FROM PGAA TO PGAI: FROM BULK ANALYSIS TO ELEMENTAL MAPPING

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Kivonat

Értékes műtárgyak archeometriai vizsgálata során az elsődleges követelmény a műtárgy épségének megóvása. A neutron ideális "vizsgálati eszköz", mivel elektromos semlegessége miatt képes az anyag mélyebb rétegébe behatolni, és ott különböző magreakciókban részt venni – a minta károsítása nélkül. Mind a neutronbefogáson alapuló módszereket (Neutrontomográfia – NT, Neutronaktivációs Analízis – NAA, Prompt-gamma Aktivációs Analízis – PGAA és a Neutron Rezonancia-befogásos Analízis – NRCA), mind a neutronszóráson alapuló módszereket (Repülési Idő Neutrondiffrakció – TOF-ND és a Kisszögű Neutronszórás – SANS) korábban már alkalmazták archeometriai kutatásokban.

2006-ban "Ancient Charm" elnevezéssel egy új nemzetközi kutatási programot indított az Európai Közösség, melynek célja a fent említett "neutronos" módszerek egyesítése értékes műtárgyak térbeli szerkezet- és összetétel-vizsgálatára. A hagyományos (tömbi) PGAA-t elsőként a Budapesti Kutatóreaktor $5 \cdot 10^7$ n/cm$^2 \cdot$s^1 intenzitású neutronnyalábján fejlesztjük tovább a képalkotás (PGAI) irányába. A vizsgálatokra szánt reprezentatív műtárgyakat a Magyar Nemzeti Múzeum, a római Villa Adriana és a leideni Nemzeti Múzeum gyűjteményéből választjuk.

Abstract

When investigating a valuable artistic object, the first and foremost requirement is to keep it intact. Neutrons, elemental particles having zero electric charge can enter deep into the irradiated material, and they can undergo different nuclear interactions, without causing any damage of artefacts. Both the neutron capture-based methods (i. e. Neutron Tomography – NT, Neutron Activation Analysis – NAA, Prompt Gamma Activation Analysis – PGAA and Neutron Resonance Capture Analysis – NRCA) and the neutron scattering-based methods (i. e. Time of Flight Neutron Diffraction – TOF-ND and Small Angle Neutron Scattering – SANS) have been previously applied to archaeometric research.

In 2006, a new European Commission funded project with ten collaborators, called Ancient Charm, was launched with the aim of combining the above mentioned neutron based methods to achieve 3-D imaging and elemental mapping of museum objects with complex structures. The first experiments to develop bulk elemental PGAA towards elemental mapping and imaging of complex objects (i. e. to work out PGAI) will be attempted at the Institute of Isotopes, on the $5 \cdot 10^7$ n/cm$^2 \cdot$s^1 cold neutron beam of the Budapest Research Reactor. Representative archaeological objects for investigations have been chosen from the collections of the Hungarian National Museum, Villa Adriana near Rome, and the National Museum for Antiquities of Leiden.

KULCSSZAVAK: NEUTRONBEFOGÁS, NEUTRONSZÓRÁS, AKTIVÁCIÓS ANALÍZIS, DIFFRAKCIÓ, KÉPALKOTÁS
KEYWORDS: NEUTRON CAPTURE, NEUTRON SCATTERING, ACTIVATION ANALYSIS, DIFFRACTION, IMAGING

Introduction

Already in the beginning of the 20th century modern physics, scientists tried to introduce nuclear analytical methods into archaeological research. Neutrons – with zero electric charge can enter deep into matter. When passing through the substance, neutrons take part in different interactions, basically in neutron capture and neutron scattering. The Hungarian chemist George Hevesy has worked out the basics of Neutron Activation Analysis (NAA), which has been applied to archaeometry in the 1950s. The principal nuclear reaction of the analysis is the radiative capture of a neutron by the atomic nucleus. Following the neutron capture, atomic nuclei emit characteristic γ-radiation, which can be utilised for element identification. Recently, NAA is considered as routine analytical method, applied in many laboratories connected to research reactors. Some examples are: the Budapest Research Reactor; Institute of Nuclear Techniques, Budapest

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University of Technology and Economics; Warsaw Research Reactor, Technical University of Delft, the Netherlands; Research Reactor Centre, University of Missouri, USA.

