

NEUTRON ACTIVATION ANALYSIS OF ARCHAEOLOGICAL POTTERY SAMPLES OF LARGE SIZE, INCLUDING PIECES OF LOW SYMMETRY SHAPE: HOW TO GET ACCURATE ANALYTICAL RESULTS IN A PRACTICAL WAY

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Abstract.

The feasibility of the instrumental neutron activation analysis of entire pieces of archaeological pottery, using low thermal neutron fluxes, is examined and a new approach for the non-destructive analysis of entire pottery objects by INAA, using the conventional relative method, is described. The proposed method relies in the preparation of a comparison standard, which is a nominally identical replicate of the original object to be studied. INAA of small samples taken from that replicate allows determining its composition for the elements to be analyzed. Then the intact sample and intact standard are irradiated together with the neutrons from a nuclear reactor neutron beam, using a suitable turntable facility and monitored by neutron flux monitors. Finally, after proper decay times, the induced activities in sample, standard and flux monitors, are successively measured, by high-resolution gamma spectroscopy, using a high-efficiency germanium detector. In this way, several complicating effects such geometrical efficiency, neutron self-shielding and gamma ray attenuation are avoided and the need of complicated mathematical corrections is not needed. A potential advantage of the method is that it can be fully validated. Quantitative experiments using 7 – 13 hours of irradiation of pairs of 750 grams replicates, at low neutron fluxes of $3.9 \times 10^6 \text{ n cm}^{-2} \text{ s}^{-1}$, followed by 100000 to 200000 seconds of counting in front of a 70% relative efficiency HPGe detector, led to recoveries between 90% and 110% for Sc and La. Another experiment, using pairs of replicates of small solid mud anthropomorphic objects, (weighing about 100 grams each), irradiated by 8 hours at a neutron flux of $10^9 \text{ n cm}^{-2} \text{ s}^{-1}$, led to recoveries better than 90% and 110% for As, Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, La, Lu, Rb, Sb, Sc, Sm, Ta, Tb, Th, Yb and U, showing that the proposed method is suitable for LSNA of entire pottery or mud archaeological objects.

1. INTRODUCTION

Non-destructive and reliable quantitative elemental analysis, of intact archaeological pottery objects, is very important because it would provide valuable information for provenance studies and authenticity assessment, without damaging those precious cultural objects by of taking samples from them.

Large Sample Neutron Activation Analysis (LSNAA), proposed by Bode *et al* [1, 2], and others [3], is a very promising option for nondestructive analysis of cultural objects. Nevertheless, the accurate LSNAA of entire pottery objects, with masses of up to one kilogram or more as well as of arbitrary, nonsymmetrical shapes, constitutes a nontrivial scientific and technological challenge.

To overcome this challenge, the application of the internal monostandard method has been proposed by Dasari *et al* [4] and the use of Monte Carlo calculations has been proposed by Stamatelatos *et al.* [5], for the estimation of calibration factors, for neutron self shielding and gamma ray detection efficiency effects.

In this report, we propose a different approach, consisting of the application of the conventional relative INAA method, adapted to the analysis of large samples with arbitrary shapes [6]. In fact a practical and reliable way of performing accurate, nondestructive INAA of large and nonsymmetric, archaeological pottery objects is to use a reference object

irradiated simultaneously with the original pottery piece (a replicate of it) with well known chemical composition, and made with the same nominal size, shape and weight as the original. In this way, as a working hypothesis, it was expected that correction factors for neutron self shielding and gamma ray detection efficiency effects will cancel.

For the preparation of the replicates, we trusted on the high skill level of our Peruvian ceramists (local ancient technology), while for the composition issue, several small subsamples were taken from the replicate, with a small diameter tungsten carbide drill. Then the trace elements composition were determined by k_0 based INAA [6-9], with the highest possible accuracy.

2. EXPERIMENTAL PART

The experimental details have been published elsewhere [6] and are briefly mentioned again here, for sake of completeness.

Twelve replicates of a Mochica pottery object, with masses ranging between 700 and 800 grams, approximately, were prepared by a local artisan, using a homogeneous clay of fine texture (Fig. 1). After weighing, all samples were superficially cleaned with a soft brush and stored in labeled polyethylene bags. Powder ceramic was extracted with a carbide drill from different parts of each replicate, and mixed to get composites with masses of about 1 gram. These samples were placed in clean glass containers, homogenized, dried and analyzed by k_0 based INAA [6-9].



FIG. 1. Replicate of a Mochica pottery object.

