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Neutron-based techniques applied for non-destructive quantitative characterisation of ancient mosaic tesserae

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Abstract **– The conservation and preservation of cultural heritage need by now non-destructive analytical methods for the characterisation of materials, detection of degradations and authenticity assessment.**
The interaction properties of neutrons with matter make neutron-based techniques suitable for non-destructive studies of ancient artefacts since they cannot be replaced. A quantitative bulk characterisation of the chemical composition of ancient mosaic tesserae, dating from 2nd to the 11th century AD and coming from different geographical areas (Greece, Italy, and Syria) has been conducted through Neutron Resonance Capture Analysis (NRCA) combined with Neutron Activation Analysis (NAA). The NAA analysis returns the bulk composition in terms of major, minor and trace elements, while NRCA reveals the presence of particular elements, like antimony, in agreement with NAA results.

I. INTRODUCTION

Several analytical techniques are actually employed in the field of Cultural Heritage to characterize constituent materials, production methodologies, dating and provenance of the artefacts. Non-destructive analyses are generally requested.

Concerning the investigation of objects elemental composition, Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) and Electron Probe Microanalysis (EPMA) techniques are often performed but they are invasive. Also, X-Ray Fluorescence (XRF) is widely used for non-destructive investigation but sample preparation can be requested, and only small superficial areas are analysed. Mosaic tesserae are inhomogeneous objects, thus XRF cannot return a complete bulk characterization of the mosaic samples.

The novelty of the present study is the application of non-destructive neutron-based technique to obtain a quantitative description of the bulk composition of the mosaic tesserae. Neutron beams are a unique probe for non-destructive investigations in materials science. Neutrons sense the differences between isotopes of the same element and provide exceptional features in the penetration of many materials, making them adapt for bulk studies, while other probes can in general only cross surface layers. In contrast to other forms of radiation, they are also highly sensitive to some light elements such as hydrogen and sodium. Neutron-based techniques do not require any particular sample preparation.

We performed neutron-based analysis at the ISIS Neutron and Muon Source (UK) [1].

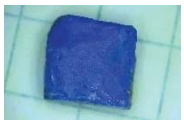
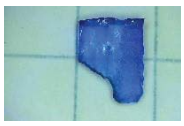
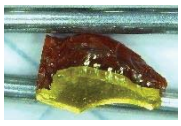
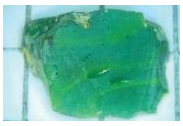
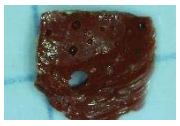
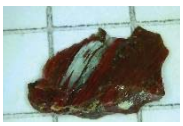
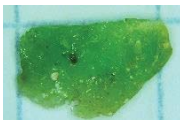
Elemental analyses have been conducted by Neutron Activation Analysis (NAA) [2] [3] and Neutron Resonance Capture Analysis (NRCA) [2] [4] [5].

Glass mosaic tesserae are heterogeneous materials composed of vitreous matrix and crystalline phases and produced from selected raw materials (generally minerals) with various functions, such as colorants, decolourants and opacifiers. The glass colour is mainly due to the presence

of small quantities of transition metal ions such as iron, cobalt or manganese in particular oxidation states, which cause selective absorption of electromagnetic radiation in the visible band [6]. Coloured glass is originally translucent; the opacity can be obtained through the dispersion of crystalline phases or the presence of bubbles scattered in matrix [7]. Different compounds were used through the centuries to make glass opaque such as antimony- or tin-based opacifiers.

In the current study, a set of fourteen glass tesserae (Table 1) have been analysed. The mosaic tesserae have different dating and provenance and most of them are coloured and opaque. The sample set is composed by five Greek tesserae and two Syrian tesserae dating back to I-II century AD, and seven Italian tesserae from the San Vitale basil of Ravenna, dating back to the VI century AD.

Table 1. Description of the provenance and colour of the analysed glass tesserae samples.

Sample name	Sample image	Provenance	Colour
DEL1		Delos Monastery - Greece	Opaque blue
DEL2		Delos Monastery - Greece	Opaque red
DEL3		Delos Monastery - Greece	Opaque green
DEL4		Delos Monastery - Greece	Transparent blue
DAFNI		Dafni Monastery - Greece	Opaque red with a gold layer
SYG2		Syria	Opaque dark green
SYG3		Syria	Opaque green
SVR24		Ravenna - Italy	Opaque pink
SVR25		Ravenna - Italy	Opaque green
SVR26		Ravenna - Italy	Opaque red
SVR27		Ravenna - Italy	Opaque red/striped
SVP27		Ravenna - Italy	Opaque green
SVP46		Ravenna - Italy	Opaque green
SVP57		Ravenna - Italy	Opaque black

II. NEUTRON-BASED TECHNIQUES AT INES

As mentioned in the previous section, all mosaic tesserae have been irradiated at the INES beamline at ISIS, which provide a thermal-epithermal neutron flux in the order of 10^6 n/s cm^2. During irradiation, NRCA spectra have been recorded through a Yttrium–Aluminum–Perovskite (YAP) scintillator performing Time-Of-Flight measurements [8]. For each sample, a qualitative analysis of NRCA spectra is conducted by indexing the observed resonances and comparing the centre of each to tabulated libraries [9]. Correction for background contributions has been applied to the experimental data by the subtraction of an “empty” measurement (i.e., without the samples in the INES

station).

