

Neutron diffractometer INES for quantitative phase analysis of archaeological objects

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Abstract

With the Italian Neutron Experimental Station (INES) a new general purpose neutron powder diffractometer is available at ISIS, characterized by a high resolution at low d -spacings, and particularly suited for the quantitative phase analysis of a wide range of archaeological materials. Time-of-flight neutron diffraction is notable for being a non-destructive technique, allowing a reliable determination of the phase compositions of multiphase artefacts, with or without superficial corrosion layers. A selection of archaeometric studies carried out during the first year of the INES user programme is presented here to demonstrate the capabilities of the instrument.

Keywords: neutron powder diffraction, archaeometry, quantitative phase analysis, Rietveld refinement

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Neutron techniques are non-destructive and they are therefore both unique and complementary to more conventional methods for the analysis of archaeological objects. When sampling is not possible, neutron methods provide chemical, phase specific and microstructural information from undisturbed large volumes. This information provides indirect evidence on attribution and manufacturing techniques. On time-of-flight (TOF) instruments, data can be easily collected even from large objects, without previous preparation, with an experimental set-up that is normally free of sample movements [1, 2].

For quantitative phase analyses of bulk objects, neutron powder diffraction offers distinct advantages over x-ray

techniques, which are more commonly used for powder studies. To name but a few: (i) neutron analysis with a beam size of several centimetres provides averaged information from the bulk sample, rather than from surface regions; (ii) absorption by the sample can be effectively corrected [3]; (iii) for some magnetic minerals that exhibit magnetic order at room temperature, magnetic neutron diffraction is particularly useful in improving the detection limits. It is worth mentioning also a drawback of the neutron techniques: when exposing an object to a neutron beam, it generally becomes radioactive for a short time. It is a good practice to check the sample activation after short neutron irradiation intervals, assess the risk of long-term radio-activation, evaluate the required irradiation time for the object to leave the facility in a reasonable time-scale. For

instance, the residual activation of copper alloys reported in this paper is negligible; the same for iron and iron oxides.

This paper focuses on phase analysis by TOF neutron diffraction combined with Rietveld methods, applied to different materials, such as clay ceramics, iron oxide compounds and metals. Experiments on these three different classes of materials have been performed during 2006 on the diffractometer INES (Italian Neutron Experimental Station) at the neutron and muon neutron source ISIS (Rutherford Appleton Laboratory, UK). Detailed analysis results of the presented projects, including wider archaeological background information, will be published separately. The examples were selected in order to underline similarities and differences of the data analyses of different materials.

2. Experiment

The experiments have been performed on INES during its first year of user programme in 2006. The multipurpose neutron diffractometer is characterized by an excellent resolution ($\Delta d/d = 0.1\%$) in the 0.1–2.1 Å range, whilst the total d -spacing range extends up to 12 Å, providing a good coverage of the kinematical range.

The diffractometer [4] is equipped with 144 squashed ^3He detectors covering 2θ angles from 11° to 170° in the horizontal scattering plane (see figure 1). The detectors, normally grouped into 9 banks, each bank composed of 16 detectors, lie on a circle of 1 m radius from the diffractometer centre. The sample container is a large vacuum tank (80 cm diameter and about 0.5 m³ volume) that allows the study of large objects, including bulky archaeological artefacts. In addition, the sample chamber is equipped with four optical windows, to be used for instance, for a visual web-camera inspection of the sample during texture and scanning experiments. A diode laser device is also available to visualize the centre line of the incident neutron beam, which is useful when aligning samples of irregular shape.

The INES is located on the N8 neutron beamline, downstream of the spectrometer TOSCA, at a 22.8 m distance from an ambient water moderator. The long primary flight path determines the good resolving power of the instrument. The station is equipped with its own beam shutter so that it can operate almost independently from TOSCA. The neutron beam emerging from TOSCA is collimated to give a uniform square cross section of about 38 mm side length at the INES sample position. On average, a sample on TOSCA removes between 5 and 10% of the primary beam neutrons. A nimonichopper is located 9.60 m from the water moderator to filter out the high-energy neutrons. This opens at times $t_{\min} = 724 \mu\text{s}$ and closes at $t_{\max} = 10339 \mu\text{s}$ (relative to $t = 0$ when the proton beam hits the spallation target) and selects the neutron wavelength interval $\lambda_{\min} = 0.17 \text{ \AA}$, $\lambda_{\max} = 3.24 \text{ \AA}$. These values may vary slightly depending on the chopper settings and phasings.