Following [6], aliquots of about 250 mg, of each composite powdered ceramic sample, were weighed in polyethylene vials and irradiated for 20 min., together with sodium comparators, using the pneumatic transfer system of the 10 MW Peruvian Nuclear research reactor, at a thermal flux of $1.9 \times 10^{13} \text{ n.cm}^{-2} \text{ s}^{-1}$ and epithermal flux of $3.2 \times 10^{11} \text{ n.cm}^{-2}\text{s}^{-1}$. After a decay time of 5 days, a first measurement of the samples was performed for 5000–6000 s, using a Canberra GC 1518 HPGe detector (relative efficiency: 15%; FWHM: 1.8 keV at 1332.5 keV ^{60}Co). The comparators were measured for 1000 s after 6 days of decay in an identical geometry. Under these conditions, ^{76}As , ^{42}K , ^{140}La , ^{24}Na , ^{239}Np , ^{122}Sb , ^{153}Sm , and ^{175}Yb were determined. A second measurement was carried out after 15–17 days decay for 10000 s with another HPGe detector (Canberra GC 7019; relative efficiency: 70%, FWHM: 1.9 keV at 1332.5 keV ^{60}Co). The nuclides determined were ^{131}Ba , ^{141}Ce , ^{60}Co , ^{51}Cr , ^{134}Cs , ^{152}Eu , ^{59}Fe ,

^{181}Hf , ^{177}Lu , ^{147}Nd , ^{86}Rb , ^{46}Sc , ^{85}Sr , ^{182}Ta , ^{160}Tb , and ^{233}Th . A certified standard reference material, NIST 1648, was used for quality control of the procedure.

For the analysis of the entire pottery objects, the replicates were organized in pairs, three of which had very similar masses (difference of about 0.1%) and the other three with mass differences of up to about 16%. One of the replicates of each pair worked as the sample and the other one as the standard. In all cases, the replicate of higher mass was used as the standard or comparator.

Each pair of replicates was placed onto an aluminum double turntable device and irradiated at the head of a neutron beam of the nuclear research reactor (Fig. 2). Small disks of scandium and gold were attached to both the samples and the comparators, as flux monitors.



FIG. 2. Irradiation geometry of a “sample” and a “standard”.

Following [6], each pair was irradiated by 7–13 h, and measured for 100,000–200,000 s, after 3 and 10 days decay, using a 70% relative efficiency HPGe detector (Fig. 3). The scandium and gold monitors were counted for about 20,000 and 5,000 s, after about 10 and 5 days, respectively from the end of irradiation.



FIG. 3. Gamma counting geometry.

In a different experiment, a variant of the proposed method was applied to four replicates of complete small anthropomorphic solid objects of unfired clay, with masses of about 100 grams each, as well as to a pair of small clay anthropomorphic heads with masses of about 10 grams each (Fig. 4). These objects were replicated copies of original objects found in the pre-ceramic ancient city of Caral. Small subsamples of these objects were taken and analyzed by k_0 based INAA, as described before. Then the six objects, organized in pairs and with small pieces of nichrome wire as monitors, were irradiated for 9 hours, inside the port of a neutron beam of the nuclear reactor, with a thermal neutron flux of $1.4 \times 10^{10} \text{ n cm}^{-2} \text{ s}^{-1}$. No rotation of samples was applied (Fig. 5). As before, one replicate of each pair worked as “sample” and the other as “standard”. After four days of decay, the induced activities of samples, standards and monitors were measured by high resolution gamma spectrometry and the following elements were determined in those objects working as “samples”: As, Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Rb, Sb, Sc, Sm, Ta, Tb, Th, Yb and U.



FIG. 4. Replicates of mud objects from Caral.

