Radiography driven Prompt Gamma Activation Analysis and Neutron Diffraction measurements on Black Boxes designed for the 'Ancient Charm' Project

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Introduction and Objectives

The aim of the 'Ancient Charm' project (http://ancient-charm.neutron-eu.net/ach) is to reveal **3D elemental and phase images of complex museum objects** by combining different **neutron based techniques** (Gorini 2007): Neutron Radiography/Tomography (NR/NT), Prompt Gamma Activation Analysis (PGAA), Time of Flight Neutron Diffraction (TOF-ND) and Neutron Resonance Capture Analysis (NRCA). Two sets of sealed boxes were manufactured by the Hungarian National Museum

(Dúzs 2008) and by the University of Bonn, Germany (Kirfel 2008). These objects are iron and aluminium-walled cubes of 40 and 50 mm edge lengths, respectively, containing materials relevant for the compositions of complex archaeological objects. These so called 'black boxes' were analyzed by these methods in order to develop and validate a routine for combined investigations.

The results of radiography-driven PGAA and TOF-ND on one Ancient Charm black box are presented here. PGAA provides elemental compositions, while TOF-ND identifies phase distributions of metal and mineral components, both in a non-destructive way. Using a collimated neutron beam and an xyzω-moving table, the elemental or phase composition of interesting parts can be studied in the X-ray or neutron radiographies.

Methods

The technique based on systematic sample scans is called as Prompt Gamma Activation Imaging (PGAI). The PGAI is a new terminology – introduced by the project – for determining the compositions of small volumes within the sample by scanning (Kasztovszky & Belgya 2006). The actual volume is determined by the intersection of the collimated neutron beam and the viewing angle of a gamma detector. In medical imaging this kind of intersection is called *isocenter*, which is a fix-point in space and is the source of the information. In our case, it is a small volume rather than a point; therefore it is better called *isovolume*. If a sample is moved, around the isovolume fixed in space, we can collect spatially well resolved analytical information by acquiring a gamma-spectrum at each sample position. This double-collimated arrangement substantially reduces the gamma counting rate, and thus increases the experimental time. Such a measurement is usually not practical and cost-effective. The solution comes at the price of reduced spatial resolution: the removal of the gamma collimation results in a wide viewing angle of the detector covering the whole object, thus photons created along a chord-shaped volume throughout the sample are detected. This arrangement is called chord-setup. In this latter case, however, the tomographic reconstruction of the object based on back projection is necessary. The schematic drawings of the two basic measurement setups are shown in Figure 1.

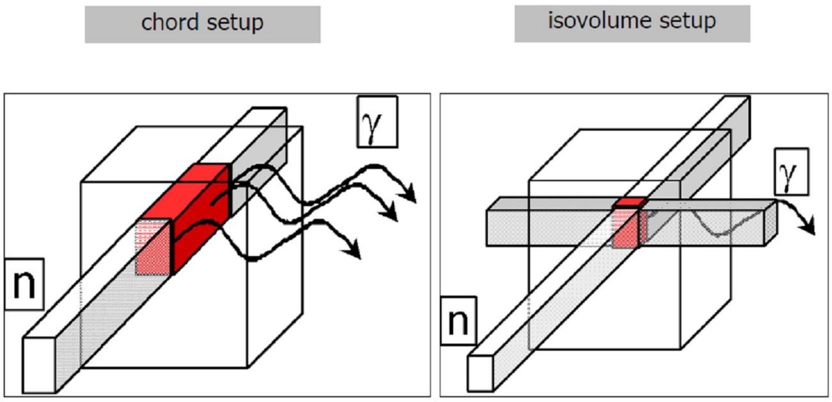

Fig. 1. Schematics of the two basic measurement setups in PGAI

(left: chord volume; right: isovolume)

Prompt Gamma Activation Imaging

In total, nine black boxes were selected for the experiments at Institute of Isotopes, Budapest (Kis et al. 2008). They represented a wide range of material and structural variability and their measurements could be completed during the available beam time.

