APPLICATION OF PROMPT GAMMA ACTIVATION ANALYSIS TO INVESTIGATE ARCHAEOLOGICAL CERAMICS

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Kivonat

A PGAA alkalmazhatóságát a kerámiák archeometriájában korábban Kolumbus előtti venezuelai szobrok vizsgálata során igazoltuk. A PGAA – mint roncsolásmentes "tömbi" módszer – jól használható a kerámiák összes fő- és néhány nyomelemének mennyiségi meghatározására. Osztályunk részt vesz a magyarországi neolit kerámia lelőhelyek felmérését célzó MÖB-DAAD együttműködésben, valamint egy inkább módszertani jellegű IAEA "Coordinated Research Project"-ben .

A MÖB-DAAD projekt keretében különböző magyarországi területekről származó kerámia töredékeket és talajmintákat elemeztünk PGAA-módszerrel. A leletek a Szarvas-Endrőd korai neolit és Tiszalúc térségében feltárt rézkori településekről származnak. Eddig Tiszalúcról 11 kerámia- és 10 talajmintát, Szarvas-Endrődről pedig 15 kerámia- és 2 talajmintát mértünk. Eredményeink szerint a mintákban meghatározhatók a fő összetevők és a nyomelemek közül a B, Cl, Sc, V, Co, Cr, Nd, Sm, Eu és Gd. A PGAA-val vizsgált minták többségét röntgen-fluoreszcens analízissel (XRF) és hagyományos neutronaktivációs analízissel (INAA) is elemezték. Előzetes eredményeink szerint a PGAA és az XRF eredmények jól egyeznek a közösen mérhető elemekre. Bár az XRF érzékenysége a legtöbb kémiai elemre jobb, a PGAA-módszer egyedi lehetőséget nyújt a bór- (B) és a hidrogén- ill. a víztartalom meghatározására. PGAA-val vizsgáltuk a kiégetés hatását az agyag összetételére. Két pár agyagminta összetételét mértük 700 ºC-on történt kiégetés előtt és után. Eredményeink szerint az égetés csak a minta víztartalmát változtatja számottevően, a többi PGAA-val kimutatható összetevőben nem észlelhető változás.

Részt vettünk az IAEA által szervezett laborok közötti összemérésben, melynek során egy kínai porcelán referenciamintát elemeztünk PGAA-módszerrel. Az összemérés eredménye szerint a PGAA-val meghatározott koncentráció értékek a legtöbb esetben jól egyeznek a névleges adatokkal.

Abstract

Applicability of PGAA on pottery archaeometry has been proved in investigations of pre-Columbian figurines from Venezuela. PGAA is a non-destructive bulk analytical method, capable to determine concentration of major- and some trace components. We take part in the MÖB-DAAD project aimed to investigate Hungarian Neolithic pottery, and also in an IAEA CRP with more methodological objectives.

Within the frame of the MÖB-DAAD project, we have analysed pottery fragments and soil samples with PGAA. The pieces have been previously excavated on Neolithic settlements of Szarvas-Endrőd and Tiszalúc region (South-East Hungary and North-East Hungary, respectively). Until now, 11 pottery fragments and 10 soil samples from Tiszalúc site; as well as 15 pottery fragments and 2 soil samples from Szarvas-Endrőd site have been measured. According to our previous experiences on ancient pottery, we are able to determine the major components (SiO_2, TiO_2 Al_2O_3, Fe_2O_3 MnO MgO CaO Na_2O and K_2O) of the bulk material. In most cases, also some accessory- and trace element concentrations, like B, Cl, Sc, V, Co, Cr, Nd, Sm, Eu and Gd can be determined. Most of the investigated objects have already been analysed with XRF and INAA too. According to our preliminary results, the agreement between the PGAA and XRF data for the common elements are good. Although XRF exhibit a better sensitivity for most components, PGAA provides the additional possibility to determine the concentration of B and H_2O.

The effect of firing on the composition of clay has been investigated, too. 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 firing procedure, the rest remain unchanged.