The interval of d -spacing (or momentum transfer Q) that is available for each detector is determined for each fixed

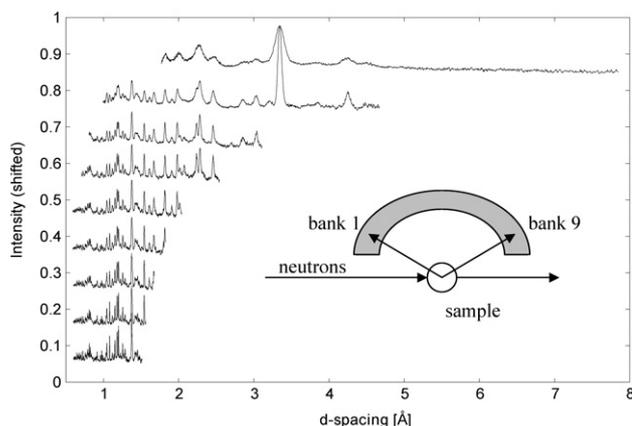


Figure 1. Nine diffraction patterns as obtained by the nine INES detector banks are shown (vertically shifted for clarity). From top to bottom: $2\theta = 11.6^\circ$ (bank 9, cut at 8 Å), 26.6° , 44.6° , 62.6° , 80.6° , 98.6° , 116.6° , 134.6° , 152.6° , 170.6° (bank 1). The sample is Otranto G1S1. A schematic view of the instrument is reported as an inset for clarity.

scattering angle 2θ as a function of neutron time-of-flight t according to

$$d = \frac{2\pi}{Q} = \frac{ht}{2mL \sin \theta} \quad (1)$$

where L is the neutron total flight path, m is the neutron mass, θ is half of the scattering angle. According to equation (1), each of the 144 detectors produces a whole diffraction pattern as a function of t , leading to different d -ranges depending on the scattering angle. The detectors are normally grouped into 9 banks for the sake of statistics, averaging over 16 detectors after conversion of the TOF scale to a wavelength scale. These focused data are then transformed into d -spacing, time-of-flight or Q scales for different analysis software applications such as GSAS [10], FULLPROF [11] or MAUD [12]. The data processing is fast and straightforwardly achieved with the ARIEL software used on all ISIS powder diffractometers. According to equation (1), the smaller the detector angle, the longer the accessible d -spacing. For TOF neutron instruments the high- d -spacing patterns are typically noisier than for angle-dispersive instruments due to the exponential decrease of the neutron flux at higher wavelengths, which in turn depends on the moderator in use. Whilst this characteristic adversely affects magnetic structure studies, it is largely compensated for structure studies by the simultaneous fitting of nine extensively overlapping diffraction patterns.

The resolution of a TOF diffractometer is given by the following formula (with the usual hypothesis of Gaussian distributed uncertainties on decoupled variables):

$$\frac{\Delta d}{d} = \left[\left(\frac{\Delta t}{t} \right)^2 + \left(\frac{\Delta L}{L} \right)^2 + (\Delta\theta \cot \theta)^2 \right]^{1/2} \quad (2)$$

where Δt , ΔL , $\Delta\theta$ are the experimental uncertainties. Hence, backscattering (high angle) detectors provide the small d -spacing range in high resolution, whereas forward scattering (small angle) detectors provide for a wider d -spacing range in lower resolution. The diffraction peak resolution of

the forward scattering detectors can be much improved by narrowing the lateral width of the incident beam, which affects the $\Delta\theta$ term, by means of motor-adjustable jaws placed between the shutter and the sample. It is worth noting that the high- d range corresponds to the region of lower peak density. Consequently, the overlap of adjacent peaks in this 1% resolution range is often unproblematic. The best resolution is obtained where it is required most, i.e. in the backscattering range of highest peak overlap. It is also worth mentioning that the resolution in backscattering is practically constant. These are considerable advantages of TOF diffractometers, especially when dealing with multiphase analyses.