After the neutron irradiation, the samples were placed in front of a High Purity Germanium (HPGe) detector to measure the induce radioactivity. Each irradiated sample has been placed at contact, at the centre of the HPGe active surface. The HPGe was housed in a lead shielding to limit the background and placed at ChipIr beamline of ISIS.

During irradiation, the beam status has been monitored by recording the current of the ISIS accelerator and by the INES beam monitor. This allows to calculate the net irradiation time and to correctly estimate the activation rate in case of beam OFF for some time intervals.

In most cases, especially when several isotopes with different half-lives were produced, the radioactivity of the samples has been measured a few times. The first measurements after irradiation have been needed to detect the γ-rays of isotopes with relatively short half-life, while measurements after the decay of short-lived isotopes have allowed higher sensitivity to isotopes with lower activity and longer decay time. For each sample, three measurements of few minutes have been performed, followed by several measurements of one hour. A prior calibration of the detector has been performed with radioactive sample of ^{137}Cs, ^{241}Am, ^{60}Co and ^{40}K.

During the neutron irradiation, the variation of the number of radioactive nuclei is given by:

$$dN = Rdt - \lambda N dt$$

where λ is the decay constant, N the number of radioactive nuclei and R is the activation rate:

$$R = \mathcal{N} \int \sigma(E)\varphi(E)dE$$

and $\sigma(E)$ the activation cross section, $\mathcal{N}$ the number of precursor isotope atoms and φ the neutron flux. The activity after irradiation (t_{irr}) is given by:

$$A(t) = R\left(1 - e^{-\lambda t_{irr}}\right)e^{-\lambda t}$$

Thus, the decays expected to occur during the measurement are:

$$n_{decay} = \frac{R}{\lambda}\left(1 - e^{-\lambda t_{irr}}\right)e^{-\lambda t_{wait}}\left(1 - e^{-\lambda t_{meas}}\right)$$

where t_{wait} is the delay between the end of the irradiation and the start of the measurement.

The net area under a specific peak gives the number of counts recorded by the detector, which is related to the number of decay events.

Finally, the number of precursor isotope atoms are derived as:

$$\mathcal{N} = \lambda n_{decay} \frac{1}{(1 - e^{-\lambda t_{irr}})e^{-\lambda t_{wait}}(1 - e^{-\lambda t_{meas}})} \frac{1}{\int \sigma(E)\varphi(E)dE}$$

III. RESULTS

Fig.1 shows the average quantitative elemental composition of the mosaic tesserae obtained by NAA. Since a thermal and epithermal neutron spectrum have been employed for the sample's irradiation, elements with a high cross-section in this energy range have been observed. Na, Mn, Sb, As, Au and Cu isotopes radioactivity have been detected by a HPGe detector and the related elemental concentrations have been evaluated.

Samples DEL4, DAFNI, SVP57 and SYG2 show the highest concentration of sodium (from 10% to 20%) while samples SVR25 and SYG3 only 2%. Sample SVP57 has the highest magnesium content among the other tesserae.