We took part in a Proficiency Test – organized by the IAEA – on Chinese porcelain reference sample that has resulted in the following outcome: Most of the identified components with PGAA agreed with the reported target values.

KULCSSZAVAK: KERÁMIA, FŐ- ÉS NYOMELEMEK, RONCSOLÁSMENTES VIZSGÁLAT, PGAA

KEYWORDS: CERAMICS, MAJOR- AND TRACE ELEMENTS, NON-DESTRUCTIVE STUDIES, PGAA

Introduction

From the Early Neolithic period, pottery production is one of the most important crafts of the prehistoric communities. Furthermore, the most abundant part of the unearthed treasure is represented by remains of pottery goods. The key questions to be answered are the characterisation of raw material sources, the separation of local products from import ones, as well as identification of workshops or production technologies.

In recent archaeology research, besides traditional typology studies, the importance of applied modern analytical techniques is continuously growing. To answer the key questions, scientist must gain information regarding the material of the object, e.g. chemical (elemental, isotopic) composition, petrography, phase structure, etc. Obviously, all of these investigations must preserve the integrity of the object, if possible.

Prompt Gamma Activation Analysis (PGAA), as a nuclear method applicable for 'bulk' analysis of a few cm^3 material, can be regarded absolutely non-destructive, and is an ideal tool to determine the average composition of ceramics. While Instrumental Neutron Activation Analysis (INAA) and X-Ray Fluorescence Analysis (XRF) are routinely applied for decades, development of PGAA in ceramics archaeometry represents the last few years' achievements.

Experimental

Since it has been described in more details somewhere else (Révay et al. 2004), we would like to mention only the basic features of PGAA. Prompt Gamma Activation Analysis is based on the capture of thermal or cold neutrons into the atomic nucleus. The experimental station is planted on one horizontal guided beam of cold neutrons at the 10 MW Budapest Research Reactor. After the upgrade of horizontal neutron guides in 2006, the current thermal equivalent neutron flux at the target position is approximately 10^8 $cm^{-2}s^{-1}$.

Samples of almost any dimensions and of physical forms can be placed in the neutron beam that is collimated to a 2×2 cm^2 diameter or smaller. 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 the whole region of the irradiated part, only the average composition of the volume is possible to determine, and we can not analyse the inhomogeneous parts separately within the beam dimensions. The correct element identification and quantitative determination of the composition are based on our PGAA library (Révay et al. 2001).

In principle, every atomic nucleus can undergo the (n,γ) reaction, although the probability of the reaction, i.e. the sensitivities for each elements varies within a wide range. In 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 minimum amount of a few hundred milligrams. Such trace components are B, Cl, Sc, V, Co, Cr and occassionally Ba.

Although other, more widespread methods, like XRF or INAA are able to identify a wider range of trace elements, PGAA is unique in determination of some light elements, like hydrogen or boron. Furthermore, 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.

One most detectable trace component is boron with a detection limit of approximately 0.1 μg/g; geochemical importance of boron in provenance of pottery requires further study. By measuring hydrogen content, on the other hand, one can obtain information regarding the firing conditions.

For a set of ceramics samples, PGAA vs. XRF results on the same material have been compared. For demonstration of the PGAA reliabilty, we show the agreement between PGAA and XRF data of one particular sample (Szarvas, locality Nr. 23). Since the two samples contained different amount of volatile material, the 'Loss on Ignation' parts were eliminated from the composition. After renormalisation of concentrations, we have found good agreement between the results from the two methods; see ***Fig. 1*** and ***Table 1***.

	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

Table 1.

Comparison of PGAA vs. XRF data on a Neolithic pottery 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.

