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k_0-Instrumental Neutron Activation Analysis Method Validation for Trace Element Determination using Environmental Reference Materials

BOON SIONG WEE*[1], SHAMSIAH ABDUL RAHMAN[2], MD SUHAIMI ELIAS[2], NAZARATUL ASHIFA ABDULLAH SALIM[2]

[1]Faculty of Resource Science and Technology, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia; [2]Malaysian Nuclear Agency, Bangi, 43000 Kajang, Selangor, Malaysia.
*Corresponding author: swboon@unimas.my
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ABSTRACT

Presently, the k_0-standardization method of instrumental neutron activation analysis (k_0-INAA) technique has become the preferred method for multi-elemental analysis due to its high metrological value. The reactor neutron parameters (α and f) for rotary rack as well as the detector efficiency were determined and used for k_o-INAA. The information is then used to compute the elemental concentration of certified reference materials (CRMs) using k_0-INAA software developed in Vietnam. This results of the CRMs analysis showed the average z-score were below the threshold value of 2 with precision of about 10% for most of the element concentrations analyzed. The result has been very promising and at present stage, the laboratory is focusing on testing this method and capacity building for our staff. In future, the k_0-INAA technique will be used to analyze air particulate, marine environmental samples, geological samples and archeological artifacts as well as to provide analytical services to clients from industries in particular.

Keywords: Certified reference material, gamma-ray spectrometer, instrumental neutron activation analysis, k_0-standardization method, reactor neutron spectrum

INTRODUCTION

Instrumental neutron activation analysis (INAA) technique has been used commonly in Europe. The Malaysian Nuclear Agency (MNA) has adopted this technique as a routine analytical method for determination of trace elements in various samples. The operation of INAA at MNA is by utilising the 1MW TRIGA MK II reactor built in the 1980s, which produces neutron spectrum consists of thermal, epithermal and fast neutrons. The normal operating power for the reactor is 750 MW with thermal neutron flux in the order of 10^{12} n $cm^{-2}s^{-1}$. Thermal neutrons produced by this reactor are mainly used in the activation of interested elements in various types of sample matrices (Wee *et al.*, 2006; Alnour *et al.*, 2015; Wee & Ebihara, 2017; Chai *et al.*, 2018). This is due to the fact that thermal neutron flux is high and the cross sections for (n,γ) reactions are large therefore they offer a good analytical sensitivity available for INAA.

In recent years, many laboratories around the world have implemented the k_o-standardization method of INAA (k_o-INAA) to complement the comparative method, which is regarded as the preferred method for INAA. The k_o-INAA is a new and improved method of INAA which was developed in 1975 and found to be suitable for multi-elemental analysis of various samples matrices without the use of standards (De Corte, 2018). This method requires simultaneous irradiation of a neutron flux monitor and a sample along with the use of k_o-factors in order to compute the element concentrations in the sample. Eventually, this method has been evaluated and well accepted by many laboratories around the world for multielemental analysis of various samples. A recent review providing more insights into the core principles, quality assurance and achievements in the continuous development of this method have been published (Greenberg *et al.*, 2011).

The advantage of this technique is attributed to the k_o-factors, which are accurately measured compound nuclear constants and they are independent of irradiation and measurement

conditions (Greenberg *et al.*, 2011). Recently, k_o-factors of various elements have been compiled and published (Jaćimović *et al.*, 2014). The k_o-factor can be determined by using Au as the comparator as indicated in Eq (1).

$$k_{0,Au}(x) = \frac{A_{sp,x}}{A_{sp,Au}} \frac{f + Q_{0,Au}(\alpha)}{f + Q_{0,x}(\alpha)} \frac{\varepsilon_{p,Au}}{\varepsilon_{p,x}} \quad (1)$$

Where,

$A_{sp,Au}$ = the specific count rate for Au
$A_{sp,x}$ = the specific count rate for element of interest *x*,
f = ratio of sub-cadmium neutron flux ϕ_{th} to epithermal neutron flux ϕ_e
Q_0 = ratio of resonance integral I_0 to thermal neutron capture cross section σ_{th}
$Q_0(\alpha)$ = Q_0 value corrected for epithermal neutron flux shape factor α
ε_p = gamma-ray detector efficiency

