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Integration of neutron-based elemental analysis and imaging methods and applications to cultural heritage research

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ABSTRACT

The present paper describes the merits of the combined neutron-based elemental analysis and neutron imaging techniques, called prompt-gamma activation imaging – neutron tomography (PGAI-NT), and illustrates its application to cultural heritage science with relevant case studies. The approach is proven to be best applicable to samples with corroded/layered/gilded/painted/coated structures where the surface weighted response would bias the analysis results obtained with simpler, more widespread, but less representative techniques (such as X-ray fluorescence spectroscopy or laser-ablation ICP-MS), as well as to answer questions related to the inner composition of a sealed object.

1. Introduction

1.1. *Evolution of neutron-analytical techniques towards use by the cultural heritage community*

One of the priorities at the Budapest Neutron Center (BNC) is to promote the collaboration between the cultural heritage (CH) experts and neutron scientists. This has been facilitated by several EU-funded transnational access (TNA) programs (NMI3, NMI3-II, CHARISMA, IPERION CH) as well as method-development projects (e.g. EU FP6 NEST ANCIENT CHARM) (Belgya et al., 2008b; Giorini et al., 2009; Schulze et al., 2010).

The EU FP7 CHARISMA and EU H2020 IPERION CH projects offer integrated access to *several instruments* located on a single campus (e.g. at BNC: imaging at RAD (Kis et al., 2015b) (i.e.Phys Proc), or NORMA Kis et al., 2015a) (i.e. NIMA), elemental analysis at PGAA (Szentmiklósi et al., 2010) or NIPS (Szentmiklósi et al., 2013), and neutron diffraction at ToF-ND (Káli et al., 2007)), or even at different radiation sources, such as neutrons, ion beams and synchrotron radiation. An innovative question-answering approach, a user “welcome desk”, and the active support by the neutron experts throughout the entire workflow made the cultural heritage users able to answer many questions by use of neutron methods.

There has been a second aspect of evolution at the facility level, also driven by the needs of the user community. Neutron techniques for elemental analysis and diffraction were originally developed to deal with point like, or at least regularly shaped, pure and homogeneous samples (Mackey et al., 1996), (Kudejova et al., 2015). In particular, prompt-gamma activation analysis (PGAA) (Molnár, 2004) has always been an excellent technique for the fully non-destructive characterization of valuable (and preferably homogeneous) artefacts, such as stone tools, glassware, pottery, bronze alloys, and coins. This research has resulted in over one hundred publications in this field (Szentmiklósi et al., 2016). A significant proportion of the cultural heritage samples are, however, neither regular-shaped nor homogeneous, e.g. painted ceramics, precious stone inlays of metals, gilding, surfaces with corrosion or patina. To make PGAA capable of analyzing such objects, an extension of the base technique was needed, where instead of bulk average composition a local elemental analysis is done and the composition determined is linked to a definite part of the object.

Another prominent technique, neutron imaging is perfect to reveal the internal structure of the heterogeneous objects (Lehmann, 2017; Lehmann et al., 2017; Schillinger et al., 2018; Szilágyi et al., 2016), with a spatial resolution far better than what neutron-based elemental analysis can ever offer. It cannot, however, provide unambiguous evidence about the materials used, since by coincidence more than one material can have the same macroscopic attenuation property. An object's internal structure and its production technology can sometimes be understood only if multi-modality imaging (Thermal neutron vs. cold neutron, Neutron vs. X-ray imaging) is applied.

1.2. *Best practices, synergies and complementarities*

Experience has showed that a multi-technique approach (Edge et al., 2015; Kasztovszky et al., 2016; Kiss et al., 2015), even if the experiments are carried out separately, offers synergies when interpreting the

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results. E.g., for alloys with more than two components, like ancient bronze artefacts, Vergard's law for binary alloys (Vergard, 1921) is not applicable. It can be extended to ternary alloys if the object is classified to a proper subcategory, such as lead-bronze, brass, tin-bronze, where different calibration curves apply (Sidot et al., 2005). With the information on the bulk average composition from a PGAA experiment, this can be done successfully (Gliozzo et al., 2017). Conversely, oxygen is hard to quantify in corroded iron by PGAA due to the low analytical sensitivity for oxygen, whereas the diffraction data can provide the experimental team with information about phases and proportions of metallic iron, oxides and hydroxide.

Reliable bulk elemental composition from PGAA or in-beam NAA can also be used on a routine basis to keep the activation risk of subsequent experiments under control (Kardjilov and Festa, 2017). For instance, the activity of 1 g of Cu, Au, Sb or Mn irradiated for 3 h in a beam of $10^8\,cm^{-2}\,s^{-1}$ thermal-equivalent slow-neutron flux (typical for PGAA) decays below the legal clearance limit within 24 h. However, if the same material would be exposed to neutrons at a beamline with a significant epithermal component (e.g. at RAD station) for 10 h during a full tomography, the sample would remain active for two weeks due to Sb-122 and Au-198 isotopes (with half-lives of 2.7 days and significant resonance integrals). This has to be considered when planning the experimental work, as the precious objects can be borrowed from museums only for a limited time and they have to be declared inactive by or shortly after the end of the user's stay at the neutron center.

