PHYSICS

STANDARDISATION OF GHARR-1 GAMMA SPECTROSCOPY SYSTEM FOR INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

The gamma-ray spectroscopy system at the Ghana Atomic Energy Commission Research Reactor (GHARR-1) Centre has been standardised with 5 standard reference materials, 6 pure elements and 5 chemically pure compounds for Instrumental Neutron Activation Analysis (INAA) using the Absolute Method. The results from the validation of the standardisation procedure using an NBS SRM 1663a Coal Fly Ash compared very well with the certified values.

KEYWORDS

Standardisation, Gamma Spectroscopy System, Instrumental Neutron Activation Analysis, Absolute Method, Standard Reference Materials.

INTRODUCTION

In neutron activation analysis, the two most common methods of quantitation are the Absolute Method and the Relative or Comparator Method. The Absolute Method uses the basic neutron activation equation and therefore relies on the nuclear constants obtained from the literature in addition to an accurate knowledge of the efficiency of the gamma detector and the neutron flux at the irradiation position. The accuracy of measurement in this mode depends therefore on the accuracy of the nuclear constants, the accurate knowledge of the efficiency of the detector, the neutron flux and the counting statistics. For most elements, the errors in nuclear constants are less than 5% [1]. Thus the overall error using the Absolute Method is about 10 - 15% [2]. With the Comparator Method, a standard containing a known amount of the element to be determined and of a matching matrix is prepared and irradiated along with the sample. The sample and its standard are then counted under identical conditions. Thus by comparing the activities of the sample and the standard and also knowing their masses, the concentration of a particular element of interest is evaluated [3]. Though the Comparator Method appears to be simple, the difficulty of obtaining standards for each element is the main constraint. The problem becomes more compounded if a multi-element analysis is involved, because preparing a multi-element standard of the same matrix and concentration as the sample under investigation is by no means a simple task. To cut down the cost of purchasing standards and also to make use of few standards together with some chemically pure compounds available, the Absolute Method of quantitation was adopted for the standardisation. With the Absolute Method of quantitation NBS standard reference materials (NBS SRM) were used as primary standards whilst the other SRM were used as secondary standards since they are not recommended to be used as primary standards because the uncertainties may be very large even for some of the certified elements [3]. Correction factors are then obtained for the various elements by comparing the measured concentrations with the SRM certified values or that of the pure element as the case may be. The correction factor for any element is the ratio between the expected and the measured values. Where an element is not available in any of the SRM, a pure sample of that element or a chemically pure compound of that element is used to obtain the correction factor. These correction factors take into account the errors in the nuclear constants, the efficiency of the detection system for the particular sample - to - detector geometry and the neutron flux at the irradiation site. In this way, there is no need for the irradiation of a sample and its standard any time measurements are to be made. The objective of this work was therefore to obtain correction factors for various elements covering a wide range of the Periodic Table which are of interest in INAA. The other parameters which need to be measured or known before adopting the Absolute Method of quantitation are:

(i) the efficiency of the detector system as a function of gamma energy
(ii) the neutron flux at the irradiation site.

In this work 5 different standard reference materials containing as many as 36 different elements put together, 6 pure elements and 5 chemically pure compounds of some key elements were used for the measurements. The work was validated with an NBS SRM 1633a Coal Fly Ash [4].

THEORY

The general neutron activation equation for calculating the amount, mj, of an element j in a sample, which has been irradiated in a neutron flux, Φ, for a time T is given by [2],

$$m_j = C_j \lambda_j M_j / [\, \theta_j (\phi_t \sigma_{tj} + \phi_e \sigma_{ej}) f_j \, \varepsilon(E_j) N_A K_j \,] \qquad (1)$$

Where $K_j = (1\text{-}\exp(-\lambda_j T))(1\text{-}\exp(-\lambda_j t_c))\exp(-\lambda_j t_d)$ (2)

and $\phi_t \sigma_{tj} + \phi_e \sigma_{ej} = \phi \sigma_j$ (3)

Cj is the photopeak counts, λj is the decay constant of the (n, λ) product radionuclide, Mj is the atomic weight of

