RECENT ADVANCES IN GLASS, STAINED-GLASS, AND CERAMICS CONSERVATION 2013

ICOM-CC Glass and Ceramics Working Group Interim Meeting

and

Forum of the International Scientific Committee for the Conservation of Stained Glass (Corpus Vitrearum-ICOMOS)

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Tulip vase: Anon. 1690–1720 (in the process of conservation), Rijksmuseum, Amsterdam, the Netherlands (Photo © Rijksmuseum)

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Introduction

Collaboration, inspiration, and exchange are an essential aspect of the conservation profession. As much as we need to be specialists, we also need to remain open to new ideas from outside our own fields. The conservation community is becoming increasingly more international and interdisciplinary, a development that, though obvious, we sometimes need to be reminded of. Furthermore, limited resources stimulate us to search for synergies that will provide unexpected opportunities to join forces across (imaginary) borders.

For the first time, the interim meetings of the ICOM-CC Glass and Ceramics Working Group[1] and the Forum of the International Scientific Committee for the Conservation of Stained Glass (Corpus Vitrearum-ICOMOS)[2] were organised as a joint conference. These organisations have much in common, including many shared members. Whereas the interim meetings of the ICOM-CC WG Glass and Ceramics have been organised every three years, the Forum meetings are held at two-year intervals. The plans for both organisations to meet in 2013 offered a rare opportunity to join forces to present the latest developments in the conservation of glass, stained glass, and ceramics, both within collections or in situ. By participating in a joint conference, the delegates will have had the opportunity to gain from the shared experience of both groups and learn from the interactions and exchanges that are a central part of the conference experience.

The aims of the conference can be summarised as follows:

- to present relevant case studies in the conservation of glass, stained glass, and ceramics
- to disseminate research results in the field of cultural heritage
- to promote the application of new materials and technologies for conservation practice, as well as tools for analysis and documentation
- to identify further research and to provide networking for future activities.

The target audience of the conference underlines its interdisciplinary nature and has included: conservators (both in museum and private practice), scientists specialising in conservation, students from all conservation disciplines, curators, and museum and heritage managers.

The overwhelming response, resulting in more than 200 participants attending the conference, has proved the power of this interdisciplinary approach and the desire of conservators and managers to communicate with a broader conservation community.

The three-and-a-half day conference included a total number of 29 oral presentations and 20 posters. The thematic sessions on research in progress and case studies reflected the cross-disciplinary nature of topics: Cracks and Fractures; Bonding and Filling; Protection and Installation; Creation and Degradation; Degradation and Treatment; Examination and Analysis. A student symposium the following day offered young professionals the opportunity to exchange their experiences – this was a novelty among our conference features.

The meeting was hosted jointly by the University of Amsterdam and the Cultural Heritage Agency of the Netherlands (RCE), with support from the Antiquities Museum in Leiden and the Rijksmuseum Amsterdam. It was exceptional to have the opportunity to visit the conservation laboratories of the Rijksmuseum and the research laboratories of the RCE in the Ateliergebouw with such a large group, to then be treated to a generous reception provided by the Rijksmuseum. 2013 has been a year of significance for the world of ceramic and glass conservation in Amsterdam. The first fully qualified graduates of the ceramic and glass conservation course at the University of Amsterdam received their final diplomas, and in the spring of 2013 the Rijksmuseum re-opened after 10 years of extensive restoration and refurbishment.

Guided tours of the conservation departments of the University and the Rijksmuseum, together with the research department of the RCE, which are housed together in the Ateliergebouw (situated opposite the Rijksmuseum), enabled delegates to experience the context of ceramic and glass conservation and conservation research in the Netherlands, as well as to digest the extensive programme and provided the opportunity for an exchange of ideas. A post-conference tour was offered to allow participants to explore stained glass in situ.

Members of the Local Organising Committee for the conference were: Renske Dooijes, Conservator of Ceramics and Glass at the National Museum of Antiquities, Leiden; Ineke Joosten, Conservation Scientist at the Cultural Heritage Agency of the Netherlands, Amsterdam; Luc Megens, Conservation Scientist at the Cultural Heritage Agency of the Netherlands, Amsterdam; and Taco Hermans, Senior Conservation Scientist/Castle Expert at the Cultural Heritage Agency of the Netherlands, Amersfoort. The team was coordinated by Kate van Lookeren Campagne, Senior Lecturer in Ceramic and Glass Conservation, University of Amsterdam.

We are very pleased that we have been able to arrange the publication of colour preprints which have been an important feature of previous Interim Meetings and Forum Proceedings[3]. All contributions have been peer-reviewed by the editors with the support from members of the conference editorial board, whom we warmly thank for their hard work and for generously sharing their expertise:
Joost Caen, Professor of Glass Conservation Studies, Antwerp University Association, Belgium; Renske Dooijes, Conservator of Ceramics and Glass at the National Museum of Antiquities, Leiden, the Netherlands; Gerhard Eggert, Professor of Objects' Conservation at the State Academy of Art and Design Stuttgart, Germany; N. Astrid van Giffen, Assistant Conservator at the Corning Museum of Glass, USA; Ineke Joosten, Conservation Scientist at the Cultural Heritage Agency of the Netherlands, Amsterdam, the Netherlands (RCE); Luc Megens, Conservation Scientist at the Cultural Heritage Agency of the Netherlands (RCE), Amsterdam, the Netherlands; Isabelle Pallot-Frossard, Director of the Research Laboratory for Historical Monuments, Champs-sur-Marne, France; President of the International Scientific Committee for the Conservation of Stained Glass; Lisa Pilosi, Conservator at the Sherman Fairchild Center for Objects Conservation, The Metropolitan Museum of Art, New York, USA; Chair of ICOM-CC; and Secretary of the International Scientific Committee for the Conservation of Stained Glass; Sebastian Strobl, Professor of Stained Glass Conservation at the Department of Conservation and Restoration, University of Applied Sciences, Erfurt, Germany, and Vice-president of the International Scientific Committee for the Conservation of Stained Glass; Norman H. Tennent, Professor of Conservation Science at the University of Amsterdam, Amsterdam, the Netherlands.

We also thank Hidde Heikamp and Hemmy Clevis from SPA Uitgevers as well as Gary Anderton for his hard work in ensuring conformity and accuracy in the text.

We know from experience that well-edited and well-produced preprints make the content of the conference available also to all those in the conservation community who are unable to attend the meeting, as well as to future generations.

We are convinced that 'Recent Advances in Glass, Stained-Glass, and Ceramics Conservation 2013' will prove to be a milestone in developing collaboration between related conservation specialisations. It will provide the opportunity to cross borders – both physically and professionally – and inspire cross-fertilisation between different cultures as well as different fields of conservation.

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Notes

1. Glass and Ceramics is one of the working groups of the Committee for Conservation of the International Council of Museums (ICOM-CC). Its members are interested conservators, conservation scientists, and curators. More information about the working group can be found on our website, www.icom-cc.org.
2. The International Scientific Committee for the Conservation of Stained Glass (Corpus Vitrearum-ICOMOS) gathers conservation scientists, conservators, curators, art historians and architects, interested in the conservation problems of stained glass windows in situ and in collections (see also: http://lrmh-ext.fr/sgc/?lng=en).
3. Some of the most recent conference publications include:
   Glass and Ceramics Conservation 2007, preprints of the interim meeting of the ICOM-CC Working Group, Nova Gorica, Slovenia, 27–30 August 2007, ed. Lisa Pilosi, Nova Gorica: Goriški Muzej Kromberk, 2007. Now available on the website: http://www.icom-cc.org/51/news/?id=156#.UioGPj8UnAF (accessed 6 September 2013).
   Glass and Ceramics Conservation 2010, preprints of the interim meeting of the ICOM-CC Working Group, Corning, New York, USA, 3–6 October 2010, ed. Hannelore Roemich, Corning, NY: ICOM Committee for Conservation in association with The Corning Museum of Glass, 2010.
   The Art of Collaboration: Stained-Glass Conservation in the Twenty-First Century, Corpus Vitrearum USA, Occasional Papers II, eds. Mary B. Shepard, Lisa Pilosi, and Sebastian Strobl, Turnhout: Brepols, 2010.

Cracks and Fractures

Peculiar Pictures – Wilhelm Geilmann and the Weathering of Glass

Gerhard Eggert

Keywords:
Geilmann, Wilhelm; gel layer; glass deterioration; glass analysis.

Abstract

Geilmann's (1956) classical German paper on 'The Weathering of Glass in the Soil' is an unmatched extensive wet microchemical and microscopic study and is reconsidered here. A related photo album with 454 (of around 2000) of his micrographs has been rediscovered recently. Because of the sample preparation, the photos show much more details of peculiar weathering phenomena and their variety than we usually see today under the stereomicroscope. Examples discussed are 'chatter marks', crack patterns, the surface below the weathering zone, and brown staining. Despite the large progress in analytical instrumentation, there has not been much progress in the theoretical understanding of the observed phenomena since then. A new approach is needed.

Introduction

This conference is devoted to 'Recent Advances', but these are based, as always, on earlier ones. In some cases, the potential of the latter still has to become fully exploited to strive for future developments and new discoveries. The work of the microanalytical chemist and microscopist Wilhelm Geilmann (1891-1967) on archaeological glass and its deterioration is a paradigmatic example. It should be reconsidered, as his observations are still widely unexplained today.

Scientific Interests of Wilhelm Geilmann

After obtaining his PhD in chemistry and after the First World War, Geilmann started as an assistant in the Institute of Agricultural Chemistry at his alma mater, the University of Göttingen, Germany. From 1923 to 1950, he worked in the Institute of Analytical Chemistry in Hannover. In 1950, aged 59, Geilmann followed his former student Fritz Straßmann, discoverer of the nuclear fission of uranium, to the newly founded Chemical Institute in Mainz. More details on his biography can be found in Bode and Straßmann (1951), Anonymous (1961), and Bode (1966).

As the staged portrait (figure 1) illustrates, the classic microscope was important for his work, something which he shares with modern conservators (but not generally with chemists). His picture book for qualitative microanalysis of inorganic substances (*Bilder zur qualitativen Mikroanalyse anorganischer Stoffe*: 1st ed. 1934, Leipzig: Voss; 2nd enlarged ed. 1954 and 3rd ed. 1960, Verlag Chemie: Weinheim) used precipitation reactions to identify ions by characteristic crystal shapes under the microscope. Along with Fritz Feigl's *Spot Tests in Inorganic Analysis* (last ed.: 6th rev. and enlarged English ed. 1972, Elsevier: Amsterdam), it has been widely used in chemical laboratories (including those dealing with conservation) for qualitative inorganic microanalysis before the age of the scanning electron microscope (SEM) with energy dispersive X-ray analyser (EDX).

A major aim of Geilmann was to develop microanalytical methods that have the same precision as normal wet chemical analysis. This fitted nicely into his interest in what we today call 'archaeological sciences'.

A number of his publications (all written in German, see Bode 1966 for citations and BCIN [www.bcin.ca] for abstracts) dealt with bronze finds (including their corrosion), archaeological textiles, and wall paintings. His sometimes rough method of sampling seems a bit more like 19th than 20th century science: 'There is nearly no visit of a church or a castle, where he doesn't pull out his pocketknife to steal small pieces of wall (plaster) with original painting' (Anonymous 1961, possibly meant humorously but certainly with a basis of truth).
With his special interest in industrial glass analysis (published in *Glastechnische Berichte*, the journal of the German Society for Glass Science and Technology [Deutsche Glastechnische Gesellschaft, DGG]), it is no wonder that Geilmann also made great efforts in the analysis of historical glass. From 1953 to 1962, Geilmann published a series of seven papers entitled 'Contributions to the Knowledge of Old Glasses' in the same journal. The first three and the last paper dealt with archaeometric questions. In communication number I (Geilmann and Jenemann 1953), varying phosphate contents between 0.1 and 4% were correctly ascribed to the different alkali sources (mineral or plant ash soda, wood ash) of historic glasses. Manganese was found to vary greatly in glass (0.0 to 3% Mn_3O_4) and in West German beechwood ashes (0.1-10%). Discussing historical recipes (Theophilus, Biringuccio, and Agricola), Geilmann and Brückbauer (no. II: 1954) concluded that even a high manganese oxide content does not prove it to be an intentional addition. Full analysis of some 50 historic glasses, beechwood ashes, and reconstruction melts were given in Geilmann 1955 (no. III). Not all beechwood ashes (from different places) are rich enough in potassium to be suitable for glass production, which might be the reason for the use of fern ash or refined potash. Correcting earlier opinions in the literature, cobalt was found to be present in all dark-blue glasses of all provenances using spectrographic analysis (no. VII: Geilmann 1962).
Judging from today's knowledge, all his conclusions are sound and still valid.

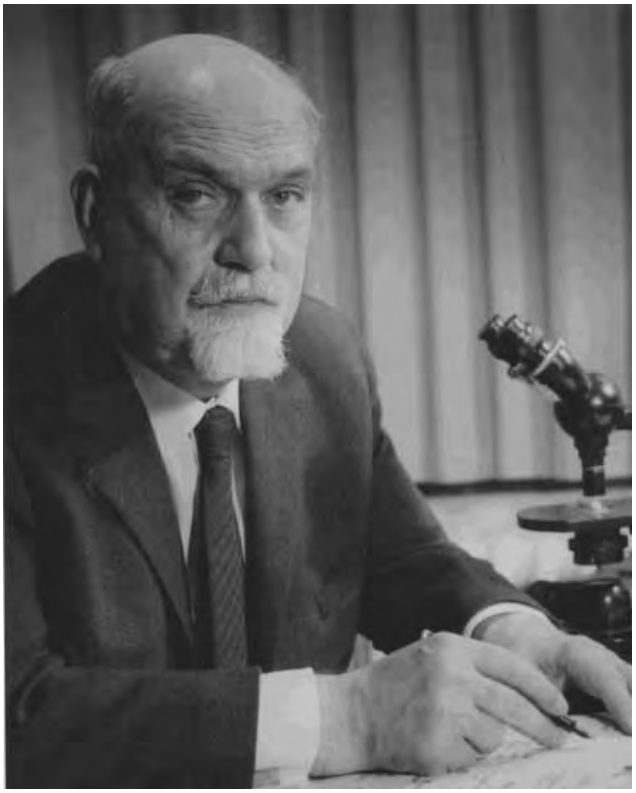

Fig. 1. Staged portrait of Wilhelm Geilmann (see Bode 1966; photo: Gesellschaft deutscher Chemiker)

Geilmann's Research on the Weathering of Glass

The other publications in the series described weathering phenomena. In no. V (Geilmann, Berthold, and Tölg 1960), the formation of gypsum ($CaSO_4 \cdot 2H_2O$) and syngenite ($K_2Ca[SO_4]_2 \cdot H_2O$) in the weathering crust of church windows was reported. No. VI (Geilmann 1960) described deep etching in old cracks on a Roman window glass. He depicts branched twig-like cracks (his figures 4 and 5), which he ascribes to mechanical forces during cracking of the pane. Newton, Halloway, and Hench (1981, figures 1 and 3) later also found them on Roman glass and could reproduce the 'feather-cracks', by making a short scratch on a microscope slide and bending it (1981, p. 356; see also Newton and Davison 1989, p. 140, figure 4.2). Unfortunately, no reference to Geilmann's paper was made.
Most important are the unmatched extensive chemical and microscopic investigations of the deterioration of glass in the soil (no. IV, Geilmann 1956). This is a classical paper that is widely referenced in publications on ancient glass deterioration (e.g. Wihr 1977; Newton and Davison 1989, pp. 154-155; Römich 1999; Roemich and others 2003; Bellendorf and others 2010). Written in German - as was still usual for German scientists in the 1950s - many details are today practically lost for an international audience. A short communication based on this article in the company journal of Zeiss that was also translated for its English edition (Geilmann 1960a) is only a poor substitute.

Geilmann identified the chemical nature of the weathering zone as a 'gel layer'. Because alkali or alkaline earth metal ions (Na^+, K^+, Ca^{2+}, Mg^{2+}) are leached out, silicon is relatively enriched in the weathering layer. As titanium dioxide is neither extracted nor absorbed, it can be used as an unchanging reference value for the behaviour of other elements during weathering. Unfortunately, the TiO_2 content is quite low and, therefore, has a high analytical relative error. Nevertheless, Geilmann states that, in absolute terms, silicon is also lost from the weathering layer because of the low but existing solubility of silica in water. He also noted 'hills' of redeposited silicic acid on the glass surface. Despite his expertise in agricultural chemistry, he is not aware of the solubilising ability of humus components or root exudates (e.g. benzene-1,2-diol, also called pyrocatechol) acting as complexing agents for silica. Although discussed by Rottländer (1989, pp. 59-62; see also Glas 1997) for the weathering of ceramics and flint, this effect seems to be neglected in research on the weathering of archaeological glass even today.
For better microscopic inspection, Geilmann removed iron and manganese deposits as well as humic acid (partially) with nitric acid and hydrogen peroxide. Staining with basic dyes such as methylene blue helped to differentiate structures in the weathering zone as they are absorbed by silicic acid gels, but not by unweathered glass. He also used polished thin sections (cut parallel to the surface or as cross-section) for his study. Sometimes, replicas made with a lacquer impression technique showed a resolution of surface details better than the original under the microscope. Details of this technique were published by Geilmann and Tölg (1955) and later were re-invented by Werner, Bimson, and Meeks (1975) for use in the scanning electron microscope.
A variety of layered structures of lamellae, either flat or in weathering cones, in combination with brown staining by iron and manganese oxyhydroxides, were illustrated (Geilmann 1956). Although most of what Geilmann saw were cracks, he had no fracture mechanical approach to this problem. He noted similarities of the periodical banded structure of precipitates with Liesegang rings known from gel precipitation.
Geilmann (1956, p. 166, note 2) announced that he would give his some 2000 (!) micrographs to the DGG library. Indeed, a photo album calligraphed *'Wilhelm Geilmann. Bilder zur Glasverwitterung. Band 2. Gläser 15 – 31. Mainz 1955'* on the title page was found in the library (Geilmann 1955a) by the author. That album contains 454[1] b/w microphotographs without any captions or other text except page numbers. The old printed 'DGG Bibliothekskatalog. Frankfurt 1957' (deadline for acquisitions: 31 Dec. 1956) indeed lists this Vol. 2 on p. 29, but no other of his albums are mentioned. The printed addendum 'Bibliothekskatalog, Nachtrag 1' (Frankfurt 1968) with new acquisitions until 30 June 1967 also does not mention any other album. Unfortunately, no trace of Vol. 1 or the potential Vols. 3 & 4 could be found in the DGG library or the University of Mainz (institute, libraries, and archive). Klaus Beyermann and Günther Tölg, then students of Geilmann and today renowned, retired professors for analytical chemistry, could not help either, although they were named as original investigators, but not authors, at the beginning of Geilmann's (1956) article.
Despite their missing context, the photos still give a better impression of what glass corrosion can look like than our usual stereomicroscopic views of untreated samples today. Scans of the album are available from the author.

