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Prompt gamma activation analysis and time of flight neutron diffraction on 'black boxes' in the 'Ancient Charm' project

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The aim of the 'Ancient Charm' project is combining neutron tomography, prompt gamma activation analysis, time of flight neutron diffraction and neutron resonance transmission to generate elemental, and phase compositions of complex museum objects in 3D. To develop a protocol for such investigations, complex test samples were constructed and then analyzed by each method. The 'black boxes' are sealed iron and aluminum walled cubes, containing 2D or 3D arrangements of materials relevant for the compositions of archaeological samples. The experimental results obtained from bulk PGAA at BNC and TOF-ND at ISIS on two selected boxes are reported.

Introduction

In 2006, a European Commission funded project started with ten participating scientific institutions. One of the ultimate goals of this three-year project, called 'Ancient Charm' is to develop 3D imaging of elemental- and phase-compositions of considerably complex museum objects by combining various neutron analytical methods. All of these methods, such as neutron tomography (NT), prompt gamma activation analysis (PGAA), time of flight neutron diffraction (TOF-ND) and neutron resonance capture analysis (NRCA) are individually already in use at large research facilities. One of the project tasks being organized in work packages is to develop prompt gamma activation imaging (PGAI) from PGAA, and to combine it with NT and TOF-ND.

In order to establish a protocol aiming to combine NRCA, tomography, PGAA and diffraction data collected on the same archaeological object, test samples constructed with varying degrees of complexity were analyzed by the different methods. Two series of closed and sealed 'black boxes' were manufactured by the Hungarian National Museum (HNM) and by University of Bonn, Germany. The contents of the boxes were planned and constructed using material types frequently occurring in archaeological context. The first set consists of ten iron cubes of 40 mm edge length (labeled as H-I, …, H-X). The second set (labeled as D-I, …, D-X) consists of similar pieces but made of aluminum and with edge lengths of 50 mm. The compositions and distributions of the filling materials are known exclusively to the constructors. As a first step towards the imaging method, we applied both conventional 'bulk' PGAA and conventional 'bulk' TOF-ND on selected regions of the objects, guided by neutron tomography (NT) and X-ray tomography data. On the other hand, NRT can thus provide a two-dimensional maps of neutron resonance absorption from which the composition of the unknown sample can be derived.

In this paper, we report on the comparison of PGAA and TOF-ND results obtained for two 'black boxes' as examples.

The PGAA measurements were performed at the Budapest Neutron Centre (Budapest, Hungary), the TOF-ND measurements at the ISIS Facility, Rutherford Appleton Laboratory (Chilton, UK).

Experimental

In order to select the appropriate sections on the objects, tomography data were collected at the research reactor FRM-II in Garching, Germany, in cooperation with the ANTARES group (neutron tomography) and at the Center for X-ray tomography at the University of Ghent (X-ray tomography).[2]

Prompt gamma activation analysis

Three aluminum and two iron boxes were investigated with the conventional PGAA at the Budapest Neutron Centre. The neutrons leaving the

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reactor core are cooled with a cold neutron source and are then guided to the PGAA/NIPS system, situated as far as 30 m away from the reactor wall.[3]

At the PGAA unit, the maximum available beam size is 20×20 mm^2, and the beam intensity is approximately $7 \cdot 10^7$ $cm^{-2} \cdot s^{-1}$. The neutron beam can be collimated to different cross sections with a minimum of 5 mm^2. Prompt- and delayed gamma-photons are detected with a 27% efficiency n-type HPGe detector, surrounded by a BGO annulus, in anti-Compton mode. The spectra are collected with Canberra S100 multichannel card and evaluated with a Hypermet PC.[4]

Selected sections of the boxes were irradiated with a cold neutron beam of 44 mm^2 area cross section. The boxes were placed into the chamber with one side in line with the neutron beam.

No gamma and neutron self-absorption corrections were taken into account at this stage of the analysis. Thus, the compositional results can be considered only as qualitative information.

Time of flight neutron diffraction

Neutron diffraction experiments were performed on three different diffractometers at ISIS, on ROTAX,[5] GEM[6] and INES.[7] The time of flight neutron diffraction (TOF-ND) method[8] makes use of the polychromatic beam of neutrons possessing wavelengths over a broad wavelength range. For all three diffractometers, the scattered neutrons are registered by detector banks at low and high scattering angles, i.e., each measurement on one of the instruments yields several diffraction patterns covering different crystallographic d-spacing ranges.

For the data collection on the black boxes, the size of the incident beam was set to typically 10×10 mm^2, apart from INES where a larger beam size of 40×40 mm^2 illuminated most of the box. The diffraction patterns were analyzed semi-quantitatively by identifying the metal and mineral phases by their Bragg peak positions. The identified phases by TOF-ND are given in Table 1.

