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Analysis of SMELS and reference materials for validation of the k_0-based internal monostandard NAA method using in-situ detection efficiency

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ABSTRACT

Three synthetic multielement standards (SMELS I, II and III) and two reference materials (RMs), SL-3 and Soil-7 of IAEA were analyzed for validation of the k_0-based internal monostandard neutron activation analysis (IM-NAA) method utilizing in-situ relative detection efficiency. The internal monostandards used in SMELS and RMs were Au and Sc, respectively. The samples were irradiated in Apsara and Dhruva reactors, BARC and radioactive assay was carried out using a 40% relative efficiency HPGe detector coupled to an 8 k MCA. Concentrations of 23 elements were determined in both SMELS and RMs. In the case of RMs, concentrations of a few elements, whose certified values are not available, could also be determined. The % deviations for the elements determined in SMELS with respect to the assigned values and RMs with respect to certified values were within $\pm 8\%$. The *Z*-score values at 95% confidence level for most of the elements in both the materials were within ± 1.

1. Introduction

In recent years the k_0-based neutron activation analysis (k_0-NAA) method is gaining importance for the analysis of samples and reference materials, since it requires a single comparator to determine concentrations of the elements in the samples [1–3]. It involves simultaneous irradiation of a sample and a neutron flux monitor, such as gold, and the use of a composite nuclear constant called k_0 [1]. Important input parameters in k_0-NAA are: (i) two neutron flux parameters namely sub-cadmium to epithermal neutron flux ration (f) and epithermal neutron flux shape factor (α), and (ii) absolute detection efficiency (ε). The α and f values of irradiation sites of a nuclear reactor are determined by bare or cadmium ratio method [1,3,4]. For samples of various geometries, it is difficult to reproduce geometry-matching standard for the determination of absolute detection efficiency. Geometric efficiency by solid angle [5] and gamma ray transmission [6] methods are used for standard geometry samples, which need elaborate procedures. In the k_0-NAA approach, efficiency ratio rather than absolute efficiency is used. In view of this the use of in-situ relative detection efficiency, obtained by using γ-rays of one or more activation products produced in the sample, obviates the need of determination of absolute detection efficiency. A k_0-based internal monostandard prompt gamma-ray NAA (PGNAA) method for the analysis of non-standard geometry samples was standardized by Sueki et al. [7], where they used in-situ efficiency by utilizing γ-rays from the monostandard having limited energy range. An internal comparator method was standardized by Lin and Henkelmann [8] for analyzing irregular geometry biological samples, where they have used external gamma ray standards for efficiency calibration. A k_0-based internal monostandard NAA (IM-NAA) method using in-situ relative detection efficiency was standardized in our lab to analyze samples of small as well as large sizes with non-standard geometries [9–13]. In this method, an element present in the sample was used as a monostandard to take care of neutron flux perturbation, if any, inside the sample. This method uses in-situ relative detection efficiency for concentration calculations which takes care of γ-ray self-attenuation and geometrical effects and thus makes the method geometry independent. To cover the energy range of interest, combination of activation products having two or more γ-rays were used to obtain the in-situ relative detection efficiency. In this method, normally a major or a minor element present in the sample is chosen as a monostandard. However, a trace element present in the sample can also be chosen as a monostandard if any of its isotopes has suitable nuclear properties like higher isotopic abundance and (n,γ) cross-section and its activation product has favorable half-life and higher gamma ray abundance. Since this method gives elemental concentration ratios with respect to the internal monostandard, a priori knowledge of concentration of the mono standard is required to arrive at the absolute concentrations. In some cases, concentration ratios are adequate to interpret the results. However, it is essential in most of the cases to arrive at the absolute concentrations. In special cases like in alloys and metals where all the major and/or minor elements are amenable to NAA,

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absolute concentrations are arrived at by a mass-balance procedure as in the cases of metals and alloys like 1S-aluminium, zircaloys and stainless steels [10–12]. In some cases a suitable monostandard is homogeneously mixed with the sample before irradiation. The validity of IM-NAA method, which is the aim of the present work, could be ascertained by analyzing control samples/(certified/standard) RMs and comparing the elemental concentration ratios with respect to the monostandard with the corresponding ratios obtained from certified values.

Though, k_0-NAA is being practised in many laboratories around the world since 1975, still this approach needs to demonstrate the quality of results vis-à-vis QA/QC measures. The first step is the validation of the method using suitable control samples. For validation of k_0-NAA, synthetic multielement standards (SMELS) were introduced by INW and KFKI-AEKI [14,15]. SMELS have a polymeric matrix spiked with a total of 33 elements in three groups namely SMELS I, II and III according to the half-lives (short, medium and long-lived respectively) of activation products. The details of SMELS along with the assigned concentration values and the uncertainties at 95% confidence level are given in Refs. [15–17]. SMELS were used at CDTN/CNEN Brazil for validation of k_0-IAEA software [18].

The present paper deals with the analysis of SMELS (I, II and III) and two RMs namely IAEA Soil-7 and IAEA SL-3 using Au and Sc as internal monostandards, respectively, for the validation of the IM-NAA method using in-situ relative detection efficiency. The % deviations from assigned/certified values as well as Z-scores at 95% confidence level were determined. Concentrations of a few elements which do not have certified values in the RMs are also determined in the present work.

