APPLICABILITY OF PROMPT GAMMA ACTIVATION ANALYSIS TO ARCHAEOMETRY OF POTTERY

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Abstract: *Based on our first experience, reported here, Prompt Gamma Activation Analysis (PGAA) is useful when applied to pottery archaeometry. PGAA is a non-destructive bulk analytical method, and able to determine concentrations of most major- and some trace components (B, Cl, Sc, V, Co, Cr, Nd, Sm, Eu and Gd). Selected objects from many geographical sites have been analysed with PGAA, XRF and INAA. The agreements between the PGAA and XRF data for all sites are good. In this paper, we give examples of our PGAA investigations on ancient ceramics. We also took part in a Proficiency Test – organized by the IAEA – on a Chinese porcelain reference sample.*
Keywords: *ceramics, major- and trace elements, non-destructive studies, PGAA*

INTRODUCTION

Starting from the Early Neolithic period, pottery production is one of the most important crafts of prehistoric communities. Pottery remains represent the most abundant part of the unearthed treasure from the Early Neolithic. In archaeometric studies, the key questions to be answered are the identification of raw material sources, workshops, technologies, and the separation of local products from imported ones.

In recent years, the importance of applied modern analytical techniques is continuously growing relative to traditional typological studies. Scientists seek to gain information regarding the material of the object, e.g. chemical (elemental, isotopic) composition, petrography, phase structure, etc., preferably with non-destructive tools.

Prompt Gamma Activation Analysis (PGAA), a nuclear method applicable for 'bulk' analysis of a few cm^3 material, is regarded to be absolutely non-destructive, and is an ideal tool to determine the average composition of ceramics. As addition to the well-known Instrumental Neutron Activation Analysis (INAA) and X-Ray Fluorescence Analysis (XRF), PGAA represents the last few years' advance in ceramics archaeometry.

EXPERIMENTAL

In this section we briefly summarize the basic features of PGAA, referring to an earlier publication by *Révay et al. 2004* for the details. Prompt Gamma Activation Analysis is based on the capture of thermal or cold neutrons into the atomic nucleus. In principle, the capture or (n,γ) reaction can take place on every atomic nucleus, although with different probabilities. It means that the sensitivities for different elements vary within a wide range. In many practical cases, like investigation of various volcanic- or sedimentary rocks, soils, glass or ceramics, we are able to quantify the major components and some important trace elements from a sample size of only a few hundred milligrams. Such trace components are B, Cl, Sc, V, Co, Cr and occasionally Ba.

The experimental station is located at the end of a horizontal guided beam of cold neutrons at the 10 MW Budapest Research Reactor. Following the upgrade of horizontal neutron guides in 2006, the thermal equivalent neutron flux is approximately 10^8 $cm^{-2}s^{-1}$ at the target position.

Samples of almost any dimensions and physical shape or form can be placed in the neutron beam which is collimated to a maximum area of 20 mm ×20 mm. If necessary, the beam size can be reduced to a few mm^2 spot. The most important advantage of PGAA is that it does not require any sampling or treatment of the object; various parts of larger objects can be investigated this way.

The characteristic prompt- and delayed gamma radiation is detected by a complex HPGe-BGO detector system. By careful analysis of the recorded γ-spectra, one can quantify the elemental composition of the sample. Since emitted gamma photons arrive from deeper layers of the irradiated part as well, only the average composition of the volume can be determined. One can not separately analyse the inhomogeneous parts lying within the beam dimensions. The element identification and quantitative calculation of the composition are based on our PGAA library (*Révay et al. 2001*).

Table 1 Comparison of PGAA vs. XRF data on Neolithic pottery samples from Szarvas, location Nr. 23. Major components are in wt%, trace elements in µg/g. The XRF measurements were done by Heinrich Taubald, Tübingen University.

	PGAA	XRF
SiO_2	73.2±0.5	71.9
TiO_2	0.81±0.02	0.77
Al_2O_3	12.1±0.3	11.9
Fe_2O_3	4.6±0.1	4.4
MnO	0.15±0.004	0.14
MgO	2.1±0.2	2.01
CaO	2.6±0.1	2.7
Na_2O	2.2±0.07	1.98
K_2O	2.1±0.05	1.95
Nd	39±4	33
Sm	4.1±0.1	5
V	97±14	87

Although other, more widespread, methods like XRF or INAA are able to identify a wider range of trace elements, PGAA is unique in being able to determine of some light elements, like hydrogen or boron. One of the most detectable trace component is boron, with a detection limit of approximately 0.1 µg/g; however, the geochemical importance of boron in the provenance of pottery has not been discussed in the literature yet. On the other hand, by measuring hydrogen content, one can obtain information regarding the firing conditions.