When applying different neutron instruments at different beamlines, or even at separate neutron centers, to the same CH object, the sampling volumes are not necessarily geometrically coincident and the penetration depths of the various radiations might differ (fast/thermal/cold/monochromatic neutrons, X-rays, charged particles), making inexact the merging of the available data. So there is a clear advantage to integrate multiple functionalities into a single instrument and analyze the object in several ways at once at the same beamline, in the same position, but with multiple means of detection. This paper presents the recent efforts to integrate the non-destructive, position sensitive elemental analysis (prompt gamma activation imaging, PGAI) with neutron imaging (radiography, NR or tomography, NT) (Belgya et al., 2008a, 2008b) at the NIPS-NORMA station (Kis et al., 2015a) of the BNC.

2. Experimental

The Budapest PGAA lab has 20 years of experience with analysis of various CH objects. Most samples with masses of a few grams and size of a few cm could fit well into our sample chamber, and, thanks to its modular structure, it can be partially taken apart to accommodate objects up to 50 cm in diameter. The extension of this well-established technique towards non-homogeneous samples was facilitated by making simultaneous use of a well-shielded gamma spectrometer, a neutron imaging camera placed downstream and a computer-controlled sample stage, all aligned around the isocentre (the geometrical intersection of the beam axis, the perpendicularly placed gamma-detector's symmetry axis and the vertical axis of the rotation stage of the sample positioner). PGAI-NT is therefore a combination of neutron imaging and element analysis, where the image is used i) as a visual feedback for sample positioning, ii) as a link between the structure and the local composition, as well as iii) for correction for large-sample effects in non-destructive elemental analysis of non-homogeneous objects.

It is often more time-effective to avoid the point-wise scan of the entire object (Belgya et al., 2008b) with a few mm-resolution and to probe selectively only certain well-defined parts, e.g. regions of interest in the 3D space. This approach is called Radiography/Tomography-driven PGAI. If a real object is made of only a few distinct homogeneous parts (e.g. a restoration patch on a restored object), then localized prompt-gamma measurements made only at a few points could already be conclusive.

NIPS-NORMA (Kis et al., 2015a), the completely redesigned successor of the Ancient Charm PGAI-NT pilot setup (Szentmiklósi et al., 2009), was commissioned in 2012 to become the first permanent and routinely operating PGAI-NT facility in the world. The major technical features of the NIPS-NORMA station have been published (Kis et al., 2015a; Szentmiklósi et al., 2013); here only the most important facts are summarized. The samples can be accommodated in a sample chamber with dimensions of $200 \times 200 \times 200\,mm^3$, and irradiated by cold neutrons (flux: $2.7 \times 10^7\,cm^{-2}\,s^{-1}$ beam cross-section up to $43 \times 43\,mm^2$, beam divergence (L/D ratio): 233–1833). The images are taken with an Andor iKon-M camera with 16 bit bin depth and typical spatial resolution of 230 μm. The prompt-gamma radiation is detected with a 23%-efficient, Compton suppressed high-purity germanium detector system placed inside 100–150 mm thick lead gamma-ray shielding. A neutron slit can shape the impinging beam to any rectangular form.

The projections are flat-field and dark-image corrected and reconstructed with the OCTOPUS 8.9 software (Cnudde and Vlassenbroeck, 2017). Afterwards, the 3D rendering and visualization is performed using VG Studio MAX 3.1 (Volume Graphics, 2017). The gamma spectra are evaluated with Hypermet-PC (Fazekas et al., 1996) or with PeakFit (Szentmiklósi, 2017) if batch processing is required, and the elemental concentrations are calculated with the Excel macro ProSpeRo (Révay, 2009).

3. Results and discussion

3.1. Analysis of archaeological iron

In the very first cultural-heritage-related study of the newly constructed NIPS-NORMA station the earliest known iron artefacts, three small beads dated to 3200 BCE, from Gerzeh, Egypt, presently owned by the University College of London, Petrie Museum of Egyptology (Inv. No: UC10738, UC10739 and UC10740), were investigated. We have demonstrated with the detection of specific element signatures that these beads were made of meteoritic iron, and shaped by hammering the metal into thin sheets before rolling them into tubes (Rehren et al., 2013). The study revealed the advantages of neutron and complementary X-ray methods to determine the nature of the material even after complete corrosion of the iron metal. Our conclusions were later confirmed by Johnson et al. (Johnson et al., 2013) using X-ray based techniques only.

A similar methodology was used in another study, where it was possible to establish a correlation between the longitudinal chlorine profile and the degree of corrosion in archaeological iron nails (Watkinson et al., 2014). After excavation, oxidation forms ferrous chloride and hydroxide, which cause cracking, fragmentation and break-up of the objects. The thick corrosion layer and the intact iron core were easy to separate in the 3D neutron images, much more recognizable than in X-ray radiograms, allowing us to correlate the corroded layer's thickness with the higher local chlorine content. This was a clear indication about the driving force of the corrosion. So the experiment confirmed that the PGAI-NT technique provides comparable results to the previously used chlorine-analysis approach by ion-selective electrodes, but in a non-destructive way.

3.2. Analysis of sealed pottery

Neutron techniques have significant advantages in the analysis of archaeological materials, including greater penetration depth and lower elemental detection limits, over other modalities, not only for heavy-metals, but already for lower-Z materials, found e.g. in ceramics and organics. A good example is an Eighteenth Dynasty (XVth c. BC) Egyptian sealed pottery vessel stored at the Museum of Aquitaine (Bordeaux, France, inventory number 8608) that has been investigated using Terahertz-frequency (THz) electromagnetic radiation, X-rays and