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Minimizing sample sizes while achieving accurate elemental concentrations in neutron activation analysis of precious pottery

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ABSTRACT

We have demonstrated in this study that the combination of micro-sampling and various methods in NAA is an ideal method of quantifying trace elements in pottery. Methodologies in thermal and epithermal NAA in conjunction with Compton suppression has resulted in a wide range of elements with sample weights of only 10 mg. These results will help develop new and improved methods of analysis of precious pottery and ceramics while preserving as much of the pottery pieces as possible.

1. Introduction

Manufacturing containers, body adornments, paintings, sculptures, etc. are one of the major characteristics of human endeavor transposed into art. Being able to achieve provenance of these objects gives modern humans the link to past lives of major cultural groups and civilizations. The field of archaeological forensics has been very active for the past century and a half. When analyzing pottery, ceramics, and other archaeological finds, neutron activation analysis (NAA) is one of the two preferred methods (the other being ICP-MS) for elemental analysis due to the large number of elements that can be measured precisely and accurately using a small sample size. Some recent studies of the application of NAA include pottery (Bedregal et al., 2014) Majolica ware (De la Vega et al., 2013) and ancient bricks (Dasari et al., 2013). An excellent overview of nuclear techniques for cultural heritage research has been published by the International Atomic Energy Agency (International Atomic Energy Agency, 2011). The current methodologies usually require about 100–400 mg of the specimen to acquire representative results. Typically these quantities for NAA are relatively large when dealing with precious pottery or rare shards from broken pottery vessels, the most common artifacts found during excavation of archaeological sites. NAA can be done with much smaller samples but a sample too small may not reflect the bulk composition. Recently the application of NAA to microgram scale of solid samples has been explored for extraterrestrial samples (Sekimoto et al., 2015). To test this hypothesis in a pilot project 10 mg samples from Tunisian pottery were examined by NAA to ascertain if samples at such small quantities could indeed give representative and meaningful results. Typically sample sizes less than 100 mg are considered to be subject to inhomogeneity. If these initial results proved to be successful in this pilot study, then the next step would be to retrieve about 10 mg from different spots on the pottery. The Tunisian pottery was previously analyzed by NAA at the Archaeometry Laboratory of the Hebrew University so that their composition was known with great precision.

2. Experimental

For this experiment it was important to analyze pottery whose composition was already known from independent NAA measurements. To this end five pottery shards previously analyzed by NAA at The Hebrew University of Jerusalem were chosen. These shards were chosen for no other reason than that they were available for resampling. The samples of five different pieces were already ground into a fine powder and homogenized and were received at the Nuclear Engineering Teaching Lab.

2.1. Sample preparation

In order for each sample to be irradiated using four different methods of irradiation, four sub-samples of each of the five pottery samples were created by weighing approximately 10 mg (a range from 9 to 11 mg) using a 5 decimal Mettler Toledo balance. The calibration of the weighing balance was done using a certified 1.00000 g standard. The stability was measured to be about 0.00075 mg before the commencement of this work. Each sample was carefully placed into 0.25 cm^3 polyethylene vial to ensure identical irradiation and counting geometry, and then into a 1.0 cm^3 polyethylene vial. To monitor and normalize the neutron flux during sample irradiations molybdenum

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wires were weighed and packed together with the samples for medium-lived isotopes, cobalt wires for long-lived isotopes, while aluminum wires were prepared for short-lived isotopes (Landsberger and Dayman, 2013). NIST 278 (Obsidian Rock), NIST 1633a (Trace Elements in Coal Fly Ash), and NIST 1633b (Trace Elements in Coal Fly Ash) were prepared as quality control for the reference materials and Ohio Red Clay was used as the comparator standard because it has been extensively used as an interlaboratory standard in archaeometric investigations of pottery (Kuleff and Djingova, 1998).

2.2. Irradiation, counting and analysis

All samples were irradiated at the 1.1 MW TRIGA reactor in the Nuclear Engineering Teaching Laboratory at University of Texas, Austin. Counting of the samples, reference material and standards was done using the Canberra reverse electrode coaxial germanium detector which is surrounded by an annular 25.4 × 25.4 cm^2 NaI(*Tl*) detector for the Compton suppression acquisition. Spectra acquisition was done in both Compton suppressed and normal modes using two interface modules supported by ORTEC Maestro's® acquisition and display software. A complete description of the Compton system is given elsewhere (Ahmed et al., 2010). The spectra were then analyzed with the analysis software NADA (Landsberger et al., 1994). Together with the samples, reference materials and the Ohio Red Clay standard flux wires were simultaneously irradiated. The different types of irradiation, decay and counting procedures correlating to specific elements analyzed are shown in Table 1.

