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HIGH-FLUX PROMPT GAMMA ACTIVATION ANALYSIS BASED TECHNIQUES FOR NON-DESTRUCTIVE ELEMENTAL ANALYSIS OF CULTURAL HERITAGE OBJECTS

Introduction to PGAA

Standard PGAA

PGAA is a younger sister of the Neutron Activation Analysis (NAA) being used efficiently since the 1970s. When performing NAA (proposed already in 1936 by G. Hevesy and H. Levi), objects are immersed into a neutron field close to a neutron source (usually a position in a moderator tank of a research reactor) for a given time. After transferring the sample to a well-shielded gamma-ray detector, the delayed gamma rays characteristic to individual elements are detected. First, the short-lived isotopes are identified (few minutes); then, the sample is left for some time to let these short-term signals decay completely. After that time, the isotopes with about hours of decay time are identified in another data acquisition round. Next, a few days of decay are required to start the usually last data acquisition for the long-term isotope identification and quantification. This acquisition can run up to days until a sufficient counting statistics is achieved. NAA is certainly one of the best non-destructive methods for trace element analysis.

The dif ference of the PGAA technique compared to NAA is the simultaneous irradiation of the sample by thermal or cold neutrons (the colder the neutron energy, the better the probability of the neutron being captured by the target nuclei) and the detection of prompt gamma rays by a high-purity germanium detector (HPGe). Its disadvantage compared to NAA is that neutrons are flying around the target during the gamma ray detection, resulting in a much higher spectral background – hence, the detection limits of traditional NAA are for the most elements unbeatable.

However, two advantages also exist: 1) The results are immediate; already during irradiation the major

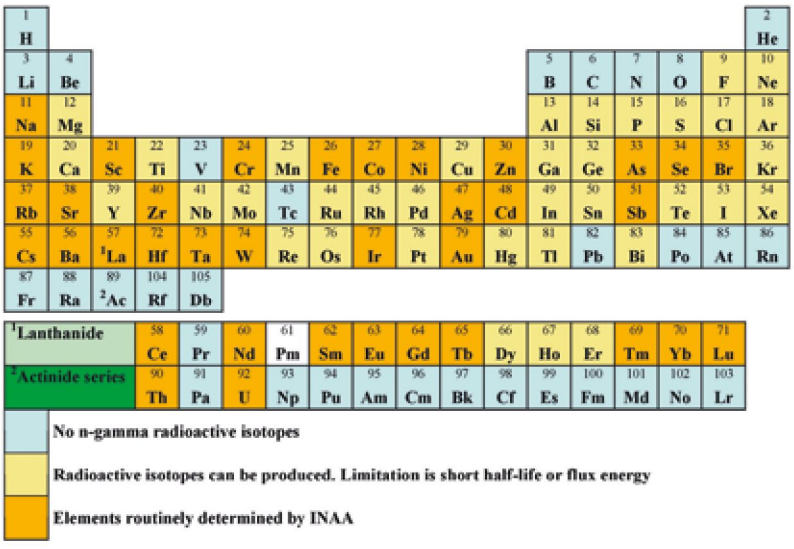

Fig. 1 Table of elements detectable with the Instrumental Neutron Activation Analysis (INAA). – (Courtesy of N. Eby [2007]).