A wide angular range coverage on a TOF instrument gives the possibility of performing fast texture analysis. Such a quantitative statistical analysis of preferred orientations of crystallites within the bulk can represent a signature of the working history of, for instance, a copper alloy. Casting and typical working processes such as hammering and annealing are expected to produce, for a given lattice structure, specific orientation distributions and associated pole figures. The pole figures can be constructed from a sequence of diffraction patterns obtained from different sample orientations [5]. If a significant angular coverage is provided, the sample does not need to be mounted on a rotating goniometer [6], thus greatly improving the practical aspects of the experiment, especially when bulky samples are under consideration. In the case of INES, a full (horizontal) detector coverage is provided in one of the two angular dimensions, thus only one sample rotation around one axis, defined by the incoming neutron beam, is required. The subject of texture analysis on INES will be covered in a forthcoming publication.

3. Archaeo-material studies on INES

In the following, the reliability of INES for quantitative phase analyses on different kinds of archaeological materials will be illustrated by means of three specific studies. The examples have been selected from experiments carried out in 2006, the first year of user programme on INES. In that period nearly half of the user's beamtime on INES has been accredited to proposals in the field of archaeometry. The selected experiments cover three material classes for which neutron analyses are particularly suited:

- Multiphase ceramic pieces,
- Materials containing magnetic phases,
- Metal alloys with corrosion phases.

3.1. Medieval sherds (Otranto, Italy, 7–9th century AD)

On the Adriatic coast of the south of Italy, in the region of Salento, close to Otranto, there is an important Byzantine ceramic production centre, one of the few pottery workshops excavated in Italy that can be attributed to the Early Middle Age. At the site, two stratigraphic structures of the production centre have been found and ^{14}C dated: (i) one from the 7–8th century AD, which includes the remains of three Byzantine kilns, (ii) one from the 8–9th century AD. The presence of production rejects in the latter, and the similarity of shapes and

clay among the finds from both layers suggests a *continuum* of production in the area [7]. At the site, a variety of ceramic artefacts can be recognized: transport amphorae, cooking pots, basins, lead glaze ware and other objects belonging to domestic life. There are strong indications that the clay mixture was prepared with local raw materials, taken from a number of possible deposits distributed throughout the Salento region. The measurements reported here are part of a wider project, aiming at investigating aspects of attribution and firing temperature ranges on a set of Medieval finds from specific sites in the Salento region. TOF diffraction and SANS [8] studies are being carried out on a large series of ceramic pieces. Furthermore, the research project aims at linking the ceramic groups to clay deposits in the Salento region by detection of minor phases and trace elements in the clay by means of prompt gamma activation analysis.

Quantitative multiphase analysis can also supply the basis for an initial characterization. The mineral composition of the ceramic indicates the transformations that occurred upon heating, hence the structure analysis allows us to estimate maximum firing temperatures [9]. However, when dealing with ancient ceramics we must keep in mind that although the thermal process of firing proceeds towards some equilibrium state, most often, due to the relatively low firing temperatures and the short duration of the process, true equilibrium might never be attained. Therefore, the degree of the ceramic transformation is related to factors such as particle size, firing time/temperature, firing atmosphere, gas distribution in the kiln. The mineral phases can be different for different parts of the ceramic, between the inner and the outer parts, and between the thinner and the thicker parts. A range of firing temperatures may be obtained depending on the position of the piece of the furnace. With neutron diffraction, the variation of the mineral contents in different parts of a ceramic piece can be studied, therefore helping to understand the firing process.

