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An innovative neutron spectroscopic imaging technique: mapping the elements distribution inside the bulk of archaeological artefacts

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***Abstract* – This work highlights the significant advances in neutron imaging at the ISIS Neutron and Muon Source, specifically focusing on the development of the nuclear technique Neutron Resonance Transmission Imaging (NRTI). NRTI combines the sensitivity to elemental and isotopic composition with detailed morphological information, utilizing the epithermal portion of the neutron flux. Unlike standard neutron radiography/tomography, NRTI allows for the identification and localization of specific elements and isotopes within an object's volume without physical sampling. The technique preserves detailed time and energy information for each pixel of the detector, enabling enhanced analysis and visualization of elemental distribution and composition. A case study related to Cultural Heritage is presented to demonstrate the effectiveness of NRTI in non-destructive investigations of inhomogeneous artefacts, specifically focusing on the excavation finds related to the first testimony of ancient brass production in Milan, Italy.**

I. INTRODUCTION

Within the field of neutron imaging, significant advances are being made at the ISIS Neutron and Muon Source to enhance a transmission imaging technique. This technique, named Neutron Resonance Transmission Imaging (NRTI) aims to provide both imaging and spectroscopic information about the elemental and isotopic composition and distribution inside the bulk of an object.

NRTI exploits the epithermal portion of the neutron flux, which is not yet widely used in neutron imaging. This technique is an extension of the well-established Neutron Resonance Transmission Analysis [1-3] and combines the sensitivity of NRTA to elemental and isotopic composition with detailed morphological information obtained through a time- and space-resolved detection system [4,5]. What sets NRTI apart from standard neutron radiography/tomography is the possibility to locate specific features within an object's volume and identify and localize specific elements and isotopes with enhanced contrast compared to others, without the need for physical sampling. Additionally, each pixel of the detector used for NRTI contains the full unintegrated transmitted spectrum, preserving detailed time and energy information, unlike neutron tomography where the spectrum is typically integrated over the time/energy range by the neutron camera [6].

These unique characteristics, combined with the non-destructive nature of the method, make NRTI a promising and powerful imaging tool for applications in the field of Heritage Science, expanding the potential of neutron imaging by enabling enhanced analysis and visualization of elemental distribution and composition in materials and artefacts. In particular, NRTI is a striking technique for the investigation of inhomogeneous materials.

This work presents a case study of NRTI in the field of Heritage Science, demonstrating its effectiveness for non-destructive imaging investigation of heterogeneous samples.

In 2009, the excavation in Corso of Porta Romana 20, Milan (Italy) conducted by Soprintendenza Archeologia, Belle Arti e Paesaggio di Milano unearthed numerous

fragments of metals and crucibles connected to brass production and datable between the end of I and the beginning of II century AD. These excavation finds are the first testimony of at least one brass workshop activity in the ancient Roman city of Mediolanum [7,8]. In fact, brass production was widespread throughout the Roman Empire [9] and well documented in England, Germany, and France [10-12], but it was completely unknown in Italy.

To disclose evidence of brass casting and confirm the composition of the metallic finds in a non-destructive way, a set of crucible fragments (Fig. 1) has been investigated with neutron-based techniques, described in Section III.

These crucibles consist of mass-produced terracotta pots, coated with a thick layer of refractory clay. Inside, traces of copper and zinc heating can be found, as they were brought to high temperatures to liquefy the alloy and then thrown it into moulds to make brass appliques for furniture and ornamental objects.

A subset of the unhearted crucible fragments clearly shows metallic deposition on their surfaces while in others brass inclusions can be inside the bulk. Therefore, to investigate non-destructively inside the volume and considering the thickness of some centimetres of the samples, neutron techniques have been chosen as the method of analysis.

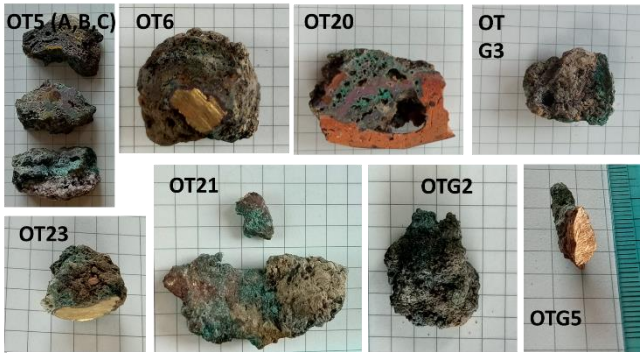

Fig. 1. Pictures of the 8 crucible fragments analysed through neutron resonance absorption spectroscopy techniques.