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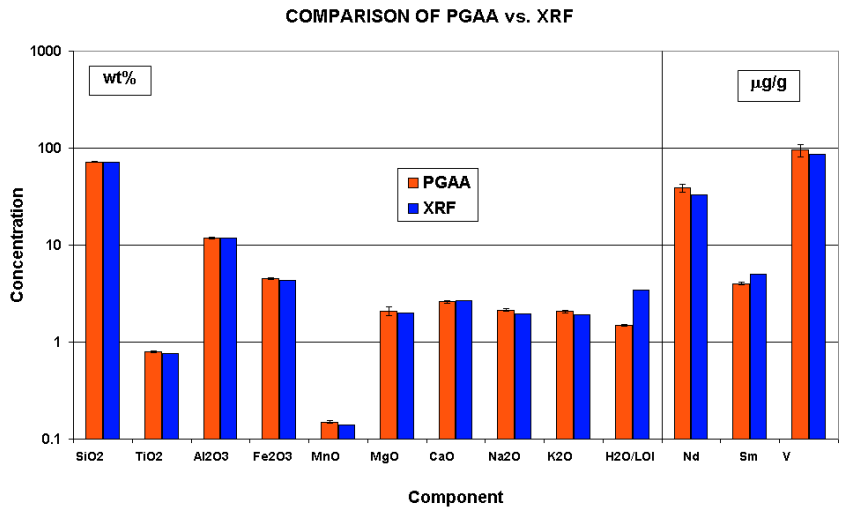

Fig. 1.

Comparison of PGAA and XRF results on a Neolithic pottery from Szarvas, location Nr. 23. The XRF measurements were done by Heinrich Taubald, Tübingen University. The concentration values are in logaritmic scale, with the error bars, where applicable.