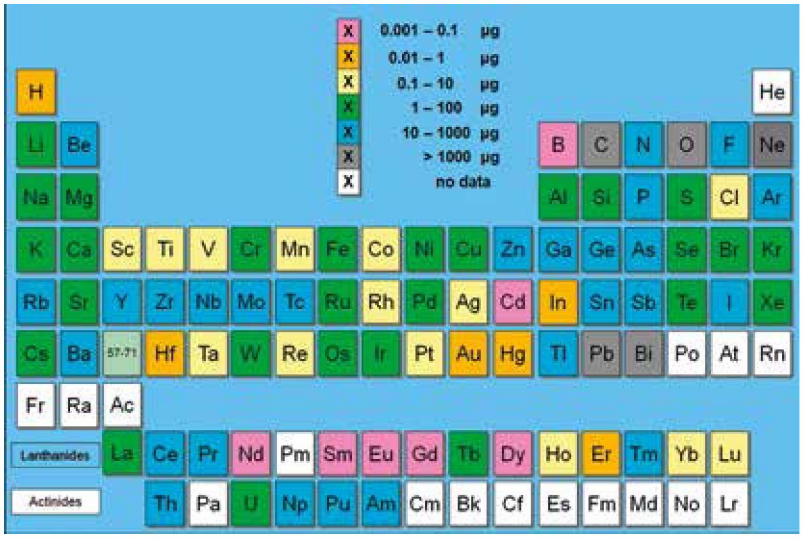

Fig. 2 Overview of elements detectable with PGAA and expected detection limit range. – (© by the authors).

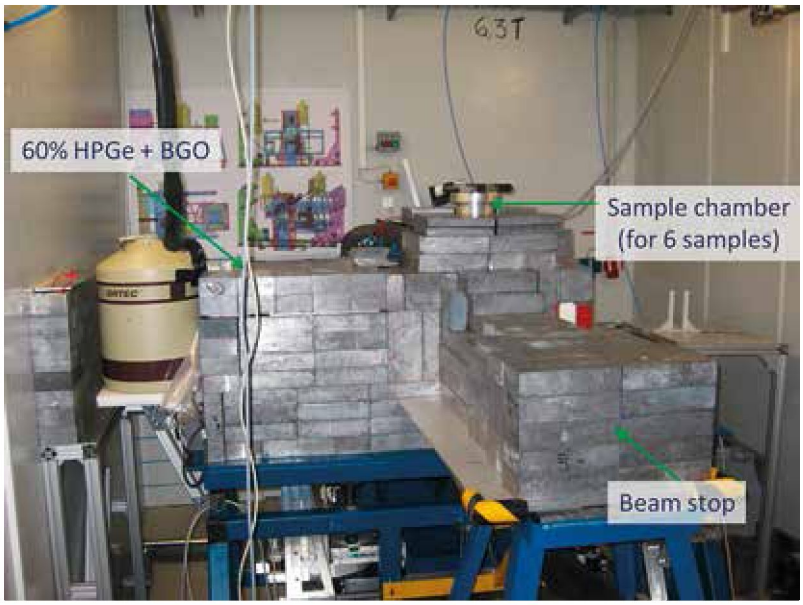

Fig. 3 PGAA instrument in a concrete bunker heavily shielded by lead to minimize the background signal. – (© by the authors).

and minor elements are revealed qualitatively. For quantitative analysis, about 30 min-6 h irradiation of an object is necessary together with a spectrum fitting procedure – e. g. in HyPC (Revay et al. 2001; HyPC 2014) and subsequent elemental analysis e. g. with ProSpeRo (Revay 2009); 2) NAA cannot »see« well or at all light elements like H, Li, B, C or N. Pb cannot be determined by NAA either (**fig. 1**). For these elements, PGAA is a complementary method to NAA (**fig. 2**). PGAA can be regarded as a trace-element technique for a few selected elements like: H, B, Cd, In, Hf, Hg, Sm, Eu, Gd, Dy or Er. Even Cl can be detected in a range of 10 ppm. A thorough description of the PGAA method is summarized in (Molnár 2004).