Several samples have been analysed both on INES and ROTAX at ISIS in order to verify the reliability of the quantitative analysis on instruments with different resolution and intensity characteristics. Ceramics samples are typically composed of high- and low-symmetry phases. A piece of archaeological pottery may therefore need to be measured as long as 12 h on INES in order to identify minority phases and to perform a quantitative phase analysis. Nevertheless, with nine detector banks on INES providing largely overlapping d -spacing ranges, a quantitative Rietveld analysis is robust and reliable. A simultaneous fit of the nine spectra for one sample has been performed for each sample using GSAS [10]. An example of fit is presented in figure 2 for four of the nine banks. The phases include: quartz, orthoclase, plagioclase, gehlenite, hematite, magnetite, diopside, spinel/hercynite and illite/muscovite. The structure models as specified in [8] have been taken from the *Inorganic Crystal Structure Database* (ICSD) [13]. Ca-rich bytownite was used to model the plagioclase peaks. We have used a structure model for muscovite in order to describe and account for illite/muscovite peaks in the diffraction patterns. Illite and muscovite are structurally related, and thus display peaks at similar reflection

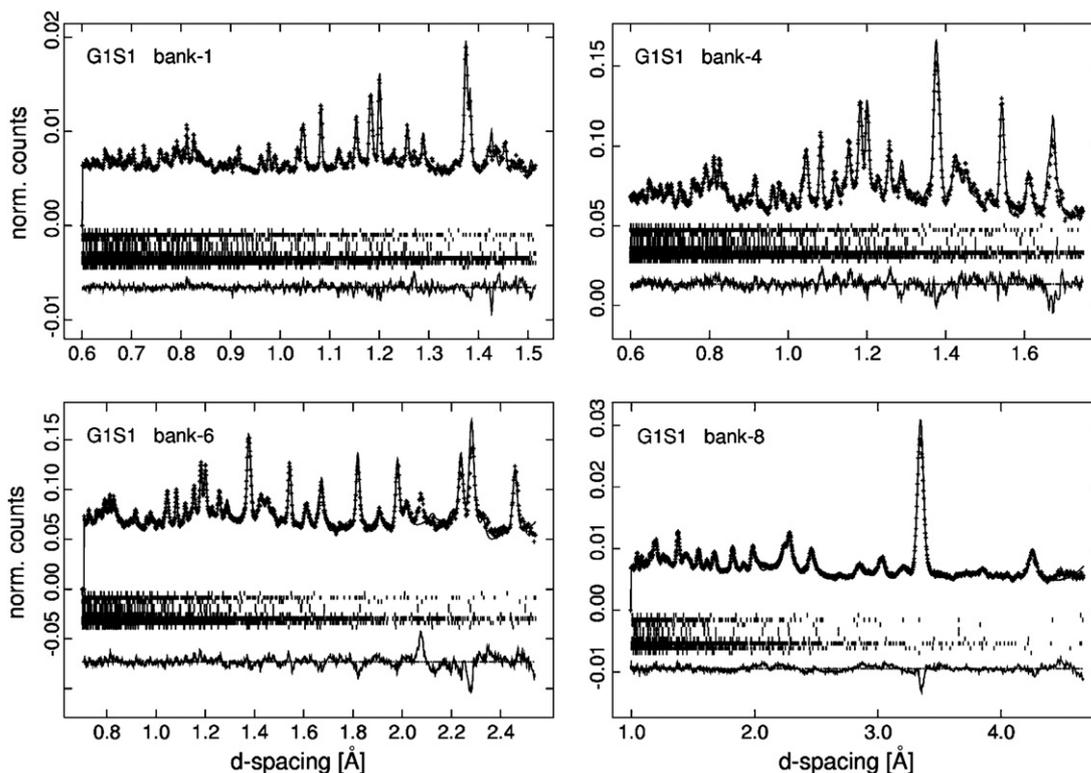


Figure 2. Rietveld data analysis of an Otranto ceramic sample. From top left, clockwise, are displayed four of the nine banks that have been fitted simultaneously: bank 1 ($2\theta = 163.1^\circ$), bank 4 ($2\theta = 109.1^\circ$), bank 8 ($2\theta = 37.1^\circ$) and bank 6 ($2\theta = 73.1^\circ$). The structural model contains nine mineral phases, which are detailed in figure 3. The top line in each inset is given by data (circles) and fit (line). Below, the ticks represent the peaks belonging to each of the nine phases, and have been reported only in order to give an idea of the high degree of superposition that is present in such a complex multiphase sample as a ceramic. The line at the bottom is given by the difference between data and fit.

