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Full paper

The ANCIENT CHARM project at FRM II: three-dimensional elemental mapping by Prompt Gamma Activation Imaging and Neutron Tomography

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The aim of the EU FP6-funded ANCIENT CHARM project has been the development of new, and the integration of existing element-sensitive imaging methods utilizing neutrons. We present here the methodology and the first implementation of 3D elemental mapping at the Prompt Gamma Activation Analysis instrument of the research reactor FRM II, in order to determine spatially-resolved elemental abundances in samples. After the design, optimization, and characterization of the new setup, measurements were successfully completed on archaeological objects of historical significance from the collection of the Hungarian National Museum.

Introduction

Neutrons are an ideal probe for elemental composition and structure analysis of samples due to their deep penetration into materials. This feature makes them especially suitable for the non-invasive investigation of bulky samples from the fields of geology, material science, crystallography, or archaeometry. The ANCIENT CHARM Project (*Analysis by Neutron resonant Capture Imaging and other Emerging Neutron Techniques: new Cultural Heritage and Archaeological Research Methods*) [1,2] started in 2006 with the aim of establishing a European-wide interdisciplinary collaboration to improve the existing, and to develop new neutron-based techniques for 3D elemental imaging of cultural heritage objects. In order to achieve this goal, the well-established Neutron Tomography (NT) [3] technique has been adopted and three novel imaging techniques were invented.

The first one uses slow neutrons and is a 3D extension of the Prompt Gamma Activation Analysis (PGAA), referred as Prompt Gamma Activation Imaging (PGAI) [4,5]. The two other techniques take advantage of resonances in the epithermal neutron range: a 2D/3D extension of Neutron Resonance Capture Analysis (NRCA) [5,6], referred as Neutron Resonance Capture Imaging (NRCI), and a tomographic technique with epithermal neutrons called Neutron Resonance (Transmission) Tomography (NRT) [5,7,8]. The present paper focuses on the integration of slow-neutron-based techniques, i.e. the PGAI and NT.

The first stage of the method development, including procedures for calibration, sample handling and software development, were performed earlier at the PGAA and NIPS facilities of the Institute of Isotopes (presently Centre for Energy Research HAS) in Budapest, Hungary [9], using a replica sample. Based on this experience, the setup was rebuilt at the PGAA station of the Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II) in Garching, Germany. This installation was used for the 3D elemental mapping of real archaeological samples, as the hundred times higher neutron flux here made the measurement already feasible.

Methods and Instrumentation

PGAA is a nuclear analytical technique that utilizes the characteristic prompt γ-rays emitted immediately after the neutron capture for the non-destructive determination of elemental and/or isotopic composition of samples [10]. In contrast to Instrumental Neutron Activation Analysis (INAA), the gamma-ray spectra are recorded during the irradiation of the sample. PGAA has been routinely used so far for bulk analysis only. To acquire localized information, a sharp collimation of the neutron beam down to a few millimeters was applied. Thereby the irradiation is limited to a small chord throughout the sample. The sample is then placed on a multi-axis sample stage that allows (at least) a two-dimensional scan [11,12]. To achieve the resolution in the third dimension, the solid angle of the gamma-ray detector must be reduced to a few square millimeters. The geometrical intersection of the collimated neutron beam and of

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the collimated field of view of the gamma detector defines the so-called *isovolume*, i.e. the source of the analytical information. This is depicted in fig. 1.

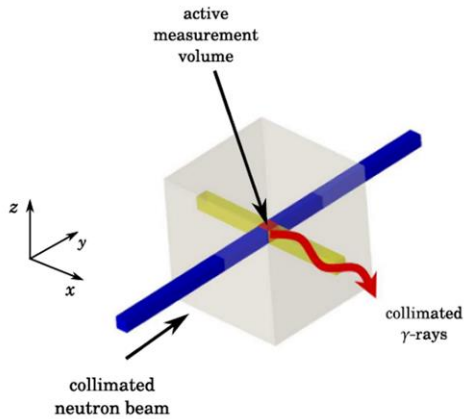

Fig. 1. Definition of the isovolume for the 3D PGAI measurements.