PGAA instrument at MLZ

The PGAA instrument (**fig. 3**) at the research reactor FRM II of the Heinz Maier-Leibnitz Zentrum (MLZ) in Garching is located at the end of about 50 m long curved neutron guide and offers the highest neutron flux reported at large facilities with up to $6 \times 10^{10}\,cm^{-2}\,s^{-1}$ thermal equivalent. Thus, objects with masses less than 1 mg can be analysed in rea-

sonable times (irradiation less than 12 h). The high flux can be reduced if necessary (e. g. for larger samples) down to about $1 \times 10^8\,cm^{-2}\,s^{-1}$ th. eq. to keep an optimum gamma-ray count rate at the detector (not to saturate it). Six objects can be measured in one batch; they are fixed with PTFE strings at a PTFE ladder (**fig. 4**) and positioned inside of the sample chamber, which can be evacuated. PTFE material consists only of the elements carbon and fluorine. Both elements have very low neutron capture cross section to keep the additional (but inevitable) background-to-signal ratio as low as possible. The schematic floor view of the PGAA instrument is shown in **figure 5**. For detecting the characteristic gamma rays, a high-purity germanium detector (HPGe) is introduced perpendicularly to the neutron beam direction and collimated by a heavy lead shielding to only see the irradiated object. The detector is shielded against neutrons by boron- and ^{6}Li-containing materials, which are both very strong neutron absorbers. Gamma rays are blocked from the detector by thick lead walls. In this way, the background signal is strongly reduced. The next step in reducing the background – which otherwise increases the detection limits of the PGAA technique for all elements – is achieved by using an active shielding in form of a scintillator surrounding the HPGe detector. Both detectors are electronically connected in anti-coincidence mode and reject each signal detected simultaneously (so-called Compton suppression). A typical spectrum acquired by our Compton-suppressed HPGe detector is presented in **figure 6**.

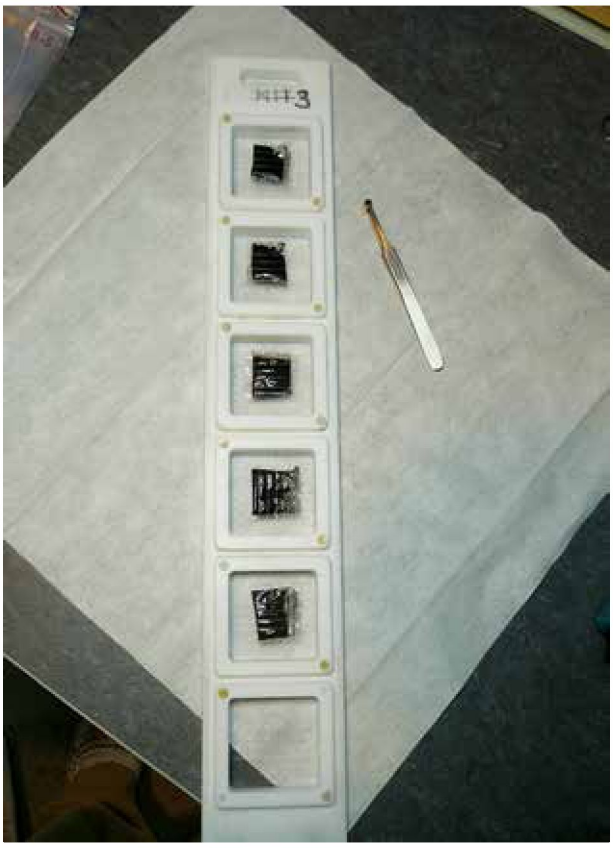

Fig. 4 PGAA sample ladder made of FTPE can accommodate up to six samples measured automatically in one batch in possibly evacuated sample chamber. Five homogenized clay crucible samples (see **fig. 7**) are sealed in FTPE foil here. – (© by the authors).