II. METHODS

From a set of about twenty crucible fragments, six of them have been selected based on their size (a few centimetres of thickness), weight (as a rough indication of the presence of metallic inclusions in the volume) and superficial morphological properties to request access for elemental analysis through neutron resonance absorption spectroscopy at the INES beamline of the ISIS Neutron and Muon Source (UK).

The analytical approach of neutron resonance absorption spectroscopy is based on the presence of sharp peaks, known as resonances, at which the neutron-induced reaction cross-sections increase by several magnitudes. For each nuclide, resonance structures appear at specific energies univocally determining a fingerprint for the presence of an element and/or an isotope in the material [6].

Two analytical techniques based on this type of interaction are currently available at INES: Neutron Resonance Capture Analysis (NRCA) and Neutron Resonance Transmission Imaging (NRTI). Both methods are based on Time-Of-Flight (TOF) measurements with epithermal neutrons (0.5 eV - 10 keV) exploiting the pulsed nature of the ISIS neutron source.

A. Neutron Resonance Capture Analysis

NRCA is particularly useful for detecting impurities whose capture cross-sections are very intense at low energies: even parts per million (ppm) of elements with resonances between 1 and 10 eV can be detected [13]. The technique relies on TOF measurement of the prompt γ-rays emitted after neutron capture reactions in the material under investigation [2,3]. The arrival time of the γ cascade following the neutron capture reaction is recorded on the detector instead of performing standard energy spectroscopy. Thus, the time of flight (and therefore energy) of the neutron captured by the sample is determined. The resulting TOF spectrum is characterised by (n,γ) resonance absorption peaks, whose positions in time or energy are analysed for determining qualitative information about the sample elemental composition.

At the ISIS spallation source, NRCA experiments are routinely performed at the INES beamline with a detection setup composed of 3 Yttrium Aluminium Perovskite (YAP) scintillator crystals coupled to silicon photomultipliers and positioned above the sample stage at about 1 m distance from the sample position [14]. The resonant capture experimental setup is optimized for providing a qualitative and semi-quantitative evaluation of the composition of an object and relative isotopic concentration, with a low limit for the sensitivity for almost-in-traces elements.

B. Neutron Resonance Transmission Imaging

The NRTI technique is an innovative TOF imaging method currently undergoing further advances and calibration at the INES beamline of the ISIS Neutron and Muon Source (UK). The NRTI is based on the resonant absorption of incident neutrons with the same energies as the nuclear resonances of the nuclide cross-sections constituting the sample and on detecting the transmitted epithermal neutrons through the object. A schematic layout of the NRTI operating principle is represented in Fig. 2.

The typical structure of the transmitted neutron beam presents negative dips whose positions in time/energy correspond to the absorption resonances responsible for neutron removal. By indexing the position of these dips,

elemental and isotopic identification can be achieved through comparison with the total cross-sections of elements available in a nuclear database.

Morphological and spectroscopic information can be obtained simultaneously with this technique thanks to the use of a space- and time-resolved detector based on the neutron Gas Electron Multiplier (nGEM) technology. The active area of the nGEM detector is 10×10 cm^2 and its pixel size is 0.8×0.8 mm^2. However, the effective area of investigation is limited to the transverse size of the INES neutron beam, which is 3.2×3.2 cm^2.

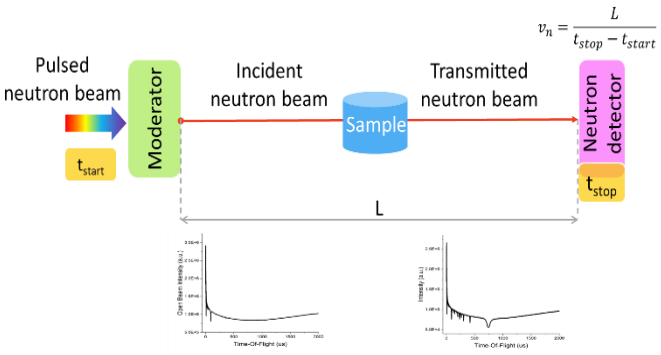

Fig. 2. Schematic representation of the NRTI technique based on TOF measurements. Spectroscopy measurements are possible by tracing back the neutron velocity (and therefore energy) using the known neutron flight path L and its time of flight.

The NRCA technique can also be extended to imaging, as previously explored in [15]; however, in this case, it is necessary to collimate the neutron beam and this reduction in beam size makes it necessary to optimize the efficiency of the detection systems. Neutron Resonance Capture Imaging (NRCI) generally requires time-consuming and bulky scanning of the sample at a collimated epithermal neutron beam. Therefore, the spatial resolution is strongly affected by the collimation of the neutron beam [15].

