



## Characterisation of medieval yellow silver stained glass from Convento de Cristo in Tomar, Portugal

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### ABSTRACT

Yellow decoration effects in stained glasses using silver staining were first applied in the beginning of the 14th century. The glass piece being decorated was usually painted on its side intended to be facing the exterior environment, and then fired to temperatures between 500 and 650 °C, resulting in colours ranging from pale lemon to deep orange. Stained glass fragments painted by this process and belonging to the Convento de Cristo, in Tomar, Portugal, were characterised using micro-PIXE, and complemented with other analytical techniques, namely UV–Vis spectroscopy and XRF. Preliminary analysis showed that a mixture of Ag and Cu was used for the production of the yellow staining.

In order to understand this staining process and the influence of the firing temperature on the resulting colours, several soda and potash glasses with compositions similar to those of medieval glasses were produced and characterised. The role played by the addition of Cu in the final colours was also investigated.

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### 1. Introduction

The development of the technique of yellow silver staining occurred in the early fourteenth century and was first described by Antoine de Pise [1]. The technique consisted in applying a diluted Ag salt in the reverse (i.e. the surface facing the exterior) of a clear or coloured glass which was then fired at temperatures between 500 and 650 °C, below the range the grisailles were submitted to (~700 °C) [2,3]. During firing, Ag penetrates into the glass by ion exchange with K or Na. The Ag cations are then reduced to their metallic state nucleating into clusters that grow and coalesce to a colloidal distribution of sub-microscopic particles with diameters between 10 and 200 nm [3–7]. The Ag nanoparticles formed will interact with light and, through selective absorption, become responsible for the bright colours observed, varying from pale to bright yellow or orange.

The final colour is known to depend on parameters such as oven temperature, firing time, the type of paint and even the composition of the glass in which it is applied, as these parameters influence the sizes, shapes and distribution of the Ag nanoparticles [3]. Care must be taken with the firing time, since a too lengthy

heating may allow particles to grow to sizes comparable to the wavelengths of light destroying the colouring effects intended. As for the influence of the source of Ag ions, a recent study by Jembrih-Simburger et al. [4] concluded that AgNO<sub>3</sub> and Ag<sub>2</sub>SO<sub>4</sub> are the Ag salts that render the glasses with stronger, more bright and vivid colours.

In 2009 a set of 423 stained glass fragments was found during a conservation intervention taking place in the choir of the church of the Convento de Cristo, in Tomar, Portugal. Built in the 12th century the convent suffered several renovations along the centuries. Probably dated from 1510–1518 the fragments of the stained glasses now found may have been produced during the intervention campaign carried out in the reign of King Manuel I [8]. The fragments were taken to the laboratory, assembled, classified according to their formal characteristics (colour and iconography) and finally grouped in smaller sets, to facilitate the analysis and study of the yellow silver staining used. In line with this classification and grouping preliminary analysis was performed by micro-XRF allowing selecting fragments for further detailed characterisation using micro-PIXE mapping complemented with optical absorption measurements in the UV–Vis range.

As the now found glass fragments are of the high lime mixed alkali silicate glass type (average composition (by weight): 60% SiO<sub>2</sub>; 18% CaO; 10% Na<sub>2</sub>O + MgO; and 6.5% others), both soda and potash glasses with compositions similar to those of medieval glasses were produced in order to address the influence of the addition

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of Cu to the Ag staining process and the dependence on the glass type.

## 2. Experimental

In the fragments from the Charola of the Convento de Cristo in Tomar three distinct tones can be observed: pale yellow, bright yellow and orange. Through preliminary analysis with  $\mu$ -XRF, the presence of a mixture of Ag–Cu in all the analysed fragments was unveiled (cf. Fig. 1), similarly to what had already been observed in stained glasses from Monastery of Batalha (Portugal) that were produced in the 15th and 16th centuries [9]. In order to better understand this staining process and reproduce the colours, several soda and potash glasses with compositions similar to medieval glasses were produced to a total of 25 samples but differing in the type of glass, kind of painting and/or firing temperature, while keeping the heating time approximately constant. The following experimental procedure was adopted:

(a) Production of eight samples of potash glass and seventeen of soda glass, with the following compositions by weight: 52%  $\text{SiO}_2$ , 20%  $\text{CaO}$ , 2%  $\text{MgO}$ , 2%  $\text{Al}_2\text{O}_3$ , 2%  $\text{P}_2\text{O}_5$  and 22% of either  $\text{K}_2\text{O}$  or  $\text{Na}_2\text{O}$  for potash or soda glass, respectively.

