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Light through glass: The spectrum of Late Antique glass from Cyprus

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ABSTRACT

In this paper we have studied by optical spectroscopy the 5th–7th century glass material from three early Christian sites in Cyprus: Yeroskipou, Maroni *Petrera* and Kalavasos *Kopetra*. The glasses could be grouped into six chemical types: Levantine 1, HLIMT, two types of HIMT (named HIMTa and HIMTb), Egypt 1 and HIT. This work presents the first extensive application of in situ absorption spectroscopy to ancient glasses. UV absorption edge, Fe^{2+} concentration and colour coordinates are optical parameters that help identifying glass composition because there exists a link between chemical groups and UV–vis–NIR spectral shapes. This allows to select samples for chemical analysis on the basis of diverging optical properties rather than using *ad random* or subjective naked-eye strategies groups. Furthermore, optical spectroscopy offers an insight into the redox conditions under which the glasses were melted. We also show why the common practice among glass archaeologists to associate certain colour to specific chemical compositions can lead to misinterpretation of the glass consumption.

1. Introduction

The interest of technological and chemical studies on ancient glass is that they help in getting knowledge on the material culture of ancient societies and on their trade networks and economy(Brems et al., 2013; Freestone, 2008).

Up to now most archaeometrical research on glass has relied on the chemical characterisation of material Janssens, 2013. In the last years our group has worked intensively on the feasibility of the application of optical spectroscopy to this study field (Meulebroeck et al., 2010a,b, 2011, 2012; Ceglia et al., 2012a,b, 2013, 2014). Glass colour is an important characteristic and transmission spectroscopy provides a good insight into the adopted technology. Colour is imparted by several transition metals and both the redox state and the coordination geometry of the metal ions affect the final hue (Weyl, 1976; Bamford, 1977; Möncke et al., 2014). Most Roman/post-Roman glass is coloured by unintentional iron addition as impurity in the sand. Consequently, the redox conditions of the melt are significant for determining the final aspect of a glass artefact (Meulebroeck et al., 2012). Moreover, the determination of the furnace conditions allows to better understand the continuous evolving skills applied in ancient glass making (Ceglia, 2014). Recently, we have cross-calibrated synchrotron X-rays absorption near edge spectroscopy (XANES) and optical spectroscopy in order to build a quantitative procedure for ferrous ions in ancient glass (Ceglia et al., 2015). We have also showed, how portable and lab optical spectrometers can be equally employed (Meulebroeck et al., 2010a).

In a recent paper we have carried out the chemical characterisation of the glass from three early Christian sites in Cyprus: the basilica of Ayioi Pente at Yeroskipou (400–650 AD), near Paphos, Maroni *Petrera* (450/500–650 AD) and Kalavasos *Kopetra* (550–650 AD) (Ceglia et al., 2015).

Cyprus was supplied with raw glass or finished objects by both Egyptian and Syro-Palestinian primary producers. Nevertheless, while in Yersokipou there is a consistent amount of both Levantine and Egyptian materials, Egyptian glass is limited in Maroni *Petrera* and nearly absent in Kalavasos (Ceglia et al., 2015). This consumption pattern corroborates research on pottery which showed that East Cyprus was connected to the Syro-Palestinian coast, while West Cyprus was more oriented towards the Aegean areas and Egypt Winther Jacobsen, 2004. However, there is a more captivating way to interpret the data in terms of chronological evolution of the glass imports. The Egyptian HIMT – High Iron Manganese Titanium – glass was present in the island in the 5th century AD, but seems to be no longer imported or produced by the mid-6th century when Kalavasos *Kopetra* flourished (Ceglia et al., 2015). HLIMT – High Lime Iron Manganese Titanium – glass, a new Egyptian production of the 6th century, appears to have taken its market share (Ceglia et al., 2015). Conversely, Levantine glass was regularly

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produced and supplied to Cyprus as it is found in consistent amounts in all three sites studied (Ceglia et al., 2015).

In this paper, we show the first extensive application of in situ absorption spectroscopy to the glass material from the three earlier mentioned Cypriot sites. We define the optical parameters that help identifying compositional groups prior to sampling. We also show why the common practice among glass archaeologists of associating certain colour to specific chemical compositions can lead to misinterpretation of the glass consumption (Jackson and Price, 2012).

2. Experimental

In the last years, we have carried out two in situ campaigns with a portable optical spectrometer on the Late Antique glass material from Cyprus. We have recorded UV–vis–NIR spectra on 416 "naturally" coloured glass fragments.

The first campaign was carried out in the Paphos District Museum, where we have analysed 206 naturally coloured glass fragments from the early Christian basilica of Ayoyi Pente at Yeroskipou. For the second campaign, we went to the Larnaca District Museum, where we have studied the excavated materials from the Late Antique sites of Maroni *Petrera* and Kalavasos *Kopetra*, where we have obtained the optical spectra of 144 and 67 glass fragments from the respective sites.