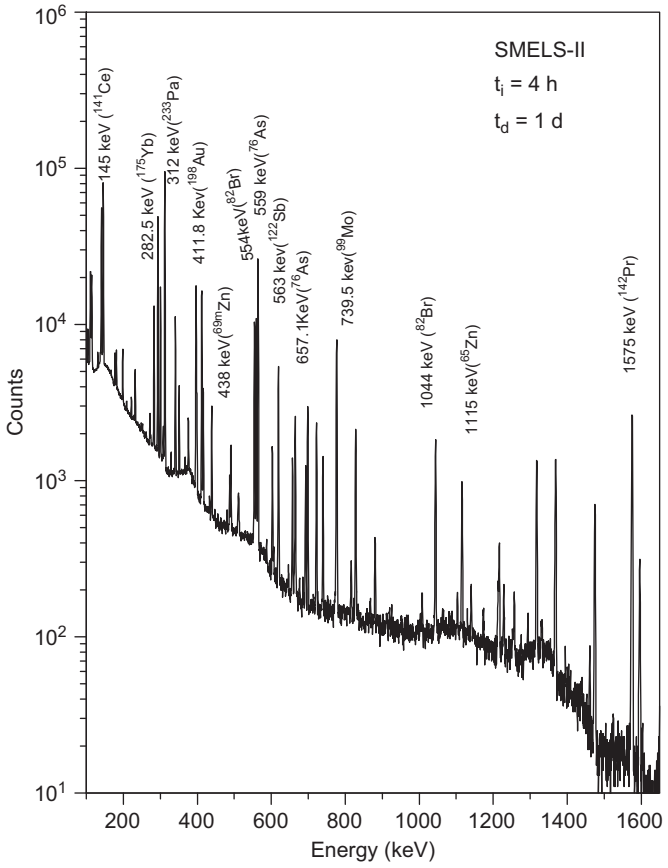

Fig. 1. Gamma ray spectrum of neutron activated SMELS-II sample.

2. Experimental

Sub-samples in the mass range 50–100 mg were used for irradiation. SMELS were used as received for sub sampling. Gold standard (ICP standard) solution was dried on Whatman filter paper and prepared with identical geometry to the samples. Irradiations of SMELS (30 min–5 h) and RMs (7 h) were carried out at E8 position of Apsara reactor, BARC. In addition, the RMs were also irradiated at tray rod position of Dhruva reactor, BARC. The thermal equivalent neutron flux values at E8 position of Apsara reactor and tray rod position at Dhruva reactor are about 5×10^{11} and $5\times10^{13}\,\mathrm{cm^{-2}\,s^{-1}}$, respectively. For characterization of irradiation sites, flux monitors namely In, Au, Co, Mo, Zn and Zr were irradiated without and with (0.84 mm) cadmium cover. Samples were assayed for radioactivity by high-resolution γ-ray spectrometry using a 40% relative efficiency HPGe detector coupled to a 8 k-multichannel analyzer (MCA). Samples were counted at distances of 10–12 cm with respect to the end cap of the detector. A typical γ-ray spectrum of neutron irradiated SMELS-II sample is given in Fig. 1. Peak areas were evaluated using the peak-fit software PHAST, developed at our institute [19].

3. Calculations

The ratio of mass (m) of an element (x) to mass of the internal mono standard element (y) in the sample by the k_0-based IM-INAA method is given by Eq. (1),

$$\frac{m_x}{m_y}=\frac{\left((S.D.C)(f+Q_0(\alpha))\right)_y}{\left((S.D.C)(f+Q_0(\alpha))\right)_x}\frac{P_{Ax}}{P_{Ay}}\frac{(\varepsilon_\gamma)_y}{(\varepsilon_\gamma)_x}\frac{k_{0,\mathrm{Au}}(y)}{k_{0,\mathrm{Au}}(x)}, \tag{1}$$

where P_A is the net peak area under the gamma line of interest, S the saturation factor, D the decay factor, C the counting factor for correcting the decay during counting period, $Q_0(\alpha)$ the ratio of the resonance integral (I_0)-to-thermal neutron cross-section (σ_0) corrected for α, $k_{0,\mathrm{Au}}$ is the literature $k_{0,\mathrm{Au}}$-factor [20] and ε_γ the relative detection efficiency and is obtained by following expression:

$$\ln\varepsilon_\gamma=k_j+\sum_{i=0}^{m}a_i(\ln E_\gamma)^i \tag{2}$$

where a_i's are the coefficients of the polynomial of order m and k_j a constant characteristic of the jth nuclide. In the calculations, a second order polynomial (m=2) was found to be adequate for obtaining a reproducible detection efficiency curve with minimum χ^2 value. The details of in-situ efficiency calibration are given elsewhere [9,10]. The α values of E8 and tray rod positions were obtained by the cadmium ratio method using multi and dual monitors, respectively, and the f-values were obtained by the cadmium ratio method using Au monitor. The α and f-values obtained for E8 position of Apsara reactor were 0.035 ± 0.003 and 50.0 ± 1.4, respectively [21] and for tray rod facility of Dhruva reactor were 0.11 ± 0.02 and 76.3 ± 2.3, respectively. The relevant nuclear data were taken from Ref. [20]. Details of steps involved in the concentration calculation in IM-NAA using internal monostandard concentration can be found in our earlier publication [13].

4. Results and discussion

For obtaining in-situ detection efficiency calibration, it is essential to use the activation products which have two or more than two γ-rays. In the case of SMELS activation products namely