With systematic scanning of the object a set of gamma spectra is obtained, from which the distribution of the elements can be deduced with a few-mm resolution. This technique is called Prompt Gamma Activation Imaging (PGAI).

In order to avoid the need to completely scan large objects at high spatial resolution, which would be highly time-consuming, a more efficient two-step approach was applied. It consists of an imaging step with a fast technique to distinguish the different (homogenous) parts, followed by the PGAI measurement with an adequate spatial resolution. This is smaller than the size of the detail one expects but still large enough to measure the main and minor elements in a reasonable length of time. The adopted solution consists therefore of 1) imaging the object by X-ray or neutron tomography with a good spatial resolution, 2) performing a bulk analysis by PGAA to identify the elements present in the sample, 3) measuring the region of interest by PGAI. Such solution is well applicable to archaeological samples. Many cultural heritage objects were manufactured from several parts, but each of them are to some extent homogeneous. The combination of NT and PGAI on the same instrument, performed subsequently, without even removing the object from the setup, is what we call PGAI-NT.

The Ancient Charm PGAI-NT setup at FRM II

For PGAI-NT measurements, modifications to the existing FRM II PGAA setup [13] had to be done. The PGAA facility is located at about 52 m far from the reactor core, at the end of beamline NL4b [14]. The neutron guide is looking at the cold source (25 K), and its last 7 m are elliptically tapered to focus the beam onto a small spot and thereby to increase the neutron flux. At the sample position a cold neutron-spectrum with an average energy of 1.83 meV (about 6.7 ˚A) and a flux of 1×10^{10} n/cm^2/s was available. Two Compton-suppressed HPGe spectrometers were in use for the gamma-ray spectrum acquisition [13].

For the position-sensitive experiments, the whole sample chamber, including the ^{6}Li-polymer shielding materials, was removed, in order to free up the space for the 4-axis (x, y, z, ω) sample stage mounted below the sample position and for the PCO 1400 BW CCD tomography camera placed further downstream. It had 1600×1200 pixel with 14bit greyscales, but during the measurements we used a Binning Factor of 2, resulting in 800×600 effective number of pixels. The spatial resolution was about 640 μm [15]. In order to obtain a parallel beam for imaging, the whole setup was moved away from the end of the beam guide and the neutrons were transported to the new sample environment through a 1.60 m long boron-lined flight tube that had a set of boron-loaded rubber apertures. This way an L/D ratio of 168±10 could be achieved [15]. In front of the sample chamber a removable neutron pinhole collimator (2 mm in diameter) made of enriched ^{6}Li-polymer was placed to switch between the neutron radiography/tomography mode and PGAI mode [16].

For gamma spectra acquisition, a Compton-suppressed Ortec n-type HPGe detector with 60% relative efficiency was used. The Pb collimator in front of the gamma-ray detector was changed to a narrower one. The aperture was rectangular with a constant width of 3 mm and a variable height changing stepwise from 9 to 15 mm in every 5 cm of the length. This geometry does not deteriorate the vertical resolution, as it is fixed by the dimension of the collimated neutron beam. On the other hand, the horizontal resolution is dependent on the energy of the gamma-rays measured [9]. A XIA Pixie4 digital acquisition system recorded the events.

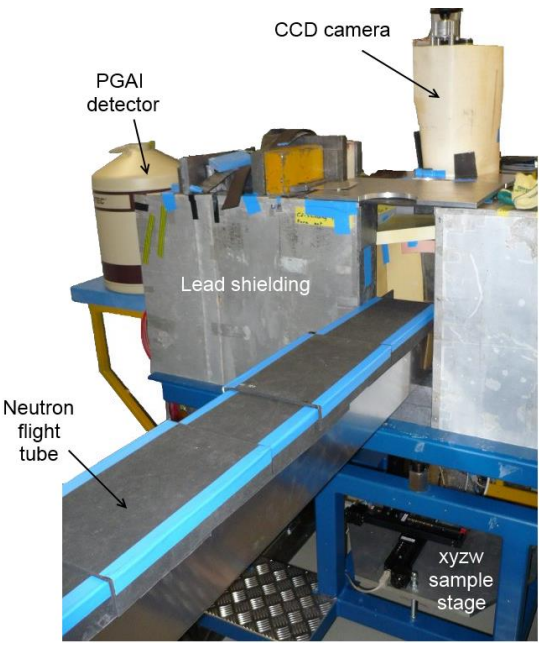

Fig. 2. The photo of the PGAI-NT pilot setup. The neutrons fly from the lower left corner towards the CCD camera