By referring to Eq (1), the reactor neutron parameters namely α, f, Q_0 along with gamma-ray detector efficiency ε_p are important input information for the calculation of k_o-factor. The determination of α can be done following the "Cd-ratio", "Cd-covered", or "bare-irradiation" methods. While, f is determined using the "Cd-ratio" method. The details of these methods were described by De Corte (2018). These reactor neutron parameters were dependent on irradiation condition and type of reactor. Practically, the accuracy and precision of the k_0 standardization method is dependent on the calibration of the gamma spectrometer efficiency, reactor's neutron parameter α and f, and the A_{sp} of the gold monitor. With all the parameters determined, the k_o-factor is then used for the calculation of elemental concentration $\rho(x)$ in various samples through Eq (2).

$$\rho(x) = \frac{(N_p / WtSDC)_x}{A_{sp,Au}} \frac{1}{k_{0,Au}(x)} \frac{f + Q_{0,Au}(\alpha)}{f + Q_{0,x}(\alpha)} \frac{\varepsilon_{p,Au}}{\varepsilon_{p,x}} \quad (2)$$

Where,

N_p = neat peak area
W = weight of the sample
t = measuring time
S = saturation factor
D = decay factor
C = correction factor for decay during counting

Upon introducing the concept of k_o-standardization method, the evaluation of the method has to be conducted prior to its implement it as a routine analytical procedure in a laboratory. Thus, this paper aims to use various certified reference materials to validate the k_o-INAA method and to discuss factors affecting the results. Once this method is validated, the use of k_0-INAA will be able to reduce the use of expensive certified reference materials and to improve the quality of analytical data.

MATERIALS AND METHODS

Efficiency Calibration of Gamma-Ray Spectrometry

The gamma-ray detectors calibrated for this experiment was the Ortec GEM20180 detector with GammaVision software. The detector were calibrated using standard gamma-ray point sources ^{241}Am, ^{133}Ba, ^{137}Cs, ^{57}Co, ^{60}Co, and ^{152}Eu with gamma-ray energy ranging from 59.5 keV to 1408.6 keV. The standard point sources and detector distance was set at 12 cm for counting. The net peak areas for the respective gamma-ray energy were used to plot the efficiency curve for the detector as shown in Figure 1. The efficiency curve for the detector was plotted in a logarithmic scale fitted to fourth order polynomial equation. The polynomial coefficients of the detector efficiency were then used for the computation of the real activity to measure radioisotopes in samples and consequently the elemental concentration using the k_o-software.

Determination of Reactor Neutron Spectrum Parameters

The thermal, epithermal, fast neutron, α and f for RR irradiation facility was determined using "Bare", "Cd-Ratio" and "Cd-covered" methods using Al-0.1% Au wire (diameter 0.5 mm, IRMM) and Zr foil (99.8%, thickness 0.254 mm, ADVENT Research Materials Ltd.) as monitors. The relevant nuclear data can be obtained from literature (Jaćimović *et al.*, 2014). The flux monitors (about 2 mg) were irradiated for 1 hour at the rotary rack (RR) of reactor. The flux monitors were measured using the calibrated gamma-ray spectrometers at suitable distance from the detector to avoid coincidence summing effects.