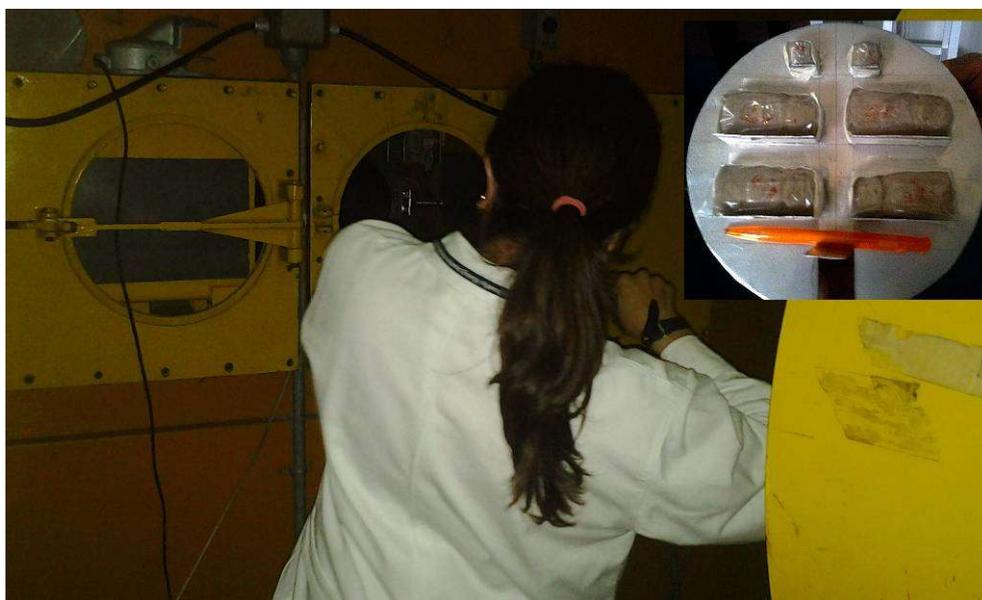


FIG. 5. Irradiation geometry for the replicates of mud objects from Caral.

3. RESULTS AND DISCUSSION

A key aspect of working with pairs of replicates, for developing the method, is that the concentrations of trace elements, for the “standard” and the “sample” are already known, through the k_0 based INAA, performed on the powder composite samples, taken from each object. This fact allows determining the recovery for each element analysed in the “sample” by the proposed method, which constitutes an assessment of trueness. Such assessment could not be possible, of course, when working with real samples, because taking samples from the precious original objects would be forbidden.

For the experiments performed on pairs of replicates of a Mochica pottery object, in reference [6] it has been shown that recoveries between 90% and 110 % were obtained for lanthanum and scandium, and between 80 % and 120 % for arsenic, potassium, sodium and europium. At the same time, poor recoveries, between 70 % and 130 %, were obtained for Sb, Sm, Cs and Fe, which are comparable to the recoveries reported in reference [5]. In the case of our proposed method, it was suspected that one important cause of poor recoveries was the poor counting statistics, arising from the low neutron fluxes used in the irradiations.

In a previous paper [10] it was shown that after irradiation of for a typical pottery sample of about 1 kg, for 45 minutes, at a thermal flux of about 10^9 n.cm⁻².s⁻¹, analytical signals are obtained, by gamma spectrometry, with counting statistics better than 1%, for ⁷⁶As, ¹³¹Ba, ¹⁴¹Ce, ⁶⁰Co, ¹³⁴Cs, ¹⁸¹Hf, ¹⁴⁰La, ²⁴Na, ¹²²Sb, ⁴⁶Sc, ¹⁵³Sm and ²³³Pa, whereas ⁵¹Cr, ¹⁵²Eu, ⁴²K, ⁸⁶Rb, ¹⁷⁵Yb and ⁶⁵Zn can be detected with counting statistics within 1% and 2%. Also, the statistics of measurement are relatively poor (ranging from 3% to 10%) for ¹⁷⁷Lu, ¹⁴⁷Nd, ²³⁹Np, ¹⁶⁰Tb and ¹⁸¹Ta.

Figure 6 shows the recoveries obtained for the replicates of the mud objects from Caral. It is remarkable to observe that these recoveries range between 90% and 110% for all determined elements, being indeed, better than 94 % and 106 % for many of the elements which are important for provenance archaeological studies. These results constitute a good evidence of the importance of the counting statistics, on the fitness for purpose of LSNAA applied to archaeological entire pottery objects.