Samples and sample supports

One goal of the project was to design universal sample supports with the following properties:

- suitable for small objects with different geometries;
- provide a firm support without damaging the valuable objects during measurement and transportation;
- keep a unique position, with neutron detectable reference markers, during the measurements performed even at different

research centres;

- influence to the measurements as low as possible.

The sample holders, made of low-Mn Al alloy (AW6060), were designed and produced by the University of Cologne and the Hungarian National Museum. The sample holder with the fibula is shown in Figure 3.

For a unique alignment in 3D space, a set of at least 4 non-coplanar reference markers is necessary: one is on the top of a separate pole standing on the baseplate of the support and the other three are fixed on the poles of the supports. The markers were pins with Gd surface-coating, as Gd has an exceptionally high contrast for cold/thermal neutrons. The details of the procedure is presented in the Electronic Supplementary Material.

The sample, a disc fibula from the 6th century (HNM Inventory number: 76.1.45), was provided by the Hungarian National Museum, Budapest, for a comprehensive analysis. The fibula was found in an excavation at the ancient cemetery Grave A279, Kölked-Feketekapu, Hungary dated to the second half of the 6th century AD [18]. It has a diameter of 31 mm, a thickness of about 20 mm, and weighs 20.08 g. The structure of the fibula consists of an outer ring, presumably made of iron, and the main round part formed by radiate gold cells with garnet (almandine) inlays. A pearl of unknown composition is present in the centre. The back plate was assumed to be bronze [19].

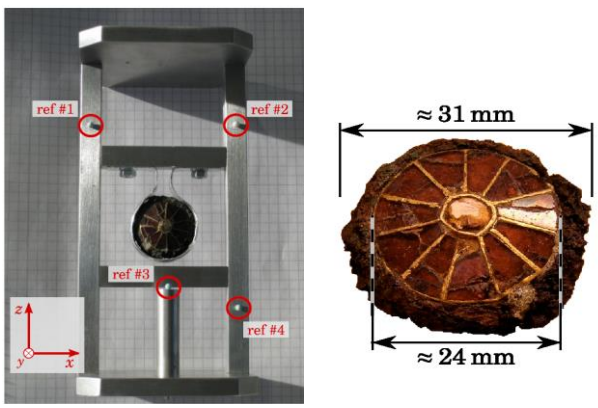

Fig. 3. Sample holder with the object under study. Highlighted are the Gd reference markers.

The archaeological questions were related to the uncommon material choice of that time, i.e. iron and gold. It was not known whether the unusual iron band is part of the original design or some later repair [19, 20]. The fibula, by its form, is a common type of the Merovingian world from the river Seine to the Danube dated to the first half of the 6th century. Overwhelming part of these fibulas were made with silver and not of gold paillons (thin leaf of a metal), hence the confirmation of the presence of gold in the fibula is of great archaeological interest. Furthermore, the composition of the pearl as well as the underlying binding material was also to be determined. The production technique together with the elemental composition of the sticking material of the garnet inlays may identify the workshop by comparison with (invasive) chemical analyses available for both Western and Eastern examples. The measurements could possibly help in understanding the origin of this population, their contacts and social status (Germanic people in the Avar empire).

Result and Discussion

The study of the fibula was started with a short PGAA run to determine the major components of the bulk and to estimate the potential activation from the neutron irradiation. The analysis identified Fe (64.5 wt%), S (15.3%), Au (7.9%), Cu (7.2%), H (2.2%), Al (1.2%), Ag (0.9%), Mn (0.7%) and Cl (0.1%). Subsequently, a full neutron tomography (NT) of the object was performed (parallel beam option, 601 projections per 180°, exposure time 6.5 sec per projection), followed by the PGAI measurements to investigate the most interesting parts of the object.