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the target element, Φj is the isotopic abundance of the isotope of interest, σtj, σej, σj are the thermal, epithermal and the effective cross-sections for the (n, λ) reaction, f_j is the gamma yield (number of gamma-rays/100 disintergrations), $\varepsilon\ (E_j)$ is the efficiency of the detector for gamma-ray of energy, E. N_A is the Avogadro's Number (6.023×10^{23} atoms/mole), and t_c and t_d are the counting and the delay (cooling) times respectively. The nuclear constants in equation (1) are λ, M, Φ, σ, f and N_A. Equation (1) may be expressed in a simple form as,

$$m_j = D_j C_j / (\phi \varepsilon(E_j) K_j) \qquad (4)$$

Where $D_j = \lambda_j M_j / (\theta_j \sigma_j f_j N_A) \qquad (5)$.

The constant D may be calculated for any element by obtaining the nuclear constants from any current nuclear data books [1, 5]. Knowing D, Φ, $\varepsilon(E)$ and K, and also by measuring C, the amount, m, of any element in the sample may be obtained using equation (4). Thus if the quoted concentration of an element in the SRM is m_{std} and the measured value is m_m, then the correction factor, F_o, is obtained from the relation,

$$F_o = m_{std} / m_m \qquad (6)$$

To obtain a more accurate value for F_o, more than one SRM containing that element, or chemically pure compounds, or pure samples of that element are irradiated and the average value F_{coor} obtained. Hence the corrected value, m_{corr}, of any measurement may be obtained from the experimentally measured value m_{exp}, as,

$$m_{corr} = F_{corr}\, m_{exp} \qquad (7).$$

Thus having determined correction factors for the elements of interest in INAA covering a wide range of the Periodic Table, equation [7] may be used to obtain accurate values for the concentrations of any element in a sample without measuring any standards.

EXPERIMENTAL

Sample Preparation

The reference materials used for the measurement were categorised into four groups, (1) Biological (Orchard leaves), (2) Environmental (Soil, Lake sediment), (3) Geological (Manganese ore), (4) Chemically pure elements or compounds (5% Cu - Al alloy, etc.). Table 1 gives the detailed description of the samples used for the measurement, their purity and the masses of the analyte samples used in each case. The analyte samples for each group were prepared by weighing the amount indicated in Table 1 from the homogeneously ground sample. They were then wrapped in thin polythene foils, put into polythene capsules and sealed with a hot soldering iron. For the multi-element samples six replicate analyte samples were prepared, two each for short irradiation, medium irradiation and long irradiation respectively. For the chemically pure elements or compounds, duplicate analyte samples were prepared for each element.

Sample Irradiation

Irradiation of the samples was done using the GHARR-1 reactor operating between 10-15 KW and at neutron flux in the range of $1\text{-}5\times10^{11} ns^{-1}cm^{-2}$. Each of the capsules was sent into the reactor for irradiation by means of a pneumatic transfer system operating at a pressure of 65 psi. The irradiation was also categorised according to the half-lives of the elements of interest. At the end of the irradiation, the capsules were returned from the reactor, allowed to cool down until the activities have reached the acceptable level for handling. Each of the samples was then placed on the detector for counting. Table 2 shows the irradiation schemes and corresponding (n, γ) product radionuclides.

Qualitative and Quantitative Analysis.

The PC-based gamma - ray spectroscopy system consists of an N-type High Purity Germanium (HPGe) detector model GR2518, an HV Power Supply Model 3103, a Spectroscopy Amplifier Model 2020, all manufactured by Canberra Industries Inc., a Silena EMCAPLUS Multi-Channel Analyzer (MCA) Emulation Software Card and a 486 micro-computer for data evaluation and analysis. The detector operates on a bias voltage of 3000 (-ve) V, and has resolutions of 0.85 keV and 1.8 keV for Co-60 gamma-ray energies of 122 keV and 1332 keV respectively [7]. The relative efficiency of the detector is 25%. By means of the MCA, the spectra intensities for the samples were accumulated for some pre-set times. The qualitative analysis which involves the determination of the various elements in the samples and the quantitative determination of their concentrations were achieved using the Gamma Spectrum Analysis Software SPAN 5.0 [8].