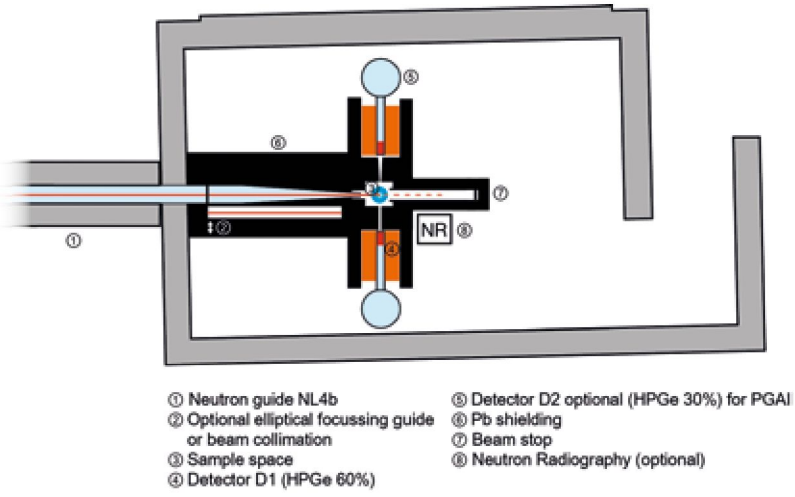

Fig. 5 Floor view of the PGAA instrument with the exchangeable units for PGAI and neutron imaging. – (© by the authors).

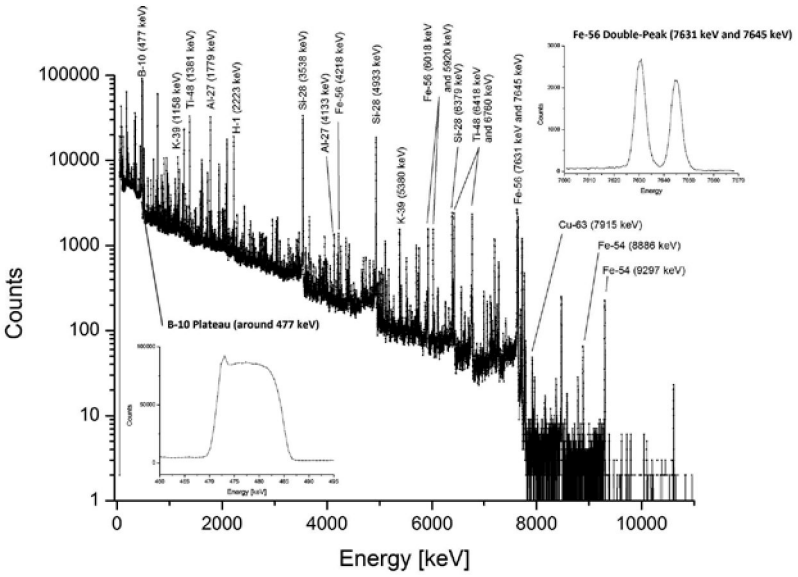

Fig. 6 A typical PGAA spectrum. Here an example of one clay crucible sample presented in fig. 4. – (© by the authors).

Fig. 7 **a** intact clay crucibles found near Preslav, Bulgary. – **b** some broken clay crucible pieces from Nadarevo near Preslav were homogenized and measured with the PGAA technique. – (© by the authors).

Examples for standard PGAA measurements

Provenance study on clay crucibles in Shumen region, Bulgaria

Very often the provenance and trade routes in ancient times are questioned (Zöldföldi et al. 2006). At MLZ a similar project ran in 2013 (Kudejova et al. 2014). Three new metal centers were discovered near Preslav, the former capital of Bulgaria (Doncheva et al. 2013). Not only metal objects were discovered, but also clay crucibles (fig. 7a-b). The local archaeologists raised the question of provenance of these crucibles – if they were imported or made by local people. To answer this question, 30 crucibles and 10 soil samples from local clay mines were measured by PGAA for major, minor and trace elements. After a thorough analysis, it was confirmed that the crucibles were fabricated locally.

