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Validation of HYPERMET PC code for the k_0 - NAA standardization method using a Ghana's Miniature Neutron Source Reactor

A.N. Adazabra,^{1,3*} S. A. Bamford,² B.J.B Nyarko^{2,3}

¹Department of Applied Physics, Faculty of Applied Sciences, University for Development Studies, P. O. Box 24, Navrongo, Ghana

²Department of Nuclear Science and Application, Graduate School of Nuclear and Allied Sciences, University of Ghana, Legon – Accra, Ghana

³National Nuclear Research Institute, Ghana Atomic Energy Commission, P. O. Box LG 80, Legon – Accra, Ghana.

ABSTRACT

The aim of this work was to evaluate the applicability of the generally accepted automated spectral analytical FORTRAN – based Computer software, to the already validated k_0 – NAA standardization method in our laboratory using Ghana's MNSR. Two matrix multi-element reference materials, NIST 1547 Peach Leave as a biological sample and IAEA Soil – 7 as an environmental sample, were analyzed in order to evaluate the performance of the program. The precision and accuracy of the analytical procedure were determined and generally found to be within 14% confirming the accuracy of the results. Satisfactory performance between the measured and certified elemental concentrations was also widely established. HYPERMET PC 5.12 program, was therefore found to be particularly powerful in automated spectral analysis using a miniature neutron source reactor.

Keywords: Automated spectral analysis, k_0 standardization method, HYPERMET PC program, Nuclear Research Reactors and Multi-element analysis

INTRODUCTION

Instrumental Neutron activation analysis (INAA), which is generally recognized as the "referee method" of choice when new procedures are being developed, is a sensitive analytical method capable of quantifying many elements simultaneously [1]. It is a valuable tool in analytical traceability and method validation and has many applications in the life sciences, physical sciences and commercial analysis [2]. The analytical method described by Rossbach et al., [3] as "being the workhorse in nuclear analytical laboratories whenever an intense neutron source for irradiation of samples is available", is also a non-destructive and high - precision multi-element determination method with a high degree of accuracy, selectivity, flexibility and reliability.

Nyarko et al., [4] validated the application of the INAA method at Ghana Research Reactor – 1 (GHARR – 1) based on two widely used standardization methods (relative and the k_0 – NAA). Since then, hundreds if not thousands of samples and or standards have gone through neutron activation analysis in our laboratory mainly due to the numerous advantages of this analytical method [5, 6].

However, even though the neutron flux at the irradiation channels of GHARR – 1 is well established to possess long – term stability and homogeneity with very little variation of about 1% [7], certified concentrations of elements in the same multi-element standards are reported differently by authors using the same facility. For instance, Ca, Mn, Mn, Na and K in standard reference material (NIST 1571) Orchard Leaves was reported differently by Nyarko et al.,

[4] and Alhassan *et al.*, [8]. More to the point, some multi-element samples present very complex multiplets (complex spectra) which may have curved, stepped or backstepped background and peaks with different Full Width at Half Maxima (FWHM) that can be very cumbersome and time consuming for manual analysis. Again, manual net peak areas determination introduces personal errors in the analytical processes.

For these reasons, an increased applicability of routine INAA with quick turnaround time by automation of the counting and data evaluation process to increase sample throughput and standardizing the procedure is a great challenge at our INAA laboratory. A PC based free code HYPERMET, which has gained general acceptance in spectral analysis and is applied with success in numerous Prompt – Gamma Activation Analysis (PGAA), Neutron Activation Analysis (NAA), and other gamma-spectroscopy laboratories is therefore investigated at GHARR – 1 for automation of spectral data acquisition [9]. The governing principle of this code has been to achieve reliable results through automatic fitting by requiring minimal input from the user in order to save manpower and minimise human errors [10]. It is therefore hoped that, this code should strongly promote the harmonization of analytical results from our INAA laboratories by eliminating bias related to the complex spectra data acquisition and personal errors in data analysis.