Discussion

It is unclear to what labelling list the subtitle 'Gläser 15-31' in the photo album refers. For the glasses analysed chemically, he used the same numbering system as in communication number III (Geilmann 1955). Samples were divided in five groups: 1 - Egyptian and Arabic glasses; 2 - Roman glasses from the Rhine-Main area; 3 - German window glasses 10th to 16th century; 4 - German vessel glasses 14th to 18th century; 5 - French church windows 15th to 17th century. Sample numbers combined the group number with the number of the sample in the group, e.g. 4,12 for the twelfth sample in group 4. However, no group has numbers 15 to 31. It is possible that there was simply not much context known for the samples used for microscopic study.
Nevertheless, even the album does not tell which picture belongs to which glass on this numbering list. Places left free[1] might mark the start of pictures of the next glass. No photo has a caption with additional information of any kind. Three photos in the album (106b, 64b, 110a) could be identified in the publication (Geilmann 1956, figures 46, 50, and 54) with slightly varying image sections (here depicted as figures 10, 2, and 9, respectively). For these, some more information (e.g. the magnification used) can be extracted from the captions and the text.
An example is album photo 64b (figure 2), which has been published as 'Bild 50' by Geilmann (1956, p. 165) with the caption 'Weathering on a 17th cent. glass, magn. x200',

without giving a sample number. He explicitly noted the similarity to precipitation in gels in the text and simply noted without further comment: 'Enough details arise from the picture'. So he left further interpretation to the imagination of the reader.
Despite these severe limitations, the photos might still today inspire discussions. Here are some examples.

'Chatter Marks'

A series of shortened 'horseshoe' or 'scale-like' cracks seen under the microscope have been interpreted by Lindig (1999) as resulting from scratches caused by the movement of tools relative to glass in the hot state. Lierke (1999; 2009, p. 56/110) sees this as evidence for her theory of the role of the potter's wheel in the manufacture of glass in the hot, plastic state. She assumes that scratches had originally produced 'horseshoe' cracks as has been reported for sliding spheres (see also Jebsen-Marwedel 1936, figure 438): '…the shanks of the horseshoes are molten back by the internal heat, only shortened marks remain.' (Lierke 2009, p. 110). The literature on glass production flaws (Jebsen-Marwedel 1936, figures 414 and 419) also depicts 'serial cracks' (German: *Reihensprünge*) resulting from rapid local cooling of glass by contact, e.g. with metal (no scratches involved).

Nevertheless, Pilosi and Wypyski (2002, pp. 104-105) presented examples of 'chatter marks' from the inside of a Byzantine bowl whose 'gather ... would not have come into contact with any surface during hot working of the vessel'. Ghering and Turnbull (1940) produced a series of 'percussion crescents' (no shanks!) with various softer metal tips on cold glass, better visible after etching. Lierke's conclusion (2009, p. 110) that such cracks must be indeed 'hot scratches' is obviously not warranted for all these series of cracks.
A number of photos on the first pages of the album show this phenomenon and give an impression as to how variable it may look, including the degree of corrosion (figures 3 and 4. Compare with Lierke 2009, p. 56; Fréchette 1990, figure 4.6; Ghering and Turnbull 1940, figures 1 and 2 and 4–9; Jebsen-Marwedel 1936, figures 414 and 419).
A closer inspection of details (e.g. Do all cracks start at the same height or every second? Are they circular segments ['crescents'] or 'horseshoes'? Are they flat or zigzag?) and more and better micrographs (higher magnification) might lead to diagnostic criteria and future advances in the distinction between hot and cold cracks and between quenching and scratching. Additionally, microfocus X-ray computed tomography may be able to visualise the three-dimensional run of the crack below the glass surface (part of a cone surface?). Geilmann himself made no comment on this peculiar feature that he had seen so often.

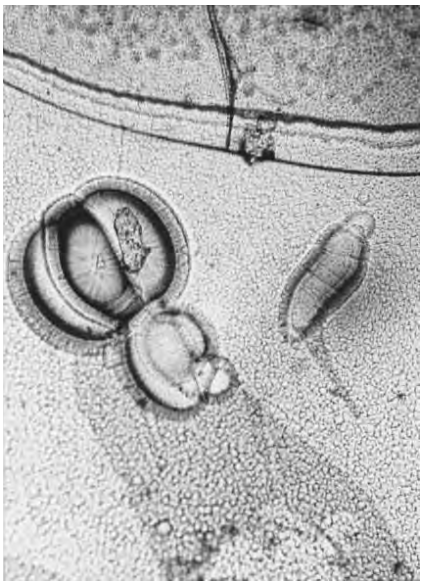

Fig. 2. Weathering on a specimen of 17th century glass, magn. 200x (Photo: 64b, Geilmann 1955a).

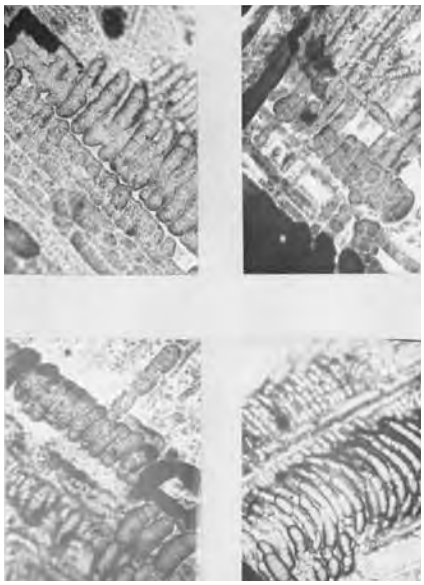

Fig. 3. Photos showing 'chatter marks' heavily etched by corrosion (Photo: page 12, Geilmann 1955a).

Fig. 4. Less etched example of 'chatter marks' (Photo: 3a, Geilmann 1955a).

Craquelure

A closer look at crack patterns tells us that they do not all look the same and they may contain hidden information (Eggert 2006).

Geilmann (1956, p. 146, figure 4) showed that a polygonal pattern of shrinkage cracks is formed in weathered zones of glass when slowly heated to 400–500°C, but not in unweathered glass. Photo 38c (figure 5) shows a similar cellular pattern.

Figure 6 shows a crack system in the gel layer where the sequential development of the cracks can be seen: later cracks end at earlier cracks.

The 'stretched' pattern in photo 21b (figure 7) really looks peculiar. The angle of bifurcation between cracks depends on the ratio of the principal stresses in the surface (Fréchette 1990, figures 3–16). However, the pattern looks more like sequential development of cracks than bifurcation.

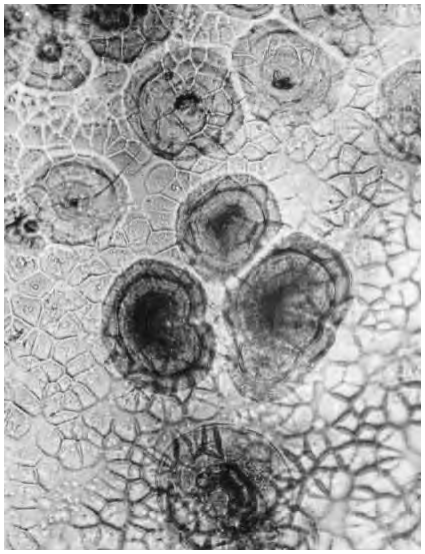

Fig. 5. Cellular shrinkage pattern (Photo: 38c, Geilmann 1955a).

Fig. 6. Sequential development of a crack system – later cracks end at earlier cracks (Photo: 23a, Geilmann 1955a).

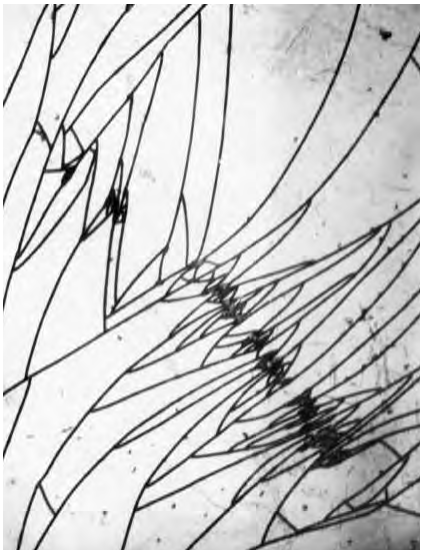

Fig. 7. Elongated crack pattern (Photo: 21b, Geilmann 1955a)

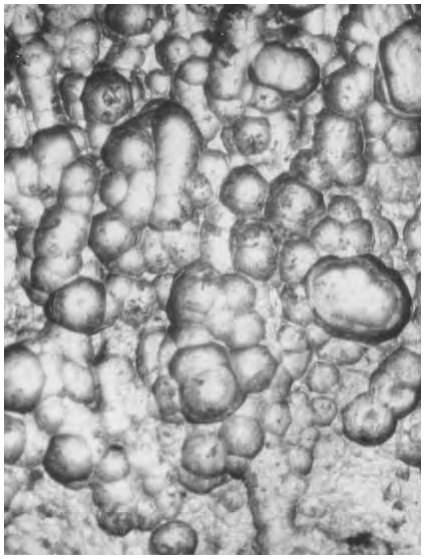

Fig. 8. Negative impression of a glass surface on a lacquer replica (Photo: 116a, Geilmann 1955a)

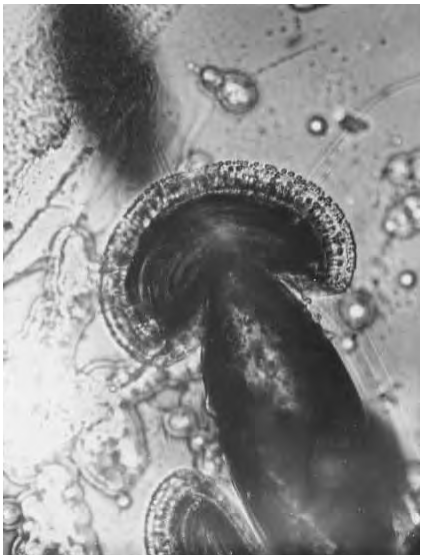

Fig. 9. Banded spot with a corona developed on the tip of an elongated bubble, magn. x200 (Photo: 110a, Geilmann 1955a)

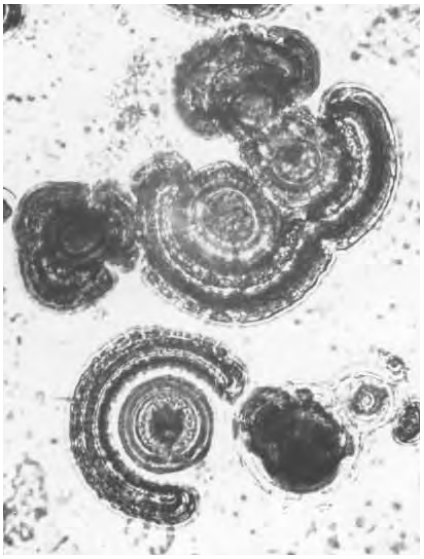

Fig. 10. Banded spots with not fully circular coronas on a Roman 2nd/3rd cent. glass from Cologne, magn. x350 (Photo: 106b, Geilmann 1955a).

Why do cracks then end with a low angle instead of 90° (Eggert 2006, figure 6)? Another elongated, but different structure is the 'cicada's wing' pattern in Kaifeng Ru ware glaze (Wood 1999, pp. 126–129).
Only a fracture mechanical approach could help to understand the pattern and its underlying causes.

Surface and/or Spot Weathering?

Surface weathering leads to stacks of parallel, straight lamellae. Near the unweathered glass, they become more and more wavy. After removal of all weathering layers, the glass surface is totally covered with round etch pits. They can be better seen in the negative of lacquer replicas as in photo 116a (figure 8); for comparison, see Geilmann 1956, figure 40 (identical to Geilmann 1960a, figure 6). Viewed directly through lamellae in the microscope in transmitted light, the optical effects of the hemispherical or ellipsoid pits led to the erroneous description of comb-like structures of lamellae in the literature (Geilmann 1956, p. 162).
Geilmann, Berthold, and Tölg (1960) counted up to 5200 (!) weathering centres per mm^2. Are the flat lamellae really formed by an even attack on the surface or later when individual weathering cones merge into a gel layer and develop lamellae on drying?

Brown Staining

Many photos in the album show brown staining in circular banded agate-like spots. According to Geilmann, the spots are nearly always covered by a transparent top layer of weathered glass that often shows cracks. Iron and manganese leached out of the glass network are precipitated as oxyhydroxides (e.g. $MnO_2 \cdot nH_2O$) when oxygen for oxidation has access. Geilmann explicitly refers to the Liesegang rings observed in precipitation reactions in gels. The album has two photos that were also used in the publication. Figure 9 (Geilmann 1956, figure 54) shows a banded spot with a corona developed on the tip of an elongated bubble. Figure 10 (Geilmann 1956, figure 46) illustrates banded spots with separate not fully circular coronas on a Roman 2nd/3rd century glass from Cologne.
Weber, Eggert, and Watkinson (2007, p. 39) also found black-brown concentric rings within the surface layer in their sample FRA5. SEM-EDX analysis showed that, in this case, they were not related to manganese oxyhydroxide, but possibly iron sulphide. It is clear from this study that many more samples need to be analysed with modern instrumental methods. A mathematical model describing banded precipitates on historical glass is still missing.

Conclusion

Layered weathering structures can now be grown in the laboratory on model glasses (Bellendorf and others 2010, p. 140; Roemich and others 2003). However, an overall theory (possibly including fractals and fracture mechanics for the description of banded precipitations and layered structures) matching the variety of observations on glass finds is still missing. A fresh view on Geilmann's pictures might inspire our search for scientific explanation. As our current understanding is still limited, the peculiar weathering phenomena documented by Geilmann deserve a re-investigation using modern analytical tools in order to achieve future advances.

Acknowledgements

The author is grateful to the Deutsche Glastechnische Gesellschaft (DGG) library (unfortunately since 2011 no longer open to external visitors) and to Liane Anders-Gorczyza (former DGG librarian) for scanning the photo album.

Notes

1. The album (Geilmann 1955a) contains 116 pages, each with 4 photos. For identification, these are cited here with the handwritten page number and their position (a: top left, b: top right, c: bottom left, d: bottom right). From the max. 116 x 4 = 464 positions for photos, the following ten are unoccupied: 20d, 35d, 48d, 52c, 52d, 64c, 64d, 70c, 70d, 107d.

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Photo credits

Fig. 1: GdCh, Figs. 2-10: Geilmann 1955a.

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A Special Kind of Crack Pattern on Historic Glass – Exploring the Causes of 'Sugaring'

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Keywords

glass deterioration; archaeological glass; crizzling; sugaring; fracturing

Abstract

Archaeological glass may develop a variety of degradation phenomena, including fractures and micro-fissures. An advanced state of corrosion is known as 'sugar glass', which refers to fractures that result in the disintegration of the glass into millimetre-size fragments. The shape of the fragments is similar to granulated sugar. This paper focuses on investigations into historic glasses and laboratory experiments undertaken in order to determine the main factors influencing this type of deterioration. Two model glasses were exposed to artificial weathering tests to explore the influence of aqueous solutions with different pH values, variations in humidity, as well as the significance of different surface properties and thickness of a glass. The results show that the constant presence of water or moisture is the dominant parameter that influences the development of 'sugaring'.

Introduction

Several terms are used to describe corrosion phenomena found on glass artefacts including dulling, crusting, iridescence, cracks, and fissures (Davison 2003; Roemich 1999a). The formation of fine cracks on glass objects in a museum environment is known as *crizzling* (Brill, Hanson, and Fenn 1998; Richter 1998; Kunicki-Goldfinger 2008; Koob 2012). Crizzling occurs due to imbalances in the glass composition and affects a wide spectrum of glasses, colourless vessel glass from the 17th to the mid-18th century being the most affected. The cracks are formed initially at the surface of the glass and are a result of the leaching of alkalis that have reacted with water in the air. If humidity fluctuates, the process is accelerated. *Craquelé* on stained-glass windows is caused by outdoor weathering, occurring mainly on mediaeval glass. The micro-cracks are again limited to the leached layer, which can reach a thickness of a few hundred micrometres (Roemich 1999a). In contrast, stained-glass windows from the 18th and 19th century can be affected by internal fractures, which are not limited to the glass surface. Some of the fractures penetrate through the glass bulk, making the glass physically unstable (Sloan 1999; Wittstadt and Mottner 2009). In Cologne Cathedral, for example, nearly all the orange and yellow glass pieces from two windows dating to the 19th century are affected by internal fractures; the size of fragmentation varies between 0.5 cm (figure 1) and more than 5 cm across one piece. A similar type of fragmentation is reported on a group of colourless Roman glass from the excavation in Bochholz, the Netherlands (Huisman and others 2008). There, an advanced state of fragmentation has been detected and was described as *sugaring*. The affected glass is endangered by micro-fractures on the surface and/or in the bulk glass leading to various states of fragmentation; these are classified as follows according to the size of the fragments: 0.5 cm to 1 cm across is referred as strong fragmentation, 0.1 cm to 0.5 cm as very strong fragmentation, and less than 0.1 cm as total disintegration.