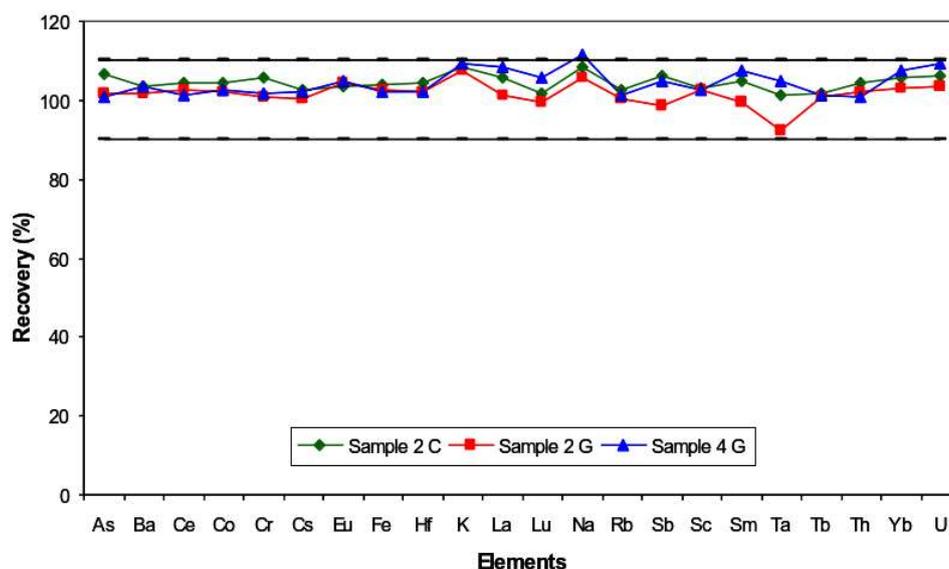


FIG. 6. Trueness assessment for the LSNAA of replicates of mud objects from Caral.

Radiological safety aspects are also very important. For example, as reported in reference [10], a typical pottery sample of about 1 kg, irradiated during 45 minutes, at a thermal flux of about $109 \text{ n.cm}^{-2}\text{s}^{-1}$, the in-contact measured gamma dose, after a decay of ten days, was about 0.8 mSv/h, which is about twice the maximum allowed dose for nonexposed personnel. The main cause of that dose was ^{46}Sc , which suggests that a typical archaeological pottery sample object should be kept in custody by about two or three months before being released back to the museum. This constitutes a major issue, especially if several samples from a museum have to be analysed, because it is necessary to consider that the archaeologists will probably want to have access to the irradiated pottery pieces, as soon as possible. Thus, a possible solution, to be studied in the future, would be keeping the neutron fluency as low as possible, while improving the peak counting efficiency, as much as possible.

4. CONCLUSION

The traditional multi-comparator method of INAA is suitable for the accurate, nondestructive determination of several elements in entire pottery objects. A key condition is the use of a replicate of the pottery object, as a reference object, to be irradiated simultaneously with the sample, and measured using the same counting geometry as for the sample. The replicate must have nominally the same weight, shape and dimensions as the sample (inside a practical tolerance of few percent) and a well known chemical composition for the elements to be analyzed.

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REFERENCES

- [1] R. M. W. Overwater, P. Bode, J. J. M. De Goeij, J. E. Hoogenboom; Feasibility of Elemental Analysis of kilogram-size samples by instrumental neutron activation analysis. *Anal. Chem.* 68 (1996) 341-348.
- [2] P. Bode, R. M. Overwater, J. J. M. De Goeij; Large-sample neutron activation analysis: Present status and prospects; *Journal of Radioanalytical and Nuclear Chemistry* 216 (1997) 5-11.
- [3] X. Lin, R. Henkelmann; Instrumental neutron activation analysis of large samples: a pilot experiment; *Journal of Radioanalytical and Nuclear Chemistry* 251 (2002) 197-204.
- [4] K. B. Dasari, R. Acharya, K. K. Swain, N. Lakshmana Das, A. V. R. Reddy; Analysis of large and non-standard geometry samples of ancient potteries by internal monostandard neutron activation analysis using in situ detection efficiency; *Journal of Radioanalytical and Nuclear Chemistry* 286 (2010) 525-531.
- [5] I. E. Stamatelatos and F. Tzika and T. Vasilopoulou and M. J. J. Koster-Ammerlaan; Large sample neutron activation analysis of a ceramic vase; *Journal of Radioanalytical and Nuclear Chemistry* 283-3 (2010) 735-740.
- [6] Bedregal PS, Mendoza PA, Cohen IM, Baltuano OR, Montoya EH., Neutron activation analysis of archaeological artifacts using the conventional relative method: a realistic approach for analysis of large samples. *J Radioanal Nucl Chem* 291 (2012):37-42.
- [7] De Corte, F. *The k_0 Standardization Method*. Habil. Thesis, University of Ghent. 1987.

- [8] P. Bedregal, P. Mendoza, M. Ubillús, E. Montoya. “k₀-INAA method accuracy using Zn as comparator” Nuclear Instruments and Methods in Physics Research A; 622 (2010) 419 – 424.
- [9] E. Montoya, P. Bedregal, P. Mendoza, M. Ubillús, B. Torres, I.M. Cohen; The development of the k₀ method in Peru: past present and future perspectives; Nuclear Instruments and Methods in Physics Research A; 622(2010):381-384.
- [10] P. Bedregal, M. Munive, P. Mendoza, A. Revilla, J. Gago, I. M. Cohen, E. Montoya; “Estudio sobre la factibilidad de empleo del análisis por activación neutrónica en cerámicos arqueológicos enteros: Parte 1: Aspectos de precisión de resultados y de seguridad radiológica del proceso. Proyecciones 7-1 (2009) 65-73.