

# Synchrotron Radiation as a Probe for Copper Oxidation States in Glass

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## Keywords

historical glass; decay; non-destructive; synchrotron radiation

## Abstract

*In this study, synchrotron radiation was used to explore the relationship between degradation of some historical glasses of different provenance and dating and the oxidation state of their colouring agents. The oxidation states of copper in red and green glasses were monitored by recording spectra at the Cu K-edge by X-ray absorption near edge structure. Promising results with this new analytical tool may extend our knowledge about glass decay.*

## Introduction

All glasses, including archaeological glasses and stained glass, develop decay phenomena with time that are strongly related to their chemical composition and the surrounding environment (Roemich 1999; García-Heras and others 2003). Understanding these phenomena helps to optimise restoration and conservation procedures and to improve preservation strategies such as creating optimal storage or exhibition conditions.

Analytical techniques commonly used to study glass decay include scanning electron microscopy, optical microscopy, or X-ray fluorescence (Carmona, Villegas, and Navarro 2006; Kanngiesser and others 2008; Melcher, Wiesinger, and Schreiner 2010). The role of glass-colouring agents during degradation processes is difficult to examine because their concentration is below the detection limit of these techniques. They may be leached out like other components from the glass or remain in the degraded surface unchanged or in a different state of oxidation. Characterisation of these chromophores using synchrotron X-ray techniques may offer new insights into the decay process of these glasses.

In this research, we have focused on copper ions, as an example for colourants in glass. The oxidation state (OS) of selected samples was studied using X-ray absorption near-edge structure (XANES) at the Cu K-absorption edge. The goal was to explore the OS of copper related to the colour and state of preservation of the samples.

## Experimental Section

### Samples

The samples analysed consisted of historical glasses dating from the first century B.C. to the eighteenth century A.D. from different locations in Spain (see table 1). All samples were coloured using copper ions with different OS (Cu 0 and I for red glasses and Cu II for green ones) and showed different degrees of surface decay (from almost non-degraded to heavily corroded).

### Analytical Techniques

X-ray absorption spectroscopy (XAS) measurements were performed at the beamline BM25 (Spanish-SpLine) at the European Synchrotron Radiation Facility (ESRF). XANES spectra at the Cu (8.9 keV) K-edge in fluorescence mode at room temperature were recorded without prior preparation of the glass. Samples were placed at 45° to incident X-rays, and the fluorescence signal was collected using a multi-element solid state detector. Four to seven scans of all samples were collected for signal averaging. Additionally, Cu powder oxides and a metallic foil were measured as reference compounds.

### Results and Discussion

The red samples exhibit different degrees of deterioration: sample Mi-3 is heavily corroded with an iridescent surface and abundant interconnected craters; sample To-5 is lightly degraded with some pits homogeneously distributed on the surface; sample Vi-2 shows an almost unaltered surface. XANES spectra of the three fragments (Mi\_3, To\_5, and Vi\_2, figure 1(b)) show important differences when they are compared to those of the reference compounds (figure 1(a)). Sample Vi\_2 shows a XANES spectrum similar to the Cu foil reference, indicating the presence of metal ( $\text{Cu}^0$ ) nanoparticles, while the Mi\_3 and To\_5 spectra exhibit the characteristic edge resonance of  $\text{Cu}^{1+}$  in  $\text{Cu}_2\text{O}$ .