MATERIALS AND METHODS

Standard Preparation

Two reference materials, Peach leave (NIST, 1547) and IAEA, soil – 7 obtained from National Institute of Standards and Technology (NIST) and International Atomic Energy Agency (IAEA) respectively in the range of 200 – 250mg were carefully wrapped in polyethylene films and located in polyethylene vials. Again, accurately weighed amounts of gold solution ~20 µg were prepared into a pre – clean 2.0 mL polyethylene vials, capped and heat – sealed. All the vials were then located in 7 ml polyethylene tubes stacked with cotton and heat – sealed for irradiation.

Irradiation

Irradiation of the reference materials and the ultimate comparator (gold) were carried out in the inner (No. 2) irradiation site with Ghana's Miniature Neutron Source Reactor (MNSR). Ghana's MNSR also known as Ghana Research Reactor – 1 (GHARR – 1), is a tank – in – pool reactor which was developed and constructed by the China Institute of Atomic Energy, (CIAE). GHARR – 1 uses highly enriched uranium (90.2% ²³⁵U) as fuel, light water as both a moderator and coolant, and beryllium metals as reflectors [11]. Irradiation of the reference materials were accomplished with the reactor operating at half thermal power (15kW) which corresponded to a pre-set neutron flux value of 5.0×10^{11} n.cm⁻²s⁻¹, on the control console at this irradiation site. As a way of reducing uncertainties due to γ – attenuation and neutron self – shielding effects, all materials were kept as small as possible. Irradiation times were varied depending on the radionuclides presents [12].

Counting and analysis of reference materials

The irradiated standards after appropriate decay periods were ascertained for their gamma activities using a PC based gamma-ray spectrometry system. The system consists of a Canberra N-Type HPGe detector Model GR2518 of relative efficiency of 25% to NaI detector and an energy resolution of 1.8 keV at 1332.5 keV γ -ray of ⁶⁰Co, an 8k MAESTRO Multichannel Analyser (MCA) and an Emulation software, MAESTRO (for spectral accusation). The other associated electronics consisted of an H.V power supply model 3105, a spectroscopy amplifier model 2020, all manufactured by Canberra Industries Inc. and a NIM power supply unit model PS01-B manufactured by SILENA.

The detection efficiency for the γ – ray spectrometer was calibrated with an IAEA mixed standard radionuclide solution containing ⁶⁰Co, ²⁴¹Am, ¹⁰⁹Cd, ⁵⁴Mn, ⁶⁵Zn, ⁸⁵Sr, ²⁰³Hg and ⁵⁷Co. The measured detection efficiencies were fitted by a polynomial function [13, 14]. As a way of reducing uncertainties caused by pile – up effects and random coincidence, the sample-to-detector distance was kept and maintained at 7.2 cm from the top of the detector surface during measurement. Care was taken to account for the counting losses by keeping the dead time around 10% at the start of counting of the samples. The spectral intensities of the comparator and the reference materials were then accumulated for a pre-set time on the MCA card and save in a file with chn extension. These files were then loaded into the HYPERMET PC version 5.12 program for analysis. The approximate widths and energy values of two dominant peaks Ca and K were used for analysis of Peach leaves while that of Al and Ca was used for IAEA, Soil – 7.

RESULTS AND DISCUSSION

A detailed description of the implementation of the k_0 – NAA standardization method at GHARR – 1 had previously been discussed by Nyarko *et al.*, [4] and hence, it was not presented here. Nuclear constants such as k_0 – factors and resonance integrals were taken from literature [15]. Irradiation site constants (i.e. neutron flux ratio, f and neutron deviation factor, α) had been previously determined using the cadmium ratio method [16]. The k_0 – NAA

standardization method based on Hodgahl convention was used for calculation of elemental concentrations. Correction factors such as neutron self shielding and gamma attenuation were found to be negligible and hence were not considered.

