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5th GLASSAC International Conference
TECHNICAL ART HISTORY

A tale of two industries:
The manufacture of bottle and window glass in England from the 17th to the 20th centuries

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Field of interest: archaeometry

Introduction

Glass has been manufactured in Europe for several millennia. In the post-medieval period (16th to 20th centuries) glass was produced for three main sectors: tableware (drinking cups, etc), flat glass (windows and mirrors) and containers (mainly bottles). Each sector has, at various times, had different requirements and found different technological solutions, although each has tended to borrow solutions developed in other sectors. This paper focuses on bottle glass and window glass manufacture in England from the mid-17th century to the 20th century.

Bottle Glass Manufacture

The 17th century saw the emergence of the 'English' bottle which came to dominate container glass production. While bottles had existed before, the 'English' bottle was thick-walled and narrow-necked allowing them to be effectively sealed and so enabling their use for storage and transport. The earliest bottles (dating to the middle of the 17th century) are made of a high-lime, low-alkali (HLLA) glass of the same composition that was also used for ordinary or common window glass (as well as the cheaper varieties of tableware). From the early 18th century onwards the composition of this HLLA glass began to shift with increasing amounts of iron and aluminium and decreasing amounts of phosphorus, due to the increased use of clay, bricks, rocks, slag and other cheap materials (Dungworth 2012a). The nature of the glass employed in the production of bottles in England was for many years constrained by a system of taxation which allowed the use of only the cheapest raw materials. The repeal of the Excise duties and regulation on the English glass industry in the 1840s freed glassmakers to use whichever raw materials they preferred. For most of the 19th century two basic recipe types were used: the first continued the 18th century tradition of using the cheapest possible ingredients for the production of dark green bottles for wine and beer (still essentially a HLLA glass), while the second made use of better quality materials to produce colourless or lightly tinted glass bottles for spirits and soft drinks (a soda-lime-silica glass). The use of HLLA glass came to an end in the early 20th century when the bottle industry underwent mechanisation — HLLA glass set too quickly for automatic bottle-making machines.

Window Glass Manufacture

Window glass was manufactured in England from (at least) the 14th century onwards. Medieval window glass was made using sand and the ash of plants readily available in the forested areas where glass manufacture was concentrated. This medieval forest glass contained relatively low levels of silica and so was not chemically durable. The same type of glass was also used for the manufacture of common tableware.

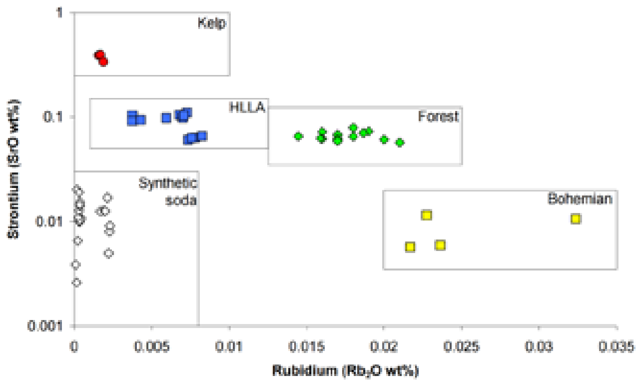
In England a significant change in glass production occurred in the later 16th century with the arrival of glassmakers from France. They brought a new style furnace and produced a new type of glass (HLLA); and again, the same glass was used for windows and common tableware. HLLA glass was used for almost all windows until the end of the 17th century (there is a small amount of evidence for the use of *façon de venise* glass for glazing the houses of the ultra-rich).

The end of the 17th century sees the emergence of a new mixed alkali glass based on the use of seaweed (kelp) ash (Dungworth 2013). This glass type is easily recognised through its relatively high strontium content (~0.5wt% SrO). There is a strong correlation between the use of kelp in window glass manufacture and the use of the crown technique for forming the glass. Both of these phenomena suggest an increasing concern with the transparency of glass.

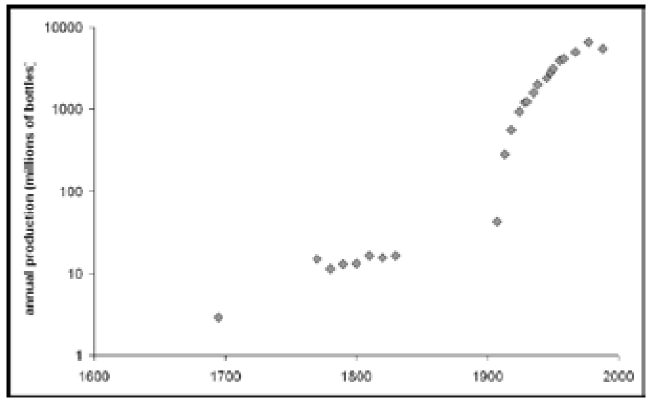
Kelp ash glass dominated window glass manufacture in England until the 1830s when the Leblanc process (for making sodium carbonate from sea salt) was introduced. Within a few years all window glass manufacturers had abandoned kelp (and any other plant-derived flux) in favour of soda ash. All window glass made after the 1830s is a soda-lime-silica glass and is characterised by the virtual absence of phosphorus (an unintentional component of all plant ash glasses).

The mechanisation of the window glass industry in the early 20th century was initially faced with problems (the glass devitrified and became cloudy) but these were resolved by the use of a proportion of magnesium to replace the calcium in the glass (Dungworth 2011).

The use of portable XRF allows the non-destructive, *in situ* analysis of historic windows (Dungworth 2012b; 2012c) which can indicate which panes of glass are original and which are later replacements (*eg* Girbal and Dungworth 2011; Dungworth 2017).



Conclusions



Although mid-17th-century bottles and windows were manufactured using exactly the same raw materials, from the late 17th century these two industries began to move apart. In some cases this was driven by customer requirements, in others it was driven by the manufacturers' desire to reduce costs, and in others it was constrained by a legal and taxation framework. The latter is probably responsible for the almost complete absence of technological change in the English glass industry during the peak years of the Industrial Revolution.

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Cobalt and potassium structure and degradation pathways in painted works of art

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Field of interest: Technical art history/conservation

Abstract

Smalt is a cobalt-potash ground-glass made by mixing a roasted cobalt ore, a potassium-rich flux, and sand at high temperatures. In oil paintings, smalt often discolors from a deep blue to a grey-yellow color. Typical of alkali silicate glass, smalt is sensitive to humidity: an ion exchange reaction between hydrogenated species (H^+) in the environment and the alkali (Na^+ and K^+) content of the glass leaches potassium/sodium from the smalt. The potassium depletion causes a reorganization of the atomic structure, and changes the coordination symmetry of the cobalt ions, resulting in the observed color change. In contrast to this visible degradation in oil paint, smalt-containing blue passages in illuminated manuscripts – which typically use glair or gum arabic as a binding medium for pigments – remain a vivid blue. This observed difference in color-fastness is the motivation for our research into how binding media other than oil affect the degradation process of smalt.

We posit that the degradation mechanism of smalt is affected by (i) the binding medium in which it is dispersed, and (ii) the chemical composition of the Co-blue potash glass. The study of smalt formulations with variable K_2O content, dispersed in several different binding media, as a function of aging can help elucidate the degradation mechanism.

Potassium and cobalt K-edge XANES were selected as they allow simultaneous examination of the coordination geometries of the metals involved, and their distribution within heterogeneous paint layers, which can determine the correlation between potassium leaching and cobalt coordination symmetry within the glass matrix. These synchrotron measurements are complemented by laboratory analysis (FORS, ICP-MS, GC-MS and FTIR). This work increases our understanding of the effect of binding media on the degradation mechanisms of smalt and, by extension, of other glass-based pigments.

Keywords: Smalt, Potash glass, Potassium leaching, XANES

Fig. 1 Left: Murillo, The Vision of Saint Francis of Paola, about 1670. Oil on canvas. ***Right:*** Master of the Murano Gradual, Saint Jerome extracting a Thorn from a Lion's Paw, 15th C. Tempera and gold leaf on parchment. The J. Paul Getty Museum, Los Angeles.

Introduction

Smalt is a cobalt-containing, high potassium ground-glass pigment used in painted works of art from the 15th century to the present day. Smalt is made by mixing *zaffera* – a roasted cobalt ore – with a source of silica and a fluxing agent (*i.e.*, potassium or sodium) at high temperatures (Muhlethaler and Thissen, 1969, Stege, 2004, Santopadre and Verità, 2006, Robinet et al., 2011). The composition of the final smalt is variable, with 66-72 wt% SiO_2, 10-21% K_2O, and 2-18% CoO (Santopadre and Verità, 2006). When used in oil, smalt can often discolor from a deep blue to a grey-yellow color (Boon et al., 2001, Spring et al., 2005, Robinet et al., 2011, Robinet et al., 2013). Such discoloration is observed *e.g.,* in the sky in Murillo's *The Vision of Saint Francis of Paola* (***Fig. 1***, left). In contrast, in several illuminated manuscripts, such as an illumination by the Master of the Murano Gradual (***Fig. 1***, right, red boxes), areas painted with smalt are still a vivid blue. Notably, illuminated manuscripts typically use glair (denatured egg white protein) or gum arabic as a binding medium for pigments, avoiding the use of a siccative oil. This difference in colorfastness motivated our research into understanding whether and how different binding media affect smalt's degradation. Better understanding the differences in chemical speciation and degradation pathways, by comparing the chemical environments in which smalt is found, may inform conservation decisions for all works of art containing smalt, and by extension, other glass-based pigments. As with other alkali silicate glass, smalt is sensitive to humidity: an ion exchange reaction between hydrogenated species (H^+) in the environment and the alkali (Na^+ and K^+) content of the glass results in potassium leaching from the smalt pigment particles (Verità et al., 2000). In oil paintings, this ion-exchange reaction involves water (from past periods of high humidity), free fatty acids in the drying oil binding medium, or a combination of both (Robinet et al., 2011). The depletion of potassium from smalt causes a reorganization of the atomic structure, and a change in the coordination symmetry of the pigment's cobalt ions. In the original pigment, the high basicity of the K-silicate glass supports the formation of covalent-bonded tetra-coordinated complexes. In such coordination, cobalt (II) ions act as network formers (such as the SiO_4 tetrahedra) and the resulting glass is characterized by an intense blue color. The loss in basicity, resulting from potassium leaching, leads to the transition of cobalt (II) ions from tetrahedral to octahedral symmetry (Boon et al., 2001, Robinet et al., 2011, Weyl, 1957). Moreover, the interaction of the leached potassium ions with the oil binding medium promotes the formation of potassium soaps – water-insoluble compounds containing alkali or heavy metals in pigments or drying agents combined with carboxylic acids in the organic medium (Robinet and Corbeil, 2003).

The study of artificially aged smalt formulations with variable K2O content, dispersed in several different binding media, can help elucidate the smalt degradation mechanism, allowing us to explicate the effects of (i) the binding medium in which it is dispersed, and (ii) the chemical composition of the Co-blue potash glass.

Methodology

Most published work to date that examines this complex system has focused on the transition metal center but hints at the importance of the alkali metal: studies using cobalt K-edge XANES (Cianchetta et al., 2012, Robinet et al., 2011) indicate that leaching of potassium from the glass structure induces changes in the Co coordination and thus potassium is important in the degradation process.

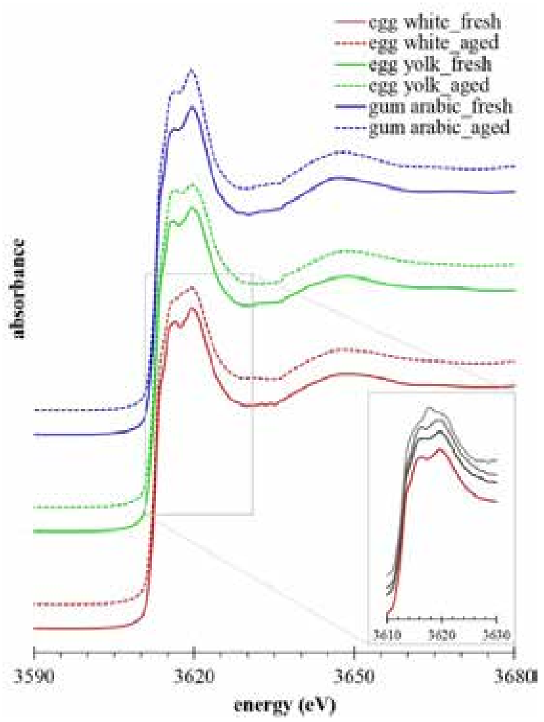

Fig. 2 Average Potassium K-edge XANES spectra of smalt dispersed in egg white, egg yolk and gum arabic, collected during the pilot study. Inset: three different spectral shapes observed in egg white, the binding medium most prone to variation among those tested.

The use of potassium K-edge XANES to investigate the changes occurring to the degrading smalt was explored during a pilot study at SSRL beam line 14-3, in which samples of a commercially available smalt dispersed in three different binding media – egg white, egg yolk, gum arabic – and painted on a polyester substrate were studied. One sample of each was artificially aged at 60°C and RH 80% for 140h; a second sample of each was left unaged. As shown in ***Fig. 2***, direct comparison of the aged to the unaged samples suggests that variation in the potassium K-edge XANES fingerprint of smalt in certain binders are apparent after even a short artificial aging period. In particular, gum arabic does not show appreciable changes while a variation in intensity and/or peak position is visible in the case of egg. Although the interpretation of the characteristic absorption features is complicated by the limited use of potassium K-edge XANES in the literature and consequent lack of reference materials, the pilot study validated the approach by highlighting a different behavior of smalt when dispersed in egg or gum.

Potassium and cobalt K-edge XANES are ideal approaches to determine the correlation between potassium leaching and cobalt coordination symmetry within the glass matrix by allowing simultaneous examination of the coordination geometries of the metals involved, and their distribution within heterogeneous paint layers. Complementary laboratory analysis (FORS, ICP-MS, GC-MS, FTIR) help complete the picture of the physical properties and chemical degradation of smalt in multiple binding media.

Conclusions

These investigations provide insight into which processes and/or chemical species impact the degradation of smalt, becoming a model for future pigment degradation studies. By providing critical knowledge to better understand the role of binding media in smalt degradation, these studies will inform conservation practices to limit the discoloration of smalt.

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Renaissance Venetian enamelled glass. An analytical investigation to understand their technology and to distinguish genuine from copied artefacts

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Field of interest: Renaissance Venetian glass, Archaeometry

Abstract

Venetian enamelled glass is one of the most significant subjects of the art and technology of Renaissance glassmaking. An analytical study using non-invasive and micro-invasive techniques on a wide selection of enamelled glass artworks from museums and archaeological finds is in progress. The aim is to characterise the materials and technology of genuine Venetian Renaissance enamelled glass production and to identify specific features allowing these objects to be distinguished from contemporary *façon de Venise* products and 19th century copies and fakes.

Keywords: Venetian glass, Enamels, Glass technology, Analysis

Fig. 1 Genuine enamelled Venetian Renaissance artworks from the Louvre collections belonging to the *cristallo* group (R15 left) and to the *vitrum blanchum* group (R29 right).

Introduction

Since 2009, the authors have been involved in a research project concerning enamelled and gilded Venetian Renaissance glass. These objects were made in Venice from the late 15th through the 17th centuries and were imitated in other European glassmaking centers during this period (*façon de Venise* glass). Furthermore, copies and fakes of the Renaissance enamelled Venetian glasses have been made in Murano and other European glass factories up to the present day.

Indeed, in spite of the interest shown by collectors, museums and specialists for more than a century, questions still remain to be answered about Venetian enamelled glass. Many pieces in the collections are of uncertain provenance and their authenticity is still being debated.

The purpose of the project is to establish, through quantitative chemical analysis of the glass and enamels, technical criteria that enable Venetian Renaissance enamelled glass to be distinguished from *façon de Venise* production and later copies and fakes. The database being developed is the first to be dedicated to this subject. More than 80 genuine Venetian Renaissance enamelled items (including archaeological fragments) and objects of doubtful provenance belonging to the French collections (mainly from the Louvre museum) up to the present day were analysed.

Non-invasive ion beam in PIXE-PIGE modes (C2RMF) was used for the artefact analyses, while micro-invasive SEM-EDS (LAMA) was used where micro-sampling was allowed.

Results discussed in recent papers, were compared with the analyses available in the literature for Venetian and *façon de Venise* items and with the recipes to make glass and enamels reported in Renaissance treatises written by Venetian glassmakers. Compositional groups were established including typical Venetian Renaissance recipes (*cristallo*, and *vitrum blanchum*, ***Fig. 1***) and others that are not Venetian Renaissance.

Conclusions

The research is being extended by analyzing a larger number of enamelled glasses from French collections, well dated items from France and Liechtenstein, as well as enamelled glass fragments datable to the Renaissance in archaeological contexts coming from Italy (Padua) and different places in England. These fragments allow to establish a reference analytical database of Venetian Renaissance glass and the investigation of both the structure and the colouring technique of the enamels using polished cross sections analyzed by SEM-EDS.

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Overview of glass chemistry and technology in late antique Cyprus

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Field of interest: Archaeology/Archaeometry

Abstract

In this work we will summarize the work carried out in the last years by our group in the field of glass archaeometry. In addition we will discuss the forthcoming research results that will extend our work. We present the multi-analytical approach based on UV-vis-NIR absorption spectroscopy, XANES spectroscopy, EPMA and LA-ICP-MS to investigate the Cypriot glass industry in the late antiquity. The variety of techniques used let us investigate technological aspects such as origin of the colour and reducing conditions as well as provenancing raw glass and recycling. Cyprus is located in very close proximity to the primary factories of raw glass, therefore it offers an interesting point of view on the distribution of glass. Because of its geographical proximity to primary production areas, on the island we can find basically all glass types circulating in the Mediterranean area in this period. In addition to very common glass compositions, i.e. Levantine, HIMT and Foy 2, we found also more rare material, such as Egypt 1 glass, rarely exported outside Egypt, and high-Al glass probably manufacture in the Anatolian peninsula.

Keywords: Late-Antiquity, Archaeometry, LA-ICP-MS, EPMA, UV-vis-NIR

Introduction

In 2011 we started working on the archaeological and archaeometric study of the late antique glass from Cyprus, with a focus on early Christian basilicas dated 5th-7th century AD. We focussed our attention on Cyprus because the island constitutes a very interesting case study to investigate the glass industry of the first millennium AD as a whole. As it is well known, in Roman and early medieval times glass was produced in large factories located in the Eastern Mediterranean areas, in particular Egypt and the Levant [1]. In late Antiquity the island was an important hub on the East-West and South-North trade routes because of its central geographical position in the eastern Mediterranean and the prevailing sea currents. Supported by a continuous economic growth this prosperous Roman province displayed an increasing building programme of early Christian basilicas between the 5th and mid-7th century AD.

We worked exclusively on the south-west coastline of the island as it was impossible to study and sample material in the northern areas due to the current political problems. Initially we have had the chance to work on the sites of Maroni Petrera, Kalavasos Kopetra, and Yeroskipou, while very recently we had the opportunity to sample material from Ayios Kononas for chemical analysis. Currently we are also working on the glass finds of the site of Ayia Mavri and Katalymata to enlarge the geographical distribution of the sites and develop an extensive view on the local glass distribution.

In *Fig. 1* we show a map of the island reporting all the sites mentioned in the text.

Our research is based on the use of optical spectroscopy. This approach offers interesting insights into technological aspects of glass production, such as the reducing conditions and colouring. The technique requires a light source, optical fibres to transport the light to/from the sample and a spectrometer connected to a laptop. Being available in devices of reduced dimension, optical spectroscopy can be transported to carry out measurements *in-situ*.

In order to develop a methodology based on optical spectroscopy we compared the determination of Fe^{2+} and Fe^{3+} in glass obtained by XANES and UV-vis-NIR absorption spectroscopy on reference glasses made in the laboratory [2]. In addition we put in relation the spectral features of glass, such as colour, Fe^{2+} concentration and UV absorption edge, with the chemical composition obtained by EPMA on real archaeological glasses. Once the methodology was establish we could interpret the spectra of more than 400 naturally coloured glass fragments coming from Yeroskipou, Maroni-Petrera and Kalavasos-Kopetra to assign glass samples to specific chemical groups which allows to evaluate the glass consumption and distribution on the island [3].

Chemical analysis still plays a paramount role to investigate questions such as provenance, recycling and identify single batches. For the glass fragments of Maroni, Kalavasos and Yeroskipou we used EPMA for major and minor elements [4], while more recently we have reanalysed all the material for trace elements with LA-ICP-MS. The latter technique has been used also on 40 samples selected in Ayios Kononas, a rural site in the Akamas peninsula.

As expected all the glasses have a soda-lime-silica composition. However, by comparing the material found on the island with material from the same period we could identify some of the most common glass groups circulating in the 5th-7th century in the Mediterranean (see for example [5]). Most of the glass has Levantine, HIMT and Foy 2 compositions. In addition, Egypt 1 and HIT glass was also found on the island. In Ayios Kononas a very rare high-Al glass fragment (about 13% of Al_2O_3) was found and which was probably produced in the Anatolian peninsula where several glasses with this type of composition have been found [6]. This glass is also characterized by the high lithium and boron, i.e. 95 ppm 710 ppm respectively.

Conclusions

The approach with UV-vis-NIR spectroscopy and chemical analysis permits a comprehensive study of glass remains. The spectroscopic data give information on the origin of colour and on the reducing conditions applied to the glass melt. Moreover, since the instruments are portable, the measurements can be carried out directly in the storage rooms without need for sampling. In this way, more material can be studied and a better interpretation of the glass consumption can be extrapolated. This information is of paramount importance for glass archaeologists as they can re-evaluate ancient connection networks between producers and consumers of goods.

The chemical composition shows that in Cyprus circulate all the main glass types manufactured in the 5th-7th century. However, probably due to the proximity, there is a larger amount of Levantine material compared to the Egyptian material. Foy 2, HIMT and Egypt 1 glass were imported into the island but in lower amount. In addition there is a chronological evolution between the HIMT and Foy 2 consumption. HIMT was produced and distributed in the 4th-5th while Foy 2 in the 6th-7th century. The exceptional presence high Al glass, an Anatolian production so far never found outside this region, shows that very likely in the north of the island there were connections with the Anatolian peninsula.

In terms of colours and redox, Levantine glass is mostly light blue with about 50% of iron in the Fe^{2+} state. However the glass can assume several colours according to the redox conditions under which was produced. As the redox conditions get more reducing the formation of sulphide ions is promoted reacting with the remaining Fe^{3+} to form the Fe-S complex. Even small amounts of this chromophore affect very strongly the colour inducing a shift to blue-green, green, green-yellow, amber, brown according to its concentration. Conversely HIMT and Foy 2 are very homogeneous: they are both yellow-green but HIMT has a stronger saturation. Because of large additions of manganese all the glasses belonging to these two groups are strongly oxidized, with about 85-90% of the iron in the Fe^{3+} state. Egypt 1 glass has a beautiful deep green colour due to the large amount of iron (about 1.6 wt%) in a mix state Fe^{2+}/Fe^{3+}, but one fragment there is a streak of yellow-green in it. By the analysis with optical spectroscopy it is evident that this is due to the Fe-S complex, therefore to locally more reducing conditions.

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The use of glass in medieval pigment making

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Field of interest: Glass history, Technical art history

Introduction

The use of glass, under many forms and with different functions, in medieval recipes for the production of pigments to be used in medieval manuscripts' illuminations, is discussed.

The Portuguese book "O Livro de komo se fazen as kores das tintas todas" (LKSK), in English "The book on how to make all the colours", dated to the 15th century will be examined as a case study. This book, which is a compilation of several recipes that can be traced back to the 13th century, has been the subject of interest of several scholars (Afonso, Cruz, & Matos, 2013; Matos & Afonso, 2014; Melo & Castro, 2016; Strolovitch, 2010), and is currently in the focus of a larger project being developed at the Department of Conservation and Restoration from the FCT/ UNL (Melo & Castro, 2016).

The purpose of the current study is to identify those recipes in the manuscript that mention glass, directly and indirectly, in many forms and functions. Thereby, we intend to gain a better understanding of the presence and importance of glass in the medieval scriptorium.

Keywords: Glass vessels, Glassmaking furnaces, Pigment recipe book, Medieval period

Discussion of ideas and possibilities

The manuscript's first recipe, "Oro Musiko" (mosaic gold) mentions a glass vessel that is required for the making of a gold coloured pigment (Melo & Castro, 2016; Strolovitch, 2010). This colour was meant to imitate gold in order to substitute this expensive material in illuminated books, and it consists of tin (IV) sulphide (SnS_2). The recipe describes that, after all the required ingredients are gathered and mixed, the mixture must be filled into a glass container. This glass vessel must be wrapped in clay in order to withstand the fire. As soon as the pigment forms and the vessel has been cooled down to room temperature, the mosaic gold is retrieved by breaking the glass vessel (Melo & Castro, 2016; Strolovitch, 2010). The recovered pigment that should look like a golden bar has then to be ground up well into a powder suitable for paint.

There are three possible interpretations of the use of the glass vessel in this recipe: 1) glass was such a common material and circulating in the national territory in such an abundancy that it was affordable to destroy a glass vessel; 2) mosaic gold was such an important and valuable colour that it was acceptable to destroy a glass vessel, even if the latter was comparatively valuable; and 3) parts of the broken glass may have deliberately been grinded together with the pigment, in order to enhance its brightness. Considering the scarcity of glass assemblages in Portugal that can be dated to the medieval period, and the relatively small number of glass fragments found in such assemblages, the 2nd and 3rd proposed hypotheses seem more likely. The recipe to make the mosaic gold was recreated in our laboratories without grinding the glass along with the pigment (Melo & Castro, 2016), but this hypothesis should be tested and compared with published analyses of this pigment from historical illuminated manuscripts. It should be added that this pigment was indeed found in Portuguese illuminated books (*e.g.* ***Fig. 1***) (Melo & Castro, 2016).

The second reference related with glass appears in Chapter Ten with a recipe to make very fine "Azarcão", in English red lead. In this recipe, it is described that after placing the needed ingredients in a vessel, this vessel has to be taken specifically to a glass furnace and be placed there for twenty-two days. After this period the pigment is ready to be used. However, no information regarding the temperature is given. Due to the experiments performed with the purpose of reconstructing the making of red lead from lead white, it was understood that placing the vessel inside the glass furnace, where the temperatures can vary between 700º and 1000º C, would result in the volatilization of the lead and consequently the loss of the main recipe component (Melo & Castro, 2016). In order to obtain red lead from white lead, the required temperature is around 470º C, so the vessel should have been placed outside the furnace or in a specific chamber, for instance an annealing chamber. We can discuss several factors that make this recipe really interesting, like the fact that a probable connection or proximity between glassmakers and other artisanal professions existed. Other important fact is the direct reference to a glass furnace. The book LKSK is written in Portuguese and the majority of the colourants described in the book can be found in Portuguese illuminated books so one can propose that the production of these colours were made in national territory. This implies the existence of glassmaking furnaces in Portugal in the 15th century, fact already proposed by Vasco Valente (Valente, 1950). But this simple reference to a glassmaking furnace seems also to suggest that these furnaces were probably easy to find in the Portuguese territory in the 15th century. Moreover, considering the temperature at which this pigment must be made one can propose that the artisan

a

b

c

Fig. 1 (a) Example of mosaic gold in a Book of Hours, Ms. 22, f.74, Palácio Nacional de Mafra (PNM), and (b) respective detail (available in http://www.dcr.fct.unl.pt/sites/www.dcr.fct.unl.pt/files/ArquivoDigital/). (c) Mortar and pestle made in glass, dated to the 17th century (Kerssenbrock-Krosigk, 2008, p. 145).

making the colourant knew that in order to obtain red lead from white lead, a high temperature was necessary, one close to the temperature the glass annealing chambers and so the advice of the glassmaker to choose the place in the furnace could be considered.

This supposed connection between artisans from different fields such as glassmaking and the book illuminating recipes, can be seen through an alchemist veil. Alchemy was practiced by scholars and workers from different areas, including the production of pigments and the making of innovative glass formulations like ruby glass (Smith, 2008), and alchemy was probably the common knowledge that connected these areas.

Conclusions and future work

From the point of view of glass history, we believe that the study of recipe books from different fields and from different chronological periods can bring new and exciting information about the importance and usage of glass objects.

Concerning the case study of the book "O Livro de komo se fazen as kores das tintas todas" LKSK presented here, it is discussed by Matos & Afonso (2014), that the names given to certain objects are not consistent along the book, and different designations are used when in reference to the same object, which might suggest that in certain recipes glass vessels were also used but not directly mentioned. From what was discussed above and looking carefully to the remaining recipes it is possible to imagine the usage of glass in its preparation. The presence of glass in Portugal during the medieval period needs to be further investigated. In the historically made reproductions of recipes collected from the book LKSK, glass vessels were often used for all kinds of compounds mainly because of its chemical inertia with a great number of substances. Moreover it is also worth mentioning that utensils like mortars and pestles were made in glass (see ***Fig. 1***) (Kerssenbrock-Krosigk, 2008, p. 145).

As future work, it will be important to study glass assemblages from monasteries that had scriptoria in order to gain knowledge about the glass objects which were used there. It is important to know what glass objects were available to the monks in order for them to create their beautiful colours and illuminated books. Based on the manufacturing of certain colours it is expected to bring new insights on the use of glass objects as a container material during the medieval period, especially in monasteries with scriptoria where the illumination books were made.

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Hispano-Moresque architectural glazes in the context of medieval glass technology

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Field of interest: technical art history / glazes

Introduction

Hispano-Moresque architectural tiles were extensively used in Portugal and Spain, during the 15th and the first half of the 16th centuries. Their rich patterns comprise mainly five colours – tin white, cobalt blue, copper green, iron amber, and manganese brown – which are all obtained from high lead glazes with the addition of specific metal oxides (Coentro *et al*., 2014). These different coloured glazes are physically separated on the tile surface, either by a dark manganese-brown line (believed to contain a greasy substance such as linseed oil), which is known as the *cuerda seca* technique, or by a ridged contour line that acts as "wall" in the *arista* technique (*Figure 1*).From the study of two Portuguese Hispano-Moresque tile collections – the National Palace of Sintra (PNS) and the Monastery of Santa Clara-a-Velha (SCV), in Coimbra – the glaze technology is analysed in the context of coeval glaze, glass, and enamel production. Starting with the colour palette and with special emphasis on tin-opacified glazes, the aim of this communication is to present a short summary of the process of technological transfer that contextualises these glazes.

Keywords: Lead glazes, Tin-opacified glazes, Hispano-Moresque, µ-PIXE, LA-ICP-MS

Methodology

This work is part of a larger project aiming at characterising and comparing Portuguese and Spanish Hispano-Moresque tile collections. A multi-analytical, minimally invasive methodology was employed. Here, the results of two analytical techniques are discussed: micro-Particle-Induced X-ray Emission (µ-PIXE) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). The analyses were performed on glaze samples (1-3 mm wide) mounted as cross-sections in epoxy resin (Araldite® 2020) and polished in Micro-Mesh® sheets up to grit 8000. By analysing the glazes in cross-section, it was possible to avoid the corroded surface as well as the glaze-ceramic body interface layer.

Results and discussion

High-lead glazes (ca. 40-60 wt.% PbO) were identified in all analysed samples and can be divided into two types: "transparent" and tin-opacified. Silica (SiO_2) and lead oxide (PbO) are the major constituents of the glazes making up to 90 wt.% of the total composition. They show an inverse correlation, with higher SiO_2/PbO ratios for tin-opacified glazes (mostly white and blue ones). The decrease in PbO is compensated by a higher Na_2O content as a fluxing agent in tin-opacified glazes. Potassium, unlike sodium, was found to be present in variable amounts both in transparent and in tin-opacified glazes.

This is consistent with a glaze technology that followed the Islamic tradition introduced in the Iberian Peninsula from the 8th century onwards. The use of lead glazes is believed to have started in the Roman Empire or in China, between the 1st century BC and the 1st century AD, and then spread to Europe and the Middle East. Alkaline glazes and glasses were also used in Medieval Europe along with lead glazes. However, in the Iberian Peninsula only lead-glazed ceramics have been unearthed so far, the significant availability of galena (PbS) in the region being appointed as one of the major factors for this, along with the advantages that lead glazes present, such as less susceptibility to defects and a higher glaze brilliance (Tite *et al*., 1998; Trindade, 2007).

The analyses of these Hispano-Moresque glazes have identified and quantified most SnO_2 contents between 6 wt.% and 10 wt.%, with variable degrees of homogeneity. Use of SnO_2 as opacifier represents the most important innovation brought by the Muslim occupation (8th-15th century) to glaze technology, turning the Iberian Peninsula into an important ceramic production centre from at least the 13th century onwards.

1 † *in memoriam* of our co-author and dear friend Vânia Solange F. Muralha

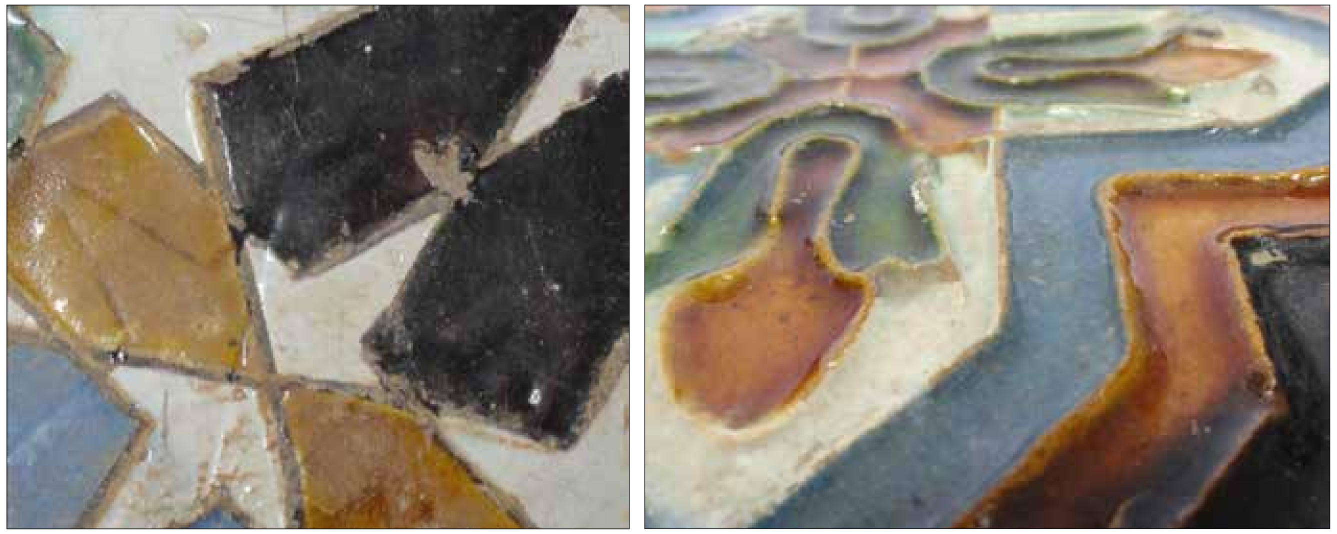

Fig. 1 Details of a a *cuerda seca* (a) and an *arista* (b) tiles illustrating the five colours identified in Hispano-Moresque glazes: white, blue, green, amber and brown.

However, tin-based opacifiers were used since Roman times and tin was used in white enamels and glass mosaics since the 4th century AD. The question remains on why this technology took almost five centuries to be adopted to ceramic coatings, since the earliest evidence of tin-opacified ceramics comes from the 9th century Iraq (Tite *et al*., 2008).

The pictorial layer is composed of five colours: white, blue, green, amber and brown. The transition metals identified are those known to be responsible for the colours – cobalt for blue, copper for green, iron for amber and manganese for brown – the very same found in Byzantine glass mosaics, as well as in medieval Limoges enamels used on metal decoration (Drayman-Weisser, 2003; James, 2006).

The influence of metal decoration on ceramics is not restricted to the colours and one can see a parallel between *cloisonné* and *cuerda seca*, as well as between *champlevé* and *arista* techniques for separating the different coloured glazes. However, the *arista* technique appears as an innovation exclusive to architectural tiles as an evolution from 13th century Gothic lead-glazed monochromatic tiles used in France and England (Trindade, 2007).