Chlorine in archaeological iron artefacts

PGAA is a suitable tool for the analysis of trace amounts of chlorine. In case of archaeological iron objects, the detection limit for chlorine is around 10 ppm. So, PGAA helps to answer the question connecting the corrosion of iron objects after excavation with the amount of chlorine located on/in its rough surface (Watkinson et al. 2014; Wagner et al. 2014). Two long-term projects are currently running at MLZ with the aim of understanding the corrosion mechanisms and to help preserving the valuable object by special treatments (Gebhard et al. in prep. and follow-up project to Schmutzler 2012). The chlorine amount in excavated samples is measured first (**fig. 8**) and then, the same objects are measured after the conservation procedure (e. g. leaching in alkaline solutions, heat-treatment, etc.). Hundreds of samples were already investigated at the PGAA instrument at MLZ. Here, the high-intensity neutron flux significantly reduces the irradiation time while keeping the detection limit for chlorine as low as possible.

Fig. 8 Roman nails from 2nd-3rd century excavated in Güglingen, Germany, analysed for the chlorine content before desalination treatment. – (© by the authors).

Safety issues

Before every experiment, all samples have to be registered in a sample tracking system at FRM II. The parameters concerning each sample (including the expected elemental composition) must be entered by the user and a possible neutron activation of each sample is then calculated based on the entered data. These data are discussed with the user prior to every measurement to ensure that all samples can leave the facility in a reasonable time (up to one month). There are only few problematic elements, which can delay the radiation clearance of the object because of its residual activity: cobalt, silver and large amounts of copper or zinc.

Valuable cultural heritage objects are usually handled by couriers of the museum or the collection exclusively in every step of the measurement procedure at MLZ as well as during any local transportation. Special sample holders must be discussed and produced before the experiment, as described e. g. by Kudejova (2008). After the measurement, as a rule, every object leaving the experimental place in the controlled area has to be checked by the radiation protection office for residual activity. Prior to this clearance check, valuable objects are deposited in a transport box by the courier and the radiation protection staff handles the box (or case) only. Less valuable objects are carefully handled by local staff according to the standard procedures until radiation protection clearance is given.

Advanced PGAA-based techniques

Most of the cultural-heritage objects can be well measured with standard PGAA described above. However, the high intensity of the neutron flux allows performing more complex or complementary measurements.

In-Beam NAA

The intense neutron flux at the PGAA instrument is almost comparable to activation fluxes in the reactor cores of small reactors. However, the neutron spectrum is much »cleaner« concerning the epithermal

