



Roman glasses coloured by dissolved transition metal ions: redox-reactions, optical spectroscopy and ligand field theory



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ABSTRACT

A collection of Roman glass samples from Ancient Messene, Greece, was analysed non-destructively for colouring elements and non-colouring additives such as fining agents, opacifiers and decolorizers, by comparing the chemical composition with the observed optical spectra. The resulting information on ion speciation is important for the discussion of technological parameters such as the applied melting temperatures or the prevalent redox conditions. Speciation also helps to distinguish intentionally added dopants from impurities. This knowledge might be used in provenancing the raw materials. The Roman assemblage under study included purple coloured Mn³⁺-containing glasses, but also samples with high levels of colourless Mn²⁺. Manganese ions can either be considered a residue of recycling, or are indicative of an intentional addition, either as a fining or as a decoloring agent. Antimony oxide was either added as a fining agent, resulting in good quality transparent glasses, or as crystalline antimonates which act in glass mosaic *tesserae* as opacifiers. The much weaker molar extinction coefficient and the partial reduction of blue Cu²⁺ to colourless Cu⁺ explain why CuO is a weaker colouring agent than CoO. The colours of iron-bearing glasses range from light blue to green and from yellow to dark brown, reflecting a complex interplay between redox conditions and the presence of sulphur in the glass melt.

Quantitative speciation of dopants will be reviewed on the basis of the ligand field theory. The different transition probabilities will be demonstrated on differently doped soda lime silicate glasses which were prepared for this purpose in the laboratory.

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1. Introduction

The study of archaeological glasses is frequently concerned with the colour characterization of the artefacts. The colour of a transparent glass is caused either by the absorption of light by chromophores or through scattering of light by nano-particles (Bamford, 1962, 1977; Bates, 1962; Duffy, 1990; Ferguson, 1970; Kühne, 1976; Weyl, 1951; Wong and Angell, 1976). In this paper the focus is on absorption phenomena. Roman vitreous fragments from Ancient Messene in Greece were examined (Papageorgiou and Zacharias, 2012; Papageorgiou et al., 2012) in the context of the electronic transitions which account for the observed colour and its

intensity. The interpretation of the optical spectra allows a qualitative and quantitative determination of colouring ion species in glasses.

When discussing the impact of colour not only the quantity of a certain metal oxide in the glass (concentration) must be considered: the fractions of the metal ion's oxidation state (valence) and the stereochemistry (coordination) also reveal important information. In general, the colouring intensity produced by the *d* electron transition metal ions, e.g. Co²⁺, Cu²⁺, Fe²⁺, Fe³⁺, or Mn³⁺, is several magnitudes lower than those of charge transfer transitions, such as occur between sulphur and iron in the [Fe^(III)SO₃]-chromophore (Bamford, 1977; Bates, 1962; Duffy, 1990; Ehrst et al., 2001; Green and Hart, 1987; Schreurs and Brill, 1984; Weyl, 1951; Wong and Angell, 1976) or of inter-valence charge-transfer transitions as between Fe²⁺ and Fe³⁺ (Duffy, 1990; Schütz et al., 2004).

For example, glasses often contain small quantities of iron, usually as an impurity with levels of ca. 0.3 wt% as iron oxides (Beltsios et al., 2012). Fe²⁺ is a blue and Fe³⁺ a yellow chromophore. The ratio of these two iron species depends on the glass

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composition but also on the redox conditions of the melt, such as air atmosphere, melting temperature, and melting time (Leister and Ehrh, 1999). Some ion species have a colouring impact in one oxidation state but appear colourless in another. For instance, monovalent copper is colourless, but the divalent ion gives a blue turquoise colour. If high levels of Cu^+ ions are found in blue glasses, Co^{2+} ions are most likely the colouring ions and copper ions comprise an impurity from the cobalt-minerals used in glass preparation. In this case, CuO might be a useful provenance marker (Gliozzo et al., 2010; Mirti et al., 1993; Papageorgiou et al., 2012). Manganese ions can either be present as purple Mn^{3+} , a strong colourant, or as nearly colourless Mn^{2+} , a residue from refining or from its use as decolourizer. Likewise, antimony may act either as opacifier or as fining agent. Lead is known as a yellow colourant in crystalline pigments such as *Neaple's Yellow*, but can act as glass former when higher concentrations are incorporated directly in the glass matrix (Mecking, 2012).

