Nuclear Analytical Chemistry: Developments and Applications

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Abstract

The article gives a brief summary of developments and applications of nuclear analytical methods namely (i) single comparator Neutron Activation Analysis (k0-NAA), (ii) k0-based Internal Monostandard NAA (IM-NAA) for large size and non-standard geometry samples including reactor materials, (iii) k0-based Prompt Gamma ray NAA (PGNAA) for non-destructive analysis of materials for low Z elements and neutron poisons, (iv) instrumental and chemical NAA (INAA and CNAA) methods for total and/or species concentrations of elements namely As, I and Se and (v) Particle Induced Gamma ray Emission (PIGE) methods for non-destructive determination of F in borosilicate glass and Li in ceramic samples.

Introduction

The k0-based NAA method was adopted at the Radiochemistry Division in the year 1995, for multi-element determination in various matrices [1-4]. This method is more attractive than relative method, as it uses a single comparator like gold instead of multielement standards. This method needs reactor and detector-based input parameters namely sub-cadmium to epithermal neutron flux ratio (f), epithermal neutron flux shape factor (α) and absolute detection efficiency of the detector (ε) in addition to nuclear constants like k0 and Q0 [2,3]. The k0-NAA was standardized by determining f and α for the irradiation sites of research reactors at BARC and determining the k0-factors for some analytically important isotopes, validated by analyzing reference materials (RMs) of different origin and applied to samples of diverse matrices [1-10]. Routine analysis by conventional NAA and k0-NAA deals with small size samples (tens of mg-500 mg). Often sub-sampling of solids and small size sample analysis are questionable in terms of true analytical representation. In this case, large size sample (g-kg scale) analysis is advantageous for better analytical representativeness. A k0-based Internal Monostandard NAA (IM-NAA) method, using in-situ relative detection efficiency, was developed for the analysis of large size and non-standard geometry samples and applied to nuclear reactor materials, wheat grains, uranium ore and archaeological potteries [11-16]. IM-NAA method was also applied to small size samples of diverse matrices including meteorites [17] and uranium ores [18]. Our expertise on k0-method was advantageously utilized, to carry out R&D work on k0-based Prompt Gamma ray NAA (PGNAA), using neutron beam facilities at Dhruva reactor [19-23,4]. R&D work on PGNAA includes determination of prompt k0-factors, analysis of RMs, compositional analysis of nuclear structure materials, meteorites and cement standard and determination of H in zircalloys and B in RMs, chemical compounds and borosilicate glass samples. The R&D work on k0 methodologies in NAA and PGNAA was carried out for the first time in India.
R&D work on $k_0$-NAA and IM-NAA

Irradiation positions of Apsara (core and thermal column, TC), CIRUS (self serve, SS, and pneumatic carrier facility, PCF), Dhruva (PCF), and AHWR critical facility (CF) were used. Neutron monitors like Au, Zr, In, Mo and Zn were used for neutron spectrum characterization. The $k_0$-NAA method was validated by determining concentrations of about 30 elements in several Reference Materials (RMs) [3] obtained from IAEA NIST & USGS and applied to many samples including ruby [1], beryl and emerald [5], sediments [6], manganese nodules and encrustations [7,8], cereals [9], medicinal and edible leaves [10]. For NAA of short-lived activation products, PCFs at CIRUS and Dhruva reactors were used. The $k_0$-factors of the short-lived nuclides (half-lives – 11 s to 37 min) for the elements namely F, Se, Sc, Al, V, Ti, Cu, Ca, Mg, I and Cl with respect to gold ($^{197}$Au) were determined [24]. For validation of the IM-NAA, Synthetic MultiElement Standards (SMELS) and IAEA RMs SL-3 and Soil-7 were analyzed using Au and Sc monostandards respectively [25]. Concentrations of 23 elements were determined and the % deviations were within ±8% with respect to certified values.

Large Sample NAA (LSNAA)

The IM-NAA method was applied for the analysis of some large and non-standard geometry samples (2-100 g), as shown in Fig. 1. This includes nuclear fuel cladding cum structure materials namely zircalloys (zircaloy 2 and 4) [11,12], stainless steels (SS 316M, D9 and SS 304L and BCS RMs) [11,13,14], 1S grade aluminium [11], wheat grains [14], uranium ores [15] and ancient clay potteries [15,16]. The results of Zircaloy 2 and SS-316M are given in Table 1. The elements determined in zircaloy samples are Zr, Sn, Fe, Cr, Ni, In, Mn, As, Co, W and Ta whereas in Stainless steel samples, the determined elements are Fe, Cr, Ni, Mo, Mn, Co, As and W. Since all the major and/or minor elements Zr, Sn, Fe, Cr and/or Ni in zircalloys and Fe, Cr, Ni, Mn and/or Mo in SS were amenable to NAA, concentration values were obtained by mass balance approach. The results are in good agreement with the literature/reported compositions. In the case of 1S aluminium, impurities could be determined as the mass of the sample was entirely due to Al.