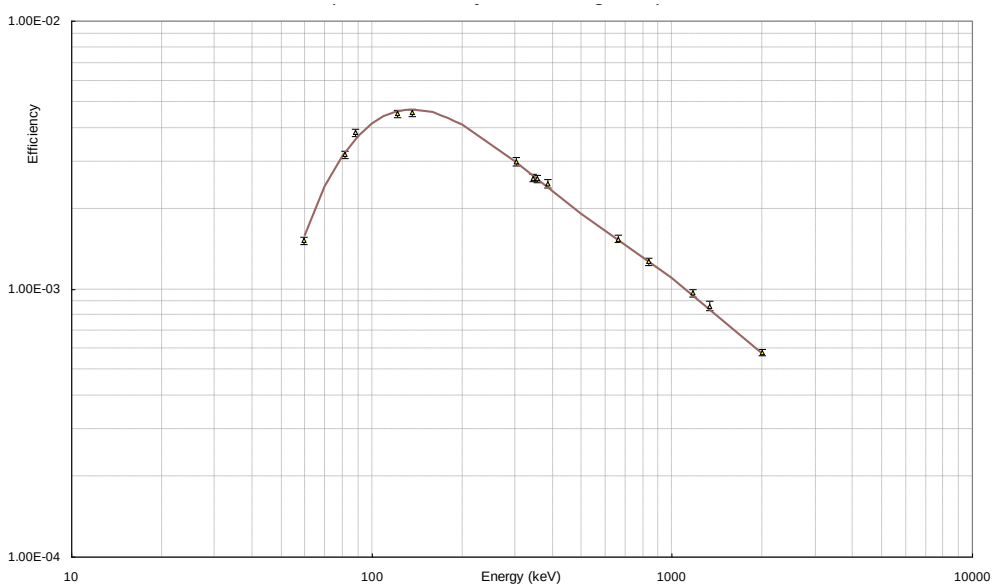

Figure 1. The efficiency curve at 12 cm of the Ortec GEM20180 detector

The counting time was ranged from 5 minutes to 1 hour. The gamma energy lines for the respective monitors were compiled and used to compute the reactor neutron flux and neutron parameters required for k_o-standardization method. The values of α and f were calculated based on the mathematical solutions obtained from literature Alnour *et al.*, 2013; Ho *et al.*, 2016) and showed in Eq (3) and (4), respectively.

$$\alpha + \frac{\sum_{i=1}^{N}\left\{\left(\log \bar{E}_{r,i} - \frac{\sum_{i=1}^{N}\log \bar{E}_{r,i}}{N}\right)\left(\log Y_i - \frac{\sum_{i=1}^{N}\log Y_i}{N}\right)\right\}}{\sum_{i=1}^{N}\left(\log \bar{E}_{r,i} - \frac{\sum_{i=1}^{N}\log \bar{E}_{r,i}}{N}\right)^2} = 0 \quad (3)$$

Where,

$$Y_i = \frac{\left(\log \bar{E}_{r,i}\right)^{-\alpha}}{\left(F_{Cd,i}R_{Cd,i} - 1\right)Q_{0,i(\alpha)}\frac{G_{e,i}}{G_{th,i}}}$$

$$f = (F_{Cd}R_{Cd} - 1)Q_{0,i(\alpha)}\frac{G_e}{G_{th}} \quad (4)$$

Where,

i = denotes isotope 1, 2..., n
$\bar{E}_{r,i}$ = effective resonance energy in eV
F_{Cd} = cadmium transmission factor
R_{Cd} = Cd-ratio [$=A_{sp}/(A_{sp})_{Cd}$]
$Q_{0,i(\alpha)}$ = resonance integral ($1/E^{1+\alpha}$) to 2,200 ms^{-1} cross-section ratio [$=I_{0(\alpha)}/\sigma_0$]
G_e = correction factor for epithermal neutron self-shielding
G_{th} = correction factor for thermal neutron self-shielding

Analysis of Certified Reference Materials

The k_o-standardization method is assessed by analyzing different types of CRMs from International Atomic Energy Agency (IAEA), and National Institute of Standards and Technology (NIST). The CRMs used in this experiment are IAEA Soil 7 (soil), IAEA 312 (soil), IAEA SL-1 (lake sediment), NIST SRM 1575a (pine needles), and NIST SRM 1632c (Bituminous Coal). These CRMs were weighted approximately 0.1 – 0.2 g and irradiated at RR facilities with Au standard solution as flux monitors attached to each sample. The reason for using Au standard solution is to reduce the cost while maintaining the accuracy and precision of the analytical results. It has been shown that both Al-Au wires and Au standard solution yield results in agreement with the certified values.