The blue glaze in *cuerda seca* and *arista* tiles is very characteristic with its light cerulean shade and opacity. The majority of the blue *cuerda seca* and *arista* glazes display a Fe-Co-Ni-Cu association, as determined by µ-PIXE and LA-ICP-MS. Copper may be linked with the raw material used for obtaining cobalt, or it could be added intentionally. As an example, a blue enamel recipe from Antonio Neri (*L'Arte Vetraria*, 1612) includes copper (*ramina di tre cotte*) along with cobalt (*zaffera*) (Vilarigues & Machado, 2015). During the 9th century, cobalt blue became profusely used by Muslim ceramists, who had the raw materials available "nearby" in one of the most important cobalt deposits in the world, Qamsar, in today's Iran. Cobalt is believed to have been introduced in the Iberian Peninsula during the 13th century, although its origin is still a matter of discussion. By then, both the Middle Eastern and the European (Saxony) cobalt mines were known in the Muslim Kingdom (which included part of the Iberian Peninsula), as referred by Abu l'Qasim's ceramic treatise (Kessler, 2012; Trindade, 2009). A small group of the blue glazes analysed displays arsenic contents above 1000 µg/g and bismuth contents above 500 µg/g. The presence of As is associated with cobalt exported as zaffre from the Saxony region (Germany) from the beginning of the 16th century onwards (Gratuze *et al*., 1996). This is consistent with a later chronology attributed to these tiles, since the group is composed exclusively of *arista* samples.

Conclusions

Hispano-Moresque tiles represent a time of great cultural changes. Their technology incorporates Islamic and Christian influences, which is visible in the colours displayed and glaze compositions found, as well as in decoration techniques. To better understand the glaze technology and its evolution, one must look at the coeval glass and enamel technologies as well, as the colour palette is the same and even the methods for separating the colours are influenced by the metal arts.

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Investigating a Byzantine technology: experimental replicas of Ca-phosphate opacified glass

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Field of interest: archaeology/archaeometry

Abstract

The archaeometric examination of mosaic glass tesserae has recently become of great interest, and more attention is given to the textural examination. The glass coloring and opacification techniques so far identified in ancient glass are relatively homogenous from the early glassmaking until the end of the Roman empire, when a major change occurred. From the 5th century onward, Sb- based pigments were substituted by other compounds, such as Ca-phosphate, probably introduced in the form of powdered bones. This compound is found in Byzantine mosaic tesserae and associated to large quantities of gas bubbles; a previous study aimed at the characterization of the opacifier highlighted the presence of a reaction rim enriched in sodium at the glass/inclusion interface, but to date little is known about the technology of production of this specific kind of opacifier.

To understand the production technologies of glass opacified with bone powder, experimental replicas were made under laboratory conditions using a silica-soda-lime base glass. Bovine bones were selected in order to minimize the variables depending on the species or the individuals; both cortical and trabecular portions were selected. Different thermal pre-treatments of the bones were tested, and batches were melted with different firing and cooling rates at different temperatures. The experimental samples thus obtained were prepared in polished sections and analyzed by means of optical microscopy (OM), scanning electron microscopy (SEM-EDS) and Raman spectroscopy in order to guarantee the textural, mineralogical and qualitative chemical analysis of the opacifying phase and the comparison with the archaeological samples.

Keywords: bones; Ca-phosphate; opaque glass; Byzantine

Thermal properties of the modernist enamels and stain glasses from the city of Barcelona

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Field of Interest Technical Art History, Conservation

Abstract

The aim of this project is the study of the thermal properties of the Modernist (late 19th and early 20th century) stain glasses and enamels from the city of Barcelona. This study is a part of a thesis dedicated to the materials and methods used in the production of enamels, grisailles and yellow stains with special regards to their degradation mechanisms. During this period enamels were mainly used to colour areas of the glasses although colour base glasses were also employed. Enamels were used not only to colour but also to give opacity adding micro-crystallites with a large refraction index.

We dispose of the collection of the raw materials, including enamels, grisailles and yellow stains, used for the production of the decorations by one of the most important enterprises responsible of the production of most to the stained glasses of the Modernist period in Barcelona, Granell y Cia[1].

One of the main issues in the conservation of the decorative layers (enamels and grisailles) is the quality of the adherence and this depends on the thermodynamic properties of both substrate glass and decorative layers. Among the most relevant thermodynamic property to measure is the glass transition, glass deformation and glass softening temperatures as they give the range of adequate firing temperatures to obtain adequate adherence of the decorative layers. Above the glass transition temperature, the glass behaves as a liquid although showing a large viscosity, and as a consequence, atomic diffusion coefficients, necessary for a good reactivity of the enamels and the background glass, show a great increase. Nevertheless the glass deformation temperature of the base glass has not to be reached in order to avoid it. On the contrary, the enamels should be fired at a temperature close to their softening point to allow their adherence to the base glass.

Finally, the physical properties of the glasses, enamels and grisailles are essentially determined by their chemical composition. For this reason the chemical composition of the raw materials, as well as, of enamels and grisailles obtained from them will be determined by SEM-EDS for major elements and also LA-ICP-MS for the trace elements. Moreover, the presence of particles, crystalline precipitates, bubbles, that is generally speaking, the microstructure is also known to affect the degradation mechanisms. This is also investigated by Optical and SEM.

Results

The blue enamels are those showing more conservation problems (mainly layer losses). We will present the first data obtained from the blue enamels used in the Modernist workshop, Granell y Cia.

The base glass of the period is a typical soda-lime glass with a glass transition temperature (determined for a viscosity of 10^{12} Pa·s) of about 581°C and a Deformation point (viscosity of $10^{10.5}$ Pa·s) of about 613°C[2]. These temperatures determine the optimal firing temperature range.

The workshop used four different blue enamels (E33, E114, E115 and E122) corresponding to different manufacture companies, Wengers, Lacroix and l'Hospied respectively. They have different chemical compositions as shown in the table. In all the cases is a B-Si-Zn-Pb glass with a cobalt base pigment. However the enamels show a different glass composition and pigment characteristics.

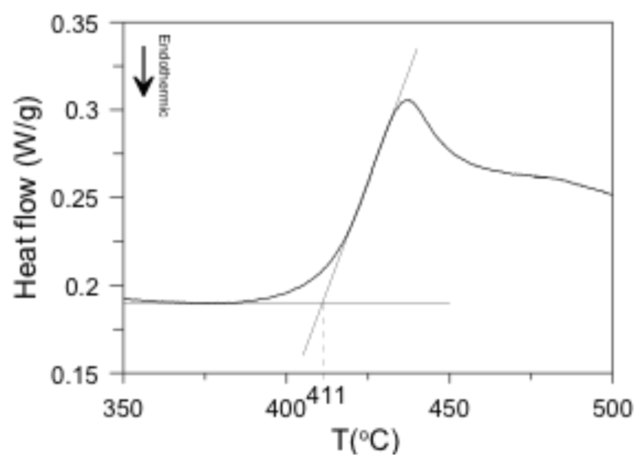
The glass transition temperature and softening point of the enamels is different and cannot be estimated from the composition and has to be measured. The glass transition temperature of the glasses was determined by DSC at 20K/min heating rate, in a Netzsch F404 Pegasus. The DSC curve is shown in the figure for the enamel E33, for which the glass transition temperature determined is 411ºC. The softening temperature is typically at about $1.5 \cdot T_g$, therefore, the firing temperature should be of about 615ºC. This temperature is very close to the base glass deformation point.

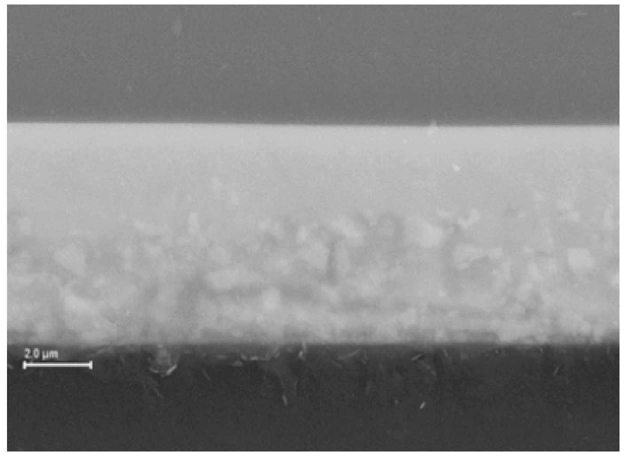
For this enamel the pigment is formed by particles of $CoAl_2O_4$, (see figure) this pigment is a cobalt aluminate known as cobalt blue; it is produced by synthesis at 1200ºC of the corresponding oxides, and was used for the decoration of porcelain, transparent glazes or as a pigment.

Table LA-ICP-MS analysis of the blue enamels. The standard deviation over three measurements is given brackets.

	%wt	B_2O_3	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3	CoO	ZnO	SnO_2	PbO
Wengers	E33	11.1	2.76	0.53	13.9	11.4	0.118	0.70	0.35	7.7	9.2	0.16	41.9
		(0.3)	(0.1)	(0.01)	(0.6)	(0.1)	(0.002)	(0.03)	(0.01)	(0.1)	(0.1)	(0.01)	(0.3)
Lacroix	E114	15.4	0.64	0.009	1.4	8.7	0.27	0.43	0.04	0.29	15.1	0.5	57.2
		(0.2)	(0.05)	(0.002)	(0.1)	(1.2)	(0.02)	(0.02)	(0.01)	(0.04)	(0.9)	(0.1)	(0.4)
	E115	18.2	0.65	0.010	0.46	7.7	0.267	0.43	0.045	0.84	14.6	0.17	56.5
		(0.3)	(0.01)	(0.001)	(0.02)	(0.1)	(0.002)	(0.01)	(0.007)	(0.09)	(0.4)	(0.03)	(0.3)
L'Hospied	E122	3.8	0.15	0.037	0.8	23.2	0.039	0.24	0.07	0.12	0.22	0.008	71.2
		(0.2)	(0.05)	(0.001)	(0.1)	(1.2)	(0.007)	(0.05)	(0.01)	(0.02)	(0.03)	(0.001)	(1.5)

ppm	P	Ti	Cr	Mn	Fe	Co	Ni	Cu	As	Sb	Ba
E33	150	245	162	73	2444	60290	732	52	204	368	75
	(16)	(3)	(12)	(4)	(85)	(1062)	(10)	(6)	(3)	(13)	(2)
E114	32	91	19	16	312	2247	28	18	6.9	60	90
	(26)	(4)	(5)	(1)	(51)	(302)	(4)	(3)	(0.4)	(3)	(20)
E115	22	85	10	43	349	6617	79	75	13	38	65
	(1)	(6)	(5)	(6)	(9)	(680)	(7)	(12)	(3)	(2)	(6)
E122	360	68	42	25	496	934	48	58	7.7	133	42
	(37)	(17)	(24)	(1)	(85)	(154)	(8)	(2)	(0.5)	(6)	(1)





Left: DSC thermal curve obtained for the E33 enamel showing the glass transition temperature.

Right: SEM image of a cross section of the E33 enamel showing the presence of cobalt aluminate particles close to the external surface.

Acknowledgements

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The creative process of applying grisaille in stained glass

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Field of interest: glass in architecture

Abstract

This article introduces a reflection on a glass painting technique used since the earliest days of stained glass art, known as grisaille. The first stained glasses, the way we perceive them to this day, first appeared in the medieval period, in the huge cathedrals where biblical narratives were displayed to spread this knowledge. To create scenes illustrating miracles with landscapes, people and animals resulted in figurative images that demanded drawing expressive details, such as traces and strokes made on the glass surface, which was coloured in its own vitreous mass. In order to study the multiple applications of grisaille we intend to examine selected works by two century-long tradition studios in the creation of stained glass, the Oficina Antunes in Portugal, and the Casa Conrado, owned by Conrado Sorgenicht in Brazil, highlighting its painting techniques, especially the differences in the way the paint is placed on glass and its resulting effects.

Keywords: Stained glass, Grisaille, Glass painting

Fig. 1 and 2 - Details of Casa Conrado stained glass, sepia grisailles to black on colourless glass and coloured grisailles on coloured and colourless glass. (Photos: Regina Mello).

Introduction

The grisaille, used even today in the creation of stained glass, consists in painting over a glass plate and taking it to the kiln in order to fixate the ink. Beginning in the Middle Age, this technique was mainly used for shading effects which imprinted a certain volumetry to faces, hands and draping's, which ended up giving it the name grisaille (grisalha), from the same french word, a feminine noun which means gray (Burtin-Vinholes,1999). "Grisaille was to make a window in mainly clear, colourless glass and to paint it with foliage in brownish-black enamels" (Klein, Lloyd, 1992). Due to its nature of enhancement of the drawing, the draping gives sense to the images, amplifying the visual sensation of tridimensionality. One of the oldest surviving examples of this painting on glass is the head of Christ from the eleventh century from Wissembourg Abbey. The design of the head is achieved by painting it with varying concentrations of brown grisaille and then wiping away areas for highlights (Wylie, Cheek, 1997).

The manufacturing of a stained glass requires a card with the chosen image, which is then amplified on paper to real size, and where the leaden rails are drawn determining the cullet's' size. The glasses are then recut with or without colored plates, dressed in the leaden rail and welded to constitute the sustainment mesh. After we cut the glass and before it is affixed to the mesh, the cullets where the grisaille will be applied are sorted for painting. We came across stained glass where the grisaille was painted using only sepia and black tones, leaving the bright

Fig. 3 and 4 - Stained glass of the church Santo António dos Congregadas, Plácido Antón Antunes, 1927, and detail of the Stained glass in S. Miguel church. (father and son, João Baptista and Aquino Antunes worked on this stained glass).

colours to be seen through the vitreous mass, underlining the idea of shadows and of greyish; in other cases one uses grisailles of transparent colours such as silver yellow, red and translucent blue as background in a first firing, and as a trace in a second stage (Brown,O'Connor,1991).The peculiarity of this technique resides in the complete filling of the glass surface with layers of uniform paint, which when dry is bit by bit removed with special brushes, causing the manifestation of light and bringing back the glass' transparency. This action reveals an inversion of the painting logic, which always puts the paint on the canvas or paper (Trublard,Callias Bey,2010).

Casa Conrado, a pioneer studio in the art of stained glass in Brazil, has created more than 600 stained glass sets, mostly in the states of São Paulo, Rio de Janeiro and Minas Gerais. Conrado Sorgenicht departed from Essen, North Germany, and arrived in Brazil in 1875, establishing his stained glass studio in 1889. Three generations of stained glass artists came next, and they developed a distinguished style, engaging with Brazilian art and architecture, making stained glass for churches and public buildings such as markets, schools and hospitals, as well as private homes (Mello, 1996).

It was a performance similar to that of the Oficina Antunes, which was also a three-generation studio established in the city of Porto since 1906, having Plácido António Antunes creating the stained glasses of the Church of Santo António dos Congregados in 1927(***Fig. 1***), the second generation starting with João Baptista Antunes – who began working with his father in 1936 (Vieira, 2003) – and the third generation with João Aquino Antunes, who started to work with his father in the 50s (Almeida, 2012) .

Aquino Antunes, a graduated painter, says that the way of painting the grisaille varies from person to person. This studio is still functioning, and has created countless stained glass works in more than 420 different places, and the vast majority of these places have a great number of stained glass sets, and are not just in Portugal, but all over the world. As an example we might mention the churches of Porrino, in Spain, and of Ludlow, in Massachusetts, in the US.

Conclusions

Though applied in a strikingly similar way to this day, the grisaille has evolved in its expressiveness and in the artistic way in which it is applied, constituting its own language, characteristic of the studio which created the stained glass, as a token of authenticity. In the early days of his work, in Brazil, Casa Conrado fashioned itself after the European models which it brought from Germany, making more use of the coloured grisaille, as can be seen by the stained glasses affixed to the older churches. Eventually it started to value more the colour of the vitreous mass, using the grisaille for shading in tones ranging from sepia to black (Melllo, 1996). The Portuguese atelier has kept itself faithful to European traditions, but subtle differences can be noted in the application of the painting techniques, which could vary according to the artist which coordinated the atelier in each period, and in the third generation the artist João Aquino Antunes devoted himself to creating stained glass works of his own, being the portuguese artist with the bigger body of work in this field (Almeida, 2011)

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Stained glass iconostasis: fragile 'Munich Glass' in Ukraine

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Field of interest: art, glass in architecture

Abstract

Stained glass iconostasis is a unique Arts and Crafts ecclesiastic feature, which was executed by the Königlich Bayerische Hofglasmalerei F.X. Zettler for the domestic St Nicholas Church in Kharkiv, Ukraine, in 1905. Although having lost some fragments, it has been the only survived stained glass iconostasis of the *fin de siècle*, incorporating 'Munich glass' and Orthodox iconography. After investigation of the iconostasis *in situ* in October 2016, the research discovers new evidences, which leads to the reconstruction of the original scheme of stained glass and to the iconography's attribution.

Keywords: Stained glass iconostasis, Iconography, the Königlich Bayerische Hofglasmalerei F.X. Zettler, the Church of St John the Baptist's Head, Kharkiv, Ukraine.

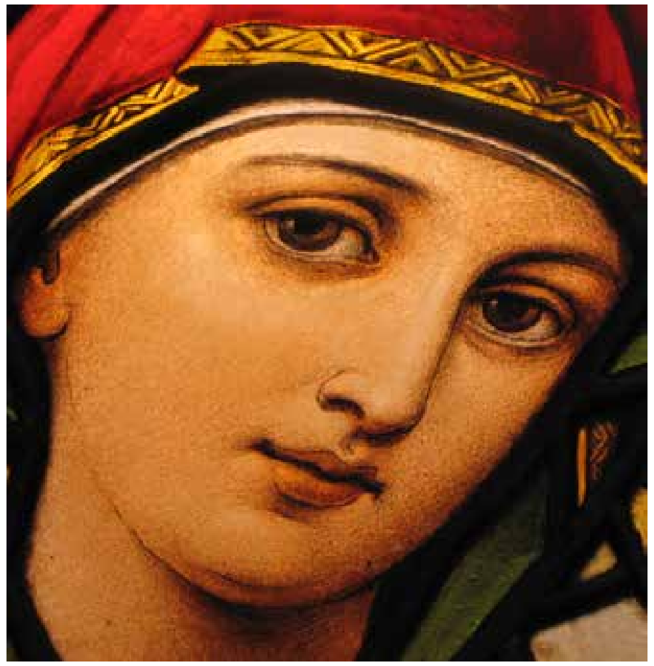

Fig. 1: Virgin Mary (fragment). Stained Glass Iconostasis. K.B. Bayerische Hofglasmalerei F.X. Zettler, 1905. The Church of St John the Baptist's Head, Kharkiv, Ukraine. Photograph 2016

Introduction

At the turn of the 19th and the 20th centuries, the Königlich Bayerische Hofglasmalerei F.X. Zettler was flourishing, having executed 12,532 stained glass windows in forty years 1870–1910 (Fischer 1910: p. 105–106). Over 8,000 stained glass windows were commissioned by the clients from the former Russian and Prussian Empires in total value of about five million (Fischer 1910: p. 105). Among them, there were two stained glass iconostases. Iconostasis, generally, is the symbolic alter wall with the iconographic system that marks the border between the heavenly and earthly in the Orthodox Church. Although traditionally made of wood, iconostasis's system had been transforming and shaping new forms at the *fin de siècle*. They could be made of marble, porcelain or crystal glass, in tune with the local Arts and Crafts movements. Iconostasis made out of stained glass became, however, an exceptional ecclesiastic feature in decoration of the Orthodox Church (***Fig. 1***). In 1898, the K.B. Bayerische Hofglasmalerei F.X. Zettler executed the first stained glass iconostasis for the military St Julian of Tarsus Church (1895–1899) in Tsarskoe Selo, St Petersburg, Russian Empire (Fischer 1910: p. 82). The Russian painter Nikolay Koshelev (1840–1918), *alma mater* of the Imperial Academy of Arts in Sankt Petersburg (Kondakov 1915: p. 100), wrote the iconographical scheme for the iconostasis (Baranovskiy 1993: p. 12), while the cartoons for the overall architectural design were developed by the architect Vladimir Kuritzin (Fischer 1910: p. 82) and 'Architecturzeichner' Josef Baumann (Fischer 1910: p. 82, 106). Although the iconostasis was completely lost with outbreak of the revolution of 1917, its cartoon *(Stadtarchiv München)* and authorship's attribution became a valuable source for the research of the survived iconostasis in Kharkiv, Ukraine.

According to the signature on the stained glass, the Königlich Bayerische Hofglasmalerei F.X. Zettler executed this iconostasis in 1905 (***Fig. 2***). It was commissioned by Alexander Yuzefovich, the owner of the newspaper *Yuzhnyi Kray,* for his domestic St Nicholas Church, 13 Sumska Street, Kharkiv (Grymalyuk, 2009; Shulika, 2010). The original architectural interior sketch of the St Nicholas Church gives the compositional impression of the overall alter (Paramonov 2007: p. 61) where iconostasis was originally placed. Following the traditional iconographic system, the iconostasis initially consisted of the six lights and the Holy Door in the centre: St Naum and St Alexander – Archangel Gabriel – Virgin Mary – Holy Door (Evangelists) – Christ Pantocrator – Archangel Michael – St Nicholas. After the turbulent years

Fig. 2: Stained Glass Iconostasis (fragment). K.B. Bayerische Hofglasmalerei F.X. Zettler, 1905. The Church of St John the Baptist's Head, Kharkiv, Ukraine. Photograph 2016

of 1918–1919 in Kharkiv with the church dissolution, the iconostasis survived in the local museum and only in 1943 it found a new home in the Church of St John the Baptist's Head, Kharkiv. The stained glass iconostasis was enlarged by two lights to fit the size of the church and reconstructed as followed: St Naum and St Alexander – St Nicholas – Archangel Gabriel – Virgin Mary – Holy Door (Annunciation and Evangelists) – Christ Pantocrator – Archangel Michael – St John the Baptist (new light) – St Athanasius and St Miletus (new light). The emerging evidence, however, points to the complex situation, which requires the reconstruction of the lost original 'Munich glass' fragments, e.g. St Luke and St Mark on the Holy Door, and the iconography's attribution of the new icons. The comparative visual analysis of the stained glass iconostasis in Kharkiv with the archival cartoon and the photograph of the stained glass iconostasis of Tsarskoe Selo, Sankt Petersburg, indicates the similarities in the ornamental patterns of the stained glass as well as in the iconographical style of glass paintings of Virgin Mary, Pantocrator and seraphim. This leads to the hypothesis that some iconographical sketches of the first iconostasis were applied to the Kharkiv's one. Nikolay Koshelev was not personally involved in the painted glass production though the K.B. Hofglasmalerei F.X. Zettler most possibly used his icons' drawing for the stained glass iconostasis in Kharkiv. He was an artist who worked in various genres: portraiture, landscape and iconography; and was particularly strong with the church interior design while executed numerous ecclesiastical sketches for decorations. The iconography of the other authentic iconostasis's lights illustrates more conservative and characteristic for F.X. Zettler glass painting style, whilst stained glass of the new lights, which are dated by the second part of the 20th century sharply contrasts in glass quality, colour pallet and painting style comparing with the original one.

Conclusions

Although iconostasis has been an archetypal meaningful structure of icons, stained glass iconostasis was a revolution in Arts and Crafts. It is the iconographical representation of the divine world, which is not only facing the person, but also shines through natural light. The stained glass iconostasis of the St John the Baptist's Head Church in Kharkiv, Ukraine, is the only authentic stained glass iconostasis of the *fin de siècle* though it is preserved in its tri-stylistic compilation of glass paintings and requires restoration. Further research on 'Munich glass' might lead to the reconstruction of the lost original fragments as well as to the reestablishment of the stylistic and compositional unity.

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New development: mouth blown UV protective window glass

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Field of interest: Glass in architecture

The challenge

Over the last years, the demand for UV protective glass for valuable art objects and historical furnishings has increased. UV rays damage organic material (textiles, wood, paper) but also modern adhesives which are based on organic materials. Until now the only solutions available were based on organic foil material or a coating of nanoparticles. The coating on the glass is not scratch-proof, over time the foils age and lose their effect. On this basis the author, a managing partner of a glass manufacturing company sought for a solution using glass. He developed a glass in which the UV protection is integrated and is not subject to aging. Thus, during the renovation of the Wittenberg town church, as part of the Luther Decade, the apse was to be glazed to protect the valuable Lucas Cranach Altar from UV rays. The second project was the UV protective glazing for York Minster, UK. 24 meters tall and about the size of a tennis court, the 311-panelled "Great East Window" is the largest expanse of medieval stained glass in Britain and regarded as one of the great pre-Renaissance treasures of European art. The east window of York Cathedral (GB) was fitted with a protective glazing of restauro®-UV in order to protect the adhesives used during the repairs from UV rays.

The manufacture of the glass

The manufacturer, Glashütte Lamberts, is a family owned company in that produces mouth blown sheet glass for restoration. The production of UV protective glass (brand name: restauro ® UV), has been submitted for a German and subsequently European patent (1). Therefore it`s composition and the processing can be explained only in general. It begins with the gradual mixing of the normal glass ingredients e.g. sand, soda, lime plus cadmium sulfite and zinc sulfite in a glass batch facility. The melting process is done in a ceramic pot at temperatures of up to 1420°C. One feature of the process is that, in the classic way, i.e. with the use of a glassmaker's blowpipe, the functional glass (see above) is combined with a normal basic glass. As most colored glasses the restauro®-UV is manufactured as a flashed glass. This 2-layer portion of glass is firstly formed to a balloon, later to a large cylinder (***Fig. 1***). After cutting the cylinder lengthwise, reheating and flattening the glass, the first step of manufacturing the UV glass is finished. The second and final step is a defined temperature treatment. At a temperature of more than 600 degrees Celsius and over a certain period of time sulfite colloids are built up in the glass. They form the UV barrier. This UV-glass is available in approximately 50 x 60 cm (2 - 3 mm thickness). It can be used for traditional lead glazing as well as double glazing or laminated glass. During production, the manufacturer observes the highest quality. Each sheet undergoes an on-site quality control before shipment. In addition, samples from each batch are checked for transmission by an independent laboratory. Typical testing equipment is Lambda 12. Test reports can be made available to customers. Tests are cross checked by peer review.

Fig. 1 Production of the 2-layer portion of glass, firstly formed to a balloon, later to a large cylinder

Dr. Hubert Drexler, a graduated chemist, with many years of practical experience in the glass and raw materials industry, contributed his well-founded knowledge of process optimization and significantly shaped the development of this UV protective glass by optimizing the mixtures and accompanying the manufacturing process. His scientific education and the know-how gained during many successful research projects at renowned industrial companies proved to be very valuable. His very special knowledge of the transmission spectrums for colored glasses formed the basis for a systematic report on the correlation between the UV protective properties of the functional glasses manufactured and the relevant parameters in the manufacturing process. The testing laboratory, IGR Göttingen, is a neutral and independent company and has modern equipment including SEM-EDX, ICP-OES, FT-IR and UV-VIS. The development and manufacturing process of restauro®-UV was accompanied analytically by the external laboratory. The main task was the chemical analysis of the glasses produced with the ICP-OES and the measurement of the UV protection with the UV-VIS. Because of the pending patent detailed analysis cannot be published.

Table 1: Luminous transmittance, CIELAB color space and transmission data of two versions of restauro® UV and a standard- floatglass

Parameter	restauro® UV (1) (2 mm)	restauro® UV (2) (2 mm)	floatglass (4 mm)
LT (D65/2°)	90,40%	90,43%	89,50%
a* (D65/2°)	-1,62	-1,14	-1,26
b* (D65/2°)	+3,08	+2,03	0,33
wavelength [nm]	**restauro®-UV (1) (2 mm)**	**restauro®-UV (2) (2 mm)**	**Floatglas (4 mm)**
350	0,0%	0,0%	73,3%
355	0,0%	0,0%	79,1%
360	0,0%	0,0%	82,5%
365	0,0%	0,0%	84,7%
370	0,0%	0,0%	85,2%
375	0,0%	0,0%	84,9%
380	0,0%	0,0%	84,2%
385	0,0%	0,0%	85,5%
390	0,0%	0,0%	87,2%
395	0,0%	7,6%	88,2%
400	0,0%	40,2%	88,8%
405	6,4%	68,1%	88,9%
410	39,9%	78,3%	88,8%
415	70,0%	82,4%	88,6%
420	80,4%	84,4%	88,4%
425	83,8%	85,6%	88,5%
430	85,2%	86,5%	88,5%
435	86,1%	87,0%	88,4%
440	86,6%	87,4%	88,4%
445	87,1%	87,6%	88,7%
450	87,5%	88,0%	88,8%
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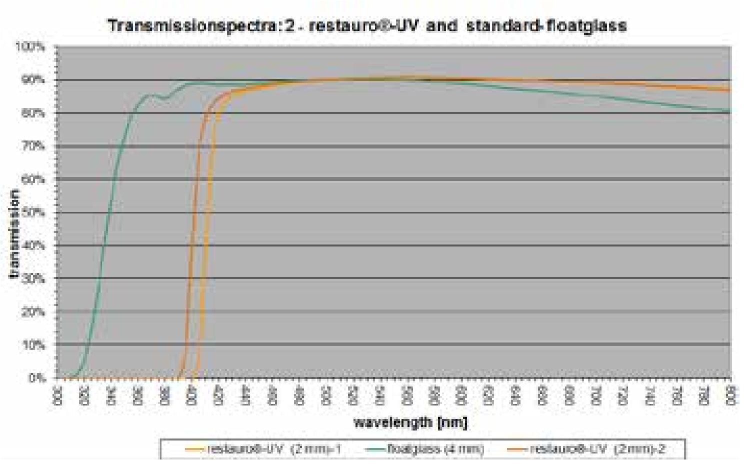

Fig. 2 Transmission of restauro®-UV and standard float glass.

Features of the glass Optical Properties

This innovative development, the mouth blown UV protective restauro®-UV glass, where the UV protection could be integrated directly into the glass without any kind of surface coating, offers a 100% UV protection at less than 380 nm. Between 380 nm and 405 nm, so already in the range of short wave visible light, the protection is between 95% and 100%. If the protective properties exceed 380 nm (WHO defines UV range between 100 nm and 400 nm (2) with a tendency towards visible light, for physical reasons the resulting color is slightly yellow.

Properties/durability

In the context of the German norm (DIN 5031-7: UV-range 100 – 380 nm) the glasses manufactured are almost colorless. This is important for the usage as window glazing in museums. In comparison to foil solutions restauro®-UV achieves a higher color neutrality. See (3). To make sure that the UV-protection effect is long lasting the manufacturer conducted a solarisation test with Heraeus Xenotest 450 as radiant source. Samples were exposed over 1,000 hours to Xenon light between 315nm and 400nm at an intensity of 48 – 52 W/m^2. Transmission of the UV-spectrum did not change after the probation period. Colour changes were not observed. The transmission of visible light is 90% with a reflection of 8%. All results were obtained from random samples with a standard thickness of 2,9 mm and relate to those only.

The case study: protective glazing for the East Window of York Minster, York/UK

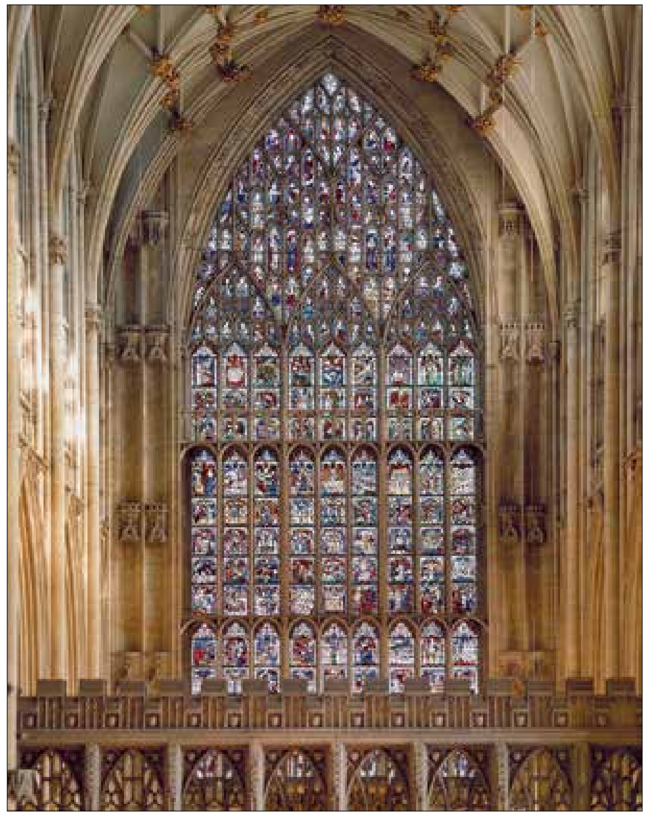

Fig. 3 East Window of York Minster, York/UK.

Requirements for the protective glazing of the East Window

After several years of restoring the stained glass windows dated 1405 – 1408 it was clear that the window would need more than a weather shield.

"Previous protective glazing has acted as a weather shield and kept glass, pigments, lead and conservation materials dry, but has not been an adequate barrier to Ultra Violet radiation. This impact on any epoxy resin used in the conservation of the stained glass leads to a yellowing discoloration of that resin after prolonged exposure." (4).

So the usage of the UV sensitive adhesive for the restoration was the major reason for the need for UV protective glazing. Without UV protection, the restoration would be again in a bad shape in the not too far future. (see (5): constglas). Costs involved would be high for renewing the restoration every 25 to 50 years. As Mark Hosea, director of York Minster said: "We are delighted to be at the forefront of this new cutting-edge technological advance, which represents a wise investment in the long-time care of the building." (***Fig. 3-6***).

The adhesive used

Araldite ® is one of the state of the art glues used in restoration of stained glass windows. For a certain period of time the repair work looks transparent and perfect. As all epoxy Araldite ® contains organic material which becomes yellow over time and deteriorates. Examples from the West Window of Altenberg Cathedral show the impact of UV rays on the adhesives (***Fig. 4***) (7). All parts where Araldite® was used became yellow.

Analysis of several windows and the used adhesives by Fraunhofer Institut during the Constglass Project show the general problems of epoxy (5). So for good reasons the responsible persons at York were afraid of facing another major restoration in few decades.

Glazing problems

For the protective glazing YGT wanted a system without major impact on the lime stone tracery and frames of the windows. "Traditional" solutions with a film laminated between two sheets of glass have double the weight of one sheet and require strong fittings. To use strong fittings means to drill new holes in the lime stone which may cause further damage. Furthermore, thicker lead lines would be necessary which adds to the weight problem. Using a glazing system where the major lines of the stained-glass window are copied to the protective glazing the glazier needs to cut the shaped pieces out of the glass. For a double layer film solution, this means that the glazier has to cut on both sides plus the film. This means at least double the time = double the cost for the labor. Using the UV protection glass means to avoid the weight, the cutting and the leading problems.

Aesthetic issues

More than the sole protection against weather and UV rays protective glazing plays an important role in the appearance of the cathedral. The so called "mirror effect" must be avoided. "In common with other cylinder glasses (…) the glass has all the movement and character of a mouth-blown material (…)" (8).