Sugaring is known to most archaeologists and conservators dealing with glass. For example, the LandesMuseum in Bonn has a collection of vessel glasses including plates, bowls, and bottles dating to late Roman times.

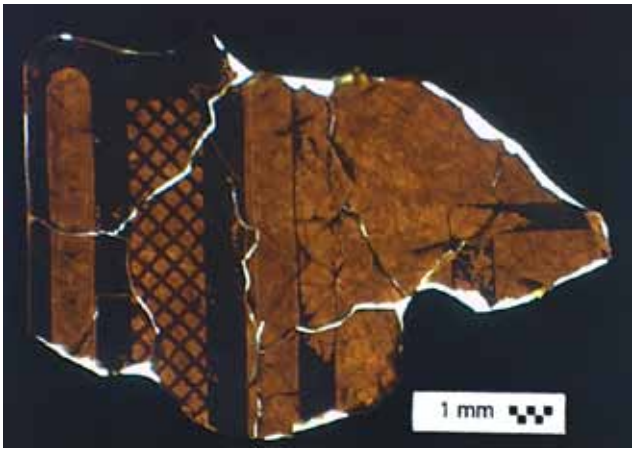

Fig. 1. Fragments of a stained glass window from Cologne Cathedral, Welterfenster, c.1865. Fractured pieces are endangered by numerous internal fractures (photo: authors).

Around 5% of these objects are affected by internal fractures or sugaring. Some severely degraded fragments were left in blocks of soil. Without appropriate treatment, they would disintegrate and fall into pieces. Before proposing suitable conservation measures, we need to understand the structure of the cracks and the reason for their formation.

In general, the formation of crack patterns could be related to the glass, or rather to specific environmental parameters. The phenomenon of sugaring seems to be predominant in glassware manufactured during Roman times, as was indicated by the survey of artefacts in the LandesMuseum Bonn. Huisman and others (2008) compared the composition of sugared colourless glass fragments with bluish-green almost pristine pieces from the same Roman excavation site. The formation of internal fractures and sugaring was observed to occur in alkali glasses that had comparatively low levels of network stabilisers, principally calcium. If the percentage of calcium (a stabiliser) in the glass composition is too low, this can also lead to crizzling and internal fracturing on mosaics and stained-glass windows (Verità 1998; Müller 2003; Kunicki-Goldfinger 2008; Wittstadt and Mottner 2009; Koob 2012).

Apart from the chemical composition, the shape and thickness of the object may also have an influence on the degree of fragmentation. Thicker parts of bottles such as spouts and handles are often more fragmented than thin-walled parts within an object. Also, plates and bowls that are usually thicker than bottles often suffer more from sugaring than bottles. A possible explanation is that thick-walled glass absorbs the stresses arising during contraction and swelling of the superficial gel layers less effectively than thin-walled glass (Huisman and others 2008). It is also thought that the curvature in handles and the bottom of vessels brings stress in the glass and accelerates fracturing (Schöfer 2012).

Internal fracturing has also been associated with micro-fissures, for example those caused by cold working of the glass (Pilosi and Wypyski 2002). Since the crack pattern is found on some objects specifically in the area of the cut decoration, it is also assumed that cracking is due to heating during grinding (Lierke 1999, p. 25). Eggert (2006, p. 72) describes a sugared glass (the outer surface of a bowl) where the cracking was not related to internal fracturing and suggests that corrosion may have caused this degradation pattern, perhaps combined with a selective weathering of pre-existing scratches. In spite of these case studies that relate sugaring with localised stress, there are also affected objects that have not experienced any mechanical processing.

The development of sugaring is certainly also related to environmental impact and appears to be promoted by the presence of water. Some authors presume that cyclic changes of wet and dry environment (e.g. purging of soil) might accelerate the formation and propagation of micro-fractures (Huisman and others 2008). The role of the pH is not clear but has been taken into consideration (Huisman and others 2008).

Even though single aspects of sugaring have been described by the authors mentioned above, the overall degradation mechanism is not yet understood. The influence of individual parameters on glass degradation can best be explored through laboratory experiments, where single parameters can be controlled and modified systematically. Since the history of archaeological glass fragments always remains an unknown factor in the overall equation, model glasses can be used to determine the influence of glass composition and technology on deterioration. For example, investigations on model glasses have been performed, to study the phenomena observed on stained-glass windows (Roemich 1999b). Furthermore, synthetic glasses were used to examine the influence of pH and soil components, leading to a better understanding of the formation of iridescent effects and laminated layers on archaeological glass (Roemich and others 2002; Bellendorf and others 2010). This paper describes the application of new types of model glasses especially designed to simulate sugaring. Environmental parameters such as pH, temperature, and humidity as well as material properties such as glass composition, surface roughness, and the thickness of samples were modified in laboratory experiments to explore their role in the formation of this phenomenon.

Experiments and Analytical Techniques

For this project, two types of glasses were used (MDS8-H and MK1; see table 1).

Samples were prepared by melting pure raw materials into glass blocks (6 cm x 3 cm x 2.5 cm) and cutting the blocks into plates with a thickness between 0.3 mm and 6 mm. For individual experiments, the glass surfaces were left rough to represent what normally occurs after cutting (saw-cut surface) or samples were polished by briefly heating them with a gas flame (fire-polishing for 2 minutes) or by mechanical polishing with grinding paper.

Polarised light microscopy was performed with a Leica DM RX/E to document surface features with up to 200x magnification. Cross-sections were prepared by embedding the samples in epoxy resin (EpoFix, Struers), followed by cutting and polishing. Scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS) was performed by using a Zeiss EVO LS10 coupled with Swift-ED from Oxford Instruments.

For the laboratory exposure, programme samples were subjected to artificial ageing by immersing them in aqueous solutions of different pH (pH 3–13) in ambient conditions. In addition to the storage in water (pH 7), the adjustment of pH values was performed using HCl (pH 3, pH 5) and NaOH (pH 9, pH 13). The influence of temperature was investigated with exposure in a neutral solution by heating the jar to 80°C or cooling to 10°C. Degradation related to high relative humidity (RH) was explored by exposing the samples in a climate chamber with 98% RH and temperatures again ranging between 80°C and 10°C. Long-term exposure in desiccators with RH between 20% to 98% was realised using conditioned absorber materials (Silicagel E, PROSorb) or a saturated salt solution ($(NH_4)_2SO_4$ for 80% RH), as well as a jar filled with water placed next to the samples (98% RH). The desiccators were stored at 30°C in a heated cabinet to gain results faster than those that would be obtained with exposure at ambient temperature.

Sample	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	MnO	MgO	CaO	PbO	CuO	S	Cl	Σ
Model glasses													
MDS8-H	71.9	0.9	0.7	18.9	2.9	n.a.	n.a.	0.8	n.a.	3.0	0.9	n.a.	100.0
MK1	70.6	0.6	0.7	18.3	2.8	n.a.	n.a.	3.3	n.a.	3.0	0.7	n.a.	100.0
Fractured archaeological glasses													
Beaker, late Roman, 1975, 158 (Staatssammlung, München)	72.9	1.7	n.a.	17.8	0.4	n.a.	n.a.	5.8	n.a.	n.a.	n.a.	n.a.	98.6
Plate, 3rd A.D. (OV05 /1023, LVR-Bonn)	75.7	n.a.	n.a.	17.4	n.a.	n.a.	n.a.	5.3	n.a.	n.a.	n.a.	n.a.	98.5
Bowl, 4th A.D., (HA 132, 152-15, LVR-Bonn)	71.4	1.6	0.6	14.8	0.3	1.4	0.6	6.7	0.5	n.a.	0.2	n.a.	98.1
Bowl, 4th A.D. (HA 132, 165-29, LVR-Bonn)	65.1	5.5	0.3	21.9	0.3	0.9	0.9	4.1	n.a.	n.a.	n.a.	n.a.	98.9
Beaker, 1st A.D. (Ni 1996/127, 1014-16, LVR-Bonn)	71.6	1.2	n.a.	20.8	0.2	0.7	0.6	3.6	n.a.	n.a.	n.a.	n.a.	98.8
Bottle, 4th A.D. (HA 132, 146-9, LVR-Bonn)	69.8	2.0	0.5	16.9	0.6	1.1	0.8	6.8	n.a.	n.a.	n.a.	n.a.	98.5
Plate, 2nd A.D. (RGM 67,807, RGM-Köln)	70.2	2.3	0.7	20.5	0.4	n.a.	0.0	4.7	n.a.	n.a.	n.a.	1.2	100.0
Bottle, late Roman (H 5699, Martin von Wagner, Würzburg)	70.2	1.5	0.8	15.4	0.5	1.5	0.6	7.6	n.a.	n.a.	0.3	n.a.	98.4
mean value	70.9	2.0	0.4	18.2	0.3	0.7	0.4	5.6	0.1	n.a.	0.1	0.2	98.8
Mean value of Roman glass (Wedepohl 2003)													
1th - 5th AD (n=781)	69.1	2.4	0.7	17.5	0.6	0.6	0.5	6.8	n.a.	n.a.	n.a.	n.a.	98.1

Table 1. Glass composition (wt.%) of model glasses and fractured archaeological glass evelautaed by SEM-EDS, as well as the mean composition of Roman glass.

Investigation of Deteriorated Glass Artefacts

Several glass artefacts had been investigated by visual inspection, and selected samples were further examined using light microscopy and SEM-EDS. The shape and size of the crack pattern can vary significantly not only between different objects, but also between different areas within one object. The fractures run from the surface through the bulk of the glass, sometimes crosslinking and sometimes ending in the glass bulk. Mostly the fracture lines have a dynamic shape (twisting) instead of being straight. Fractures and micro-fissures make the glass physically unstable, especially when fracture lines are straight. The fractures can be different in appearance: they can appear bright (reflecting light and being comparable to the typical appearance of mechanically induced cracks), include some matt sections as 'dark lines', or are not well-defined with a cloudy appearance. In other cases, fractures are coloured (mostly yellow–brown comparable to a yellowed epoxy bond). The glass object in figure 2 shows an example with bright as well as yellow fractures. The bottle is mechanically instable but not yet consolidated.

The surface of archaeological glasses with internal fractures can show additional degradation phenomena, which are known from other glasses without fractures, such as crusting. Analytical investigation of cross-sections with light microscopy and SEM confirm the initial investigations above. The cross-section of another sugared fragment (Roman glass, sample H 5699, Martin von Wagner Museum, Würzburg; figure 3) shows an advanced stage of fragmentation according to Huisman's classification. Several fractures cross the bulk glass. These pass straight through the glass, whereas others crosslink at the surface. The fractures are different in width; some are completely filled with gel glass, while others show gaps and the accumulation of corrosion products. Published data of fractured ancient glass (e.g. Brill, Hanson, and Fenn 1998; Schlick-Nolte and Werthmann 2003; Huisman and others 2008) suggest that the affected glasses can be classified as soda–lime glasses. Our own analysis using SEM-EDS confirms that the content of flux is nearly the same and that the percentage of calcium oxide is somewhat lower than for average Roman glasses. The silicon content is approximately 70 wt%. The difference with the mean glass composition of Roman glass is minor, but does have a tendency to be paired with lower contents of calcium (table 1). Future investigations on fractured samples will be necessary to confirm this tendency.

Fig. 2. Glass bottle with internal fractures; the overview (left) and the close-up (right) shows the characteristic crack pattern; strong fragmentation/sugaring, especially at the spout (HA 132_146-9, dated 4th century A.D. (Photo: LVR-LandesMuseum Bonn).

Fig. 3. Cross-section of sugared glass sample (Roman glass, sample H 5699, Martin von Wagner Museum, Würzburg, Germany). Top: light microscopy in transmission light. Bottom: SEM-image (Photo: authors).

Results From Laboratory Experiments With Model Glasses

Influence of Glass Composition

The chemical composition of the model glasses was chosen in order to achieve sugaring of the glass. For this reason, for both model glass types, the content of alkaline earth oxides is low; this is similar to original archaeological glasses on which sugaring was observed (see table 1).

Glass MDS8-H is similar to type MDS8, which had been designed to simulate fractures encountered on blue Baroque enamels from the Green Vault in Dresden (Wagner, Frischat, and Hellmold 2005). MK1 was designed explicitly to simulate sugaring. The difference between MDS8-H and MK1 is the content of CaO: 0.8 wt% CaO in MDS8-H and 3.3 wt% for MK1. Both model glasses are blue, due to their copper content (3 wt%).

Fig. 4. Model glass MK1 (top) and MSD8-H (bottom) after artificial weathering, macroscopic image in transmitting light (Photos: authors).

Samples of MK1 and MDS8-H (both having a rough surface and no special polishing) were exposed to the same artificial ageing conditions at 60°C and 98% RH. Images in transmission light (figure 4) were taken after 4 days for MK1 and after 1 day for MDS8-H, when the crack patterns became clearly visible. The crack patterns were sugar-like in both cases and similar to the ones found on the original glass (figures 1 and 2). Type MDS8-H reacted faster and showed a smaller crack pattern compared to model glass MK1.

Influence of Aqueous Solutions With Different pH Values

It is known that the degradation of glass is primarily related to the presence of water and is strongly influenced by the pH of a solution. Burial experiments with model glasses have showed that the formation of specific corrosion phenomena depends on the surrounding pH of the soil (Bellendorf and others 2010; Roemich and others 2002). For the simulation of sugaring, pH in the range of pH 3–13 was studied.

Visual inspections of the model glasses were carried out after storage for 10, 35, or 50 days. It was found that the degree of damage was roughly comparable in the entire range from pH 3 to pH 13. Contrary to other glass compositions, it can be stated that the formation of internal fractures on this type of glass appears to be independent of pH.

Influence of Temperature and Relative Humidity

The speed of chemical processes such as selective leaching increases with a rise in temperature. Buried objects experience slow variations in temperature. In Europe, for example, at a depth of 8 metres or more, the temperature remains constant at around 9°C all through the year (Scheffer and Schachtschabel 1998).

To evaluate the influence of the temperature on the formation of fractures, model glasses of type MDS8-H with a thickness of 2 mm were exposed to 10°C, 20°C, and 40°C. One set of samples was immersed in water, while another set was stored at high RH (atmospheric weathering at 98% RH). To simulate atmospheric weathering, samples were exposed to a temperature of 80°C. The samples were inspected regularly. To obtain an indication of the development of the damage, the moment when fractures first became clearly visible was recorded. The results are summarised in figure 5.

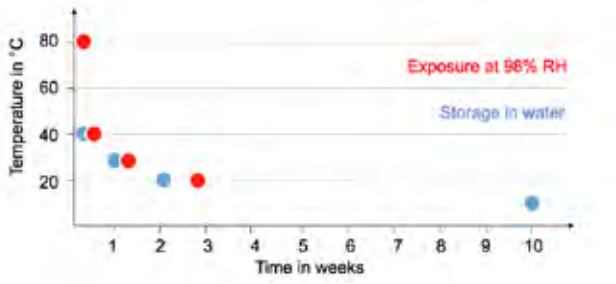

Fig. 5. Time after first signs of damage became visible after exposure of model glass MDS8-H at different temperature (blue dots for experiment with samples immersed in water and red dots for exposure at 98% RH).

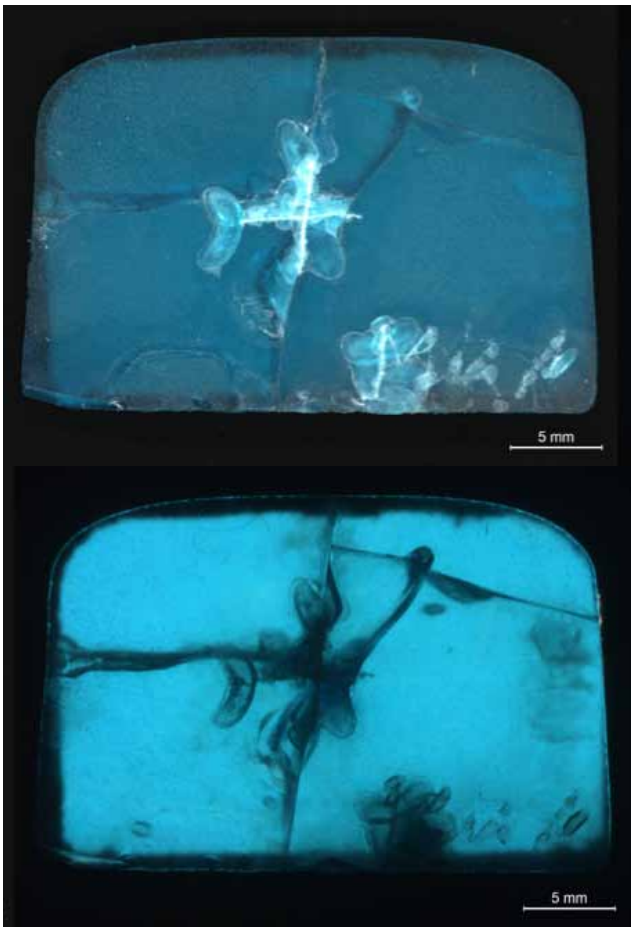

Fig. 6. Model glass MK1 after weathering (80°C, 98% RH, 19 h) in reflecting (top) and transmitting (bottom) light (Photo: authors).

At a given temperature, the deterioration process on samples stored in aqueous solutions begins earlier than samples that have been exposed to atmospheric weathering. This becomes more evident at lower temperatures. Model glasses immersed in water and stored at 40°C showed the first signs of fracturing about 3 days earlier than the samples that had been exposed to 98% RH. For samples stored at 20°C, the difference was about 6 days. An increase in temperature leads to an acceleration in the development of fractures and seemed to follow an exponential run of the curve/process. For samples immersed in water at 10°C, fracturing began after 10 weeks. At 20°C, the first signs of fracturing were already observed after 2 weeks. Where there was an increase in temperature to 30°C, samples started to crack after 1 week and, at 40°C, after about 2 days.

Influence of Different Relative Humidity/Presence of Moisture

Archaeological glasses are often exposed to very humid conditions. In areas with high ground-water levels or shorelines, the pore system of the soil is saturated with water. Apart from the top soil layer (around 30 cm) where water can easily evaporate, the degree of saturation with water in lower ground levels of middle European soils is more than 90% RH (Knight 1996; Scheffer and Schachtschabel 1998).

