NEUTRON DIFFRACTION ANALYSIS OF 'BLACK BOXES'

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Abstract

The Ancient Charm *project addresses several aspects of neutron analyses of archaeological materials, with the specific aim to developing neutron activation and neutron diffraction into imaging methods. One of the central techniques is element determination by Neutron Resonant Capture Analysis (NRCA), besides the more established Prompt Gamma Activation Analysis (PGAA). Neutron diffraction is another technique employed in this project, for mapping the spatial distribution of crystallographic phases in a sample.* Ancient Charm *provides the prospect of combining several of these analytical neutron methods with neutron radiography in order to obtain a comprehensive characterisation of the interior of an artefact. This paper reports on neutron diffraction results on 17 of so-called 'Black Boxes', closed cubes containing geometrical arrangements of materials such as metals, minerals, ceramics, and organic matter. The measurements were carried out at the pulse neutron source ISIS at the Rutherford Appleton Laboratory in the United Kingdom. The aim of this 'Black Box' study was to identify strengths and weaknesses of neutron diffraction for analysing archaeological objects and to develop a best practice for a combined use of analysis methods for different combinations of materials*.

Kivonat

Az Ancient Charm *program keretében a régészeti leletanyag neutronfizikai alapokon történő vizsgálatának számos lehetőségét próbáljuk ki, a neutron analitikai vizsgálatok (aktivációs analízis, diffrakció) képalkotási lehetőségeinek gyakorlati kifejlesztésére. Az egyik legfontosabb technika a Neutron Rezonancia Befogási Vizsgálat (NRCA), a másik, már jobban kidolgozott eljárás a Prompt Gamma Aktivációs Vizsgálat (PGAA). A neutron diffrakció olyan eljárás, amelyet a projekt keretében arra alkalmazunk hogy feltérképezzük a minta belsejében kijelölt területek fázisösszetételét. Az* Ancient Charm *program lehetőséget ad többféle neutron alapú analitikai módszer együttes alkalmazására, neutron radiográfiával kiegészítve, hogy a műtárgy belsejének összetételéről részletes ismereteket szerezhessünk. Ebben a cikkben 17 kísérleti próbatest, ún. 'fekete doboz' neutron diffrakciós vizsgálatáról számolunk be. A zárt próbatestekben különféle fémeket, ásványokat, kerámiát és szerves anyagot helyeztek el, szimulálva geometriailag kontrollált körülmények között a tényleges régészeti leletekben előforduló vegyes összetételű tárgyakat. A vizsgálatokat a Rutherford Appleton Laboratory (Nagy-Britannia) ISIS nevű neutron forrásánál vizsgáltuk. A 'fekete dobozok' vizsgálatának célja az volt, hegy megismerjük a neutron diffrakciós vizsgálatok lehetőségeit, előnyeit és hátrányait, régészeti tárgyak vizsgálatára és kifejlesszünk egy eredményes módszertant a különböző vizsgálatok együttes alkalmazására*.

KEYWORDS: NEUTRON BASED IMAGING ANALYSIS, EXPERIMENTS, NEUTRON DIFFRACTION

KULCSSZAVAK: NEUTRON ALAPÚ KÉPALKOTÁSI TECHNIKÁK, KÍSÉRLETEK, NEUTRON DIFFRAKCIÓ

Introduction

Neutrons are a very suitable probe for the non-destructive examination of undisturbed objects and bulky samples made from materials as diverse as ceramics, pigments, glasses, pure metals and alloys. The most important property for material testing is that neutrons have a high penetration power due to the kind of probe-material interaction. In fact, neutrons easily pass through relatively thick samples and transport information about the interior in general and about internal parts in particular that are not visible from the outside. This is an essential characteristic of the neutron techniques, in the case that the analysis of the archaeological object has to be non-destructive.

Several neutron methods are available for the examination of objects, among them elemental analysis and structure analysis methods. An EU-sponsored research project, called ANCIENT CHARM, aims to develop neutron-based techniques into non-invasive methods for 3D imaging of the elemental concentrations and phase compositions of cultural heritage objects (Gorini 2007). The main emphasis of the project is on the development of a relatively new technique, Neutron Resonance Capture Analysis (NRCA) (Postma et al. 2004). This technique has already been frequently used at the neutron source GELINA in Geel, Belgium. One of the tasks in the project is the installation of NRCA on a high-intensity neutron source, the accelerator based pulsed neutron source ISIS in the United Kingdom. For NRCA, the sample is irradiated with 'epithermal' beam, i.e.

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relatively fast neutrons, which activate the sample and prompt it to emit gamma radiation, which is particularly strong for certain element specific 'resonance' energies. The intensity of the emitted gamma radiation at a resonance informs about the concentration of the respective element in the irradiated part of the sample. Traditionally, NRCA is applied with wide neutron beams, several centimetres in diameters so that not much position-information of the elements is obtained. It is one of the goals of ANCIENT CHARM to further develop NRCA into a method with a much higher spatial resolution. In the same way and in parallel, other methods are being developed into imaging methods, Prompt Gamma Activation Analysis (PGAA) at the research centre in Budapest and at the research reactor in Munich, as well as Time-of-flight Neutron Diffraction (TOF-ND) at ISIS. The aim of the 'Ancient Charm' project is also to combine these methods with Neutron Tomography (NT) in order to generate a consistent set of 3D images of the internal elemental and phase compositions of complex museum objects.