Sample	Weight (mg)	Irradiation time (h)	Na	Mn	As	Sb	Au	Cu
DEL1	24,98	22,2	7,1% ± 0,2%	0,196% ± 0,007%	n.d.	4,70% ± 0,01%	n.d.	n.d.
DEL2	29,25	5,3	7,4% ± 0,2%	0,093% ± 0,002%	0,015% ± 0,001%	0,057% ± 0,002%	n.d.	8,6% ± 0,5%
DEL3	6,91	4,8	7,2% ± 0,2%	0,128% ± 0,004%	n.d.	1,9% ± 0,1%	n.d.	n.d.
DEL4	5,71	17,0	10,3% ± 0,3%	0,014% ± 0,002%	0,870% ± 0,006%	0,42% ± 0,01%	n.d.	n.d.
DAFNI	3,56	12,6	11,1% ± 0,3%	0,35% ± 0,01%	n.d.	n.d.	0,032% ± 0,001%	n.d.
SVR24	4,01	6,9	7,4% ± 0,2%	0,086% ± 0,006%	0,38% ± 0,02%	8,3% ± 0,3%	0,007% ± 0,001%	n.d.
SVR25	22,5	21,0	2,4% ± 0,1%	0,025% ± 0,001%	0,052% ± 0,002%	0,65% ± 0,01%	n.d.	n.d.
SVR26	1,80	18,4	8,3% ± 0,2%	0,45% ± 0,02%	0,036% ± 0,003%	0,055% ± 0,004%	n.d.	n.d.
SVR27	7,25	5,3	9,2% ± 0,2%	0,240% ± 0,007%	0,032% ± 0,002%	0,074% ± 0,004%	n.d.	n.d.
SVP27	18,48	22,8	5,1% ± 0,1%	0,012% ± 0,001%	0,0032% ± 0,0004%	0,0031% ± 0,0003%	n.d.	n.d.
SVP46	1,63	17,0	9,4% ± 0,3%	0,133% ± 0,007%	n.d.	0,0450% ± 0,004%	n.d.	n.d.
SVP57	4,95	18,2	19,2% ± 0,5%	2,88% ± 0,06%	n.d.	4,1% ± 0,1%	n.d.	n.d.
SYG2	14,70	7,5	15,5% ± 0,4%	0,019% ± 0,001%	n.d.	n.d.	n.d.	n.d.
SYG3	34,36	5,0	2,0% ± 0,1%	0,0057% ± 0,0003%	0,00366% ± 0,0003%	0,005% ± 0,001%	n.d.	n.d.

Fig. 1. Table of the chemical composition of the mosaic tesserae (weight %) obtained by NAA. (n.d.=under detection limit).

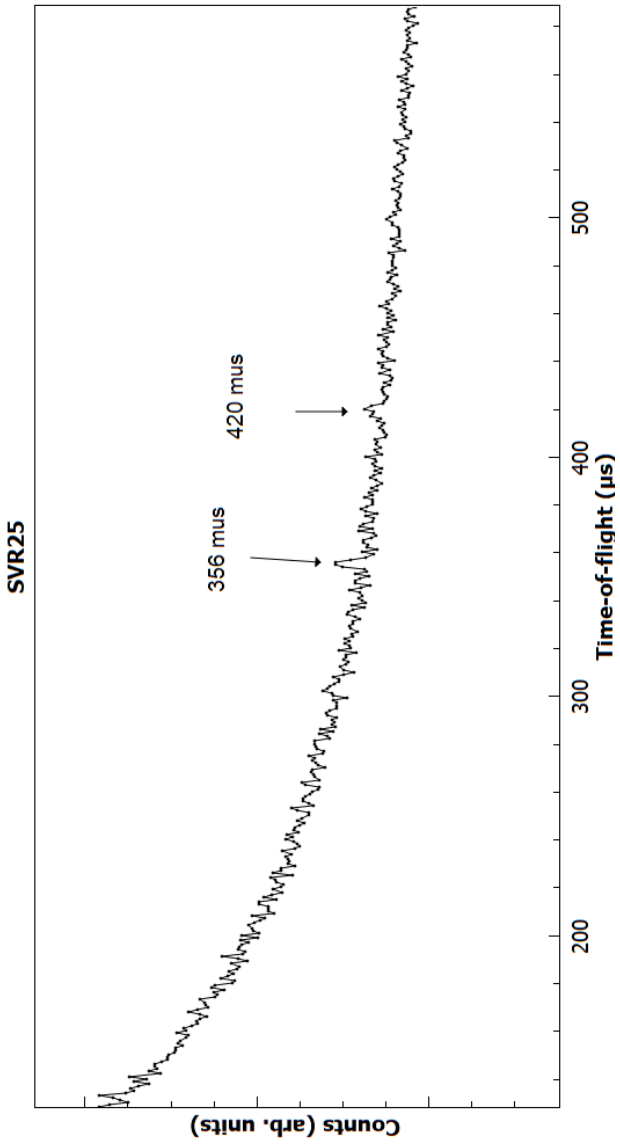


Fig. 2. NRCA spectrum of sample SVR25 showing the Sb peaks at 356 and 420 µs.