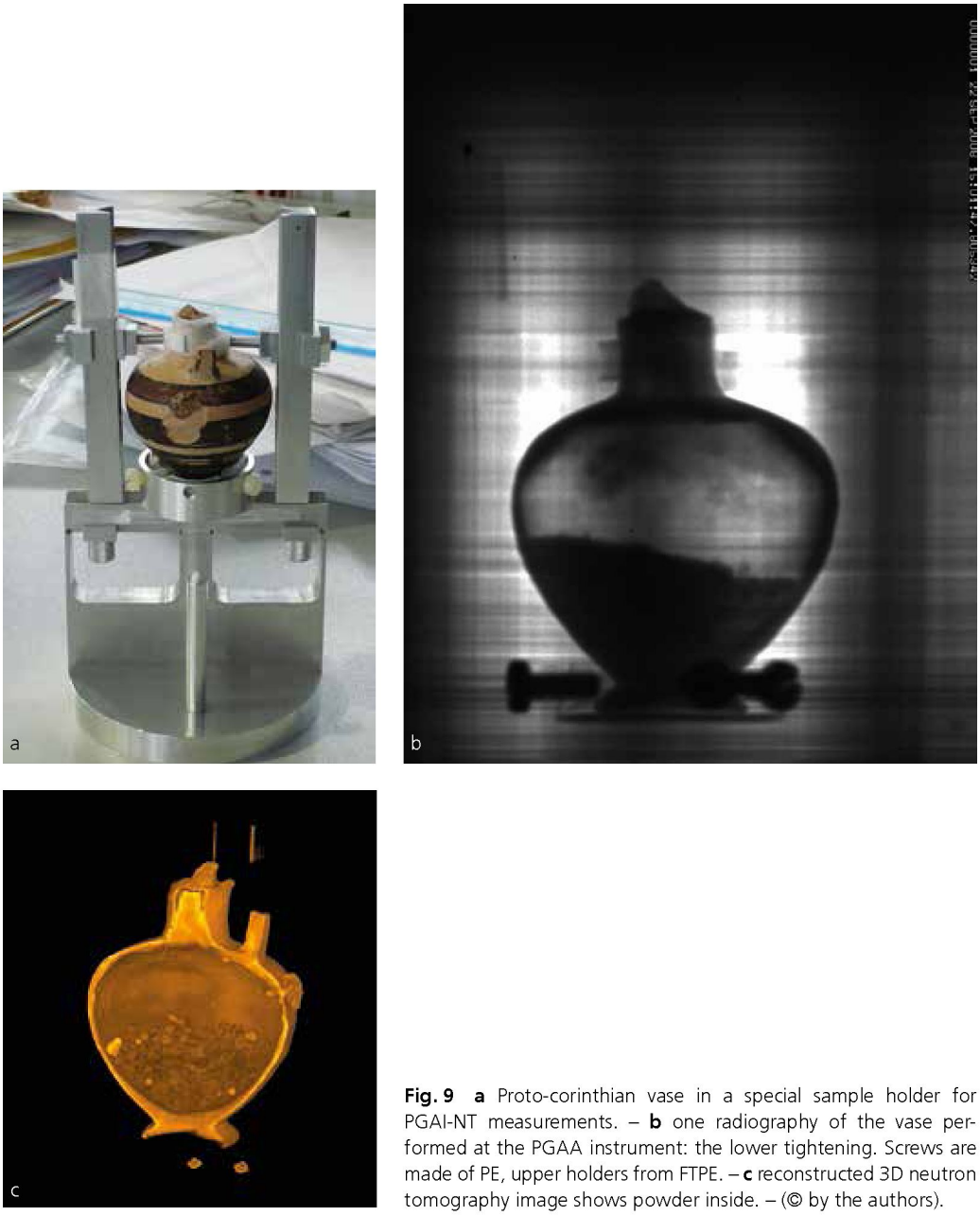

Fig. 9 **a** Proto-corinthian vase in a special sample holder for PGAI-NT measurements. – **b** one radiography of the vase performed at the PGAA instrument: the lower tightening. Screws are made of PE, upper holders from FTPE. – **c** reconstructed 3D neutron tomography image shows powder inside. – (© by the authors).

part of the neutron spectrum. Neutron Activation Analysis can be performed directly after the PGAA measurement by switching off the beam and counting the sample activation immediately or by bringing the sample to our new low-background counting chamber next to the PGAA instrument – providing higher efficiency and lower background signal (Revay et al. 2015). The transport time takes not more than 60 s – fast decaying isotopes like ^{28}Al (2.2 min) can be detected as well and with better detection limit than directly with PGAA.

PGAI-NT

Prompt Gamma Activation Imaging combined by Neutron Tomography (PGAI-NT) is a position sensitive method revealing the composition of the object on spots of interest (Belgya et al. 2008a; 2008b; Schulze et al. 2013). First, a standard neutron tomography of the object is performed and the 3D structure is visualised (Schillinger, this volume; Kardjilov et al. 2006). Then the neutron flux is collimated to a pencil beam of e. g. 2 × 2 mm^2, and the