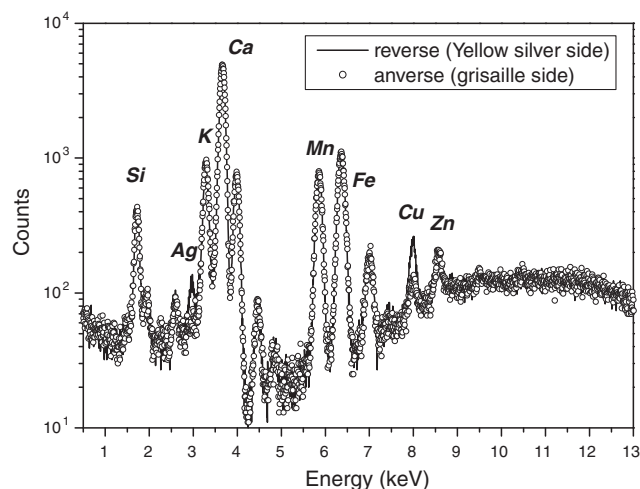
(b) Melting of the various oxides at 1300 °C in crucibles of Pt/Rh in an electric furnace for 24 h; next the molten glass was poured onto a metal plate at room temperature and levelled in order to obtain a uniform sheet of approximately 3 mm in thickness.

(c) Cutting the glass sheets with diamond-coated blades and then polishes them with SiC abrasive paper Micro-Mesh™ until a final 4000 mesh.

(d) Painting four samples of each type of glass with a mixture of 10% arabic-gum and: (i)  $\text{Ag}_2\text{SO}_4$  (Riedel-de Haen®); (ii) mixture of  $\text{Ag}_2\text{SO}_4$  (Riedel-de Haen®) and  $\text{CuO}$  from Fluka Chemika (2:1 ratio by weight).

(e) Painting nine soda glass samples using the same binder and: (i) three with a mixture of the  $\text{Ag}_2\text{SO}_4$  and  $\text{CuO}$  but in a 1:1 ratio by weight; (ii) three with a layer of Ag sulphate followed by an overlayer with Cu oxide solution – (Cu/Ag); iii) three with a layer of Cu oxide followed by an overlayer with Ag sulphate solution – (Ag/Cu).

(f) Firing the samples at 500, 550, 600, 650 and/or 700 °C, for 10 min, followed by cooling to room temperature.



**Fig. 1.** Spectra obtained from opposite sides of a glass fragment containing yellow silver stain. The spectrum from the anverse face of the glass fragment (the grisaille side) was obtained from a region not containing any visible traces of grisaille.

All the samples produced underwent cross-sectional  $\mu$ -PIXE analyses to obtain the profiles of Ag and Cu in the glass matrices, and UV–Vis spectroscopy for determining the intensity and the wavelength of absorption bands. The same analyses were carried out in five fragments from the Charola of the Convento de Cristo, chosen in order to have a representative colour sampling of the whole set of fragments. The chosen fragments were labelled as O3, O6 (pale yellow), O13, O10 (bright yellow), and O5 (orange). In the orange fragment, O5, an iridescent greenish layer is visible at the surface, which is also present on some of the samples produced and annealed at higher temperatures.

The results of the analysis of the laboratory produced samples and of the historical fragments were compared, trying to interpret the technical and production conditions of the past. To understand the diffusion of Ag and Cu ions in the glass, three different factors were considered: the type of glass, the type of paint and the firing temperature.

For  $\mu$ -PIXE characterisation, the laboratory samples were cut with a diamond-coated blade and the exposed surface cleaned with alcohol and analysed. The elemental distribution maps and line-scans performed on the stained glass fragments and sample cross-sections were obtained using a 2 MeV  $\text{H}^+$  microbeam with  $\sim 100$  pA intensity, delivered by a 2.5 MV Van de Graaff accelerator, and focused to  $\sim 3 \times 4 \mu\text{m}^2$  by an Oxford Microbeams triplet system. The X-rays were collected with an 8  $\mu\text{m}$  windowed Si(Li) detector with 145 eV energy resolution positioned, in the vacuum chamber, at 135° to the beam direction. An additional 50  $\mu\text{m}$  thick Mylar foil prevents backscattering protons from entering the X-ray detector. Beam scanning control and data handling were performed using OMDAQ V5.2 software package [10].