When the emitted gamma photons are detected during irradiation, not only the delayed gammas, but also the prompt gammas can be measured. This way, in principal, almost every chemical element can be identified. This kind of activation analysis with external neutron beam is called Prompt Gamma Activation Analysis (PGAA). Although PGAA is less sensitive for many trace elements than NAA, some important elements, like H, B, Cl, Cd, Sm, Gd and Eu can be measured more effectively. PGAA is best applicable for non-destructive investigations of stone, pottery, metal and glass objects. The number of PGAA laboratories in operation is less than twenty all over the world among which the Budapest laboratory achieved significant results in archaeometry (Anderson and Kasztovszky, 2004).

A similar neutron capture reaction takes place, when the samples are irradiated with epithermal neutrons (with energies higher than a few hundreds meV). At epithermal energy range the neutron capture can be resonance-like with very high probability. By detecting the characteristic gamma emissions, the quantitative identification of components is possible. The method is called Neutron Resonance Capture Analysis (NRCA). NRCA is absolutely non-destructive too, and applicable mainly for heavier elements, like Cu, As, Zn, Ag, Sb and Sn. NRCA is a perfect tool for investigation of bronze objects, and complementary to PGAA (Blaauw et al., 2005). The only laboratory, where NRCA is practised can be found at the Institute for Reference Materials and Measurements, Geel, Belgium.

Diffraction methods, in general aimed to explore the atomic structure, or to identify different phases within a variety of solid materials. More specifically, Time of Flight Neutron Diffraction (TOF-ND) can be applied for investigations of alloys (e.g. bronze, Ag-Cu) or pottery in order to reveal some information about the production techniques. Prominent examples for archaeometric applications performed at the ISIS laboratory, United Kingdom, and were reported by Siano et al, 2006. The other neutron-based scattering method, Small Angle Neutron Scattering (SANS) is applicable to investigate larger scale order in various materials, with very preliminary archaeometric applications (Botti et al., 2006).

The above mentioned activation and scattering methods aimed to determine composition or structure of various objects, but they are usually not applied to provide spatial distribution of the components or phases within the object. There exist some neutron-based imaging methods on the other hand. Neutron Radiography or Neutron Tomography (NT) is designed to visualise the inner structures of composite objects, based on the differences of neutron absorption for different elements. The obtained image is similar to a more common X-ray radiogram, but components of lighter elements (H, water, organic or air) can be separated in the two- or three dimensional images. Significant appliers of NT work in Europe at the Paul Scherrer Institute, Villigen, Switzerland (Deschler-Erb et al., 2004), at the ILL in Grenoble, France, and at the FRM-II in Munich, Germany.

The Ancient Charm project

The neutron-based analytical methods, described in the previous section are either capable to provide an average chemical (elemental or isotopic) composition of a bulk sample, or they can reveal a two- or three dimensional image of the object with a limited resolution. It implies that a comprehensive method, which integrates the advantages of the previous ones, would be desirable.

With this intention, European research groups have worked out a large scale scientific program, to provide a new, comprehensive neutron-based imaging approach, which will be applied for the 3D imaging of elemental and phase composition of objects selected as a result of a broad scope archaeological research (G. Gorini, in press). The title of the project is 'ANCIENT CHARM' – is an acronym for **A**nalysis by **N**eutron resonant **C**apture **I**maging and other **E**merging **N**eutron **T**echniques: new **C**ultural **H**eritage and **A**rchaeological **R**esearch **M**ethods.

The accepted research program started in January 2006 and lasts for 36 months as ADVENTURE project under the New and Emerging Science and Technology (NEST) programme of the 6^{th} framework of the European Community. The participating institutes are the following: *Universitá degli Studi di Milano-Bicocca*, the *Universitá degli Studi di Roma Tor Vergata*, the *Reinische Friedrich-Wilhelms Universität Bonn*, the *Universität zu Köln*, the *Technical University Delft*, the *Leiden University*, the *Institute for Reference Materials and Measurements* in Geel and the *Central Laboratory of the Research Councils* in Didcot. Two institutes are involved from Hungary – the *Hungarian National Museum* and the *Institute of Isotopes of the Hungarian Academy of Sciences*. The tasks have been organised into workpackages, which will be performed by various working groups.

The research institutes, which exploit the benefits of large scale facilities, offer their technical support to develop new methods for Cultural Heritage research.