RESULTS AND DISCUSSIONS

The results obtained from the measurement of the correction factors for 41 are shown in Table 3. The results show that the correction factors for 17 elements fall within 0.95 - 1.05 indicating that the uncertainties in the nuclear constants and the measurable parameters such as efficiency of the detection system, the neutron flux and the counting statistics add up to only 5%. The uncertainty for 17 others were between 5 -20% while 5 elements, Cr, Eu, Mo, Nd, and Ta showed uncertainties greater than 20%. Table 4 also shows the results obtained from the measurement of the concentrations of 25 elements in the NBS SRM 1633a Coal Fly Ash for the validation of the standardisation procedure. The measured values gave good agreement with the SRM certified values, since of the 25 elements whose concentrations were measured, 8 of them, Al, Ba, Ce, Fe, Hf, Na, Sc and Zn showed deviations less than 6% from the certified values. These elements, Co, Cu., Mg, Mn, Mo, and V also showed deviations between 6 - 10%, Ca, K, Rb and Sr also showed deviations between 10 - 15%, whilst As, Cr, Eu, Ga, Sb, Ti and U showed deviations greater than 15%. It has been recommended [6] that the sensitivities of the following elements, As, Ba, Mo, U and Zn may be increased if epithermal neutrons are used and that Ga is best determined using epithermal neutrons.

Table 1: The materials used, their purity and the masses of the analyte samples.

MATERIAL	DESCRIPTION	PURITY (%)	ANALYTE SAMPLE MASS (mg)
ORCHARD LEAVES	NBS SRM No. 1571	-	150-250
SOIL	IAEA - SOIL - 7	-	100-150
LAKE SEDIMENT	IAEA - SL - 1	-	100
MANGANESE ORE	BCS CRM No. 176/2	-	50
5% CU-AI ALLOY	BCS CRM No. 216/2	- *	50
+COAL FLY ASH	NBS SRM - 1633a	-	250
GOLD (Au)	FOIL	100	4 - 8
SILVER (Ag)	FOIL	100	5
CADMIUM (Cd)	FOIL	100	50
$Na_2 SO_4$	POWDER	$\geq$99	50
$HgCl_2$	POWDER	$\geq$99	50
$Ni(NO_3)_2.6H_2O$	POWDER	$\geq$99	50
SiO_2	FUMED	-	56
KBr	POWDER	98.5	50
TUNGSTEN (W)	FOIL	100	13 - 16
COBALT (Co)	POWDER	$\geq$99.8	50
ALUMINIUM (Al)	PELLET	100	400 -500

*USED FOR THE VALIDATION

Table 2: The irradiation scheme adopted and the corresponding (n, y) products.

TYPE & HALF-LIFE OF (n, γ) PRODUCT RADIONUCLIDE	NEUTRON FLUX x 10^{11} $ns^{-1}cm^{-2}$	IRRADIATION TIME T (M)	DECAY TIME t_d (M)	COUNTING TIME t_c (S)	(n, γ) PRODUCT RADIONUCLIDE
SHORT - LIVED $20S \le T^{1}/_{2} < 20M$	1 - 5	0.5 - 2	2 - 10	600	Al-28, Br-80, Ca-49 Mg-27, V-52, Cu-66 Ti-51, Ag-108, Sb-122
MEDIUM- LIVED $20M \le T^{1}/_{2} < 5H$	5	10	20 - 60	600	Ba-139, CI-38, Dy-165 I-128, Mn-56, In-116M, Sr-87M, Si-37, Zn-7IM Ni-65, Ru-105, Eu-152M
MEDIUM-LIVED $5H \le T^{1}/_{2} < 5D$	5	60	1 - 3D	1000 - 3000	As-76, Br-82, Au-198 Cd-115, Cu-64, Ca-47 Ce-143, La-140, Na-24 W-187, U-239, Sb-122, Sm-153, Zn-69M, Zr-97, Hg-199M, Pd-109, K-42 Ho-166, Yb-175, Mo-99
- LONG-LIVED $T^{1}/_{2} > 5D$	5	6 H	3 - 14	3000 - 5000	Ag-110M, Cr-51, Fe-59, Ce-141, Hg-203, Hf181, Nd-149, Yb-177, Rb-86

Tables 3: The results of measurement of the correction factors for 41 elements.