UV–Vis spectra were obtained with a Perkin Elmer® Lambda 35 spectrometer, covering the wavelength region from 190 to 1100 nm, with a 1 nm resolution.

Whenever necessary, the compositions of glasses were determined by XRF using an ArtTAX, Intax® spectrometer equipped with an air-cooled low-power X-ray tube with a Mo target and an XFlash® Peltier cooled silicon drift detector of 130 eV energy resolution. Polycapillary X-ray lens allow the primary X-ray beam to be focused down to 70  $\mu\text{m}$ .

## 3. Results and discussion

### 3.1. Optical absorption spectrometry in the UV–Vis

Visually, the final colours obtained with the several laboratory samples showed that for potash glasses a yellow colour could be obtained only with the Ag–Cu mixture in the ratio 2:1, whereas for soda glasses bright colours were obtained with Ag staining in the whole range of firing temperatures used (500–650 °C). Here, bright colours were also obtained with the Ag–Cu mixture in 2:1 ratio and firing temperatures up to 550 °C. All the other soda glass samples, stained either with the 1:1 ratio mixture or recurring to the layer-overlayer scheme, result in very similar colours that are independent of the firing temperature, but always with too dark hues.

These samples and the historical glass fragments were analysed through optical absorption spectrometry in the UV–Vis range. The results are summarised in Table 1. Analysis of this table clearly shows that in all cases one or two strong absorption bands are detected at wavelengths in the range 418–488 nm. Furthermore, some trends seem to emerge: (i) for all the glasses produced in the laboratory and fired at temperatures below 600 °C, a strong absorption band is detected centred at wavelengths in the range 435–453 nm; (ii) generally, for the same type of glass, as the firing temperature increases, these bands tend to have their locations

**Table 1**

Surface plasmon resonance band positions extracted from the UV–Vis spectra recorded for the glasses studied in this work.

		500 °C (nm)	550 °C (nm)	600 °C (nm)	650 °C (nm)	700 °C (nm)
Potash glass	Ag	N	N	434	428	
	Ag + Cu (2:1)	443	435	428	420	
Soda glass	Ag	N	436	430	421	
				460	460	
	Ag + Cu (2:1)	453	448	421	445	
				460		
	Ag + Cu (1:1)			425	425	425
				460	473	488
	Cu/Ag			424	429	428
					462	455
	Ag/Cu			428	431	N
				460	457	
Tomar	1 band		418 nm (fragments O3, O6, O13)			
	2 bands		422 nm and 465 nm (fragment O10)			
			422 nm and 478 nm (fragment O5)			

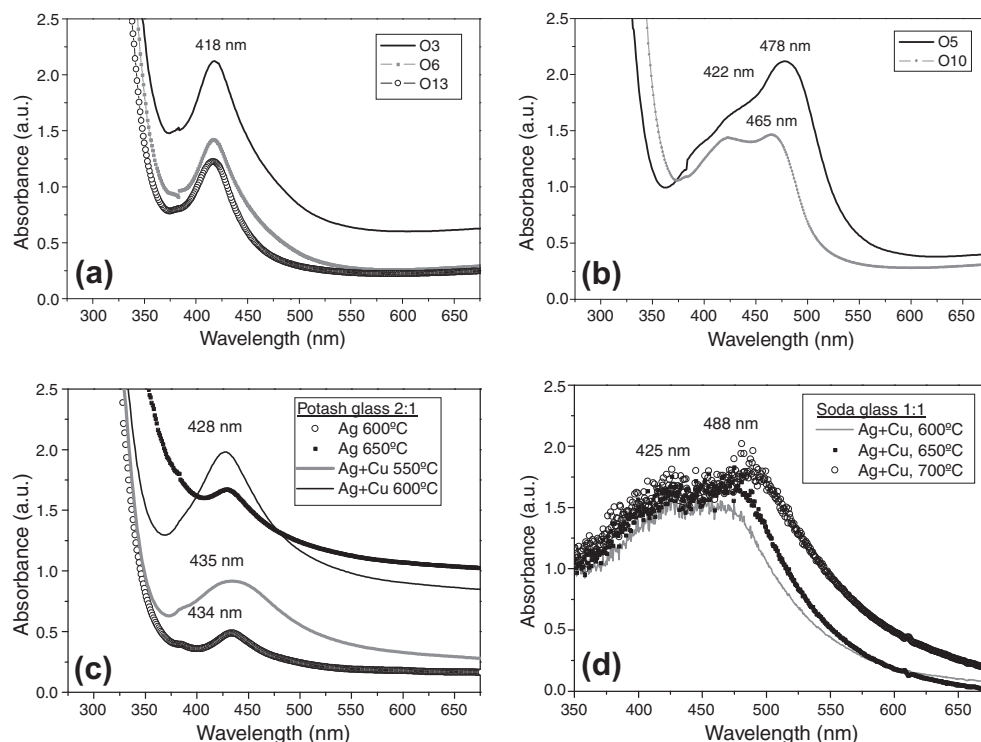
N: not established, due to spectral noise