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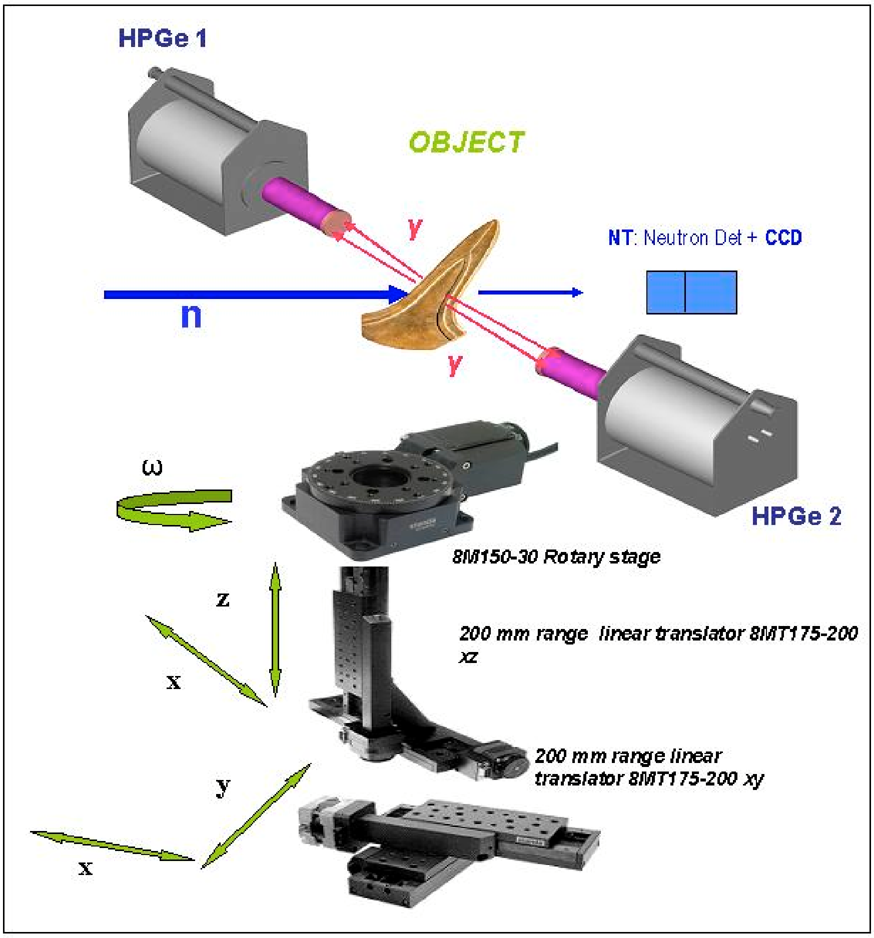

Figure 1.

The conceptual design of PGAI experimental station at the cold neutron beam of the Budapest Research Reactor.

Museologists of the Hungarian National Museum take a leading part in the beginning of the research. In workpackage 1, we have to harmonise the archaeologists' requirements and the performance of methods, in order to choose the most adequate objects for investigations. We can select objects from the wealthy collections of the National Museum (i.e. Palaeolithic, Roman, Migration period collections). The objects should be optimal to attain significant experimental results according to their material, size and structure. The analytical results, on the other hand, will be fed back to the methodological developments. Furthermore, the obtained results have to be unique and important for archaeological research.

One valuable candidate for investigation is a disc fibula unearthed during the excavation of a 6th century A.D. migration period settlement next to Kölked, Hungary. The photos of the fibula was published in "Archeometriai Műhely" by Kasztovszky & Belgya, 2006. Disk fibulas with almandine inlays had been imported into the territory of the Avar Empire. They originated from the Frankish settlement area. Among these types, the main iron structure with silver or gilded silver covering plates is very rare (Kiss 1996; Salamon & Erdélyi 1971). These fibulas are assumed to be produced by Merovingian workshops. We would like to answer the following questions with the help of 3-D elemental mapping (PGAI): *1*, Whether the main structure was made of gilded silver and, consequently the iron band could be reparation, or the object belongs to the rarer group of iron disc fibulas. *2*, What is the material of the filling material of the cells and that of the decorated metal foil below the almandine plaques. *3*, It would be interesting to know the exact form and the material of the white pearl in the middle.

Besides the Hungarian treasure, artefacts from Leiden University and from Rome University will be studied. Before analysing real archaeological objects, experiments will be run on artificial test objects (cubes with unknown inner composition, in practice) and later on master copies of art objects. These replica objects will be produced by the partners from the Hungarian National Museum and the Bonn University.

From 'bulk' PGAA to the three dimensional elemental mapping (PGAI)

When we perform a routine PGAA investigation, a 20-400 mm^2 cross-section beam is applied. Usually, the detected major and trace components –

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as average values – provide reliable information to characterise homogeneous objects, such as stones, glass and metals. Within the frame of ANCIENT CHARM we wish to extend the PGAA and similarly the NRCA towards 3D elemental mapping. How can we 'focus our eyes' on small parts like grains, pearls, inlays, gild, etc.? How can we map these details in composition with our neutron beam?