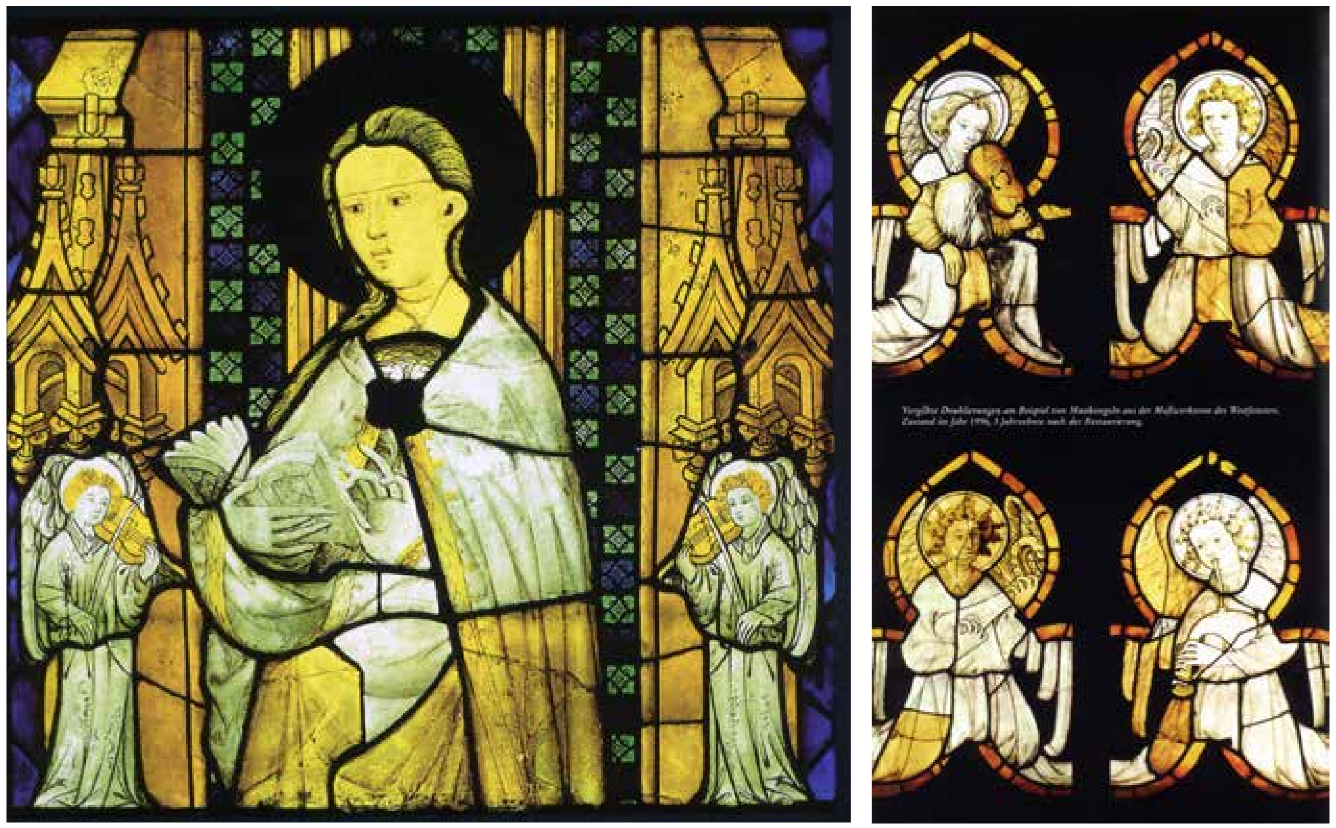

Fig 4. Examples from the West Window of Altenberg Cathedral show the impact of UV rays on the adhesives.

The sampling

After exchanging samples and counter samples during the run of 2013 YGT and the manufacturer agreed on the thickness and the color of the UV protection glass.

Thickness

For the project the normal thickness of restauro ® UV of 3 mm +/- 0,3 mm was appropriate as no protection against vandalism was required.

Color

A selection of almost white to slightly yellow tinted glass was selected. It goes well with the tone of the lime stone façade.

Shipment of the glass to York

The first shipment of 3 crates of UV glass arrived at the workshop in York on 14th February 2014. A few days later the production manager of the manufacturer and the author came to York to discuss the quality of the shipment with YGT. A first preselection made by YGT had showed an almost 30% share of "too yellow glass". "Too yellow" was not the result of any colorimetric analysis but the impression of the glaziers. After a thorough discussion about the conservational concept it was decided to use 90% of the glass and to mix the tints in order to get the best aesthetic result.

Glazing

Cutting and leading of the UV glass went without any problems. Major breaks while cutting the glass were not observed. All shipments to York were on time and the glazing and the installation of the protective glazing were always within the time schedule.

Summary

restauro® UV is a new development in the glass industry. It protects all material, especially organic, from UV radiation up to 400 nm. Protective glazing of York Minster´s East Window was one of the first projects, until today the by far biggest project. All requirements of YGT were fulfilled at highest satisfaction. As Sarah Brown, director of YGT said: "It is reassuring to know that we are now able to offer total environmental protection for all aspects of the conserved window." (8)

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(1) German patent (pending): DE 102013105643A1

(2) www.unep.org/pdf/solar_index_guide.pdf

(3)

Sample	CIE L*
Sample 1	92,34
Sample 2 restauro UV	92,65
Sample 3	92,41

(4) http://www.yorkminster.org/about-us/news/ground-breaking-new-material-used-in-york-minster-conservation

(5) http://www.constglass.fraunhofer.de/uploads/media/CONSTGLASS_Product_Matrices_01.pdf

(6) Telegraph & Argus, Thursday 23rd January 2014

(7) email Ivo Rauch to the author: „… attached please find two photos showing the Altenberg west window. The window has been made before 1397 and restored in 1970 by Oidtmann, Linnich.

During the restoration many glasses were completely laminated onto clear duplication panels using Araldite (probably Araldite 362/362 (?), but the newer Araldite yellow as well ...). In the photos all white areas (eg. the shoulders, hand & book of Maria) are not doubled. The rest of the characters was doubled and is now yellow ... … The photo of the tracery is from: Uwe Gast / Daniel Parello / Hartmut Scholz: Altenberg Cathedral, Regensburg 2008. There is also a description of the yellowing damage (page 11).

The other photo (Maria) is from a Peters Glasstudios publication. Today, we would (of course) not apply the Araldite on the whole area; but it is also the current state of the art to repair the cracks using Araldite which yellows in the same manner.

(8) Sarah Brown, Apocalypse, The Great East Window of York Minster, 2014, p. 57

Glass as an artistic material on exterior façade in 21st century architecture

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Field of interest: Glass in architecture

Abstract

The design of façades on the buildings in 21st century has been a quite important part of buildings designs. The discovery of new materials and the developments in technology have been the basis of generating new opportunities in architectural design sphere. Glass has been considered as one of the oldest construction materials although a lot of new materials have been discovered, and it continues to maintain its importance and is approved as a symbol of contemporary façade in architecture. It is known that in building façade design in 21st century, glass production methods such as hot glass-blowing, casting are used for innovative façade suggestions as well as float glass production methods. Many properties of glass such as color, light transmittance, refraction and reflection of light add the qualifications of a material with almost no alternatives to glass in innovative surface design. In this study, the examples with in the sphere of architecture, where the glass is used as an artistic element on exterior façade construction and coating, are going to be analyzed and evaluated both in terms of technique and form.

Keywords: Architecture, Façade, Glass, Surface Architecture, Architectural Glass Art

Introduction

Glass is recognized as one of the most important construction materials of contemporary architecture since it provides a special intermediate layer between the interior and exterior space, due to its being transparent and many other properties it adds to the structure. A lot of properties have been added to the space in architecture in parallel with the developments in glass technology [1]. Fire control and sound control are among the primary ones of these properties, more than that creating comfort in the space is aimed [2]. In addition to effort to create comfort in the space, glass is also used as an aesthetical element which enriches architectural surfaces by using different application methods and unique expression ways. The volume of architectural surface and its relationship with the gaps, questioning basic design elements used on the surface such as color, form and light have attributed a more colorful, more dynamic architectural practice to occur [3].

When contemporary architectural designs are analyzed, it is seen that glass is used in many different types aside from flat glass. Glass bricks, channel shaped glass, glass profile, pressed glass, curved glass and cast glass are some of these applications, and they are industrial glass construction materials [4]. In addition to industrial glass products glass produced in studios have started to be used in architectural structures along with

Fig. 1 Hierve Diseñería, glass façade example which is composed of blown units completely, Mexico City, 2005

Fig. 2 Netherlands Institute for Sound and Vision, Hilversum, 2007

the art perception changing in 21st century, custom production designs and period of innovation. There are also surfaces which are created with dichroic glass and borosilicate glass tubes [5].

Today glass surfaces are developed with different techniques and material usage as a result of new solution pursuits for modern architectural practices and they are completely created with glass-blowing methods. There are over seven thousand glasses which are shaped with glass-blowing method on the building in Mexico City called "Hierve Diseñería" by Architect Alejandro Villarreal. Each glass on the front façade is supported by EPDM (a kind of rubber which is used in automotive industry and is resistant to weather conditions), which is made in a workshop in Guadalajara, Jalisco by craftsmen, and this is fixed via a traditional stud with a stainless-steel wire. Each wire carries 27 globes maximum which are fixed on concrete construction at the top of the building and on structural steel elements at the bottom. This practice is quite different from classical front façade practices. The use of glass as a screen covering the surface by utilizing its properties such as opacity and reflection is quite different from classical front façade practices in terms of newly created façade suggestion and using blowing – glass on the façade [6].

Another example where glass is used as an artistic element is Netherlands Institute for Sound and Vision building. Glass front façade of the building is composed of original TV images obtained from the archives of the institute. Relieves on glass panels on the façade, which composes of 2100 pieces, are composed with slumping glass method at 820°C. The quality of light coming through contemporary vitrified windows is obtained in the building via glass façade and a textured surface is added to the building. Iconic images of Holland TV history appear and disappear throughout the day as a result of the refraction of sunlight on glass surface [7].

Conclusions

The possibilities of using glass in contemporary architecture are almost limitless. The ideal world we try to create stimulates the mind by addressing emotions and encourages us to think that we are a part of the created world. Today, the use of glass as an artistic element in the façades is an answer to the physical, intellectual and emotional quests of man.

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Architectural glass in the 18th to 20th centuries in Iran

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Field of interest: glass in architecture

Abstract

In this research we study the Orsi windows as one of the significant elements in the Iranian architecture during the centuries 18th to 20th. Orsi windows reflect and refer to the Islamic and the Iranian ancient religious and the beliefs concerning the function of light in interior spaces, creating a dynamic and spiritual atmosphere for the inhabitance of a building.

Keywords: Orsi widows, Light, Ancient Iranian beliefs

Introduction

Handmade glassware has a long history in Iran and it goes back to the first millennium BC [1]. Since then, Iran retained its position in the development of glassware making until the Mongol invasion in 13th century, when glass making had a cessation for one and half centuries because the majority of glassblowers immigrated to the west. Then after some years, from sixteenth to nineteenth centuries, kings of Safavid[1] dynasty and Qajar[2] dynasty gave a special attention to renovate traditional arts like glass art [1]. Orosi, Arasi or Orsi are sash windows, resulting of craftsman skills in Safavid era in Iran. There is no evidence of producing Orsi windows or sash windows before Safavid era in Iran, and the oldest examples of sash windows in Iran were found from Safavid era and after that time. In Safavid and Qajar era, Orsi windows were a kind of luxurious decoration which was used in different places like houses, Mosques, schools, Hussainiyas[3] [2] [3].

Orsi windows are mix of wooden Girih tiles[4] with colorful pieces of glass [4]. The passing of light through the colored glass brings spirituality to the interior space and enlarge its actual size (***Fig. 1***). In addition, Orsi in Iranian architecture has a special value because its function refers to the light allegory in the Iranian ancient religious and beliefs. Before the advent of Islam in Iran (637–651), many religions like Zoroastrianism and Manichaeism and Mithraism used the metaphor of light to illuminate their doctrines [2]. In Islam, light is a symbol of God and there is a chapter with the name of light in Quran[5]. In this chapter God introduces himself as a light of earth and heaven:

"Allah is the Light of the heavens and the earth" [Quran 24:35].

Light is in contrast with darkness and one of the most significant elements in ancient Iranian religions is the victory of the light over devil darkness [5]. Traditionally Iranian have a hatred of darkness and they tried to bring light inside their houses, worship places and almost all interior places. They bring light into interior places considering the climate of the place – Iran is a big country and has 4 different climates (cold; hot and arid; semi-arid and humid; and mild climates). Architectures in 18th to 20th centuries in Iran consider two types of elements in designing Orsi windows based on the specificity of climates: first, light controllers and second, light amplification. About two-thirds of Iran's are in the hot, arid and semi-arid climate, light controllers were considered fundamental in the structure and organization of Iranian architecture [5]. Iran climate conditions and specific religious beliefs in Iranian ancient architecture resulted in an inward seeking architecture, where one can see no opening in external walls while the inside façade is full of windows facing the courtyard [6]. Orsi windows are movable panels which are opened by sliding vertically or horizontally, instead of flipping on the heels round (***Fig. 2***); this feature resulted minimum amount of occupied place during opening and closing [4]. They

1 Safavid dynasty (1501–1736) was one of the most significant ruling dynasties of Persia (modern Iran) after the fall of the Sasanian Empire during the Muslim conquest of Persia in the 7th century AD, and "is often considered the beginning of modern Persian history"

2 From 1785 to 1925.

3 Hussainiya is a congregation hall for Shia commemoration ceremonies, especially those associated with the Remembrance of Muharram.

4 Girih tiles are a set of five tiles that were used in the creation of Islamic geometric patterns using strapwork (girih) for decoration of buildings in Islamic architecture

5 Sūrat an-Nūr (Arabic: سورة النور, "The Light") is the 24th sura of the Qur'an with 64 ayat.

Fig. 1 Haj Agha Ali's house in Rafsanjan, Kerman, Iran. Gajar Era. © Sara Lava.

Fig. 2 Dolat abad Garden, Yazd, Iran. Built in 1747. © Mahdi Taheri.

Fig. 3 Nasir Al Mulk Mosque, Shiraz, Iran. Built in Qajar era. © Mohammad Nouri.

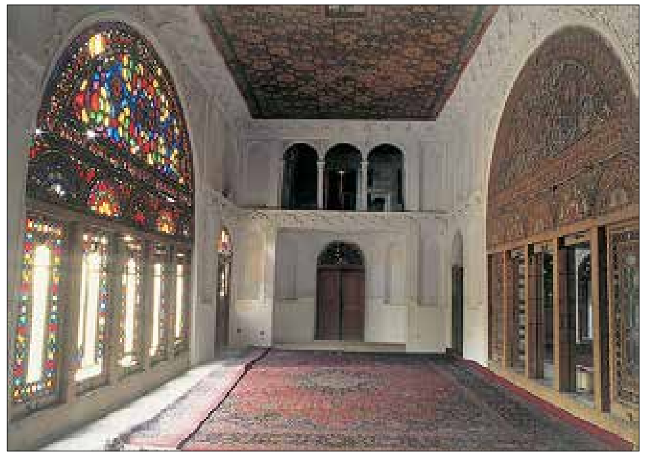

Fig. 4 Aminiha Hosseiniyeh, Qazvin, Iran. Built in 1858. © Marziye Falahnejad.

are designed to be a part of the architectural decoration which manage the light by a handful of wooden details containing tiny pieces of colored glass. Different colors used in each piece of glass have psychological impact on human behavior [7]. In addition, "mild" colors control and balance the intensity of light. According to the Islamic beliefs, colorful light is a symbol of God's holy presence in the interior architectural design. Nasir ol Molk Mosque (***Fig. 3***) in the city of Shiraz is a good example which was built from 1876 to 1888, by the order of Mirzā Hasan Ali (Nasir ol Molk), a Qajar ruler. The Western bedchamber of the mosque has seven doors in wooden colorful glass connecting to the courtyard of the mosque. This mosque is acknowledged as the pink mosque because of using considerable pink color tiles in its interior design. In this mosque people can feel and experience the effects of light, observing dynamic images appear and change continuously, depending of the weather and the position of the light. Also dynamic images of colored light are a symbol of God's presence.

Designers of Orsi windows used abstract geometrical shapes due to the prohibiting use of human images in Islamic arts. This geometrical shapes with different angles from each other, create sound effects, and therefore Orsi windows have acoustic resonance effect which is the subject of acoustic science [4] [8]. Orsi windows also limit the visibility from the outside to the inside of the houses and provide privacy in the interior. This characteristic of Orsi windows leads architectures to use them inside the houses as a dividing wall too; for an instance, in Aminiha Hosseiniyeh (***Fig. 4***) Orsi windows are employed as a dividing wall inside the house and are also used for dividing the rooms from courtyard. At last it shouldn't be unmentioned that based on the experience of the ancestors and those who have used the Orsi windows, these kind of windows prevent the appearance of annoying insects and reptiles inside the houses by creating colorful lights [8].

Conclusions

Orsi windows are important elements in traditional Iranian architecture in 18th to 20th centuries. The special characteristic of Orsi windows is the attractive light reflection in interior spaces, referring to Islamic and the Iranian ancient religious and beliefs. Beside its beautiful effect on exterior and interior design of a building, it also creates a dynamic environment with colorful lights and have acoustic resonance effects. Moreover, Orsi windows provide a safe atmosphere for interior inhabitance - mostly by women - by making visibility limitations and also by keeping reptile and insects away to enter the house because of colorful lights.

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The detriments of the contemporary stained glass from Estonia

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Field of interest: stained glass

Abstract

The purpose of the presentation is to introduce modern stained glass detriments and explain the reasons for their occurrence, but also to draw attention to graphical and structural aspects of their design, poor quality of materials and inadequate knowledge and skills applied during their preparation and their impact on the life of stained glass.

The research looks at these issues through the summer of 2016, when MTÜ Gerlachus (Eve Koha and Elise Lekarkin) was working on the restoration-conservation of the Muhu St Catherine's Church south stained glass window from the second half of the 20th century. The stained glass window consists of six larger rectangular panels, two sharp arcs and one quatrefoil shaped panel. The total size is about 3 m^2. The author of stained glass design is the artist Eeva Jänes.

All the stained glass detriments are examined and analysed. Reasons why lesions occur in new stained-glass are set out because ignoring the structural principles of stained glass are the most important causes of the damages incurred specifically in the Muhu stained glass. The church south window's structurally weak points are the horizontal breakdowns passing through, and also the concentric circles of the composition (***Fig. 1***).

In these areas the load accumulated in lead began to bend them and the stained glass stability deteriorates and the pieces of glass start to drop out from the lead came. Without intervention this might end with destruction of the entire stained glass.

Broken pieces or cracked glass within the stained glass are the most common damages, but the reasons for this might vary. Usually it is vandalism, or the impact of natural forces, but for the stained glass in Muhu the main cause of the damage were the structural problems related to the construction.

Another important reason for the stained glass detriments occurrence is the poor quality of the glass material itself and poor skills of craftsmen. Inaccurately cut pieces of glass do not fit tightly together in the lead-came, which also contributes to the stability of the stained glass. The handmade rolled glass plates for stained glass were imported in the1980s and 1990s from Latvia or Lithuania. The glass plates were in beautyful colours, but often curved and therefore had stress inside the glass – which means that the annealing was bad. It was the reason why some of the cut stained glass pieces were cracked.

The stained glass panel lead-cames were not filled with putty. Filling would have added the rigidity to the panel and defended the lead-cames and the accumulation of moisture between them due to corrosion.

There were also not enough iron bars to support the stained glass panels, which would have prevented the panel from sagging.

In this regard, parallels are brought of Muhu stained glass and located in the ceiling mirror mosaic stained glass lighting damage in Paide Cultural Centre cafe from 1987.

The entire conservation-restoration process of the Muhu Church stained glass window — repairing detriments and strengthening the overall condition of the stained glass is briefly introduced. In the same thread the aesthetic aspects considered to be important from the use of glass as transparent material viewpoint are treated.

During the conservation-restoration process, it was possible to relieve the stained glass in the structural design flaws and and strengthen the general state of the stained glass (***Fig. 2***).

The glasses removed from the lead-cames first needed cleaning of the dirt accumulated on them. On the violet tone glass there were brown stains, which were very difficult to remove during the cleaning. This refers to the manganese damage, which means that manganese in gathering on the glass surface. This damage will certainly be examined separately.

The corroded and stretched and twisted lead-cames throughout the entire stained glass were replaced and soldered. Also, were replaced missing and damaged glass pieces with new glass with suitable colours and textures, choosing the tone as accurate as possible, because the human eye reacts to colour the most.

Inaccuracies and bumps of the pieces of glass were straightened by grinding in order to fit them tightly together in the lead came.

Fig. 1 Muhu St Catherine's Church south stained glass window before the conservation-restoration. Photo: J. Kilumets

Fig. 2 Muhu St Catherine's Church south stained glass window after the conservation-restoration. Photo: K. Saar

For the overall reinforcement reason of stained-glass window the lead-cames were puttied to protect them against moisture.

The special red copper reinforcement tapes were added to the inside horizontal run of lead came.

For the same purpose the circle-shaped stainless steel bars were added to support the concentric circles.

The topic review also identifies that "life" of stained glass windows depends very much on the design of the stained glass for monumental structural fundamentals that have to be taken into account, in-depth knowledge and skills in the manufacture of stained glass and the quality of the materials used.

Finally, the question is posed whether in such a situation it is justifiable to carry out conservation-restoration of stained glass, or to announce a competition for a new stained glass window and to replace the previous one?

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Scottish medieval monastic and ecclesiastical window glass

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Field of interest: Window, glass, Medieval, Post-Medieval, Scotland, Compositional analysis

Abstract

There has been little scientific investigation of either medieval and post-medieval window glass or domestic glass production in Scotland (Kennedy et al., 2013). There is no physical or documentary evidence to show that glass was manufactured in Medieval Scotland before the establishment of the first documented post-medieval glasshouse in East Lothian in 1610 (Turnbull, 2001). This leads to the assumption that all window glass was imported to Scotland before this time.

Scientific analysis of window glass by Scanning Electron Microscopy – Energy Dispersive Spectroscopy (SEM-EDS) and portable X-ray Fluorescence (p-XRF) was carried out on 250 glass shards from 13 medieval monastic and ecclesiastic medieval sites across Scotland, typologically dated to between the 13^{th} – 15^{th} Centuries. In addition nearly 200 fragments of window glass, excavated from a range of domestic settlement types - from simple dwellings and farmsteads to larger houses and castles - across Scotland, dated to post-medieval late 15^{th} to late 18^{th} Century C.E. contexts were also analysed.

Chemical analysis was used to quantitatively or semi-quantitatively identify the concentrations of the main and trace elements in the glass which have been interpreted to provide information about the raw materials that the glass was made from and, consequently, the changing technologies used to make the glass. Chemical composition of Scottish glass has been compared with similar scientific studies of glass from England, Ireland and Western Europe.

This work is the first major study of the composition of medieval and post-medieval window glass used in Scotland and confirms that glass from a number of different regions in Europe was sourced and imported to Scotland to glaze cathedrals and monastic buildings. There is a transition from forest glass used in the 13^{th} and 14^{th} centuries to the use of high-lime low alkali (HLLA) glass in the 15th and 16th centuries. HLLA window glass was imported to Scotland from continental Europe as early as the mid-15^{th} Century. Window glass from Scotland during the seventeenth century shows a wider range of composition than that observed in England (Dungworth, 2011). Glass with both a HLLA and a mixed-alkali kelp-fluxed composition were found but also a range of transitional compositions. This included a HLLA 2 type glass with higher levels of sodium compared to that found in English window glass, possibly products of Scottish manufacture. Kelp also appears to have been in use from the middle of the seventeenth century as an additional flux in a HLLA 2 glass. This points to a time of considerable experimentation and introduction of new raw materials into glass making in Scotland.

Keywords: Window Glass, Medieval, Post-medieval, Scotland, Compositional Analysis

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Glass: the medium and the metaphor The crossover approach of the glass museum GlazenHuis

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Field of interest: glass art, glass museum, curatorial

Introduction

In 2007, I was invited by the City of Lommel in northern Belgium with the challenge to set-up GlazenHuis, a glass museum with a hot glass studio (***Fig. 1***). Ten years later, we can proudly look back on a diversity of twenty-three exhibitions, hundreds of workshops, dozens of studio projects with artists and designers and a yearly summer residency program as well as the International Glass Prize, a triennial competition for glass art and design.

The fundamental idea of this material-oriented museum was – and still is- that the label "glass museum" should not limit the scope of our activities. On the contrary, we believe that by using "glass" as the common thread throughout our initiatives it allows us to present different stories beyond the conventional categories. We surpass and encompass such common dichotomies as science and art, design and craft, contemporary and historical, decorative and functional. Unexpected connections emerge amongst paintings, photography and video works as well as performance, theatre, poetry and music. They all make a statement in respect to the material glass, in a physical, visual or metaphorical sense (***Fig. 2***).

Also the International Glass Prize (IGP), a project initiated by the Charlotte van der Seijs Foundation, implemented a corresponding crossover approach. From the first edition in 2012, the IGP has generated internationally an enormous response and has been instrumental in boosting the careers of young artistic talents. Next to the worldwide promotion of the

Fig. 1 Glass museum GlazenHuis, Lommel, Belgium (2007). Architect Philippe Samyn and Partners. Photo: Marie-Françoise Plissard

Fig. 2 The Glass Archive (2005-2015), collection of 100 novels all featuring the word glass in the title, Jerome Harrington

Fig. 3 Self-Container No.1 (2015), Rui Sasaki, residency prize winner, International Glass Prize

Fig. 4 Finale I (1990), Wim Delvoye, exhibition XY, GlazenHuis 2017. *Photo: Studio Wim Delvoye*

glass museum this was an advertisement for glass as a narrative material and its establishment in the domain of contemporary art (***Fig. 3***).

This year's tenth-anniversary exhibition entitled XY (X for 10 and Y for years) is the twenty-fourth show at the glass museum GlazenHuis. Referencing this, we have invited twenty-four artists and designers who bring an update of the use of glass within the field of fine and applied arts in Belgium. The impressive list of attending artists underlines the relevance of the material glass in contemporary art. In contrast to many other countries, Belgium has realized to anchor glass in the field of visual arts through internationally renowned artists such as Wim Delvoye (***Fig. 4***), Jan Fabre, Koen Vanmechelen, Hans Op de Beeck and Ann Veronica Janssen. Their consent to participate in this exhibition testifies to the reputation our museum has built up during the last ten years.

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Glass sculptures meet public in public spaces

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Field of interest: Glass Art, Sculptural Glass, Glass art in Public places

Abstract

Public spaces are identified as areas that breathe with and for the community, displaying a wide array of artworks that have an influential role on artists. Art is an individualexpression that creates an increase in awareness of our surroundings and permits an interaction within the public. The impact of an artwork on the viewer depends primarily on its originality, be it by the artist's use of alternative methods with usual forms and material or his/her use of unusual material to create a classic object.

I use glass as my main art material and test its infinite style and form in every work I create. As one knows glass is basically made up of sand and fire. It is formed by technique yet the final process is guided by the artist's feelings and rhythm. It is not easy to render one's spirit into a work of art yet when one is able to master the knowledge, then it is possible to convey a spiritual message throughout the production.

I personally create my glass pieces using hot glass layers and create forms before cooling with momentary inspiration. Using glass and metal together I bind two contradictory elements by applying the hard and cold characteristics of metal together with glass, which is transparent and fragile.

My approach in creating public sculptures is based on bonding with individuals for whom these works are created. I envisage each part of my work as the core that makes up the mass, just like individuals that create a community. All my sculptures are large as I dedicate them to the large public they are commissioned for.

Keywords: Public space, Glass art, Glass sculpture, Modul

Fig. 1-2 Secret of Rose Garden, Göztepe Park, ISTANBUL, Yasemin Aslan Bakiri

Fig. 3 Heaven Glory "Emirgan Park" ISTANBUL, Yasemin Aslan Bakiri

Introduction

The giant tulip sculpture I created for Emirgan Park in Istanbul is made up of small glass v parts shaped as tulips. I used coloured hot glass technique in its production.

Tulip resonates with the Turkish historic culture and the use of glass in rendering the massive sculpture with a fragile element as glass evokes a certain awe in the onlooker.

I used a similar approach in the sculpture at Hidiv Kasri by applying tiny glass roses in order to create a 3 meter high sculpture. The technique is coloured hot glass applied on carcass.

The work is also related to the architectural structure that exists in terms of the relationship with the environment. The projections in the works have strengthened the relation with the environment.

Conclusions

All the possibilities of glass would pour out my hands, my knowledge and my experiences, becoming and language of colors that strong fragility between counterparts and imbalances would re establish the balance, concluding that through these means.

We would understand each other.

Fig. 4 The Only Love of Rose Garden, Khedive Palace, ISTANBUL, Yasemin Aslan Bakiri

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Acknowledgements

I would like to express my gratitude to Municipilaty of Istanbul, who commisioned me about doing my art works in Public Spaces.

Glass foam works created from recyclable glass bottles, conservation vessels and waste glass paints

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Abstract

Today glass conservation vessels and window glasses take an important place in recycled materials. With the developing modern technology and the increase of consumption, cheap and extensive raw glass materials found on earth, gave the glass recycling an important role. At the same time, innovative glass designs that are of great importance brought healthy products and beverage consumption together with itself.

In the glass bottles and conservation vessels there is a great amount of colour range. So it is possible to treat colourful glass foam as a medium for artistic productions. Artists can create fine-art products only by utilizing from glass foam blocks on the on the one hand, and they may create three-dimensional (3D) glass objects by gathering plain float glass on the other. In order to reflect the aesthetic role of any artistic work, soda-lime silicate glasses can also be applied to the glass foam blocks on the same work to highlight the colour, volume and transparency features of the two materials.

Another feature of colourful glass foam is its light mass and its physical resistance, reliable and stable appearance. Its porous formation and structural visually with its different sized pores, will create different effects in artistic works. Giving shape to the glass foam is very easy and suitable for other operations like drilling, engraving, carving, assembling, joining, thus remarkable and interesting glass works can be created. Glass foam can be combined with different techniques like kiln casting and slumping, as also being used in mixed media works to produce interesting works. Colour and structure diversity can be achieved by the use of consumption glass and paints without of the original glass colours. The idea of creating artistic objects, was carried out together with the scientific research and development and laboratory investigations. Many tests and applications were made during this research. The physical compatibility of massive and foamed glass are of high importance. With its extraordinary texture, the glass foam creates a different taste and feeling.

As a result, artistic glass works created by using foam glass will create a different point of view in the mind of people which are related with glass art and design.

Keywords: Glass foam, Recycle, Art work, Environment, Glass Art, Glass Packaging

Introduction

Waste is not a thing to be thrown away, however, as Migoni et. al. stated "Nowadays, increased sensibility to environmental issues together with the orientation toward the reuse of waste materials open to a wide range of new eco-compatible products"[1]. Glass art contains many technical and technological components. In recent years there have been new quests in glass art with different technical works. "Foam glass" which is an insulation material, has been produced since 30 - 40 years and is being developed with different structures.

Japanese artist, architect Yoshiaki Kojiro first evaluated glass foam as an art material. He still produces his works using glass foam. Artist; Kojiro, Y has met by "Foam Glass" while he was working on the construction of the Japanese railway. He has tested his ability to do artistic work from glass foam. He has made works by mixing glass foam and transparent glasses. He has his own specific studies.

Fig. 1 Ekrem Kula, Offbeat (48x30) 36 cm Foam glass with glass fiber, 2014 Photo Serhat Özdemir

Fig. 2 Yoshiaki Kojiro Kiln Work(48x16) H 54 cm 2005 Photo: Hans- Joachim Becker [2]

Fig. 3 Damien Francois Foam Glass Pate de Verre (16,5 x 14.4) 8 cm 2012 [3]

Waste Statıstıc In Turkey

Fig. 4 The annual amount of waste per capita in Turkey is 416 kg. 2012. *Photo: Orhan Gazi Keskin, 2017*

Another reason is the claim of using Glass Foam together with GFT "Glass Fiber Techniques" that I have developed.

In this study, common glass packaging such as colored and colorless soda, beer, wine, window glass to capture the interest in the production and recycling of glass in our country includes the main theme of this work. Investigations have been carried out on the process of recycling glass pellets into glass foam.

The use of glass foam material as art material obtained in this way is to emphasize the indispensable color and form of art. Application works include three-dimensional forms and emphasized the contrast of art objects in features such as color, colorless, matte, bright, transparent, opaque, smooth, rough, small, big, empty, and full.

Fig. 5 Ekrem Kula, Glass foam figure (16 x 35) 45cm Glass foam 2015, Photo: Murat Paktur

Fig. 6 Ekrem Kula Breeding (10x34) Glass foam, 30 cm, With Float Glass, 2015, 2014, Photo: Serhat Özdemir

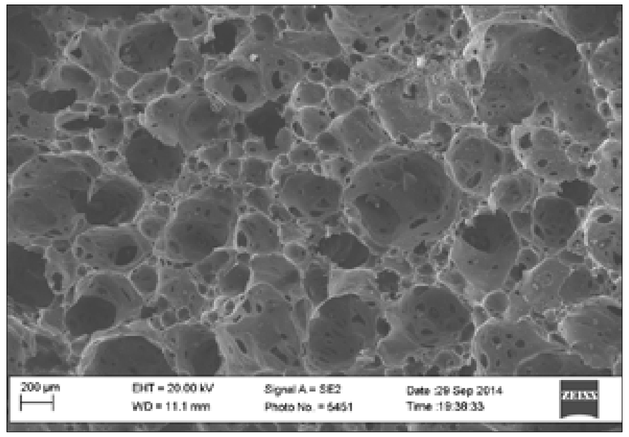

Fig. 7 SEM images of soda-lime silica glasses which shows pore structures, 200 µm, WD 11,1 mm, 2014, Anadolu University

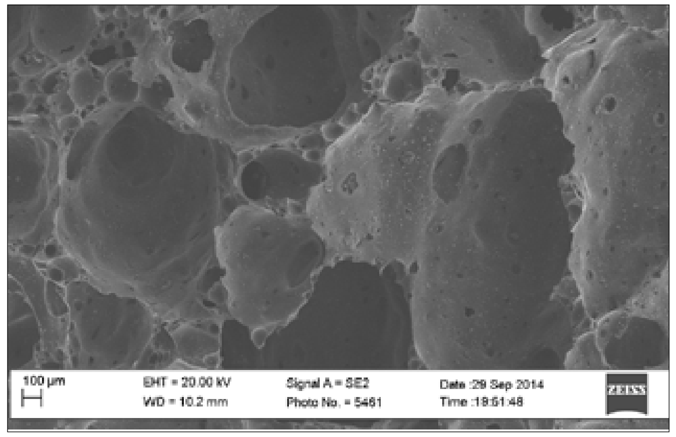

Fig. 8 Details of pores and columns whch can be seen from SEM image of soda-lime glass, 20 µm, WD 11,1 mm, 2014, Anadolu University

Fig. 9 Examples of glass foam obtained from different kind of bottles – From left to right: cobalt mineral water bottle, coloring with MnO, Beer bottle, green mineral water bottle, 2015

Fig. 10 Glass foam which is obtained from Sweden recycle glass. Pores can be seen in glass foam.
Photo: Murat Paktur, 2015.

Conclusions

This work draws attention to the creation of artistic glass art with another structural change by processing recycled glass materials. If we consider that many industrial products and artifacts are art materials today, the foam glass obtained from glass powder may also be a material for sculpture. When it is fired again, it is a light weighting material that is more robust, can be shaped and has natural appearance.

As a researcher and hands on practitioner, in the department I work for, the Glass Fiber Technique (GFT), presented in the previous figures, has been developed. Furthermore, there is a rising desire to apply Glass Foam and GFT in a single work to reflect the aesthetic delicacy and attract the artists to contribute innovative applications for visual glass culture.

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Production and application of ceramic decal technology on vitreous substrate

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Field of interest: glass art, glass in architecture, ceramics, printmaking

Abstract

Despite their frequent use in architecture and advertising, images printed on glass are very rarely of a finely crafted quality. Instead, low quality printing solutions such as laminated paper or photomechanical silkscreen print, is the common choice. However, images on vitreous surfaces have a rich history, going back to industrial approaches, first in the ceramic industry, in the 18th century. The present project aims at researching and integrating simple methods of printing and molding into the studio glass practice. There is today an immense potential for extending the scope of fine art printing on glass by combining the creative flexibility of the digitally processed image and the autographic image, using handmade transfer papers to carry the visual content.

Keywords: Glass, Image, Fine art printing, Decals

Introduction

One major concerns of this project, to enlarge the scope of established modes of print creation, brought about by the incorporation of simple transfer techniques into the realms of fine art print.