The results of elemental concentrations of the certified materials (IAEA, Soil – 7 and NIST 1547, Peach Leave) using HYPERMET PC version 5. 12 automated spectral analytical software are presented in Table 1 and Table 2. The uncertainties associated with the measurements, U_{lab} were determined as expanded uncertainties ($k=2$). Those associated with the certified values, U_{cert} were taken from their certificates. Even though the precision calculated as the percentage relative deviation (%RSD) and accuracy determined by the percentage relative error calculation had been reported previously by authors using this facility [17,18,19], for validation of the automated spectral analysis, these parameters were determined again.

The precision of the results was satisfactory with relative standard deviations varying from 0.10% to 11.11% for IAEA Soil - 7. That of NIST 1547 Peach leaves ranged from 0.26% to 12.50%. Thus, most of the measured concentrations were within a precision of 13% which reflects the reproducibility of the measured values. A perusal of Table 1 and Table 2 show that, most of the relative errors were lower than 14% confirming the accuracy of the results obtained by this analytical method. The detection limits were calculated based on an equation proposed by Curie [20]. These limits were well below the detected concentration levels as manifested in the Tables.

Table 1. Results of the analysis of IAEA Soil – 7 using k_0 – NAA standardization method (in $\mu\text{g/g}$)

Element	$(X_{lab} + U_{lab})$	RSD (%)	RE (%)	$(X_{cert} + U_{cert})$	Detection limits	E_n number
As	13.40 \pm 1.30	9.70	2.29	13.1 \pm 1.4	0.051	0.16
Co	9.10 \pm 0.71	7.80	2.25	8.9 \pm 0.89	0.003	0.18
Cr	58.50 \pm 4.30	7.35	-2.50	60 \pm 12.6	0.140	0.11
Cs	5.60 \pm 0.30	5.36	3.70	5.4 \pm 0.76	0.008	0.24
Cu	10.40 \pm 0.90	8.65	-5.45	11 \pm 1.98	0.060	0.28
La	30.00 \pm 2.20	7.33	7.14	28 \pm 1.2	0.171	0.80
Mn	651.00 \pm 30.00	4.61	3.17	631 \pm 28	1.801	0.49
Rb	54.00 \pm 6.00	11.11	5.88	51 \pm 4.6	0.783	0.40
Sb	1.71 \pm 0.10	0.10	0.59	1.7 \pm 0.20	0.001	0.00
Sc	8.60 \pm 0.75	8.72	3.61	8.3 \pm 1.1	0.037	0.23
Sm	5.00 \pm 0.05	1.00	-1.96	5.1 \pm 0.36	0.024	0.28
Th	9.10 \pm 0.40	4.40	10.98	8.2 \pm 1.1	0.091	0.77
U	2.80 \pm 0.20	7.14	7.69	2.6 \pm 0.55	0.002	0.34
V	76.10 \pm 5.00	6.57	15.30	66 \pm 7.26	1.035	1.15
Zn	110.00 \pm 12.00	10.91	5.77	104 \pm 6.2	1.328	0.44

Relative standard deviation (RSD), Relative Error (RE), Measured values (X_{lab}), Certified values (X_{cert}), Measured uncertainty (U_{lab}) and Certified uncertainty (U_{cert}).

Table 2. Results of the analysis of NIST 1547, Peach leave using k_0 – NAA standardization method (in $\mu\text{g/g}$ unless otherwise stated)