On the NIPS station of Budapest Research Reactor, the positioning of the samples was carried out using a moving table and based on the radiography images taken with the mounted neutron tomograph. The beam size used for analytical purposes was either 2 mm × 20 mm or 2 mm × 10 mm. The height of the collimator aperture was chosen to fit the geometry of the selected section and to optimize the measurement time. The typical acquisition time varied between 200 sec and 3600 sec, depending on analytical sensitivity of the investigated materials. All boxes measured on this station were studied in chord geometry, while four of them were also examined with isovolume setup.

General features of the NIPS system:

- Flux: 7×10^7 $cm^{-2}s^{-1}$ cold neutron beam narrowed by a neutron collimator
- Hundreds of gamma spectra depending on spatial resolution; 200 – 3600 sec per spectrum
- Accurate positioning of interesting parts of the boxes based on neutron radiography images
- Neutron penetrating depth: in the order of centimetres
- No self-absorption correction yet ➔ qualitative or semi-quantitative elemental composition

Chord features:

- Higher count rates
- Best applicable for elongated parts of boxes
- Lower spatial resolution

Isovolume features:

- Low count rates
- Applicable for point-like parts of the box
- Smallest isovolume used: 2.3 mm ×2.3 mm × 5 mm

Time of Flight Neutron Diffraction

The complementary information content of time-of-flight neutron diffraction (TOF-ND) method was exploited in several cases in order to reveal the phase compositions of the sections investigated if the elemental compositions from PGAA did not provide the full information on the metal or mineral phases. Neutron diffraction experiments were performed on two diffractometers at ISIS, on ROTAX (Kockelmann et al. 2000) and GEM (Day et al. 2004). The TOF-ND method (Kockelmann & Kirfel 2006) makes use of the polychromatic beam of neutrons possessing wavelengths over a broad wavelength range. For both 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 collections on the black boxes, the size of the incident beam was set to typically 10 mm × 10 mm. The boxes were measured at several points where the neutron and X-ray tomographies indicated particular features. A more detailed description of the TOF-ND analysis on the black boxes is given by Festa et al. (2008).

Main features of the TOF-ND systems:

- no sample preparation
- large objects can be analysed

- millimeter spatial resolution
- bulk analysis (average)
- similar to XRD
- crystalline materials
- quantitative phase + structure analysis
- texture and strain in metals

Results

Iron (H-VI) box: According to the X-ray radiography and neutron radiography images taken from different views, this box is divided into four sections of equal sizes with a crossing pair of separating sheets (Fig. 2). Based on the different transmissions observed by radiography, the four sections apparently contain different materials. Moreover, a strong neutron absorber fibre-like material is placed in section (1+2). All four section materials were analysed by PGAI and TOF-ND. Details of the identified elemental and crystalline components are summarized in Table 1. With PGAI the fibre-like material in section (1+2) was identified as Ag. Predominantly Si was found in section 3 and Fe in section 4, whereas Na and Cl in section 5. Since the molar ratio of Na and Cl in section 5 is 1 to 1, it was asserted that this section contains pure sodium chloride. There were signals of Al in two measurements carried out in section (1+2) and 5. It is due to the Al plate covering the sections. The measurement at the crossing points of the sheets confirmed the presence of Cu.