To simulate the influence of different amounts of moisture or cyclic changes of moisture, model glasses were placed in desiccators with 20% RH, 40% RH, 60% RH, 80% RH, and 98% RH at 30°C. The samples were investigated using transmitted light, which allows fractures to be visualised and photographically documented. In addition, light microscopy was performed. During the test period of 20 weeks, the samples stored at 20% RH did not change at all. All other samples showed crystallisation at the surface that could be observed with light microscopy. Sugaring occurred only on the samples stored at 80% RH and 98% RH; where there was exposure to very high humidity, the deterioration began earlier and developed much faster than on samples stored at 80% RH.

In order to explore the influence of fluctuating versus constant conditions, the following experiment was set up. One set of model glasses was stored permanently at 98% RH in an ambient temperature for 96 hours. A second set was exposed to cyclic conditions with an alternating wet (98% RH) and dry (30% RH) atmosphere at ambient temperature (one wet and dry cycle lasted 12 hours and was repeated 16 times). After 192 hours, both sets of samples were exposed for 96 hours to 98% RH.

Visual examination in transmitted light revealed that the glass plates stored at constant high humid conditions

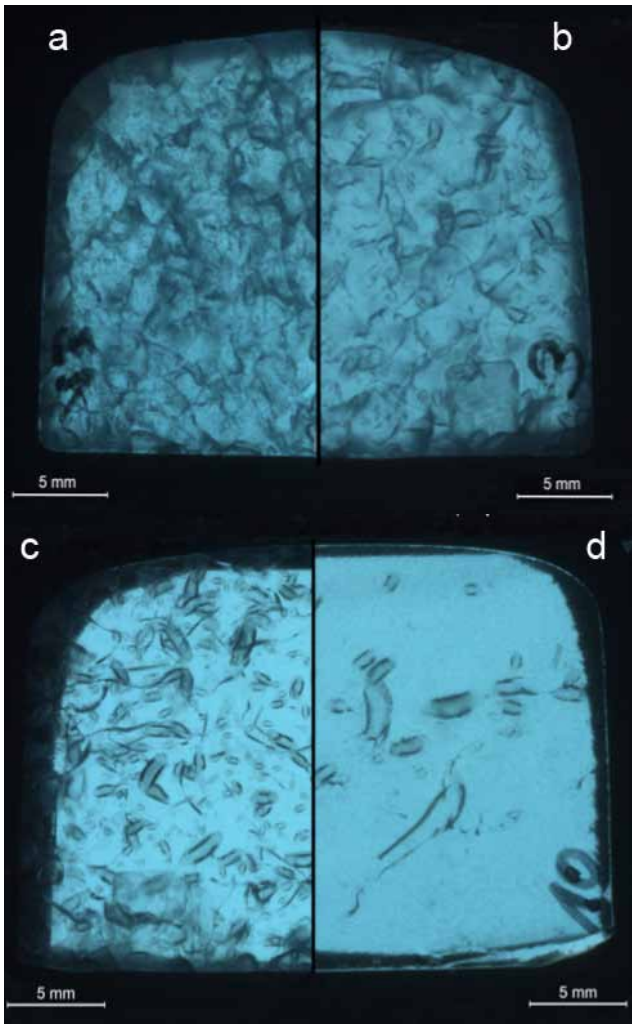

Fig. 7. Model glass MDS8-H after weathering (60°C, 98% RH, 24 h): the extent of sugaring depends on different surface treatments: (a) sand paper grain size 500, (b) rough surface resulting from the production, (c) mechanical polishing grain size 2000, (d) smooth surface achieved by fire-polishing for 6 min (Photo: authors).

showed much more fracturing than the samples exposed to cyclic conditions. It can therefore be stated that alternating wet and dry conditions do not promote sugaring, at least not at the early stages of the deterioration process.
Samples that reached an advanced state of sugaring became physically unstable and disintegrated during the drying process.

Influence of Surface Properties

It can be assumed that the condition of the glass surface has an influence on the development of damage phenomena. To test this, an experiment was designed to compare the results from model glasses where the surfaces had been treated differently. Some sample surfaces were roughened with single scratches or sand paper with different grain sizes. Other samples had a rough surface resulting from the production process or a smooth surface achieved by fire-polishing. After accelerated weathering of these samples, the damage phenomena were compared.
On samples that had been mechanically damaged, the fractures followed the pattern of the scratches (figure 6). The model glass plates with a rough surface developed fractures significantly earlier than the polished samples (which had been either mechanically polished or fire-polished). An example is given in figure 7, which shows model glasses treated with sand paper of large grain size. Here we see that the roughest surface has the worst state of sugaring after accelerated weathering. These samples developed many fractures, leading to a darker, opaque appearance. Samples with a rough surface resulting from production also had many fractures, but they did not become opaque. A significantly lower state of deterioration with limited fracturing was observed on the polished samples. Model glasses treated by fire-polishing stayed transparent and showed only some initial signs of fracturing.
When the accelerated weathering of the samples shown in figure 7 was prolonged, all model glasses developed the same crack pattern, except for the samples with a fire-polished surface. Samples treated by fire-polishing showed a delayed deterioration and a slightly different form of fragmentation producing larger fragments.

Dependence of Fracturing on Sample Thickness

The tendency for thick-walled vessel parts to develop fractures (Huisman and others 2008) was simulated in an experiment. Samples of type MDS8 (with a rough surface) with thicknesses of 2 mm, 4 mm, and 6 mm were weathered (exposed to 98% RH at 40°C for 10 days), and the degree of damage was investigated visually and using SEM cross-sections. This experiment showed that fracturing was comparable for all test specimens and, therefore, was not related to the thickness of the material.
When considering the results of this research project, the comparability of model and original glass samples has to be discussed. All model glass samples were cut from one glass block that has undergone the same production-related cooling and had no additional thermal treatment.

Complex-shaped historic objects with thicker and thinner parts may have experienced additional stresses during production. This aspect is included in ongoing experiments in order to simulate more correctly the damage observed on originals.

Summary and Conclusion

The crack pattern of sugaring is known to specialised archaeologists and conservators, but the deterioration mechanisms are not yet fully understood. The aim of this research was to study the factors influencing the formation of sugaring. Investigations using SEM on cross-sections of historic glass objects showed that the micro-fractures are often filled with gel glass or corrosion products. For conservation purposes, this is an important observation. The penetration of consolidants into such cracks would have little effect, and other techniques to bring stabilisation will have to be applied.
The significance of several parameters that may influence the formation of sugaring was explored in various experiments that successfully reproduced deterioration phenomena that are comparable with archaeological glass artefacts.
There are various ways in which the results of the laboratory tests can be related to historical glass. The two model glasses created were of similar composition but differed in the percentage of calcium oxide. The model glass with a lower CaO content (type MDS8-H) proved to be more sensitive to deterioration, since the sugaring effect developed earlier during artificial ageing. Further, this type of model glass showed a crack pattern smaller than that of type MK1. It is evident that a low percentage content of stabilising network modifiers plays an important role in the development of sugaring.
The most important parameter for the development of the fractures is the presence of water – the more humid the environment, the earlier fracturing occurs and the faster the damage proceeds. Fluctuating humidity seems to result in better preservation conditions as compared with a permanently very humid environment. A dry environment will provide the best conditions. The sugaring that developed on model glasses proved to be unaffected by fluctuations in pH values in the range of pH 3–13. This is a surprising result, since glass degradation in aqueous media is highly dependent on pH values.
The simulation experiments in this study successfully reproduced sugaring as observed on archaeological glass. An even more accurate analysis of the progress of fracturing may be achieved when more samples are applied in each experiment, by the use of more advanced analytical techniques, and the testing of glass samples with various compositions.
The use of model glasses is essential for laboratory testing. Samples with defined damage phenomena could prove helpful for further experiments, such as for the evaluation of the influence of cooling rates on crack pattern as well as for testing conservation treatments and storage conditions for sugared historic glass objects.

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Non-destructive Analysis of Altered Gold-leaf Glass Tesserae From the Mosaics of the Daphni Monastery, Greece

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Keywords:
glass; gold-leaf glass tessera; corrosion phenomena; PIXE

Abstract
The published data on analysis of gold-leaf glass tesserae are limited and usually focus on the composition of the glass. In this study, altered gold-leaf glass tesserae from the Daphni monastery (dated to the 11th century) were examined macroscopically and microscopically. Degradation phenomena were studied on the surface and near the interface with the gold leaf. The paper highlights the non-destructive investigation of the micro-morphology of corrosion layers using optical and scanning electron microscopy and provides some preliminary compositional data from investigation with micro-proton induced X-ray emission spectrometry.

Introduction
Glass mosaic tesserae with metal leaf (gold/silver or their alloys) are a unique type of tesserae due to their manufacture technique: a metal leaf is enclosed between two layers of transparent glass, the support glass and a second thin layer, the top glass (often described by the Italian term *cartellina*). Gold tesserae were used in abundance in Byzantine wall mosaics. So far, studies have focused mostly on technological issues (Fiori and others 1989; Verità 1991; Verità 1996; Brill 1999; Carbonara, Muscolino, and Tedeschi 2000; Verità and others 2000; Moropoulou and others 2002; Verità, Renier, and Zecchin 2002; Verità, Profito, and Valloto 2002; Verità 2006; Arletti, Fiori, and Vandini 2010; Verità and Santopadre 2010; Silvestri, Tonietto, and Molin 2011; Conventi, Neri, and Verità 2012).
Research on glass tesserae in general (coloured and metal-leaf tesserae) has shown that their preservation is influenced by the composition of the glass, the conditions at the monument and previous conservation treatments applied to the mosaics (Verità 1996; Verità 2000). The degradation mechanism proposed (Verità 2000; Verità and others 2000) was based mainly on weathering, i.e. the leaching of glass due to condensation phenomena, as localised corrosion was rarely detected. With low durable glasses, micro-cracks form over time in the leached layer creating further leached layers around them, while water evaporation facilitates the crystallisation of salts inside the micro-cracks promoting their propagation into the glass. However, the influence of water infiltration through the mortar was not excluded, and alterations on the side of the tesserae embedded in the mortar have been reported (Verità and others 2000).
The detachment of the top glass, a phenomenon that occurs only on metal-leaf glass tesserae, has been studied and attributed to the alteration of the glass in contact with the metal leaf due to poor adhesion between the three layers. The only published condition assessment (Verità and others 2000) concerned all categories of glass tesserae. As a result, this project was conceived with the aim to specifically study gold-leaf tesserae non-destructively in order to evaluate the surface condition and link the macroscopic and microscopic morphology of decayed tesserae.
Optical microscopy and scanning electron microscopy (SEM)

are appropriate tools to document the morphology of altered tesserae. In addition, micro-proton induced X-ray and γ-ray emission spectrometry (μ-PIXE/PIGE) was available to explore the chemical composition of glass. This publication is presenting part of a PhD research project (Loukopoulou and Moropoulou 2012a; Loukopoulou and Moropoulou 2012b; Loukopoulou and Moropoulou 2013).

Experimental Work

The Monastery of Daphni (dated to the 11th century) in Athens, Greece is an important monument of the Byzantine period; it is included in the UNESCO World Heritage List, because of its architecture and wall mosaics decoration. Tesserae from its Katholikon (church), which had been detached at different periods mainly due to natural disasters that caused severe damage to the monument, were available for this study. The selection of samples was based on the classification established *via* optical examination. The selected altered tesserae exhibited variations in surface condition along with different corrosion phenomena. Investigation was focused on the top surface, as decay alters tesserae appearance considerably.

Photographic documentation during macroscopic examination was carried out using a digital camera (Olympus, SP-560UZ). For microscopic examination, a digital portable microscope (Dino-Lite, AM211, with adjustable focus and magnification from 10x to 200 x) and a stereo microscope (Olympus SZ61 with digital camera Olympus C-7070, wide zoom, 7.1 megapixels) was used.

Analysis was performed by a FEI Quanta 200 scanning electron microscope using a large field detector. The samples were documented with secondary (SE), backscattered (BSE) and mixed (Mix) images (an overlay of backscattered and secondary electron image). The simultaneous viewing of a given area in the three observation modes facilitated the detection of compositional differences and enabled a better understanding of areas with complicated topography. Tesserae were analysed as entire pieces without applying a conductive coating. In order to facilitate analysis, a conductive custom-made holder of the samples was used, made of a cushioned piece of polyethylene foam covered with aluminium foil.

μ-PIXE/PIGE was carried out using the scanning nuclear microprobe installed at the 5 MV Van de Graaff electrostatic accelerator of the Institute of Nuclear Research of the Hungarian Academy of Sciences (ATOMKI-HAS) in Debrecen, Hungary. The tesserae were analysed as-received and were folded in aluminium foil before being fixed onto the sample holder.

Results

The transparent glass used to create the gold-leaf tesserae facilitates the optical examination of the gold leaf, and consequently any alteration that occurs at the interface is apparent if it produces a visual change. In addition, the stratification of the altered areas due to losses near the edges and at the top surface of the tesserae was revealed. Altered areas will be described by using the terms stratum, zone, layer or lamina. However, as glass corrodes in a multilayered fashion, we do not generally refer to only one layer/lamina, etc.

Optical Examination of the Surface

The tesserae showed physical and chemical deterioration along with the detachment of the top glass and the partial or complete loss of gold leaf. Physical damage usually included fissures and fractures of the top glass–along with losses around the edges but rarely involved the total break of the tessera. Macroscopically, the top surface of the tesserae exhibited the phenomena of decayed glass commonly described as a dull or iridescent surface, a whitish surface (milky) with opalescence, as well as dark discolourations in brown areas or layers (Newton and Davison 1989, pp. 154–159; Cronyn 1990, pp. 130–134; Davison 2003, pp. 183–186).

The most distinctive phenomenon observed was the greyish alteration of the gold tesserae surface, shown in figure 1. It is noteworthy that the phenomenon is limited to areas with gold leaf in the middle. The corrosion front in the case of the greyish or the pearly (whitish with opalescence) surface appeared to proceed from the perimeter of the tessera. Microscopically, the corrosion layers of the glass were not always visible on the top surface but rather on the sides of the tesserae. The top glass often exhibited a dull surface with fine depressions or a thin translucent external layer with occasional fine granular products and/or light iridescence. Moderately or heavily decayed tesserae demonstrated a more uneven texture with depressions isolated or in abundance and a surface that was either slightly rough with light iridescence or quite even with haziness and indication of

exfoliation. In other tesserae, surfaces with fairly unaltered areas (based on the undisturbed view of the gold) combined with more decayed ones, which exhibited different corrosion phenomena, were detected.

Occasionally a thick opaque layer, with strong discolouration (dark brown colour) was observed on heavily decayed tesserae (figure 2). The microscopic examination of the external thick brown layer revealed the presence of darker spots and less discoloured areas with banded semicircular zones and circular features similar to pitting. In addition, similar darkened areas were observed on tesserae with differently preserved sections, possibly indicating an initial stage of the layer's formation. On the same tesserae, along with the dark discoloured areas, the surface exhibited hazed regions with iridescence or opalescence as well as areas of detached external planes where sporadic well formed pits were detected. Moreover, rough areas with opalescence and occasional micro-pits were observed. The unevenness of the surface was created by closely packed small crevices that were partly crusted with whitish products. Depending on the angle of light, these areas also exhibited some iridescence with a metallic shine, probably due to the remains of a thin corrosion layer.

On tesserae with a greyish surface appearance, the top glass exhibited a transparent to translucent external zone that transformed near the gold layer to an opaque greyish layer with a strong shine (figure 3). The greyish zone exhibited an uneven, undulated surface with lumps that cast a shadow on the glass layer during inspection under raking light. A darkened layer was detected beneath the gold leaf (on the support glass) and, occasionally, on top. The dark layer on the support glass was usually almost black, while on top of the gold leaf it showed a more brownish colour.

Gold/glass Interface

Microscopic examination of the sides of the tesserae facilitated the study of the glass/gold interface in section. In many cases, this was possible due to the incomplete preservation of the altered areas. On tesserae with light corrosion, a thin whitish layer was detected at the gold interface, while on more decayed examples the altered zones were broader with wavy layers and occasional voids between the corroded glass and the gold leaf. A dark discolouration of the layers was detected frequently near the gold leaf or throughout the whole thickness of the altered zone, although there were also tesserae that exhibited only a light brownish hue. Sometimes the quality of bonding between the two glass layers varied among the different sides of the same tessera. This influenced the condition of the glass at the gold/glass interface, causing advanced decay that was also visible on the top surface. In general, the bonding of the two glass layers was pristine in areas where the gold leaf was absent, and only in some cases limited corrosion was detected.

Fig. 1. General view of the top surface of a gold-leaf tessera with greyish alteration. Glass areas with no gold in the middle appear transparent with an aqua hue (stereo-micrograph 20× magnification) (Photo: Polytimi Loukopoulou).

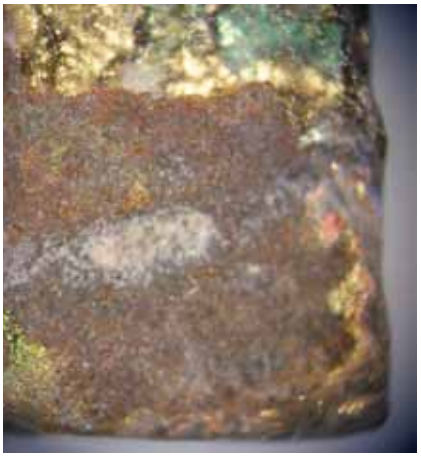

Fig. 2. Remains of a dark brown layer on the top surface of a tessera (stereo-micrograph 50 × magnification) (Photo: Polytimi Loukopoulou).