The focus of the present paper is on neutron scattering, or more precisely, neutron diffraction analysis. In principle, diffracted neutrons can give information on the microscopic structure of a material in terms of crystalline phase abundance (e.g. minerals or metals), of the microstructure, of texture or porosity, and other structural properties. Structure parameters and phase composition(s) of a material are often related to the fabrication methods and treatments that a materials has seen, to the deformation history of the material, and to the corrosion behaviour and corrosion environment. For example, the phase composition of a ceramic object depends on the firing conditions; the microstructure of a metal object depends on the mechanical and thermal treatment during manufacture or usage. The application of neutron diffraction as a non-destructive archaeometric tool to study ceramic and metal artefacts was proposed a few years ago. The characterisation potentials were initially investigated on ceramics (Kockelmann et al. 2001) and archaeological bronze objects (Siano et al. 2002) using the powder diffractometer ROTAX at the pulsed neutron source ISIS. It is important to emphasise that neutron diffraction 'sees' mostly crystalline material, though also glassy materials leave traces in the diffraction data. As for NRCA, quantitative analysis by TOF-ND is typically performed using large neutron spot sizes of several square centimetres. This large beam illumination is sometimes considered an advantage of the neutron analysis because it can provide a representative overview of the sample material, averaged over a large illuminated volume. Neutron diffraction analyses are typically performed on one or several analysis points, either to check for homogeneity of the material or to survey a complex object composed of several parts of different materials. This non-destructive surveying of an object is limited by the available neutron flux, the available beamtime on the diffractometer, by the collection time, and last but not least, by the size of the diffracting volume, i.e. the size of the neutron sampling volume. This volume is defined by the beam cross section area multiplied by the sample extension along the given primary beam direction. It normally takes an one hour 'shot' to analyse one spot, i.e. the sample at a given position and orientation, so that the non-destructive inspection of an object rather than a few 'shots' needs several hours beam time.

For many archaeological objects, a systematic mapping of phases and structures rather than a few 'shot' is highly desirable, often even indispensable for obtaining useful information. Many cases require spatial resolution in the sub-millimetre range. It is obvious that the requirement for high-resolution diffraction imaging is difficult to meet, simply because neutrons are highly penetrating, which is just why they are used for non-destructive testing in the first place. There are essentially two approaches to achieve diffraction imaging, depending on the signal used for mapping. The signal can be extracted from the direct beam (transmission), or from the scattered beam (Bragg diffraction). The transmission techniques, being essentially modifications of conventional radiography/tomography, are fast, since the full object can be simultaneously illuminated. Scattering techniques are typically slow because of the low neutron fluxes compared to X-ray sources and because of the limited access to the diffracted neutrons due to the limited and expensive coverage of the space around a sample with detectors. A complete mapping of an object by neutron diffraction is therefore rather the exception than the rule, and it can only be done with comparatively low spatial resolution in the order of millimetres. In contrast, neutron tomography can produce images in the sub-millimetre resolution range. However, the attenuation images provide merely attenuation contrasts while they can not deliver direct information on the type and structure of materials. That is to say, radiography and tomographies often show high-contrast details of features inside objects but there is no clue to the elemental and structural consistency of the feature. This is why neutron diffraction methods are important; they can give the colours in the radiographies a physical and structural meaning. Consequently, it is generally desirable to use both tomographic and scattering methods aided by the elemental information that can be retrieved from activation methods such as PGAA and NRCA.

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Table 1 - Analysed Black Boxes at ISIS. Instruments used by TOF-ND: time-of-flight neutron diffraction. PGAA: prompt gamma activation analysis. XR: x-ray radiography. NR: neutron radiography

Box	TOF ND	Complementary methods	Appendix Table
D-II (Al)	ROTAX	XR, NR	Table 1
D-IV (Al)	ROTAX	PGAA,XR	Table 2
D-V (Al)	ROTAX	PGAA, XR, NR	Table 3
D-VI (Al)	ROTAX	PGAA	Table 4
D-VII (Al)	ROTAX	PGAAXR, NR	Table 5
D-VIII (Al)	ROTAX	XR, NR	Table 6
D-IX (Al)	ROTAX	XR, NR, NRCA	Table 7
D-X (Al)	ROTAX	XR, NR	Table 8
D-XI (Al)	ROTAX		Table 9
H-I (Fe)	GEM, INES	PGAA, XR, NR	Table 10
H-II (Fe)	GEM, INES	XR, NR	Table 11
H-III (Fe)	GEM, INES	PGAA, XR, NR	Table 12
H-IV (Fe)	GEM, INES	PGAA, XR, NR	Table 13
H-V (Fe)	GEM	XR, NR	Table 14
H-VI (Fe)	GEM, INES	PGAA	Table 15
H-VIII (Fe)	GEM	PGAA, XR, NR	Table 16
H-IX (Fe)	GEM, INES	XR, NR	Table 17

An overview of aspects and techniques of neutron diffraction imaging is given in Kockelmann & Kirfel 2006.

In the present paper, we report on the neutron analyses of test samples, the so called 'Black Boxes', which were analysed by the different techniques, including neutron diffraction. These test objects are sealed iron or aluminium-walled cubes of 40 and 50 mm edge lengths, respectively, containing 2D or 3D arrangements of materials relevant to the compositions of archaeological samples. One and the same samples were measured with different probes (fast neutrons and slow neutrons, X-rays), different techniques (PGAA, TOF-ND, NT), on different instrument stations, and at different neutron sources in Europe, the Institute of Isotopes in Budapest (Hungary), ISIS (UK), FRM-II Munich (Germany), and GELINA Geel and Ghent (Belgium). The goals of the Black Boxes analyses were to:

- obtain more insights into the potentials and weaknesses of the different methods
- develop a ‘best practice’ procedure of combined efforts,

both with respect to different combinations of materials.