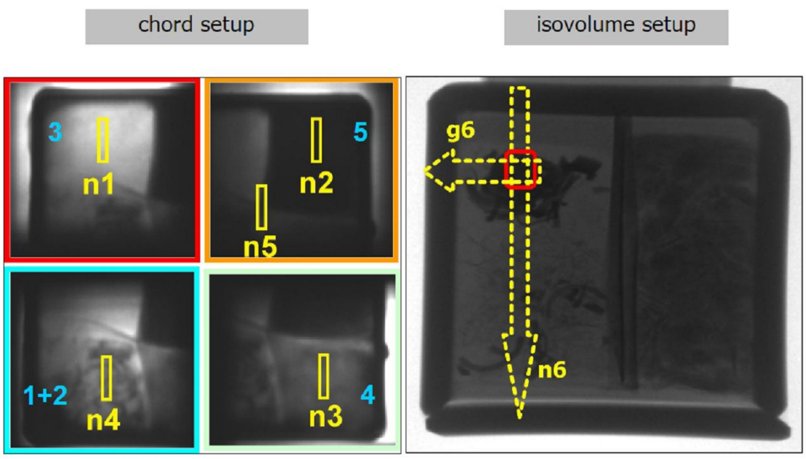

Fig. 2. PGAI measurement points for box H-VI (left: chord volume; right: isovolume)

These results reasonably agree with the TOF-ND results. TOF-ND has identified gypsum and talc in all sections, probably as filling material. This result may indicate a misalignment or it may indicate that talc powder leaked from (1+2) into other compartments. TOF-ND identified quartz in section (1+2) and 3, quartz and sodium chloride in section 5, iron oxides (wuestite, magnetite) in section 4, and Al or Ag in section (1+2) (see Table 1). TOF-ND can not distinguish between Al and Ag, which have the same structure and almost the same lattice parameters. Based on PGAI results, the material proved to be Ag. The wuestite (FeO) could probably be part of the iron box walls. TOF-ND shows an fcc-phase in some points with clearly larger lattice parameters than pure copper, indicating the presence of a copper alloy such as bronze or brass. The identification of Zn by PGAI decides for brass rather than bronze.

Table 1. Details of the composition of the box H-VI.

Nr.	Nominal composition	Meas. type and Nr. of PGAI beam	PGAI results*	TOF-ND results (Festa et al. 2008)
1+2	Ag in talcum	chord: n4 isovolume: n6	H, Si, Cl, Mn,Fe, Cu, **Ag**	quartz (SiO_2), gypsum ($CaSO_4(H_2O)_2$), talc ($Mg_3(OH)_2$ (Si_4O_{10})), Al or Ag, based on PGAI: Ag
3	sand	chord: n1	H, B, Na, Al, **Si**, Cl, K, Ti, Mn, Fe, Cu	quartz, gypsum, talc, Al or Ag, Cu-type fcc (bronze, brass)
4	iron grit	chord: n3	H, B, Al, Cl, Mn, **Fe**	gypsum, talcum, Cu-type fcc (bronze, brass), wuestite (FeO), magnetite (Fe_3O_4)
5	salt	chord: n2	**Na**, Al, **Cl**, Cu	quartz, halite (NaCl), gypsum, talc, Cu-type fcc (bronze, brass)
6	Al plate	-	-	
7	Cu sheets	chord: n5	H, Na, Al, Si, Cl, Mn, Fe, **Cu**, Zn, Ag	halite (NaCl), gypsum, talc, Al or Ag, Cu-type fcc (bronze, brass), wuestite (FeO)

* : Elements in bold face are major components, others are in smaller quantities

Conclusion

PGAA and TOF-ND are standard non-destructive methods for elemental and phase analyses. They provide information averaged over the irradiated volume. However, narrowing the neutron beam to a few millimetres makes chord or isovolume setups possible and provides localized information on the sample.

According to our experiments on the black boxes, the methods (PGAI, TOF-ND, and NR/NT) provide complementary information, none of them being sufficient for characterising a composed material alone. NR/NT produces high-resolution 2D/3D images that are required to survey the object for its geometrical structure and attenuation features. The contrast in the NR/NT images provides chemical and structural interpretation only if information from PGAI and TOF-ND is added. PGAI can 'see' the elements in the chord and/or isovolume, which is an important analysis requirement in characterisation of archaeological objects. TOF-ND is phase sensitive and can identify structures and phases, for example distinguish carbon phases and oxides in iron objects.

For a quantitative analysis, neutron self-shielding and gamma self-absorption corrections should be introduced using Monte Carlo calculations.

Acknowledgments

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