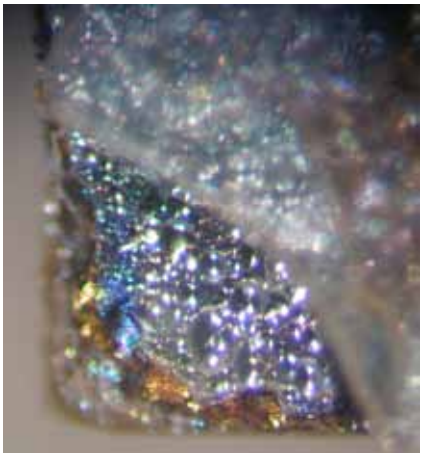

Fig. 3. Exposed stratigraphy of a tessera with greyish alteration as seen on a broken edge near the corner; transparent external zone, opaque greyish internal zone with undulated surface and fractions of the gold layer near the edge (stereo-micrograph 90 × magnification) (Photo: Polytimi Loukopoulou).

Optical examination demonstrated that the appearance and condition of the altered gold tesserae is the combined effect of corrosion at the external surface of the glass and at the interface with the gold leaf.

Micro-morphology of Altered Glass Areas

SEM revealed different corrosion phenomena on the external surface of the tesserae. The morphology of the top glass was classified in three general groups: (a) tesserae with an uneven surface with depressions isolated or connected in a polygonal fashion and the occasional preservation of a thin external layer; (b) tesserae with most of the surface covered by a thick stratum with multilayer sub-structure; and (c) tesserae with a surface that exhibited fairly unaltered glass, along with local decayed areas.

On the contrary, the top glass showed the same morphology in all the samples near the interface with the gold leaf. At the broken edges, the glass layer presented a smooth, sometimes conchoidal fracture near the external surface and a multilayer structure of corrosion close to the gold leaf. These layers exhibited an undulated surface with globular augmentations resembling the appearance of minerals with a botryoidal habit (figure 4). On lightly to moderately decayed tesserae, a thin zone of alteration was revealed; however, on heavily corroded tesserae, most of the edges were occupied by the botryoidal layers. The differences observed by optical microscopy based on colour and shine vanished on SEM images. Tesserae with greyish appearance usually demonstrated an external surface with depressions and laminated alteration with botryoidal layers close to the gold leaf.

The support glass typically exhibited advanced corrosion where it was in contact with the gold leaf and a multilayer structure with smoother morphology deeper in the glass. The deeper layers of the support glass demonstrated an uneven surface with depressions at the place where the top glass exhibited globular augmentations. Here it showed an inverted or mirror image of the *botryoidal* morphology.

When in contact with the gold leaf, the support glass displayed either a layer of inverted *botryoidal* surface or more often a rough surface of a honeycomb structure with open cells. The morphology of the surface, as shown in figure 5, also incorporated areas with banded zones of multiple parallel laminas that developed vertically towards the surface. The surrounding areas of the banded zones had a smooth or uneven surface along with 'islands' of better-preserved glass. The uneven surfaces were created by large crevices, probably due to the collapse of the smaller open cells of the structure. Moreover, the surface of the glass was frequently rough near the edges, and on many areas an abundance of granular impurities was detected.

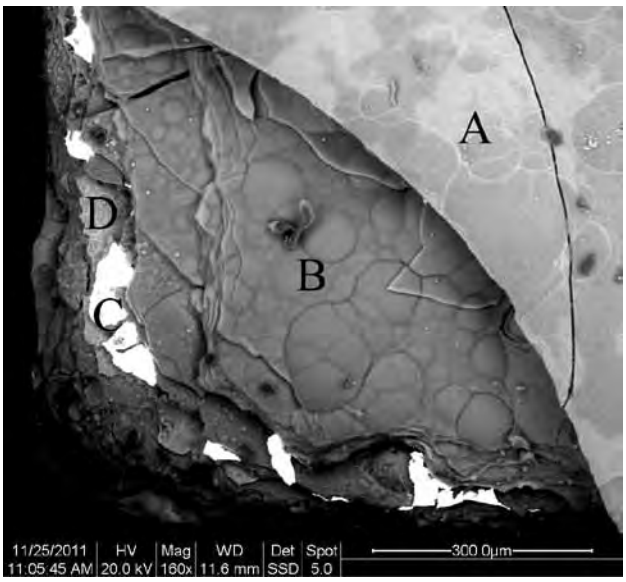

Fig. 4. SEM-BSE image of the same area illustrated in figure 3. (A) Top surface (not original due to local detachment of external stratum), (B) botryoidal altered layers, (C) fractions of the gold leaf and (D) exposed surface of the support glass (Photo: Polytimi Loukopoulou).

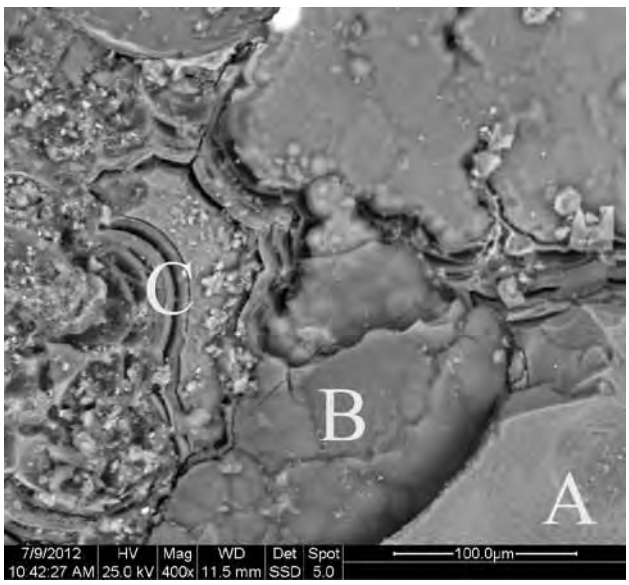

Fig. 5. SEM-BSE image. (A) external surface of the top glass; (B) internal zone of the top glass with botryoidal altered layers; (C) exposed surface of the support glass with a honeycomb structure and banded zones of multiple parallel laminas along with an abundance of impurities (Photo: Polytimi Loukopoulou).

Examination of the Exposed Interface on a Tessera With Detached Top Glass

One of the most challenging cases was a tessera with light decay on which the top glass was detached during initial sorting, making it possible to retain the two glasses for further investigation. The uncovered surface of the support glass exhibited iridescence and localised small bands with a yellowish-brown discolouration, gold leaf remnants with coloured spots, residuals of the top glass layers and few areas where the surface was detached. SEM of this surface revealed the most complex images due to the presence of the various features and the altered areas of the top and the support glass.

The top glass remnants exhibited a *botryoidal* texture (figure 6), while the support glass showed decay in the form of an incipient honeycomb structure. The support glass in contact with the gold leaf also showed zones of parallel laminas with a semicircular shape along with 'islands' of pristine glass. Moreover, on the uncovered surface of the support, small areas of pristine glass surrounded by banded zones were frequently detected. These 'islands' of unaltered glass, usually with a diamond shape, followed a pattern in the form of the gold-leaf cracking network (figure 7). These areas were quite small and possibly indicated that the gold leaf was fissured; as a consequence, the two glass layers were directly joined. This is considered to provide additional evidence that better preservation of the glass is achieved in areas without gold in the middle.

Micro-PIXE/PIGE Analysis

The micro-PIXE/PIGE analysis was used mainly to determine non-destructively the composition of the glass on the well-preserved gold-leaf tesserae. However, a few altered tesserae were also analysed. In the context of this paper, the results of micro-PIXE from tesserae with a greyish surface are discussed. The sample exhibited a broad altered zone with discoloured (blackened) corrosion layers at the interface with the gold. Figures 8–10 show the elemental distribution maps (relative colour maps) of gold, manganese and iron, respectively, from the edge of the sample. At the interface with the gold, a higher concentration of manganese and iron can be seen; this indicates that the dark discolouration of the corroded layers could be attributed to the presence of those last two elements.

Discussion

The phenomena of micro-cracks on the surface (similar to crizzling) and the collapse into small fragments under light pressure as reported for deteriorated tesserae from indoor mosaics (Verità 2000; Verità and others 2000) were not detected on the detached gold-leaf tesserae of the Daphni mosaics.

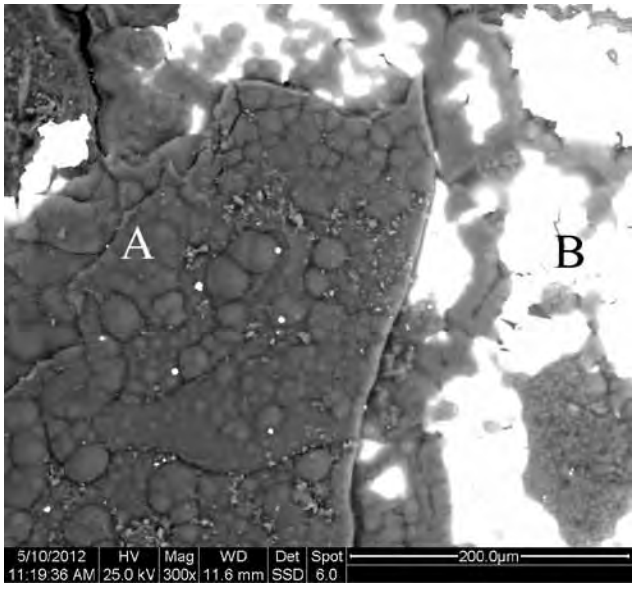

Fig. 6. SEM-BSE image. (A) fraction of the corroded top glass with botryoidal texture and (B) the exposed gold leaf (Photo: Polytimi Loukopoulou).

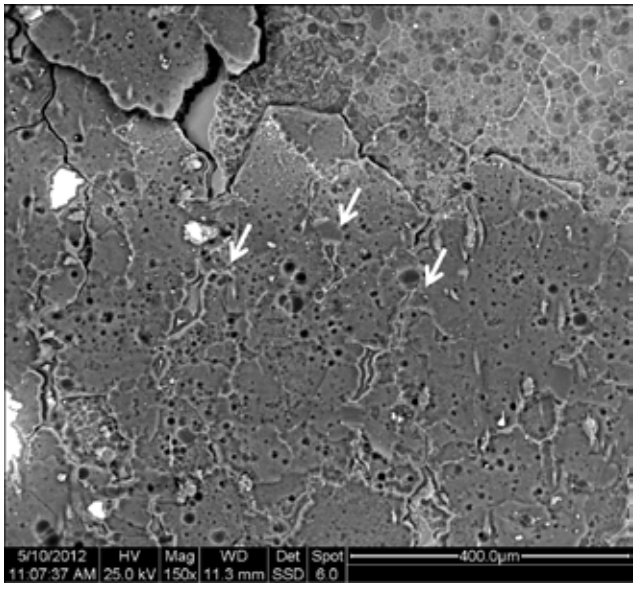

Fig. 7. SEM-BSE image. The surface of the support glass exhibiting 'islands' of unaltered glass (a few indicated by arrows) following a pattern (Photo: Polytimi Loukopoulou).

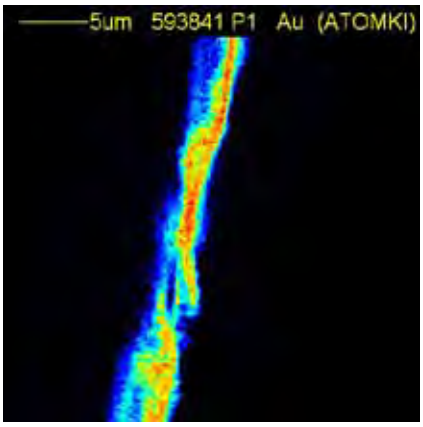

Fig. 8. μ-PIXE element distribution maps from the edge of an altered glass tessera. Relative colour maps ranging from low concentration (dark blue) to high concentration (bright red). μ-PIXE element distribution map of gold (Photo: Polytimi Loukopoulou).

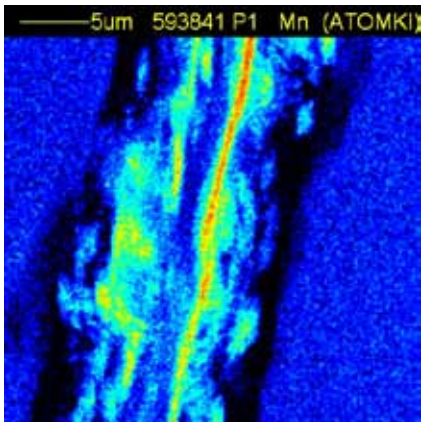

Fig. 9. μ-PIXE element distribution maps from the edge of an altered glass tessera. Relative colour maps ranging from low concentration (dark blue) to high concentration (bright red). μ-PIXE element distribution map of manganese (Photo: Polytimi Loukopoulou).

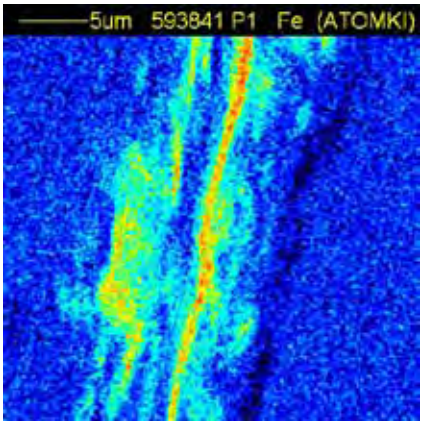

Fig. 10. μ-PIXE element distribution maps from the edge of an altered glass tessera. Relative colour maps ranging from low concentration (dark blue) to high concentration (bright red). μ-PIXE element distribution map of iron (Photo: Polytimi Loukopoulou).

Some of the gold-leaf tesserae exhibited degradation similar to archaeological glass, indicating perhaps that, prior to the detachment from the wall, they had undergone alteration not only due to weathering but also due to a more direct contact with water.

Generally, glass corrosion has been studied using SEM coupled with X-ray fluorescence spectroscopy of polished sections and rarely the surface. Further, during analysis, emphasis is usually given to the chemical composition rather than the morphology. In an attempt to describe the micro-morphology of the layers, the term *botryoidal* has been borrowed from mineralogy, where it is used for crystalline materials and describes a pattern that is visually similar to what we observe on tesserae. The term botryoidal has also been used by Morgenstein, Wicket and Barkattet in 1999 (p. 1197 and 1198) in order to describe the textural features of the layers detected on altered glass samples from Egypt.

Geilmann (1956, figs. 39–41; see Eggert 2013, this volume, for details on Geilmann's work) documented microscopically such surfaces below the weathering zone of archaeological glass. According to his observations, the layers near the unweathered glass become more and more wavy, and after their removal the exposed glass surface was covered with round etch pits. It is interesting to notice that his negative impression of the glass surface as presented on a lacquer replica has an undulated surface similar to the *botryoidal* layers. Moreover, surfaces with comparable micro-morphologies have been revealed in recent studies of excavated glass finds although they have not always been similarly described (figure 7 in García-Heras and others 2005; figure 2 in Gulmini and others 2009; figure 7 in Barbera and others 2012).

Preliminary analysis of the darkened corrosion layers of glass in contact with the gold leaf attributes the discolouration to the presence of manganese and iron. This is in accordance with the phenomenon of browning or manganese staining of excavated glass objects and stained-glass windows. Manganese-rich areas were described by Geilmann as early as 1956 and subsequently by many researchers (e.g. Shaw 1965; Newton 1971; Alten 1988; Cox and Ford 1989; Cox and Khooli 1992; Macquet and Thomassin 1992; Cooper, Fox, and Perutz 1993; Cox and Ford 1993; Libourel, Barbey and Chaussidon 1994; Schvoerer and others 1995; Knight 1996; Römich 1999; Sterpenich and Libourel 2001; Silvestri, Molin, and Salviulo 2005; Doménéch-Carbó and others 2006; Gulmini and others 2009) and investigated further by several others (Doménéch-Carbó, Doménech-Carbó, and Osete-Cortina 2001; Watkinson, Weber, and Anheuser 2005; Farges and others 2007; Weber, Eggert, and Watkinson 2007; Schalm and others 2011). The discolouration of glass is attributed to the formation of iron and manganese oxyhydroxides in the altered glass areas.

Conclusion

The corrosion of gold-leaf glass tesserae occurs both on the external surface and at the interface with the gold. Examination indicated that the presence of gold leaf influ-

ences the condition of glass at the interface. The combined effect of the glass corrosion at the exterior and at the interface is the key factor explaining the current appearance and condition of the gold-leaf glass tesserae.

Microscopic examination has demonstrated its potential as an initial tool for the systematic research of the gold-leaf tesserae decay. Analysis with SEM verified the finds of microscopic examination and provided details of the micro-morphology of corroded glass. The multi-layered morphology of corroded areas was revealed, and layers or surfaces with different characteristics were detected and described.

The most distinguishing phenomenon producing radical changes in the appearance of the gold-leaf glass tesserae was the modification into a greyish surface resembling a silver-leaf glass tessera. This was attributed to the corrosion of the glass at the interface with the gold: preliminary results of μ-PIXE analysis of the altered glass layers indicated an enrichment of manganese and iron.

This research is still in progress. Compositional differences of the altered areas will be studied. In addition, analysis of cross-sections will be carried out in order to evaluate the results of non-destructive investigation and obtain additional information.

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Bonding and Filling

The Consolidation of Cracks and Fissures in *Dalle de Verre*: Assessment of Selected Adhesives

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Keywords
adhesives; consolidation; bonding; *dalle de verre*

Abstract
Dalle de verre windows, created from 1930–1940 onwards, consist of glass pieces with a thickness of approximately 2 to 5 cm, set in a matrix of (reinforced) concrete. Besides the degradation of the concrete, the windows suffer mainly from a complex three-dimensional form of cracking of the glass elements. The cracks need to be consolidated in order to ensure stability and improve transparency. A selection of possible adhesives was evaluated: Araldite® 2020, Hxtal NYL-1™, Fynebond, Paraloid® B-72, LV740, A18 and 0R-G®. An attempt has been made to objectively compare these adhesives using a bench-marking system. None of the adhesives appears to be suitable for in situ application; sufficient penetration of the adhesives can only be realised with the help of vacuum techniques.