Here, we report on the results of the diffraction analyses on altogether 17 Black Boxes, in comparison with results from other methods, i.e. from neutron radiography and X-ray radiography (Kudejova et al 2007; Kudejova 2008) and PGAA (Kis et al. 2008). In most cases, and at different stages (experimental, data treatment) of the analyses, complementary information from the other techniques was definitely needed to efficiently determine the correct structural composition of a Black Box by diffraction. The paper is organised as follows: **section 2** contains a short description of the samples. In **section 3**, we describe the experimental aspects of the TOF-ND analysis at the ISIS Facility at the Rutherford Appleton Laboratory (Chilton, UK). **Section 4** deals with some of the crystallographic information and peculiarities of the diffraction experiment, as far as important for understanding the diffraction results on the boxes. In **section 5** we discuss the experimental results, mainly referring to the tables in the appendix.

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In **section 6** the diffraction results are discussed in comparison to results from the other methods as well as to the true compositions of the boxes (reality check) (Kirfel (2008), Dúzs (2008)) revealed after completion of the analyses. Finally, **Section 7** summarises the learned lessons, and draws conclusions of the Black Box analyses. In the appendix, the bulk of the analysis results for each box is summarised in tabulated form. The first part of each table reports on the own diffraction results. These are compared in the second part with information obtained from other methods and also with the now disclosed composition of a box.

Black Boxes

Two sets of sealed Black Boxes were manufactured by the Hungarian National Museum (HNM), Budapest and by the University of Bonn, Germany, respectively. The contents of the boxes were according to the plans and designs proposed by the archaeologists and conservators of the HNM, using typical materials often found in an archaeological context (Hajnal 2008). The first set consists of ten iron cubes of 40 mm edge length (labelled as H-I through H-IX, wall thickness 1 mm; Dúzs 2008). The second set (labelled as D-I through D-XII; Kirfel 2008) comprises twelve aluminium boxes with wall thickness of 1 mm and dimensions of 50 mm. The compositions of the internal parts, the filling materials, as well as the individual layouts were unknown to the experimentalists. The boxes represent increasing levels of complexity, with geometrical 2D or 3D arrangements of different materials.

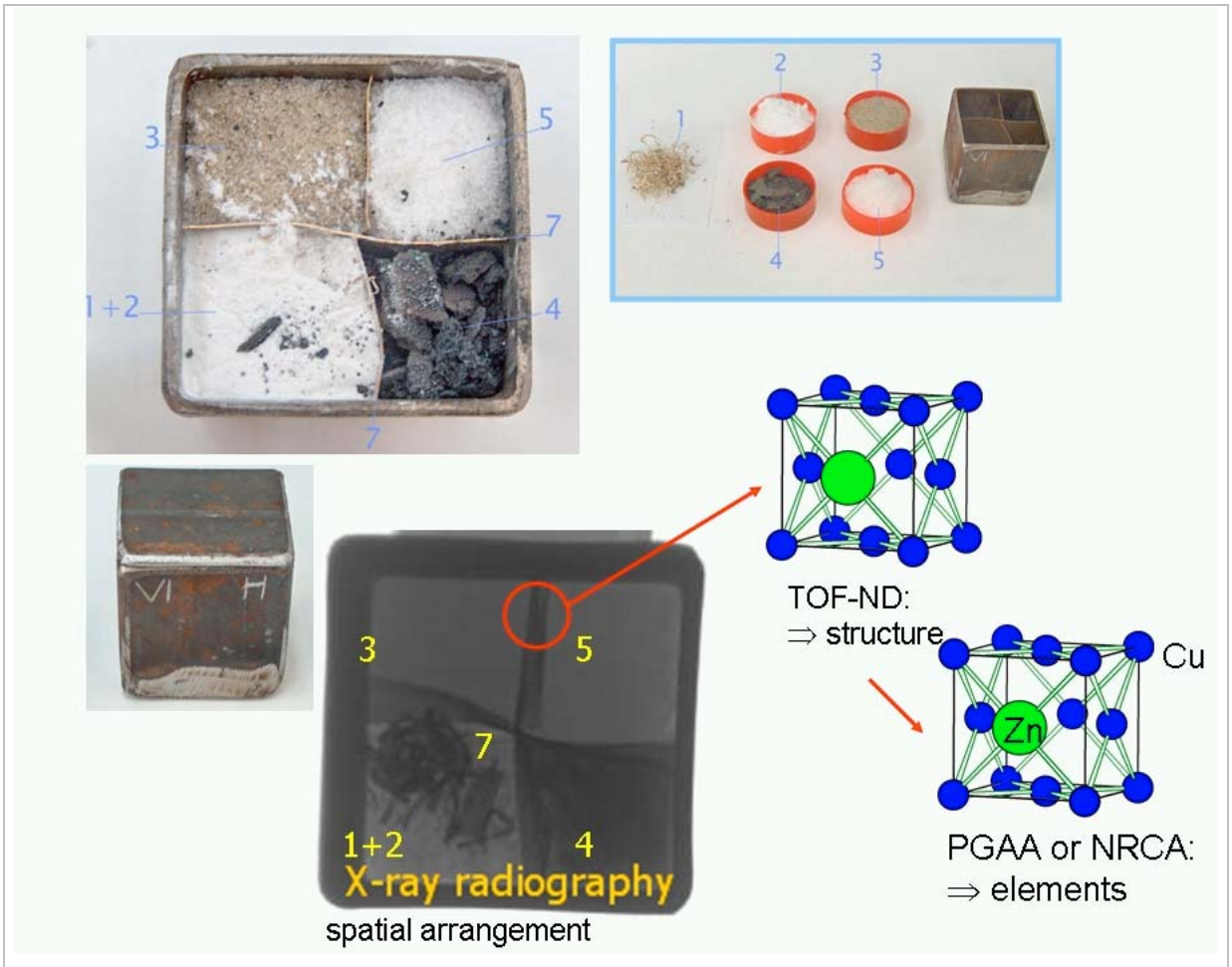


Figure 1.