Results and discussion

Three aluminum and two iron boxes were chosen for analyses with PGAA and with TOF-ND. The radiography images of one iron box and one aluminum box selected as examples are displayed in the parts (A and B) of Fig. 1, and discussed in details (Table 1). On the left side of the figure one can notice the directions of the impinged neutron beam (numbered arrows) for the PGAA measurements, while on the right side of the figure numbers indicate the analyzed regions by TOF-ND.

Table 1. Elemental (with PGAA at BNC) and phase (with TOF-ND at ISIS) compositions of the selected black boxes. Numbering is according to that in Fig. 1

Analyzed part	PGAA	Analyzed part	TOF-ND
H-VI. Box			
1	H, Si, Al, K, Cl, Ti, Ag	1	quartz, gypsum, talcum, Al or Ag, Cu-type fcc (*bronze, brass*)
2	H, Na, Cl (Na/Cl~1)	2	quartz, salt (NaCl), gypsum, talcum, Cu-type fcc (*bronze, brass*)
3	H, Si, Cl, Cu, Ag	3	gypsum, talcum, Cu-type fcc (*bronze, brass*), wuestite (FeO), magnetite (Fe_3O_4)
4	H, Cu, Si, Cl, Ag	4	quartz (SiO_2), gypsum ($CaSO_4(H_2O)_2$), talcum ($Mg_3(OH)_2$ (Si_4O_{10})), Al or Ag
		5	salt (NaCl), gypsum, talcum, Al or Ag, Cu-type fcc (*bronze, brass*), wuestite (FeO)
D-VI. Box			
1	Fe, Cu, Na, Cl, Ca, Si	1	NaCl, Cu-type=fcc, *a*=3.592 Å, steel (Fe) or copper (Cu)
2	Al, Cu, Fe, Na, Cl, Si, Ca	2	bcc-Fe *a*=2.845 Å (ferrite + cementite), in calcite+quartz
3	Cu, Na, Cl	3	NaCl, small fcc peaks *a*=3.6 Å
4	Cu, Na, Cl	4	calcite, quartz ("failed shot")
5	Al, Na, Cl, Si, Ca	5	NaCl
6	Fe, Na, Cl, Si, Ca	6	calcite (75wt%), quartz (25 wt%)
7	Fe, Na, Cl, Ca, Si		
8	Fe, Na, Cl, Ca, Si		
9	Cu, Na, Cl		
10	Cu, Na, Cl		

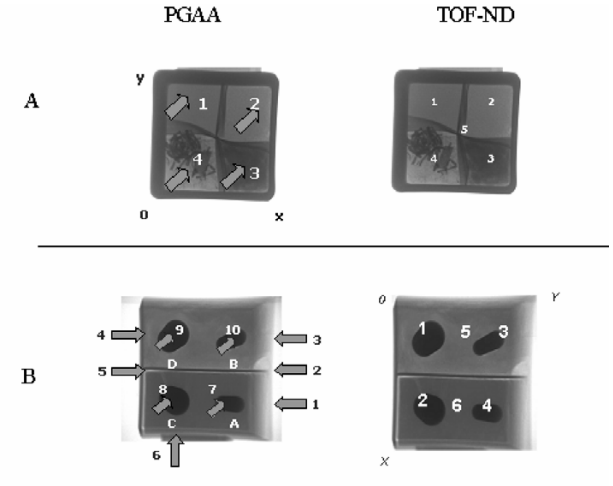

Fig. 1. X-ray radiography images of the H-VI. (A) and D-IV. (B) boxes with the investigated points. The radiographs were taken at the center for X-ray tomography, University of Ghent. For PGAA and TOF-ND measurements the numbering of parts of the images is different in the case of D-IV. (B) box

Iron box, labeled H-VI.

According to the X-ray radiography images taken from different view, this box is presumably divided into four sections of equal sizes with a pair of crossing sheets (Fig. 1A). All four sections' materials were analyzed by PGAA (Fig. 1A, left). The same sections and the crossing point of the sheets were also analyzed with TOF-ND (Fig. 1A, right). Details of the identified elemental and crystalline components are summarized in Table 1. With PGAA, predominantly Si was found in the sections 1 and 3, Na and Cl in section 2, whereas the fibre-like material may be identified as Ag chippings in section 4. Since the molar ratio of Na and Cl in section 2 is 1 to 1, we assert that this section contains simply sodium chloride.

These results quite reasonably well agree with the TOF-ND results (Fig. 2). TOF-ND has identified gypsum ($CaSO_4$ $(H_2O)_2$) and talc in all sections, probably as filling material. TOF-ND identifies quartz in section 1, quartz and sodium chloride in section 2, iron oxides in section 3, and Al or Ag in section 4 (Table 1). TOF-ND cannot distinguish between Al and Ag which have the same structure and almost the same lattice parameters. TOF-ND shows an fcc-phase in some points with clearly increased lattice parameters with respect to pure copper, which indicates the presence of a copper alloy such as bronze or brass. The presence of wuestite (FeO) could probably be explained as being part of the iron box walls.