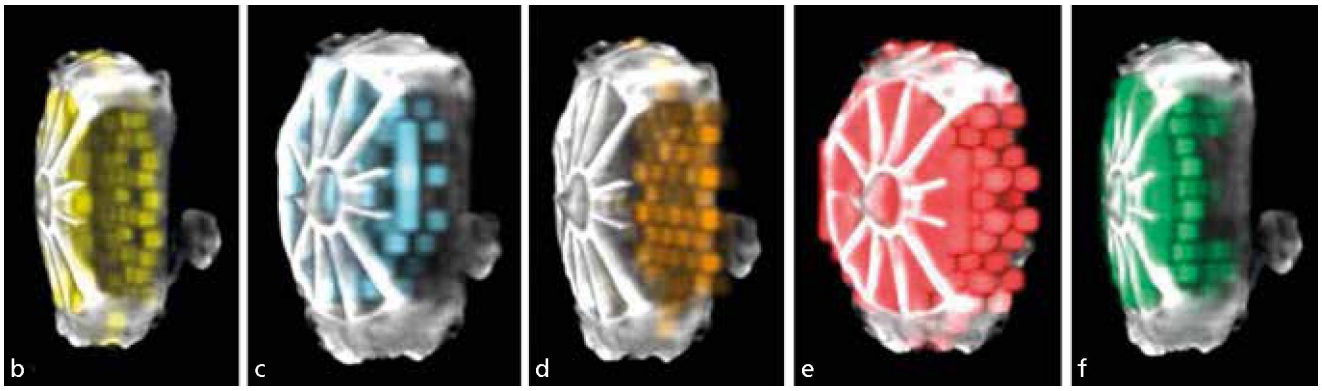

Fig. 10 **a** German disc fibula (25 mm in diameter). – **b-f** distribution of following elements in the fibula: b gold; c silver; d copper; e iron; f sulfur, measured by PGAI and merged with the neutron tomography 3D image. – (After Schulze et al. 2013).

HPGe detector is strongly collimated to a slit of $2 \times 10\,mm^2$. In this way, an irradiated volume of about $2 \times 2 \times 2\,mm^3$ (so-called voxel) is visible to the detector. Using the tomography's 3D image for PGAI navigation, we scan the object point by point to produce the 3D elemental map of it. Since the scanning by PGAI is very time consuming, a high-intensity neutron flux is essential. Usually only selected inner parts of the object are scanned.

Proto-Corinthian vase

An ancient Greek vase of Proto-Corinthian style (ca. 600 BC) with the height of about 6 cm found near Cerveteri, Italy, was investigated for its sealed content. A special sample holder was created for the valuable object (**fig. 9a**). Then a set of neutron radiography measurements was performed (**fig. 9b**) at the PGAA instrument and a 3D tomography image was reconstructed (**fig. 9c**). Finally, the neutron beam was collimated to a pencil beam of $2.3 \times 2.3\,mm^2$ and the unknown inner content was irradiated for 90 min for the PGAA analysis. The elemental analysis of the ceramic vase wall was performed later with the same conditions (90 min, pencil beam) for comparison (Schulze 2010). A qualitative analysis was performed only for the major components of the sealed powder, which are: Ca, K, H, Mn and Fe. It is assumed that the powder was some ancient cosmetics.

Disc fibula

A German disc fibula with gold lining and almandine inlays from the 6th century was excavated at an ancient cemetery in Kölked-Feketekapu, Hungary (**fig. 10a**). This object of about 25 mm in diameter was chosen for a thorough 3D scan of its internal structure elements. Again, the neutron tomography was performed at first. Since the fibula was expected

Fig. 11 Bronze relief by Lorenzo Ghiberti in a sample holder for tangential irradiation for PGAA. – (© by the authors).

to be symmetrical and the PGAI measurements were time consuming, only one quarter of it was scanned (Schulze et al. 2013). Three layers were scanned into the depths of the fibula to differentiate the elemental composition of the front surface, the filling and the rear part respectively. The results are presented in figure 10b-f.

Surface analysis

In a special case of a large bronze object, only the surface layer of about 1 mm was of interest for the conservators. Typical non-destructive surface methods like XRF or PIXE cannot analyse such thick layers, only surface layers of maximum 30 µm are possible. Two independent methods – laser ablation cleaning and Rochelle salt cleaning – were used to clean the deposited layer caused by air-pollution on one of the gilded bronze relief by Lorenzo Ghiberti (Festa et al. 2009). The collimated neutron beam, as described in the previous paragraph, was used, but only the surface of the bronze head was tangentially touched by the neutron beam (fig. 11). The most important task was to determine the chlorine signal measured in all three regions of the bronze head. According to the PGAA results, only the part cleaned by Rochelle salt was below the detection limit of PGAA, compared to the part cleaned by laser ablation, which still contained detectable trace concentrations of chlorine next to the expected elements Cu, Au and Hg.