PGAA inherently allows us to develop elemental mapping in three dimensions. If we reduce our beam to a few millimetre size, and also detect the emitted γ-photons from a very narrow solid angle, we can 'cut' a certain part from the body of the object. Moving the object in front of the beam – practically rotating around a vertical axis and translating vertically and horizontally with an automated system – we can map each part of the object. The design of experimental station at the Budapest cold neutron beam is shown on **Fig. 1.** PGAA measurement of each section will result in one individual spectrum, but one has to keep in mind that reducing the beam size will result in loosing the intensity, thus the acquisition time might be considerably longer. From the step of collecting the required spectra, it is 'only' computer work – although not an easy one – to construct the three dimensional elemental 'map' of the object. This technique is called Prompt Gamma Activation Imaging (PGAI). To perform complete 3-D mapping of a whole object with PGAI, however, is very time consuming, thus it is plausible to combine it with the much simpler neutron tomography (NT), which, in turn can provide a resolution of some 100 µm. The idea is to get an overall picture of the object with NT first, and then to focus on the sections of interest with PGAI.

However, the above described principle of investigation is much more complicated in reality. As we mentioned, the atomic nuclei not only capture but also scatter the neutrons. Scattering of neutrons will cause the beam to diverge, thus the theoretical quality of image will decrease in reality (**Fig. 2**). The ratio between the capture and scattering events depends on the ratio of the absorption and the scattering cross-sections, which is different from one material to another.

It is obvious that prior to the measurements of real objects, one must perform simulation calculations to choose the feasible compositions from the everyday practice and also need to run test measurements on simple but significant artificial model objects. On **Fig. 3** we show three characteristic examples for Monte Carlo simulation of neutron transport in silver, nickel and cellulose. The calculation is done, supposing a 2 mm × 2 mm neutron beam incident in "Z" direction. The dots represent the neutron capture events in "X-Y" and "X-Z" planes for each material.

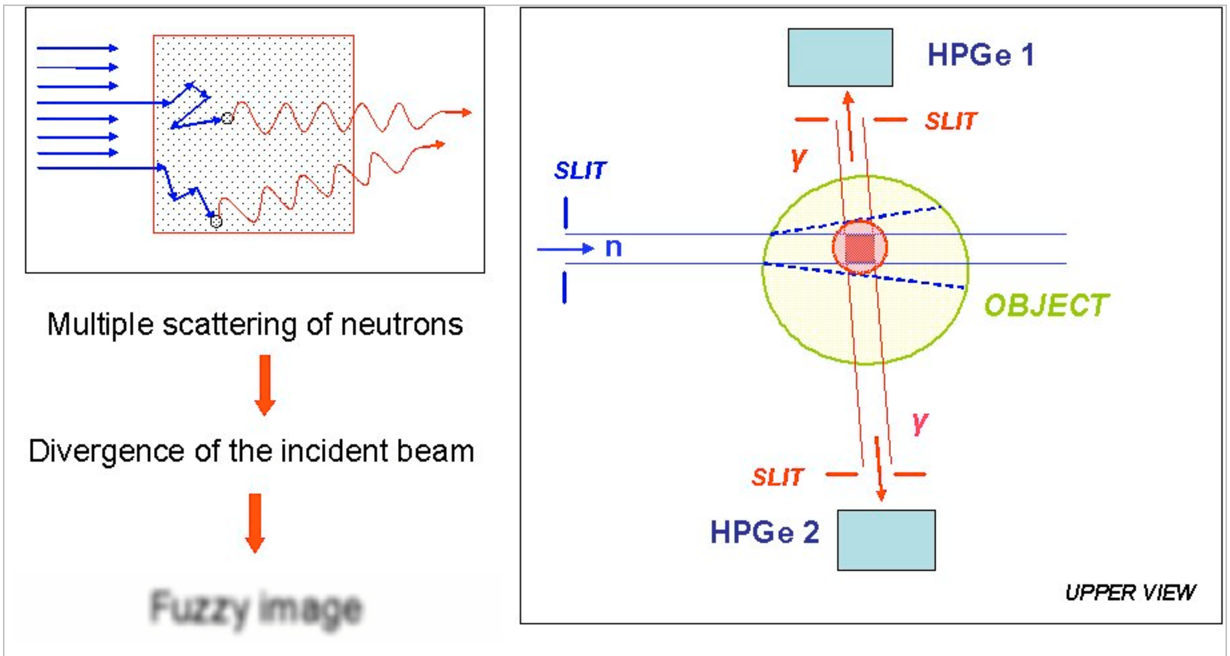

Figure 2. Effect of neutron scattering on the image quality.

