

Application of INAA and PIXE for analysis of archaeological pottery samples

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Introduction

Analysis of archaeological artifacts like potteries, bricks and tiles by nuclear analytical techniques (NATs) like instrumental neutron activation analysis (INAA) and ion beam analysis (IBA) is very useful for obtaining simultaneous multielement profiles at major to trace concentration levels. Archaeological studies are often focused on provenance studies to establish whether they are from same or different origin [1-2]. The preliminary information is obtained by the physical appearance and the confirmation of provenance is mainly done by chemical composition analysis. The artifacts like pottery, bricks, stones, coins and paints are often analyzed for their provenance. Potteries are widely studied since they have a strong correlation with the clay/soil source from which they are prepared and this fact might be true for bricks also as they are made from clay /soil [2]. Elemental concentration ratios of Al to Sc (due to non-volatile nature) La to Ce (due to their similar geochemical properties) are used for preliminary grouping of the pottery samples. The key elements used for grouping are: (i) Na, K, Ca, Rb and Cs, (ii) transition elements like Ti, Sc, Cr, Co and Ni (iii) rare earth elements (REEs). Among these, REEs and metallic elements at trace levels are most useful because they are highly insoluble and immobile and their patterns often remain unchanged. In the present work, a comparison study of analysis of pottery samples k_0 -based internal monostandard NAA (IM-NAA) [3-4] and PIXE using proton beam was carried out [5]. The validity of methods was examined by analyzing IAEA RM SL-1 (lake sediment). Ancient pottery samples were collected from excavated Buddhist sites of Andhra Pradesh.

Experimental

For NAA work, pottery sample was ground homogenously and 150 mg of sample was packed in aluminium along with IAEA RM SL-1 (control) and RM SL-3 (reference standard) separately. Sample and RMs were irradiated (for 6 h) in self serve position of CIRUS reactor of BARC, Mumbai at a neutron flux of $5 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$. Radioactive assay was carried out using a 40% relative efficiency HPGe detector coupled to 8k MCA. PHAST peak fit software was used for spectrum analysis to get peak areas.

In the case of PIXE, proton beam of 2.5 MeV energy (current about 10 nA) obtained from the FOTIA (Folded Tandem Ion Accelerator), BARC, Mumbai was

used for our work using internal PIXE method [5]. Sample mass of 400 mg was mixed with cellulose (binder) in 1:1 ratio along with yttrium oxide (1200 ppm of Y). The purpose of mixing yttrium oxide powder is to monitor the variation of beam current during irradiation. The resultant mixture was compressed using a 2 ton hydraulic press into pellets of 20 mm diameter and about 1 mm thickness. Pellets were placed on an aluminum ladder in the PIXE chamber at 45° to the beam direction and X-rays were analyzed using a peltier cooled Si(Li) detector of resolution 180 eV at 5.9 keV X-ray of Mn.. Typical spectra obtained for irradiated pottery sample by INAA and PIXE are given in Fig.1.

Calculations

In IM-NAA, concentration ratios were calculated with respect to Sc (using 889 keV of ^{46}Sc) using following expression,

$$\frac{m_x}{m_y} = \frac{(S.D.C)_y \cdot P_{Ax} \cdot \varepsilon_y \cdot (f + Q_0(\alpha))_y \cdot k_{0,Au}(y)}{(S.D.C)_x \cdot P_{Ay} \cdot \varepsilon_x \cdot (f + Q_0(\alpha))_x \cdot k_{0,Au}(x)}$$

the ratio of the mass (m)/concentration of the element x to y present in the sample. where P_A is the net peak area under the gamma peak of interest, S is the saturation factor, D is the decay factor, C is the counting factor used for correcting the decay during counting period, ' f ' is ratio of thermal to epithermal neutron flux ratio, $Q_0(\alpha)$ is the ratio of the epithermal to thermal cross section corrected for epithermal neutron flux shape factor (α), $k_{0,Au}$ is the literature k_0 -factors with respect to gold and ε is the, here, relative Insitu detection efficiency, details of which are given in ref. 4. GUPIXWIN software was used for PIXE spectrum analysis. A relative method using current normalized count rate was used for concentration calculation.