Construction of Black Box H-VI and X-ray radiograph. Dimension: 4 x 4 x 4 cm3. The radiograph was used to guide the TOF-ND analyses and PGAA analysis. In the highlighted case, neutron diffraction identifies a copper alloy fcc phase as the material of a dividing wall, whilst PGAA is necessary to detect the presence of zinc as alloying element.

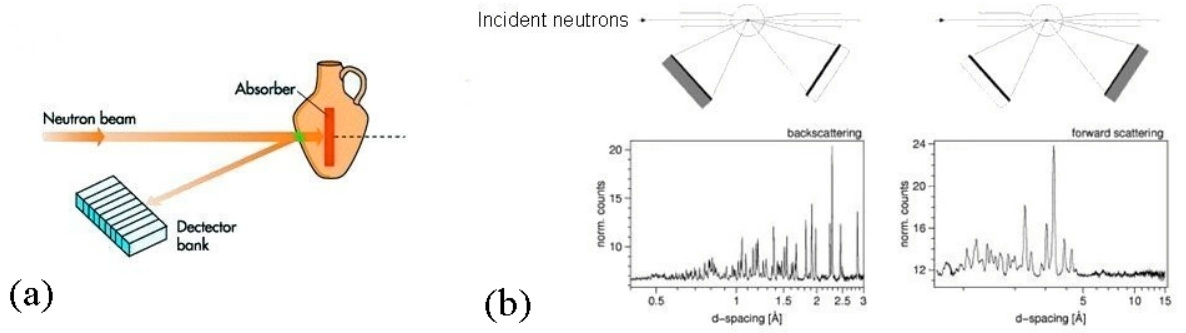


Figure 2.

(a) TOF-ND schematic; (b) patterns collected with detectors at different angles provide different d-spacing ranges with different d-resolutions

The combination of different materials in a particular box was not always following realistic compositions in an archaeological context, but rather chosen to test the capabilities and limitations of the utilised neutron methods, by realising varying degrees of complexity. In this sense, the Black Boxes served as samples in a round-robin for testing the different neutron methods and examining the degree to which the results from the different methods can be combined and made consistent.

Figure 1 shows one of the H-boxes and schematically highlights the complementarity of radiography, structure analysis by TOF-ND and element analysis by PGAA and NRCA. Details of all Black Boxes and their constructions can be found in the same issue of AM (Kirfel, 2008; Hajnal, 2008; Dúzs, 2008).

Experimental

Figure 2a illustrates the basic set-up of a time-of-flight neutron diffraction (TOF-ND) experiment. A neutron beam hits a stationary sample. The 'thermal', relatively slow, neutrons interact with the atoms in the material. Most of the neutrons pass through the material or are absorbed, some of the neutrons are scattered by the nuclei of the atoms and collected with one or more neutron detectors. Elastically scattered neutrons, i.e. those that have not changed their energy during the scattering process, carry the information on the structure of crystalline material. The TOF-ND measurements were carried out on the diffractometers ROTAX (Kockelmann et al. 2000), GEM (Day et al. 2004), and INES (Imberti et al; 2008) at the ISIS Facility, at the Rutherford Appleton Laboratory (Chilton, UK). ISIS is a pulsed neutron source, and as such, capable of providing a sequence of sharp neutron pulses (50 pulses per second), which are required for the TOF technique. Neutrons, after interaction with the sample, are recorded by detectors arranged in banks that measure both the 2Θ scattering angle and the flight time. The data for each bank are converted into a diffraction pattern, neutrons versus crystallographic d-spacing (Å), which are comparable to conventional X-ray powder diffraction patterns (**Figure 2b**). Each detector bank produces a separate histogram; but all histograms for one 'shot' can be entered into the data analysis procedure. The 'backscattering' pattern (see left pattern in **Figure 2b**) has a special relevance for the Black Box analysis because neutrons are scattered (reflected) back into the detector and provide information even if the box contains highly absorbing material. For the forward scattering bank (right pattern in **Figure 2b**) the primary neutron beam, as well as the scattered neutrons, have to cross the full length of the sample so that forward scattering data are much more prone to absorption effects.

Figure 3 shows schematics of the three ISIS instruments used for the Black Box analysis. Although these instruments use the same type of technique they have different characteristics, performances and setups as given in the figure.

Figure 3.

ISIS TOF-diffractometers ROTAX, GEM and INES, with some instrument characteristics.

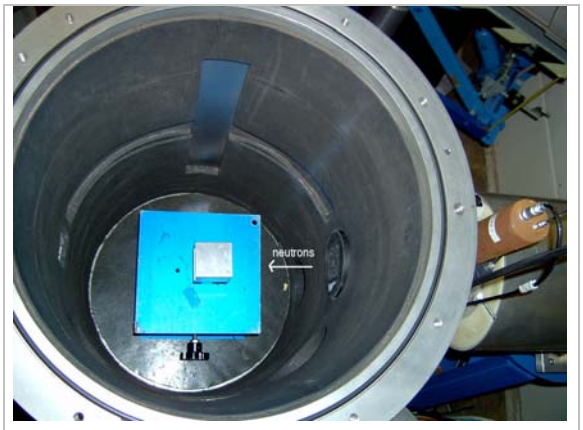
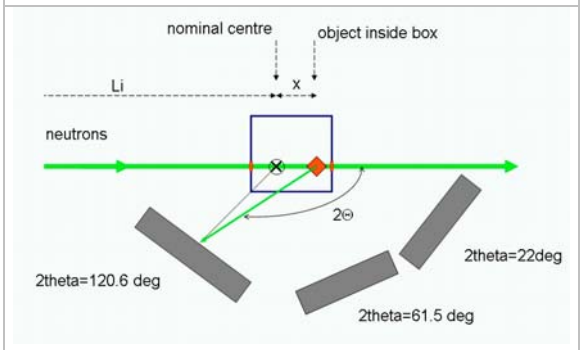


Figure 4.