Archaeometry has been used to answer a variety of technological questions about the use and selection of raw materials, the modus of kiln operation, or re-cycling issues, etc. (Rehren, 2008; Henderson, 2013). However, many archaeometric studies of vitreous materials rely solely on information obtained from the analysis of the chemical composition. Optical spectroscopy provides a non-destructive method which can easily be applied to vitreous materials to obtain not only qualitative, but also quantitative information on transition metal ion species and their redox ratios. So far, only a small number of papers have applied absorbance studies for dopant speciation in archaeological glasses while utilizing all information from the ligand field theory or the different transition probabilities of the various ions (e.g. Bingham and Jackson, 2008; Green and Hart, 1987; or Mirti et al., 1993; Schreurs and Brill, 1984). Therefore, the examination of the Roman assemblage under study will be supplemented by a more general discussion regarding the interpretation of UV–Vis spectra of coloured glass samples. The focus will be on the oxides of cobalt, copper, manganese, iron and antimony which are responsible for the majority of the existing colour variations in antique glasses. Overall, the study aims to combine chemical and optical spectroscopy data for an advanced characterization of archaeological glass colouration.

2. Materials and methods

2.1. Roman samples (Papageorgiou and Zacharias, 2012; Papageorgiou et al., 2012)

The archaeological assemblage discussed in this paper belongs to the Roman and Protobyzantine periods (1st to 5th century AD) and was excavated in Ancient Messene (Peloponnese, Greece). Ancient Messene is an important ancient city in terms of its size, form and state of preservation and represents one of the biggest restoration projects in Greece today. It was founded in 369 BC by the general Epameinondas from Thebes who had trounced the Spartans at the battle of Leuktra in 371 BC. The new capital of independent Messenia comprises not only sanctuaries and public buildings, but also imposing fortifications, domestic quarters and funerary monuments.

When Pausanias visited Ancient Messene in the 2nd c AD, it was a prosperous political and cultural centre (Papahatzis, 1974). From AD 212–394 the archaeological record is short of historical information, indicative of the decline of the city (Themelis, 2002a). The latest layers of destruction and abandonment of most of the city's buildings followed the collapse of the Roman Empire and are dated at about AD 360/70. However, towards the end of the 4th c AD, a thriving Protobyzantine settlement was established in

the area of the *Asklepeion* and remained active until the end of the 6th c AD. Its domestic quarters extend along the eastern side of the ancient complex and in the remains of at least five big houses two rooms preserved a significant amount of glass residues which are considered to be evidence of the existence of a glass workshop in the city of Messene (Themelis, 2002b). These include glass chunks, droplets and test pieces. The existence of glass specialists is assumed from these glass remnants, a fact that was verified by the discovery of a funerary inscription of the glassworker *Agathonymos* (Bardani, 2002). Most coloured samples are vessel glass sherds from public building contexts. The collection, however, includes other glass objects such as a fragment of a window pane, a stirring rod and a glass test piece. The latter comes from the Protobyzantine settlement where the glass workshop was located. Several coloured translucent and opaque mosaic *tesserae* uncovered at the temple of Isis and Serapes could be studied archaeometrically. These *tesserae* were in all probability part of the walls' decoration. The samples, along with their chemical composition are listed in Table 1 for further details see also Papageorgiou and Zacharias, 2012 and Papageorgiou et al., 2012.

2.2. Remade model glasses

The standard glass NCS, a soda lime silicate glass with 74 SiO_2 –16 Na_2O –10 CaO in mol%, is perhaps the best characterized material in modern glass chemistry. Coloured NCS glasses were prepared from 50 g batches from the high purity reagents SiO_2 , CaCO_3 , Na_2CO_3 and doped with 0.1–3 wt% of different transition metal compounds such as MnCO_3 , CuO , Fe_2O_3 , or NiO . The nominal composition of each model glass can be found in Table 2. The glasses were melted in alumina crucibles in a conductive heated electric furnace at 1350 °C for 3 h and afterwards poured either on preheated brass or graphite blocks, and in both cases annealed from 500 °C to room temperature with a cooling rate of about 2 K/min. Polished, 1 or 2 mm thick, plane parallel samples plates were prepared for optical characterization.

2.3. Optical spectroscopy

Optical absorption spectra were recorded on commercial double beam spectrophotometers which employ a deuterium lamp as light source for the low wavelength region and a tungsten halogen lamp for higher wavelengths respectively (Shimadzu, UV-3102; Perkin Elmer, Lambda19 and Lambda950). The spectra were obtained in the transmission mode from 200 to 3000 nm, where the absorbance, $A_\lambda = \log(T_0 - T)$ was recorded with an error <1% (T and T_0 : transmission with and without the sample). The Roman samples were measured by the same method with small masks to ensure that the probe beam focused on a good quality sample area which also had a favourable thickness for transmission measurements. The Lambda950 was also used in the transmission mode using an integration sphere. Comparison of the well-polished model glasses confirmed that identical spectra were obtained by all different measurement set ups. For every measurement, the empty sample holder with the selected mask was used as reference for the auto zero spectrum. The use of very small masks might decrease the signal to noise ratio and might enhance spectral discontinuities at the wavelengths where the lamps or monochromators are changed; therefore, larger masks were preferred whenever possible. The smallest masks had dimensions of 2×4 mm and were placed in the centre of the instrument's probe beam.

Opaque samples were analysed in the reflectance mode using the 15 cm diameter integration sphere of the Lambda950.

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