26.1	0.7	-
5	Zn	150	-	163	15	130.4	3.5	130.4	3.8	-
6	Rb	190	-	201	17	211.7	6.1	211.8	6.6	-
7	Cs	9.6	-	9.4	0.5	9.6	0.3	9.54	0.36	-
8	Ce	105	-	118	4	98.1	2.6	105.4	3.7	-

9	Eu	1.9	-	1.6	0.1	1.62	0.04	1.65	0.06	-
10	Hf	4.6	-	4.3	0.2	4.54	0.13	4.53	0.16	-

\*Reference Element

## 5. CONCLUSION

A procedure for determination of in situ relative detection efficiencies for internal monostandard neutron activation analysis has been proposed. The element concentration found in some standard samples were in good agreement with certified values. The method is promising as it has been successfully applied to a nonstandard geometrical sample. However, further analysis of large samples of various geometry is required to verify and optimize the method.

## ACKNOWLEDGMENT

The authors are thankful to Ministry of Science and Technology of Vietnamese government for financial support through the ministerial-level project coded DTCTB-01/18-VNCHN.

## REFERENCES

- [1] Nguyen Canh Hai, Nguyen Nhi Dien, Vuong Huu Tan, Tran Tuan Anh, Pham Ngoc Son, Ho Huu Thang, "Determination of elemental concentrations in biological and geological samples using PGNAA facility at the Dalat research reactor", *J Radioanal Nucl Chem*, 319 (3), 1165-1171, 2019.
- [2] Rahat Khan, Shayantani Ghosal, Debashish Sengupta, Umma Tamim, Syed Mohammad Hossain, Sudha Agrahari, "Studies on heavy mineral placers from eastern coast of Odisha, India by instrumental neutron activation analysis", *J Radioanal Nucl Chem*, 319 (1), 471-484, 2018.
- [3] Jan Kamenik, Filipa R. F. Simoes, Pedro M. F. J. Costa, Jan Kucera, Vladimir Havranek, "INAA and ion-beam analysis of elemental admixtures in carbon-based nanomaterials for battery electrodes", *J Radioanal Nucl Chem*, 318 (3), 2463-2472, 2018.
- [4] Pasquale Avino, Geraldo Capannesi, Luigina Renzi, Alberto Rosada, "Physiological parameters affecting the hair element content of young Italian population", *J Radioanal Nucl Chem*, 306 (3), 737-743, 2015.
- [5] Sudarshan, K.; Nair, A. G. C.; Goswami, A. J. Radioanal. "A proposed  $k_0$  based methodology for neutron activation analysis of samples of non-standard geometry", *J Radioanal Nucl Chem*, 256 (1), 93-98, 2003.
- [6] A. G. C. Nair, R. Acharya, K. Sudarshan, S. Gangotra, A. V. R. Reddy, S. B. Manohar and A. Goswami. "Development of an internal monostandard instrumental neutron activation analysis method based on in situ detection efficiency for analysis of large and nonstandard geometry samples", *Anal. Chem.* 75, 4868-4874, 2003.
- [7] Manh-Dung Ho, Quang-Thien Tran, Van-Doanh Ho, Dong-Vu Cao, Thi-Sy Nguyen, "Quality evaluation of the  $k_0$ -standardized neutron activation analysis at the Dalat research reactor", *J Radioanal Nucl Chem*, 309 (1), 135-143, 2016.

# XÁC ĐỊNH HIỆU SUẤT GHI TƯƠNG ĐỐI CHO PHƯƠNG PHÁP PHÂN TÍCH IM-NAA ĐỐI VỚI CÁC MẪU CÓ HÌNH HỌC KHÔNG CHUẨN

NGUYỄN DUY QUANG<sup>(1)</sup>, TRỊNH VĂN CƯỜNG<sup>(1)</sup>, TRẦN TUẤN ANH,<sup>(1)</sup>  
HỒ VĂN DOANH<sup>(1)</sup>, NGUYỄN THỊ THỌ<sup>(1)</sup>, HỒ MẠNH DŨNG<sup>(2)</sup>

<sup>(1)</sup>*Viện Nghiên cứu Hạt nhân, 01 Nguyễn Tử Lực, Tp. Đà Lạt, Lâm Đồng*

<sup>(2)</sup>*Trung tâm Hạt Nhân Tp. Hồ Chí Minh, 217 Nguyễn Trãi, Quận 1, Tp. HCM*

*Email: duyquang1691@gmail.com*

**Tóm tắt:** Phương pháp phân tích chuẩn nội đã được nghiên cứu phát triển và áp dụng ở nhiều nơi trên thế giới. Khi áp dụng trong các kỹ thuật INAA và PGNAA, phương pháp chuẩn nội đặc biệt hiệu quả đối với các mẫu lớn, hình học mẫu không chuẩn và mẫu vật liệu hạt nhân. Một trong các ưu điểm nổi bật của phương pháp chuẩn nội là loại bỏ được các hiệu chỉnh cho hình học mẫu cũng như hiệu ứng tự suy giảm của chùm gamma trong mẫu. Tuy nhiên, độ chính xác của kết quả phân tích phụ thuộc vào việc xác định hiệu suất ghi tương đối trong mỗi lần đo. Do đó, việc xây dựng đường cong hiệu suất tương đối là một trong các vấn đề được quan tâm hàng đầu trong phương pháp phân tích chuẩn nội. Báo cáo này chỉ ra một phương pháp đơn giản và tự động để xác định hiệu suất ghi tương đối của đầu dò, sử dụng các tia gamma đặc trưng của một hoặc nhiều sản phẩm kích hoạt trên dải năng lượng quan tâm. Việc xác định hiệu suất ghi tương đối này có thể áp dụng cho kỹ thuật phân tích INAA và PGNAA.

**Từ khoá:** *INAA, PGNAA, phương pháp chuẩn nội, hiệu suất tương đối, mẫu không chuẩn.*