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PROMPT GAMMA-RAY NEUTRON ACTIVATION ANALYSIS BY THE ABSOLUTE METHOD

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In this study an investigation into the applicability of the absolute method in Prompt Gamma-ray Neutron Activation Analysis (PGNAA) was undertaken. Although the system parameters are adequately characterized, the scatter in nuclear data for a number of elements is significant. For our particular experimental set-up the K-factors were calculated for a number of elements using both Au and Fe as monostandards. A comparison was made between the calculated and experimentally determined K-factors and from this comparison the feasibility of the absolute method in neutron prompt gamma-rays can be realized for a number of elements.

Introduction

Prompt Gamma-ray Neutron Activation Analysis (PGNAA) is routinely used as a complementary technique to conventional neutron activation analysis for the elemental analysis of B, Cd and some rare earth elements at trace levels as well as for H, Cl, S, etc., at percent levels. PGNAA often requires long irradiations and to handle so many standards as in the comparator method is not only cumbersome and time consuming, but is a source of additional errors during preparation, mixing, dilution and counting of the standards. The usual practice is to use standard reference materials (SRM) or certified reference materials (CRM) as multi-elemental standards. These reference materials are not always available and difficulties may arise when one is to analyze a new type of material which has a different elemental composition from the reference materials available or when the element sought has no certified value. An inherent source of error is the possible change of the certified concentration data with time as more data are accumulated.

An investigation into the possible applicability of the absolute method in PGNAA was undertaken. In order to establish the absolute or rather the non-comparator method good and accurate knowledge of all the nuclear and system parameters involved and reliable and reproducible experimental conditions are needed. In practice

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this means evaluation of all the parameters in the activation equation with good accuracy and precision. As a completion to our previous study on system characterization we attempt here to evaluate the nuclear data used and their suitability for application in the absolute method of analysis. In our work on system characterization, a thorough study was carried out.[1,2] In the study the effect of orientation and displacement of the target (sample) on the geometric solid angle (reproducibility) of the experimental set-up were reported and a measure of tolerance on reproducibility in activity quantification was discussed. The non-uniformity of the induced activity and its effect on the geometrical factor and the variation of this factor with target position were also reported. In evaluating the detector efficiency for volumetric sources, the effective solid angle[3] was calculated using a Monte Carlo program. A major portion of the change in the detector efficiency with target (sample) diameter is a geometrical change, but the dependence of the detector efficiency on gamma-ray energy compels the determination of other factors in addition to the geometrical solid angle. Combining all of these factors gives the effective solid angle which, when applied to the experimentally obtained point source efficiency, yields the detector efficiency for volumetric sources (samples).[4] Although the system parameters are adequately characterized, we try here to check experimentally the reliability of our knowledge of nuclear data.

Experimental

Using the flux convention of STOUGHTON and HALPERIN,[5] the gamma-ray detector response (D) at a particular energy can be written as:

$$D = \left[\frac{N_0 m}{A}\right] \epsilon_\gamma \, I \, \theta \, t_i \, \Phi_{th} \left[g \, \sigma_0 + I_0' \frac{\Phi_{epi}}{\Phi_{th}}\right] \tag{1}$$

where N_0 – Avogadro's number,
m – mass of sample in gram,
A – atomic number,
ϵ_γ – detector efficiency,
I – photons emitted per 100n captured,
θ – isotopic abundance,
t_i – irradiation (counting) time,
Φ_{th} – thermal neutron flux,
σ_0 – thermal cross-section (2200 m · s^{-1} neutrons),
g – Westcott constant,

I_0' – infinitely dilute resonance integral defined as

$$I_0' = \int_{\mu kT}^{\infty} \sigma(E)\, dE/E,$$

Φ_{epi} – epithermal flux per unit lnE.

In a thermal beam the epithermal contribution is small and for nuclides with small resonance integrals, the sensitivity index $\sigma_0 I/A$ gives an indication of the analytical sensitivity, Table 1.

An experimentally determined sensitivity for our set-up (Fig. 1) is given as follows:

$$S = \left[\frac{D}{mt_i}\right] \qquad c \cdot g^{-1} \cdot s^{-1} \qquad (2)$$

Table 1
Comparison of the sensitivity index ($\sigma I/A$) as reported in the literature