shifted towards lower wavelengths; (iii) only in glasses fired at temperatures of 600 °C or above, two absorption bands develop with the centre of the system grossly located close to 440 nm, with only a slightly different separation between both bands (of less than 40 nm); (iv) for the historical glass fragments either a single band shows up, centred at 418 nm (cf. *fig. 2*), or two absorption bands are recorded, the higher energy one at 422 nm, the one of lower energy peaking at 465 nm or 478 nm, depending on the fragment analysed. These observations are consistent with the presence of sub-microscopic particles of dimensions grossly around tens of nm. In fact, it is known that the yellow silver staining of sil-

icate glasses gives rise to absorption bands from 410 nm to somewhat longer wavelengths, depending on the type of glass. These are explained as originating from surface plasma resonance oscillations of the free electrons confined in Ag nanoparticles, with the number, position and width of the bands depending on the dimensions and shapes of the particles formed [3–7]. The development of a single band has been described in the context of a distribution of spherical particles, while the appearance of two bands may imply either a bi-modal distribution of (very nearly) spherical particles or a distribution of particles with non-spherical symmetry.

Following the discussion above, and from the fact that the spectra of fragments O3, O6 and O13 present a single absorption band, centred at 418 nm, well in the range characteristic of yellow Ag stained glasses, the presence of Ag nanoparticles can be inferred. These are most probably very nearly spherical, with dimensions of the order of 10 nm. In fact, taking the estimated 30 nm FWHM for this SPR (surface plasmon resonance) band, we calculate with the help of the Mie theory a value of 8 nm for the diameter of spherical particles [11].

On the contrary, the spectra of the fragments O10 and O5 show two absorption bands (cf. *Fig. 2*) pointing to the formation of nanoparticles with either two different size distributions or a single distribution of non-spherical shapes, similarly to the findings reported elsewhere [12]. This remains an open question at the present stage. Although the appearance of two absorption bands in the spectra of the glasses produced in the laboratory with addition of Cu, and fired at high enough temperatures (600 °C or higher) might also be explained by considering two different distributions of different particles of Ag and Cu, respectively, this seems very unlikely. In fact, since colloidal dispersions of Cu particles in these types of glasses usually give rise to a single absorption band located around 565 nm, a displacement as large as 100 nm in wavelength would be very surprising and difficult to explain.



**Fig. 2.** UV–Vis spectra obtained for the stained glass fragments and for some of the laboratory glasses: (a) a single band at 418 nm can be noticed for fragments O3, O6 and O13; (b) the two band absorption spectra from fragments O10 (at 422 nm and 465 nm) and O5 (at 422 nm and 478 nm); (c) single bands observed for the potash glass painted with Ag + Cu in a 2:1 ratio and with only Ag at the firing temperatures indicated in the graph; (d) example of the two-band formation as for the case of soda glass painted with Ag + Cu in a 1:1 ratio, fired at high temperatures.

Finally, the observed displacements of the absorption bands towards lower wavelengths as the firing temperatures increase, may be explained by a growth of the Ag particles to smaller final dimensions, which is supported both by Mie theory and the observations by Mock et al. [12] using TEM.

### 3.2. PIXE spectrometry

In order to assess the extension of Ag and Cu diffusion, the  $\mu$ -PIXE technique was applied to cross-sections of all laboratory samples and to the five selected fragments of stained glass.