While the introduction of the image to ceramic decoration has a long history dating back to the earliest times where a simple wood stamp could be used to print, repeat shapes, create patterns, (SCOTT, 2012), it was, however, with the development of the printmaking and the printed image, that the imaging content was perfected and refined. Around 1750, images engraved on copper plates were transferred to on glazed ceramic surfaces using bat printing (HILDYARD, 1999). After that, another method emerged, the potter's tissue, for transferring images to underglaze ware. Later, in 1796 the lithographic process was discovered by Alois Senefelder, and was also adapted for use on pottery. Today, screen printing and digital processes dominate the ceramic decoration industry. Digital printing technologies have undergone a strong technological development in the last two decades. The production of commercial decals is quite common nowadays. There are specialized companies dedicated to the graphic creation and production of decals for ceramic and glass industries, developing products in the scope of customizing pieces of china with advertising, logos and brands.

Architectural glass is perhaps the area where printing onto glass has had greater visual impact and has been most highly developed by artists (PETRIE, 2006), such as Brian Clark, Amber Hiscott, David Pearl and Alexander Beleschenco.

Considering glass surfaces offer rich possibilities to work with printed image due to its transparency, quality and physical presence, this project focus on the production of intermediate surfaces for enlarging the scope of printmaking technique. Commonly referred as decals, within this project optimized for a fine art print context, it allows transferring the image on two-dimensional and three-dimensional glass supports. A second aim, however, is to exceed the specifically technological dimension of the print/glass opposition, and to explore the way in which this binary might also be used by artists to specify a conception of thinking as backgrounded by the body's liveliness and interference related to the use of different media and obviously the very presence within an workshop space.

The project was conducted in two different workshops: glass and printmaking at FBAUP and also at VICARTE FCT / UNL facilities. It all started with the preparation of paper transfer, with comparative tests, aiming to evaluate the behavior of different types of papers, associated with different coating formulas, like vegetable gums, animal glues and synthetic glues. After that, tests were developed related with ink and covercoat materials. On those prepared decal papers, we printed with glass inks though screen printing, intaglio and flexographic plates. Tests have confirmed several advantages in the use of an intermediate surfaces between drawing process and particular modes of thinking through intaglio, as opposed to the more regular solution of direct screen printing. With regard to glass molding, the printed image was applied on flat glass, curved glass, between two sheets of glass, on pâte-de-verre surfaces, inside cast and sandcasting glass, on flamework spheres and on glass blowing pieces, testing single-firing and multi-firing processes.

Fig. 1 Preparing transfer paper. Gelatin sizing application whith brush.

Fig. 2 Ink preparation, mixing enamel powder and pine oil medium, for oil based screenprinting.

Fig. 3 Printing from flexography plate, with glass enamels, to handmade transfer paper. That plate was also used to make a mold in which the glass was molded.

Fig. 4 Kilncasting piece, Birdwatching (Ana Margarida Rocha, 2016), with etching prints decals, applied on magnifying lenses.

Conclusions

If one compares direct printing on glass with transfer papers and decal procedure, several advantages arise: portability, flexibility, and adaptation to different rigid surfaces and objects with complex curvatures, due to the plastic nature of the cover coating.

This research proves the possibility of producing these special papers, from scratch, customized for the fine art practice. The choice of paper, coating, paints, binders and sealants, allows the free combination of techniques and materials, selected through the aesthetic and functional intentions of the author.

One major topic analysis through this project, is how to recover and renew modes of print creation previously used in industrial and fine art printing contexts. Tests conducted have brought about the aesthetic diversity and the remaking and reshaping of elected techniques into the realms of fine art print. While silkscreen as dominated original modes, through an archeology of the techniques of the past, used in ceramics, lithography, it is possible to allow the artist direct engagement with the physical interests and freedom found in intaglio printmaking and successfully transfer such images, with soft modulations, delicate lines without loss of information or resolution. In practical terms, artists can use the inks and papers used in these media without much constraints. Also, from the point of view of print aesthetics, specifically hand crafted printing qualities and approaches can be maintained which add further interest on the impact of such images.

Passing to the application of these images to glass, the possibilities are also vast, related with incasing the images on glass mass or playing with deformation and expansion of the images on glassblowing and flamework processes. So, it is concluded, handmade decals, within this project developed as an expressive tool of great interest, offer a greater opportunity for combining many print surfaces enlarging the scope of traditional fine art print on to glass surfaces.

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Acknowledgements

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Reflection and illusion in glass art; mastering artist Jin Hongo and his works

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Field of interest: Glass Art, Sculptural Glass Works

Abstract

Glass, as a medium of art, owns the features which provide the glass to be a special material to create powerful effects of light and transparency in artistic works. When used in the artistic aspect, it can be observed that some glass artists use their scientific knowledges to create powerful glass works by using the reflections of the light. The information about light and how it is reflected by mirrors and is breaked by glass lenses, play an important role in the creation of such kind of illusionist glass art works.

In this presentation, the glass and its optical features are introduced firstly. Some glass works which aim to create effects of illusion and their creators, glass artists will be mentioned during the presentation. Artistic investigations about reflection and perceptual illusion take part in some of personal glass works. The artistic approach of Jin Hongo, with his special geometrical style in his art works and his sensitive use of the light in this case, will be emphasized in the paper.

Jin Hongo creates his artistic works that he created by using the medium glass, with the idea by saying: "...reflections are also happening in your mind, that is to say that your experiences and knowledge you have had are reflected on yourself in your thoughts, judgments and philosophy. In that sense we are all reflected images of ourselves, or we are all illusion of ourselves."

The opportunities that the glass provides as an artistic medium as a material, are very wide. Personal thoughts about the future of designing artistic works, created by using effects of reflection and illusion achieved through the usage of the medium glass, will be discussed in the conclusion part.

Keywords: Glass art, Sculptural glass, Geometry, Reflection, Illusion

Fig. 1 Work created by Tiina Sarappu and Eeva Kasper, Frauenau, Germany, http://eevakasper.squarespace.com/#/imaginary-space/

Introduction

Reflection and Illusion in Glass Art

In this part, the scientific reality of reflection and its application in glass art will take place.

Artists Creating the Effect of Illusion trough their Art Works

Chosen artists that are using the effects of reflection to create illusions in their artistic glass works will be introduced in this part.

Jin Hongo and His Works in the Aspect of 'Reflection and Illusion in Glass Art'

The emphasis will be given on Jin Hongo's work; a glass artist that is creating his works with the power of geometry. Light effects and mirror reflections are some of the ways he creates reflection and expresses himself by his artistic works.

Fig. 2 Portrait of Jin Hongo inside of his geometric glass work J.Hongo (Personal Communication, February, 8, 2016)

Fig. 3 Jin Hongo and his geometric double man-size work "Bright Technology", 2004 J.Hongo (Personal Communication, February, 8, 2016)

Conclusions

The future of the glass art in the aspect of creating illusion will be discussed.

In the part of conclusion, artistic works of Jin Hongo will be inspected more deeply and the latest projects of the artist will be mentioned.

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Acknowledgements

I would like to express my gratitude to Professor Jin Hongo, who informed me about his art works and the meanings they refer, works personally.

The contribution of the science of glass to the artistic expression

Fatma Ciftci

Field of interest: Glass Art, Glass Science

Abstract

In this statement, author discusses how the sciences of glass contribute to the expression of art glass.

I'll make a remark on conceptual meaning of the artwork based on physical and chemical properties of glass. How the process of forming glass affects the conceptual meaning of a glasswork. This artwork is self-portrait that material is glass and made with kiln casting technique. Glass is fragile and transparent material, which is corresponding self. Technically in this self-portrait, the face is hollow and light gets through the hollow and makes it visible. Self makes a room for its existence in life fluency and light as a soul makes it alive.

Kiln casting technique requires a mold. Glass can pretend like a liquid in high temperature (melting point) and take the form of requested. Glass is a material that changes its molecular structure when expose by melting temperature. It is related to life fluency, which shapes humankind. Glass annealing process which gives time to harmonise the new molecular structure, relates human-life relation as requires time for positive result through traumatic experience. It's the process of regenerating the inner peace of the artist and reflects her on self-portrait.

I offer an alternative view to chemical and physical properties of glass.

Keywords: Artistic glass, Art glass, Science of glass

Fig. 1 Selfportrait / Technique: Casting. Size: 26x28x6 cm / Year: 2016 / Medium: Glass. Exhibited: 44A Gallery, Istanbul

A glass garden

Francesca Giubilei

Art Curator

Field of interest: Contemporary Art In Glass

Abstract

Since 2013 I am collaborating with the Australian artist Rosslynd Piggott in a project that extends her artistic research, based primarily on drawings and paintings, into the use of glass, in particular the engraving, as a new language to through which she can communicate her ephemeral and evanescent world. Glass, she says, not only helps to translate the appearance of her works of art, but, more importantly, it communicates her feelings for two of her favorite subjects, flowers and gardens.

Rosslynd Piggott decided to work in glass because of her interest in the metaphysical potential of this material and its beguiling and elusive properties, in particular its transparency and interaction with light. Glass contains and reveals, it has paradoxical properties of solidity and fluidity, and it conjures a sense of multiple space. For her as a painter who works with many layers of fine transparent paint, glass has an immediate relationship to her work. Piggott is not a glass artist. She approached glass with the fascination of a painter whose work extends into a variety of materials in order to explore their possible evocative relationships by the means of spatial installations.

This paper intends to show and explain the results of the collaboration between Rosslynd Piggott, the glass engraver Maurizio Vidal and myself. The glass objects were created in Murano. They are composed of glass plates engraved in several layers with botanical images. A mirror at the back of the stack of glass plates adds depth and substance by its reflection and refraction properties. Engraved glass and empty space alternate, and the mirror not only creates a vertiginous effect, but also presents an image of the viewer, albeit in a distorted and ambiguous shape. The viewer can immerse into a garden, a space for imagination, immateriality, wonder, and pleasure.

Keywords: Glass, Mirrors, Engraving technique, Contemporary art, Flowers

Fig. 1 "Garden fracture: Mirror in Vapour" 2013- 2016
Murano glass, slumped mirror, engraved clear glass

Fig. 2 "Mirror Shift: Wisteria" 2016
Engraved mirror and glass with avventurina

Coloring studio glass by metal oxides

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Field of interest: art

Abstract

Color is a kind of language for giving some impressions by art work. Glasses in some colors cannot be purchased easily. In this study transparent glasses were colored by adding micro sized metal oxides in a studio environment. Waste glasses can also be used for this kind of process. As the first step of glass coloring, waste clear glass was ground to a micron size and then one or more metal oxides were added to the glass batch. Then the batch was melted. Soda lime silica glasses were selected as waste. The process of coloring the glass was affected by some important variables: the most important of these factors were: the composition of the glass and coloring agents in the recipe (usually metal oxides) and their proportions, the kiln atmosphere (reducing or oxidising) and the heat treatment. In this process, different amounts (0.001% - 10%) of coloring agents (mixture of MnO_2 and CoO) were added to the glass batch in order to produce a variety of purplish blue tones. Additionally, to observe the effect of temperature, glasses were melted at 1100°C, 1150°C and 1200°C. The color changes in the glass as a function of the amount of added oxides and melting temperature were examined. Also the colors of the produced glasses after melting was examined by technical (measuring LAB) and classical (observation relative to the reference sample) methods. Beside these, thermal properties were investigated. The results of the study gave information about important properties of the colored glasses. According to these conclusions, decisions can be made on using these glasses together or separately in various shaping techniques to create artistic works in the studio environment. Also optimization of the firing schedule was realized based on these data. Coloring of waste glass by metal oxides was achieved by the study.

Keywords: Glass, Glass art, Glass coloring, Glass for studio, Glass thermal properties

‘Inside Painting’ suggested as a new model for contemporary glass art

Jianyong Guo

Field of interest: Contemporary painting glass

Abstract

My PhD research (2016) has been an art-based practice-led project focused on Chinese ‘inside painting’ in glass art. It has attempted to create a ‘new model’ for Chinese traditional inside painting through the creation of contemporary glass artworks. This research mainly used studio-based art practices, inspired by traditional inside painting of Chinese snuff bottles, traditional Chinese painting and calligraphy, influenced by Taoism, together with Western glass painting, printing and calligraphy in order to reduce some of the existing limitations of traditional methods. The methods of glass making for this research covered blowing (***Fig. 1***, *Waiting*), casting (***Fig. 2***, *Young Girl)*, flame work, fusing, slumping, incorporating ‘outside’ painting combined with ‘inside’ painting, and printing combined with inside painting.

Traditional inside painting techniques have developed over more than 200 years into a popular form of Chinese folk art, often based on glass snuff bottles with painted decoration on the inside. The craftsmen who make these pieces usually pay more attention to inside painting skills and overlook their own artistic expression. The designs used tend to be repetitive and copies of existing designs from other media such as ink painting or photographs. In this research, a body of inside painted glass works was produced to show how the glass form and painted content were combined This work also helped to establish possible ways to reduce the limitations of traditional inside painting of Chinese snuff bottles. It is hoped that this research will promote the development of traditional inside painting and lead to inside glass painting developing as a strand of the contemporary glass arts.

Keywords: Practice-led, Inside painting, Snuff bottle, Taoism, Contemporary glass art

Fig. 1 Jianyong Guo, Waiting, blown glass, inside painting, 55x15x15cm (each), 2015.

Fig. 2 Jianyong Guo, Yong Girl, cast glass, inside painting, 30x20x12cm, 2016.

Red glass revisited – a short review of the work made in Vicarte Laboratories

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Field of interest: glass science in art

Abstract

In this communication various examples of red glass obtained either through usual production processes or using innovative techniques are described.

Cadmium and selenium mixtures are commonly used to obtain red glasses, however due to their toxicity the use of other elements, such as gold and copper can be an alternative. The red colour of gold and copper glasses is caused by the interaction of electromagnetic radiation with metallic nanoparticles.

Conventional synthesis methods were used in our Laboratories by adding to a soda-lime silicate glass composition either gold and tin oxide as a reducing agent[1] or purple of Cassius. One interesting experiment was made using a recipe found in a batch book of the Factory “Gaivotas”. An almost clear glass was obtained, which formed an original amethyst glass when heated at 650ºC. With further heating to 700ºC a gold ruby glass was obtained.

Gold and copper ruby glasses were also produced without using any conventional reducing agent. In a first approach a batch composition doped with gold or copper, prepared using very pure compounds, was melted at 1500ºC. A transparent clear glass was obtained which did not strike at any temperature. After irradiating with gamma rays[2] or by infrared irradiation using a nanosecond laser[3] a brown colour was obtained, mainly due to F centres. Further heating using different annealing conditions gave origin to red colours with different hues. Using the same glass composition two hooks were made by a Vicarte artist. When the glass was heated in the glory hole, gold was reduced, which resulted in a red glass under transmitted light and brown under reflected light. The Lycurgus cup, a Roman vase of the 4th century, also exhibit two colours, however the colour observed under reflected light is green instead of brown. In this case it is known that the glass has small amounts of gold and silver.

Other processes were studied. Copper mirrors production and further heating, dip coating of glasses in solutions of gold and copper and the use of spray pyrolysis with copper acetate over a heated plate also gave rise to copper and gold ruby glasses.

Keywords: Ruby glass, Gold, Copper, Metallic nanoparticles

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Proceedings of the 5th GLASSAC International Conference

ARCHAEOLOGY AND ARCHAEOMETRY

Vidros da terra - Glass from the Earth The contribution of archaeology to the history of medieval and early modern glass in Portugal

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Field of interest: Archaeology, History of Glass

Abstract

Archaeological investigation over the last 35 years has made significant contributions to our understanding of production and consumption of glass in medieval and early modern Portugal. Combining typological, stylistic and archaeometric approaches, the study of relevant archaeological assemblages of post-Roman glass made possible to propose hypotheses about origins and places of production, while iconography and documentary sources helped in understand its significance in the Portuguese society.

Keywords: Archaeology, History of glass, Typology, Iconography

Introduction

Since the end of the 19th century the scholars investigating the history of Portuguese glass attempted to answer a central question: was it possible to recognize a "national character" in the glass originating in the country?

Fig. 1 Portuguese glass at the Aveiro exhibition in 1882. From Gomes and Vasconcelos 1883

Joaquim de Vasconcelos, in the catalogue of the exhibition on Portuguese decorative arts promoted in 1882 in Aveiro (*Exposição distrital de Aveiro em 1882. Reliquias da Arte Nacional*), listed some fundamental points that needed to be addressed: the documentary sources as the main (or even only) resource available to substantiate the existence of the Portuguese glass production preceding the beginning of the 18th century; the difficulty of identifying a distinctive character of the glassware created by the national furnaces; the feeling that - although basically unknown - the products of the Portuguese workshops always had an utilitarian nature and that the best-quality and luxury glasses were necessarily imported from abroad.

These issues remained largely unresolved for decades. Studies of Portuguese social and economic history showed that at least from the 15th century onwards glass manufacturing had, along with other activities, an important role in the country. Nevertheless, little trace is left and it was hard to relate these written sources to any set of material of possible national origin.

As a matter of fact, these questions continued almost unanswered until archaeology gave a strong boost to glass studies in Portugal. It happened during the 1980s, when increasing interest in preserving, classifying, and studying materials from medieval and modern archaeological contexts and the concomitant awakening of Industrial Archeology introduced substantial innovations in the discipline. The Glass Working Group of the AAIRL - Association of Industrial Archeology of the Lisbon Region, founded in 1980, was the driving force behind several outstanding initiatives, such as exhibitions, conferences, and investigation of post medieval furnaces.

Currently investigation of post-Roman glass from archaeological excavations carried out in Portugal make it possible to paint a less simplistic and more detailed panorama of the use of glassware in this country during medieval and early modern times. In addition to the questions mentioned above, others arose, guiding us in the formulation of the objectives of our investigation. What is the extent of the dissemination in Portugal of models and technological know-how from regions where glassmaking was possibly more developed? In the written documents dated to 16th and 17th centuries, the allusions to the arrival in Portugal of valuable glass produced in Venice and in the main European glassmaking centers abound: might it be

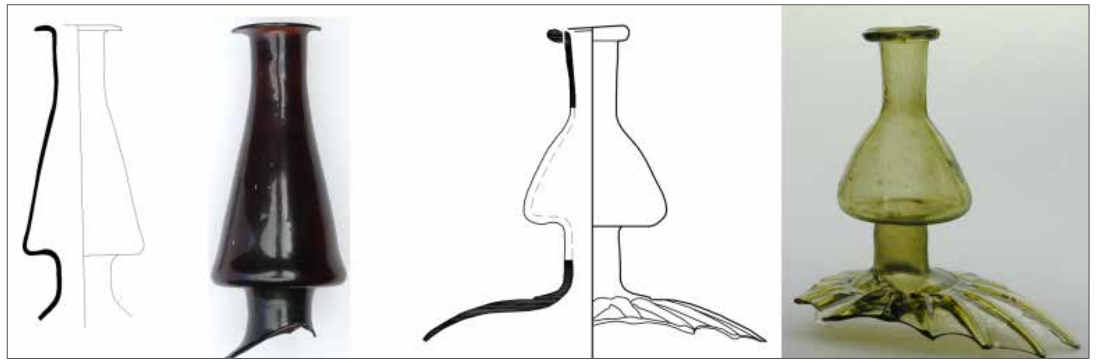

Fig. 2 Fragments of gourd bottles from the Monastery of Sta.Clara-a-Velha, Coimbra. 17th century.

possible to more comprehensively research and document these imports?

The systematic study of hundreds of finds coming from several archaeological sites from the 11th to the 17th century provided information that helped answer the above questions. Relating archaeological data with archaeometry, iconography, and documentary sources increased our understanding of the production, use and diffusion of glass objects in Portugal in the pre-industrial era.

Factors of continuity and innovation in the use of glass in Portugal over the centuries have been explored. The glass dated to 11th-13th centuries, related to the Muslim occupation, shows some similarities with glass supposed to have originated in Al-Andalus. During the 14th and 15th century the analogies with contemporary European glassware predominate, while in the 16th and 17th centuries a greater stylistic individualization appears. Identification of the provenance of glassware thought to be imported has allowed us to confirm that the commercial streams brought to Portugal mainly Venetian and *façon de Venise* glass. However, the influx of imported goods did not prevent the development of local glass productions.

Regarding the identification of a "national character", we emphasized the distinctive use of bracelets, a practice that relates Portugal to Spain in evident absorption of customs of the Muslim world, and the occurrence of objects showing peculiar shapes, such as gourd bottles.

Conclusions

The archaeological approach has contributed substantially to the reconstruction of the production and circulation of glass in medieval and early modern Portugal. Although some chronological and geographical gaps still need to be filled, it is possible to follow the use and diffusion of glass objects in the country from the 11th century onward and to understand their significance in Portuguese society. The combination of typological, stylistic, and archaeometric analyses make it possible to propose hypotheses about their origins and their places of production, considerably improving our understanding of this significant heritage.

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Origins of stained glass in the great east window of York Minster, UK

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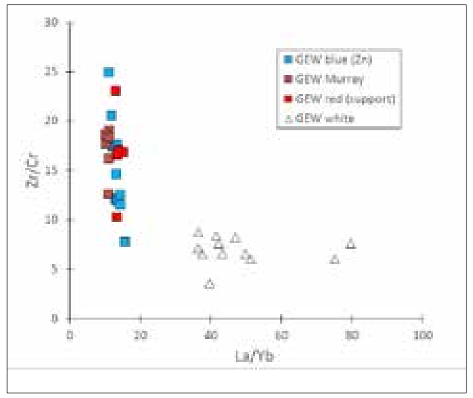
Field of interest: archaeometry

Abstract



Created by the master glazier John Thornton of Coventry between 1403 and 1405, the Great East Window (GEW) is the largest expanse of stained glass in the UK, comprising 311 individual panels, each containing hundreds of fragments of glass. It tells the history of the World from beginning to end, based upon the Books of Genesis and Revelation. The window is currently the subject of a major conservation project, which has involved its dismounting and the removal of the glass from the lead calmes. During the conservation process, the opportunity has been taken to sample glass from selected panels while they are in the conservation studio and subject them to physico-chemical analysis to determine their technologies, provenances and durabilities.

This paper focuses upon the provenance of the glass used in the window. The analysis progressed in a hierarchical fashion, so that large numbers of samples were analysed for major elements using SEM-EDXA or EPMA, a sub-sample for trace elements by LA-ICP-MS and a relatively small number for neodymium and strontium isotopes by thermal ionization mass spectrometry (TIMS).

A number of base glass compositions are recognized in the GEW. Two major glass types are original. Both contain around 11% K_2O, but the blue, red and murrey colours have higher CaO (c. 22%) and lower MgO (c. 4%) than the whites (15% CaO, 7% MgO). The white glasses show a higher enrichment in light rare earth elements (LREE; La/Yb) and lower Zr/Cr. Analysis of glass from late medieval workshops in England reveals that the products of a number of these in both Staffordshire and the Weald show similar LREE enrichment and low zirconia. Elemental and isotopic data combine to indicate a specific workshop in the Midlands as the probable source of the white glass. The coloured glasses do not match the English sources and are likely to have been imported. Comparison of these results with a number of other windows attributed to John Thornton, from York Minster, Coventry Cathedral and Hampton Court (Hertfordshire) indicate that Thornton used the same sources of glass over a considerable period. As far as we are aware, this is the first time that it has been possible to assign the manufacture of glass used in a major medieval window to a specific workshop.

Keywords: Medieval Glass Production, Stained Glass, Trace Elements, Neodymium isotopes, Strontium isotope

Analytical investigation of 14th century stained glass windows from Santa Croce Basilica, Florence. Glass types and weathering phenomena

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Field of interest: Stained windows glass, archaeometry, deterioration

Abstract

The *Basilica di Santa Croce* (Basilica of the Holy Cross) is the major Franciscan church in Florence (Italy) and the largest Franciscan church in the world. The construction began in 1294 and the church was consecrated in 1442. Since the beginning the Basilica became one of the most important religious centers and the most prominent families in Florence had their chapel in the church sumptuously decorated with frescoes and glass stained windows painted by the masters of that time. In the church there are 22 stained glass windows. During the last ten years the Opera di Santa Croce started a restoration campaign of some of the stained glass windows. In this paper the archaeometric data collected from six of the most important stained glass windows are compared. According to stylistic studies the six windows belong to a period spanning from the first/second decade to the end of the fourteenth century.

Keywords: Stained glass, Chemical composition, Degradation

Introduction

In Table 1 the stained glass windows taken into consideration for this study are described. Dating and attributions are based on extant documents and/or stylistic studies.[1]

The six windows belonging to a period spanning over the entire fourteenth century, are part of an extensive glazed complex in the Franciscan church of Santa Croce, described by Giuseppe Marchini as among Italy's *"most important centers for the quantity and quality of [stained-glass] expression"*[2].

Table 1

Reference	Name	Position	Dates	Attribution
I	Biblical Kings	apse central window upper section	1380	Agnolo Gaddi
		apse central window lower section	1320-1340	Jacopo del Cosentino
sII	Saints	apse right window	1380	Agnolo Gaddi
nII	Saints	apse left window	1380	Agnolo Gaddi
sII sup	Franciscan Saints and Popes	Bardi Chapel	1317-1334	Master of Figline
nII sup	Genealogy of the Virgin	Tosinghi-Spinelli Chapel	1330-1334	Master of Figline or pupil
nVIII	St. Sigismund and Saint Kings	Bardi di Mangona Chapel	1332-1335	Taddeo Gaddi (cardboard)

Fig. 1 Panel n 5 (lower part) - window nVIII St. Sigismund

Only one of these windows (nVIII) is signed by the master glassmakers with the following latin inscription *"HOC OPV(s) FECIT FRATER GHERARDINU(s) ET FRATER VBALDV(s) DE VITRO DE FLORE(n)TIA" "This work has been done by monk Ubaldo de Vitro and monk Gherardino Pillecti of Florence"* (***Fig. 1***). The other windows were attributed to different masters working on frescoes in the different chapels. In most of the cases scholars proposed that the painter contributed not only to the creation of the cardboard but to the painting of glass, especially for the faces and details of the figures (***Fig. 2***).

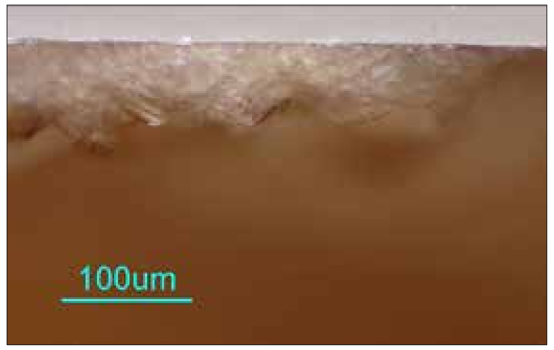

Fig. 3 Window sVII Optical micrograph of the polished cross section of a yellow sample (C5)

Fig. 2 Panel n 3 (upper part) - window sII St. Francis (before restoration)

From each stained glass window micro-samples of glass, representative of the colors, weathered areas and materials due to past interventions were taken. The glass microsamples were observed under the optical microscope and images at different magnifications were acquired. Subsequently, cross sections were investigated by SEM-EDS and EPMA. FT-IR and XRD were employed to analyze samples taken from weathered glass layers or materials used in past interventions.

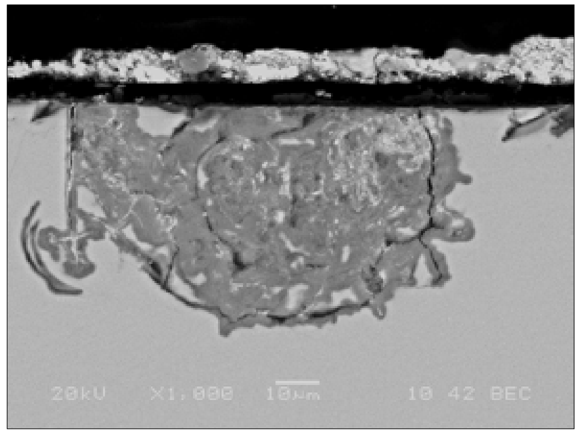

Fig. 4 Apse, left window; SEM micrograph in BSE mode of the polished cross section of a red sample (A4)

Conclusions

The analyses of glass samples from six stained windows from the Santa Croce Basilica in Florence gave a unique opportunity to investigate one of the most important cycles of 14th century Italian stained windows. An important aspect of this work was the possibility of comparing the composition of glasses of similar color coming from the different stained glass windows attributed to different periods and artists working in the complex of Santa Croce.

The analyses made it possible to study the composition of the glasses, identifying several types of potash-lime glass (included a potash-lime-lead group of green glasses), soda-lime glass (red glass excluded) and less abundant, mixed-alkali glass. By comparing these results with the analyses performed on other Italian stained windows of the same period it was possible to outline both similarities and differences.

Finally, the analyses allowed the weathering phenomena to be evaluated, assessing the state of preservation in relation to the type of glass (***Figs. 3 and 4***). Materials used in past restorations were identified.

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The authors gratefully acknowledge also Americo Corallini of the Studio Fenice, Bologna, in charge of restauration of three glass stained windows (sII sup, nII sup, nVIII) and the Studio Forme, Rome, in charge of the restoration of the apse stained windows, for supplying samples for analysis and for helpful discussions.

Study of Picenes beads from two Iron Age necropolises

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Field of interest: archaeometry

Abstract

Two sets of beads coming from two Picene necropolises and dating back to between the 9th and the 6th centuries B.C. have been investigated by applying a totally non-invasive and non-destructive approach. The collections are composed of glassy, shell and bone-based beads. The use of Reflectance Spectroscopy allowed the determination of the main chromophores used to color the blue glass beads, while Raman Spectroscopy resulted crucial in the determination of hematite as the coloring phase in a red bead and the differentiation of the glass- based samples from those obtained by other materials. In addition, X-Ray diffractometry was used to identify the opacifiers in the white and yellow beads.

Keywords: Glass beads, Bronze Age, Reflectance Spectroscopy, X-Ray Diffraction

Introduction

Studies carried out in the last decades permitted a definition of how historical populations were distributed along the Italian Adriatic coast from the beginning of the Iron Age to the Romans conquest. Two main ethnic groups existed: Jalepigi and Sabelli, which were in turn divided into various tribes, including Picenes, living in the current coastal area of the Marche and of the northern Abruzzo regions between the 1st millennium B.C. and the 3rd century A.D.

The excavations of two Picene necropolises in Novilara (PU) (Figure 1) and Matelica uncovered various grave goods including many colored glass beads. The first includes more than 300 tombs dating back to between the 9th and the 7th century B.C.; the latter (MC) (***Fig. 1***), indeed, also contains tombs dating to the 6th century B.C.

The proposed study concerns a totally non-invasive characterization of a selection of glassy beads coming from a wider set of 210 samples including also shell and bone-based artifacts.

Analytical Methods

Reflectance spectra were collected using a portable fiber optic spectrophotometer Quest-U by B&W Tek Inc. (Newark, DE, USA), connected to a tungsten light source through a Y shaped bundle of 7 silica glass fibers (Ø= 200µ each) entering a SMA 905 probe (3 mm^2). Spectra were taken in the 370-950 nm interval, averaging 30 cycles of 45 ms each and maintaining both the incident and detecting angles at 45° from the surface normal, not to include the specular component. A Labsphere teflon (99% diffuse reflectance) standard was used for calibration, after a dark acquisition.

Raman spectra have been acquired by means of a portable Raman spectrometer BWtek i-Raman 785S matched with an Olympus BX51 microscope equipped with a 40x planar objective. The spectrophotometer uses a 785 nm diode laser of variable power (3-300 mW) in the fixed spectral range 175-3000 cm^{-1}, with a nominal spectral resolution of 4.5 cm^{-1} and spectra were collected using integration times of 60 sec and 5 accumulation cycles to improve the signal-to-noise ratio.

X-ray diffraction (XRD) experiments were performed on whole samples using MoK_α radiation on a Bruker AXS Smart diffractometer equipped with an APEX II CCD area-detector. Diffraction rings were integrated using the Fit2D software (Hammersley et al., 1996; Hammersley, 1997).

Discussion of the Results

Reflectance spectroscopy gave information about the use of different chromophores used in blue glass beads: as expected spectra of the darker samples contain the typical features of tetrahedral Co^{2+} ions, while data obtained from the two light blue beads available, coming from the Matelica necropolis, showed no traces of this metal but only the spectral profile deriving from the presence of Cu^{2+} ions (***Fig. 2***). As known from literature, turquoise glass was commonly used during the Bronze Age, while cobalt started to be employed as a colorant during the Final Bronze Age in association with copper and then became the dominant metal to obtain dark hues due to its high colouring efficiency (Henderson, 1988; Billaud & Gratuze, 2002; Gratuze & Picon, 2006; Shortland &Schroeder 2009, Panighello et al., 2012).

Both Reflectance and Raman Spectroscopy allowed the identification of hematite as the colouring agent of the only red bead available, coming from the Novilara necropolis. This is a very peculiar result, since no literature data have been reported

Fig. 1 Satellite view with localization of the two sites, Novilara and Matelica.

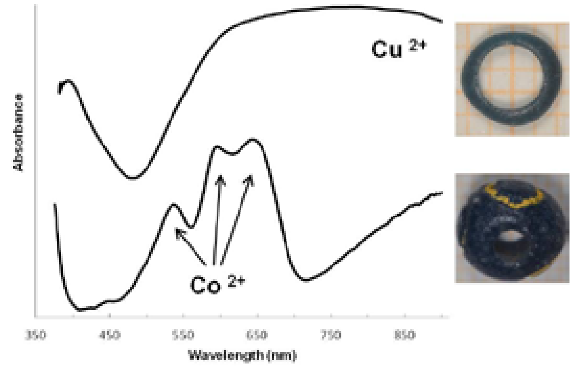

Fig. 2 Absorbance spectra of two glass beads from Matelica (upper) and Novilara (lower) necropolis colored by Cu^{2+} and Co^{2+} ions, respectively.

so far, to the best of our knowledge, about the use of hematite in glassy beads dated to the Iron Age.

White and yellow samples were mainly studied by XRD: in both cases the use of traditional opacifiers such as Ca and Pb antimonates was demonstrated. Yellow samples in particular displayed the presence of lead pyroantimonate ($Pb_2Sb_2O_7$), whose diffraction peaks could be well distinguished over the broad glass structure; on the contrary, the collection of patterns from white samples, exhibiting a black surface decorative coating, gave results that were more difficult to interpret.

Conclusions

The main aim of this research was to obtain the greatest amount of data to characterize glass artifacts according to a totally non-invasive way. The proposed procedure has been adopted for a large set of glassy beads coming from two Picene necropolises in order to verify the feasibility of this kind of approach, combined with techniques such as X-Ray Diffraction, normally employed under a micro destructive analysis. Collected data allowed the determination of the chromophores employed in blue glasses and the discovery of the introduction of hematite in a red sample from the Novilara necropolis. In addition, the opacifier crystalline phases were successfully determined by using X-Ray Diffraction on whole samples.

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Glass recycling in the first millennium AD: a spatial-temporal approach

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Field of interest: archaeometry, archaeology of glass, glass recycling

Abstract

We have now reached a critical mass in published chemical data for the composition of ancient and historical glasses, particularly for the first millennium AD Mediterranean. For the journal *Archaeometry* alone, the average number of papers reporting the chemical composition of glasses has risen from 0.5 per issue (1970-1997) to 1.2 per issue (1998-present); similarly, a quick search of the scientific papers listed in Web of Science™ using key terms 'glass' and 'archaeology' returns 164 results for the years 1998 to 2017, compared with just 18 for the years 1970 to 1997 (for more details on these figures, see Duckworth forthcoming). Key compositional groups of glass have been defined and these have been linked to geographical provenances and to the use of certain raw materials in glassmaking.

Now that this point has been reached, we might – like the physicists of the late nineteenth century – ask whether all that remains is to fill in the details, run more analyses, and essentially refine the conclusions we already hold. As did the physicists of the early twentieth century, however, we are likely to discover that the current state of knowledge conceals a far more complex reality. In the case of glass composition, a key challenge to traditional provenance studies and their conclusions is the past practice of recycling.