Element	Energy, keV	SENFTLE et al.[6]	LONE et al.[7]
B	477	326.000	–
Cl	788	0.097	0.140
Cl	1164	0.102	0.187
K	771	0.017	0.028
Ca	1942	0.006	0.008
Ti	342	0.036	0.003
Ti	1382	0.083	0.088
Fe	352	0.005	0.005
Fe	692	0.002	0.002
Fe	1261	0.001	0.001
Fe	1725	0.004	0.004
Cd	559	25.670	15.850
Sm	333	32.340	38.150
Sm	439	17.790	21.410
Sm	738	3.600	4.260
Sm	1170	1.720	1.810
Gd	247	55.150	–
Gd	944	10.540	32.750
Gd	1185	14.750	33.750
Dy	186	1.115	1.176
Dy	538	0.405	0.428
Au	216	0.049	0.049
Au	262	0.029	0.029
Hg	3681	0.530	1.525
Hg	661	0.089	0.084
Hg	1693	0.160	0.265
Hg	2002	0.142	0.132
Hg	2640	0.080	0.073

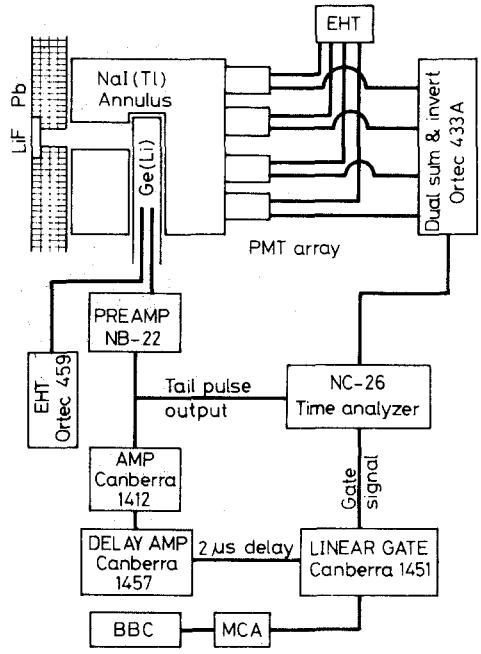

Fig. 1. A block diagram of the compton suppression spectrometer

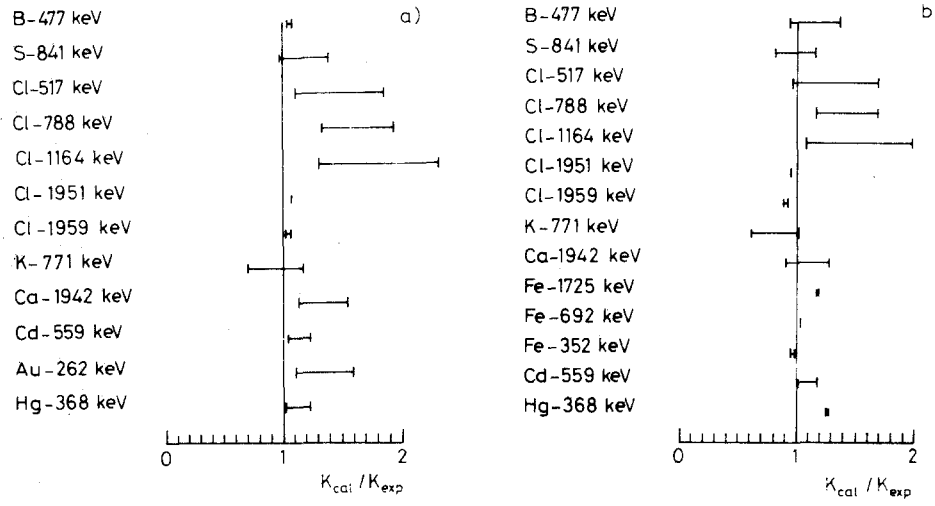

Fig. 2. Variation of the experimental and calculated K-factor using Fe (a) and Au (b) as single comparators (monostandards)

The sensitivity (S) is usually obtained by measurement of standards which are interference-free matrices or simple compounds. The sensitivity is a function of the element, gamma-ray energy, yield (I), neutron flux and detector efficiency of the system but is not a function of the sample. Experimentally determined sensitivities

Table 2
Elemental sensitivities of the PGNAA set-up

Element	Energy, keV	Sensitivity, $c \cdot g^{-1} \cdot s^{-1}$
B	477	14 000 ±2 300
S	841	1.06± 0.27
Cl	517	20.0 ± 0.5
Cl	788	14.5 ± 0.3
Cl	1164	12.5 ± 0.3
K	771	1.88± 0.35
Ca	1942	0.28± 0.03
Fe*	352	0.75
	692	0.22
	1261	0.12
	1725	0.15
Cd	559	4 439 ± 328
Au*	194	6.2
	214	11.9
	237	6.0
	248	9.1
	262	9.0
	381	3.5
Hg	368	57 ± 4

*For Fe and Au the errors obtained from repeated measurments were found to be less than 2%.

for a number of elements are shown in Table 2 and normalized to the boron sensitivity for the sake of comparison with other facilities as in Table 3.