The irradiation time for all samples was 6 hours followed by cooling time of 4 days to 2 weeks for determination of various radionuclides. All irradiated samples were measured at suitable geometry using calibrated gamma-ray spectrometers. The concentrations of trace elements were computed using k_o-software and the values were compared to certified values. The accuracy of the k_0-INAA method is assessed using z-score by comparing experimental results to those of the CRM values (Alnour *et al.*, 2015). The z-scores were calculated according to Eq (5).

$$z - score = \frac{x - c}{\sqrt{u_x^2 + u_c^2}} \quad (5)$$

Where,

x = experimental results
c = certified or recommended values
u_x = uncertainty of experimental results
u_c = uncertainty of certified or recommended values

RESULTS AND DISCUSSION

Efficiency Calibration of Gamma-Ray Spectrometry

The detector efficiency was fitted to appropriate functions and analysed by the k_0 software. The function to express detector efficiency at 200 keV to 2000 keV is a linear function, while those at lower gamma energy are fitted to polynomial equation (Alnour *et al.*, 2016; Ho *et al.*, 2016). The applicability of the fitting equation of the efficiency curve is examined by counting known point standard source at the 12 cm sample-detector distance.

Determination of Reactor Neutron Spectrum Parameters

The reactor neutron parameter α and f were determined by "bare" and "Cd-covered" method as described by De Corte (2018). The thermal flux, α and f for RR irradiation site are $(2.29 \pm 0.09) \times 10^{12}$ n/cm^2.s, $(1.57 \pm 0.55) \times 10^{-2}$ and 17.2 ± 0.9, respectively. A previous study (Alnour *et al.*, 2013) showed that the thermal flux, α and f for RR irradiation site are $(2.33 \pm 0.08) \times 10^{12}$ n/cm^2.s, $(1.92 \pm 0.80) \times 10^{-2}$ and 18.85 ± 0.24, respectively. It is obvious that the lower f value for the TRIGA MK II reactor signifies a less thermalized neutron available at the irradiation sites. The reactor neutron parameter α and f obtained in the reactor irradiation position are slightly lower than the value measured in Dalat Triga MK II reactor (RR: α = 0.073 and f = 37.3) (Ho *et al.*, 2016). The reactor neutron parameters and gamma spectrometer efficiency are input parameters into the k_0-Dalat software apart from other routine input data such as counting time, irradiation time, sample's weight, counting and irradiation of gold flux monitor are required for the running of the software. Overall evaluation of the applicability of the k_0-Dalat software for the intended purpose was done by analyzing certified reference materials consisting of soil, sediment, coal, and biological matrices. This is to cater the future use of the k_0-INAA in analyzing various environmental samples comprising similar matrices.

Analysis of Certified Reference Materials

The results of the analysis of CRMs were presented in Tables 1 and 2. The total combined numbers of elements determined for these CRMs were 27. In Figures 2–6, the vertical bars represent the 95% confidence intervals as indicated by the reference material manufacturers whereas the average deviation between experimental and literature values are indicated by a point, and the uncertainty (± 2σ) is represented as Y-error bars. The overlapping of the Y-error bar with the vertical bar signifies the z-score of less than |2|. For results to be acceptable, a z-score of within ± 2 is anticipated (Wee *et al.*, 2006; Khairudin *et al.*, 2014).

The analysis of IAEA Soil 7, IAEA 312, IAEA SL-1, and NIST SRM 1632c showed that most of the elements could be determined with good agreement with the certified values. The range of z-scores for the elements analyzed in IAEA Soil 7, IAEA 312, IAEA SL-1 and NIST SRM 1632c were 0.03 – 1.95, 0.32 – 1.02, and 0.06 – 2.04, 0.12 – 1.72, respectively. The element Cr in IAEA SL-1 showed 20% deviation from the certified value. This might be due to the presence of ^{147}Nd which interfere with ^{51}Cr. On the other hand, Zr result was not reported in this study as it has large deviation from the certified values in IAEA Soil 7, IAEA SL-1 and NIST SRM 1632c. This is due to spectral interference from ^{152}Eu, ^{154}Eu, and ^{160}Tb (Neisiani *et al.*, 2018). Similarly, inaccurate results on Zn also indicated interference from ^{46}Sc, and ^{152}Eu, which required proper correction measures (Wassim, 2013).