(a) Black Box in the ROTAX sample chamber. The neutron beam is coming from the right;

(b) schematic experimental set-up (for details, see text). Li is the flight path of the incident neutrons, in meters.



There are, however, some common characteristics for all the measurements: the boxes were mounted on a platform or moving table inside a sample chamber to change the point of impact of the neutron beam and its direction relative to the boxes own coordinate system. The data were collected at standard ambient temperature conditions. Only for some boxes, the sample chamber was evacuated; otherwise measurements were performed in air. The air scattering turned out to be irrelevant. Neutron and X-ray radiographies were used as guides to select the most interesting 'shots' for TOF-ND analyses. The beam size was typically 10 x10 mm^2 except for INES where a beam of 40 x 40 mm^2 was used. Alignments were performed by eye, data collection times lasted between minutes and two hours at most, and data were collected with all available detectors of the instrument.

Correspondingly, in the analyses, all data were taken into account, even though in the following, only selected portions of the diffraction patterns are shown.

Figure 4 shows a photo of one of the boxes on a moving table inside the ROTAX sample chamber. The schematic highlights the following features of the experiment:

- The beam size was typically 10x10 mm^2.
- The detectors collect data from a neutron 'chord' through the whole of the sample.
- If a scattering volume element inside the box is laterally displaced from the nominal centre of the diffractometer, then Bragg peak positions of that material are shifted to different d-values in the pattern. In Fig. 4, the displacement 'x' translates into different d-spacing shifts for the different detector banks. Hence, also the Bragg peaks from the walls of the cubes are shifted with respect to the nominal Al or Fe (database) positions, respectively. Then, in case of a weak neutron-absorbing material inside the box one observes double patterns at backscattering and forward scattering angles. Is, however, the material strong neutron-absorbing, only single Al or Fe Bragg peaks are observed at backscattering angles.
- On one hand, the d-spacing shifts hamper the identification of a phase. On the other hand, these 'x'-shifts can also be used to reconstruct the spatial distribution of the material in an extended object (Gutmann et al. 2006):

  $\Delta d/d = x * \cos(\theta) / L_2$, where Δd is the distance between the observed and the nominal peak position, d is the d-spacing, in Å, L_2 is the distance between sample position and detector, and θ is half the scattering angle.
- Because of the peak shifts for horizontal displacements, accurate lateral positioning of the box in the sample chamber is important in order to obtain signals from the material at the focus. However, without secondary collimation, scattering contributions from other sample parts in the beam cannot be avoided. A vertical shift of the material or sample does not affect the position of the diffraction peaks.

Figure 5 shows for one of the Black Boxes a section of a neutron diffraction pattern collected on ROTAX.

The art of analysing a neutron diffraction pattern obtained from a multi-component sample is to disentangle the different patterns generated by the constituent 'phases', minerals, metals or other crystalline compounds. In the case of the Black Box analyses, the crystalline phases were generally identified by pattern comparison with a database of mineral and metal phases. Semi-quantitative analysis was performed by Rietveld fitting with GSAS (Larsen & von Dreele 1986; Young 1993).

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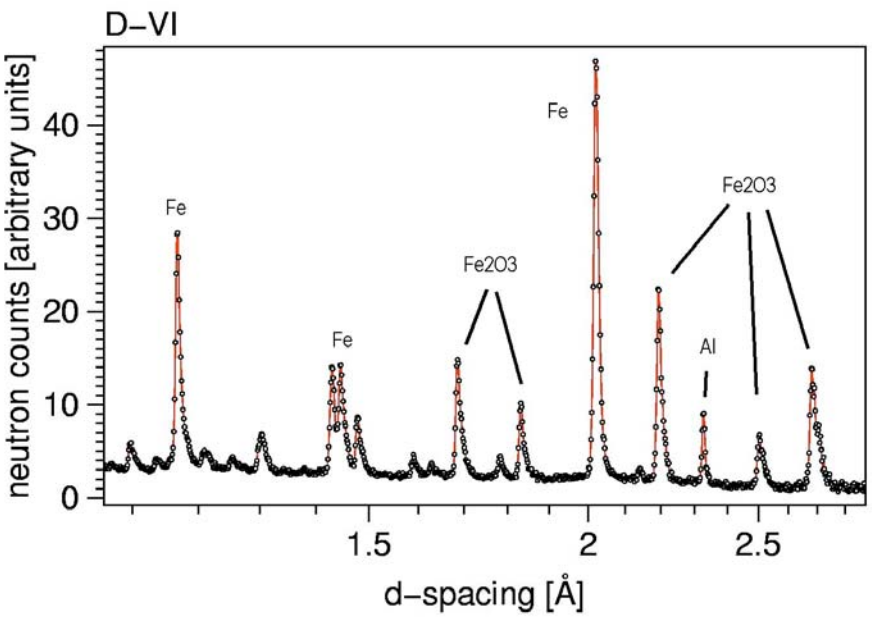

Figure 5.
A TOF-ND pattern of Black Box D-VI

The GSAS analysis suite is used to check the measured neutron patterns against theoretical single phase database patterns, and thus to confirm or reject the presence of an assumed phase. A full quantitative analysis is difficult and actually impractical due to the above described peak shifts caused by off-focus scattering because Rietveld programs cannot account for different off-centre displacements of different phases in the same data set.