positions in the diffraction patterns, in particular a pronounced peak at 4.5 Å. Therefore, it is difficult to distinguish the two structures if only small amounts are present in the mixture. Since there is no illite structure model available, and since muscovite is expected to exhibit strong preferred orientation, the obtained weight fractions indicate the presence of this phase in small or large quantities rather than being reliable weight fractions. Several spinel-type phases have been considered. Because of the restriction of GSAS to nine phases these spinel models could not be implemented in the model. Spinel and hercynite on the one hand, and magnetite and maghemite on the other hand give similar diffraction patterns, the latter two with strong magnetic Bragg peaks. For spinel/hercynite and magnetite/maghemite the refined lattice parameters indicate which phase is present. In most cases the lattice parameter indicates the presence of spinel (rather than hercynite) and maghemite (rather than magnetite). Other refinement parameters were: phase fractions; one common Debye–Waller factor for all the minerals. A detailed account of the phase analysis results will be reported in a forthcoming paper. A direct comparison of the phase identifications and quantitative phase analyses on the same samples from INES and ROTAX is displayed in figure 3, in general showing good agreement of results.

3.2. Mesopotamian seals (from about 2000 BC to about 650 AD)

In many civilizations seals were used as a signature in commercial exchanges. They were carved from various stones and pressed into soft clay to identify their bearer or to seal off jars, doors, etc. Cylindrical seals (see figure 4) are typical of ancient Mesopotamia. The *De Liagre–Böhl* collection of the Dutch Institute for the Near East (NINO) houses about 150 seals, 13 of which were selected for this study and visually identified as hematite. The seals were acquired at the beginning of the last century and they are unprovenanced.

In the *Old Babylonian Period* (about 2000–1600 BC) there was a sharp increase in the use of iron oxide stones as raw material for cylinder seals [14]. This increased use of the iron oxide in this period has not yet been satisfactorily explained. Assyriologists have demonstrated the term ‘hematite’ to correspond to the Akkadian word *šadānu*, which means ‘stone from the mountains’. Indeed, essential in the hematite research is the question of provenance, given that excavation data and cuneiform sources only give circumstantial evidence. On the other hand, provenancing of iron oxides does not have a long scientific history. As the material is relatively ubiquitous, accurate measurements of a significant number of