(n, γ) PRODUCT RADIONUCLIDE	γ - RAY ENERGY (KeV)	ELEMENT	MEASURED CORRECTION FACTOR (F corr)
Al - 28	1779	Al	0.951
Ag - 108/Ag - 110	633/885	Ag	1.030/0.912
As - 76	559	As	0.884
Br - 80/Br - 82	616/777	Br	1.062/0.835
Ce - 143	293	Ce	0.839
Co - 60M	59	Co	0.824
Cr - 51	320	Cr	0.689
Ca - 49/Ca - 47	3084/1297	Ca	1.024
Ba - 139	166	Ba	0.834
Fe - 59	1099	Fe	0.863
Dy - 69	95	Dy	0.947
Eu - 152M	842	Eu	0.759
Hf - 181	482	Hf	0.740
K - 42	1525	K	1.046
Mg - 27	844	Mg	1.123
Mn - 36	847	Mn	1.010
Na - 24	1369	Na	0.904
Mo - 99	141	Mo	0.453
Cd - 115	336	Cd	1.009
Au - 198	412	Au	0.941
Cu - 66/Cu - 64	1039/511	Cu	0.551/0.974
Hg - 197M	134	Hg	0.971
Si - 31	1266	Si	1.041
Rb - 86/Rb - 88	1077/1836	Rb	0.904

Table 3(contd.)

Nd - 147	91	Nd	0.777
Sb - 122	564	Sb	0.881
Sc - 46	889	Sc	0.951
Sm - 153	70	Sm	0.945
Sr - 87M	388	Sr	0.921
U - 239	75	U	0.825
V - 52	1434	V	0.024
W - 187	480	W	0.1003
Yb - 175	396	Yb	0.921
Ti - 51	320	Ti	1.143
Zn - 69M	439	Zn	0.835
Zr - 95	757	Zr	0.824
Ta - 182	68	Ta	0.008
Tb - 160	879	Tb	1.113
Cl - 38	1643	Cl	1.008
Ni - 65	1482	Ni	0.9488
S - 37	3104	S	0.7865

Table 4: Comparison of the INAA values with NBS SRM 1633a Coal Fly Ash.

ELEMENT	NBS SRM 1633a COAL FLY ASH (ppm)	THIS WORK (ppm)	ELEMENT	NBS SRM 2633a COAL FLY ASH (ppm)	THIS WORK (ppm)
Al	14.0	14.3 ± 0.2	Mg	0.455	0.411 ± 0.007
As	145 ± 14	175 ± 3	Mn	190	204 ± 8
Ba (%)	0.150	0.148 ± 0.005	Mo	29	27.1 ± 2.8
Ca (%)	1.11 ± 0.01	1.40 ± 0.12	Na (%)	0.17 ± 0.01	0.18 ± 0.02
Ce	180	171 ± 18	Rb	131 ± 2	151 ± 26
Co	46 ± 1.4	43.1 ± 2.2	Sb	7.0	9.2 ± 0.1

Table 4 (Contd)

Cr	196	151 ± 8	Sc	40	39.4 ± 3.5
Cu	118	125 ± 35	Sr	880 ± 30	919 ± 89
Eu	4.0 ± 0.04	3.1 ± 0.1	Ti (%)	0.80	1.16 ± 0.05
Fe (%)	9.4	9.4 ± 0.2	U	10.2 ± 1.0	15.1 ± 0.8
Ga	58	74 ± 4	V	300	320 ± 11
Hf	7.6 ± 0.5	7.2 ± 0.7	Zn	220 ± 4	233 ± 28
K (%)	1.88 ± 0.04	2.19 ± 0.05			

CONCLUSIONS

Correction factors for 41 elements have been obtained for the standardisation of the gamma spectroscopy system at GHARR-1. The results of the measurements of the concentrations for 25 elements in an NBS SRM 1633a Coal Fly Ash for the validation of the standardisation procedure showed good agreement between the certified values and the experimentally measured values. Of the 25 elements whose concentrations were measured, 14 showed deviations of less than 10% representing about 56%, whilst a total of 18 showed deviations of less than 15%, representing about 72%. Since the Absolute Method avoids the measuring of standards together with the samples anytime measurements are to be made, it is a useful method when Instrumental Neutron Activation Analysis is adopted for commercialization. It is also advantageous to adopt this method when only a few SRM are available.

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