For a set of ceramic samples we have compared PGAA vs. XRF data for major components and traces identified with both methods. To demonstrate the reliability of PGAA we present the agreement between PGAA and XRF data for two samples from one particular location (Szarvas, locality Nr. 23). Since the two samples contained different amounts of volatile material, we have eliminated the 'Loss of Ignition' part from the composition. After renormalisation of the concentration values, we have found good agreement between the results from the two methods (**Table 1**).

In addition, we took part in a Proficiency Test organized by the International Atomic Energy Agency (IAEA), on a Chinese porcelain reference material that has resulted in the following outcome: all the components identified with PGAA agreed with the reported target values, except for Na, which we have quantified with a significant deviation from the target value (**Table 2**). A possible explanation of this deviation is the unlucky interference of the Na 472.2 keV prompt gamma line with the irregularly wide B 477.6 keV line (**Fig. 1**). This interference must be taken into consideration more carefully to get accurate sodium concentration data.

Table 2 Comparison of concentration 'target values' with the result of PGAA in an IAEA Proficiency Test. Major components are in wt%, trace elements in µg/g.

	PGAA	XRF
SiO_2	67.2±0.6	67.5±0.7
TiO_2	0.97±0.02	0.95±0.04
Al_2O_3	24.3±0.5	23.9±0.4
Fe_2O_3	2.7±0.07	2.7±0.1
MnO	0.029±0.001	0.026±0.001
CaO	0.74±0.04	0.62±0.05
Na_2O	0.56±0.02	0.44±0.02
K_2O	2.4±0.06	2.3±0.2
H_2O	0.83±0.02	-
B	84±1.5	-
Sc	18±3	14.9±2.5
V	148±13	107±6
Nd	65±5	51.9±7.2
Sm	6.5±0.2	8.7±1
Gd	7.2±0.3	-

INITIATED PROJECTS APPLYING PGAA ON ARCHAEOLOGICAL CERAMICS

Archaeometry of Neolithic pottery: a MÖB-DAAD project

In a co-operation between Tübingen University and the Hungarian National Museum, archaeological ceramics and geological samples from different Hungarian Neolithic sites and their geographical surroundings have been collected. The aim of this project was to compare the mineralogical, petrographic and geochemical composition of ceramics and local sediments, which are considered as potential raw materials for pottery making, in five selected localities: Vörs (SW-Hungary), Kup (W-Hungary), Szarvas-Endrőd (SE-Hungary), Aggtelek-Baradla (N-Hungary), Tiszaszőlős-Domaháza (E-Hungary). (*Taubald et al. in press*)

As a methodological aspect of the research, analytical data obtained by XRF, INAA and PGAA have been compared (see above). So far, 15 pottery fragments and 2 soil samples from Szarvas-Endrőd, as well as 11 pottery samples and 10 soil samples from Tiszalúc have been investigated with PGAA. The number of the analysed samples is still small; in the future, we plan to continue PGAA of selected Neolithic pottery samples.

The effect of firing on the composition of clay has also been investigated. Two pairs of clay samples before and after firing at 700 ºC were measured by PGAA. It has been shown that only the water content changes significantly during the firing procedure; the rest remains unchanged.

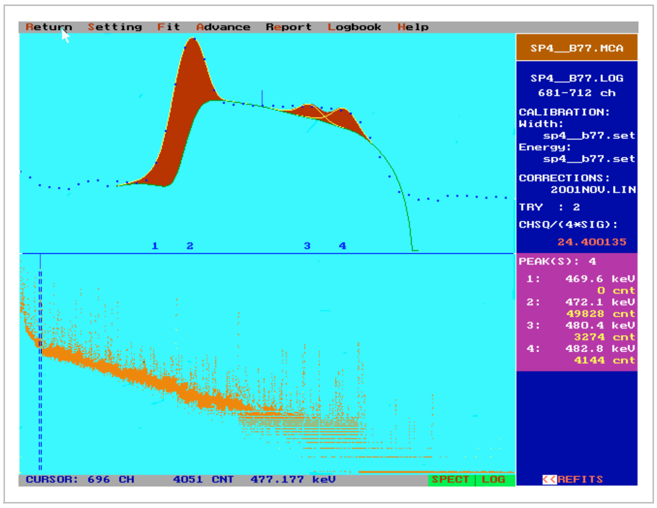

Fig. 1 Interference of the Na 472.2 keV prompt gamma line (line Nr. 2) with the broad B 477.6 keV prompt gamma line during spectrum evaluation

In the next step, we will design a series of controlled firing experiments in order to follow the change of the clay's composition under various conditions (i.e. maximum temperature, heating speed, the time kept on maximum temperature).