The analysis of biological sample NIST SRM 1575a, however, showed only four elements (As, K, Mn, Zn) with satisfactory results with their corresponding certified values. Many elements such as Ba, Co, Cs, and Sc were undetected due to their low concentrations. The z-score for K in NIST SRM 1575a was 6.30 but the actual variation was -11% from the certified value. This was due to small uncertainty values for both measured and

Table 1. Results of this study (Exp.) and certified values (Ref.) for NIST SRM 1632c and IAEA Soil 7. All concentration values (dry weight) are reported in mg/kg except stated otherwise

NIST SRM 1632c						IAEA Soil 7					
Element	Exp.	±	Ref.	±	z-score	Element	Exp.	±	Ref.	±	z-score
As	5.75	0.31	6.18	0.27	0.52	As	14.1	0.3	13.4	0.8	0.76
Br	16.6	0.5	18.7	0.4	1.72	Ba	143.3	69	159	32.5	0.21
Ce	10.5	3.0	11.9	0.2	0.24	Br	8.3	0.6	7	3.0	0.43
Co	4.27	0.85	3.48	0.53	0.40	Ca (%)	16.9	1.2	16.3	0.85	0.42
Fe	7741	604	7350	110	0.32	Ce	62	4	61	7	0.19
K	1223	199	1100	33	0.30	Co	10.1	1.6	8.9	0.9	0.64
Sb	0.473	0.043	0.461	0.029	0.12	Cs	5.8	0.8	5.4	0.8	0.36
Sc	3.00	0.08	2.91	0.04	0.59	Eu	1.1	0.2	1	0.2	0.27
Th	1.59	0.34	1.40	0.03	0.29	Fe (%)	2.70	0.65	2.57	0.05	0.20
U	0.642	0.191	0.513	0.012	0.34	K (%)	1.33	0.05	1.21	0.07	1.34
						La	29.5	0.4	28.0	1.0	1.37
						Lu	0.4	0.05	0.3	0.1	1.08
						Mo	3.0	1.5	2.5	1.6	0.20
						Na	2597	16	2400	100	1.95
						Nd	36	13	30	6	0.41
						Rb	58	20	51	5	0.35
						Sb	1.7	0.1	1.7	0.2	0.03
						Sm	4.6	0.0	5.1	0.4	1.34
						Tb	0.6	0.3	0.6	0.2	0.06
						Th	8.4	0.8	8.2	1.1	0.11
						U	2.0	0.4	2.6	0.5	0.90
						Yb	2.4	0.2	2.4	0.4	0.08

Table 2. Results of this study (Exp.) and certified values (Ref.) for IAEA SL-1, NIST SRM 1575a and IAEA 312. All concentration values (dry weight) are reported in mg/kg except stated otherwise

IAEA SL-1						NIST SRM 1575a					
Element	Exp.	±	Ref.	±	z-score	Element	Exp.	±	Ref.	±	z-score
As	30.8	0.5	27.6	2.9	1.07	K	3707	22	4170	70	6.30
Ba	612	80	639	53	0.28	As	0.0450	0.0149	0.039	0.002	0.40
Ce	100	2	117	17	1.00	Mn	446	18	488	12	1.93
Co	20.0	0.9	19.8	1.5	0.09	Zn	37	21	38	2	0.06
Cr	124	4	104	9	2.04						
Cs	7.5	0.6	7.0	0.9	0.44						
Eu	1.5	0.2	1.6	0.5	0.10	IAEA 312					
Fe (%)	6.46	0.08	6.74	0.17	1.49	Element	Exp.	±	Ref.	±	z-score
Hf	4.3	0.4	4.2	0.6	0.11	Th	94.9	4.1	91.4	10.1	0.32
K (%)	1.44	0.06	1.45	0.21	0.06	U	15.2	0.9	16.5	0.9	1.02
La	48.4	0.3	52.6	3.1	1.36						
Lu	0.51	0.02	0.54	0.13	0.20						
Na	1734	12	1700	120	0.28						
Rb	94	9	113	11	1.39						
Sb	1.40	0.07	1.31	0.12	0.60						
Sc	16.8	0.1	17.3	1.1	0.45						
Tb	1.11	0.21	1.40	0.46	0.58						
Th	13	0.5	14	1	0.73						
U	3.96	0.27	4.02	0.33	0.15						
Yb	3.58	0.16	3.42	0.55	0.28						
Zn	264	22	223	10	1.70						