Introduction
The introduction of the *dalle de verre* technique in 1929 can be credited to Jean Gaudin (1879–1954) (2006). Until 1940, several prototypes and patents were filed inter alia by Auguste Labouret (1871–1964). In Belgium, the first *dalle de verre* creations can be seen in the Mine Churches of Zwartberg (1939) and Beringen (1942) (De Vis and others 2011). In both cases, the ravages of time become very evident and conservation treatments will be needed in the years to come. A common problem is the presence of complex three-dimensional cracks in the glass elements. These cracks result in a loss of stability and transparency (figure 1). Unfortunately, there is a lack of practical experience in the treatment of the glass elements present in *dalle de verre* windows.

This investigation aimed to evaluate the possibilities available to consolidate these cracks using materials that are commonly accepted or are currently under development for the conservation of window and vessel glass. The major difference with other glass consolidation problems is that the ideal consolidant for *dalle de verre* should penetrate several centimetres into the glass, while for window glass and vessel glass this penetration is restricted to several millimetres. Furthermore, the consolidants for *dalle de verre* need to be applied in situ, which distinguishes this treatment from usual workshop applications.

Experiments and Methodology of Evaluation
The mechanism of penetration of an adhesive into a crack can partially be declared by physical laws such as capillary forces ($h = \frac{2\gamma \cos\Theta}{\rho g R}$), where h is the height of the capillary tube, γ is the adhesive–air surface tension, Θ is the contact angle, ρ is the density of the adhesive, g is the gravitational field strength and R is the internal radius of the crack, and Poiseuille's law ($\Phi = \frac{\pi R^4}{8\eta}\frac{\Delta P}{L}$), where Φ is the volumetric flow rate, R is the internal radius of the tube, η is the (dynamic fluid) viscosity of the adhesive, L is the length of the crack and ΔP is the pressure difference between the two ends of the crack.

Different experiments were undertaken to explore the effect of these properties on the penetration of a selection of adhesives:

- Experiment 1: Wetting and spreading properties (γ and θ)
- Experiment 2: Differences in viscosity (η)
- Experiment 3: Capillary penetration potentials (h)
- Experiment 4: Influence of gravitational force (g).

Only the penetration ability was used as an evaluation criterion. The resistance of the adhesive to ageing (yellowing, loss in strength) and the reversibility of the adhesive were not incorporated into this study; these properties have already been studied by others (Jägers, Römich and Mueller-Weinitschke 2000, p. 137; Coutinho and others 2009, pp. 127–133). The result of each experiment was evaluated by means of a bench-marking system, based on the strategic 'balanced scoreboard' approach used in economic studies (Baima and Berrada, 2005; Caen, De Vis and Tennent 2010, p. 137). This method of ranking provides an unbiased procedure by which the various parameters (to be defined individually for each project) can be weighted in accordance with their importance. As a result, an objective evaluation can be made. For each experiment, the goals and requirements were defined as listed in table 1. To give an example: an adhesive that penetrates more than 50 mm in the gravity experiment (4) achieves 5 points, when it penetrates less (20–50 mm) only 3 points or even only 1 point in case of very superficial penetration (> 10 mm). This quantification of the results makes it possible to compare the adhesive more objectively, even though the choices made in the scoring system do not eliminate all bias. Based on the four above-mentioned experiments (each contributing with a maximum of 5 points to the overall score of an adhesive), a maximum of 20 points can be achieved. In order to have a reliable and qualitative consolidation, a minimum of 15 points (75%) should be obtained.[1]

Fig. 1. Detail of the dalle de verre Jacobus window, St Albert church, Zwartberg (Belgium), 1939. The originally yellow glasses lost their transparency and brightness due to the formation of cracks and fissures (Photo: K. De Vis).

		Araldite ® 2020	Hxtal NYL-1™	Fynebond	Paraloid® B-72 (5 wt%)	Paraloid® B-72 (10 wt%)	LV 740 (Bohle)	OR-G®	A18
Experiment 1: Wetting and spreading properties (γ and θ)									
> 30°		1	1	1	1	1	1	1	1
> 20°		3	3	3	3	3	3	3	3
Not measurable		5	5	5	5	5	5	5	5
Results experiment 1: max. 5		**1**	**1**	**3**	**5**	**5**	**5**	**3**	**5**
Experiment 2: Viscosity and penetration measurements of epoxy resins (η)									
Penetration decrease > 50%		1	1	1	In this experiment, only epoxy resins were measured				
Penetration decrease > 25%		3	3	3					
Penetration decrease > 12.5%		5	5	5					
Results experiment 2: max. 5		**1**	**3**	**5**					
Experiment 3: Capillarity penetration potentials (h)									
3a Maximum penetration in capillary tubes									
≥ 10 mm	600 µm	1	1	1	1	1	1	1	1
	1000 µm	1	1	1	1	1	1	1	1
	1400 µm	1	1	1	1	1	1	1	1
≥ 20 mm	600 µm	3	3	3	3	3	3	3	3
	1000 µm	3	3	3	3	3	3	3	3
	1400 µm	3	3	3	3	3	3	3	3
≥ 50 mm	600 µm	5	5	5	5	5	5	5	5
	1000 µm	5	5	5	5	5	5	5	5
	1400 µm	5	5	5	5	5	5	5	5
Results experiment 3a: max. 15		**1**	**1**	**3**	**4**	**2**	**4**	**2**	**2**
3b Capillarity – Velocity of penetration									
≥ 60 s	600 µm	1	1	1	1	1	1	1	1
	1000 µm	1	1	1	1	1	1	1	1
	1400 µm	1	1	1	1	1	1	1	1
30–60 s	600 µm	3	3	3	3	3	3	3	3
	1000 µm	3	3	3	3	3	3	3	3
	1400 µm	3	3	3	3	3	3	3	3
≤ 30 s	600 µm	5	5	5	5	5	5	5	5
	1000 µm	5	5	5	5	5	5	5	5
	1400 µm	5	5	5	5	5	5	5	5
Results experiment 3b: max. 15		7	7	3	13	15	11	11	15
Results experiment 3: max. 5		**1.3**	**1.3**	**1.0**	**2.8**	**2.8**	**2.5**	**2.2**	**2.8**
Experiment 4: Influence of gravitational force (g)									
90° TOP	Penetration > 10 mm	1	1	1	1	1	1	1	1
	Penetration > 30 mm	3	3	3	3	3	3	3	3
	Penetration > 50 mm	5	5	5	5	5	5	5	5
45° TOP	Penetration > 10 mm	1	1	1	1	1	1	1	1
	Penetration > 30 mm	3	3	3	3	3	3	3	3
	Penetration > 50 mm	5	5	5	5	5	5	5	5
0° BASIS	Penetration > 10 mm	1	1	1	1	1	1	1	1
	Penetration > 30 mm	3	3	3	3	3	3	3	3
	Penetration > 50 mm	5	5	5	5	5	5	5	5
45° BOTTOM	Penetration > 10 mm	1	1	1	1	1	1	1	1
	Penetration > 30 mm	3	3	3	3	3	3	3	3
	Penetration > 50 mm	5	5	5	5	5	5	5	5
90° BOTTOM	Penetration > 10 mm	1	1	1	1	1	1	1	1
	Penetration > 30 mm	3	3	3	3	3	3	3	3
	Penetration > 50 mm	5	5	5	5	5	5	5	5
Result experiment 4: max. 20		2	1	4	6	0	7	0	0
Results experiment 4: max. 5		**0.5**	**0.3**	**1.0**	**1.5**	**0.0**	**1.8**	**0.0**	**0.0**
Total results except epoxy: max. 15		–	–	–	9.3	7.8	9.3	5.2	7.8
Total results all adhesives, max. 20		3.8	5.6	10.0	12.4	10.4	12.3	6.9	10.4

Table 1: Summary of scores from the benchmark system; higher points reflect better results of the adhesive.

Selection of Conservation Materials

For the experiments, the following seven adhesives were chosen: (1) Araldite® 2020, (2) Hxtal NYL-1™ and (3) Fynebond (all three are epoxy resins), (4) Paraloid® B-72 (5 and 10 wt% in a mixture of solvents consisting of di-acetone-alcohol (70 wt%) and in acetone (30 wt%)) and the (5) UV-curing LV740 (Bohle) (two acrylates) as well as two consolidants (6) A18 and (7) OR-G®. During the experiments, the adhesives were applied once and used as delivered by the supplier or producer without changing any parameter or addition of solvents, in order to keep as much control as possible on the products and to control their natural ageing behaviour. Product specifications are listed at the end of this article.

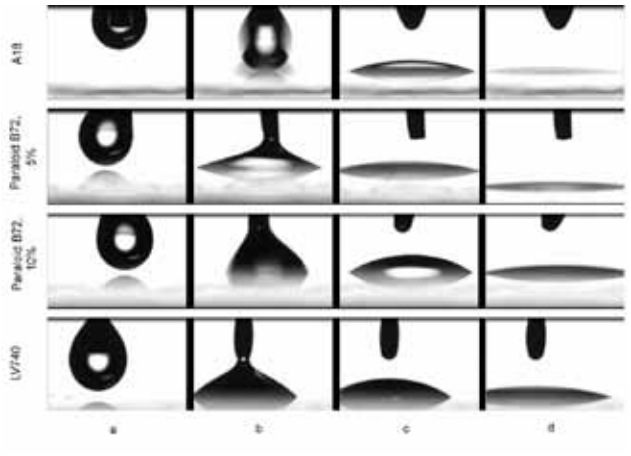

Fig. 2. The spreading of four adhesives (A18, Paraloid® B-72 (5 and 10 wt%) and LV740 viewed with a Contact Angle Measurement instrument called 'EasyDrop' (Krüss GmbH): (a) drop on a needle, (b) first contact with the surface, (c) first spreading and (d) liquid on the glass (Photo: K. De Vis).

Results of the Individual Experiments

Experiment 1: Wetting and Spreading Properties (Influence of γ and θ)

The contact angle measurements of the selected adhesives were performed using the Contact Angle Measurement instrument EasyDrop of Krüss GmbH (range: between 1 and 180°, angle resolution: ± 0.1°, drop volume: 2 µl controlled by means of a liquid dispenser). After depositing a drop of the adhesive on a (microscope) glass substrate, the image of the drop is captured through a CCD camera. The form of the drop on the glass substrate is analysed with appropriate software using a Laplace–Young curve fit of the captured image (Goossens 2012).

The EasyDrop could not be used to test the low viscosity adhesives (A18, Paraloid® B-72 (5 and 10 wt%) and LV740). The contact angles were beyond the detection limit of 20–25°. This means that the adhesive spreads out easily over the glass surface and eventually into cracks in the glass. The results for these adhesives are depicted in figure 2, which shows four successive steps in the experiment. The first image shows the drop of adhesive on the needle (a), followed by the first contact (b) and the proceeding spreading of the fluid (two steps: c and d) on the glass substrate. The other adhesives (Araldite® 2020, Hxtal NYL-1™, Fynebond and OR-G®) had measurable contact angles between 27.1 and 43.4°, respectively:

- Araldite® 2020: 43.4 ± 1.0°
- Hxtal NYL-1™: 33.0 ± 1.4°
- OR-G®: 29.7 ± 2.4°
- Fynebond: 27.1 ± 1.1°.

It was concluded that two groups can be distinguished among the adhesives. The wetting properties of acrylates and A18 can be considered to be very good (contact angle < 25°), whereas the other adhesives show inferior, but still good results. A remarkable outlier is Araldite® 2020 with a contact angle of 43.4 ± 1.0°.

Experiment 2: Viscosity and Penetration Measurements of Epoxy Resins (Influence of η)

The viscosity of an adhesive or consolidant can be influenced by various factors such as the type of polymer, its concentration in solution, its molecular weight, the polarity and the viscosity of the applied solvent as well as the ambient temperature (Kucerova and Drncova 2009, p. 151).

In conservation practice, an epoxy resin and hardener are mixed in a fixed ratio depending on the type of epoxy. Conservators often stir the epoxy mix for a variable amount of time and use the epoxy until it loses its fluidity. In an attempt to define and quantify this, the viscosity and penetration depth of Fynebond, Araldite® 2020 and Hxtal NYL-1™ were measured as a function of time. The other adhesives were excluded from this test, as their setting begins immediately with evaporation of their solvents. This is different for epoxy resins which set by chemical reaction (Horie 2000, p. 5). All viscosity measurements were executed by means of an MCR301 Rheometer (rotational modus; 20°C; spindle speed: 5 RPM; gap width: 1 mm; adhesive volume: 1 mL; time: 400 min).

In figure 3, the results are presented for each of the three epoxy resins. Generally, they were obtained immediately after mixing epoxy resin and hardener. Araldite® 2020 can be considered to be the adhesive with the lowest viscosity, followed by Fynebond and Hxtal NYL-1™. After four hours, the viscosity of the latter increased by 48% (from around 1.5 to around 2.2 Pa s), whereas the viscosity of the other epoxies increases respectively by 22% (Fynebond) and 28% (Hxtal NYL-1™) and reached levels of, respectively, 1.6 and 0.65 Pa s. Although this limited increase in viscosity suggests a good penetration as a function of time, in reality the opposite was observed. The penetration depth between two microscope glasses decreased by 41% (Hxtal NYL-1™), 45% (Fynebond) and even 61% for Araldite®2020! As a conclusion for this experiment, it can be stated that the penetration of Araldite®2020 is acceptable, but it loses this capacity as a function of time.

Experiment 3: Capillarity Penetration Potentials (*h*)

The experimental determination of the penetration depth of the adhesives into cracks in original *dalle de verre* glass elements was rendered impossible by the irregularly shaped and heterogeneous glass. A more simple experimental system was therefore employed. Glass capillaries with a diameter of 600 µm, 1000 µm and 1400 µm and a length of 15 cm were used to simulate (simplified) cracks. These commercial capillaries do not completely fulfil the conditions of *dalle de verre* windows containing a complex three-dimensional network of cracks with variation widths between about 5 nm and 2 mm, but they do permit comparison of the capillarity of different conservation materials, thus providing an indication of their expected properties in situ.

The capillary tubes were dipped into the same amount of adhesive and, in a single measurement, the achieved penetration depth and the time required to achieve this depth were recorded. The results are depicted in figures 4 and 5.

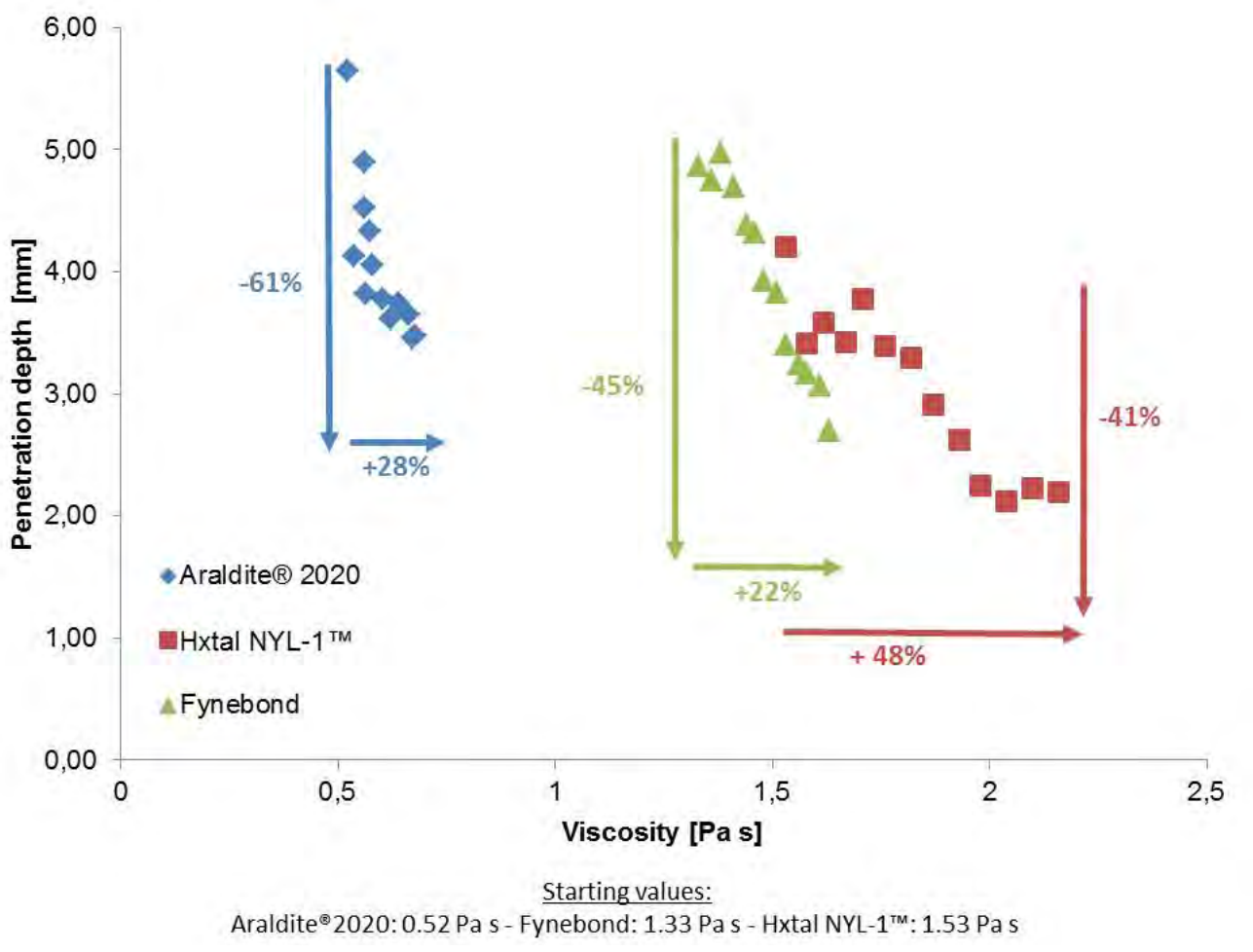

Fig. 3. Plot of viscosity {Pa s} versus the maximum penetration depth {mm} for three epoxy adhesives (Figure: K. De Vis).