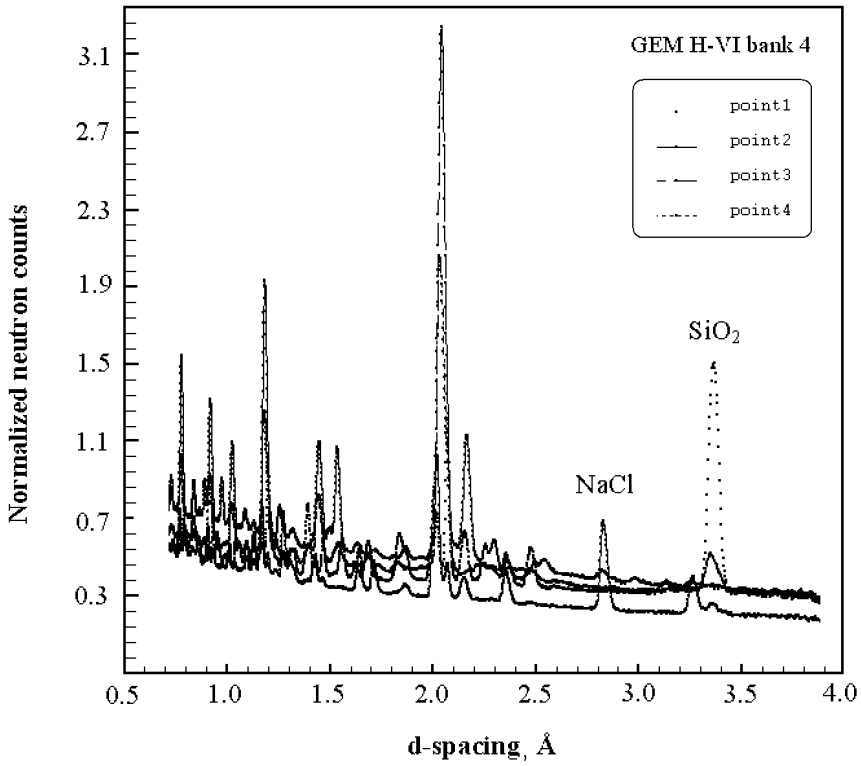

Fig. 2. TOF-ND spectra, taken at GEM, ISIS, UK. Four points on H-VI. black box have been analyzed

Aluminum box, labeled D-IV

The X-ray radiography images show that this box is divided into two parts of equal size. Each compartment contains two cylindrical rods (Fig. 1B). Based on both PGAA and TOF-ND measurements, the 'A' and 'C' rods are made of iron, while the 'B' and 'D' are made of copper. TOF-ND shows that the iron phase is ferrite (bcc iron), rather than steel. The iron Bragg peaks in 'A' in the TOF-ND data are missing, probably because the collimated neutron beam missed the rod during the experiments. It is also important to note that TOF-ND has difficulties to distinguish between copper and steel (fcc-iron) which have the same structure and similar lattice parameters. TOF-ND suggest that the filling material surrounding 'B' and 'D' is sodium chloride, while that around 'A' and 'C' consists of 75 wt% calcite ($CaCO_3$) and 25 wt% quartz (SiO_2) (Table 1). There are no clear indications, neither in the PGAA nor in the TOF-ND data, of the composition of the dividing sheets between the two sections. Missing signals could indicate that the separating walls are made up of Al, like the outer walls. The aluminum contribution observed in the No. 5 PGAA measurement may originate from both the box wall and the dividing sheets.

Conclusions

PGAA and TOF-ND are non-destructive techniques that can be regarded as standard methods for bulk elemental and phase analysis. They both provide information averaged over the irradiated volume, which is primarily determined by the neutron beam dimension. PGAA with a wide beam is fast, but the spatial resolution is not sufficient to reveal fine details inside the objects. Furthermore, for a quantitative composition analysis, neutron self-absorption correction will be introduced, using Monte Carlo calculations.

According to the experiments on the black boxes the methods (PGAA, TOF-ND and NT) provide complementary information, none of them being is sufficient alone. NT produces high-resolution 3D images that are required to survey the object for attenuation features. The contrast features in the NT images obtain a chemical and structural interpretation when information from PGAA and TOF-ND is added. PGAA can 'see' the elements in the bulk which is an important analysis requirement in archaeological sciences. TOF-ND is phase sensitive and can identify structure and phases, for example distinguish between the different oxides of iron.

According to the aims of the Ancient Charm project, the next step is to use a 'pencil beam' (narrow beam of the order of 1 mm diameter) to perform systematic scanning of large objects.

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