The analytical study of glass recycling has recently gained important ground, especially for sample sets in which the patterns are clear (for example, Jackson and Paynter 2015). Yet current approaches to recognizing recycling rely upon chemical markers indicative only of some recycling practices, notably the mixing together of two different glass types. Used alone, a sample by sample approach to recognizing recycling cannot offer clues as to the extent of recycling 'like with like', or the relationship between glass object types and position on the '*chaîne opératoire*' of glass recycling. My approach involves a combination of experimental and synthetic data, using published papers on glass composition to approach the small details indicative of recycling patterns over a large geographical area and temporal span. The initial results of the synthetic approach will be presented in this talk, and I shall discuss their place in the more complex and nuanced understandings of glass production and trade which are increasingly possible thanks to the volume of data now being generated.

Keywords: Recycling, Roman glass, Early Medieval glass, Mediterranean, Archaeometry

Introduction

For the archaeologist, recycling can be viewed as an invisible process; an ever-present possibility which must be taken account of, but which leaves few material traces. For the archaeological scientist, it can be an obstacle, obscuring the relationship between materials and their provenance, and blurring the distinction between compositional groups. Yet recycling is also a social act, and its study can offer insights into human relationships with materials and technology. This paper presents the preliminary results of a project aimed at the identification and – as much as is possible – quantification of glass recycling practise in the first millennium AD Mediterranean.

From the 1st century AD, glass was produced on a massive scale. Compositional and archaeological research has established that by the 4th century, primary glass production was mainly concentrated in the Levant and Egypt, where it was made to set recipes in large batches, then broken down in 'raw glass' chunks and traded to numerous smaller centres to be worked into form locally. Scientific analysis of glass should thus be straightforward, with certain compositional features (e.g. the ratio of one element to another) being characteristic of their production centres. The situation is complicated, however, by the existence of a parallel trade in broken glass ('cullet') for recycling, as reflected by the literary figure of the scrap glass peddler, and by the identification of shipwrecks with quantities of scrap glass (Silvestri et al. 2008).

Given that the primary fusion of glass requires specific raw ingredients, higher temperatures and more fuel than does secondary working or re-melting, we might envisage an economic incentive to recycle, particularly for the lower status or less well-connected glassworker. Yet we remain ignorant of almost all of the details of recycling: on what scale was it practised? Was it more common outside the core glass making areas? How controlled was it, and were additional raw ingredients necessary to counter loss on reheating? Were recycled glasses reserved for the production of certain objects? Was it a response to scarcity, or part of normal glass production practise?

These questions are being addressed by a large-scale approach which combines explicit testing of assumptions about glass composition with the vast banks of data published in recent years (at the time of writing this abstract, I have collated over 6000 data points from publications dated to 1999 and later). Compositional evidence for recycling may be most apparent

over the *longue durée*, and increase with distance from the core production zones. The wide geographical and temporal limits of this project are thus crucial to its success, in spite of obvious difficulties related to the combination of data from many sources, and the many lacunae in sample selection and analysis to date.

Conclusions

Significant recent advances in compositional analysis have gone a long way to identifying primary production centres for raw glass, but the potential for these data to also address the secondary working and manipulation of glasses has yet to be fully exploited. This is being approached by the collation of published data on 1st-11th century AD glass compositions into a database categorized by date, object type, site and geographical coordinates. The dataset, which will eventually be made available online, allows the plotting over time of the recycling 'markers' currently being tested by ongoing experimental work.

Data are also being mapped in a geographic information system (GIS), to trace the relationship between recycling and spatial factors such as distance from core production areas. By combining the database, GIS mapping, experimental testing (ongoing), and regional case studies (ongoing), it is becoming possible to assess the locations and periods in which glass recycling was most prominent, and to tackle social questions, such as whether recycling was primarily a response to scarcity. The results presented, though preliminary and subject to further interpretation, thus feed directly into our understanding of Roman and early medieval society, and its relationship with the cycles of transformation and renewal undergone by material culture.

Acknowledgements

The work presented is being undertaken thanks to the award in 2015 of a British Academy postdoctoral fellowship. I received generous assistance in designing the project from a number of individuals, including Ian C. Freestone (UCL), David J. Mattingly and Colin Haselgrove (University of Leicester), and after the award was granted, from the attendees of a one-day workshop on glass and metals recycling held at the University of Leicester in May 2015.

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Archaeovitreological analysis by PIXE/PIGE of glass fragments from Miranduolo, Chiusdino, Italy

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Field of interest: Archaeometry

Abstract

Twenty transparent glass fragments (colourless, yellow, azure and green hues) from Miranduolo have been analyzed by Particle Induced X-Ray Emission and Particle Induced Gamma-Ray Emission (PIXE/PIGE). The fragments are dated from mid-13th to mid-14th century AD, when the first Tuscan glass-making workshops emerged. All the glasses are of Na-Ca-Si composition, with 6 being made with unpurified Levantine plant ash, 12 made with purified Levantine plant ash, 1 with Barilla plant ash, and 1 with natron (with high magnesium). Continental calcite has been added to the glass batch as glass stabilizer in order to make the glasses more stable and resistant to corrosion.

Keywords: Archaeovitreology, Medieval glass, PIXE/PIGE, Tuscany

Introduction

Twenty transparent glass fragments (colourless, yellow, azure and green hues) have been analysed by PIXE/PIGE. The glasses have been archaeologically excavated from the Miranduolo site, Tuscany, Italy and dated from mid-13th to mid-14th century AD (Period II, with three phases). Miranduolo is a hilltop village, continuously inhabited from 7th to mid-14th century AD. Through its course, Miranduolo was expressing the strength of the aristocratic families over farmers and metalworkers. During the second half of the 13th century AD, Miranduolo witnessed an attempt of reconstruction and revitalization, even though in the reduced form of a lordly residence. With the first half of the 14th century AD, only residual settlement forms survive and the site is gradually abandoned. In Tuscany, 13th/14th century AD was a period when the first regional glassmaking factories were established. At Miranduolo, no *in situ* glass production has been recovered (Valenti, 2008).

Experimental

The PIXE/PIGE analysis was carried out at MTA Atomki, Debrecen, Hungary at the 0° beamline of the 5 MV Van de Graaff accelerator. The measurement setup included an SDD, a Gresham type Be-window Si(Li)detector, and a Canberra HPGe 40% Gamma-Ray detector; the accumulated charge was monitored using a beam chopper and a collimated PIN diode to detect the backscattered particles. An irradiating beam of 3.2 MeV focused down to ~ 5 µm x 5 µm with a current of 50-100 pA was applied. Each sample was measured on 2-4 spots. The scan size of each spot was 1 mm x 1 mm. The standard glass reference materials included NIST 610, Corning A and Corning B, and a series of pure metals and a layered sample (6 µm thick Ti foil on 50 µm Ni). The PIXE spectra were evaluated with the GUPIXWIN software. The elemental concentrations were normalized to 100% where needed.

Results

The chemical maps of all glasses shows a homogeneous composition, consistent with VP-SEM-EDS (Posedi, I., Schiavon, N., Mirão, J. & Fronza, V., 2016b). The average Miranduolo glass composition is 63.94 wt% (min. 59.37 – max. 67.69 wt%) of SiO_2, 15.76 wt% (min. 11.86 – max. 20.53 wt%) of Na_2O, 6.62 wt% (min. 2.17 – max. 9.41 wt%) of CaO, 2.43 wt% (min. 1.24 – max. 5.82 wt%) of K_2O, 3.42 wt% (min. 1.86 – max. 6.84 wt%) of MgO, 3.13 wt% (min. 1.57 – max. 4.99 wt%) of Al_2O_3 and 1.33 wt% (min. 0.55 – max. 1.95 wt%) of Fe_2O_3. In total, there are 6 ULpa-Na-Ca-Si (Unpurified Levantine plant ash soda-lime-silica glasses), 12 PLpa-Na-Ca-Si (Purified Levantine plant ash soda-lime-silica glasses), 1 UBpa-Na-Ca-Si (Unpurified Barilla plant ash soda-lime-silica glass) and 1 HMgn-Na-Ca-Si (High magnesium-natron soda-calcium-silica glass) glass compositions (***Fig. 1***).

Positive correlation of CaO with MgO (r= 0.8360, R^2=0.6989) and Sr (r= 0.8519, R^2=0.7257), and no correlation of K_2O with CaO (r=0.2453, R^2=0.0602) nor MgO (r=0.0824 R^2=0.0068) suggest addition of calcite to the batch (Barkoudah and Henderson, 2008; Harrison, D.J., Inglethorpe, S.D.J., Mitchell, C.J., Kemp, S.J., Chaodumrong, P. & Charusibandhu, M., 1998). When plotting CaO against Br, a positive correlation would suggest addition of the sea shells as a source of lime in the glass (Schiavon, N., Candeias, A., Ferreira, T., Da Conceicao Lopes, M., Carneiro, A., Calligaro, T., & Mirao, J., 2012) multi-analytical approach combining the high sensitivity of SR-mXRF, the light element capability of PIXE/PIGE under a helium flux and the spatial resolution of BSEM + EDS was used to characterize chemical composition and corrosion of glass samples (first to fourth centuries AD. On the other hand, the negative correlation of CaO and Br with r=-0.6729 and R^2=0.4527 found in Miranduolo glasses seems to imply that the calcite was of continental origin (***Fig. 2***).

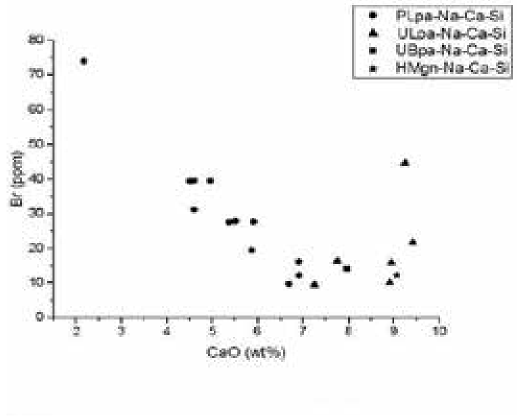

Fig. 1 Bi-plot of K_2O (wt%) and CaO (wt%) of Miranduolo samples with marked glass compositional groups

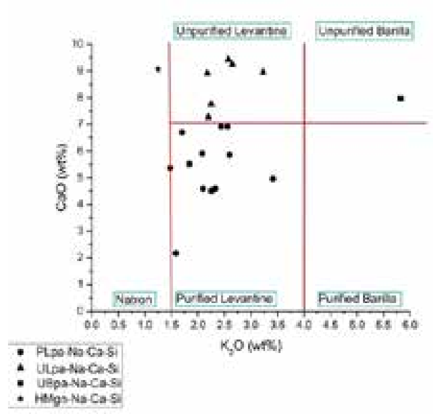

Fig. 2 Bi-plot of CaO (wt%) and Br (pmm) of Miranduolo samples with marked glass compositional groups

According to the glass groups, there is no apparent correlation with the silica source used, except for 3 ULpa-Na-Ca-Si glasses (MD 12, MD 21, MD 143) that have SiO_2≤62 wt%, Al_2O_3≥4.5 wt%. A distinction can be seen for the Fe_2O_3/Al_2O_3. Purer silica sources with Fe_2O_3≤1 wt% have been used exclusively for ULpa-Na-Ca-Si glasses, while 1 wt%<Fe_2O_3≤1.4 wt% is used for both Lpa-Na-Ca-Si glasses, but for PLpa more impure silica source has been used with Fe_2O_3>1.4wt%. MgO≤3.1 wt% is determined for PLpa-Na-Ca-Si, except for MD 272 which has 4.10 wt%. For ULpa-Na-Ca-Si glasses MgO>3.2 wt%. Fe_2O_3/TiO_2 and TiO_2/Zr display a strong positive correlation, respectively r= 0.7298, R^2= 0.5326 and r=0.7390, R^2=0.5462. This was investigated further with LA-ICP-MS due to higher sensitivity to Zr. The Al_2O_3/Zr plots indicate that for all glass types low (≤65 ppm) and medium (65-130 ppm) Zr values are common, while high Zr values (≥130 ppm) are only present in ULpa-Na-Ca-Si glasses (Posedi, I., Schiavon, N., Mirão, J. & Fronza, V., 2016a). Only two samples: MD 24 and MD 259 are colourless. Comparing the ratio of the Fe_2O_3/MnO interesting results occur. This ratio has been taken into account due to the fact that iron impurities cause tints in glass and MnO (0.3 – 0.8 wt%) indicates intentional addition as decolourant. For colorless samples MD 24 the ratio is 1.52 and for MD 259 1.73. But the samples MD 66 has the ratio of 1.48 and MD 257 1.58, while MD 272 and MD 276 have the ratio of 1.30 and 1.29 and they are colored.

Conclusions

The Miranduolo glasses have been procured since the establishment of the village in the 7th century AD, as no *in situ* glass factory has been recovered. Due to the fact that regional Tuscan workshops have been established from mid-13th century AD, it is clear that at Miranduolo, the investigated glasses have been procured upon the establishment of regional glassmaking centers. Meaning that the previous tradition of obtaining the glasses outside the region has been abandoned. What can be deduced is that the glass masters used local silica and possibly local calcite sources, knew the ash purification processes, possibly consciously adding decolourants to obtain different hues and added calcite to the batch. The addition of calcite made the glasses more stable and rose the melting temperature of the glass and more fuel was needed to obtain such temperatures, making the glass production more expensive. A clear proof of the use of different silica sources between ULpa-Na-Ca-Si and PLpa-Na-Ca-Si also indicates different production practices for different glass sub-types. They generally managed to produce high quality glass that was resistant to corrosion using standardized 13th-14th century tableware typology. Due to the fact that no distinction in production can be detected through time (three phases of Period II at Miranduolo), the same glassmaking procedures were used at least for a century.

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Analytical investigation of Renaissance Venetian enamelled glass. Potential and limits of portable X-ray fluorescence

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Field of interest: Archaeometry, Renaissance glass, Enamels

Abstract

In this work the analysis of enamelled and gilded Venetian Renaissance glass masterpieces from Italian Museums by using a non-invasive, portable X ray fluorescence technique (pXRF) was carried out. This research is part of a wider project called *Cristallo*, and aims at proving the reliability of pXRF in the quantitative evaluation of glass matrices in order to identify compositional differences able to discriminate copies and fakes of Renaissance enamelled Venetian glasses, like the so called *façon de Venise glass*. Promising results were obtained in the quantification of glass matrices and in the semi-quantitative enamel composition, making this technique a profitable solution for in situ chemical analysis.

Keywords: Venetian glass, Enamels, pXRF, Chemical analysis

Introduction

Enamelled and gilded Venetian Renaissance glass masterpieces are exhibited in museums all over the world (***Fig. 1***). These objects were made in Venice from the late 15th through the 17th centuries and were imitated in other European glassmaking centres during this period (*façon de Venise glass*). Copies and fakes of Renaissance enamelled Venetian glasses have been made in Murano and other European glass factories up today.

In spite of the interest shown by collectors, museums and scholars, several questions are still being debated as to the authenticity of many pieces in the collections. A research project called *Cristallo* was started in 2009 in the attempt to provide answers to these issues.

In this framework, quantitative chemical analyses were performed by PIXE-PIGE, a non-invasive and non-destructive analytical method, on a number of masterpieces mainly from French collections. This analytical method was made available at the Laboratoire du Centre de Recherche et de Restauration des Musées de France. SEM-EDS analyses of micro-fragments sampled from broken objects or from archaeological fragments were also performed at the LAMA laboratory.

As illustrated in another paper presented at this Conference, more than 80 objects were quantitatively investigated for the chemical composition of the glass object and of the enamels.

Compositional groups typical of Venetian Renaissance recipes (*cristallo* and *vitrum blanchum*) and groups other than Venetian Renaissance were identified [1,2].

Fig. 1 The Barovier's cup held in the Glass Museum of Murano

The impossibility to extend the PIXE-PIGE analysis to all the interesting items available is clear. Many objects cannot be moved from the collections or involve prohibitive transport and insurance costs. Therefore, chemical analysis by portable X-ray fluorescence (pXRF), a non-invasive, non-destructive analytical method, seemed appropriate for this kind of items. Despite recent and continuous advances, the limitations of this technique for the analysis of vitreous materials are well known [3,4,5]. For instance, only elements with an atomic weight higher than silicon can be quantitatively measured with a certain reliability; light elements such as sodium and magnesium cannot be detected, and aluminium and phosphorous show unacceptable limits of detection. In addition, important interferences (peak overlap) occur for certain elements, etc. Nonetheless, with reference to an available database of quantitative chemical compositions of genuine Renaissance Venetian, *façon de Venise* enamelled objects and later copies and fakes, the intention was to ascertain which kind of information can be obtained by pXRF analysis.

Materials and methods

pXRF measurements were performed with a handheld EDXRF Thermo (Waltham, USA) NITON spectrometer XL3T-900 GOLDD model, equipped with an Ag tube (max. 50 kV, 100 μA, 2W), large area SDD detector, energy resolution of about 136 eV at 5.9 keV (***Fig. 2***). The analysed spot had a diameter of 3 mm and was focused by a CCD camera, with a 2 mm working distance. The total time of analysis was 120 s and the instrument was held in position with a moving stage allowing millimetric shifts, in order to reach the desired probe-to-sample distance. The obtained spectra were processed with the commercial software WinAxil, derived from the IAEA software QXAS. The quantitative analysis was improved by calibrating the device by using reference standards. Successively, a wider approach was used, applying the fundamental parameter method (Rousseau algorithm [6]) to take into account different real situations during the analytical in situ operations.

Fig. 2 Experimental set up of the pXRF in situ measurements

In order to verify the accuracy, precision and limits of detection of pXRF, preliminary analyses were performed on reference glasses of known composition (NIST, Corning and Stazione Sperimentale del Vetro CRM) including the same elements of interest for the analysis of the Renaissance Venetian objects. Then, pXRF measurements were carried out on Venetian Renaissance enamelled masterpieces from Italian museums (Musei Civici d'Arte Antica, Bologna; Castello del Buon Consiglio, Monumenti e Collezioni Provinciali, Trento; Museo del Vetro, Murano -Venezia). A number of enamelled glasses made in Murano late 19th - early 20th c., imitating Renaissance artworks were also analysed.

Discussion

The results show a good quantitative agreement with the standards, demonstrating the reliability of the non-invasive pXRF analytical technique for glass chemical analysis, despite the impossibility of determining some light elements. The precision in the evaluation of the dark matrix makes it possible to measure with good accuracy other elements present in the glass such as potassium and calcium, colourants (Co, Cu, Fe, Mn) and their related elements, and opacifiers and related elements. On the other hand, the analysis of the applied enamels turned out to be more complex. During the data evaluation, it was impossible to quantitatively discriminate between the contribution of the components of the enamel and of the underlying glass; further investigations are required. Anyway, the semi quantitative analyses of enamels have been useful to discriminate fakes, by identifying finger print elements such as As, Sn, Sb, Cr, Zn.

Conclusions

The possibility of obtaining reliable quantitative chemical analyses of some components of the glass of the artworks was verified. Viceversa, only qualitative and/or semi-quantitative analytical data were obtained for the enamels, due to the peculiarity of the enamelling technique.

The results obtained allow us to conclude that, despite its limits, pXRF can help to identify copies (fakes) made in the 19th-20th c. with different materials, as well as items belonging to compositional groups classified in the database of Venetian Renaissance enamelled glass. In this case, the type of cobalt ore used to colour blue glasses and enamels can be recognized, allowing the dating of items before or after 1520-30.

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Preliminary non invasive study of Roman glasses from Jesolo (Ve), Italy

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Field of interest: archaeometry

Abstract

Archaeological excavations in Jesolo (VE, Italy) follow each other since sixties, when the first evidences of an Early Medieval church (6th-7th century) were found. During the last decades investigations lead to the collection of a large amount of glass fragments, including many tesserae, dating between the 4th century and the 12th A.D.

A selection of glass fragments and mosaic tesserae coming from the excavations performed in 2014 in locality *Le Mura* (Jesolo) were studied by means of reflectance spectroscopy to individuate the chromophore ions, in particular Cu^0, Cu^{2+}, Co^{2+}, Fe^{2+} and Fe^{3+} were found in both the transparent and opaque samples. Images taken under UV light (λ_{ex}= 365 nm) show a quite strong green fluorescence of some samples and the chemistry of a selected set of findings (***Fig. 1***) allowed to assess the use of costal sands and Natron as raw materials.

Fig. 1 Glass findings from the Jesolo excavations.

A green cup fragment decorated with blue drops displayed different compositions for the substrate, belonging to the HIMT class, and the applications whose matrix is enriched in flux content.

Moreover, the use of high resolution close-up images permitted to observe the presence of two red lines under the blue glass drops, probably used to align them. The analysis of a red and of a green mosaic tesserae evidenced the presence of high iron quantities in the first case, and of lead in the second one, the latter also exhibiting an unusual shape that, together with the very high lead content (24.8 wt%) lead to hypothesize the reuse of a material originally employed for enamels.

This study carried out by non invasive analytical technique permitted the acquisition of preliminary data to carefully project further methodological actions involving other non invasive analysis coupled to micro invasive ones, in order to obtain archaeometrical information to be related to the archaeological results.

Keywords: Roman glass, Reflectance Spectroscopy, EDS, SEM

Chemical and textural investigation of the glass tesserae from the baptistery of Tyana (Khemerisar)- Turkey

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Field of interest: Archaeology/ archaeometry

Abstract

The ancient city of Tyana (today Kemerhisar, Turkey) lays in the south-eastern part of Cappadocia. Despite its inland position, the city lays in a strategic position, connected to central Europe and eastern Mediterranean coast. The excavation of the ancient Roman and Byzantine settlement brought to light a Christian church with a baptistery that, on the basis of stylistic and historical data, is dated to the 5th -6th century CE. The floor of the baptistery was decorated with a figurative mosaic, partly preserved; mosaics also probably covered the walls and vaults of the same building. The excavation brought to light a set of detached tesserae of various shades of blue, green, red, yellow, black and gold. To clarify what kind of glass was employed in the mosaic, 46 tesserae were selected for the archaeometric analyses. Textural and chemical characterization was conducted on polished section by means Scanning Electron Microscopy and Electron Microprobe; X-ray Powder diffraction was conducted on a selection of tesserae to determinate the opacifying phases involved.

In the majority of the tesserae glass composition and opacifiers are consistent with the dating of the mosaic, demonstrating that the decoration was realized employing new tesserae, produced with fresh, contemporary glass and coloured/opacified with contemporary technologies; a small group of samples, mostly gold tesserae, is consistent with Roman base glass and – when opaque- Roman production technologies, suggesting that in those cases older tesserae were re-used; a single black tessera is made of obsidian of probable local origin, and no sign of glass recycling was identified, which allows concluding that Tyana, despite its inland location, was well connected to the main trade routes, and was easily supplied with fresh glass.

Keywords: Mosaic, Byzantine, Tesserae, Archaeometry, Tyana

Conservation of glass at the Corning Museum of Glass: training and future developments

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Field of interest: Conservation of Glass, education, training and practical.

Abstract

The Corning Museum of Glass has become the center for training in the conservation of glass objects. For almost 20 years the museum has accepted student interns, trainees, and conservational professionals from all over the world for training. Training is offered in both theory and practice, and includes work with a variety of glass objects, from ancient to modern. Hands-on experience is given in cleaning, use of adhesives, filling losses, and preparation for exhibition.

Keywords: Glass, Conservation, Training, Adhesives, Research

Introduction

The Corning Museum of Glass has become the center for training in the conservation of glass objects. For almost 20 years the museum has accepted student interns, trainees, and conservational professionals from all over the world for training. Training is offered in both theory and practice, and includes work with a variety of glass objects, from ancient to modern.

The program includes lectures and seminars on the technology and manufacture of glass as well as how it preserves and deteriorates, which is integral to its conservation. Instruction and hands-on experience is given in the handling, movement and installation of glass, including objects designated for exhibition, loan or storage. Special focus is also placed on the deterioration of historic glasses, as evidenced by crizzling. This problem is examined with recommendations for possible treatment and long-term storage.

Every intern and trainee experiences the many active and passive approaches that we offer for the care and preservation of glass. The major topics that are covered include the care, cleaning, and treatment of glass, including disassembly of old repairs, re-assembly, and restoration, preparation for exhibition and long-term storage. Mastering the use of adhesives and the resins used for filling losses in glass is certainly the most challenging of the conservation skills and needs to be balanced with the ethics and aesthetics of conservation/restoration.

An optional opportunity is also available for each intern to carry out a Research Project. Possible topics include: library research and study: preparation of a detailed bibliography; survey of a glass collection the Corning Museum of Glass and evaluation of condition; testing of synthetic adhesives and consolidants: acrylics, epoxies, polyester resins, commercial putties and fillers; color matching; Refractive Index matching.

Fig. 1 Roman inlaid bowl, during assembly with B-72 adhesive

Fig. 2 Conservation trainee in conservation laboratory.

Fig. 3 Tour of the new Conservation Laboratory.

Fig. 4 Conservation Laboratory currently with 4 conservators.

Research into new materials and techniques for the restoration of broken glasses continues to be a high priority, as we are now observing failure of some adhesives from their use in the early 1970's. Paraloid B-72 was introduced at the museum in 1993, and has also become one of the standard materials used both as an adhesive and for loss compensation (***Fig. 1***).

The Conservation Department and Laboratory expanded in 2009 with the addition of a second conservator and a larger laboratory. It is now easier to accommodate group tours as well as multiple interns and conservators (***Figs. 2, 3, 4***).

The Museum has also recently expanded, with the addition of a new building in 2015 which houses the Contemporary Art and Design Wing.

Conclusions

The future also looks extremely important and full of innovative opportunities for The Corning Museum of Glass. We hired a third conservator in 2017, primarily to specialize in the conservation of modern and contemporary glasses and to manage our strong commitment to outgoing Loans. With the recent expansion we already have had to cope with challenges of glass compatibility, adhesive failure, breakage from improper packing and shipping. A continuing study and documentation of these issues will provide the conservation community with a better understanding of how to manage such a large and varied collection.

The Corning Museum of Glass is an exciting and active center for trainees, conservators and professional conservators. We love telling the world about the Conservation of Glass.

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Maintenance and safeguarding of stained glass windows

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Field of interest: Conservation of stained glass windows

Abstract

Maintenance programs provide an insight into the condition of stained glass windows conserved in projects since the beginning of the widespread installation of protective glazing. In this paper two examples from the last years' workshop practice – the stained glass windows of St. Martha, Nuremberg and St. Jakob, Straubing, both in southern Germany – are presented. The examinations reveal the performance of conservation materials and the functional capability of the protective glazing from the early 1980's as well as around 2006. The impact of the former conservation measures to the present condition of the historic glass panels is discussed.

Keywords: Stained glass window, Protective glazing, Maintenance, Conservation material

Introduction

The main methods of conservation of stained glass windows as we execute in our days were fundamentally established in the 1960's to 70's. This does not only include the conservation materials but in many cases the installation of an isothermal protective glazing. Besides detailed research projects, observations during the daily workshop practice help to learn about the stability of materials and the efficiency of protective glazing in diverse conditions. Two examples of maintenance programs in the last years are presented below: the medieval stained glass windows in the chancel of St. Martha, Nuremberg and the clerestory windows of St. Jakob in Straubing both are mounted room side of an isothermal protective glazing.

St. Martha in Nuremberg was consecrated in 1385. Several patrician families donated the eight stained glass windows, which were installed in the chancel in the following years. During its long history multiple restorations and additions were carried out – inscriptions indicate dates from 1578 to 1927. The last comprehensive measure took place in the early 1980's. Workshops Frenzel and Gustav van Treeck from Nuremberg and Munich restored all stained glass windows and installed an isothermal protective glazing. The original panels were mounted in brass frames.

34 years later, restoration works at the roof structure in 2014 gave the impulse to deinstall, maintain and store all stained glass panels in the workshop van Treeck. This was a fortunate

Fig. 1 St. Martha, Nuremberg; deinstalling the framed stained glass panels

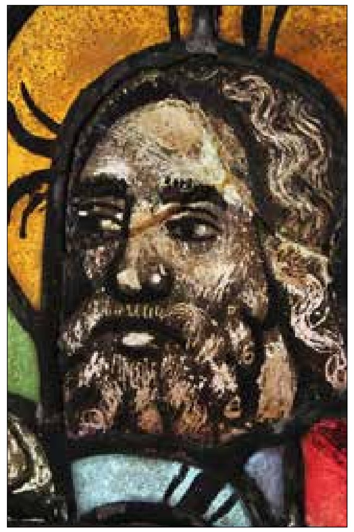

Fig. 2 St. Martha, reconstruction (part of the head) and heavily yellowed edge bonding

Fig. 3 Basilica St. Jakob; view from the organ loft

Fig. 4 Crating of the stained glass panels in St. Jakob

decision – three weeks after dismounting the valuable windows the church was destroyed by fire.

The condition of all panels was investigated on the light table and under the microscope and compared to the photographic documentation from the former conservation. Attention was centred to the constructive condition of the solder joints, frames, edge bonding of glass as well as peculiarities and new damages of the paint layers, glass substance or surfaces.

The stained glass was in a surprisingly good condition. Just few areas showed apparently new glass corrosion or efflorescence. Edge bonding materials appeared shiny yellow, but stable. Consolidation of paint layers did not show any visible alteration. This is even more remarkable, as in St. Martha there was already used an *Araldite* for edge bonding and *Paraloid B72* for consolidation of paint layers and crizzling glass. On the other hand alterations occurred in thick large-area consolidation of crizzling with *Paraloid B72*. Blebs arose especially along the lead cames and some cracks. This illustrates the disadvantage of the use of *Paraloid* B72 for thick films with its comparatively low glass-transition temperature on objects exposed to the sunlight and periodic high temperatures. Frenzel plated severely fragmented panes to clear glass with the epoxy *Araldite*. Now on a large scale use yellowing turns out to be a problem, mostly aesthetical.

The appearance of the stained glass panels as well as the observations in the church suggest that the preservation conditions provided by the protective glazing have been appropriate. Besides a sensitive dry cleaning of the surfaces, re-bonding of few glass cracks and sporadic soldering of brass frames, no conservation had to be carried out. Unfortunately the protective glazing was destroyed by fire 2014 and has to be rebuild in the course of the reconstruction of St. Martha.

Maintenance of stained glass windows from a much more recent conservation programme was realized in St. Jakob, Straubing. In the clerestory of the basilica there are four painted windows from 15th / early 16th century, one of them attributed to Albrecht Dürer, and 20 windows from around 1900. The conservation, restoration and installation of a protective glazing of the 24 windows were carried out in the years 2005 to 2009 by three different workshops.

Throughout the restoration of the interior space of the basilica, all nearly 700 panels were dismounted from the construction in 2012 and safeguarded in a storage space inside the church. This was the opportunity to undertake a first investigation of the condition of the stained glass and to verify the success of the prior conservation measures. Deinstallation took place in wintertime, under moist conditions. Especially on the north-east windows formation of ice in thick layers between protective glazing and stained glass was observed. With the beginning of heating, melting water left its marks on the back sides of many panels.

As for St. Martha, every panel was checked on the light table. Peculiarities of glass or paint layers were investigated under the microscope. Generally historic and conservation materials were in a good condition – but in comparison to St. Martha's stained glass, just 3-7 years after restoration, astonishing more conservation work had to be undertaken. Due to constructional faults brass frames were destabilised and had to be soldered. Few of the 15th century panels, situated in the north-east of the church, showed new efflorescence of glass corrosion on the back sides. Thick layers of *Paraloid B72* showed significant alterations comparably to St. Martha. A noticeably large number of edge bondings lost its adhesion and had to be re-fixed.

To avoid these occurring problems in the future, attention was turned to good ventilation of the space between protective

glazing and stained glass during the reinstallation of the panels. The operability was tested by air flow measurements.

As an important step for a long-term preservation a maintenance program is undertaken at St. Jakob in five years cycles.

Conclusions

In both cases the stained glass windows of St. Martha and St. Jakob have undergone equal conservation measures, but apparently with different long-term success. The examinations make clear that there are various parameters that influence the sustainability of conservation and protective glazing.

One of the most important parameters is the ambient climatic condition, which appears to be more stable and appropriate in St. Martha. Although observations on the stained glass windows in St. Jakob indicated functioning ventilation, the air circulation was obviously not strong and stable enough to cope with the temporarily arising amount of humidity, affecting the historic glass and conservation materials. Not often it is possible to predict the development and changing of the climatic conditions by installing a protective glazing in detail. The constructional characteristics of the windows, but also of the building as well as the local circumstances shall be taken into account. The church room in Straubing is larger than that of St. Martha and the windows, even the stained glass panels, are much bigger and in more exposed position.

Furthermore, the observations in St. Jakob illustrate that proper working and professional handling of the historic and conservation materials are required to avoid consequential damages. Despite the demonstrated deficiencies, the positive effect of the conservation and installation of the protective glazing in St. Jakob is not questioned.

The condition of the St. Martha panels allows optimistic prospects respective the widely used modern conservation materials. In adequate ambient conditions the applied materials obviously have a high durability – in St. Martha verified for over 30 years.

Maintenance programs are an important item for long-term preservation of stained glass windows. Besides detailed scientific research projects they are worth a survey of the sustainability of realized conservation measures.

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All photos: H. Pohle, Gustav van Treeck GmbH

Thermographic analysis of glasses, enamels and grisailles from stained glass windows

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Field of interest: Conservation

Abstract

Infrared thermography is a non-destructive and contactless technique which has been applied in conservation science principally on historical buildings and structures, however the studies on glassy materials are scarce. In this study, the thermographic assessment of glasses, enamels and grisailles from stained glass windows has been carried out.

Keywords: Thermography, Stained glass window, Enamel, Grisaille

Introduction

Infrared (IR) thermography is a non-destructive and contactless technique which measures the IR energy emitted from the surface of a target. The measured energy is due to the emission of the object itself as well as the energy reflected from its surroundings. It is usually represented in form of apparent surface temperature maps. The principal advantage of this technique is that the heterogeneities in the near surface region and the different materials, such as restoration products, are observable (Kylili et al., 2014, Bagavathiappan et al., 2013).

The principal application of IR thermography in cultural heritage is on historic buildings, frescos and mosaics (Avdelidis and Moropoulou, 2004, Ludwig and Rosina, 2005, Carlomagno and Carosena, 2001). Even, archaeological and historical objects such as paintings, tapestries, books and archaeological artifacts (Mercuri et al., 2011, Candoré et al., 2012) has been characterized by IR thermography. However, studies on glassy materials are scarce and they are focused on industrial purposes (Elmahdy and Devine, 2005, Yang et al., 2004).

The main objective of this study was the assessment of the behavior of different glasses, enamels and grisailles from stained glass windows.

Materials and methods

Two different stained glass windows were characterized by infrared thermography. The small "Saint George and the dragon" which was analyzed in the laboratory in winter, and the 20th century stained glass window located in the building of the headquarters of the Spanish National Research Council (CSIC) which represents the allegories of Sciences and which was analyzed *in-situ* in summer.

The thermographic analysis of the stained glass window entitled "Saint George and the dragon" was carried out with a FLIR ThermaCAM™ B4 (7.5 to 13 µm wavelength range, -20 to +130 ºC temperature range and 0.08 ºC of temperature accuracy) in transmission and reflection modes, and the 20th century stained glass window just in reflection mode. The studies were carried out by active thermography illuminating the stained glass windows during 10 min and measuring during the 20 min. The light source was a 500 Watts halogen lamp.

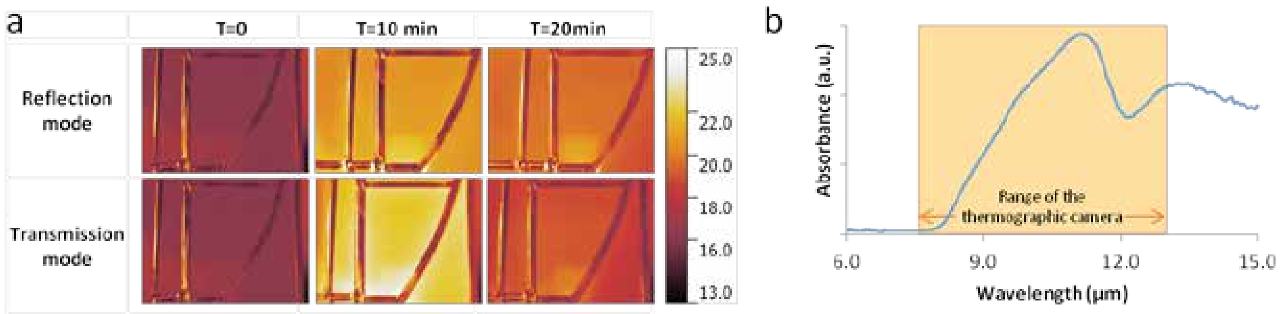

Fig. 1 a Surface apparent temperature map evolution of "Saint George and the dragon" in reflection and transmission mode at 0, 10 and 20 minutes of essay. b) FTIR spectrum of a soda lime silicate glass, in yellow tone the wavelength range of the thermographic camera.