The optical set-up consists of a spectral broadband light source, a focusing lens, an integrating sphere which collects the transmitted light and the spectrometer (Fig. 1). The light is guided trough optical fibres and the light beam spot size on the sample is smaller than 4 mm. Weathering layers often covers excavated glass and affects its optical aspect. Therefore, prior to the in situ transmission measurements about 5 × 5 mm^2 of the glass surface was polished using a hand-held Dremel rotary tool. The integrating sphere allows to collect all the light that is transmitted, minimising the effects of the curvature of the glass fragments and eventual polishing defects (Ceglia et al., 2014). Optical spectra have been normalised to 1 mm of thickness. In addition, reflection losses were subtracted in order to interpret quantitatively the spectral measurements. To normalise the spectra we have measured the thickness of each sample using a digital micrometer with 0.001 mm resolution. Although the resolution is very good, the error associated with the measurement is difficult to evaluate, since it depends on the shape of the fragment analysed. The removal of reflection losses was approximated using an average refractive index of 1.5 and the Fresnel equations (for more details see Bamford, 1977).

We have employed different equipment in the laboratory and during the two in situ campaigns. In the first in situ expedition, we have used the Avantes AvaLight-HAL halogen light source and a compact combination of two spectrometers manufactured by the same company: one for the UV–vis region, the AvaSpec-3648, and one for the IR region, the AvaSpec-256-NIR1.7. The spectra are recorded between 400 and 1600 nm. The spectral resolutions are 1.4 nm in the UV–visible and 4 nm in the infrared regions. In this campaign we have selected 69 fragments for chemical analysis by EPMA in order to be representative of the spectral groups identified. The choice of the materials was not based on typological features, but exclusively on the basis of the shapes of the recorded optical spectra.

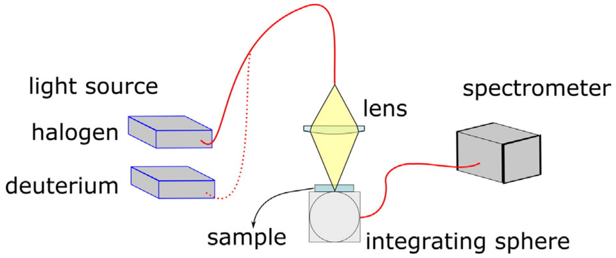

Fig. 1. Scheme of the set up used for both in situ and lab optical measurements. The light source and spectrometer used for in situ and in the lab are different (see text).

During the analysis of the spectra, we have understood that the low UV emission by the light source used during the in situ campaign was a limiting factor to gain the most information out of the spectral analysis. Therefore, we have re-measured the UV–vis–NIR spectra of 45 of the selected samples in the laboratory with two lamps as light source: a 30-W deuterium lamp emitting in the UV spectral region and a 20-W halogen lamp emitting in the visible and infrared regions. The rest of the samples were too small and a quantitative optical measurement was impossible. Overall, the first campaign gave us the tools to interpret optical spectra in function of chemical compositions.

For the second in situ campaign we have acquired a UV portable lamp, the Avantes DHS-BAL deuterium lamp, and combined it to the first one in order to analyse the full UV–vis–NIR spectral range between 200 nm and 1650 nm. On the basis of the spectral analysis, we have selected 33 samples from the Maroni *Petrera* set and 22 from the Kalavasos *Kopetra* set for chemical analysis.

From the optical spectra, we have calculated the colour coordinates in the CIE Lab system normalised to the standard illuminant D65 (Meulebroeck et al., 2010b).

3. Results and discussions

From the chemical composition, we could identify six glass types: Levantine 1, HLIMT, two types of HIMT (named HIMTa and HIMTb), Egypt 1 and HIT (Table 2). Levantine 1, HIMT and Egypt 1 are renown Late Antique chemical glass compositions (Freestone and Hughes, 2000), (Freestone, 1994), (Gratuze and Barradon, 1990). On the contrary, HLIMT and HIT were defined and discussed only recently (Rehren et al., 2010), (Ceglia et al., 2015). HIT – High Iron Titanium – glass was first described by Rehren et al. (2010), while HLIMT was defined by our group in a recent paper (Ceglia et al., 2015). The HIT group is not well defined yet and is considered to be a member of the HIMT – High Iron Manganese Titanium – family. HLIMT glass is believed to be a specific Egyptian primary production of the 6th century with precise compositional boundaries and Fe/Al and Fe/Ti ratios which clearly differ from HIMT (Ceglia et al., 2015).

In Table 1, we list all samples that were analysed chemically together with the parameters calculated from the optical spectra: Fe^{2+} concentration, UV absorption edge (UVAE), the CIE Lab colour coordinates. We also report the total amount of iron and manganese measured by EPMA in elemental wt.%, the Fe^{3+} concentration (obtained by subtracting Fe^{2+} by the total iron) and the Fe^{2+}/$\sum$Fe ratio.

Table 2 summarises the composition and optical parameters for each chemical group.

In Tables 3, 4 and 5, we list the optical parameters for all glass fragments analysed only by in situ spectroscopy. As we have explained above, the spectra taken during the first in-situ campaign are recorded only starting from 400 nm, losing the UV region. Therefore for the fragments of Yeroskipou it was not possible to extract the UVAE. Nevertheless, the calculation of the colour is not affected by the narrower spectra range.

In order to keep the structure comprehensible, we first discuss the spectra of the glasses analysed chemically. This allows us to link the optical spectra to specific ancient glass compositions and to define which parameters allow the classification of the glasses. Then, we extend our findings to estimate the chemical composition of the fragments only analysed by in situ spectroscopy.

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