As the symmetry of the fibula was confirmed by NT, it was decided to limit the PGAI experiment to only one quadrant of the fibula. The acquisition lasted for 10 days, even with this constrain. The results were afterwards extrapolated to the rest of the object. The layers behind the garnet inlays were found to be relatively homogeneous on NT reconstruction, therefore a fine scan of these layers was not deemed necessary. The defined measurement grid for element analysis is shown in Fig 4. The typical acquisition time was 10.000 seconds for each voxel.

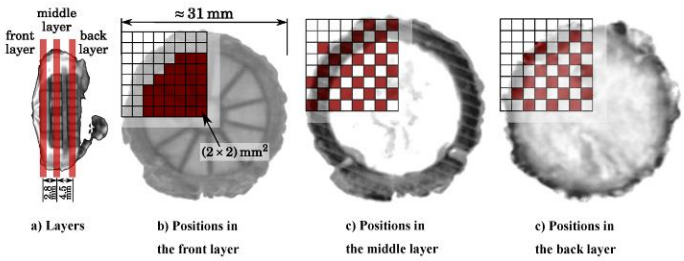

Fig.4. The defined measurement grid overlaid on the NT reconstruction for the PGAI experiment

After the analysis of raw data, the data overlay, alignment of the datasets (tomography and PGAI) was carried out. Nowdays, highly sohisticated three-dimensional visualization tools became available and are used in many branches of science to present the results [21]. The qualitative results for the significant elements are likewise presented in Figure 5.

The highlighted voxels represent regions where the given element was detected, whereas other voxels were made transparent. More detailed intensity maps and structural plots are presented in the Electronic Supplementary Material. A parallel research is ongoing to make the results of the method more quantitative [22].

The Neutron Tomography showed two different layers of the filling materials (top right image of Fig 5.) indicating that the fibula was repaired during its long use. Structure revealed by the Neutron Tomography confirmed the archaeologists' earlier speculations of the strange structure, namely the iron ring was a secondary element of this jewelry.

In the following subsections the results of the 3D element mapping are interpreted. Iron was significant in almost every voxel. The higher intensities were detected in the outer ring of the fibula and at the iron-containing garnet pieces. However the intensities were also unexpectedly high in the inner part, as due to the high corrosion of the outer ring some iron oxides could be washed into the filling lime or gypsum-like material by the moist

of the soil. Sulfur is localized mainly in the inner region of the fibula, as it is likely a component of the first layer of the binding material. The highest gold intensities were detected in the front, and surprisingly, also at the rear layers. The gold distribution found in the front layer confirmed the presence of golden backing foil of the garnet inlays. Close to the back plate the Au intensities are significant, indicating a hidden gold layer near the back plate. Copper is nearly exclusively detected in the rear part, in the secondary back plate, which confirmed the assumption about its copper-alloy, probably bronze material. Hydrogen is distributed quite homogeneously in the first and second layers. In the third one, the intensities are significantly lower than in the first layer. Hydrogen is therefore a presumed component of the filling material of the prepared fibula, thickening the former original object, and is present also in the corroded circumference. Silver is only present in the front layer and in the middle layer. Its highest intensities coincide with the positions of the inlays' backing foil.