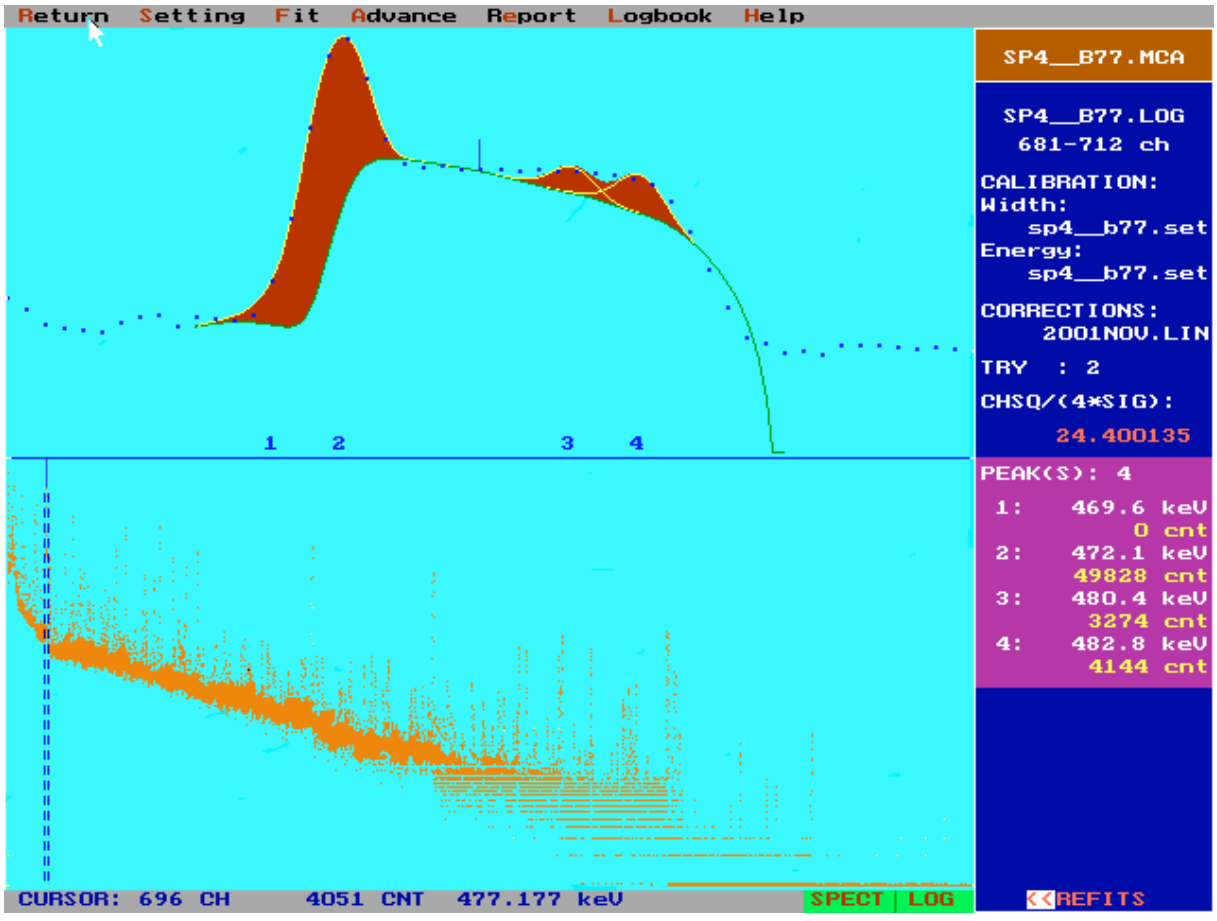

Fig 2.

Interference of the Na 472.2 keV prompt gamma line with the B 477.6 keV prompt gamma line during spectrum evaluation.

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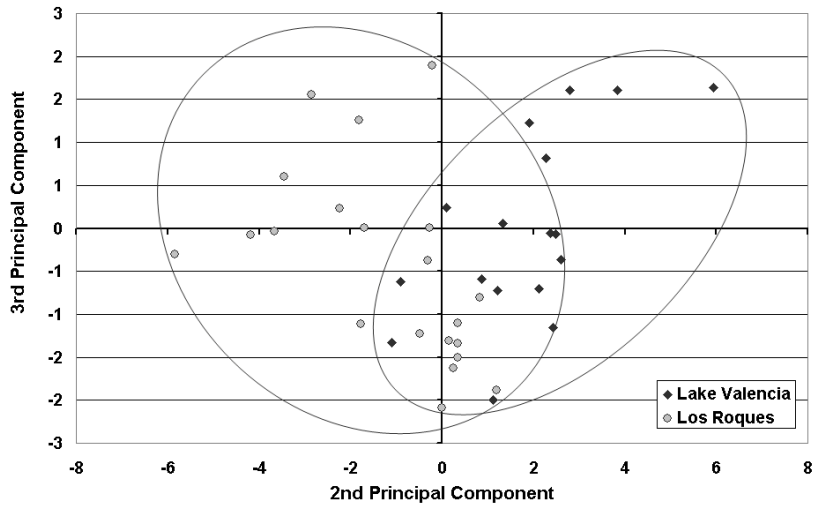

Fig 3.

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

Table 2.

Comparison of concentration 'target values' with the result of PGAA in an IAEA Proficiancy 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	-

In addition, we took part in a Proficiency Test, organized by the International Atomic Energy Agency (IAEA), on Chinese porcelain reference material that has resulted in the following outcome: all the identified components with PGAA agreed with the reported target values, excluding Na, which we have quantified with a significant deviation from the target value, see ***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, see ***Fig 2***. This interference must be taken into correction more carefully to get the precise sodium concentration data.

Initiated projects applying PGAA on archaeological ceramics

Investigation of Pre-Columbian Ceramics Figurines from Venezuela

In 2002 we have initiated an ad hoc co-operation with the Simón Bolívar University, Caracas. We have investigated fragments of Pre-Columbian figurines, produced in the 12-15th Century. The archaeological pieces have been excavated in Lake Valencia Basin (north-central Venezuela mainland) and in the Los Roques Archipelago, 140 km away from the mainland coast, where the Valencioid sites have been located on six islands. The main question was whether the occupants of the islands used local raw material for pottery production, or they imported clay from the continental area. We attempted to give an answer by PGAA of 20 figurine fragments from Lake Valencia Basin, 21 figurine fragments from Los Roques and 9 soil samples from Lake Valencia Basin area.