Results and discussion

The results obtained for IAEA RM SL-1 by IM-NAA and PIXE methods are given in Table 1. Though concentrations of 22 elements were determined, for comparison purpose results of 15 elements (Na, K, Ca, Ti, V, Cr, Mn, Fe, Co, Zn, Rb, As, Ga, Ia and Ce) are given. Using PIXE, concentrations of seven elements namely K, Ca, Ti, V, Cr, Mn, Fe, Rb and Zr were determined. The results of IM-NAA and PIXE are found to be in good agreement and also in good agreement with the certified/information values. Though, we have analyzed

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many samples of potteries, results of 14 elements in one of the representative clay potteries analyzed by IM-NAA and PIXE are given in Table 2. PIXE results (for 7 elements) are found to be in good agreement (within 8%) with that of IM-NAA. The results show that IM-NAA is powerful for many elements, and PIXE is a good alternate multielement technique for ceramic samples for medium Z elements. Further work on utilization of PIXE and PIGE is being pursued using FOTIA and other accelerator facilities.

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Table.1 Concentrations (mg kg⁻¹) of IAEA SL-1 by INAA and PIXE

Elements	Certified values	PIXE	IM-NAA
Na	1720 ± 120	ND	1810 ± 92
K	(15000)	15480 ± 461	16253 ± 369
Ca	(2500)	2595 ± 37	24009 ± 211
Ti	5170 ± 361	4800 ± 38	5231 ± 120
V	(170)	155 ± 6	181 ± 6
Cr	(104)	95 ± 3	102 ± 5
Mn	3460 ± 173	3448 ± 61	3580 ± 81
Fe	67400 ± 2022	65865 ± 164	69253 ± 1521
Co	19.8 ± 1.5	ND	19.2 ± 0.7
Zn	223 ± 9	ND	235 ± 6
Rb	113 ± 11	124 ± 7	109 ± 8
Zr	(241)	264 ± 12	ND
As	(27.5)	ND	29.3 ± 2.1
Ga	(24)	ND	23.2
Ce	(11.7)	ND	12.3 ± 0.51
La	52.6 ± 2.7	ND	53.1 ± 1.6

(): not certified / information values, ND: not detected

Table. 2: Elemental concentrations of representative pottery sample analyzed by PIXE and IM-NAA methods

Elements	PIXE Concen. (mg kg ⁻¹)	IM-NAA Concen. (mg kg ⁻¹)
Al	ND	77924 ± 654
K	25344 ± 633	25615 ± 421
Ca	33906 ± 189	33729 ± 259
Sc	ND	16.1 ± 0.3
V	ND	64.0 ± 4.8
Cr	352 ± 1.6	324 ± 6
Mn	3892 ± 84	4170 ± 186
Fe	37236 ± 70	39960 ± 165
Co	ND	4.71 ± 0.08
As	ND	5.01 ± 0.18
Rb	319 ± 31	344 ± 23
Sr	1614 ± 69	ND
Zn	ND	67.6 ± 2.1
Ba	ND	1610 ± 32

γ-ray spectrum of Pottery Samples Irradiated in CIRUS for 6h.

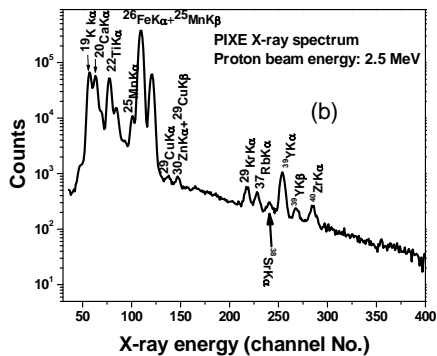
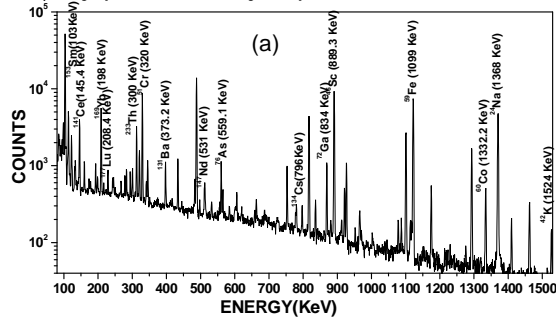


Fig. 1. Typical γ -ray (a) and X-ray (b) spectra of ancient pottery sample