The link of the Otranto Byzantine kiln to the medieval ceramics production of the Salento region (Italy)

In this co-operation with the Physics Department of University of Rome TRE, we aimed to characterise archaeological ceramics from the 7th-9th centuries, as well as clay samples with the help of PGAA. The archaeological pottery samples were excavated close to Otranto in the Apulian region of Salento, which is known as one of the few Mediterranean production centres, which can be attributed to the early Medieval Ages. Remains of a Byzantine kiln have been found on the excavation site. The objectives of the research are twofold: to differentiate among the potential clay deposits, which can be found in the Salento, and to define more precisely the raw material used in the Otranto kiln.

Previous, Small Angle Neutron Scattering (SANS) experiments at KWS2, FZ Juelich Germany and Time Of Flight Neutron Diffraction (TOF-ND) experiments at ROTAX, ISIS, UK suggested that the transport amphorae as well as the domestic objects were fired at a relatively high temperature. However, the domestic pottery group shows a broader distribution than the amphorae, both in terms of maximum firing temperature and mineralogical content. This can be due to different methods to produce the amphorae and the domestic objects. (*Botti et al. 2006*). Thus, a more complete description of the production scenario of the kiln in Otranto must include possible correlations between the firing technology (SANS, TOF-ND) and the raw materials supply strategies (PGAA) used in producing the two main classes of pottery: the transport amphorae and the tableware. These currently ongoing investigations will be published soon.

Provenance Study of Pre-Columbian Ceramics Figurines from Venezuela

In a co-operation with the Simón Bolívar University, Caracas, we have investigated fragments of Pre-Columbian figurines, produced between the 12th and 15th centuries. The archaeological pieces have been excavated in the Lake Valencia Basin (north-central Venezuela mainland) and in the Los Roques Archipelago, 140 km off the coast, where the Valencioid sites have been located on six islands. It was asked whether the occupants of the islands used local raw material for pottery production or they imported clay from the continental area. To give an answer, we have analysed 20 figurine fragments from Lake Valencia Basin, 21 figurine fragments from Los Roques and 9 soil samples from Lake Valencia Basin area with PGAA.

Several mass ratios were calculated, and bivariate diagrams were constructed aiming at classifying the objects. In addition to the characteristic elemental ratios, Principal Component Analysis (PCA) was applied to the standardised data, in order to find groups of similar elemental composition. (**Fig. 2**)

Based on PCA of all the measured samples, we found that the ceramics samples from the Lake Valencia Basin are significantly different from those from the Los Roques Islands. However, there is an overlapping between the two groups, (**Fig. 3**) (*Kasztovszky & Sajo-Bohus 2003, Kasztovszky et al. 2004*). It seems that in this case with the PGAA alone we are not able to answer to the question of provenance. In order to explain the overlapping of the two groups we probably need to seek for other characteristic chemical components, on the basis of complementary methods.

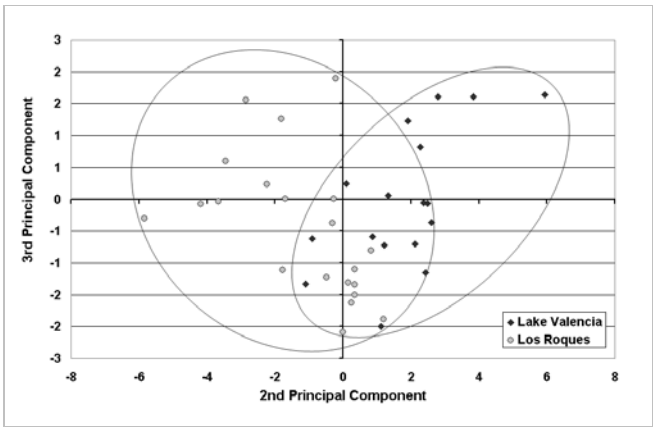

Fig. 2 Principal Component Analysis on the PGAA data set of Venezuelan ceramic figurines

FINAL REMARKS

On the basis of our projects on archaeological ceramics, PGAA, as an absolutely non-destructive 'bulk' analytical tool can play a key role, since it is able to determine all major- and some trace components, including boron. The most significant advantage of PGAA is that the analysis does not require any sample preparation. On the other hand, it is less sensitive for many of the characteristic trace elements than INAA or XRF. Consequently, the best approach is to combine the application of several analytical methods.

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