Conclusions

PGAA offers archaeologists and restorers the elemental composition of valuable objects non-destructively and in the whole volume of the object. The measurement as well as the analysis can be very fast (within one day). Major, minor components and some trace elements can be identified and quantified. The high-intensity cold neutron flux available at MLZ shortens the irradiation time and offers other investigative methods based on PGAA: if necessary, the activation of the sample after irradiation can be measured in a low-background counting chamber (in-beam NAA). If position sensitive measurement is needed, Prompt Gamma Activation Imaging can be offered combined with neutron tomography, which is used for navigation inside of the object.
The PGAA Instrument at FRM II is being rebuilt to accommodate 14 samples into the sample chamber and to speed up measurements of large amounts of small objects. We are currently working on a new design of the PGAA facility to exchange the measuring modes (PGAA, PGAI, NI, INAA) fast, reproducibly and with low rebuilding effort.

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Summary / Zusammenfassung

High-flux Prompt Gamma Activation Analysis Based Techniques for Non-destructive Elemental Analysis of Cultural Heritage Objects

Prompt Gamma Activation Analysis (PGAA) is a nuclear analytical technique suitable for non-destructive bulk analysis of precious archaeological objects. It is performed at several neutron centers all over the world, e. g. at the Heinz Maier-Leibnitz Zentrum at Garching near Munich, where the strongest cold-neutron beam is operated. PGAA is ideal for the analysis of the light elements being the main constituents of archaeological finds, while neutron activation analysis offers a complementary method for determining the trace elements, which method can also be performed in the strong beam at MLZ (in-beam NAA). PGAA can be combined with tomography and mapping to investigate the internal structure of complex objects. The technique has been successfully applied for a series of archaeological applications: provenance studies of clay crucibles, determination of trace chlorine in corroded iron objects and bronze sculptures, 3D reconstruction and elemental mapping of complex artifacts like vases and fibulae.

Techniken basierend auf der Hochfluss-Prompt Gamma-Aktivierungsanalyse für die zerstörungsfreie Analyse von Objekten des Kulturerbes

Die Prompt Gamma-Aktivierungsanalyse (PGAA) ist eine nukleare Technik, die sich für die zerstörungsfreie Volumenanalyse von wertvollen archäologischen Objekten eignet. Sie wird an mehreren Neutronenzentren in der ganzen Welt angewandt, z. B. am Heinz Maier-Leibnitz Zentrum in Garching bei München, an dem der stärkste Strahl mit kalten Neutronen betrieben wird. PGAA ist ideal für die Analyse der leichten Elemente, die die Hauptbestandteile von archäologischen Funden bilden, während die Neutronenaktivierungsanalyse eine ergänzende Methode zur Bestimmung von Spurenelementen bietet, die sich ebenfalls in dem starken Strahl am MLZ (in-beam NAA) durchführen lässt. Um die interne Struktur von komplexen Objekten zu untersuchen, kann PGAA mit Tomographie und Abtasten (Mapping) kombiniert werden. Diese Technik wurde erfolgreich in einer Serie von archäologischen Anwendungen eingesetzt: Herkunftsstudien von Ton-Schmelztiegeln, Bestimmung von Chlorspuren in korrodierten Eisenobjekten und Bronzeskulpturen sowie 3D-Rekonstruktion und Element-Mapping von komplexen Artefakten wie Vasen und Fibeln.

Keywords

irradiation with neutrons /
prompt gamma activation analysis /
gamma spectrometry / non-destructive analysis /
multi-elemental analysis /
in-beam neutron activation analysis /
prompt gamma activation imaging /
archaeological artifacts