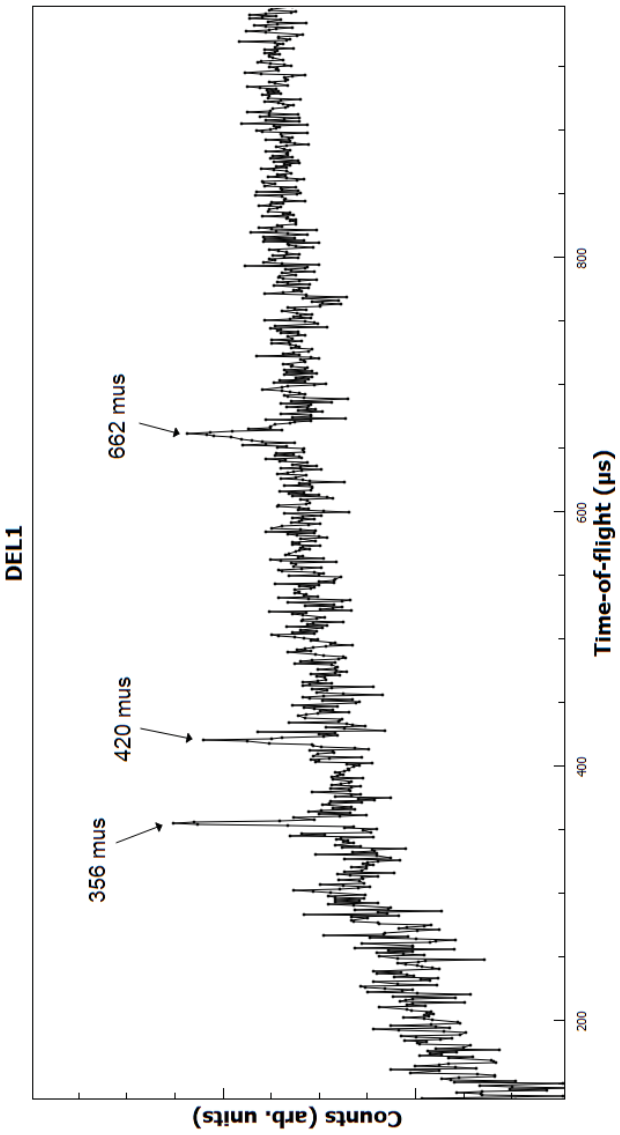


Fig. 3. NRCA spectrum of sample DEL1 showing the Sb peaks at 356, 420 and 662 µs.

High concentration of antimony has been found in samples DEL1 and SVP57 (4,7% and 4,1% respectively) and SVR24 (8,3%). In the other glass tesserae, antimony is present in low concentrations, except in sample DAFNI and sample SYG2. In these cases, the Sb signal is lower than the detection limit of the experimental system. Presence of Au has been detected and evaluated in samples DAFNI (where a gold layer is visible on the surface) and in SVR24.

The red tessera DEL2 shows a high content of copper (8,6%) accordingly to the colourant function of Cu oxides in glasses.

NRCA analysis shows the presence of antimony in samples SVR25 and DEL1 (Fig.2 and Fig.3, respectively). NRCA at the moment allows only qualitative indications of the presence of elements in the samples. NRCA spectra of the glass tesserae are characterised by a high background in the TOF range between 25 and 120 μs, due to the vitreous matrix. Therefore, resonance peaks of copper - or any other elements with NRCA signal in this range - cannot be distinguished.

IV. CONCLUSIONS

In this study, the quantitative bulk elemental composition of glass mosaic tesserae is determined in a non-destructive way by means of neutron-based techniques. Through NAA a quantitative description in terms of Na, Mn, As, Sb, Au and Cu elements is provided. It is worth mentioning that elements with high thermal end epithermal cross-section can be detected by irradiating the samples with a thermal-epithermal neutron flux. NRCA analysis encountered the vitreous matrix background issue in resonance peaks detection. Presence of antimony was detected in samples irradiated for more than twenty hours and for which NAA returns an Sb concentration around 4%.

Further investigation on the application of these neutron-based techniques to glass samples will help to understand the optimum way to obtain detectable signals for quantitative study.

V. REFERENCES

[1] https://www.isis.stfc.ac.uk
[2] N. Kardjilov, G. Festa (Editors), “Neutron Methods for Archaeology and Cultural Heritage, Neutron Scattering Applications and Techniques”, Springer, Berlin, 2007.
[3] M.D. Glascock, H. Neff, “Neutron activation analysis and provenance research in archaeology”, Meas. Sci. Technol., vol.14, No.9, 2003, pp.1516-1527.
[4] H. Postma et al., “Neutron resonance capture analysis of materials”, J. Radioanal. Nucl. Chem., vol.248, 2001, pp.113–120.
[5] H. Postma et al., “Neutron resonance capture analysis and applications”, J. Radioanal. Nucl. Chem., vol.271, 2007, pp.95–99.
[6] K. Nassau, “The Physics and Chemistry of Color. The Fifteen Causes of Color”, John Wiley & Sons, 1983.
[7] E. Basso et al., “Characterization of colorants and opacifiers in roman glass mosaic tesserae through spectroscopic and spectrometric techniques”, J. Raman Spectrosc., vol.45, 2014, pp.238–245.
[8] A. Pietropaolo et al., “A Neutron Resonance Capture Analysis Experimental Station at the ISIS Spallation Source”, Applied Spectroscopy, vol. 64, No.9, 2010, pp. 1068-1071.
[9] http://atom.kaeri.re.kr/nuchart