Comments on some experimental and crystallographic aspects of the Black Box analysis

Figure 5 shows a typical neutron diffraction pattern, here of box D-VI, which contains iron and hematite, Fe_2O_3. The neutron diffractogramm is characterised by Bragg peaks, which are quantitatively analysed in terms of peak-intensities, -positions and -widths. The data contain information on the crystal structures and magnetic structures (hematite is magnetic at ambient temperatures) as well as on texture, i.e. the orientation distribution of the crystallites in the material. Each crystalline component yields a characteristic pattern, a 'fingerprint'. For a multi-component sample, the respective single-phase patterns superpose. Non-crystalline components or amorphous materials (typically organic materials) do not give rise to Bragg peaks and are therefore not taken into account in the diffraction analysis. However, both inorganic and organic hydrogenous materials are noticeable in the diffraction data by a typical 'hydrogen background' of often large intensity originating from the incoherent (i.e. non-Bragg) scattering of hydrogen atoms.

Neutron diffraction can differentiate between different phases and modifications of a compound, as well as its corrosion products. Structural differentiation is a strength compared to elemental analysis methods. Different phases in a phase diagram of materials are distinguished, for instance, the face centred cubic (fcc) structure of alpha-brass and the body centred cubic (bcc) structure of the beta-brass phase. For many metal structures, which crystallise in the fcc-lattice, the diffraction patterns appear very similar, because the structures are isotypic and scattering is usually not measured on an absolute scale. Then, the differences between diffraction patterns are only recognisable from slightly different peak positions due to different lattice parameters. Usually, with an optimised geometry, the unit cell parameters (lattice parameters, given in Angstrom) of compounds can be determined by TOF-ND with high accuracy, for example, the fcc structures of steel (a= 3.608 Å) and copper (a=3.6145 Å), or the structures of Al (a=4.048 Å), Ag (a= 4.086 Å), and Au (a= 4.078 Å). It is obvious that for the discrimination of silver and gold, a high-resolution instrument is required. However, as mentioned above, the neutron data peaks recorded from the Black Boxes are affected by peak shifts, if the scattering happens off the diffractometer centre. This makes the measurements of lattice parameters less accurate, and differentiation between some fcc structures becomes difficult. In the case of the Black Box analysis this applies, for example, to the above-mentioned structures of copper (Cu) and steel (Fe), or to Al, Ag and Au. In such situations, it is crucial to have results from other techniques such as PGAA in order to determine the correct metal phase(s).

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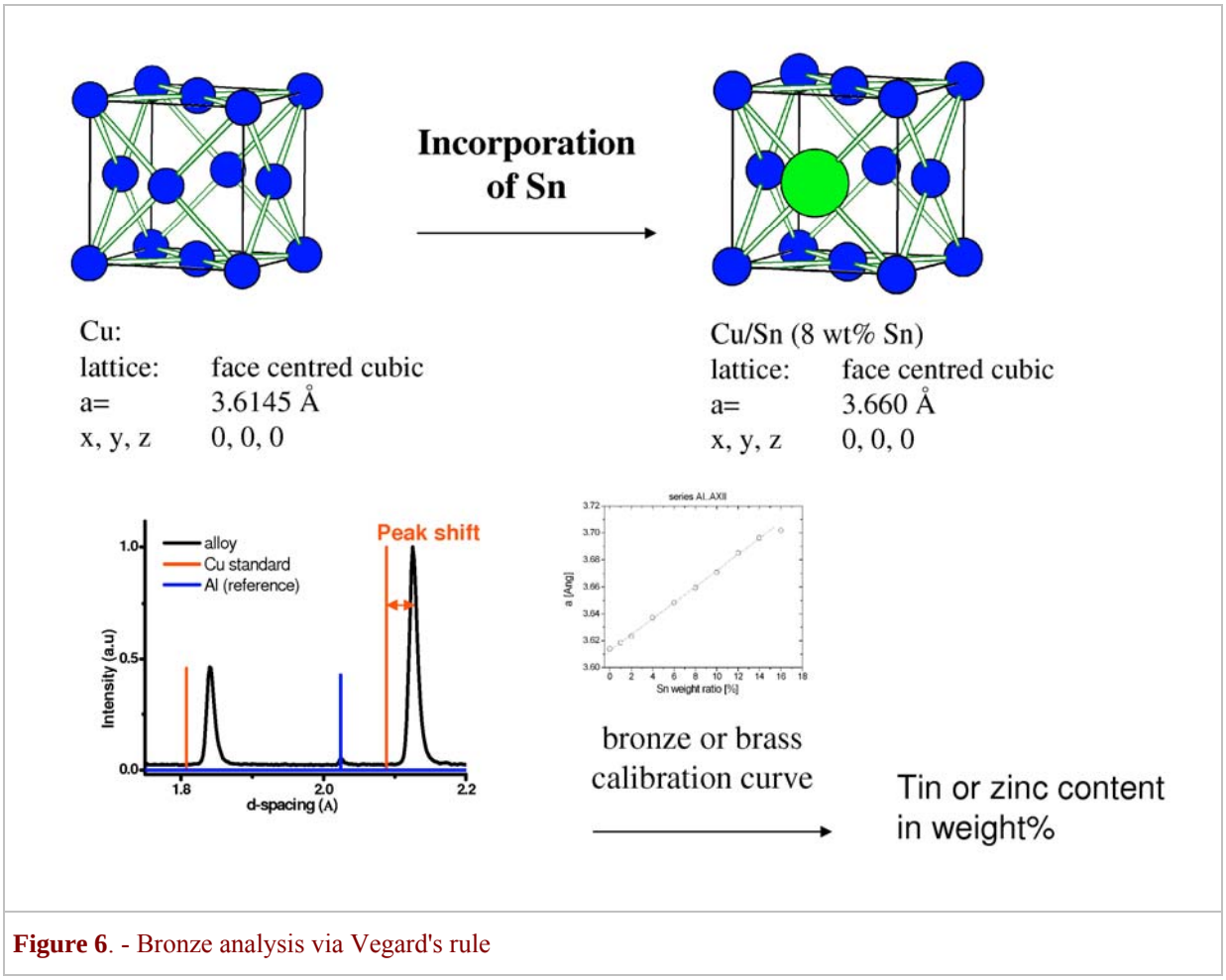