Due to the difference in experimental methods, results obtained by NRTI will always be more accurate compared to those resulting from NRCI [3]. In a single NRTI measurement, the two-dimensional map is produced as in the transmission set-up the whole area of the object is illuminated. Hence, NRTI is less time-consuming. In addition, NRTI data reduction and analysis procedures are less complicated and NRCI is currently still less established. The disadvantage of NRTI is that is less sensitive to impurities and trace elements compared to NRCI [3].

NRTI measurements of the crucible fragments lasted 2 days; each sample was irradiated for 7 hours approximately, alternating acquisitions with-in and with-out the sample for normalisation purposes. Given the clay-based composition of the fragments with traces of metallic elements, the activation that follows on these samples did not require long decay times (on the order of a few days).

III. RESULTS AND DISCUSSION

At INES, NRCA is a more optimized technique than NRTI. Therefore, preliminary bulk elemental analysis was performed with NRCA to compare the NRTI results as both methods are based on TOF measurements of epithermal neutron absorption.

The NRCA spectra of the crucible fragments are shown in Fig. 3. The composition is averaged on the entire volume of the samples. Resonance capture peaks related to the presence of Cu, Zn, Sn, Sb, As and Ag have been identified in the available TOF window of INES (20-2000 µs). The same elemental composition of the fragments has been disclosed with NRTI measurements, as shown in Fig. 4. Moreover, both techniques are transparent to the refractory material matrix, which ensures that the detection of metallic elements is not disturbed by the background generated by the matrix.

The element distribution inside the volume of a fragment can be mapped through NRTI and applying the resonance selection of a specific nuclide in the transmitted spectrum. As an example, the distribution of Cu, Zn, Sn, Sb, and Ag

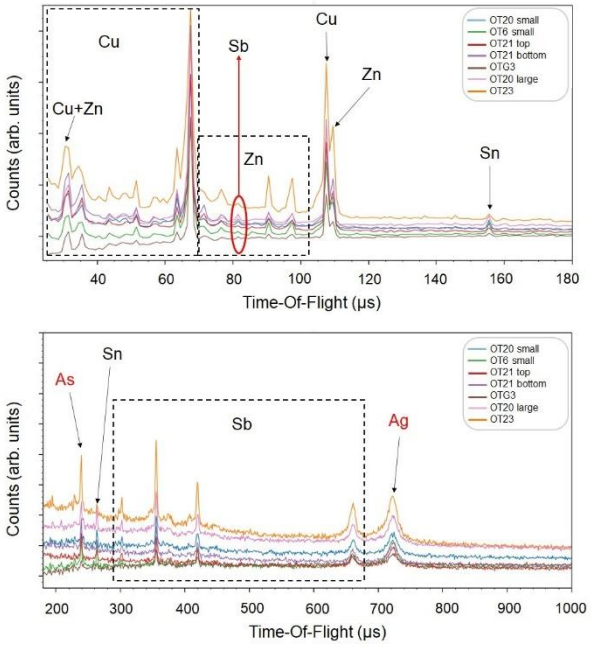

Fig. 3. Top: NRCA spectra of the crucible fragments in the TOF region 20-180 µs. Bottom: NRCA spectra of the crucible fragments in the TOF region 200-1000 µs. The region between 1000 and 2000 µs has not been reported as it does not exhibit a significant signal for elemental composition determination. Main peaks related to copper, zinc, tin, arsenic, antimony, and silver are highlighted [6].

inside the bulk of sample OT20_small is described in this work. Fig.5 shows the neutron radiography of the fragment OT20_small. Different levels of transmission can be seen due to a different composition within the bulk. By selecting the TOF range of a specific resonance dip in the relative NRT spectrum (Fig. 4), such as the Cu resonance between 35 and 40 µs, the contrast due to the absorption of neutrons by copper nuclei is enhanced in the 2D map, revealing the position of copper inside the volume (Fig. 6). The same procedure can be made with resonances related to the other elements (Fig. 6), to facilitate the visualisation of the elemental distribution even for nuclide with similar neutron attenuation coefficient.

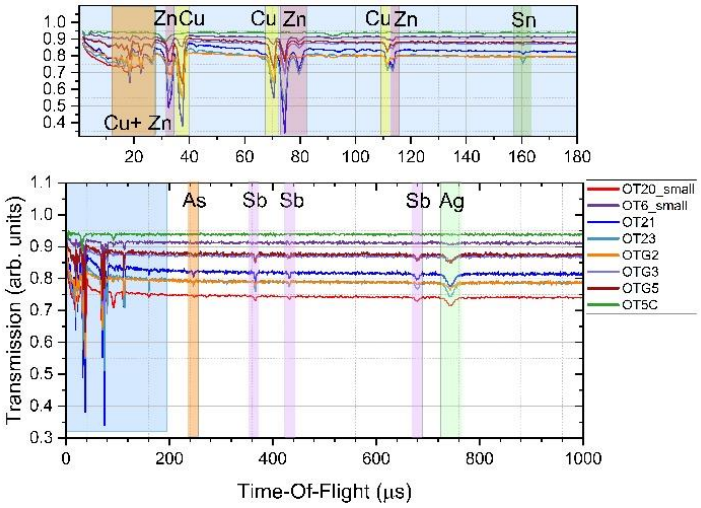

Fig. 4. NRTI spectra of the 8 crucible fragments shown in Fig.1. The qualitative composition of these fragments has been identified by indexing the resonance positions and comparing them with (n,tot) cross-section libraries [6] .