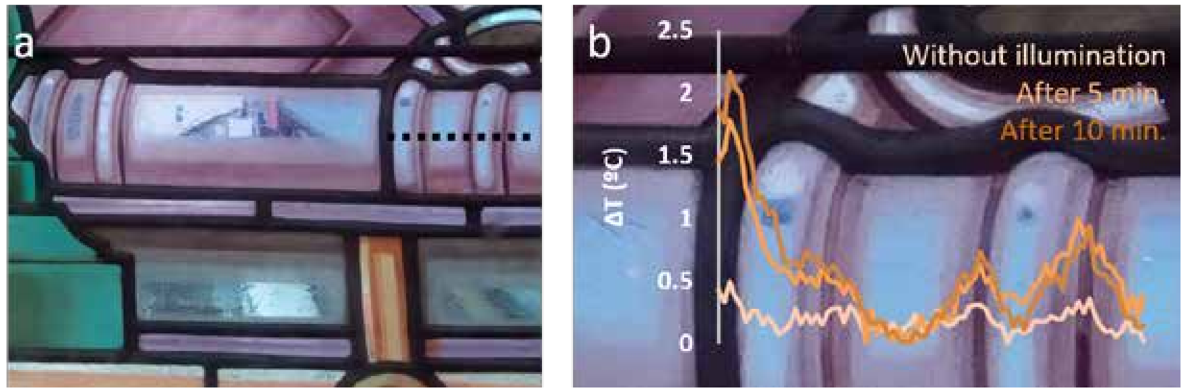

Fig. 2 a Linear analysis (dot line) in the stained glass window from the CSIC headquarters. ***b)*** Linear thermal variation in reflection mode without illumination and after 5 and 10 minutes of illumination.

Results

Glass behavior on active IR thermography in reflective mode showed a significant increase of the surface apparent temperature during the illumination (***Fig. 1 a***) because of the radiation reflection and the heating of the glasses due to the absorption of the silicate bands (***Fig. 1 b***). When the spotlight was switched off, a progressive cooling was observed (***Fig. 1 a***). In transmission mode, the surface apparent temperature experienced a higher increase because of the radiation not reflected or absorbed by the silicate bands was transmitted through the glasses. Glass heating was also produced, however this heating was less intense than in reflective mode and the cooling was faster (***Fig. 1 a***).

In painted glasses, illumination induced a higher increase of the surface apparent temperature in enamels in comparison with the glass support. This increase depended on the time of illumination, the thickness of the surface layer and its color. Higher times of illumination can characterize better the surface layers, because they can induce higher temperature variations (***Fig. 2 a and b***), however a long time of illumination can heat up so much inducing damages on the surface layer.

Thicker surface layers experienced higher increases of temperature for the same illumination conditions than thinner ones. This behavior can be related with the low transmittance of these glassy materials to long-wave IR radiation. For color variation, darker colors increased more the surface apparent temperature in comparison with those ones with lighter colors (***Fig. 2 b***). This behavior is similar to opaque materials where light colors present a higher reflectance than dark colors (Lechner, 1990). In the case of grisailles, they present the highest increase of the surface apparent temperature during the illumination because they were thick black lines.

The different temperature behavior of the supporting glasses and the surface layers makes the area more vulnerable to fissures and detachments due to their different expansion coefficient. The thermographic analyses can evaluate these areas susceptible to be altered and the suitability of the conservation measurements of historical stained glass windows.

Conclusions

Two stained glass windows have been successfully characterized with infrared thermography. Glasses presented a significant increase of the surface apparent temperature because of the warming of the glass. Enamels and grisailles experienced a higher increase of their surface apparent temperature in comparison with the glass support which depended on the thickness and color of the surface layer. The temperature difference between the glass and the surface layer can induce thermal stress, fissures and cracks which can accelerate their degradation.

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Final results of analysis of a 15th century stained-glass panel "The Throne of Grace" from the Dominican Monastery in Kraków, Poland

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Field of interest: conservation

Abstract

The conservation of the stained-glass panel depicting "The Throne of Grace" allowed a deep study of an exceptional example of Polish medieval stained-glass art. The goal was an analysis of the composition of glass, vitreous paints and corrosion crust, as well as the morphology of deteriorated layers of glass and paint layers. Instrumental techniques such as MA-XRF, SEM imaging, SEM-EDS and XRPD were applied. MA-XRF allowed a non-invasive preliminary analysis of glass and paint. The received data, collectively with SEM-EDS analysis of glass cross-sections, provided information on the technology and condition of the panel. The study was complemented with XRPD technique, which allowed the identification of the weathering products. Final conclusions contributed to a better understanding of the technology and the deterioration processes affecting the panel, thereby led to the compilation of a treatment proposal.

Keywords: Polish stained-glass, Analysis, SEM-EDS, MA-XRF, XRD

Introduction

The aim of this paper is to discuss the results of the analysis of the technology and deterioration of a medieval stained-glass panel depicting the "The Throne of Grace", originally placed in a window of the Dominican Monastery in Kraków. The investigation was performed during its conservation. The goal of the study was to gain data on different kinds of glass and paints observed within the panel, and to recognize and define deterioration processes. On the basis of the obtained information an optimal treatment proposal could be elaborated, and appropriate recommendations could be set to allow the exposition of the panel in the museum of the monastery.

"The Throne of Grace" is considered as made in a local stained-glass workshop during the first half of the 15th century and belongs to a collection consisting of twenty one medieval stained glass panels made between the 13th and 15th centuries. All panels have infills with inpaintings and borders designed by Stanisław Wyspiański (a famous Polish Art Nouveau artist) and incorporated in the first years of the 20th century. The turbulent history of the collection had a decisive impact on the state of preservation of the discussed panel. This history includes the transfer of all the panels from the church to the cloister windows (before 1820), the great fire of Kraków in 1850, which destroyed an important part of the monastery, both I and II World Wars and, finally, several previous repairs. As a result, the panel

Fig. 1 "The Throne of Grace", 15th century, Dominican Monastery in Kraków. State after conservation (Photo: P. Gąsior).

was severely damaged, hence repaired and subjected to significant visual modifications.

The condition of the panel was bad. some panes of glass were missing, the 15th-century ones were highly deteriorated and covered with deterioration products on the external side, some panes were also relocated. The paint layer, both 15th and 20th-century, was deteriorated as well.

For a full recognition of the state of preservation and degradation processes occurring on the stained-glass panel, reliable scientific research was needed. The preliminary analysis of the panel was noninvasively carried out with X-fluorescence by means of a macro scanner (MA-XRF). Glass and paints composition was analyzed with energy-dispersive X-ray spectroscopy (SEM EDS). X-ray powder diffraction (XRPD) was used in order to identify and determine the kind of corrosion crust present on the external side of glass. The added value of combining several analytical techniques was a mutual complementation of the results. While using only one method, it would not be possible to avoid false interpretations.

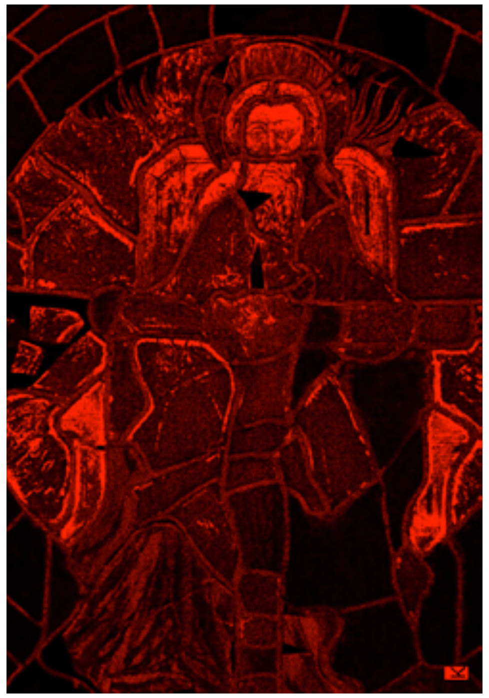

Fig. 2 MA-XRF image showing the potassium distribution (Image: M. Płotek).

Macro-XRF analysis was conducted before the conservation treatment. The obtained maps of elemental distribution provided general information on the technology of the panel. Predictably, the results showed differences in glass and paints composition between medieval and modern parts.

Complementary to MA-XRF, SEM EDS analysis was carried out on cross-sections to gain more specific information on the elemental composition of particular layers. The determined average composition of medieval base glass consisted of: 55.7 wt% SiO_2, 20.5 wt% K_2O, 13.9 wt% CaO, 2.1 wt% MgO, 1.2 wt% Al_2O_3. The composition of stable glass and 'gel layer' was also compared. A decrease of around 97 % and 96 % of K_2O and CaO, respectively was observed.

SEM images, especially BSE images allowed the analysis of the morphology of deteriorated layers of glass, as well as of the paint layers including the granulometry and the level of vitrification.

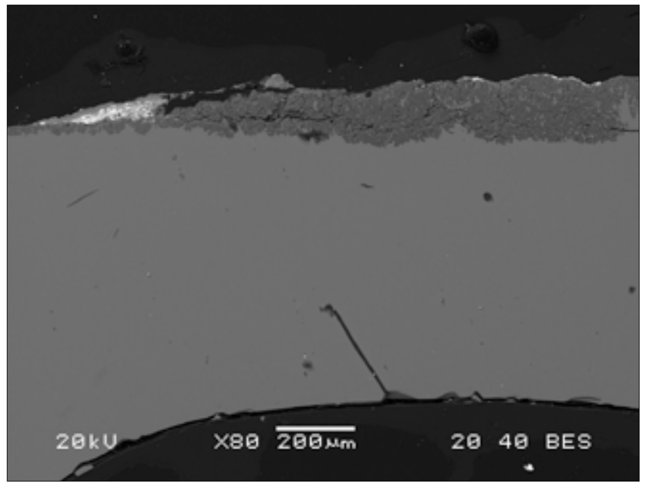

Fig. 3 SEM image (back-scattered electron detector) of the sample of the 15th century glass (Image: M. Walczak).

Manganese browning was also identified during the analysis of a sample of clear glass. Brownish areas, which were not visible to the naked eye, were revealed in cross-section under the microscope. These areas were distinguished by a higher amount of manganese and iron.

The identification of the corrosion crust observed on the external side of glass was crucial for the overall evaluation of the condition of the panel. The XRPD analysis of three samples revealed the presence of syngenite $K_2Ca(SO_4)_2 \cdot H_2O$, arcanite K_2SO_4 and gypsum $Ca(SO_4)(H_2O)_2$.

Summary and Conclusions

The instrumental analysis contributed to the identification of the materials used in "The Throne of Grace" panel and thus yielded the insight into the technology of both 15th and 20th century elements. The analysis confirmed that the medieval glass used for "The Throne of Grace" was of potash-lime type (in contrast to modern panes where also sodium was detected). It also revealed differences between modern paint layers, leading to the conclusion that at least two kinds of modern vitreous paint were used. However, the conducted analyses were not sufficient to determine the cause of significant differences in the state of preservation between 20th-century paint layers.

The stage of deterioration of medieval glass was also evaluated. In comparison to stable glass, the "gel layer" was characterized by a stronger signal from silicon, mostly followed by decrease in potassium, calcium and magnesium, and increase in aluminum. Moreover, within the deteriorated layer sulfur was observed as well. The analysis of deterioration products revealed the presence of three different chemical compounds. Such diversity is most likely related to the composition of glass, but the limited possibility of sampling excluded a deeper examination of all glass panes. Therefore, no connection between the type of corrosion product and type of glass was found. Thereby, research conclusions allowed for a better recognition of the condition of the panel, proved how severely and irreversibly damaged is the panel. Finally, resulted in the elaboration of an optimal treatment proposal and then in conservation of the artwork.

"The Throne of Grace" is so far the only panel from the Dominican collection which was analyzed. Thereby the obtained results determine the direction for further research and constitute a starting point for the analysis of the remaining panels.

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Surface roughness impact on medieval stained glass alteration

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Field of interest: stained glass alteration

Abstract

The aim of this study is to evaluate the influence of the initial roughness of a glass on its alteration and to determine the evolution of the roughness over time. For this purpose, alteration experiments of two glass samples, one polished and the other one highly rough, were carried out. The results show that the initial glass roughness has a strong impact on the alteration. If the glass has an initial smooth surface, the alteration layer will be constituted by different sublayers which will tend to scale as the alteration progresses. If the initial glass surface is very rough, the alteration will begin by digging the asperities and then homogenize, which decreases the roughness.

Keywords: Medieval glasses, , Surface roughness, Glass alteration

Introduction

The alteration of ancient stained glass windows displays several altered layer morphologies, such as cracks, scaling and pits (Carmona et al., 2006; Lombardo et al., 2010). Especially, pits were interpreted as the result of biological activity, of chemical heterogeneities or of surface defects. In order to investigate the impact of the initial surface roughness of the glass on its alteration, two samples of a medieval-type glass with a different initial roughness were immersed in ultrapure water in static condition during 6 months.

Material and methods

Two Si-K-Ca medieval-type glass coupons (51% SiO_2, 19% K_2O and 17% CaO and 13 % others) were used for this experiment. The first one, called R-, is polished up to ¼ µm and is considered as smooth at the micrometric scale. The second coupon was polished using a SiC paper with a P80 grade to obtain a high roughness and is called R+. Each of these coupons was cut in 4 samples with a geometrical surface of 2.7 ± 0.4 cm^2. One sample of each roughness was dedicated to initial characterization and the three others were placed in a PTFE reactor (one for R- and one for R+) at 30°C. Samples were immersed in ultrapure water (pH ~ 4.8) in static condition, in 0.6 L for R- and in 1.0 L for R+. For both reactors, one sample was collected after 1, 3 and 6 months of alteration.

Solid samples were characterized by interferometric microscopy to determine the average surface roughness Ra (VEECO NT1100, magnification ×10 and analyzed zone of 595×453 μm^2) and observed with miniSEM (Hitachi TM3030, 15 keV) directly at the surface or in cross-sections.

Results and discussion

Fig. 1 presents the evolution of R- and R+ before alteration and after 6 months of alteration. At the initial state, R- has a totally smooth surface (***Fig. 1a*** and ***1c***). After alteration, a significant part of the alteration layer at the center of the sample is lost due to a scaling process (***Fig. 2a***). SEM observations indicate the presence of a developed crack network and the peeling of the extreme surface (***Fig. 1b***). The cross-section at 6 months shows a thick alteration layer (14 µm) composed of several sublayers of variable thicknesses (***Fig. 1d***). In the zones where scaling can be observed, the detachment does not occur at the interface between alteration and pristine glass, but at the adherent deepest sublayer.

The behavior of R+ differs completely. The initial surface is disturbed by the polishing with the creation of defects and scratches (***Fig. 3a and 3c***). After 6 months, a heterogeneous crack network and large grooves are developed at the surface (***Fig. 3b***). Moreover, the cross-section shows the presence of these grooves in depth and the development of an important altered layer (Fig 3d), whose thickness varies between 6 and 27.5 µm according to the zones. However, there is no scaling on its surface (***Fig. 2b***).

The determination of the average surface roughness Ra was carried out by interferometric microscopy. The initial Ra value of R- is 0.009 ± 0.001 µm. This value increases to 0.5 ± 0.1 µm for 1 month of alteration, 0.7 ± 0.1 µm for 3 months and 1.8 ± 0.2 µm after 6 months for the zones keeping the entire altered layer. The zones which have lost a significant material part have a Ra value of 0.9 ± 0.1 µm. The initial surface roughness of R+ is 3.1 ± 0.3 µm and also greatly increases during the first month of alteration until 5.8 ± 1.3 µm after 1 month, but decreases at 3.7 ± 0.4 µm after 3 months and tends to stabilize at 4.1 ± 0.2 µm after 6 months.

All these results show that alteration morphology and its evolution varies as a function of the initial roughness. For R-, the surface roughness increases linearly with the glass alteration, up to a certain threshold, corresponding to the maximal textural development of the altered layer surface and to the moment when the altered layer become too fragile and flakes off. Moreover, the altered layer is constituted of sublayers separated by cracks parallel to the glass surface. This can be caused by

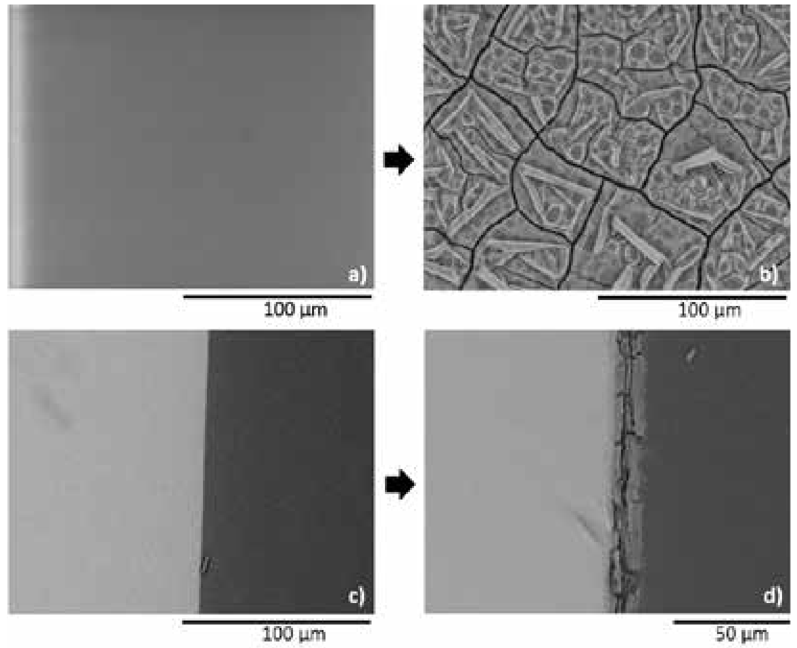

Fig. 1 Evolution of R-on SEM images (BSE): surface at a) t = 0 and b) 6 months of alteration and cross-sections at c) t = 0 and d) 6 months of alteration.

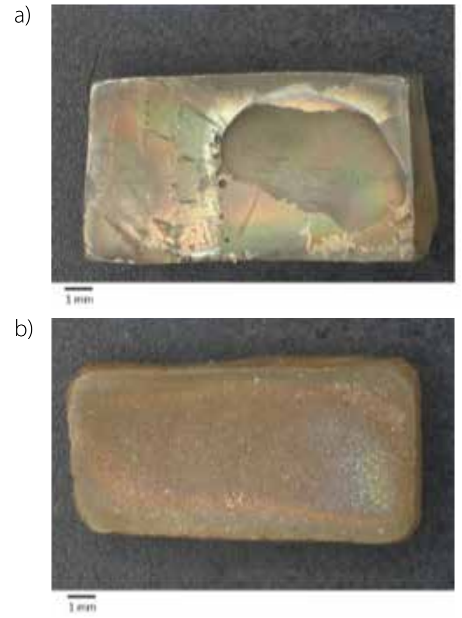

Fig. 2 Photographs of samples surface after 6 months of alteration for a) R- and b) R+

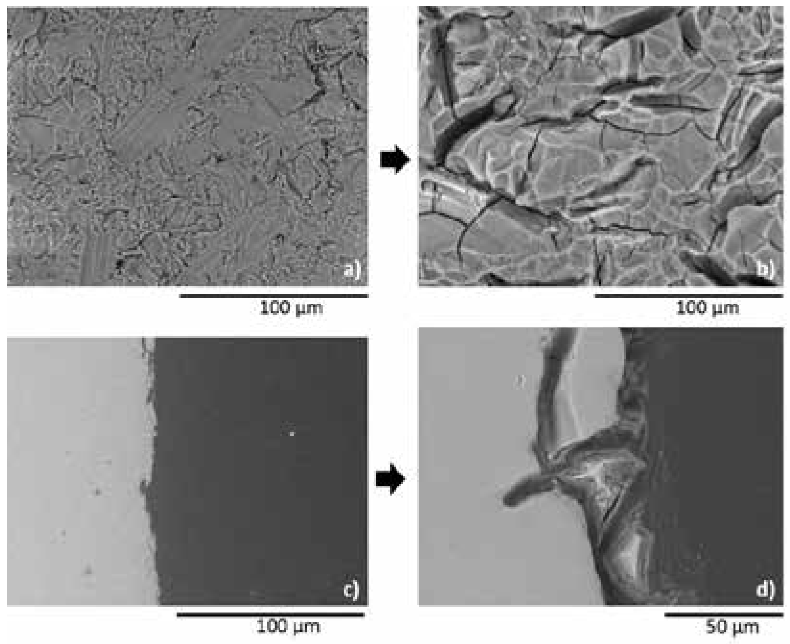

Fig. 3 Evolution of R+ on SEM images (BSE): surface at a) t = 0 and b) 6 months of alteration; Cross-sections at c) t = 0 and d) 6 months of alteration.

the gradual fragility induced by the alteration during the time, leading to the separation of sublayers and the scaling of a part of the altered layer. Flakes do not detach at the pristine glass interface but at the interface with the deepest sublayer, and the newly exposed zones have a lower roughness than the upper surface, but higher than the uncorroded sample. For R+, the Ra values are much higher than R- and reach an optimum after 1 month of alteration and then decrease and stabilize. These data seem to indicate that first the initial roughness increases due to the digging of the asperities by dissolution (water retention inside and pH increase). Then, this mechanism of dissolution allows dissolved zones to join together, leading to a relative smoothing of the roughness.

Conclusions

This study shows the strong impact of the initial glass roughness on the alteration and its evolution. The glass sample with an initial smooth surface has an altered layer constituted by different sublayers which tend to scale as the alteration progresses. The roughness increases linearly and is maximum on the areas close to flake off but much lower on the newly exposed areas. However, if the initial glass surface is very rough, the alteration begins by digging the asperities and then homogenizes them so the roughness will increase first and then decrease. Although this experiment did not represent realistic conditions for a medieval glass exposed in atmospheric conditions, the results allow to see the impact of the initial roughness on the altered layer development and its evolution. A new series of experiments with two different initial roughness exposed in real atmospheric conditions is in progress.

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Corrosion patterns of a Historical Glass Collection from Greece

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Field of interest: archaeometry

Abstract

The corrosion mechanisms of ancient glasses are a complex process (Zacharias & Palamara, 2016). The objects which have been exposed to the burial environments, usually lack coherency and transparency. The examination of excavated corroded glasses, often concludes to alkalis loss and the formation of different corrosion patterns on the surface. In this study a collection of soda lime silica glasses is examined, aiming to the characterization and classification of their corrosion patterns. The under study samples originated from the mainland Greece, Thebes.

In the present study a combination of analytical techniques, mainly non-destructive, namely LED optical microscopy (LED-OM), Scanning Electron Microscopy coupled with an Energy Dispersive Spectrometer (SEM-EDS), and Rutherford Backscattering Spectroscopy (RBS), were used to completely fingerprint the corrosion mechanisms. The analytical data provided useful information about their preservation state and the observed corrosion patterns.

Keywords: Soda-lime-silica glass, Corrosion patterns, Preservation state

Introduction

The complexity of historical glass has attracted the interest of the scientific society over the last 30 years. The studies until now have focused mostly on technological and provenance purposes. However, as complex is the glass nature the more complex is its corrosion mechanism. The two main combining factors involved in glass corrosion are the chemical composition and the environmental conditions (pH, temperature, moisture, presence of organic matter).

Aim of the Research

The research objectives are: (a) the determination of the corrosion patterns occurred; (b) the primary corrosion mechanism and (c) the characterization of the preservation state in glass with different surface finishes.

The Material Studied

The study concerns samples from a collection of glass beads, beads fragments, glass waste and core formed vessel fragments. The samples originated from the mainland Greece, Thebes. In the ancient times Thebes was a city with significant power continuously, from the Palaeolithic period until the Late Medieval Times, due to its strategic position at the Gulf of Corinth. The collection consists of 13 colored glass beads and 3 fragments of core-formed vessels. The beads were found in an ancient cemetery, discovered during the construction of a bridge in the outskirts of Thebes and are dated from Archaic to Hellenistic period (7th - 4th c. B.C.). The vessels were recovered during a systematic excavation on the O. KORDALI, N. ZACHARIAS, G.PROVATAS

Manisalis plot in Thebes's city center and dated at the Late Archaic- Early Classical Times (6th – 5th c. B.C.). The beads have a variety of coloration such as green, white, colorless, light and dark blue, brown and black, while the vessel fragments have deep blue color with yellow and white trail decoration, characteristic of the core-formed technique. All samples fall in the soda lime silica category using natron as a flux (Zacharias et al., 2008; Oikonomou, et al., 2012).

Methodology of the Research

In the present study 16 glass samples were studied using non-invasive analytical tools such as LED Optical Microscopy (LED-OM), Scanning Electron Microscopy coupled with an Energy Dispersive Spectrometer (SEM-EDS), and Rutherford Backscattering Spectroscopy (RBS) to thoroughly characterize the corrosion patterns.

In the first stage of the study, all samples were examined and documented macroscopically. The samples were categorized in three groups based on the alteration signs of their surface: (a) good – samples do not have any corrosion pattern on their surface; (b) slightly corroded – samples show corrosion patterns on the surface, no material loss and (c) medium – intensive iridescence and friable surface – material loss. The thickness of corrosion layer was not more than 1mm from the edge, so the fragments are not characterized as heavily corroded. (Brill, 1975)

LED-OM was used for the microscopic examination and documentation. Areas in which interesting patterns appear were selected for further examination. SEM–EDS was used for the microtopography examination and identification of the different corrosion patterns formed at the surface. The investigation and the comparison of the images of pristine glass and altered areas were carried out for all the samples (***Fig. 1***). The composition of the pristine and corroded glass was also determined. For the evaluation of the initial characterization of the preservation state, line scanning using a SEM-EDS and RBS performed at a Tandem accelerator was carried out. The depth profiling of the corroded area revealed the thickness of the leached layer.

Results

The corrosion patterns appearing at the samples are: iridescence, pitting - micropitting, crustation and semi opaque milky effect (***Fig. 2***). Furthermore, a gel layer formation was present. The hydrated silica layer was observed mostly at the vessels, though in some beads occurred under the iridescent layers. The formation of the gel layer is an indication of an environment of high humidity (Hench & Clark, 1978).

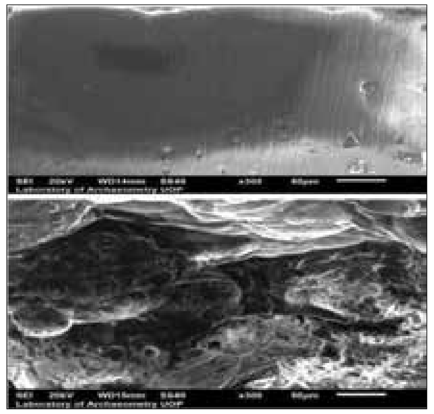

Fig. 1 Pristine and corroded areas of the same sample under SEM. The un-weathered area is smooth (up). The corroded areas (down) are covered with pits and have a spongy texture. O. KORDALI, N. ZACHARIAS, G.PROVATAS

The difference of the Na_2O on the pristine glass to the corroded was determined. The mean percentage of the alkalis loss for glass beads was 71.48 % and for vessels 93.37 %. The CaO is considered to be a stabilizer and up to 10 mol% reduces soda extraction. The molar percentage of CaO of the beads and vessels is 8.87 % and 6.27 % respectively. The vessels, which have lower calcium concentrations, are more likely to absorb water by the surface layers and corrode, than the beads (Jackson, et al., 2012).

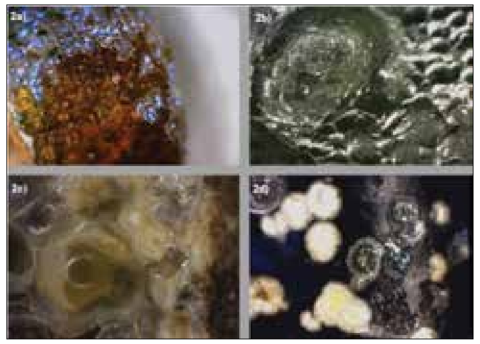

Fig. 2 Identified corrosion patterns under LED-OM: 2a (up left) iridescence, 2b (up right) pitting, 2c (down left) semi opaque milky like surface and 2d (down right) pitting with characteristic concentric layers forming local crust.

The examination was performed in four different manufacturing surfaces: even craft surface (beads), uneven surface (2 colored beads-fused surface), uneven surface (glass waste), and valleys-ridges (vessels-decoration trails). Through cross section examination of the core form vessels, it was observed that the thickness of lamination at the edge of the decoration trails was clearly bigger than the one at the blue body (***Fig. 3***). It is worth mentioning that the samples which were initially categorized at the medium preservation state were the glass waste samples. Glass waste samples and core formed vessels endorse the hypothesis that surface unevenness accelerate the decay rate.

The RBS analysis was performed in good and medium preservation state samples. For the first group, it revealed a variation of Na_2O as well as SiO_2, in different layers around 3-3.5 μm deep from the surface. The variation of the alkalis indicates, that the leaching out corrosion mechanism was in an initial stage. For the second group, RBS revealed a variation of the Al_2O_3 and CaO, which confirmed the hypothesis of the formation of Type III surface.

Since the bead samples have been buried inside a tomb, the development from outer to inner glass layers of SO_3, is an indication of contamination probably by organic residues (Palamara, et al., 2015). Natron which was the main ingredient - besides silica - for both vessels and beads, contains a small quantity of sodium sulfate. It is possible that the presence of sulfur at the samples, resulted by natron addition and augmented by organic residues contamination.

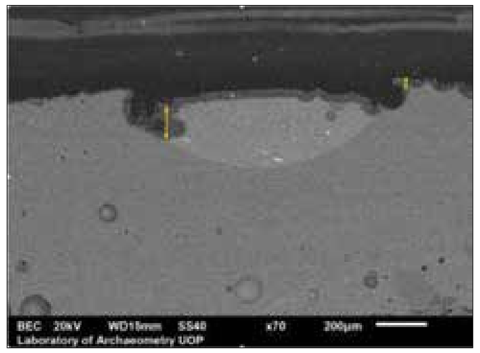

Fig. 3 Cross section of core-formed vessel sample. Under the SEM. The lamination thickness appear to be 5-6 times thicker than at the blue body.

Conclusions

The study resulted that the concentration of calcium oxide influenced the alkali leaching. A molar of CaO percentage closer to 10% reduces the corrosion mechanism. Different manufacturing technologies (e.g. beads vs. vessels) influenced the degree and extent of glass surface degradation. Using different analytical tools the corrosion depth for the vessels was determined and the preservation state was characterized. Moreover, the depth profiling information obtained by the RBS technique, for the beads, revealed a variation of the chemical composition of the leached leayers. A result that is in agreement with recent, more detailed, invasive studies (Schalm & Anaf, 2016).

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Research of a chemical treatment based on zinc salts for ancient glass objects sensitive to atmospheric degradation in museums

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Abstract

Zinc salts are known to have a positive effect on silicate glass surfaces against atmospheric alteration but the scientific bases are lacking to explain this effect. In this study we evaluate the potentiality of a treatment based on zinc salts to protect ancient glass objects from atmospheric degradation. In the meantime the mechanisms of the atmospheric alteration and the origin of the protection are investigated. To this purpose, glass replicas were aged in climatic chamber and altered layers were characterized with complementary tools (mainly SEM-EDX, Raman, NMR, SIMS). A positive effect of Zn(II) to reduce the replica glass hydrated thickness is confirmed and hypothesis are drawn to explain the results.

Keywords: Cultural Heritage, Museum Glass Objects, Atmospheric Alteration, Protection Treatment, Zinc Salt Deposit

Introduction

The deterioration of ancient glass objects by atmospheric alteration is a serious issue for the museum collections. Active degradation is indeed observed on the surface of numerous glass objects stored in museums, through macroscopic manifestations mainly like white salt deposit and crizzling, resulting in a loss of transparency and material disintegration [1,2,3]. Depending on the glass composition and the conservation conditions, the related mechanisms are not yet well understood. Until now the best protective measure applied by conservators and curators to slow down the alteration is the control of the environment (temperature, relative humidity, pollutants) within suitable museum display cases. Nevertheless, by acting directly on the glass surface, more efficient and less costly protective methods could be proposed. Inspired by an empirical industrial process aimed at protecting manufactured glass windows during their storage and transport [4,5,6], we are focusing in this study on the possibility that a small deposit of zinc salts may efficiently reduce the alteration kinetics of chemically unstable ancient glass (alkali(Na,K)–rich silicate).

To this purpose, the mechanisms underlying the atmospheric alteration as well as the protective action of zinc salts are investigated by means of ageing experiments (temperature and humidity control) on relevant ancient glass composition replicas. Even concerning the industrial process, there is no report in the literature on the mechanisms of zinc-based protective treatments. The respective effects of the ageing temperature, glass composition and zinc treatment on the morphological, structural and chemical evolution of the glass surface are evaluated.

Experimental methods and results

Three glass replicas representative of three unstable ancient glass compositions are studied: a mixed alkali (Na,K) lime silicate (late Middle-Age and Renaissance period), a soda-lime silicate (since Antiquity) and a potassium silicate with a low lime content (16th, 17th and 18th centuries). Polished glass plates (1x1x0.3 cm) and glass powders of controlled size fractions are used as starting materials.

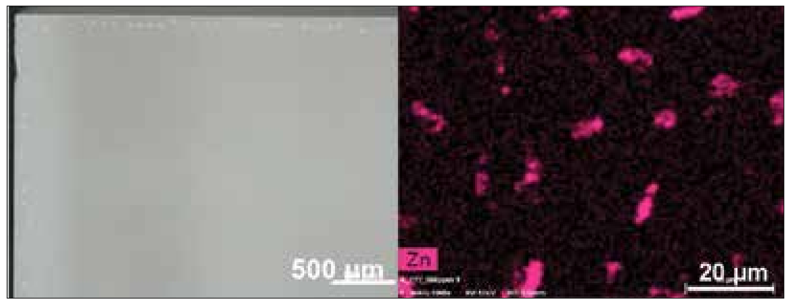

Fig. 1 Glass plate surface (not pre-altered) after a zinc salt spraying treatment (~ 1.2 µg/cm²). (a) binocular magnifier image (b) SEM image

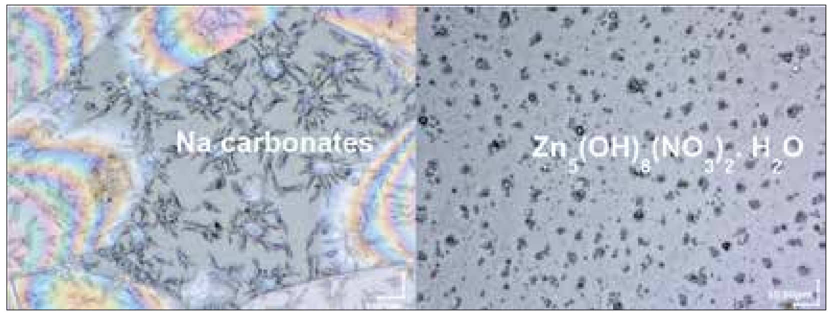

Fig. 2 Glass surface state after an accelerated ageing test (80 °C / 85 % RH / 3 days) (optical microscopy image). (a) without Zn (II) treatment (b) with a spraying treatment of zinc nitrate (about 1.2 µg/cm²) prior to the ageing.