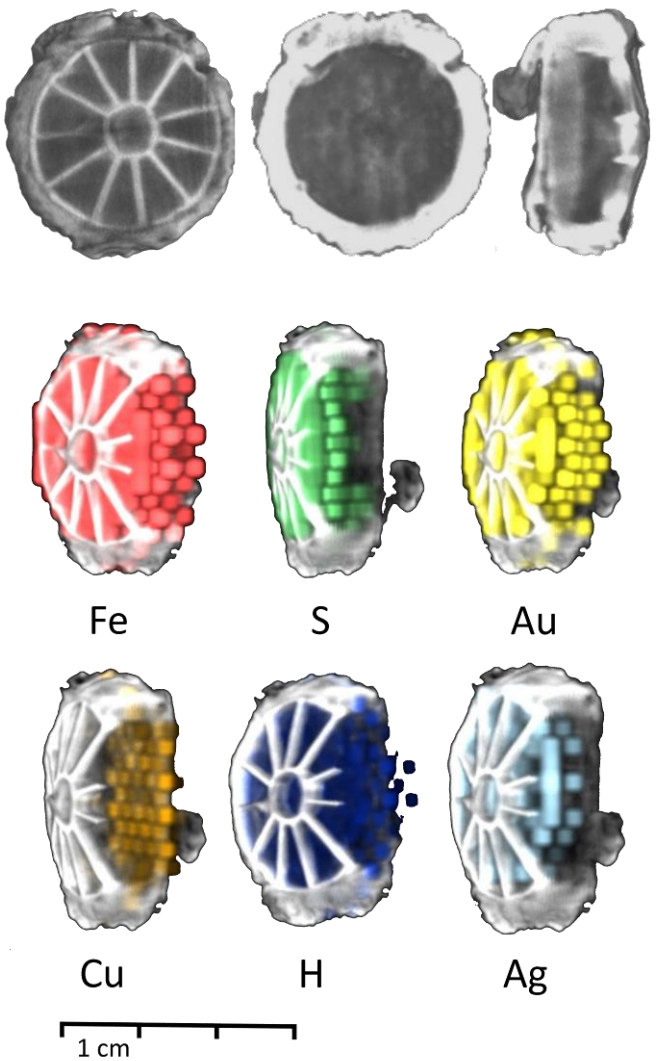

Fig.5. 3D visualizations of the structure and selected elements. The element distribution measured for one quadrant was generalized in these plots, allowed by the proven symmetry of the object (see also the Electronic Supplementary Material for futher images)

Possibly the silver can be attributed to the soldering material, which was used for sticking the cells together. As mentioned before, at that time a (gilded) silver underlay foil was much more common in such kinds of objects. Stray chlorine occurrences were seen at some distinct points on the back of the fibula and on the outer iron ring. Its presence can be explained by a surface corrosion or a modern glue used by the conservation process. In this case, the extrapolation of Cl to the whole fibula would definitely not be justified.

Conclusions

The structural and elemental mapping results discussed above could answer some of the open archaeological questions. The gold distribution was well identified with this method as well as the components of the filling material (mainly hydrogen and sulfur). Iron and aluminum can be a component of the filling material and also high signal was detected from the outer ring of the fibula and the garnet inserts. The backing foil of the garnet was confirmed to contain a smaller amount of silver in addition to the gold. The silver was presumably used for soldering the original fibula together. We can clearly see the two different layers of the filling material and slight differences in their components. Unfortunately, the composition of the pearl in the middle of the fibula is still unknown. The copper detected in that position is unlikely to originate from the pearl. Real mollusk pearls consist mainly of calcium carbonate. As long as calcium is the main component of the pearl, it should have been detected. A hypothesis is that the pearl was substituted with a glass imitation. Glass contains silicon dioxide as a major component, and silicon could not be analyzed with this pilot setup due to background issues.

After the NT analysis at FRM II it is clear that the fibula's strange structure is due to ancient repair. There are two layers of filling materials that can be seen below the cells: the first ends in the lower line of the cells, which is the original filling paste. Below this another layer can be seen that fills the whole area of the iron ring: so we can preliminary conclude that the former back plate was detached and that the addition of an iron band around the fibula was to prevent the cells from falling apart. Then the remaining space was filled with another paste, and finally a new back plate with a new needle-case (a pin to stick it up to the clothes) was attached to the fibula.

The further analyses of the components of the filling material is likely to help in determining the workshop where it has been made. The rare and valuable materials, i.e. gold and pearl, indicate the high social status of the owner and a first-class goldsmith workshop located more likely in Western Europe than in the Carpathian Basin. The application of 3D mapping by PGAI and Neutron Tomography helped us to better understand the object and early mediaeval technology in general.

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