The IM NAA method was used to analyze samples of wheat grains to investigate the applicability of large sample NAA and to examine the effect of heterogeneity on the routinely practised sub-sampling method [14]. The results indicated, that it would be better to analyze one large sample (> 1 g) instead of replicate sub samples. One of the best applications of IM-NAA is the analysis of large and non standard geometry ancient potteries for the provenance study. A total of 30 large size ancient potteries, obtained from excavated Buddhist sites of Andhra Pradesh, were analyzed [16]. The concentration ratios of 15 elements Na, K, Cr, Fe, Co, Ga, Cs, As, La, Ce, Sm, Eu, Lu, Hf and Th with respect to Sc were determined. Values of La/Ce and statistical cluster analysis using concentration ratios were used for the grouping.
R&D work on Prompt Gamma ray NAA (PGNAA)

Since 1999, we have been carrying out studies on PGNAA using thermal and reflected neutron beam lines at Dhruva reactor [19-23]. As part of the quality assurance program, prompt $k_0$-factors for isotopes of elements like $H$, $B$, $N$, $Mg$, $Si$, $K$, $Ba$, $Cd$, $Sm$, $Hg$ and $Gd$ were determined, with respect to 1951 keV gamma-ray of $^{36}Cl$, using both thermal and reflected neutron beams [19,20]. The internal mono-standard method of PGNAA was used to analyze IAEA RMs like SL-3 (sediment) and 153 (Milk powder) [21] for method validation. Composition analysis of SS 361M and BCS CRM 466 was carried out by standardless approach. It was also applied to "Jagannath meteorite" and concentrations of $Fe$, $Cr$, $Si$, $K$, $Mg$, $Ca$ and $Ni$ were determined. A methodology for correcting the self-shielding effect was standardized, which was validated with synthetic samples containing neutron poisons like $B$, $Cd$ and $Gd$. The method developed was used to determine elements namely $B$, $Ti$, $Mo$, $Cr$ and $Si$ in TiB$_2$ alloy [22] and boron in chemical compounds and borosilicate glass samples [23]. Low concentrations of boron were determined in several RMs, with a detection limit of 1 mg kg$^{-1}$ [23].

Applications of instrumental and chemical NAA methods

Thermal and Epithermal NAA (TNAA and ENAA) methods were standardized for $U$ and $Th$ in mixed oxides and zircon, $U$, $Th$ and Rare Earth Elements (REEs) in uranium ores, and trace amounts of $Th$ in uranium oxide. Trace amounts of REEs and other elements in a purified $^{241}Am$ sample could be determined by NAA. INAA and Chemical NAA (CNAA) methods were used for total arsenic and inorganic arsenic species (arsenite and arsenate) concentrations in potable water [26]. ENAA method using boron carbide filter was optimized to determine concentrations of iodine in food, food products including milk, baby foods and iodized salts and iodine values were found to be in the range of 0.16- 5.5 mg kg$^{-1}$ except for iodized salt (10-33 mg kg$^{-1}$) [27]. An anion exchange Polymer Inclusion Membrane (PIM) was used in conjunction with NAA, to determine low levels of $I$ in aqueous samples and applied to milk and milk powder sample for iodide contents [28]. Selenium (Se) in crop products from seleniferous areas of Punjab was estimated by INAA. Se concentrations are in the range of 10-670 mg kg$^{-1}$, whereas the values of wheat and mustard grains are 100 and 670 mg kg$^{-1}$, respectively [29].
PIGE methodology for low Z elements (F and Li) using proton Beam at FOTIA, BARC

Quantitative estimation of low Z elements like Be, Li, B, C, N, O, F, Si, P and S is difficult by many analytical techniques, including wet chemical methods, if the sample is difficult to dissolve. PIGE methods, with proton or deuterium beams are found to be unique due to the non-destructive nature, negligible matrix effect and no spectral interference. Recently a PIGE facility (Fig. 2) has been set up at FOTIA, BARC. We have standardized a PIGE method using 4 MeV proton beam for non-destructive determination of F in barium borosilicate glass samples [30,31]. Barium BoroSilicate Glass (BaBSG) is a potential candidate for vitrification of thoria-based nuclear waste. The prompt gamma rays of 110 and 197 keV from $^{19}$F ($p, p'\gamma$) $^{19}$F were measured by high resolution gamma ray spectrometry. Samples containing F in the range of 0.1-4 wt%, prepared at WMD, BARC, were analyzed to study the F retention in glass matrix during vitrification. In a similar way, a PIGE method was standardized for Li, in lithium incorporated $\text{Nd}_2\text{Ti}_2\text{O}_7$ ceramic sample, determination non-destructive. The prompt gamma rays of 478 and 429 keV from $^7$Li ($p, p'\gamma$) $^7$Li and $^7$Li ($p, n\gamma$) $^7$Be were used for this study. The method is promising for Li estimation in samples like Lithium nitrate and silicate without chemical destruction of sample.

Fig. 2: PIGE set up at FOTIA

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