Figure 6. - Bronze analysis via Vegard's rule

The lattice parameter of the fcc cell determined ('refined') with GSAS from the Black Box data gives a first indication of the composition of the lattice. Incorporation of an element, such as tin or zinc, into the copper lattice expands the unit cell according to the size of the guest atoms (Sn is larger than Zn). Phases with fcc- lattice parameters significantly exceeding that of copper (a=3.6145 Å), are then evaluated as copper alloys Cu/Sn (bronze) or Cu/Zn (brass). The amount of Sn or Zn can be estimated from calibration curves for copper alloy standards (Siano 2002) as soon as the type of guest element is known from PGAA (**Figure 6**).

There are well established procedures in crystallography to study single-phase samples (powders or single crystals) and also multi-phase samples in case of well defined diffraction geometry. In comparison, the analyses of the Black Boxes data present a much higher degree of complexity due to:

- Interference of different materials, crystalline and amorphous, inside a box; powders, single crystals, textured materials, compounds of high and low symmetries
- scattering contributions from sample parts off-set from the instrument centre i.e. the neutron data depend on which material is in front or in the rear of the box
- materials with different absorption properties

The fact that the materials to be analysed are inside containers that themselves give rise to significant Bragg diffraction has further consequences. Al inside an Al-box, and Fe inside a Fe-box are obviously difficult to analyse, even though the Bragg peaks from the box walls are shifted in the patterns: the overlap of peaks is too high to disentangle the patterns. Since silver has a similar lattice parameter as aluminium, it is difficult to detect and quantify silver objects inside an aluminium box. Furthermore, for most of the cases, there are double-peaks of Fe or Al from the box walls. These wall-double-peaks can, however, not be satisfactorily fitted in a standard GSAS refinement which is the main reason why a full quantitative analysis of Black Boxes data may fail to work well and why the weight fractions given in this paper must be considered as semi-quantitative estimates only.

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TOF-ND results

The tables in the appendix summarise the neutron diffraction results on seventeen Black Boxes. For most of them, radiographies were available at the time of the ROTAX and GEM experiments, and they were used to guide the TOF-ND measurements. Also, PGAA results were available for the TOF-ND analyses, and they helped to identify some of the components inside the boxes. The layouts and the material compositions of the boxes disclosed after the analyses could be compared to the diffraction analyses results. The first part of each table (a) in the appendix presents the results of the neutron diffraction analyses; the second part (b) compares the results from TOF-ND and PGAA with the actual composition of a box (reality check).

In many cases, the TOF-ND analysis succeeded in correctly and completely identifying the materials inside the boxes. In other cases, only partial information could be obtained. In a few cases, TOF-ND could not provide useful information on the contents of boxes, because data remained unexplained, were too complex or could not be analysed due to poor counting statistics. All in all, TOF-ND was relatively straightforward to provide results of metals with their generally highly symmetric structures, but TOF-ND struggled with mixtures of multi-phase 'low symmetry' components, e.g. combinations of ceramics, as in H-VIII (Dúzs 2008) .

The INES data were collected with a large neutron beam of approximately 40 x 40 mm^2, at a time when X-ray or neutron radiographies were not yet available. Hence, the entire box was illuminated during an analysis, and consequently, the data contained Bragg peaks from all components of the box. It turned out, that these data could not be analysed because of the complexity of the diffraction patterns. The INES data are therefore not taken into account and omitted from the appendix.

Discussion

Radiographic and tomographic data have proven to be essential in guiding the diffraction experiments, and saving valuable neutron beam time. In some cases, 2D X-ray radiographies were fully sufficient for the location of the features inside a box. In many other cases, 3D tomographic data were required, i.e. views from different angles. Vice versa, for a proper physical and structural interpretation of the radiographic features, TOF-ND and PGAA data were essential. In some cases, TOF-ND and PGAA yielded valuable complementary information, for example for copper alloys, where TOF-ND cannot determine the alloying elements.

It turned out that the definition of a unique object coordinate system ensuring reproducible orientation at different facilities is a very important issue if radiography, PGAA and TOF-ND data are to be combined. Objects and radiographies of them need to be provided with such a reference system, as well as with information on the incident beam direction in the radiography. This was not always the case in the current study.

Alignment of the samples on the TOF-ND instruments was not always adequate, because carried out by eye only. An accurate sample positioning device is required. Also an in-situ collection of a radiographic image, as alignment aid (like demonstrated at NIPS for PGAA in Budapest), would be highly desirable for TOF-ND. Moreover, secondary collimation would allow for selecting individual scattering volumes along the incident beam direction (see double-chord set-up Budapest, (Kis et al. 2008) in spite of intensity reduction).

Finally, the analyses should become more quantitative, rather than semi-quantitative as in the present study. This is, however, not possible without an extensive revision of the analysis software, for instance with respect to allowing for different sample offset corrections for different phases in one and the same dataset.