For short irradiations (for short-lived radionuclides), samples and flux wires were sent into the reactor using the automatic thermal pneumatic transfer (tPNT) system and the automatic epithermal pneumatic transfer (ePNT) systems. For the tPNT irradiations the samples were sent into the reactor sequentially and irradiated for 1 min at a neutron flux of ~4.5 × 10^{11} n cm^{-2} s^{-1}. A short irradiation time was used to reduce the counting deadtime which can be very high to due to ^{28}Al and ^{56}Mn. After a decay period of about 15 min, the samples were counted for 15 min on a 30% efficient germanium detector with a full-width half-maximum (FWHM) resolution of 2.0 keV for the 1332 keV photon of the ^{60}Co. Fig. 1 shows the spectra for normal and Compton suppression after a thermal neutron irradiation.

For ePNT irradiations, the samples were irradiated in a cadmium-lined shield sequentially for 2 min at a neutron flux of ~2.25 × 10^{11} n cm^{-2} s^{-1}. After a decay period of about 30 min, the samples were counted for 1 h each with the exception for Si (see Table 1). A typical comparison of the four methods is shown in Fig. 2 for two elements — titanium and strontium.

For medium irradiations the sample wires were irradiated at the 3 element (3 L) site for 4 h at a neutron flux of ~2.25 × 10^{11} n cm^{-2} s^{-1}. After a decay period of about 4 days (for medium-lived radionuclides) and then again after 2 weeks (for long-lived radionuclides) the samples were counted again for 4 h each. Samples were counted using an automatic sample changer. Fig. 3 shows the spectra for a normal and Compton suppression after epithermal medium-lived NAA.

For long irradiations, samples were arranged in a rotary sample rack

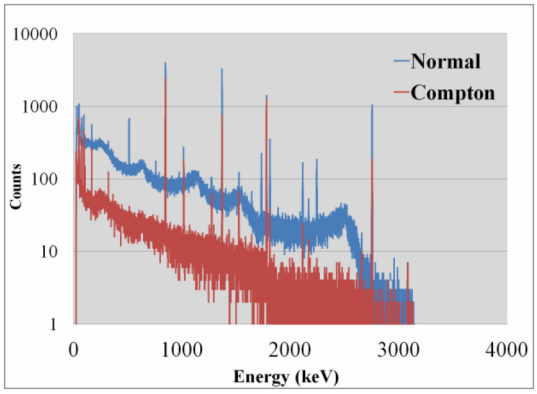

Fig. 1. Comparison of normal (upper) and Compton (lower) spectra for short-lived thermal NAA.

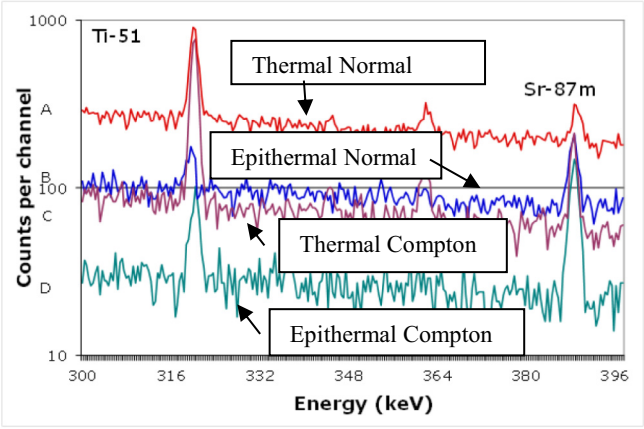

Fig. 2. Different NAA methods to determine titanium and strontium.

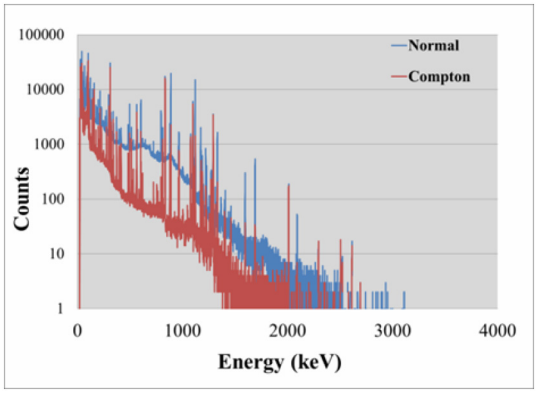

Fig. 3. Comparison of normal (upper) and Compton (lower) spectra for medium-lived epithermal NAA.

Table 1
Elements analyzed and corresponding irradiation and decay times.

Elements	Irradiation type	Count type	Irradiation time	Decay time	Count time
Al, Mn, Na, V	Thermal	Normal	60 s	15 min	10–15 m
Ti	Thermal	Compton	60 s	15 min	10–15 m
Ba, Dy, K, Si, Sr, U	Epithermal	Compton	120 s	10–30 min	15 min–1 h
As, Sb, Sm	Epithermal	Compton	4 h	4 d	4 h
Cs, Eu, Hf, Ni, Sc, Ta	Epithermal	Normal	4 h	2 w	4 h
Lu, Rb, Tb, Th, Zr, Zn, Ni,	Epithermal	Compton	4 h	2 w	4 h
Co, Fe, Yb	Thermal	Normal	4 h	2 w	4 h
Ce, Cr, Nd	Thermal	Compton	4 h	2 w	4 h