Elemental distribution maps were obtained as well as line-scans performed in order to better compare and understand the Cu and Ag diffusion profiles in the analysed samples. The values obtained are summarised in Table 2, and presented as a function of firing temperature, type of glass substrate and type of painting procedure.

Fig. 3 displays typical examples of the results, namely the elemental distribution maps and plots of the corresponding depth profiles obtained from fragment O3 and samples of potash glass with Ag + Cu fired at 500 °C and of soda glass with Ag fired at 600 °C. From Fig. 3 it can also be seen that the penetration depths of Cu and Ag in the bulk of the analysed fragment are quite similar but much shallower than recorded for the samples produced in the laboratory. The PIXE signal intensities also demonstrate that the Ag and Cu concentrations are higher in the laboratory samples than in the analysed historical fragments, as can be derived from Fig. 3, since the line intensities are normalised to the accumulated beam charges and therefore, a lower signal intensity carries larger statistical fluctuations. These observations are generally similar to what can be found in the other fragments (cf. Table 2).

Furthermore, it is found that for both the potash and soda glasses produced in the laboratory, diffusion of Ag reaches a maximum extent of approximately 300  $\mu$ m when only the Ag compound is applied at a maximum firing temperature of 650 °C.

These findings concerning the systems formed when only Ag is used to create colour, in particular in what concerns the observed relationship between single band SPR location and diffusion data, can be understood as follows. First, according to the prevailing theory of SPR absorption (Mie theory, considering spherical nanoparticles that are sparsely distributed and therefore do not have any electromagnetic coupling with each other and may then be taken as interacting independently with the electromagnetic radiation field), the SPR shift to lower wavelengths as the firing temperatures increase (while keeping firing time constant) implies that

the Ag nanoparticles form and grow to smaller dimensions when the glass is heated or fired at higher temperatures. Furthermore, considering that the diffusion of Ag increases with temperature as our results indicates, we propose that due to a faster diffusion there is effectively less time for the diffusing Ag atoms to interact and bind when forming or growing already formed Ag metal clusters, leading to smaller growth rates and thus smaller final sizes of the colloidal Ag particles at higher firing temperatures.

When instead the Ag + Cu mixture is applied, the diffusion of both species is somewhat faster in the case of soda glass, although in both types of glass (potash and soda) Ag diffuses more when fired at 600 °C. This contradicts with the idea that the higher the temperature, the greater the diffusion of Ag in the glass matrix. In fact, when Cu is present as well, the samples fired at temperatures of 700 °C, show 3–5 times less diffusion of Ag than those fired at 600 °C.

The behaviour of soda glass when painted with a Cu/Ag layer-overlayer or the reverse Ag/Cu, show that when the Ag compound is applied first onto the glass surface, Ag diffuses more. Again, at 700 °C the diffusion depth of both chemical species undergoes a strong decrease.