In view of the application, we are evaluating an easy handling treatment method by spraying a low concentrated alcoholic zinc salt solution at ambient temperature. This treatment distinguishes itself from the industrial one, for which an aqueous Zn(II) solution is sprayed on hot glass surface (around 60 °C) at the end of the float process. A small amount of Zn(II) salt crystals is then deposited homogenously on glass surface (***Fig. 1a***), mainly as zinc precipitates (***Fig. 1b***). The total amount of Zn(II) is 0.1 to 1.2 µg/cm2, as evaluated by XRF, depending of the concentration of the zinc salt solution.

The effect of this treatment is assessed on pristine glass plates and also on pre-altered ones. Ageing experiments of glass plates (treated and untreated) and glass powders are performed at different temperature (40 ºC / 50 ºC / 60 ºC / 80 ºC) at 85 % RH (vapour of H_2O) for various time periods, in a climatic chamber or in an hermetic disposal with a saturated solution of KCl.

Our results highlight the remarkable positive effect of small amount of Zn(II) deposited by spraying to slow down the hydration kinetics of the mixed alkali replica glass at 80 °C and 60 °C. At these high ageing temperatures, the altered layers thicknesses are indeed considerably reduced for the investigated ageing times. For instance, in 3 days at 80 °C and 85 % RH, the hydrated thickness is reduced by a factor of 60 with a Zn(II) deposit of about 1.2 µg/cm2 (13 µm altered thickness for the untreated glass – SEM measurement - as compared with 200 nm for the treated one – TOF-SIMS analysis). The macroscopic manifestations such as the flaking of the surface and the formation of sodium carbonates (***Fig. 2a***) are suppressed with the treatment: only zinc nitrate hydroxide monohydrate ($Zn_5(OH)_8(NO_3)_2.H_2O$) and sodium or potassium nitrates are identified on glass surfaces (Raman, DRX) when treated with zinc nitrate (***Fig. 2b***). It is worth to notice that similar good results are obtained with zinc chloride salt with which the predominant phase that forms on surface is simonkolleite ($Zn_5(OH)_8(Cl)_2.H_2O$). For lower ageing temperatures, the same zinc hydroxide precipitates are observed on surface.

Preliminary results at 40 °C after three months ageing are very encouraging for the three replica compositions. For instance, for the glass A composition, the hydrated thickness has been reduced from 800 nm to 200 nm, as determined by Tof-SIMS analysis. Tests are still under way at 40°C and at ambient temperature, for a longer periods of time, because the alteration kinetics is very low at these temperatures.

In this study, ageing temperature has obviously a strong impact on the alteration mechanisms. In particular, at 80 °C, hydrolysis of the silicate network proceeds very fast and a hydrated solid phase is formed bearing a high concentration of silanol groups and molecular water (about 10 wt% H_2O – analysis of the O-enrichment by EDX and TGA analysis) characterized by strong hydrogen bonding (^1H NMR experiments). Alkali ions mainly stay embedded in the hydrated layer in the close vicinity of silanol groups and molecular water (^{23}Na and multi-nuclear ^{23}Na-^1H NMR experiments). Only a limited alkali depletion is detected by EDX. To explain these results, we suppose that at such a temperature of ageing, the acid-base reaction with Si – O – Na (or K) sites and Si – O – Si hydrolysis occurs with water molecules strongly bonded in a "ice-like" state on glass surface: thus, Na^+ and OH^- ions are not solvated but react rapidly to form Si – OH groups and regenerate Si – O – Na reactive sites [7]. On the contrary at 40°C, the hydrolysis rate is considerably reduced and a significant alkali depletion is observed. We propose that at this low temperature alkali and hydroxide ions are completely solvated and can migrate.

With a spraying treatment method, Zn(II) on glass surface precipitate with OH^- ions stemming from the first stages of the hydration process. This reactivity contributes to neutralize and stabilize the glass surface. Thus the hydrolysis rate is limited, slowing down silicate network disintegration and in depth water penetration.

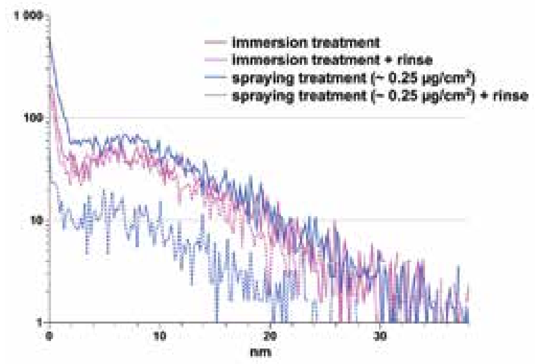

Fig. 3 Zn SIMS profile of a microscope slide after Zn(II) treatment by immersion (pink) and by spraying (blue) (~ 0.25 µg/cm²). The dotted line relates to the Zn profile when the treated glass plates are rinsed 5 min after the treatment.

Zn(II) is also detected on the surface outside the zinc hydroxide precipitates (about 0.1 µ g/cm² – EDX at very low accelerating voltage). This small amount of adsorbed Zn(II) could be responsible for a passivation effect, reducing the water diffusion into the glass network. To investigate this latter point, we compare the spraying treatment with a treatment by immersion at 60 ºC in an aqueous solution of zinc salt (pH close to 6.5) during 10 seconds. This method, similar to industrial treatments against glass alteration under atmosphere [6], allows Zn(II) to adsorb on the glass surface, at a low amount of about 0.1 µg/cm2 (from XRF measurements). By SIMS, we put in evidence the homogeneous deposition of Zn on the glass surface for both treatments, as well as the diffusion of Zn(II) into the glass near-surface porosity (***Fig. 3***). The treatment by immersion gives a similar positive result on the hydration kinetics reduction at 80 ºC / 85 % RH, confirming the hypothesis of a passivating effect induced by the adsorbed Zn(II) (***Fig. 4***). The origin of this passivating effect is not clear and research is carried out on the speciation of Zn(II) on the glass surface and its time evolution with the atmospheric ageing (in particular by Grazing Incidence X-Ray Absorption Spectroscopy at SOLEIL.

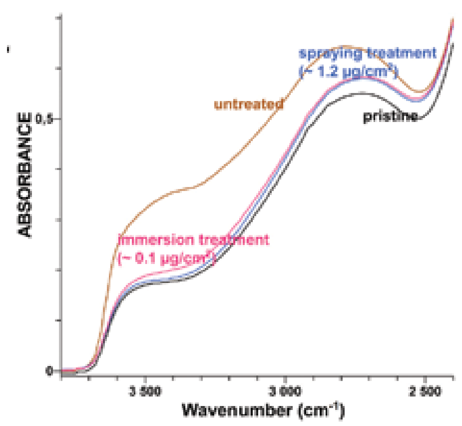

Fig. 4 Transmission FTIR spectra in the range 2400-3800 cm-1 (-OH group absorbance) of the mixed alkali silicate for pristine glass and after an ageing test (80 °C / 85 % RH / 1 day) for untreated and treated glass (by immersion (~0.1 µg/cm² and spraying (~1.2 µg/cm²)

Conclusions

A striking positive effect of Zn(II) on the reduction of the atmospheric alteration kinetics of a mixed alkali (Na,K) silicate glass replica has been clearly put in evidence on a large range of temperatures (40°C, 60 °C and 80 °C / 85 % RH). Atmospheric alteration mechanisms are strongly dependent on the ageing temperature, in particular the peculiar features of the altered layer formed at 80 °C in terms of composition (embedded alkalis) and structure (network depolymerization) are highlighted.

Hypothesis have been drawn on Zn(II) protection mechanisms and research is currently carried out to better understand the origin of the surface passivating effect. Then, it will be important to assess the long-term stability of the surface passivation, and to demonstrate the efficiency of this treatment on already altered glass surfaces. Besides, the characterization of ancient glass objects and the comparison with the aged replica gasses is mandatory to progress in the understanding of atmospheric alteration. It is another direction of our current study.

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Protecting historic window glass in Scotland - A look at planning application approval rates over a 10 year period

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Field of interest: Historic Preservation, Protection of Glass, Listed Buildings

Abstract

Conservation of built heritage in Scotland began around 1945 with many buildings being listed by the 1970s. Listed buildings and conservation areas in Scotland highlight national, regional and local importance, with the entirety of the building(s) being protected for future generations to enjoy. This research aims to help to highlight the need for protecting historic windows, one of the most vulnerable materials in buildings, and a material which is often overlooked as something that adds character or value to the building.

This research evaluates how clear historic window glass (glass made prior to the1960s with the manufacture of float glass being common post 1960s) is being preserved in historic buildings (Listed Building and Buildings in a Conservation Area). This research examined planning applications over a 10-year period (2005-2015) which involved work being done with windows. The approval, denial, and withdraw rates, help to illustrate how windows are being altered in historic buildings along with what action is being taken to encourage maintenance over replacement. To further examine the window replacement rates more in-depth, three years of applications based on the building category (Listed Buildings A,B,C and Conservation Areas) was examined to see if there were any trends with regards to approval/denial rates of window replacements in buildings based on the category, location, or other factors.

At the conclusion of this research the rates at which historic windows are being altered/replaced will help to illustrate the need for more active protection of historic windows. Along with encouraging more research in Scotland to understand the history of window manufacture nationally which will help to provide more information about the importance of preserving historic window glass.

Keywords: Historic Glass Conservation, Built Heritage

19th century stained-glass windows of two mausoleums from Belém do Pará, Brazil: a characterization study

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Field of interest: Conservation

Abstract

The mausoleums of *Assis Chermont* and *Britto Pontes* families, located in the city of *Belém do Pará* , northern Brazil, have spectacular stained glass windows produced in the late 19th century, which were commissioned from France and Portugal, respectively. These panels have been exposed to tropical weather for more than a century without any preventive conservation measure and the scientific investigation towards this valuable legacy is indispensable. Thus, the main objective of this work is to determine the chemical characteristics of 11 samples of 4 stained-glass windows from the mausoleums previously described and to identify the microorganisms existing on the biofilm which is deposited only on the surface of colourless glasses. The chemical composition was determined by WXRF. Surface's morphology and microorganisms' identification were carried out by optical microscopy. According to the analysis, the results indicate that all samples are soda-lime-silicate glass with approximately 70% of SiO_2 (***Table 1***). This fact increases their resistance to the weathering action, although some pits, opacity and iridescent areas are already visible. It was also verified that the amount of Na_2O is twice as high as K_2O, revealing the difference between this composition and another from stained glass windows produced in 19th century, studied by the literature. The biofilm is mainly composed by cyanophyceae (*Gloeocapsa Sp* and *Oscillatoria Sp*) and small animals *(Rotifera Encentrum Sp)*, as shown in Figure 1. The excreta (N and P) produced by the rotifers provide the algae with nutrients, although an excess of these compounds also contributes to the corrosion of the glass surface. Moreover, the lack of air circulation inside the mausoleum combined with the particularities of the tropical climate, contributes significantly to the development of the microorganisms. Finally, the studied stained-glass windows show a good state of conservation. However, it is necessary to regular monitor the panel's conditions, considering precipitation levels and relative humidity. This will guarantee the integrity of the panes and ensure their historical and aesthetic quality in the context of the local architectural heritage.

Keywords: Stained glass, Biodeterioration, Conservation, Soda-lime glass, Amazon region

Table 1 Samples chemical composition determined by WXRF.

Samples	Oxides wt.% (XRF)											
	SiO2	Al2O3	Fe2O3	CaO	MgO	Na2O	MnO2	K2O	PbO	Cr2O3	CuO	Other
ACM-1 (Colourless)	68,95	0,66	0,22	15,67	0,11	14,36	-	-	-	-	-	0,03
ACM-2 (Blue)	66,25	0,94	0,19	13	0,14	19,22	0,1	0,1	-	-	-	0,07
ACM-3 (Opaque lilac)	67,02	4,76	0,17	3,77	-	21,96	0,25	-	1,6	-	-	0,47
ACM-4 (Purple)	66,38	0,66	0,25	11,36	-	18,75	2,46	-	-	-	-	0,14
BPM-1 (Green)	65,38	1,12	0,46	9,23	-	21,6	-	0,48	0,49	0,57	0,47	0,2
BPM-2 (Yellow)	68,9	2,23	0,25	7,67	2,19	18,7	-	-	-	-	-	0,06
BPM-3 (Blue)	71,57	2,11	0,31	7,84	0,12	16,87	0,09	0,81	0,24	-	-	0,04
BPM-4 (Red Flash glass)	71,89	0,71	0,18	13,35	0,16	13,67	-	-	-	-	-	0,04
BPM-5 (Green)	67,92	1,77	0,24	9,72	-	17,19	-	2,21	0,55	0,18	0,14	0,08
BPM-6 (Colourless with enamel)	68,92	2,49	0,33	13,55	-	13,59	-	1,06	-	-	-	0,06
BPM-7 (Blue)	69,69	2,15	0,37	12,66	-	14,29	-	0,68	0,12	-	-	0,04

Obs.: (-) Below the detection limit.

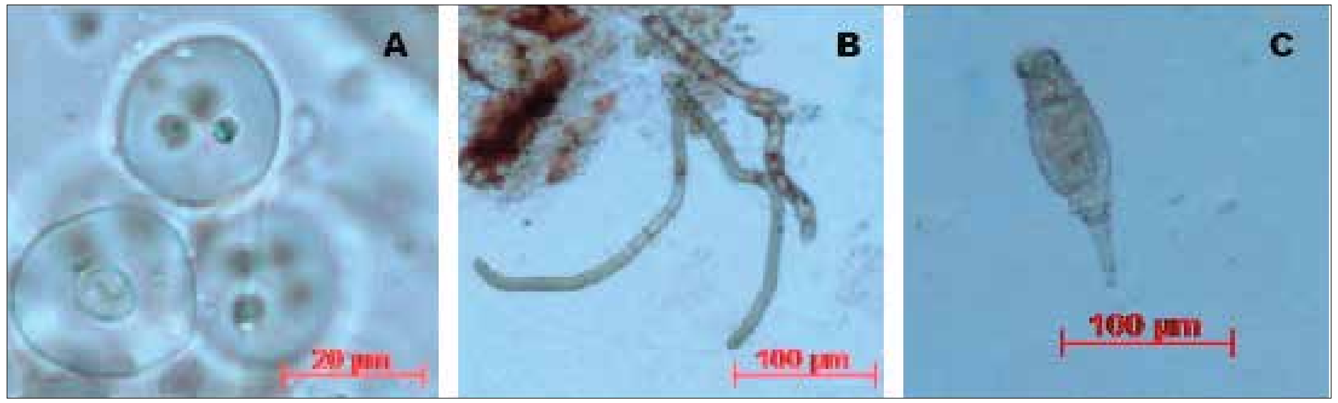

Fig. 1 Microorganisms found on Sample ACM-1: a) Gloeocapsa Sp.; b) Oscillatoria Sp.; c) Rotífera Encentrum Sp.

Organic Surface Coatings on Medieval Stained Glass and Microbiological Investigation

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Field of interest: Medieval stained glass conservation, protective glazing, climate measurement, archaeometry

Abstract

Project

Medieval stained glass has been treated with Polymethylmetacrylate coatings by Kwiatkowski[1] in Poland during the 1950s. Such treated panels were found in the Johannes Church of Torun (without protective glazing), in the Cathedral of Wloclawek (behind a protective glazing), and on glass kept in exhibition cases in the museum of Torun. Surface coatings have been detected and analyzed on the samples of Wloclawek and on samples from the museum of Torun, more than 60 years after the treatment occurred. No coatings have been found on samples in the Johannes Church, because of the direct weathering impact on the windows without a protective glazing during these years. In the SEM analysis of the coated samples evidence o microbiological growth have been found. The question to investigate was: Are organic surface coatings a source for enhanced microbiological activity?

Keywords: Medieval stained glass, SEM analysis, Microbiological investigations

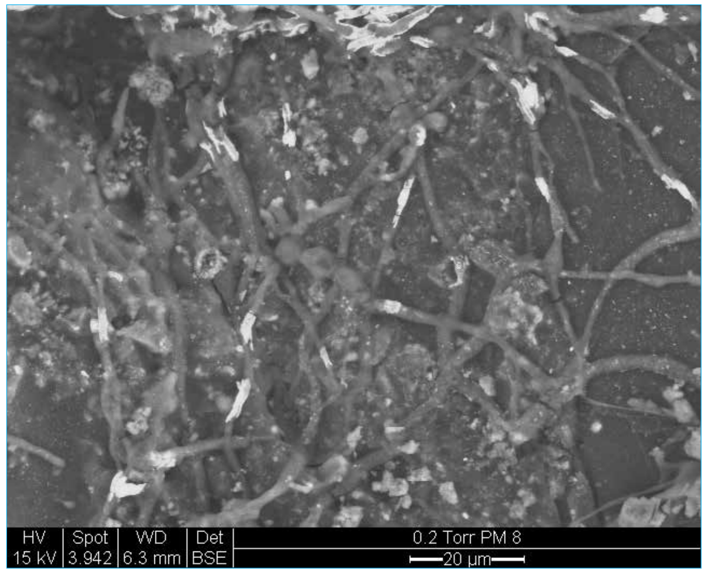

Fig. 1 Microbiological growth on a coated glass sample of Wloclawek (SEM)

[1] Annales du 2e Congr.s des Journ.es Internationales du Verre, Leyde 30 juin-4 juillet 1962, S. 137-151

Analytical Methods

Microbiological investigations were performed on samples, which contained coatings, using two strategies. Firstly, by extracting and sequencing of DNA from coated samples to detect and identify bacteria and fungi which grew on the glass surface and secondly by cultivating the bacteria and fungi under laboratory conditions using a media rich in appropriate nutrients to grow these specific bacteria and fungi.

Results

Direct DNA extraction of the bacteria found on the samples yielded no result. The second method showed that several Aspergillus strains could be identified after the cultivation using DNA sequencing of ITS regions. DNA was extracted via Phenol Chloroform and PCR was used for amplification of the ITS region. Data based identification of DNA sequences showed different types of Aspergillus in all samples (***Table 1***).

The results indicate that it can be assumed that there was no extensive contamination by fungi or bacteria if the glass was either coated or not.

Table 1: Identification of different types of fungi and bacteria

Sample	Organism	Specifikation
CW1	fungi	Aspergillus (Ascomycota)
CW2	fungi	Aspergillus (Ascomycota)
JCT1	fungi	Aspergillus spp. (A. glaucus or A. pseudoglaucus)
JCT2	fungi	Cladosporium ramotenellum, Aureobasidium pullulans, Cladosporium ramotenellum
MT1	fungi	Aspergillus (Ascomycota)
MT2	bacterium	Micrococcus luteus

CW: Cathedral Wloclawek, JCT: .Johannes Church Torun, MT: Museum Torun

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5th GLASSAC International Conference

POST-ROMAN GLASS IN THE IBERIAN PENINSULA
Vidro pós-romano na Península Ibérica
Vidrio post-romano en la Península Ibérica

The glass from Recópolis: an analytical approach

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Field of interest: archaeometry, archaeology, Visigothic Spain

Abstract

This paper examines the type of glass that was worked and used in the Visigothic city of Recópolis between the late sixth and early ninth century CE. Recópolis was an important production and consumption center with substantial archaeological evidence for glass working activities during the late sixth and into the eighth century CE. A selection of 200 well stratigraphically contextualized glass artefacts from the three glass working furnaces at Recópolis as well as the residential areas have been analyzed by LA-ICP-MS. This presentation discusses the analytical results and their historical and archaeological implications.

Keywords: Récopolis, Visigothic glass, Levantine I, Foy-2, glass workshops

Introduction

The excavations of the Visigothic city of Recópolis on a plateau on the Río Tajo near the village of Zorita de los Canes in the province of Guadalajara yielded an exceptionally large amount of glass finds. Among the finds were 3 furnaces in the commercial area of the city just south of the palatine complex, evidently dedicated to the processing of glass (Olmo Enciso, 2008). The stratigraphic evidence indicates that one of these workshops was active from the foundation of the city (578 CE) to the first half of the seventh century CE, while the activities of the second date mostly to the seventh century (600 - 700 CE), and the third furnace appears to have been active in the second half of the seventh century to about 700 CE (Olmo Enciso *et al*., 2008). The workshops seem to have mainly produced tableware (cups, plates etc.) as well as unguentaria and lamps (Castro Priego and Gomez de la Torre-Verdejo, 2008). Large amounts of glass fragments were also recovered from the residential areas, spanning the entire period of occupation from the last quarter of the sixth to the first half of the ninth century CE (Castro Priego and Gomez de la Torre-Verdejo, 2008). In order to shed light on the type of glass that was worked and used at Recópolis and its changes over time, 200 glass fragments were selected for chemical analysis. The chosen samples cover the entire range of object types, including working debris and crucibles, and span the entire period of occupation (phase R1, 578 CE to phase R6, 9th century CE). A high proportion of glass was selected from the workshops (a total of 126 samples across the 3 different workshops) to ascertain the variability of glass that was processed on site, while the remaining 74 samples come from the residential areas.

Methodology & Results

Small fragments of the glass objects were removed, embedded in epoxy resin and polished to facilitate analysis. Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS) was performed at the Centre Ernest-Babelon of the IRAMAT in Orléans (for a detailed description of the methods see e.g. Gratuze, 2016; Schibille *et al*., 2016).

Upon preliminary inspection of the analytical data all glasses are of a soda-lime-silica composition with levels of potassium and magnesium oxides generally below 1.5%, indicating the use of a mineral source of soda (Lilyquist and Brill, 1993). A total of 12 samples, all from workshop 2, have potash and magnesia levels in excess of this cut-off line (> 1.5%), which is more typical of glasses produced using a plant-ash component in addition to or instead of mineral soda. The majority of the remaining soda-lime-silica glasses appear to be associated with known primary production groups, specifically Levantine I and Foy-2. The possibilities and extent of recycling and the chronological dimensions of these practices will be explored.

Conclusions

The analytical results have significant implications for the interpretation of the glass working activities at Recópolis and the city's connectivity to the wider Mediterranean world (Olmo Enciso, 2015). The quantity and quality of glass highlight the major role of Recópolis as a glass working center during the sixth to eighth centuries. The conclusion that the raw glass originated in primary production centers in the eastern Mediterranean, testifies furthermore to ongoing commercial interactions between Visigothic Spain and the east.

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Caracterización y comercialización del vidrio en la periferia de al-Andalus (Ciudad de Vascos, Toledo)

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Field of interest: Archaeometry

Abstract

Se presentan los análisis de 150 fragmentos de vidrio de época islámica y tardoantigua procedentes del yacimiento de Ciudad de Vascos (Toledo). Se trata de un asentamiento situado en la frontera de al-Andalus por lo que resulta de gran interés para conocer las diferencias y similitudes con otros conjuntos medievales analizados en la Península Ibérica y en el contexto europeo y Mediterráneo.

Keywords: Islamic glass, HIMT, Levantine I

Introducción

El yacimiento de Ciudad de Vascos se encuentra situado en la orilla sur del río Tajo. Las excavaciones arqueológicas realizadas desde el año 1975 han revelado que fue ocupado durante la Edad del Bronce y el Bajo Imperio, convirtiéndose entre los siglos X y XI d.C. en un asentamiento urbano fortificado ubicado en la frontera de al-Andalus con los reinos cristianos. Tras la conquista castellana de la Taifa de Toledo en el año 1085 quedó abandonado hasta la actualidad (de Juan, 2016).

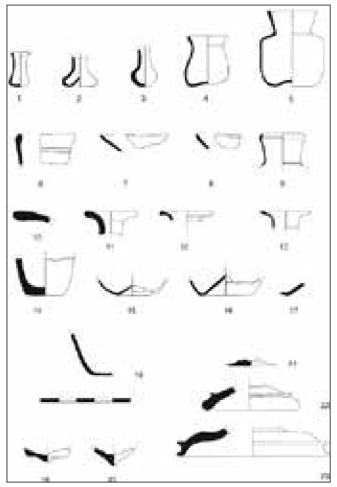

Fig. 1 Vidrios islámicos y tardoantiguos de Ciudad de Vascos (de Juan y Cáceres, 2016).

El vidrio era un material escaso entre los habitantes de este asentamiento de la periferia de al-Andalus. Este hecho, y la ausencia de restos de producción, evidencian que se trataba de un producto importado desde otras poblaciones. Los trabajos arqueológicos han permitido documentar una amplia variedad cromática de vidrios (incoloros, verdes, amarillentos, azules, blancos y púrpura) que se asocian a un diverso ajuar compuesto por vajilla de mesa (vasos, botellas y redomas), elementos de adorno (cabujones y cuentas), y de cuidado personal (sublimadores o ventosas, ungüentarios, ampollas y tapones), destacando también la presencia de algunos vidrios planos decorativos. A este repertorio hay que añadir copas y vidrios de paredes gruesas que recuerdan por su tipología a recipientes de épocas precedentes.

Con la intención de caracterizar los grupos químicos del vidrio utilizados en el yacimiento y conocer sus similitudes y diferencias con los presentes en otros lugares se seleccionaron un total de 150 fragmentos procedentes de un variado conjunto de contextos estratigráficos que se corresponden con los distintos momentos de ocupación identificados en el yacimiento.

Metodología

Las muestras analizadas comprenden la totalidad de los fragmentos de vidrio conservados en el Museo de Santa Cruz de Toledo (excluyendo las joyas de vidrio) que han sido recuperados en las excavaciones realizadas en el yacimiento en los últimos cuarenta años. Para su análisis se muestrearon pequeños fragmentos de 3mm^2 de superficie que fueron embutidos en resina epoxy y pulidos para facilitar su análisis. Las muestras fueron analizadas en el *Institut de recherche sur les archéomatériaux, Centre Ernest-Babelon (IRAMAT-CEB)* del CNRS y la Universidad de Orleans (Francia) por ablación láser con espectrómetro de masas con plasma acoplado por inducción (LA-ICP-MS), utilizando un espectrómetro de masas Element XR (Thermofisher) y una sonda de ablación laser de excímeros RESOlution M50e ArF (Resonetics) como se describe en Gratuze (2016) y Schibille et al. (2016).

Resultados

El análisis preliminar de los resultados ha permitido establecer que todos los vidrios son de tipo silicato sódico-cálcico pudiendo diferenciarse tres grupos principales de acuerdo a su composición. El grupo mayoritario (70%) lo constituyen vidrios elaborados a partir de sosa vegetal con altos contenidos de óxido de sodio (11-11%) y proporciones superiores al 1,5% en óxidos de potasio y magnesio. Este grupo de vidrios presenta una composición similar a la predominante a partir de los siglos VIII y IX en el oriente islámico (Phelps et al., 2016), y probablemente a partir del siglo IX en la Península Ibérica (De

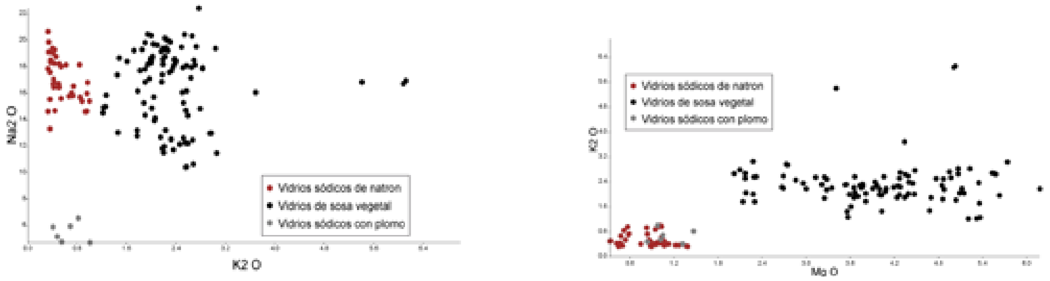

Fig. 2 Las diferencias en potasio, magnesio y sodio en los vidrios de Ciudad de Vascos permiten diferenciar los tres grupos de composición principales.

Juan y Schibille, e.p.). Un segundo grupo, que apenas alcanza el 4% del total de la muestra, se caracteriza por tener cantidades significativamente elevadas de plomo (40-48%). Vidrios sódicos con alto contenido en plomo han sido descritos previamente en el Próximo Oriente medieval (Sayre y Smith, 1963), en el norte de África y en la Península Ibérica en Córdoba (Duckworth et al., 2015) y Murcia (García, 2008). Un tercer grupo constituye el 25% del total de los vidrios analizados. Son vidrios de tradición romana fabricados con fundentes sódicos de origen mineral (natrón) caracterizados por sus bajos contenidos en óxidos de potasio y magnesio (<1,5%). Todos los ejemplares que por sus características tipológicas pueden atribuirse a época preislámica se incluyen en este grupo, mientras que en él se encuentran ausentes las formas de cronología claramente medieval. La procedencia de este grupo de vidrios hay que situarla en el Mediterráneo oriental, identificándose vidrios con altos contenidos en hierro, manganeso y titanio (HITM) de posible procedencia egipcia y vidrios con elevados contenidos de aluminio y calcio (Levantine I) de posible origen sirio-palestino.

Conclusiones

La investigación realizada ha permitido caracterizar por primera vez los tipos de vidrio consumidos y comercializados en los siglos X y XI en una pequeña población fronteriza situada en extremo norte de al-Andalus. Los resultados demuestran la coexistencia de diferentes técnicas de fabricación que posiblemente son el reflejo de la coexistencia de distintos centros productores que abastecieron al centro peninsular durante este periodo, poniendo de manifiesto la relación existente con los centros vidrieros contemporáneos del oriente islámico y evidenciando la transmisión de saberes tecnológicos entre los dos extremos del Mediterráneo. Por el contrario, la inexistencia de vidrios cálcico-potásicos en el conjunto analizado permite distinguirlos claramente de los vidrios contemporáneos en el ámbito cristiano centroeuropeo. La identificación de vidrios de natrón pertenecientes a grupos químicos bien conocidos ha permitido desechar la adscripción al periodo islámico de algunos tipos que a partir de su contexto estratigráfico presentaban dudas sobre su adscripción cronológica, ayudando a precisar la cronotipología de los vidrios islámicos del centro peninsular.

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Chemical characterisation of Islamic glass from Silves' Castle (Portugal)

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Field of interest: archaeometry, archaeology, Islamic Iberia

Abstract

Archaeological excavations conducted by one of us (RVG) since 1984 at Silves' Castle (Portugal) yielded a significant eleventh- to thirteenth-century glass assemblage. A representative cross-section of different artefact types from different well-stratified contexts was selected for LA-ICP-MS analyses. We present the analytical results as a function of the different vessel types (goblets, bowls, jugs, jars and small flasks) and different colours.

Keywords: Silves' Castle, Islamic glass, Gharb al-Andalus, Medieval fortifications

Introduction

The excavations of the early medieval fortifications of Silves' Castle produced substantial glass finds (Gomes, 2003). Typological evidence suggests that some of the glass objects might have been produced on the Iberian Peninsula, whereas others might have been imported from Syria and Egypt (Gomes, 2015). This raises the possibility that Silves was well integrated into the commercial networks of al-Andalus and connected via long-distance trade to the eastern Mediterranean.

A series of glass vessels from different contexts have been analysed for major, minor and trace elements in order to establish the chemical characteristics of the glass finds and to elucidate the relationship between vessel types and base glass composition. This will allow us to explore the geographical and chronological dimensions and key developments in the use of glass in late Islamic Silves.

Methodology & Results

The glass fragments were analysed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the Centre Ernest-Babelon of the IRAMAT (Orléans, France), using an Element XR mass spectrometer (Thermofisher) and a RESOlution M50e ArF excimer laser probe ablation device (Resonetics) as described in Gratuze (2016) and Schibille et al. (2016).

The analytical results will be compared to compositional data of glass from other Iberian sites such as Cordoba, Murcia, Pechina and Vascos (Duckworth et al., 2012; García-Heras, 2008; Jiménez Castillo 2000 & 2006; de Juan and Schibille, forthcoming). This will significantly improve our understanding of the chemical characteristics of principal glass groups in circulation on the Iberian Peninsula during the Islamic period. A high chronological resolution of the glass finds will enable us to refine the temporal developments of glass production in Iberia and its relationship to Palestinian and Egyptian glass manufacture.

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The al-Andalus Glass Project: Production and Invention in Medieval Iberia

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Field of interest: Special Day (Post-Roman Glass in the Iberian Peninsula); Archaeology/Archaeometry; History

Abstract

In this presentation we will provide the latest data and interpretations of the al-Andalus Glass Project, which since 2010 has investigated glass production in the Iberian Peninsula, from chemical, historical and archaeological perspectives. A combination of archaeological and historical synthesis, new fieldwork, and laboratory analysis will be presented.

The evidence to date paints a dynamic picture of the importation of glass, and the development of a native Iberian glass industry. Technological know-how for vitreous materials production was transmitted from the East Mediterranean and North Africa to the Iberian Peninsula where it was in some cases developed and modified, eventually also influencing the glass and glazed ceramics industries of Christian Iberia and the Italian Peninsula. The relationship between glass and glazed ceramics may have been more important than has previously been accounted for, and we are starting to trace glimpses of concomitant developments in the two technologies. New considerations to be discussed in our presentation include the location of glass workshops in urban contexts, and the degree to which glass production was controlled by the state over time.

Finally, we shall reflect on how much has been achieved in the past seven years, and consider the future directions which should be taken by researchers interested in medieval glass in the Iberian Peninsula.

Keywords: Archaeometry, Glass production, al-Andalus, Recycling

Introduction

Since the publication of Alice Wilson Frothingham's 'Spanish Glass' in 1963, there has been no synthetic work on medieval glass in the Iberian Peninsula. The al-Andalus Glass Project was established with the aim of significantly advancing our understanding of this subject, particularly the context of production, and particularly – though not exclusively – for Islamic Spain. We are approaching this through a combination of archaeological and textual sources, including glass recipes, with scientific analysis of glass fragments derived from production and consumption contexts.

To date, we have conducted a synthetic overview of medieval glass furnaces in southern Spain (Duckworth and Govantes-Edwards 2015); analysed sets of glass samples from several archaeological sites (see Duckworth et al. 2015); and examined the technical recipes of later Spanish writers in order to determine the extent to which they might inform us about practices in Islamic Spain (Govantes-Edwards et al. 2016). More recently, we have continued our programme of analytical work, and in collaboration with Dr Alberto García Porras and Prof. Kate Welham, have embarked upon two 'sister' projects, which are archaeologically investigating the context of pyrotechnological production at the palace sites of Madinat al-Zahra, Córdoba, and the Alhambra, Granada. As part of a British Academy-funded project conducted by Chloë Duckworth, we are also developing our understanding of the role of the Iberian Peninsula in wider patterns of glass trade and technology transfer, with a particular focus on the role of recycling, both in the past and in our own investigative methodologies.

Through this work we are gradually building a more nuanced picture of glass production, trade and use in medieval southern Spain, with some relevance to the entire Peninsula and beyond (e.g. Duckworth et al. 2014). While there remains much work to be done, it is becoming clear that glass and glazed ceramics production were closely related; that patterns of trade and consumption are far from simple, with recycling playing a major role; and that glass technologies were significantly more regionalized than has previously been accounted for.

Conclusions

In the past seven years, the al-Andalus Glass Project has transformed our understanding of glass production in southern Spain, and fed into broader pictures of glass production, trade and consumption in the Iberian Peninsula and beyond. Our ongoing research demonstrates the importance of considering regionality in glass production, and the significance of cross-craft interaction between glass and glazed ceramics in technological change over time. Yet much work remains to be done, and we look forward to the opportunity to engage with other scholars who are developing this, and similar fields of research.

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Aproximacion al contenido de un unguentario andalusí por GC-MS (Albalat, Extremadura, s. XII)

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Área de interés: Arqueometría

Resumen

La aplicación de técnicas analíticas al estudio de los vidrios andalusíes se encuentra todavía en una etapa incipiente. Aunque nuevos resultados obtenidos en el marco de recientes proyectos de investigación están arrojando luz sobre sus características tecnológicas y composicionales, poco sabemos sobre lo que contenían los recipientes de vidrio, utilizados principalmente en contextos domésticos. Más allá de las hipótesis que pueden plantearse en base a fuentes textuales e iconográficas y en la correlación morfológico-funcional, es posible aplicar el método de cromatografía en fase gaseosa (método separativo) acoplada a la espectrometría de masa (método estructural) para tratar de determinar su contenido. Esta técnica, cuando se aplica con un protocolo de doble muestreo, permite obtener información sobre los residuos orgánicos conservados bajo forma soluble (lípidos, aceites, resinas, ceras, etc.) e insoluble (marcadores de frutas como el ácido tartárico de la uva o fermentación alcohólica para el vino).