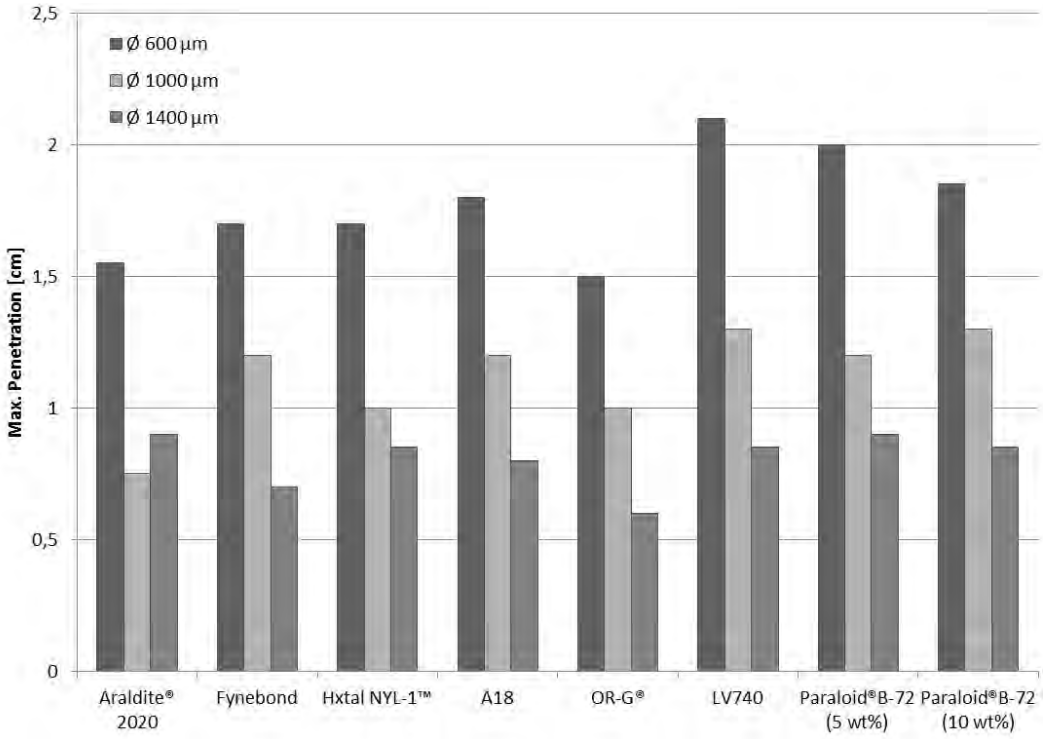

Fig. 4. Penetration depth of selected adhesives in three different types of capillaries (single measurements) (Figure: K. De Vis)

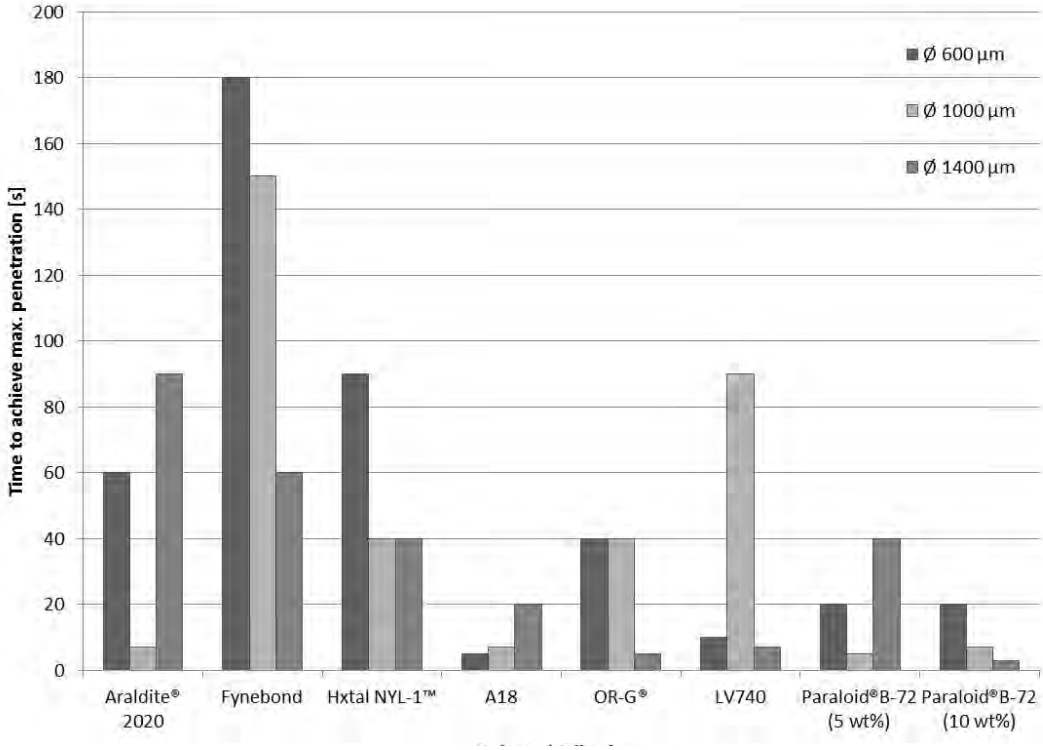

Fig. 5. Penetration velocity of selected adhesives in capillary tubes with different widths (single measurements) (Figure: K. De Vis).

The best penetration in the capillary tube of 600 µm was achieved by the UV-curing acrylic LV740 (2.1 cm) followed by Paraloid® B-72 (5 wt% – 2 cm), Paraloid® B-72 (10 wt% – 1.85 cm) and A18 (1.8 cm).
Generally, a specific consolidant shows the best penetration in the smallest capillary tube. For example, Paraloid® B-72 (5 wt%) penetrates only 0.9 cm in a capillary with a diameter of 1400 µm, while, in a tube with a radius of 600 µm, a penetration of 2 cm is achieved.
In the previous experiment, the increase of viscosity due to the polymerisation of the epoxy resins and the evaporation of the solvent in case of the other adhesives had an effect on the penetration ability of the adhesive. The quicker the adhesive reaches and covers the crack surface, the better the result of the treatment will be. Therefore, also the penetration velocity was measured.
The time to fill the capillaries was recorded during different intervals, namely 1, 3, 5, 7, 9, 20, 40, 60, 90 and 120 seconds after dipping the capillary in the adhesive and until equilibrium was attained (see figure 5). Paraloid® B-72 and A18 belong to the group of quickly penetrating adhesives: they penetrate into a tube within 20 seconds after dipping the capillary into the adhesive. This contrasts to Fynebond, which creeps slowly into the capillary tube and needs about 150 seconds to achieve its maximum penetration height. Some adhesives can be categorised as slowly penetrating adhesives in small capillary tubes, but they move more quickly into the tube once the capillary widens. This is the case for Hxtal NYL-1™.

Experiment 4: Influence of Gravity (*g*)

Again in this experiment, the complex three-dimensional shape of cracks in slab glasses were approximated in simplified form; here, two microscope glasses pressed together in a frame and positioned under different angles, 0° corresponding to a horizontal orientation of the microscope slides, 90° to a vertical orientation where the adhesive runs down and is pulled along by gravity; in the –90° orientation, the adhesive penetrates upwards, defying gravity. At –45° and +45°, the slides were oriented diagonally upwards and downwards, respectively. A constant amount of adhesive was introduced between the microscope glasses. The maximum penetration depth was measured (in mm), irrespective of the fact that the adhesives covered the complete internal surfaces of the microscope glasses or not. All tests were executed three times with all selected adhesives. The obtained averages (in mm) were fitted using the statistical measure of central tendency, called 'trimmed mean'. The major advantage of the use of a trimmed mean is that it is less sensitive to outliers than a simple numerical average (De Vis and others 2011, pp. 59–61).
In general, the impact of gravity is clearly visible as depicted in figure 6. The lower the angle of orientation (–90° à +90°), the less adhesive will penetrate into the crack.
Although *dalle de verre* are often treated in situ, these penetration depth results are also useful in the context of conservation treatments in a workshop environment of other types of thicker pieces of glass.

Summary after Four Experiments

Based on these four experiments, the scores as listed in table 1 were attributed to the different adhesives.
Considering that the maximum score that each adhesive could obtain is 20 points, it is clear that *none* of the adhesives achieves a very high overall mark. Paraloid® B-72 (5 wt%) and LV740 demonstrated the best results (around 12–13 out of 20) based on this bench-marking system.
All parameters influencing the penetration behaviour were studied under atmospheric conditions, i.e. without pressure difference ΔP between the two ends of a crack. To investigate how, in view of Poisseuille's law, this parameter may exert an influence, a final experiment was set up. It involved glass cubes with a more realistic pattern of cracks. They were consolidated under vacuum conditions. The only impregnation system based on a pressure difference that is described in the literature thus far was employed for consolidation of mural paintings (Mitronatsios and others 2010). The glass cube consolidation experiment was performed by means of a vacuum chamber and could therefore not be executed in situ.

Experiment 5: Infiltration into Glass Cubes with a Complex Crack Morphology

In this experiment, glass cubes (2.7 x 2.7 x 2.7 cm) with a complex fracture pattern were employed. These glass cubes were artificially fractured by means of a thermal shock that is automatically produced after rapid cooling of the glass sample to simulate fractured architectural glass following the system of Audrey Ougier-Simonin (2011), which involves the following steps:

1. Heating (Gobi furnace) to a maximum temperature of 300°C (the cubes were left for 1 hour at this temperature).

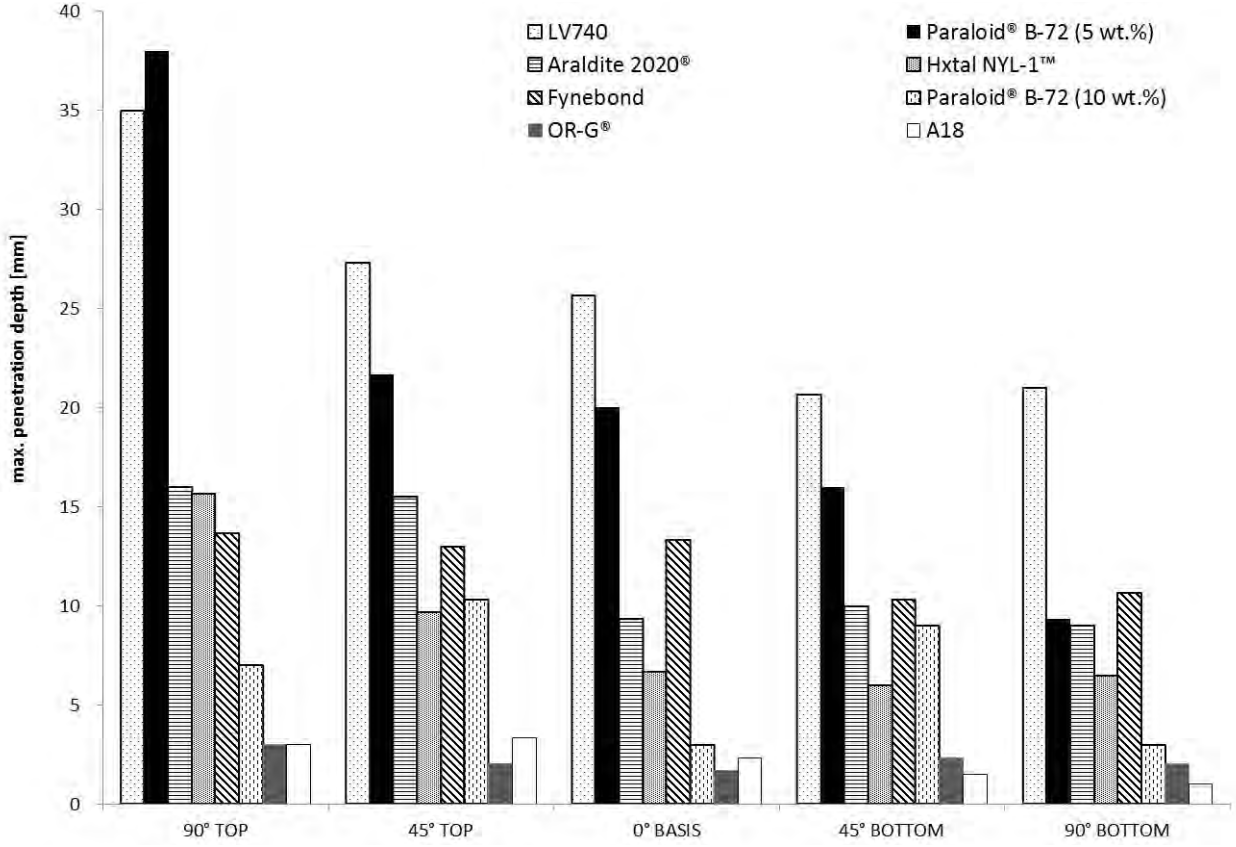

Fig. 6. Maximum penetration depth of the adhesives between two microscope glasses under different angles (Figure: K. De Vis).

2. Quenching of the cubes into distilled water at room temperature in less than 5 seconds. The thermal shock generated a differential stress field and stress relaxation, inducing crack creation and propagation.
3. Reheating up to 100°C (during 1 h) to eliminate the presence of water in the cracks of the cube.

The cracks produced by means of this protocol are very narrow, segmented and do not always reach the glass surface as the surface was cooled down extremely quickly. This cooled down layer of glass forms a seal whereas, in the cube, fractures and cracks are visible. After sealing the four faces of the cube with adhesive tape and a slight impact with a hammer, the cracks could be traced up to the surface of the glass cube.
For each selected adhesive, two cubes were consolidated by means of a different application method. Non-treated faces of the cubes were covered with tape to simulate glass embedded in concrete. In the first case, a drop of adhesive was applied on to the crack; in the second case, the glass cube was impregnated under vacuum conditions (80 kPa). In both cases, the adhesive was applied during 5 minutes on one face only of the glass cube. The time limit was selected as the amount of penetrating adhesive could not be controlled in the vacuum device.
The penetration of adhesive into the transparent glass cubes was estimated by means of a binocular microscope (ZEISS Axioskop 2 light microscope equipped with an AxioCam RC5 digital camera and Axiovision v.4.6 software).
Generally, when bonded under vacuum conditions, the amount of 'mirrors' (reflecting internal surfaces) on the crack surfaces could be reduced and the glass cubes also regained more transparency. The improvement in aesthetic appreciation of the glass cubes suggests a better penetration of the adhesives into the cracks when working under reduced pressure.

Conclusions

Dalle de verre represents a challenge for conservation research. It involves answering questions such as 'how far can the cracks be filled?' and 'how can the consolidant cure in the cracks?'

The evaluation of the efficacy of different consolidants is limited by the currently available analytical techniques. The methodology applied for this study was based on a selection of seven adhesives and consolidants with different chemical compositions. Measurements enabling a comparison of the viscosity and wetting properties of these adhesives were performed. All experiments were executed in laboratory conditions with a fixed temperature and relative humidity. In all cases, rinsed glass samples, free from contaminating materials were used, as may or may not be the case in situ.

By means of the balanced scoreboard, it became clear that only Paraloid® B-72 (5 wt%) and LV740 to some extent fulfil the requirements to consolidate this type of glass fracture. While the first tentative experiments involving vacuum-assisted consolidation showed promising results, it must be kept in mind that *dalle de verre* windows can never be treated under complete vacuum conditions when located in situ. In this respect, it may be interesting – in the frame of future research – to cooperate with colleagues responsible for the consolidation of mural wall paintings.

The conclusion is that, among the selected adhesives, no candidates were found to be adequate up until now. Neither the type of adhesive nor the technique of application is sufficient and further research is required. Furthermore, the benchmark system, as explained in this article, discussed only the physical parameters of the adhesive or consolidant. Further parameters such as reversibility, ageing properties (yellowing, brittleness), ease of treatment methodology (one or multiple layers), the probability of the consolidant to neutralise the effect of reflecting internal surfaces (called 'mirrors') to improve aesthetical issues or the need for a trained operator (conservator or technician) etc. should be added to constitute a more balanced scoreboard.

Acknowledgments

The authors are very grateful to Dr O. Schalm (University College Antwerp, Belgium) and Dr J. Dewanckele (University of Ghent, Belgium) for their help with the (analytical) interpretations.

Materials and Suppliers

- Araldite® 2020: 2-component epoxy resin (adhesive), Huntsman GmbH, Ch-Basel, technical data at http://www.farnell.com/datasheets/1640467.pdf (accessed 28 February 2013).
- Hxtal NYL-1™: 2-component epoxy resin (adhesive),Vosschemie, B-Brugge, technical data at http://www.hxtal.com (accessed 1 March 2013)
- Fynebond: 2-component epoxy resin (adhesive), Fyne Conservation Services, Schotland-Loch Fyne Argyll PA25 8BA; http://www.fyne-conservation.com (accessed 5 March 2013).
- Paraloid® B-72: thermoplastic acrylic resin (solvent: 70 wt% di-acetone-alcohol and (30 wt%) acetone), Dow Benelux, B-Terneuzen, technical data available at http://www.dow.com (accessed 5 March 2013).
- OR-G®: ORMOCER® is the protected name for a class of materials developed at Fraunhofer ISC. ORMOCER®s are inorganic–organic hybrid polymers synthesised by chemical nanotechnology, with property profiles that can be varied depending on the type of application. The ORMOCER® used in this study is an inorganic-organic hybrid polymer, a heteropolysiloxane mixed with an acrylate (Paraloid® B-72). This formula (also called OR-G®; applied in this study in a solvent mixture (Ethyl acetate:Butoxyethanol 2:1)) has been optimised for good adhesion to glass and for reversibility. It was applied as part of a multilayer protective system on medieval stained glass, for example in Cologne (see http://www.constglass.eu/, accessed on 18 February 2013). Supplier: Fraunhofer-Institut für Silicatforschung ISC, Bronnbach Branch, Bronnbach 28, D-97877 Wertheim, Germany.
- A18: The functionalised basic components used for the sol–gel process include Aluminium-sec-butylat and Triethanolamine. A18 has been developed as a consolidant for internal fractured glasses and was tested in the laboratory at Fraunhofer ISC (solvent: ethanol). So far, no case studies have been published. Supplier: Fraunhofer-Institut für Silicatforschung ISC, Bronnbach Branch, Bronnbach 28, D-97877 Wertheim, Germany.
- LV740: UV-curing acrylic resin, Bohle Benelux, Veenendaal, the Netherlands http://www.bohle-group.com (accessed 5 March 2013).