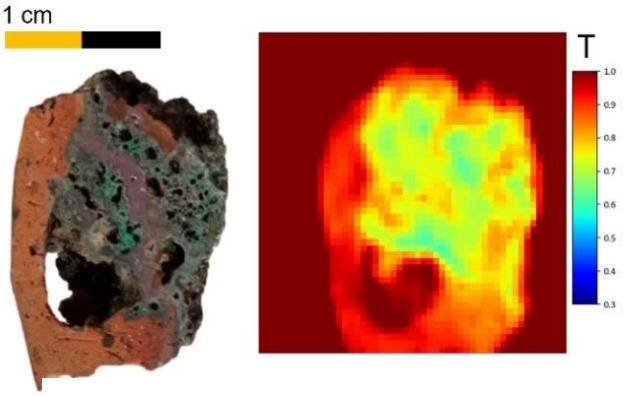

Fig. 5. Picture and transmission map of crucible fragment OT20_small. The size of all 2D maps is 3.2×3.2 cm² [6].

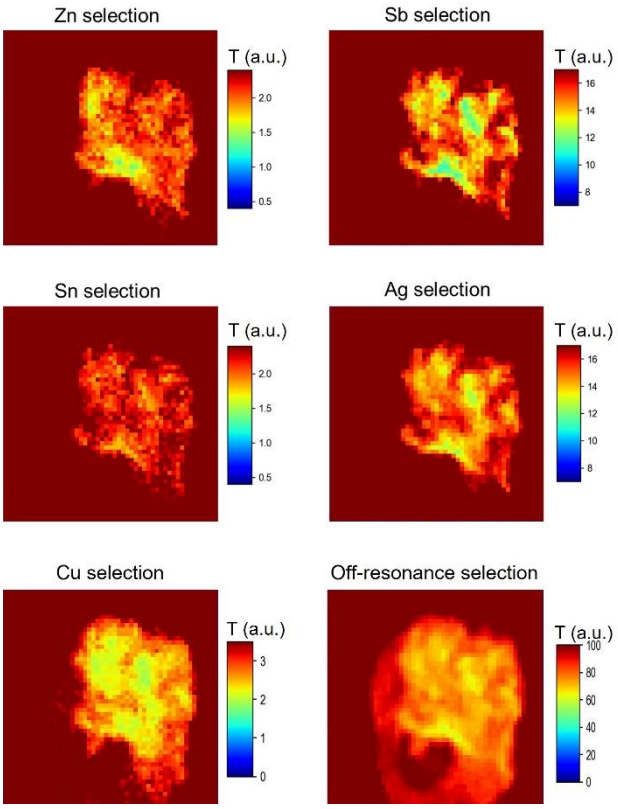

Fig. 6. NRTI maps after the selection of the main Zn, Sb, Sn, Cu and Ag resonances and of a TOF region without any absorption resonance.. The size of all the 2D maps is 3.2×3.2 cm² [6].

IV. CONCLUSION

In the field of Heritage Science, neutron resonance absorption spectroscopy is a powerful method for determining non-destructively the elemental composition of thick samples thanks to the high penetrating capability of neutrons and the presence of resonance peaks in the neutron-induced absorption cross-sections of nuclei. Neutron Resonance Capture Analysis is a well optimized elemental analysis and is routinely applied at the INES beamline of the ISIS Neutron and Muon Source.

On the other hand, Neutron Resonance Transmission Imaging is an innovative and promising technique for determining both the elemental composition and the distribution of the elements inside the bulk of archaeological objects, without the need for sampling. The application of NRTI to crucible fragments related to brass production in the ancient Roman city of Medioulanum confirms the presence of brass inclusions inside the volumes of the fragments composition. The NRCA investigation on the crucible fragments qualitatively confirms the elemental identification accomplished through NRTI.

Moreover, this kind of samples presents an

inhomogeneous distribution of Cu, Sn, Sb, Ag and As. Therefore, the feasibility of the NRTI for localizing the position of elements with enhanced contrast has been demonstrated through this case study.

To conclude the achieved results demonstrate the profitability of NRTI to perform non-destructive imaging combined with elemental analyses for investigating the composition of inhomogeneous samples.

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