In order to classify the objects, several mass ratios were calculated, and from those, which show significant classification of the objects, bivariate diagrams were constructed. In addition to the characteristic elemental ratios, Principal Component Analysis (PCA) was applied to the standardised data, in order to seek patterns of distribution of the samples within the compositional space.

According to PCA of all the measured samples, the ceramics samples, which were excavated in Lake Valencia Basin are significantly different from those, which were excavated in the Los Roques Islands. However, there is an overlapping between

the two groups, see ***Fig 3***. (Kasztovszky & Sajo-Bohus 2003, Kasztovszky et al. 2004)

Archaeometrical analysis of Neolithic pottery: a MÖB-DAAD project

Between 2005 and 2006, in a co-operation between Tübingen University and the Hungarian National Museum, archaeological ceramics and geological samples from different Neolithic and Copper Age excavation sites and their geographical surroundings have been collected. All sites are located in Hungary and have abundant scientific evidences. The aim of this project was to compare the mineralogical, petrological and geochemical composition of ceramics and local sediments, which are considered as potential raw materials for pottery making, in nine selected localities: Vörs (SW-Hungary), Kup (W-Hungary), Szarvas-Endrőd (SE-Hungary), Aggtelek-Baradla (N-Hungary), Borsod-Derekegyháza (NE-Hungary), Tiszaszőlős-Domaháza (E-Hungary), Füzesabony-Gubakút (N-Hungary), Tihanyapáti (W-Hungary) and Tiszalúc (NE-Hungary) (Taubald et al. in press).

As a methodological aspect of the research, analytical data obtained by XRF, INAA and PGAA have been compared. So far, 15 Neolithic pottery fragments and 2 soil samples from Szarvas-Endrőd, as well as 11 Copper Age pottery samples and 10 soil samples from Tiszalúc have been investigated with PGAA.

Although the number of samples is small yet, averaging the pottery vs. soil compositions suggests that pottery contains significantly higher amount of Cl and B, and lower amount of Mn what has to be explained.

The effect of firing on the composition of clay has been investigated, too. 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 firing procedure, the rest remain unchanged.

In the future, we would like to continue PGAA of selected Neolithic pottery samples. Additionally, we design a controlled firing experiment 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 recently starting co-operation with the Physics Department of University of Rome TRE, we wish to characterise archaeological ceramics from 7^{th}-9^{th} century, as well as clay samples with PGAA. The archaeological pottery samples were excavated close to Otranto in the Apulian region of Salento, one of the few Mediterranean production centres which can be attributed to the early Middle Ages. One of two stratified structures includes the remains of a Byzantine kiln. The proposed experiment aims at addressing two main issues: the attribution of the pottery finds to the Otranto kiln and a possible differentiation in the selection of the raw clay material.

Small Angle Neutron Scattering (SANS) experiments at KWS2, FZ Juelich Germany and Time Of Flight Neutron Diffraction (TOF-ND) experiments at ROTAX, ISIS, UK suggest a scenario where the transport amphorae as well as the domestic objects were fired at relatively high temperature of about 900-1000 ºC. Although the last sample group shows a broader distribution in terms of mineralogical content. This can be due to a different procedure used in the production of the amphorae and the domestic objects. (Botti et al. 2006)

The existing analysis results do not allow us to confirm the chosen groupings of the ceramic fragments which can only be achieved by determining the main and trace elements in the samples.

Final remarks

Although typological descriptions and petrographic studies of archaeological ceramics still remain the most important research tools, various kinds of analytical techniques gain more and more importance in archaeometry.

PGAA, as an absolutely non-destructive 'bulk' method, can be of a key role, since it is applicable to determine all major- and some trace components, including boron. The most significant feature of PGAA is that the analysis does not require any sample preparation, but on the other hand, it is less sensitive for a series of characteristic trace elements, than INAA or XRF. Consequently, the best approach is to combine the application of more analytical methods.

We have to remember that ceramics must be regarded as composite material with inhomogeneous distribution of matrix, temper, pores and often glaze on the surface. Therefore, other complementary methods, like PIXE or ICP-MS are also recommended.

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