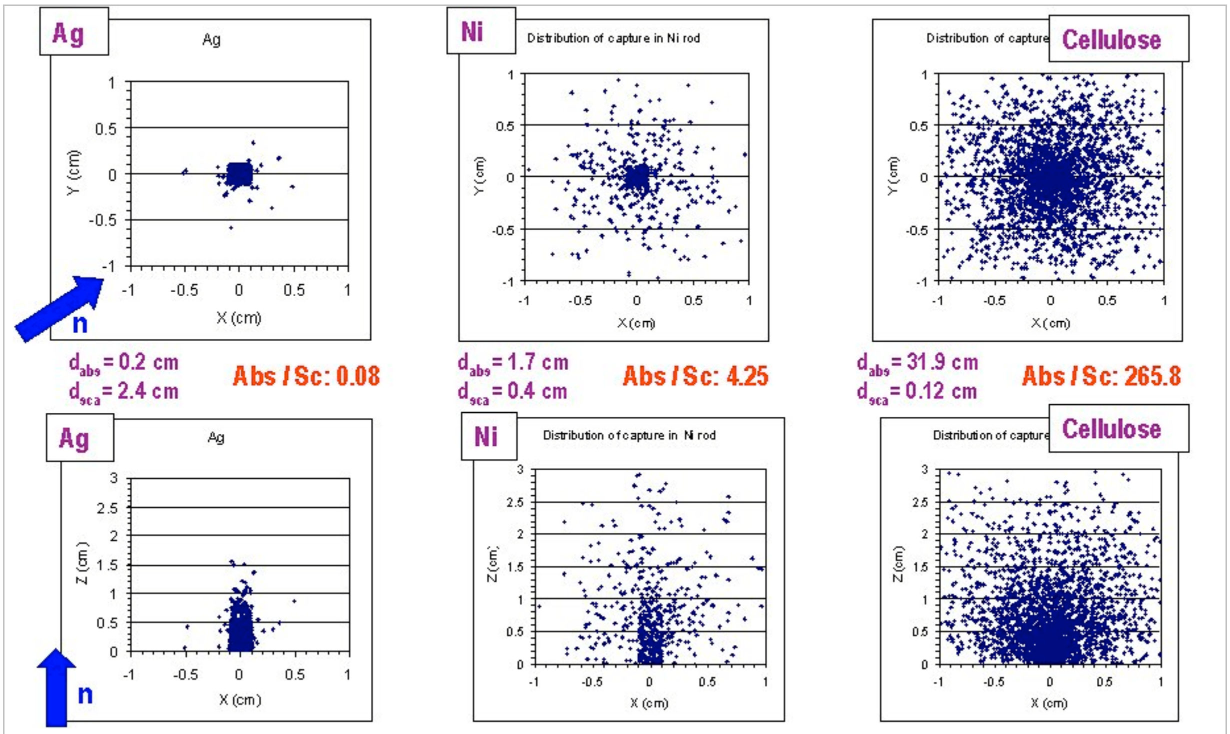

Figure 3. Monte Carlo simulation of neutron transport in silver, nickel and cellulose.

In can be seen that for cellulose, where the scattering effect is large (typically every H- and C-containing, *i.e.* organic ones) the pencil-beam will be widened, thus the image of a particular part will be fussy, as if we would make a photo in the fog. On the other hand, details behind a highly absorbing material (one practical example is silver) can not be detected, because the nuclei on the front will capture most of the neutrons within a very short distance. In case of silver this critical distance is around 1 cm. To summarise, in order to perform a reliable 3D elemental mapping, we have to fulfil a double requirement: First the incident neutron beam should not disperse too much inside the sample, and secondly it should penetrate deep enough to obtain information from inner parts.

Final remarks

Ancient Charm project is one step forward combination the existing neutron-based techniques in order to apply them in archaeometry research. Extension of the bulk analysis towards 3-D elemental mapping and imaging will raise the amount of valuable information about museum objects with fine details. The work, however, is only in the starting phase yet, we have to make some basic consideration first. Based on model calculations and pilot measurements on artificially made test objects, we have to choose the most appropriate real objects of interest. All the selection part, the construction task, the data collection part, as well as the interpretation of the results require strong and permanent collaboration between museum experts and scientists.

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