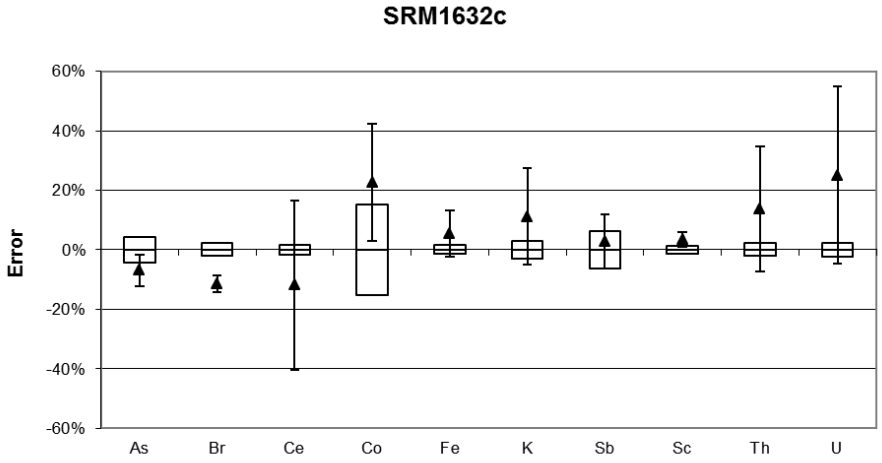

Figure 2. Comparison of experimental results (triangle symbols with error bars) with the certified values of NIST SRM 1632c

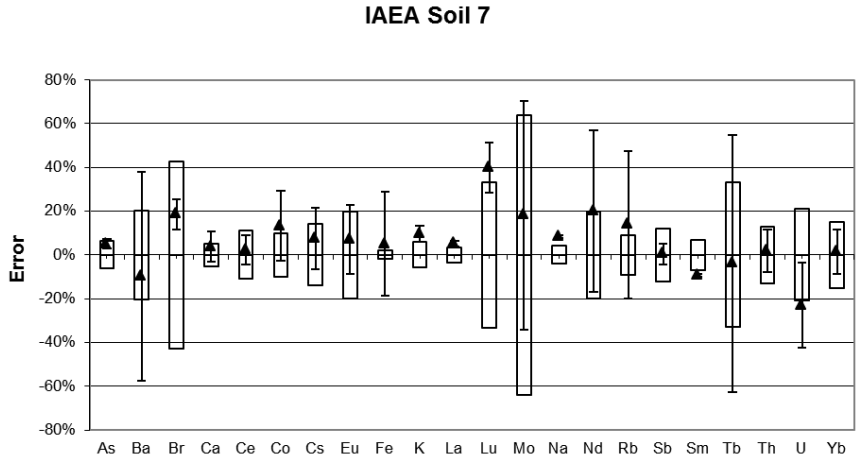

Figure 3. Comparison of experimental results (triangle symbols with error bars) with the certified values of IAEA Soil 7

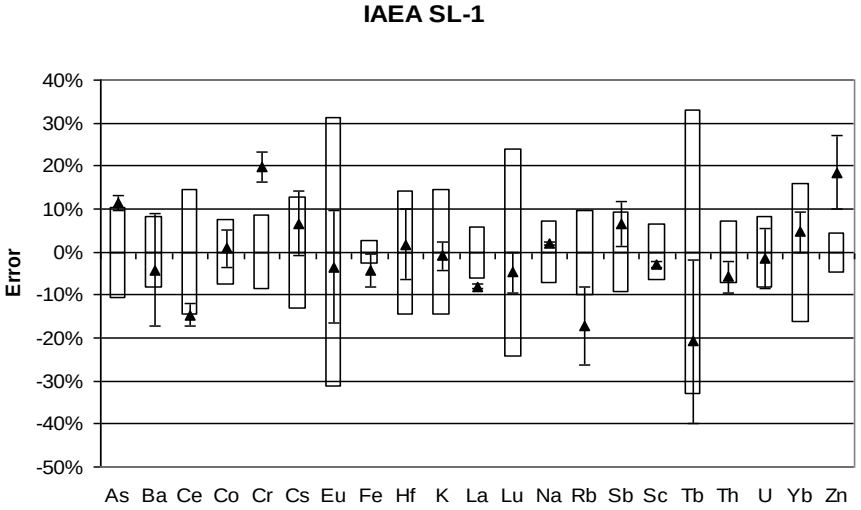

Figure 4. Comparison of experimental results (triangle symbols with error bars) with the certified values of IAEA SL-1