Exponemos aquí los resultados de un análisis realizado sobre el fondo de un ungüentario hallado en el yacimiento de Albalat (Romangordo, Extremadura), y procedente de un contexto arqueológico fechado en época almorávide, primera mitad del s. XII. Su análisis ha permitido invalidar la hipótesis inicial según la cual este frasco podía haber contenido algún líquido, tal vez un perfume. A pesar de la conjunción de varios factores adversos (ausencia de residuos visibles sobre las paredes internas, concentración muy débil de materia orgánica conservada y presencia de numerosas contaminaciones postdeposicionales), el análisis orgánico ha identificado compuestos naturales: una base grasa constituida por productos lácteos, aceite de oliva y cera vegetal, junto con marcadores de una grasa subcutánea y/o de una piel sebácea de origen animal (***Fig. 2***). Estos productos apuntan a la composición de un bálsamo, sin poder determinar una finalidad cosmética o terapéutica.

Palabras clave: GC-MS, Al-Andalus, Albalat, Unguentario, Bálsamo

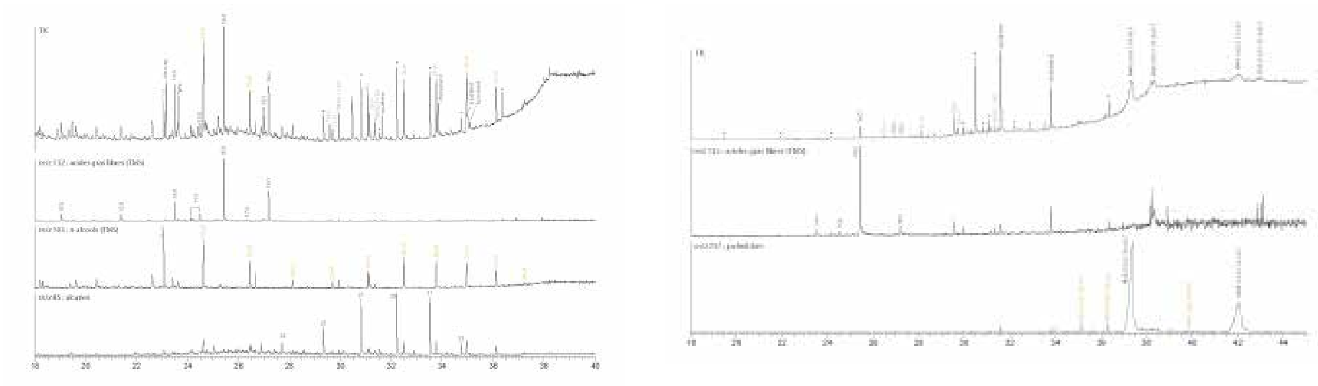

Fig. 1 Cromatógramos de los dos extractos (primer lipídico a partir del sedimento y de residuos sólidos y segundo a partir del lavado de las paredes con solvente).

Medieval Glass from Santarém (14^{th}-15^{th} centuries)

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Field of interest: *Archaeology*

Abstract

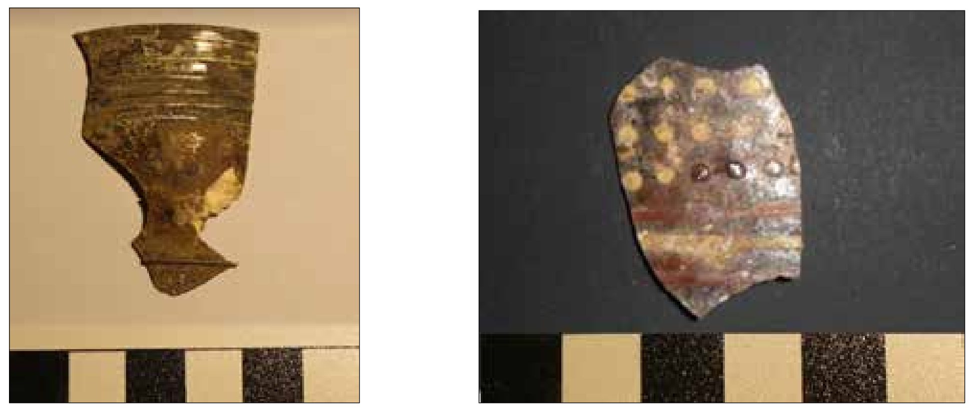
Archaeological excavations in Santarém identified a few dozen storage pits filled with domestic garbage in the late 14th and 15th centuries. Associated to these contexts hundreds of material culture elements were found such as pottery, metals and some glass objects.

Medieval glasses can be associated to different forms such as goblets, beaker shaped vessels, and bowls and what seem to be fragments of bottles. Decorations vary from concentric lines around the object's body to small dots and different colours.

The origin of these objects is yet under discussion since we have no information about the production of glass in medieval Santarém. However the resemblance of such glasses with Lisbon production may in fact indicate the acquisition in Portugal's capital. Other objects are similar to European productions.

This poster is the first news of these discoveries as well as the first approach to the consumption of medieval glass in Santarém aiming to understand what type of objects were being consumed by medieval populations.

Keywords: Glass, Decoration, Middle Ages



Glass vessels from Santarém

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Beber a la Moda: copas, tazas y otros materiales arqueológicos en Mallorca (1500-1700)

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Área de interés: Historia del vidrio, arqueología, arqueometría

Resumen

En esta aportación se analizan materiales procedentes de tres excavaciones arqueológicas urbanas realizadas recientemente que permiten conocer con mayor precisión los tipos de objetos de vidrio utilizados en Palma en la época moderna. En esta aportación se estudian estos objetos de origen catalán y probablemente veneciano y se plantean hipótesis relativas a la producción local teniendo en cuenta los materiales ya publicados procedentes de ocho excavaciones urbanas.

Palabras clave: Venecia, Cataluña, "façon de Venise", Mallorca, España

Introducción

El notario mallorquín Pau Ribas, en la contraportada de pergamino de uno de sus libros profesionales, anotó que "@ 1 setembra 1640 tinch sinquanta dos peces de vidre vanesià". Esta referencia a su ajuar vítreo formado por 52 ejemplares venecianos probablemente refleja su gusto por coleccionar y usar objetos de cierta calidad. Además, es una muestra clara de la incorporación de las modas cortesanas y de la presencia abundante de vidrios de origen italiano y a la "façon de Venise" en la isla; sin embargo la realidad material no refleja esta importancia documental, ya conocida por estudios anteriores (Capellà 2015). El corpus de objetos procedentes de Mallorca conservados de época moderna tanto por coleccionistas privados como por instituciones públicas es muy reducido. Por esta razón, para poder realizar un estudio del vidrio en el antiguo Reino de Mallorca es necesario acudir a las fuentes escritas de la época y a los materiales arqueológicos. Los objetos y fragmentos recuperados sistemáticamente en excavaciones arqueológicas de depósitos urbanos excavados en la roca en los solares de casas en la ciudad de Palma desde finales de los años 60 del siglo XX han permitido conocer una realidad material prácticamente desaparecida.

La producción vítrea insular en la época moderna estuvo determinada por la influencia directa ejercida por los talleres de Cataluña. Esta se ejemplifica con las conexiones que se establecieron mediante la importación de vidrios y la llegada de numerosos artesanos, en especial, desde Barcelona y Mataró donde se situaban los talleres más innovadores de la antigua Corona de Aragón. Los hornos de la ciudad de Mallorca realizaron en este período una producción de vidrio común y algunas producciones de vidrio artístico, que no podemos diferenciar de las catalanas. Tan solo disponemos de información arqueológica de un único taller, que estuvo activo durante la segunda mitad del siglo XVII (taller de Sa Gerreria, (***Fig. 1***). Este yacimiento proporcionó a los investigadores numerosos materiales (crisoles, herramientas, restos de vidrio, goterones y restos de piezas), que son fundamentales para la comprensión del vidrio producido en la isla. De una parte de los vidrios se ha realizado unos primeros estudios arqueométricos (Capellà y Albero 2015), totalmente preliminares que, esperemos que pronto con la colaboración de otros investigadores, puedan completarse y ampliarse con el análisis de más materiales arqueológicos recuperados en contextos de la misma época de la ciudad. Así, se podrá avanzar en un mejor conocimiento de la producción de los talleres mallorquines. Los restos de piezas localizados en este taller no

Fig. 1 Restos de elaboración, segunda mitad del siglo XVII. Excavación arqueológica de la Gerreria, Palma.

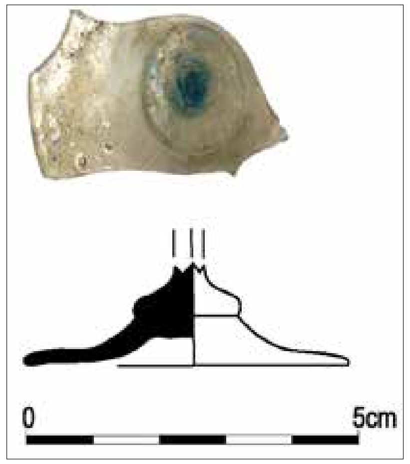

Fig. 2 Base de copa, segunda mitad del siglo XVII. Excavación arqueológica de la Gerreria, Palma.

Fig. 3 Copa con decoración de lacticinio, probablemente Cataluña, segunda mitad del siglo XVI-primera mitad del XVII.

Fig. 4 Fragmento de taza con decoración de filigrana, probablemente Venecia, segunda mitad del siglo XVI.

permiten evidenciar que se tratase de una infraestructura capaz de desarrollar las técnicas más sofisticadas "a la façon de Venise", que sí se constatan en Barcelona, aunque sí se produjeron algunas piezas con decoraciones de influencia italiana (***Fig. 2***). En este sentido, es fundamental citar que en Mallorca está documentado entre 1602 y 1605 Domingo Barovier, junto a otros miembros de su familia, que en un documento escrito afirmó haber enseñado las técnicas venecianas características de inicios del siglo XVII a los maestros mallorquines (Rodríguez 1988). Aún a día de hoy, no se ha podido comprobar, ni con documentos ni con materiales arqueológicos, la veracidad de las afirmaciones realizadas por Barovier ante las autoridades locales.

La realidad material recuperada en diferentes excavaciones de yacimientos en la ciudad de Palma, refleja la presencia de materiales que clasificamos como catalanes. Así, por ejemplo en una excavación realizada en 2015 apareció un interesante conjunto de objetos con decoraciones de cordones de lacticinio, con un ejemplar en muy buen estado de conservación, que bien podría ser producido en la isla (***Fig. 3***).

Finalmente, la realidad arqueológica ha aportado numerosos ejemplos de piezas venecianas importadas. Como es el caso de un fragmento de taza u otro contenedor con decoración de filigrana que, lamentablemente, está en mal estado de conservación (***Fig. 4***), entre otros ejemplares.

Conclusiones

Gracias a su situación geográfica, en el puerto de la Ciudad de Mallorca (Palma, en la actualidad) confluían las rutas comerciales mediterráneas que conducían desde Italia hacia el Atlántico, siendo un enclave estratégico en la distribución de materias y de hombres. Aunque el mercado insular era reducido, entre 1500 y 1700 hemos podido documentar más de 100 vidrieros activos en la isla, señal de una significativa actividad productiva. Por esta razón, el estudio de los materiales arqueológicos contribuye al conocimiento de la capacidad productiva de sus talleres, de la redistribución de producciones y también del uso que se realizó de esta preciada materia en la época.

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Vidros, do século XVI, do Poço-Cisterna de Silves

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Área de interesse: Arqueologia

Resumo

Escavações arqueológicas, conduzidas pelos signatários, no Poço-Cisterna islâmico de Silves, hoje Monumento Nacional, verificaram que aquele foi entulhado nos finais do século XVI. Entre o numeroso espólio ali exumado contam-se fragmentos de diversos recipientes (garrafas, frascos) e adornos (contas e braceletes) de vidro (***Fig. 1***), produzidos com vidro transparente ou colorido que, embora alguns estejam em exposição no Museu Municipal de Arqueologia daquela cidade, não se encontram devidamente estudados. Trata-se tanto de produções possivelmente nacionais como de outras importadas, usadas nos quotidianos urbanos de casas de populações com relativo poder económico, conforme se pode deduzir das faianças, espanholas e italianas, das porcelanas chinesas e de muitos outros artefactos a que aquelas se associavam.

Palavras-chave: Poço-cisterna, Silves, garrafa, bracelete, contas

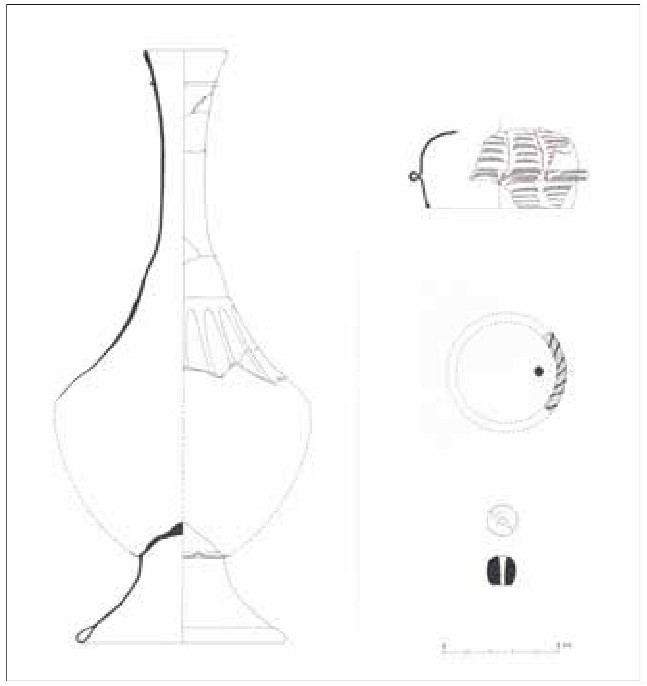

Fig. 1 Espólio vítreo do Poço-cisterna de Silves (seg. M. V.Gomes e R.V.Gomes)

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Potassium-rich glass in Lisbon in the 18th century

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Field of interest: archaeometry, history of glass, archaeology

Introduction

From two archaeological interventions performed in Lisbon (more precisely at Rua do Arsenal (LRA), where the ruins of the Côrte-Real Palace were partially discovered, and at the Roman Theatre Museum (LTR), where the remains of a middle-class house dated to the 18th century were found), a group of twenty-five colourless glass fragments was unearthed. This group of colourless glasses was analysed by µ-PIXE and proved to be of a potassium-rich composition, which relates with the Central European glassmaking tradition. The shapes and decorations of the glass fragments can find parallels with other coeval European archaeological assemblages, as well as with the glass production from the Coina Glass Factory in Portugal.

As far as it is known, until the end of the 17th century glass circulating in Portugal was of a soda-rich composition (Coutinho 2016). This suggests that Portugal followed a Mediterranean glass-making tradition, and that the trading in glass with the North and Central European areas was low or inexistent. The 18th century European glass innovations, related to the development of lead glass and potassium-rich glass, spread very fast all over the Portuguese territory and its use (and production?) quickly became almost exclusive (Pulido Valente et al. 2016; Coutinho 2016).

The information about Portuguese glass production comes in majority from historical documents, and the only excavated furnace was the Coina Royal Glass Factory, active between 1719 and 1747. According to J. Custódio, glass *à la façon de Bohème* was being produced in the Coina Glass Factory during the first half of the 18th century (see figure 1) (Custódio 2002, p.113). Concerning other Portuguese glass productions, in 1768 a contract was made between two German entrepreneurs (João Galo and João Jorge, the original German names unknown to us were adapted to Portuguese in the written documents) and the Salvaterra de Magos glass manufactory, with the intent of making its production closer to that of the Bohemian tradition (Custódio 2002, pp.52, 54).

Keywords: Potassium-rich glass, Early Modern period, Archaeometry

Results and Discussion

Analysing the shapes and decorations of the unearthed objects, fragment LTR0014 (figure 1), belongs to an octagonal flask decorated with polychrome enamels, a feature typical of Central European glass from the 17th to 18th century (see for example: Metropolitan Museum of Art, Accession Number 13.179.70a). Flasks with the same shape and very similar decorations were identified among the objects excavated at the Coina Glass Factory. One flask with this shape and a resembling motif is present in the Soares dos Reis Museum, Porto, attributed to the Marinha Grande Glass Factory (figure 1 b). The difference between the two objects is that the design on fragment LTR0014 is enamelled, while on the flask at the Soares dos Reis Museum was engraved (Custódio 2002, p.244,246). Another flask also attributed to the Coina Glass Factory can be seen in figure 1 a), presenting an enamelled motif of the Portuguese shield.

The faceted drinking glasses represented in figure 1 (fragments LTR0055, LTR0063, LTR0064, LRA0126) often appear among the LTR and LRA archaeological excavations in different sizes. These shapes were identified in the Marinha Grande Glass Factory Catalogue, which proves that these type of beakers were produced in Portugal. These shapes were also identified among the finds from the Cistercian nunnery of Clairefontaine in Belgium, showing that these models were in fashion and circulating throughout Europe (Hellemans et al. 2014).

The archaeometric study tried to answer the provenance questions. Chart in figure 2 has the representation of literature values for K_2O ***vs.*** CaO contents taken from Table X.3 (Coutinho 2016). This comparison with literature is based on limited number of data and for that reason the conclusions drawn are only tentative. The reported values for Bohemian glass have very high contents of CaO apart from one reported group (Group F). This is also true for the values reported for Polish glass from Elblag and Poznan (Hellemans et al., 2014). Fragments LTR0064, LRA0006, and LRA0076 are the only fragments that in terms of potassium and calcium oxides can be related with Polish glass from Elblag and Poznan. The great majority of fragments analysed from the LTR and LRA sets are consistent with the Portuguese production from the Coina Glass Manufactory. These fragments are also consistent with the Belgium CL1.1 group reported in Hellemans et al. (2014). However, in general, the values of titanium, manganese and iron oxides of the samples unearthed in Lisbon are lower comparing with the Belgium CLF reported values.

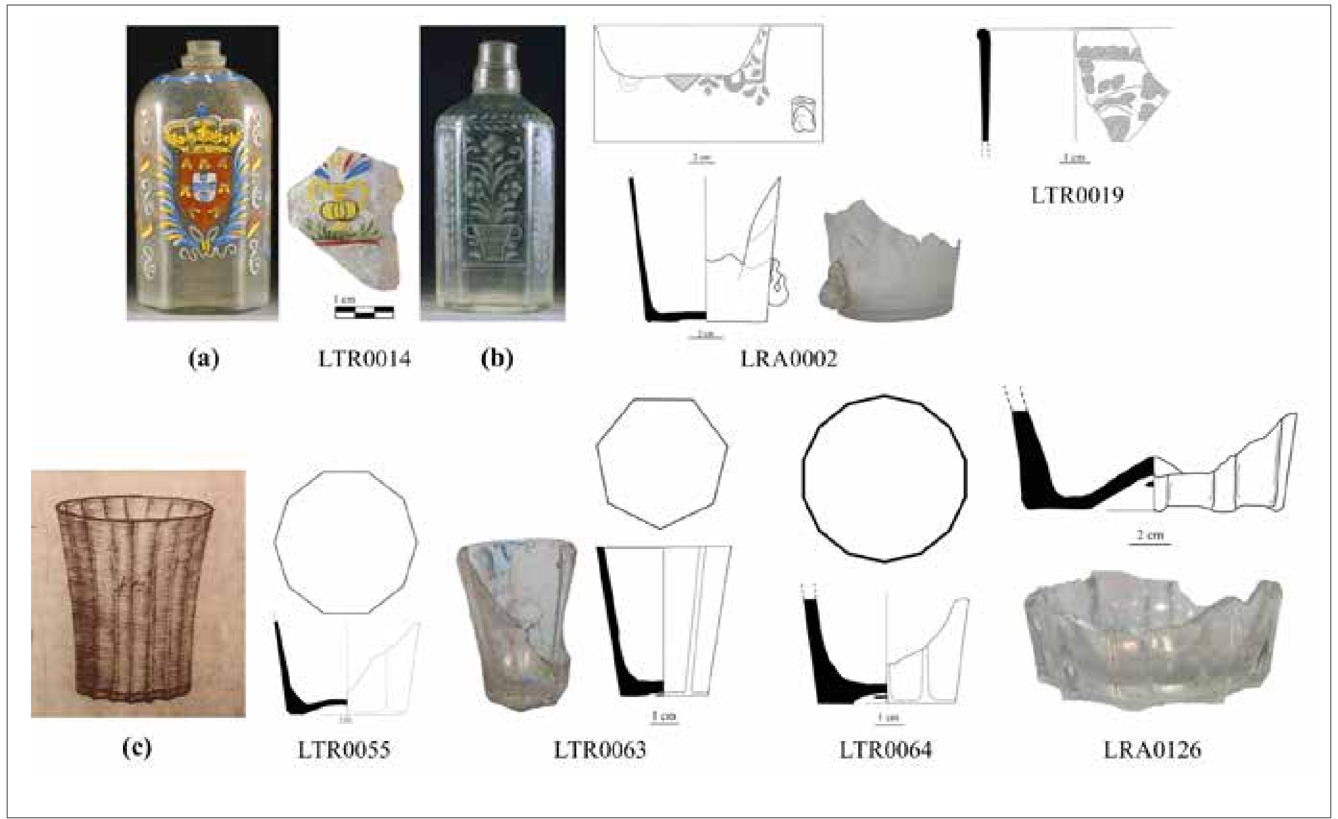

Fig. 1 *Examples of fragments unearthed in the two Lisbon archaeological excavations (LTR – Lisboa, Museu do Teatro Romano and, LRA – Lisboa Rua do Arsenal) identified with the respective inventory numbers and examples of objects found in Portuguese museums that were identified as probable Portuguese productions: (a) Polyhedral flask with enamelled decoration, attributed to Coina Glass manufactory, dated ca. 1719-1747. Accession no 342 Cer/MNSR; (b) Polyhedral flask with engraved decoration, attributed to Marinha Grande Glass Factory, dated ca. 1747-1767 (John Beare administration period). Accession no 314 Vid CMP/MNSR; both objects in Museu Nacional Soares dos Reis. (c) Drawing (unknown author) of a drinking glass dated to the mid-18th century and presented in the Catalogue II from Marinha Grande Glass Factory, print XLI.4, in (Barros 1969).*

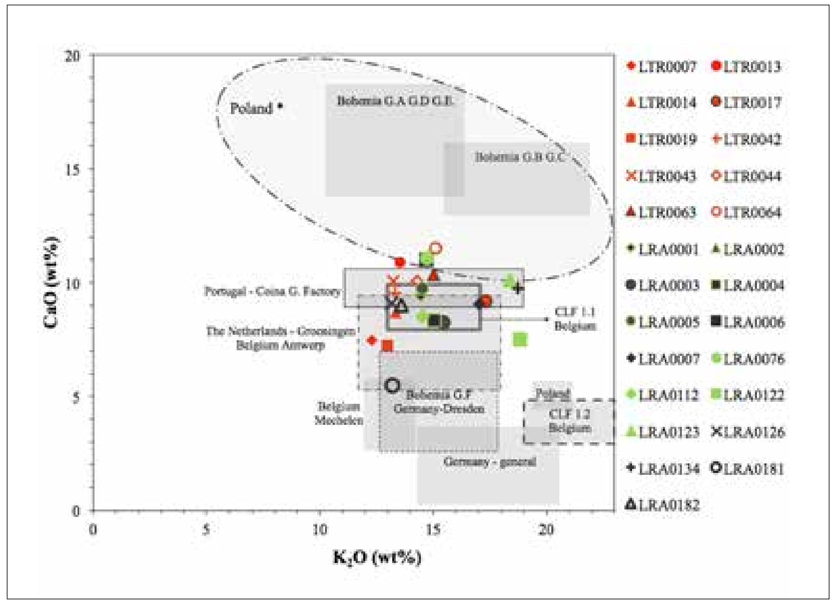

Fig. 2 Binary plot of K_2O vs. CaO concentrations, in weight percent of oxides and determined by means of μ-PIXE and LA-ICP-MS for the potassium rich glass. It is possible to observe mean values (considering the standard deviation) collected from literature and present in Table X.3 (Coutinho 2016), plus the area representing analysed glass found in Poland (Poland *), discussed in Hellemans et al. (2014) and referenced as Kunicki-Goldfinger et al, forthcoming.

Conclusions

Decorative features allow one to propose that LTR and LRA objects (ribbed beakers, engraved and enamelled vessels), were attempts to imitate glass produced in Central Europe, namely Bohemia. For the majority of these objects, a national production can be considered, and it should be stressed that Central European glassmakers worked in the Coina Glass Manufactory, as well as in the Salvaterra de Magos furnace. With this investigation, it became clearer the need for further studies on the glass that circulated in Portugal in the Early Modern period. These studies will allow one to broaden the knowledge on the trading of glass and glassmakers around Europe.

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Vidro e sociedade. A vidraria da estação arqueológica do palácio dos marqueses de Marialva nos sucessivos contextos sociais, laborais e económicos sucessivamente documentados (séc. XVII – início do séc. XIX)

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Área de interesse: Arqueometria, arqueologia.

Resumo

Júlio Dantas foi mal querido dos modernistas como Almada Negreiros. Todavia, devem-se-lhe obras que, tal como as de Júlio Dinis, são o repositório de memórias preciosas para o entendimento de certos ambientes e dos objectos que os povoaram.

O século XVIII, época charneira (do poder real absoluto, da afirmação do barroco e de monumentais remessas de ouro do Brasil) entre a época de desalento da Guerra da Restauração, na 2ª metade do séc. XVII, e as invasões francesas que deslocalizariam o poder real para o Brasil, é o da criação da Real Fábrica de Vidros cuja produção se encontra largamente representada no espólio vítreo dos marqueses. É, também, a época que melhor evoca o quase memorialista Júlio Dantas.

Todavia, o palácio, data do século XVII, como qualquer organismo vivido mereceu obras, foi sepultado pelo terramoto de 1755 e seria parcialmente reconstruído até completamente do mesmo terem desistido os marqueses a favor dos moradores menos abastados dos chamados casebres do Loreto, pelo que, no espaço que ocupou, foram encontrados objectos muito diferentes ao serviço das mesmas funções. É esta abordagem diacrónica da vidraria que, informada pela História e, por isso, apoiada em fontes escritas e iconográficas, trazemos a este forum.

A estética barroca, nos seus aspectos principais, encontra-se associada, em particular, à produção da Real Fábrica criada em 1719, sob D. João V, com o carácter de manufactura no que respeita a organização do processo produtivo. Sobreviveram-lhe, todavia, agentes das produções vidreiras anteriores, artesanais e historicamente sucessoras da melhor vidraria do século XVII, da era anterior à depressão das campanhas da Restauração, cujos testemunhos a arqueologia de campo soube recolher. Do extremo oposto do espectro cronológico data um conjunto de material a imputar, em especial, ao gosto da burguesia que timidamente aparece, nos finais do séc. XVIII, a ocupar a habitação que a urbanística renovada de Lisboa, após a reconstrução pombalina da cidade, pôs ao seu alcance, alternativa de comodidade quando comparados os apartamentos dos hôtels de coberturas à la Mansart com o desconforto dos ventosos palácios brasonados. A seriação cronológica é encerrada por vidraria já francamente industrial.

Suscitando especial curiosidade a hipótese de ter existido, no palácio, uma botica, será esta questão equacionada com base no espólio vítreo, ainda que, neste caso como nos demais, tivesse convindo examinar, também e pelo menos, a faiança associada ao vidro.

The vase offered to D. Amélia de Orléans by Émile Loubet

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Field of interest: Art and History

The deep political crisis of the 1890s in Portugal, caused by financial issues and foreign competition in the colonial empire, led Dom Carlos I (1863-1908) to initiate diplomatic actions which drew the attention of the world's great powers. According to Rui Ramos, like all European kings, the Portuguese sovereign insisted on representing a main role in foreign policy and followed this tradition, by even performing the interpreter in private conferences of Portuguese politics with foreign diplomats. One of Dom Carlos most distinctive features was precisely the fact that he was the only member of the Portuguese political class addressing external relations (Ramos 2006 : 196), on which he possessed deep knowledge.

Keywords: Dom Carlos I, Loubet, Gallé, Falize, offer

Consequently, a series of visits was exchanged between the Portuguese king and Alfonso XIII of Spain, as well as with Edward VII of England, the Kaiser William II of Germany, and, in the end of 1905, also Émile Loubet, president of the French Republic. The Portuguese king visited Paris in 1895, 1902, 1904 and 1905 (Ramos 2006: 197).

It was convenient to secure friendship and good relations with France. In the 1890s the investment of French capital in Portugal was so significant that it was even alleged that the latter country was financially dependent on the former.

On 28 October 1905, when Loubet visited Lisbon, the magazine Illustração Portugueza reported in detail the preparation of the reception and how warmly the French president was welcomed: "Mr Emile Loubet vae chegar dentro em pouco a Lisboa e a cidade prepara-se para o receber com um enthusiasmo e uma alegria sem precedentes. Engrinalda-se flores, veste-se de luz, arma-se de festa, cobre-se de bandeiras, transforma-se desde os centros mais ricos aos bairros mais afastados. Illumina-se e atroa-se com a Marselheza, n'uma ancia de mostrar a sua satisfação em guardar nos seus muros, embora por pouco tempo, o presidente da república franceza."[1] Also on October 28, the Figaro magazine reported the day of arrival : "enthusiasm manifested itself freely everywhere, the crowd sometimes even passed through the barriers of soldiers escorting the royal carriage" and "the king accompanied the president to the hall of honour of the Palace where the queen of Portugal, D. Amélia of Orléans (1865-1951) was with her court ladies, visibly moved to find her compatriot of the French Republic.

After a private lunch and a visit to the Society of Geography, the procession crossed the streets of Lisbon, where all shops were closed and the ovations to the French head of state grew as they passed. At eight o'clock in Palácio da Ajuda, a large dinner was offered to the guest's honour by the Portuguese king. According to the O Século the banquet was served in the "lavish dining-room, completely restored for the visit of Alfonso XIII, and where two tables were set for about 170 guests (...)."

Dom Carlos payed back the visit to Loubet in the following month. On 23 November, the Figaro magazine described the affectionate and enthusiastic welcome to the King of Portugal by the French. The former wrote in a letter to the Portuguese minister Luciano de Castro: "I will only tell you that even the Tsar in the best days of the Franco-Russian alliance was never received as well as I was here." (Ramos 2006: 205).

Fig. 1 The President Loubet and the Portuguese Royal Family during the former's visit to Portugal. PNA. Inv.61853.

[1] Translation: Emile Loubet will soon be arriving in Lisbon and the city is preparing itself to welcome him with unprecedented enthusiasm and joy. Flowers are wreathed as it dresses itself with light, as it dresses up for the party, as it covers itself with banners, transforms itself from the wealthiest centres to the most remote neighbourhoods. It illuminates itself and the Marseillaise roars, in an eagerness to show its satisfaction in guarding within its walls, although not for long, the president of French Republic.

Fig. 2 Vase with French roses offered by Émile Loubet to Queen Amelia, PNA. Inv.1288 e 1288/A

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During these visits, as a sign of friendship and courtesy, several diplomatic offers were exchanged, of which the most outstanding were the ones delivered at the Hotel Bristol in Paris, where Dom Carlos stayed "(...) four large boxes containing the offers of the President of the Republic to His Majesty. Above all we highlight a splendid folding screen of Gobelins, a wonderful jar of Sèvres and a large marble statue."

On November 30, 1905 the Figaro reported the President of the French Republic had already made an offer to the King before: a superb crystal jar with a gold mounting, containing bouquets of French roses in gilded silver and in its silver ribbons the words: «Émile Loubet, Président de la Républiquefrançaise, à sa Majesté la reine Amélie de Portugal » can be found. This marvel of Falize is nowadays in the King's Hall in the Bristol hotel. The piece, offered to Queen Amelia, derived from a collaboration of Émile Gallé (1846-1904) and the firm Falize Orfèvre.

Known as one of the most creative glass and ceramic makers of his time, Gallé came from a reputed family that emerged in the period of the second empire in France (1852-1870). This artist gained international fame especially since the Universal Exhibition of 1889, due to the originality of his work.

President Loubet – the 7th President of the French Republic (1899-1906) – is known for his appreciation of Gallé's artworks, among other artists. By the hands of the French head of state, work of this artist was patronized and promoted in the European courts via diplomatic offers (Olivié 1995: 235). The collaboration of Emile Gallé and Lucien Falize (1839-1897) – and later of his successors –, where the latter executed the mountings, was frequent and significant. The offers of the French Republic to the courts of Denmark, Russia, Italy, and finally Portugal should be highlighted.

The vase in *Art Nouveau* style has a cylindrical body in transparent and opaque green glass of several shades, moulded, folded and engraved; it shows a naturalistic relief decoration in its lower part, with trees and brownish glass lustre; the lower part is of a darker tone. From the tri-lobed rim, drops of glass seem to run down, and in the middle an inclusion of a metallic particle can be found (gold?). In the line of a symbolist decoration – frequently adopted in this type of pieces, unique and customised – one can read an inscription of a fraction of the poem "La voix du soir ", by Charles Guérin (1873-1907): "La bonté / calme / Des / choses / Charles Guérin ". Gallé had the habit of inscribing small poems that inspired him in the creation of his artworks, to which is attributed the French term "verre parlant ". In this case, and because it was the vase offered to Queen Amelia, daughter of the Count of Paris and great-granddaughter of the last king of France, Louis Philippe of Orleans, there is a clear allusion to his known kindness against the odds. The diplomatic visits and the offerings demonstrated also courtesy and good relations from the French Republic to the greatest figure of the monarchy, in this case to Queen Amelia.

Fig. 3 Detail of the relief decoration of trees.

Below the poem, the signature "Gallé" can be found.

The carved silver mount, that supports the vase, has the shape of an artichoke. It bears the initials "RF" (République Française) engraved on a plain surface highlighted by a laurel oval frame, from which two flags and a strip with an insignia of the French Order of the Legion of Honour, and two olive branches stand out. On each side, the inscriptions: "*EMILE LOUBET PRÉSIDENT / DE LA / RÉPUBLIQUE FRANÇAISE* ", and "*À SA MAJESTÉ / LA REINE / AMÉLIE DE PORTUGAL* " can be seen. In the back part, there is a cartouche with engraved vegetal ornaments shaped in "A" of Amelia, surmounted with a royal crown. The base of the artichoke bears the words "Falize. Orf. Paris". Concerning the "roses of France" in silver gilt, they were this way designated by the newspaper Figaro. As means of depicting love, as well as the fragility of life and feelings, there are several references to roses in literature and in art since time immemorial, and they were the most beloved flowers in France. From the 18th century, their growth in the French gardens reached large proportions and was continued for the following centuries. The best known species was the Rose Gallica.

After the foundation of the Portuguese Republic in 1910, the property of the Royal House was registered, and the vase and the branch were in the so called "Arrecadação da Senhora D. Amélia ", in the Palácio das Necessidades, later transferred to Palácio Nacional da Ajuda, where they were temporarily exposed in the "Green Room" (Sala Verde).

Fig. 4 Detail of the "vase parlant" with the lines of Charles Guérin

Conclusions

The vase was offered in November 1905, in Paris, during the state visit of Dom Carlos I, instead of Lisbon as was originally thought. In this very same year, the firm "Falize Orfèvre" was already under the administration of the three brothers André, Pierre and Jean Falize. This occurs after the unexpected death of their father Lucien, in 1897, which can lead to the hypothesis that the mounting might have been done by the offspring. In the newspaper Figaro there is an uncertainty in the description of the lower part of it, mentioning silver instead of gold. But the vase has indeed some decorative elements in silver gilt. Concerning the glass vase, it can have been made after 1897/98. Like Lucien Falize, Émile Gallé was also already deceased by 1905, the year of the visit of Dom Carlos I. However, the luxury production continued until 1906, when the widow Henriette Gallé Grim took over the business in connection with Émile Lang. During this period, several commissions were placed by European Courts and other public figures. Therefore, this vase can have been manufactured by the renowned glass artist or shortly after his death.

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