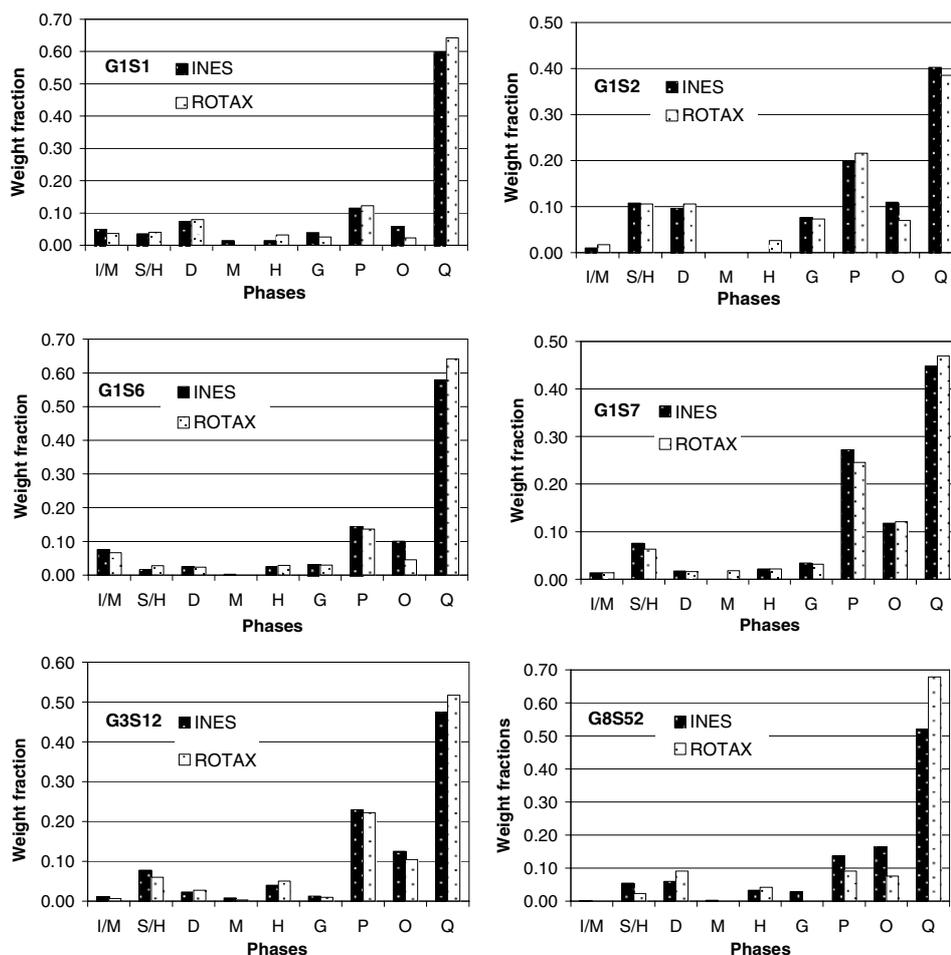


Figure 3. Comparison of phase compositions (in weight percentage, wt%) for six samples derived from INES (black histogram) and ROTAX (white histogram) data. From left to right: illite/muscovite (I/M), spinel/hercynite (S/H), diopside (D), magnetite (M), hematite (H), gehlenite (G), plagioclase (P), orthoclase (O), quartz (Q). Refer to section 3.1 for a detailed description of the structure model.

trace elements are needed to identify separate sources, and results will be compared with available geological data from the region, in a similar way to the successful provenancing of ochres [15].

On INES 11 seals from the De Liagre–Böhl collection (nos 45, 46, 47, 55, 57, 59, 61, 66, 67, 75 and 84) have been analysed. The aim of this project is to characterize this specific set of samples from the collection by a non-destructive quantitative bulk-phase analysis. The peaks at high d -spacing allow us to identify directly the main phases even with a short acquisition time of a matter of minutes. In figure 5 diffraction patterns of three Mesopotamian seals with different iron oxide compositions have been reported.

The INES data show that ten out of eleven seals are composed of iron oxides. Seven seals are pure hematite (Fe_2O_3) or hematite with small admixtures (up to 5 wt%) of phases such as quartz or magnetite (Fe_3O_4). One seal consists of mainly magnetite (63 wt%) with a high proportion of hematite (37 wt%) as a second phase. Two more objects are composed of 100% goethite (FeOOH). Seal no 55 is very intriguing. On macroscopic identification (colour, metallic

sheen, weight, cut) it appeared to be carved from iron oxide stone. However, the analysis showed it to be composed of mainly calcite (98 wt%) and quartz (2 wt%). Further analysis will demonstrate the composition of the seal in more detail. This may aid in identifying the provenance of the material. The patterns reported in figure 5 show quite clearly the fingerprint peaks that allow a quick clear identification of the major components of the seals from one of the high- d INES banks. Nevertheless, a detailed analysis evidenced in some of the seals a few peaks of small intensity that remain unidentified, and some details of the present phase analysis may need to be reconsidered once bulk elemental analysis data are available. However, given the similarity of the elemental compositions of the objects (Fe, O), it is clear that diffraction analysis is indispensable for a characterization of such objects.

In addition to the phase analysis, the atom positions of FeOOH could be obtained with better accuracy than given in the x-ray database. The lattice parameters of hematite show a slight variation, probably due to the presence of impurity elements in the trigonal structure. Also, a parameter for the peak width broadening was refined indicating significant



Figure 4. Cylinder seal no 62 shows an introduction scene before a seated goddess. The height of the seal is 20 mm, its diameter 8 mm. The style of the seal is typical of the Old Babylonian Period about 2000–1600 B.C.