In summary, related to the complexity of the samples, TOF- ND analyses were hampered by a number of circumstances:

- too large beam sizes (e.g. 10 x 10 mm^2 or 10 x 20 mm^2)
- missing secondary collimation
- inaccurate positioning and alignment of samples in the beam
- Bragg peak shifts
- errors in coordinate assignments to radiographies
- neutron absorption
- H-containing materials
- difficulties to identify complex materials and single crystals (gems, jewellery) at backscattering angles when the box is filled with a highly absorbing material

In a number of cases, TOF-ND performed well and added complementary information to radiographies and PGAA data. Some illustrating examples are:

- For box D-II, TOF-ND discovered a beta-brass alloy inside one of the copper alloy spirals. This result could only be achieved by neutrons which penetrate into the core of the wire. X-ray diffraction detected the beta-phase in the wire's interior only after grinding a piece of wire. Still, the neutron diffraction cannot tell if the beta-brass phase is in the core or in the surface of the wire

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owing to the insufficient spatial resolution. Since, however, an initial X-ray analysis of the intact wire had 'seen' only copper, one can infer that the additional phase must stem from the wire's interior.

- Extra cementite (Fe_3C) peaks were identified in the iron rods of box D-IV. The corresponding carbon content is estimated to 0.7 wt%.
- Different iron modifications (ferrite, steel) and iron oxides (FeO, Fe_2O_3, Fe_3O_4) are differentiated, as demonstrated for D-VI and H-VI.
- TOF-ND, in combination with PGAA, distinguishes between copper alloys and copper phases

All these examples demonstrate the need for diffraction experiments for the full characterisation of a material/object. At the same time, the fruitful combination of element analysis methods (PGAA) and phase analysis method (TOF-ND) is illustrated.

In many cases, the diffraction analysis was hindered by the complexity of the diffraction data, originating from the superposition of patterns from different parts of a box, when the neutron beam had been crossing several components. This shows that the beam size and the contributing irradiated volume are too big. An improved set-up would need to use a secondary collimator on the scattered beam side, following the example of the double-chord set-up at NIPS. Such a set-up is actually used at ISIS for structure and phase mapping on the engineering instrument ENGIN-X. On this instrument, a spatial resolution, of for instance 2 x 2 x 2 mm^3, is achieved by tight collimation of both incident and scattered radiation, which define the gauge volume (Kockelmann & Kirfel 2006). This set-up avoids recording sample-offset scattering and the accompanying peak shifts. The method appears ideal for the analysis of metals, but would also struggle to provide useful information for ceramics and clay minerals, mainly due to too low intensity emitted from the gauge volume.

Limited by the neutron flux, the recording of complete three dimensional maps with TOF-ND is very slow. Data collection times would be in the order of many hours up to days, which must be considered un-economical. More appropriate are linear depths scans, as for box D-VI, and profile scans on parts of the sample that have been beforehand surveyed by neutron or X-ray tomography.

The Black Boxes results highlight some aspects for analyses of archaeological objects with neutrons. Neutron analyses are non-destructive and provide information from the interior of the boxes. However, relatively low spatial resolutions compared to those of other methods such as X-ray methods need to be kept in mind when thinking about neutron projects. Even the spatial resolution of NT of typically 0.1 mm is still not good enough for many applications. Neutrons have high penetration in materials, but much depending on the material. Even for materials like Fe or copper, absorption is substantial and noticeable so that absorption corrections would have to be applied for a quantitative analysis. For hydrogen-containing minerals or water-soaked samples, the penetration depths are even as small as in the order of millimetres. Thus, for such materials, neutron attenuation plays an even more destructive role. Since the attenuation is not known before the experiment, attenuation measurements by NT are useful prior a TOF-ND experiment is performed.

Neutron diffraction provides information about the crystalline components. However, for multi-phase mixtures, e.g. a mixture of different types of pottery, the complexity of diffraction patterns can be overwhelming.

Conclusions

We have used time-of-flight neutron diffraction at ISIS to analyse components inside closed 'Black Boxes'. TOF-ND is necessary to characterise the features in radiographic data in terms of their phases and structures, information which is not available from other methods. For instance, cementite in iron is identified, which can be used to determine carbon contents. Different copper alloy phases can be identified and quantified, such as a beta-brass core inside an alpha-brass coating of a brass wire.

TOF-ND and PGAA are standard non-destructive techniques for phase or bulk elemental analysis, respectively. They both provide information averaged over the irradiated volume, which is primarily determined by the neutron beam cross section, and the extension of the object in the incident beam direction. Both methods are relatively fast with a wide beam spot, but the spatial resolution is often not sufficient to reveal fine details inside the objects. Reducing the beam size is at the expense of valuable neutron beam time, and as such often impractical. In many cases the combination of results from NT, XT, TOF-ND and PGAA can sufficiently reveal the properties of the materials. However, also in many other cases, the spatial resolution of TOF-ND is not sufficient, when scanning on a micro-meter scale is required.

The analysis of the Black Boxes suggests a best procedure for non-destructive analyses of objects:

- A conventional surface analysis technique (walls in the case of the boxes) characterises the outside of the objects as good as possible.
- X-ray radiography or neutron tomography produce high-resolution 2D/3D images that show

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the internal geometrical structure and attenuation features in quantitative terms. Radiographic data prior to the diffraction experiments are absolutely essential to guide the TOF-ND structure analysis. In many cases, X-ray radiographies will be sufficient. In-situ neutron radiography to guide the experiments would be useful.

- Collection of 1D or 2D diffraction data (3D diffraction imaging is rather lengthy and un-economical). Analyses have to be performed using a unique object coordinate system, ensuring reproducible orientation.
- Collection of elemental data by PGAA and/or NRCA is essential for a proper identification of materials.

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