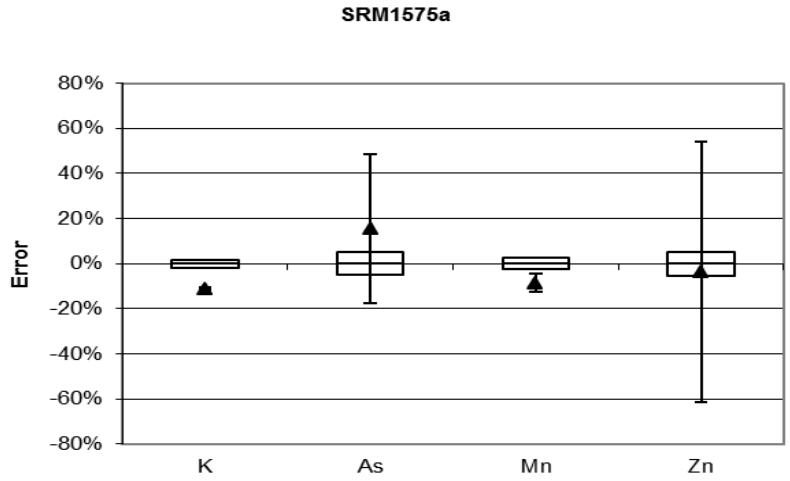

Figure 5. Comparison of experimental results (triangle symbols with error bars) with the certified values of NIST SRM 1575a

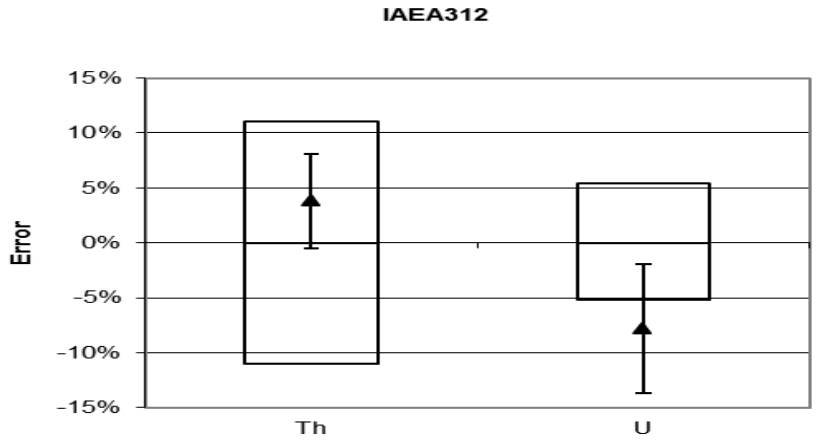

Figure 6. Comparison of experimental results (triangle symbols with error bars) with the certified values of IAEA 312

certified results. However, for the elements As, Mn, and Zn their z-scores were 0.40, 1.93, and 0.06 respectively. The analysis of biological sample is rather challenging owing to the fact that many elements are low in concentrations and high counting dead time may prevent their detection. From overall results, most elements determined in the CRMs showed ±15% deviation from the certified values with a few elements exceeded ± 20%. On the other hand, the relative standard deviations (% RSD) for majority of the elements were in the range of ± 10% showing good reproducibility of the measured values. The z-scores were calculated by comparing the experimental values with certified values were found to be less than |2| for most of the elements determined in the CRMs.

CONCLUSIONS

This study had determined 27 elements (As, Ba, Br, Ca, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Mn, Mo, Na, Nd, Rb, Sb, Sc, Sm, Tb, Th, U, Yb, Zn) in selected CRMs using k_o-INAA methods with acceptable accuracies and precisions. The results have been very encouraging and have prompted our laboratory to engage the k_o-INAA method for analysis of various environmental samples collected namely marine sediments, marine biological samples and soils. In future, it is envisaged that k_o-INAA methods will be utilised for the analysis of air particulates, historical artifacts and food samples.

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