(This figure is in colour only in the electronic version)

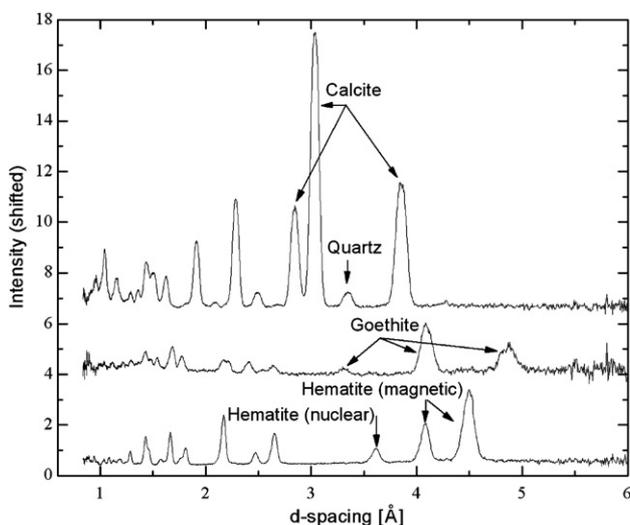


Figure 5. Bank-8 diffraction patterns for three Mesopotamian seals with different iron oxide compositions. From top to bottom: seal no 55 (calcite), no 61 (goethite) and no 45 (haematite). The peaks at high d -spacing allow us to identify directly the main phases even with a short acquisition time. For example, the presence of hematite is directly evident from the three distinct peaks between 3.5 and 5 Å (magnetic and nuclear).

particle size broadening for the iron oxide. Linewidth analyses are a particular strength of INES due to the extraordinary instrument resolution in backscattering. The linewidth of the magnetic hematite peaks follows the trend of the nuclear peaks, i.e. indicating that there is no extra (magnetic domain) broadening. It is interesting to note that for two of the seals the intensity ratios of the magnetic hematite peaks deviate from ratios calculated on the basis of the antiferromagnetic structure above the Morin transition of 260 K. This finding may indicate a requirement for a slight modification of the magnetic structure, e.g. tilting of the magnetic iron moments towards the trigonal unique axis due to impurities in the Fe_2O_3 crystal structure.

Heavy, black to dark-grey stones with a metallic sheen are usually identified as ‘hematite’, often incorrectly as our data show. Hematite, magnetite and goethite are easy to

discern by diffraction methods, be it in single-phase samples or multiphase mixtures. Neutron diffraction has a particular advantage for this study because it allows for the identification and quantification of phases in the bulk. Moreover, since for hematite and magnetite the magnetic Bragg peaks are more intense than the nuclear peaks, the magnetic scattering significantly raises the sensitivity for the detection of these phases. It is important to recall that non-destructive analysis is important when dealing with ancient unique artefacts as well as objects with delicately decorated surfaces such as the Mesopotamian seals.

3.3. Etruscan bronze objects (5th century BC)

A range of methods are used to analyse the composition of bronzes and their corrosion products. Firstly, it is useful to know what components are present in an object to confirm or refute its authenticity and to decide if it is suitable for certain kinds of conservation treatments [16].

Alloy composition, structure and corrosion products may also hint at the origin, manufacturing technology and storage conditions of the object. For instance, there are certain elemental indicators, such as lead and zinc, which can help with an initial attribution of an object. Zinc was not known as an alloying metal in antiquity [17] due to the technological difficulties of brass production. Even if the copper ore used by the Etruscans contained a considerable amount of zinc-containing minerals, zinc will escape due to its high vapour pressure at the high temperatures of the copper smelting process.

The production of zinc and brass requires special techniques. Hence, it is generally accepted that zinc was not used before the first century BC, at least not in the western part of the Mediterranean region. The Etruscans ceased production of bronzes in the second century BC. Hence, Etruscan bronzes are unlikely to contain zinc percentages larger than a fraction of a per cent. This is shown in a number of studies of well-documented Etruscan objects [18]. This observation has been used to distinguish fake from genuine Etruscan statuettes [19].

On the other hand, lead may be present in large quantities in Roman bronzes; at the time it was employed in order to lower the melting point of the alloy and as a relatively cheap filling material, while high proportions of lead are considered unusual for Etruscan bronzes.