Element	$(X_{lab} + U_{lab})$	RSD (%)	RE (%)	$(X_{cert} + U_{cert})$	Detection limits	E_n number
Ba	131.00 \pm 6.70	5.11	5.65	124 \pm 3.7	0.990	0.91
Cl	375.00 \pm 0.15	4.00	4.17	360 \pm 18	1.941	0.64
Cu	3.82 \pm 0.01	0.26	5.14	3.7 \pm 0.2	0.031	0.95
Dy	0.80 \pm 0.10	12.50	15.94	0.69 \pm 0.02	0.002	1.08
K(%)	2.40 \pm 0.05	2.17	-1.23	2.43 \pm 0.024	0.001	0.52
Mg	4405.00 \pm 100	2.27	1.97	4320 \pm 86	3.250	0.64
Mn	101.00 \pm 8.40	8.32	3.06	98 \pm 2.9	0.345	0.34
Na	23.00 \pm 1.30	5.65	-4.17	24 \pm 1.9	0.23	0.43
Sr	57.00 \pm 2.32	4.07	7.55	53 \pm 4.2	0.300	0.83
V	0.41 \pm 0.01	2.50	8.11	0.37 \pm 0.03	0.001	0.95
Zn	18.00 \pm 0.67	3.27	0.56	17.9 \pm 0.36	0.101	0.13

Relative standard deviation (RSD), Relative Error (RE), Measured values (X_{lab}), Certified values (X_{cert}), Measured uncertainty (U_{lab}) and Certified uncertainty (U_{cert}).

An E_n number performance evaluation test was conducted in order to establish an agreement between the elemental concentrations determined in the reference (certified) materials and those concentrations provided in their certificates. An E_n [21] is mathematically defined as;

$$E_n = \frac{|X_{lab} - X_{cert}|}{\sqrt{U_{lab}^2 + U_{cert}^2}}$$

Using E_n number, performance levels are normally determined as follows: $E_n \leq 1$ satisfactory performance, $E_n \geq 1$ unsatisfactory performance [22]. For the purposes of using E_n number test, recommended values – values that do not have their associated uncertainties, were not considered in this analysis.

Table 1 shows the results of the E_n number test for an environmental sample, IAEA Soil – 7. Elements such as As, Co, Cr, Cu, Rb and U recorded E_n values far below 0.50 which indicated a better performance agreement between X_{cert} and X_{lab} values. Sb showed an exact agreement between these values within two decimal points. Nuclides such as Th, Mn and La therefore had satisfactory performance. However, the performance of V was unsatisfactory. Reasons for this poor performance are not yet known and hence require further investigation. E_n number performance test for a biological sample NIST 1547, Peach leave are presented in Table 2. In contrast Table 1, all of the elements excluding Dy evaluated, only showed satisfactory performance. This can partly be explained Seiler *et al.*, [23] accession that “the composition of biological systems is so complex that the trace elements are totally masked by major constituents and hence difficult to determine”. Kubsova and Kucera [22], obtained similar results for E_n number test of real samples with most deviations being recommended elements.

In general, most E_n number performance test values were close to unity for both IAEA Soil – 7 and NIST 1547, Peach leave elements. These somehow high values could to some extent be attributed the neglect of correction factors such as neutron shielding, neutron attenuation, pile – up effects and random coincidence summing. It is therefore evident that HYPERMET PC version 5.12 program is particularly a powerful multi-element automated spectral analytical software for analysing spectra (obtained from Multichannel Analysers) from miniature neutron source reactors.

CONCLUSION

It can therefore be concluded that a general good agreement has been found between certified elemental concentration values and measured concentration values determined in this work. A biological reference material (NIST 1547, Peach leaves) and an environmental reference material (IAEA Soil – 7) used in this analysis represented the major types of samples analysed in our laboratory. To this end, three main parameters (Precision, accuracy and detection limits) were considered for the validation of the program. The precision, calculated as the percentage relative deviation (%RSD), of most of the measured data were found to be within 13% which reflected the capability of HYPERMET PC program in maintaining the reproducibility of the analytical method. Accuracy, calculated as percentage relative error (%RE), was found to be mostly within 14%. Also detection limits were also determined to be very low for most of the detected elements. It is therefore evident that HYPERMET PC version 5.12 program is particularly a powerful multi-element automated spectral analytical software for analysing spectra from MNSRs.

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