In order to realize the direct applicability of Eq. (1) for the multi-elemental analysis of samples, a K-factor method is introduced here, analogous to that used in conventional neutron activation analysis.[10] This K-factor is obtained by rewriting Eq. (1) for the element of interest at a given gamma-ray energy in comparison with a chosen comparator denoted by an asterisk (*) we get:

$$K_{cal} = \frac{A^*\theta\ I\ \epsilon_\gamma [g\ \sigma_0 + I'_0\ \Phi_{epi}/\Phi_{th}]}{A\theta^*\ I^*\ \epsilon^*_\gamma\ [g^*\sigma^*_0 + I'_0{}^*\ \Phi_{epi}/\Phi_{th}]} \tag{3}$$

Table 3
Comparison of experimental sensitivities normalized to the senstivity of boron

	This work	ANDERSON et al.[8]	HANNA et al.[9]
ϕ_{th}, $n \circ m^{-2} \cdot s^{-1}$:	$1.06 \circ 10^{10}$	$2.0 \circ 10^{10}$	$5.0 \circ 10^{12}$
CR (Au):	9.0	55.0	42.0
Element E, keV	Normalized sensitivities		
B – 477	1.0	1.0	1.0
S – 841	$1.05 \cdot 10^{-4}$	$1.02 \cdot 10^{-4}$	$1.04 \cdot 10^{-4}$
Cl – 517	$2.47 \cdot 10^{-3}$	$2.64 \cdot 10^{-3}$	$2.80 \circ 10^{-3}$
Cl – 788	$1.54 \cdot 10^{-3}$	$2.26 \cdot 10^{-3}$	–
Cl –1164	$1.24 \circ 10^{-3}$	$1.89 \cdot 10^{-3}$	$1.91 \circ 10^{-3}$
K – 771	$2.21 \circ 10^{-3}$	$2.45 \circ 10^{-3}$	$2.38 \cdot 10^{-4}$
Ca –1942	$3.88 \circ 10^{-5}$	$4.15 \cdot 10^{-5}$	$4.26 \cdot 10^{-5}$
Fe – 352	$7.43 \circ 10^{-5}$	$8.91 \cdot 10^{-5}$	$8.68 \cdot 10^{-5}$
Cd – 559	0.31	0.32	0.33
Au – 214	$1.18 \cdot 10^{-3}$	–	$1.04 \cdot 10^{-3}$
Hg – 368	$3.33 \cdot 10^{-3}$	–	$1.77 \cdot 10^{-3}$

An experimental check on K_{cal} is the K_{exp} which is given as:

$$K_{exp} = [S/S^*] \tag{4}$$

In order to determine the K-factor experimentally, a number of pure elements and simple compounds were irradiated. Au and Fe were chosen as single comparators because their nuclear data are very well known and can be shaped into the desired form for irradiation without difficulty. The neutron flux was monitored during the course of experiments and any fluctuations were taken into account.

A comparison between the experimental and calculated K-factors using both Fe and Au as single comparators was undertaken to investigate the feasibility of using the absolute method, Eq. (1) in the multi-elemental analysis of neutron induced prompt gamma-rays. The result of this comparison is shown in Fig. (2).

Conclusion

For elements where agreement between the experimental and calculated K-factor exists, the absolute as well as the single comparator method could be applied with a good degree of accuracy and precision. For elements where discrepancies are found, it

is an indication that the absolute method cannot as yet compete in accuracy with the comparator method. This is mainly attributed to the uncertainties which still exist in the knowledge of nuclear constants required, especially cross-sections and gamma yield (photons emitted per 100 neutrons captured). Nuclides whose cross-section deviate from the 1/v law in the thermal region ($g \neq 1$) should be carefully considered. For example ^{113}Cd, ^{176}Lu, Eu, ^{240}Pu, etc., exhibit resonances below or very close to the Cd cut-off energy of 0.55 eV and the contribution of the cross-section in the region μkT to E_{cd} is not negligible and should be taken into account in evaluating the total reaction rate when calculating the K_{cal} factor.

As a concluding remark, a thorough investigation in the field of the single comparator method offers a better understanding of the factors affecting the applicability of the absolute method, since it acts as a monitor on the reliability of nuclear constants when carried out on both a calculated and experimental basis and the continuously improving accuracy of nuclear data will certainly enhance the importance of the absolute method. As of now, the usefulness of Eq. (1) is still limited by the unreliability of our knowledge of nuclear data, the scatter in nuclear data for a number of elements is significant as can be seen in Table 1.

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