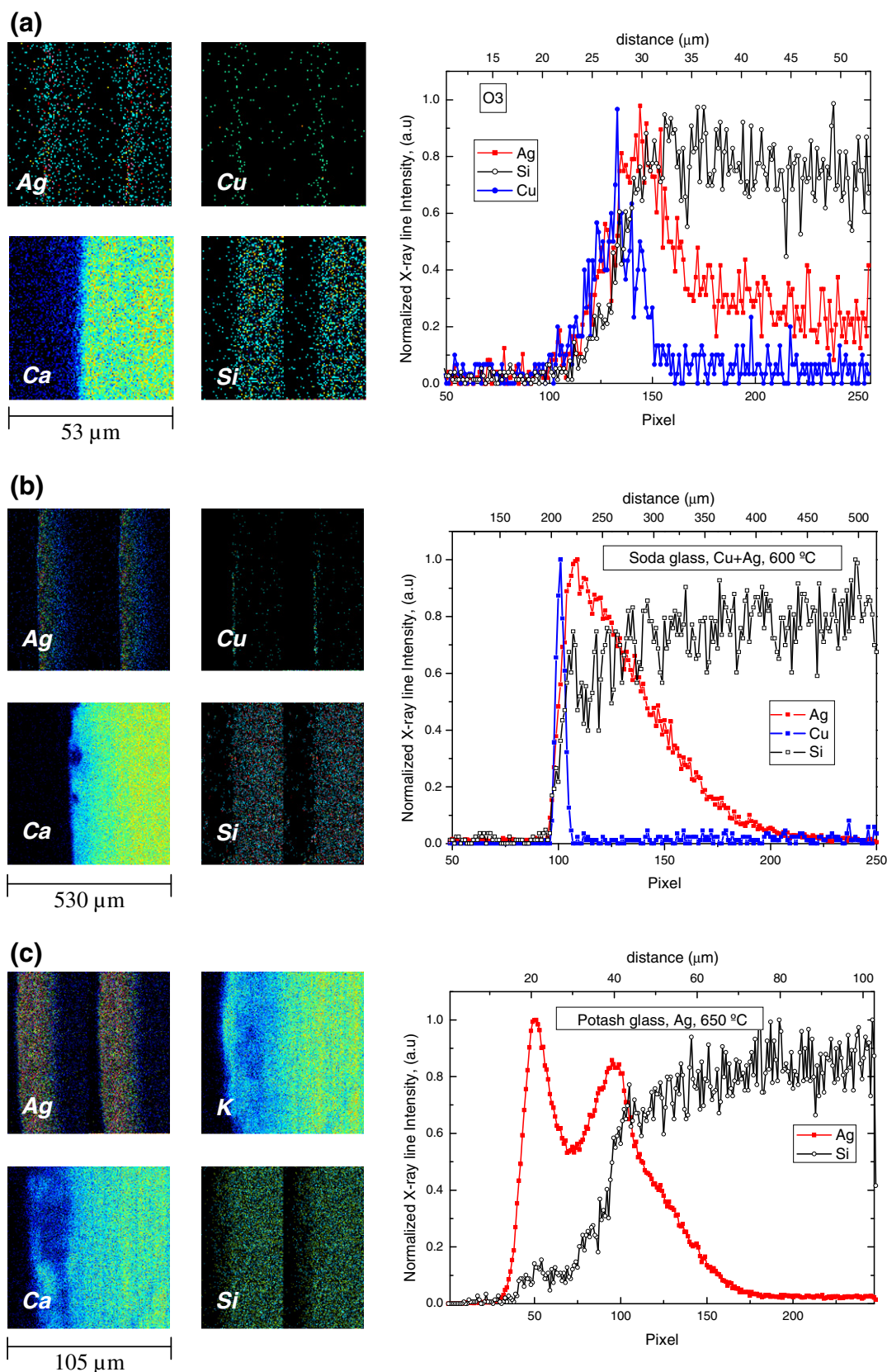
Notice, however, that Ag diffusion is always faster when only the Ag compound is used to create colour, irrespective of glass type and staining condition.

Excluding the possibility that the Cu measured in the yellow silver stained glass fragments results from grisaille contamination, as can be ascertained by the anverse and obverse X-ray spectra shown in Fig. 1, the discussion remains, if it was a planned or unplanned addition. The most well known description on the yellow silver staining medieval technique (Antoine de Pise [1]) makes no reference to the addition of Cu to the used silver salts. There is, however, a very recent compilation on the production techniques of stained glasses in Flandres from the XV to the XVIII centuries [13] where Cu is mentioned to be included in the yellow silver stain used, in order to obtain more intense and vivid colours. Intentionally or due to lack of other sources of raw materials at the time, there is the possibility that silver coins (usually in the form of a Ag–Cu alloy) could have been used for the production of silver stain. Alternatively, the use of a Cu mortar for reducing Ag to powder and then producing the necessary silver salt has also recently been referenced [14]. The use of a Cu mortar would be responsible for an unintentional contamination with Cu. In this work, the finding that the presence of Cu allows in fact to obtain bright yellow colours even for the lower firing temperatures used (up to 550 °C), leaves open the possibility that the technique of using

**Table 2**  
Ag and Cu diffusion lengths on the set of glasses from Convento de Cristo and the glasses produced in the laboratory. The data were obtained from the FWHM of the line-scans performed by PIXE.