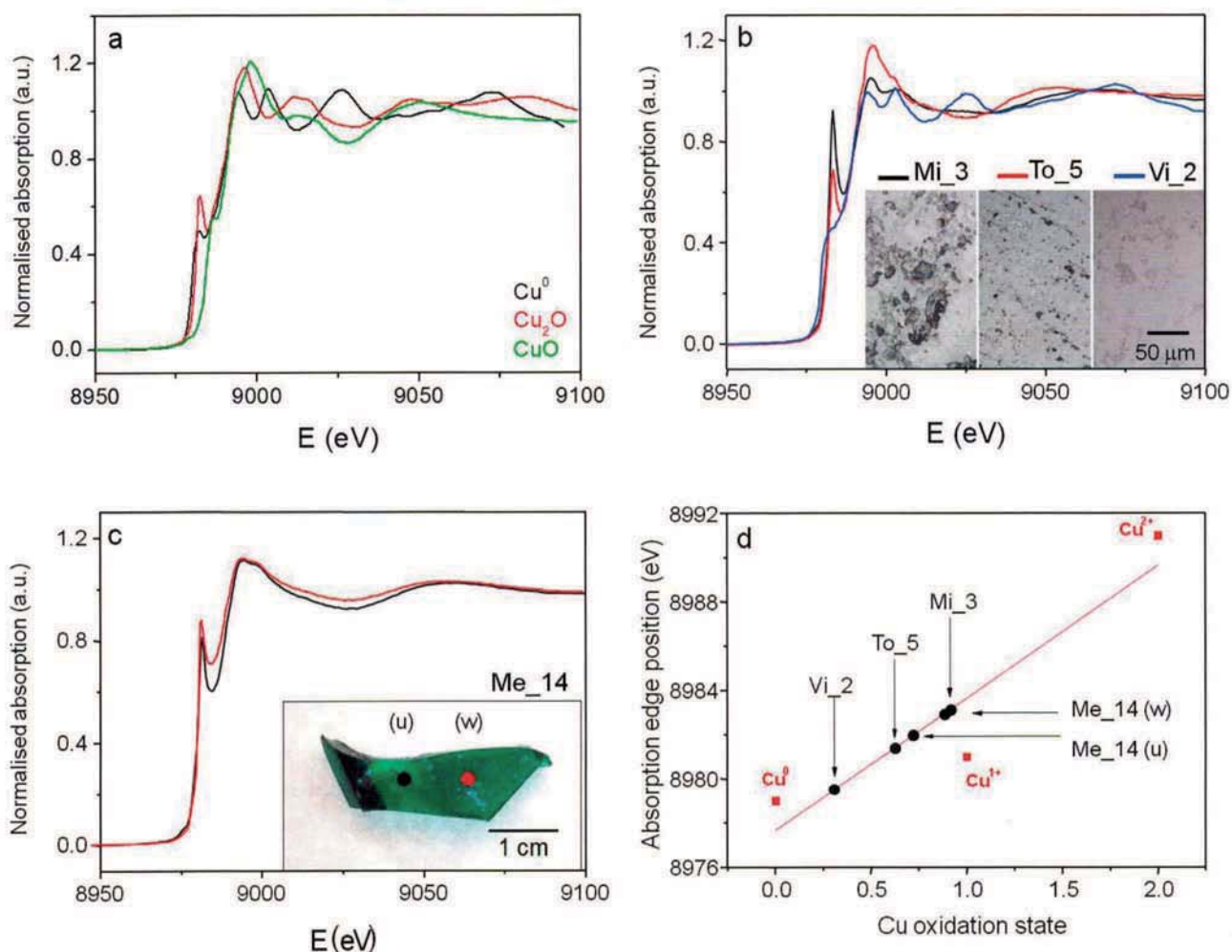


Fig. 1. Normalised Cu K-edge XANES spectra of: (a) reference compounds: metallic Cu,  $\text{Cu}_2\text{O}$  and  $\text{CuO}$ ; (b) historical red glasses: Mi\_3, To\_5 and Vi\_2 (spectra combined with light microscopy images); (c) comparison of two areas of sample Me\_14 (u – unweathered and w – weathered; spectra combined with overview image of the sample); and (d) relationship between the Cu K-edge absorption edge energy and Cu oxidation state of all samples (black points) and reference compounds (red squares).

Sample	Colour	Main Cu oxidation state	Date	Provenance	Degree of weathering
Me_14	green	Cu <sup>2+</sup>	1st century B.C.	Archaeological site of Mérida	intermediate
Mi_3	red	Cu <sup>0</sup>	15th century	Miraflores chartreuse	heavily
To_5	red	Cu <sup>0</sup>	15th century	Toledo cathedral	intermediate
Vi_2	red	Cu <sup>0</sup>	18th century	Spanish stained-glass window	almost not

Table 1. Sample description.

Sample Me\_14 shows an intense green colour characteristic of Cu<sup>2+</sup> ions (figure 1(c)). Partial flaking on one side allowed the measurement of a non-degraded surface (point named u – unweathered) compared to a degraded part (gel layer with an iridescent surface, point named w – weathered). In order to evaluate differences in Cu oxidation state because of weathering, XANES spectra were recorded. Both show an intense peak at the edge, characteristic of Cu<sup>+</sup> in Cu<sub>2</sub>O as well as a single oscillation spectral shape, indicative of highly disordered systems. The observed modification of the edge position indicates that the local order around Cu is higher in the non-corroded area, while it shifts towards higher energies in the other area, indicating the increasing presence of Cu ions in a higher OS in the degraded areas of the glass surface (point w).

Finally, the relation between the absorption edge position and the Cu OS may indicate the degree of degradation on the glass surfaces. Figure 1(d) shows that sample Vi\_2 is located near the Cu<sup>0</sup> point, indicating an abundance of Cu<sup>0</sup> colloids and almost no degradation; corroded red glasses To\_5 and Mi\_3 points are located near the Cu<sup>+</sup> point, indicating the presence of this ion as +1 OS and an intermediate superficial degradation; and the green glass Me\_14 points are near Cu<sup>+</sup> and Cu<sup>2+</sup> ions points, indicating the presence of both Cu ions in OS +1 and +2 and higher degradation.

## Conclusions

Through study of the Cu K-edge absorption energy of three red glasses (Vi\_2, To\_5 and Mi\_3), it was possible to establish a correlation between the OS and the surface decay, from non-weathered to middle and heavily corroded glasses. On different areas of the same green sample (Me\_14), it was possible to distinguish the non-corroded from the corroded areas.

Taking into account the heterogeneous surface of historical glasses and the presence of different degrees of alteration on

the same glass (e.g. pits or corrosion crusts), these results show clearly that it is possible to characterise the weathering phenomena of historical glasses from macroscopic to atomic scale in a totally non-destructive and non-invasive way. Synchrotron radiation techniques and, in this case, XAS have shown to be a promising tool to extend our understanding of glass decay. Nevertheless, a broader investigation is necessary by increasing the number of glass samples and chromophore K-edges to improve diagnostic accuracy and establish an easy-to-use methodology.

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Manuel Abuín, Aída Serrano, Jesús Chaboy, Miguel-Ángel García and Noemí Carmona

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