In this study, two non-destructive complementary neutron techniques have been employed for bulk compositional analysis, neutron diffraction and *neutron resonance capture analysis* (NRCA) [19] which is suited for bulk analysis of major and trace elements. The elemental analysis provides key information for addressing questions of provenance and authentication, whereas the structure information from neutron diffraction addresses questions of ancient materials, making techniques and corrosion. Diffraction is very strong in separating out corrosion phases and secondary phases, allowing an unobstructed view of the original alloy components. Diffraction analysis, however, only provides indirect information on the chemical composition of the copper alloy, via lattice parameter measurements and application of

Table 1. Quantitative phase analysis results for bronze samples. The weight fractions add up to 100%. The lattice parameter is used to estimate the Sn content for a Cu/Sn bronze (see the text for details). Errors of the weight fractions are typically 0.5 wt%. Due to its relatively large unit cell, lead peaks are small, thus typically the error bar is about 10% of the given value.

Artefact	Copper alloy (wt%)	Pb (wt%)	Cu ₂ O (wt%)	Lattice constant <i>a</i> (Å)	Cu (wt%)	Sn (wt%)
Patera CO-235	69.6	29.4	1.0	3.6739	89.7	10.3
Arm CO-9	93.8	4.0	2.2	3.6822	88.2	11.8

Table 2. Comparison of tin to copper ratios as determined via neutron diffraction and neutron resonance capture analysis.

Artefact	Sn/Cu (ND)	Sn/Cu (NRCA)
Patera CO-235	0.115 ± 0.003	0.130 ± 0.004
Arm CO-9	0.134 ± 0.003	0.153 ± 0.002

Vegard's law [21]. This kind of 'chemical analysis' assumes that the lattice parameter of a solid solution varies linearly as a function of the concentration of the alloying elements such as Sn or Zn. For a ternary alloy, for instance Cu with Sn and Zn, a lattice parameter measurement does not provide unambiguous elemental contents. Different is the case of lead (Pb) which does not dissolve in the copper lattice and can therefore be identified and quantified by neutron diffraction. It is worth noting that small x-ray beams are inappropriate at quantifying lead inclusions. Hence, a combination of phase and elemental analysis methods is required for a characterization of ancient bronzes.

Two samples from the National Museum for Antiquities in Leiden (The Netherlands), both considered to be of Etruscan origin, have been analysed.

- fragment of statue (arm) CO-9,
- fragment of statue (hand and patera) CO-235.

The results are summarized in tables 1 and 2.

The diffraction and resonance capture analysis results are in good agreement. Both objects are made of leaded bronzes, with about 10 wt% tin in the copper lattice, typical of classical bronzes. Neutron diffraction identifies a small amount of cuprite (Cu₂O) in both objects. No other corrosion phases are observed. Slight discrepancies in the tin/copper ratios (table 2) may be due to the fact that neutron diffraction provides indirect evidence of the elemental alloy composition. The high lead content of the CO-235 object is unusual for an Etruscan object, whereas the low CO-9 lead weight fractions agree with expected negligible or low Pb content in Etruscan artefacts. On the other hand, NRCA shows about 1 wt% zinc in sample CO-9, which raises concerns about its Etruscan attribution. Neutron diffraction cannot distinguish such an exchange of tin by zinc from a lattice constant measurement, but given the zinc fraction of 1 wt%, the corrected tin fraction is 11.3 wt% compared to 11.8 wt% for a binary Cu–Sn bronze (table 1).

4. Conclusions

The three case studies demonstrate that INES can be successfully used for phase and structure analysis of

archaeological objects. It is important to emphasize that this analysis is non-destructive and quantitative, i.e. the data can be subjected to a standard Rietveld analysis. Phase analyses on complete ceramics objects by x-ray diffraction, be it on laboratory or synchrotron sources, often suffer from radiation acceptance and texture problems which make a quantitative analysis difficult or impossible. The studies on the iron oxide seals and the bronze objects demonstrate that an elemental analysis often needs to be accompanied by a phase analysis in order to distinguish different iron oxide phases in the bulk (study on seals) or to separate alloy phases from corrosion phases (bronze study). It is worth underlining how important it is to have access to a non-destructive technique, when dealing with small, valuable objects, covered with carved figures and characters, for which any type of sampling would leave visible marks.

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