		O3 $\mu$ m	O6 $\mu$ m	O13 $\mu$ m	O10 $\mu$ m	O5 $\mu$ m
Ag		8	10	11	25	13
Cu		4	6	10	18	8
		500 °C $\mu$ m				
		550 °C $\mu$ m				
		600 °C $\mu$ m				
		650 °C $\mu$ m				
		700 °C $\mu$ m				
Potash glass	Ag	Ag	72	100	125	315
	Ag + Cu (2:1)	Ag	45	37.5	85	35
		Cu	5	4.5	10	30
	Ag	Ag	76	113	160	313
	Ag + Cu (1:1)	Ag	48.5	27	130	130
		Cu	7.5	8.5	20	60
Soda glass	Ag + Cu (1:1)	Ag	–	–	120	125
		Cu	–	–	8	112
	Cu/Ag	Ag	–	–	139	103
		Cu	–	–	8	7
	Ag/Cu	Ag	–	–	139	68
		Cu	–	–	7	6





**Fig. 3.** Typical elemental distribution maps and Ag and/or Cu diffusion profiles obtained from a micro-PIXE analysis of sample cross-section: (a) stained glass fragment O3; (b) prepared potash glass sample painted with a Ag sulphate and Cu oxide mixture and fired at 500 °C; (c) prepared soda glass sample painted with the Ag sulphate solution and fired at 600 °C.

both Ag and Cu was already known and used in the production of the stained glasses now found at Convento de Cristo, in spite of the

fact that the isolated use of a silver salt can be traced up to the XX century [9,15].

#### 4. Conclusions

Stained glass fragments of historical value found in Convento de Cristo, in Tomar, Portugal, were analysed by a combination of UV–Vis spectroscopy and micro-PIXE. Some of these, fragments O3, O6 and O13, display a single absorption band in their UV–Vis spectra, each centred at 418 nm wavelength, despite their colours varying from pale to bright yellow. Taking the measured location and characteristic width (i.e. the measured FWHM), this absorption band may safely be assigned to the formation of a colloidal dispersion of very nearly spherical Ag nanoparticles of typical dimensions of the order of 10 nm. On the other hand, fragments O10 and O5 present a two band absorption spectra, centred at 422 and 465 nm, and at 422 and 478 nm, respectively, that may indicate the formation of either non-spherical nanometer-sized particles, or a bimodal distribution of particles sizes. Only the laboratory samples fired at temperatures above 600 °C show two absorption bands in the UV–Vis spectra. As the characteristics of the yellow silver stained fragments could not be entirely reproduced, especially in what concerns the extent of Ag diffusion, we cannot definitely conclude that fragments O10 and O5 were fired at temperatures above 600 °C.

The finest yellow colours were observed in the following three different sets of laboratory samples: (a) potash glass painted with the Ag–Cu compound mixture in the 2:1 ratio and fired at temperatures between 500 and 600 °C; (b) soda glass stained with only the Ag salt and fired at temperatures between 500 and 650 °C; (c) soda glass stained with the Ag–Cu compound mixture in the 2:1 ratio and fired at temperatures between 500 and 550 °C. The role played by Cu in this process could not be attributed to the formation of Cu nanoparticles, since the surface plasmon resonance at ~565 nm could not be found in the UV–Vis spectra.

For all the samples painted either with a Cu and Ag compound mixture or in a sequence of different layers of Cu and Ag the corresponding concentration depth profiles obtained by micro-PIXE show that Ag penetrates into the glass during the annealing, leaving Cu behind and closer to the surface. It can also be noticed that the Ag diffusion extent on these samples is significantly smaller than the ones observed when only the Ag solution is used.

As to the historical stained glass fragments from the Convento de Cristo, Cu diffusion was found to be similar to that recorded for the laboratory samples, displaying, however, a much more limited Ag diffusion. An important conclusion of this work is that the set of experimental results, both the UV–Vis SPR blue shifts and the Ag diffusion profiles derived by micro-PIXE, can be understood consistently, if the transit time, i.e. the time available for atom-metal cluster interaction by diffusion, is the key parameter for the growth of the Ag nanoparticles and their final dimensions at a given firing temperature. This will determine the probabilities of binding to the clusters and thus the cluster growth rate and its final

dimensions: the higher the temperature, the faster the diffusion and the smaller the transit times. At higher firing temperatures, Ag atoms diffuse faster and have less time to interact with the forming or already formed Ag metal clusters. Binding to the clusters becomes therefore less probable, resulting in a distribution of smaller sized Ag nanoparticles, where the conduction electrons collectively absorb light (SPR) at higher frequencies (shorter wavelengths). When present, Cu plays an important role in the proposed mechanism. As shown, the Cu reduces the Ag diffusion extent, which implies more time for interaction with nucleation centres and growing aggregates. This improves the growth of more clusters to the appropriate dimensions, resulting in more effective scattering of light and thus more intense, vivid colours.

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