Notes

1. The viscosity tests were carried out only for epoxy resins. Therefore, the maximum achievable point for all other adhesives is 15. In table 1, the end quotation will be equated to 20 points.

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New Developments for Casting Paraloid™ B-72 for Filling Losses in Glass

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Keywords
Paraloid™ B-72; casting; fills; glass; loss compensation

Abstract
Conservators at The Corning Museum of Glass have developed a technique for casting Paraloid B-72 to compensate for losses in glass. By slowing down the evaporation of the solvent, it is possible to obtain films of bubble-free B-72 that can be used to make fills of losses in glass. Since the original research was published in 2011, there have been new experiments and case studies exploring the possibilities and expanding the applications of this technique, which are described in this paper. These include casting thick films of B-72, manipulating films to fill losses with complex curvatures, creating intentional bubbles and other methods to mimic textures of the glass, and using more complex moulds to create fills for cut and moulded glasses.

Introduction
Losses in glass can be very difficult to fill, particularly with very thin glass that is structurally unsound (Davison 2008; Koob 2000). For these types of glasses, the synthetic resins and casting techniques traditionally used in glass repairs can cause further damage (Down 1996; Koob 2006; Tennent and Koob 2010). For this reason, an alternative technique using cast Paraloid™ B-72 (B-72) sheets or films was developed at The Corning Museum of Glass and was first presented in 2011 at CCI's Adhesives and Consolidants for Conservation conference in Ottawa (Koob and others 2011). Epoxies and polyester resins are commonly used for fills in glass and their characteristics are well documented (Jackson 1983; Bradley and Wilthew 1984; Bradley 1990; Down 1996; Nunes de Silva 1998; Shashoua and Ling 1998; Down 2001). Despite having many properties well suited for making fills for glass, most epoxies and polyesters are known to yellow and degrade over time (Down 1984; Down 1986). Unlike epoxies, B-72 remains reversible and does not yellow over time (Feller 1984).

As was shown in the initial research, it is possible to cast bubble-free sheets or films of B-72. The films can be made transparent, translucent, or opaque and can be coloured with dyes and pigments to match a wide variety of glasses. Casting B-72 into sheets allows the fill to be inserted into or removed from the loss without disassembling the object, thus posing less risk of further damage. Since B-72 is such a stable material and since this technique is much safer for the object than many other loss compensation methods, the authors intend to adapt the technique for use in many different treatment applications. However, a basic cast B-72 film is bubble free, relatively thin, and flat, which is not appropriate for all glasses. The following new developments have addressed some of the more complicated ways to cast B-72 for filling losses in glass. These include fills for thicker glasses and glasses with more complex shapes and surface textures.

Casting Paraloid™ B-72 Into Sheets or Films
Paraloid B-72 can be successfully cast in sheets or films, without air bubbles, for use as fills in glass. When used as an adhesive for joins, excess B-72 develops bubbles along

join lines because of the rapid evaporation of solvent. By controlling the solvent evaporation rate, a bubble-free sheet of B-72 can be cast. B-72 is dissolved in acetone with the addition of a small amount of ethanol. Xylene can also be used, but is more toxic. The basic recipe is as follows:

30 g of B-72
100 ml of acetone
20 ml of ethanol (or 1–2 ml of xylene).

The ethanol is added only after the B-72 has dissolved completely. Additions such as fumed silica, pigments, or dyes used to change the translucency or colour of the film should be mixed into the ethanol before it is added to the mixture. The solution is then poured out into an open silicone mould or onto polyethylene sheeting or silicone release paper and covered or placed in an enclosed chamber. Covering the B-72 restricts, but does not stop, the evaporation of solvents. The very slow evaporation of the solvent allows the film to form uniformly, and prevents air bubbles from forming. The B-72 can be covered with a watch glass, Petri dish, or placed in one or two sealed plastic bags and should remain covered for 1–6 days depending on the size and thickness of the film and the exact solvent mixture. Very thick films or many films in the same chamber need to remain covered for even longer, up to several weeks. The film needs to be removed when it is still flexible enough to take on a curvature, but not so flexible that it collapses in on itself.
Once the film has been cast, it can be shaped to take on the desired curvature and cut to size. The fill can then be glued into the loss area with B-72 adhesive (Koob 1986) or simply with some acetone applied to the edge. The remaining solvent will take a few days to fully evaporate. The duration of this process can be reduced by placing the fill in a low-temperature oven either before or after joining to the object.

Manipulating the Appearance of B-72 Films

A basic B-72 film is cast flat and transparent without bubbles and is relatively thin. This is a good match for many glasses, but not for all. Some glasses are much thicker, or have bubbles or different textures; others have strong curvatures or moulded or cut decorations. Fortunately, B-72 can be cast in different ways to manipulate the appearance of the resulting film.

Fig. 1. B-72 casting with plaster inclusions (Photo: The Corning Museum of Glass).

Fig. 2. Making silicone moulds of pressed and cut glass (Photo: The Corning Museum of Glass).

Fig. 3. B-72 castings and moulds from pressed and cut glass (Photo: The Corning Museum of Glass).

Thick Films

It is possible to cast thick films of bubble-free B-72. First, a deeper mould is required, keeping in mind that the initial amount of B-72 poured into the mould will lose approximately 70% of its thickness (if one starts with a 30% solution). Second, more than one application of B-72 solution is usually required. The first application should fill the mould only halfway and be allowed to dry for 2–3 days, and then a new application of the 30% solution can be applied directly on top of the first application. It should also be allowed to dry partially for 2–3 days before a third layer is applied. The number of applications depends on the desired thickness of the B-72 film (and the depth of the mould). Thicknesses of 3–4 mm have easily been accomplished in this way. Tinted coloured films are made in the usual manner.

Curved Films

The curvature of the films can be manipulated either during or after the casting process. Casting the B-72 in a curved mould is possible, but it can be difficult to achieve an even thickness. It is much easier to cast a flat film and shape it by slumping over a curved surface while it is still flexible. If the film is already set, it is possible to soften it with a hot-air gun and give it the desired curvature. The use of heat to shape the B-72 film should be done away from the object. For strongly curved objects, such as the one described below, a silicone mould with the correct curvature can be made.

Textured and Bubbled Films

B-72 films can be textured to match a badly weathered or bubbly glass. The film can be textured by disrupting the surface while it is still slightly sticky with a finger or with a textured tool or piece of fabric that will not stick to the resin. If the film is no longer sticky, the surface can be made tacky with a tiny amount of acetone. Inclusions, such as small bits of plaster, can also be added (figure 1). This is best done after the B-72 solution has been poured into a mould.

Another way to texture the film is to allow bubbles to form. Case Study 1 describes how many tiny bubbles were created by removing the cast film early and driving off the rest of the solvent. Bubbles can also be allowed to form more slowly by uncovering the casting early, but leaving it in the mould or by not covering the casting until the desired amount of bubbles have formed. By allowing the bubbles to form more slowly, one has more control over their size and number. Slowly-formed bubbles tend to be larger than those described in Case Study 1. Bubbles in the film can be stretched to imitate how bubbles in glass are stretched during production. Stretching the film can be done while the casting is still flexible, but the film may contract again, leaving the bubbles less elongated. It is more effective to soften the film with heat after it has set and then stretch it, because it will stiffen faster and retain the stretched bubbles.

Moulded and Cut Glasses

B-72 films can also be used to imitate moulded or cut glass. One pressed-glass pitcher and one cut-glass decanter were chosen to mould and cast B-72 films. Moulds were made with a fast-setting silicone rubber in multiple applications (figure 2). Because the moulds were curved, they were built up with more silicone rubber on the sides to create a deeper 'reservoir' for the B-72 solution. Five applications of 30% clear B-72 were applied to each mould, every other day, thus building up the thickness of the film (as described above, in *Thick Films*). The resulting thick films were removed after another 2 days and looked very much like the original glass (figure 3). They could be cut and fitted in to a loss area in the same manner as thinner flat or shaped films.

Some initial experimentation with casting B-72 into a mould of a figurative bead has also been successful. The bead is three-dimensional, but because it is flat on one side it was possible to use an open mould. As with the moulds of moulded and cut glass, multiple layers of B-72 were applied to the mould over a number of days until the desired thickness was achieved.

Case Study 1: Intentional Bubbles to Create Texture

Although it is possible to cast B-72 films without bubbles, sometimes bubbles are desired to better match the fill to the glass. This was the case with an Islamic beaker (The Corning Museum of Glass 74.1.18; H: 12.05 cm; D: 8.82 cm) with a severely weathered surface. Much of the weathering had been lost, leaving the glass heavily pitted and very thin, down to 0.2 mm in the body adjacent to the losses. The beaker was broken into more than 35 fragments with about 5–10% of the body missing. The loss of the weathering had left many rough break edges that did not join well. The poor joins, the thinness and the losses led to the decision to fill the major

losses to provide additional support during handling. The fragility of the surface and the thinness of the glass made this beaker a good candidate for a cast B-72 fill.

A B-72 mixture was made according to the recipe described above. Fumed silica and some dry pigments were mixed with the ethanol. The B-72 mixture was then poured into premade silicone moulds, which were put into a plastic bag and sealed with tape.

Initially the intent was to use a bubble-free, slightly tinted B-72 film. However, the first casting was removed from its vapour chamber while there was still too much solvent in the film for it to remain bubble free. It was covered for 6 days (with two other large castings in the same bag). After 6 days, it was removed from its mould, placed on a paper cup and put in a low temperature oven (about 40–50°C) for about 36 hours to drive off the remaining solvent.

Fig. 4. Making a bubbled film: (a) the B-72 film is placed on a paper cup while still quite flexible and placed in a low temperature oven (40–50°C); (b) the B-72 film with many tiny bubbles (Photo: The Corning Museum of Glass).

Fig. 5. Islamic beaker (74.1.18) during treatment: (a) beaker showing losses; (b) the bubble B-72 film is placed over the loss; (c) after the shape of the loss was traced onto the film, it is cut out with scissors; (d) the fill is placed in the loss waiting to be adhered with acetone applied to the edges (Photo: The Corning Museum of Glass).

Fig. 6. Detail of the large fill after joining. The fill was done in two sections (Photo: The Corning Museum of Glass).

Fig. 7. Islamic beaker after treatment showing four of the B-72 fills (Photo: The Corning Museum of Glass).

Within a couple of hours, numerous tiny bubbles had formed on the film (figure 4). The texture created by the bubbles was actually very complementary to the surface of the object. Although the bubbles in the initial casting were accidental, the effect was easily re-created for additional fills using a similar process.

The B-72 films were placed over the losses while still flexible and the outline of the required fill was traced onto it with a permanent marker. The fills were cut out with scissors. In some cases the film had to be re-heated with a hot-air gun to soften it to make cutting easier. This sequence of steps can be seen in figures 5 and 6. The fills were placed in the areas of loss and tacked in by applying a tiny amount of acetone to the break with a soft brush. The eight largest losses were filled (figure 7).

Case Study 2: Strong Curvatures

Creating strong curvatures in B-72 fills can be challenging. For this case study, a silicone mould was made from an intact area of the object. The cast B-72 sheet was then heated with a hot-air gun while in the mould until it had the desired curvature.

The ancient Roman blown glass jar (The Corning Museum of Glass 69.1.22; H: 8.43 cm; D: 8.00 cm) has a wide shoulder near the base and tapers up to a restricted rim. The jar had been previously broken and repaired. The jar is made up of eight fragments that were joined with B-72 in acetone. There is one acute-angled loss, approximately 3 x 3.5 cm, along the shoulder (figure 8). The thickness of the jar wall varies over the profile; however, in the area of loss, it ranges from 1 mm to 2 mm. There is some iridescence on the surface of the glass, but the weathering layers seem to be fairly compact and mostly located on the interior.

The fragile nature, the presence of weathering layers, and the thinness of the glass, combined with the difficulty encountered when trying to reverse the previous fill, strongly favoured the use of a detachable fill for this object. The options available for making detachable fills included manipulating a cast epoxy or B-72 sheet or casting a plaster fill in place and using the plaster piece to cast an epoxy piece separate from the object. Cutting and shaping a cast epoxy sheet to fit in an irregularly edged loss is difficult to do. Casting a plaster piece in place would have been almost impossible due to the thinness of the glass and the complex shape of the loss. Therefore, cast B-72 film was chosen as the fill material because of the thinness of the glass walls and the potential to manipulate the B-72 to fit the complex loss.

The cast B-72 sheet was made using the method described above. A small amount of raw umber pigment, fumed silica, and ethanol was mixed with the B-72 before pouring it into an open rectangular silicone mould. The mould was tilted slightly while the B-72 set to mimic the variation in wall thickness of the area of loss. The mould was double bagged in polyethylene and a Zip-Lock bag to slow down evaporation. After five days, the film was removed from the mould and cut to a shape approximately 1–2 cm larger on all sides than the area of loss.

In order to conform the cast B-72 sheet to the curvature of the loss while minimising handling of the object, a silicone mould was made. The silicone was applied within a plasticine dam to a section of the shoulder near the area of loss that had a similar curvature. After the silicone had set, it was placed in an oven to cure for 24 hours.

A section of the cast B-72 sheet with a thickness that matched the profile of the area of loss was placed in the mould in a low-temperature oven to try to sag or slump it to adjust it to the correct shape. The cast sheet had become too stiff to slump into the acute angle required by the shoulder. Therefore the cast B-72 sheet was heated with a hot-air gun while in the mould. It could then be pressed with fingers and stretched slightly until it had attained the desired curvature without wrinkling around the edges.

The cast B-72 sheet was then allowed to cool slightly before removing it and placing it in the area of loss. The outline of the loss area was traced onto the cast sheet (figure 9).

Fig. 8. Roman jar (69.1.22) with loss on shoulder (Photo: The Corning Museum of Glass).

The piece was cut out of the cast sheet with scissors away from the object, as opposed to using a scalpel on the object, in order to avoid possible damage to the glass. The piece was then slightly re-shaped by heating in the mould again due to some distortion that occurred during cutting. The cast B-72 sheet responded well to the re-shaping. The curved piece was adhered with a solution of ~70% Paraloid B-72 in acetone. After adhering the fill in place, it was in-painted with Golden Matte Fluid Acrylics and Polymer Varnish with UVLS (Matte) to add the appearance of weathering layers (figure 10).

Fig. 9. Roman jar during treatment showing loss on shoulder, deeply curved silicone mould, and B-72 film with an outline of the fill (Photo: The Corning Museum of Glass).

Fig. 10. Roman jar after treatment. The B-72 fill was adhered with acetone applied to the edges and has been in-painted (Photo: The Corning Museum of Glass)

Further Experimentation

As discussed in this paper, B-72 sheets can be manipulated in a number of ways. Research into techniques for adapting the sheets to match various types of losses and glass is an ongoing process. Casting directly onto an object is possible, but so far has only been done for small fills. More experimentation is needed to improve how the fill areas are covered in order to slow solvent evaporation during casting and to see if it is possible to cast larger fills of B-72 directly onto an object.
It may be possible to mimic layered or 'sandwich' glasses either by casting a layered film or by joining layers of different coloured films with heat or solvents. It may also be possible to create B-72 films with colour gradations in which one colour blends into another colour. Additional research could also be done on whether cast B-72 films could be used as fills for losses to other materials, such as ceramics.

Conclusion

Casting B-72 films may not be an effective method for filling losses in all types of glass, but it has been shown to be a very successful technique for loss compensation in some glasses, especially fragile archaeological glasses of various shapes and surface textures; further, there is much potential for developing additional techniques and applications. B-72 has all the characteristics required for a filling material, notably reversibility, stability, health safety, ease of application, as well as the possibility of manipulating the appearance to match the glass including colouring, adding texture, and retouching. Gap filling with B-72 allows minimum intervention on the glass while limiting excessive handling, which makes it especially useful for very fragile glasses that would not tolerate the more invasive gap-filling methods traditionally used for glass. As the research described in this paper demonstrates, the basic technique for casting sheets of B-72 can be adapted to create thicker films and films with strong curvatures and some three-dimensionality. The surface of the films can also be manipulated to more closely resemble the glass it is imitating.

These new developments allow the technique to be applied to a larger variety of glasses. Future developments may allow even more applications for casting B-72 in the conservation of glass as well as other materials.

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Paraloid™ B-44: Studio Tests for the Reconstruction of a Tang Dynasty Model of a Horse

Hanneke Ramakers

Keywords

Paraloid™ B-44; earthenware; elevated ambient temperature; reversibility; heat-ageing

Abstract

The request to display a damaged Tang Dynasty model of a horse (weighing 20.5 kg) gave rise to this study. The standard adhesive at the Victoria and Albert Museum for bonding porous earthenware is Paraloid™ B-72 (methyl acrylate/ethyl methacrylate copolymer); however, the gallery temperature had previously approached the glass transition temperature of this adhesive. Paraloid™ B-44 (methyl methacrylate/ethyl acrylate copolymer) was considered to be a potential alternative; however, a literature search did not reveal the extent of solubility after ageing. Experiments were designed to ascertain the reversibility of joins on low-fired earthenware samples bonded with Paraloid B-44. The joins were no less reversible after heat-ageing than they were after one month of ageing at room temperature when compared to joins bonded with Paraloid B-72.

Introduction

The aim of the project was to compare the degree of reversibility of Paraloid™ B-44 (methyl methacrylate/ethyl acrylate copolymer) to Paraloid™ B-72 (methyl acrylate/ethyl methacrylate copolymer) when used as an adhesive for low-fired wares. The proposed display of a model of a horse (figure 1) gave reason to investigate suitable adhesives for a gallery with temperature peaks recorded between 35°C and 40°C. The earthenware model (Northern China, Tang dynasty, A.D. 700–800) weighs 20.5 kg and has extensive old repairs. Joins across the legs had failed as a result of impact damage during transit, requiring it to be dismantled into 37 fragments (figure 2). Treatment required the fragments to be bonded with an adhesive of sufficient strength to support the weight of the horse without the visual distraction of a stand. The standard adhesive for bonding porous earthenware in use at the Victoria and Albert Museum is Paraloid B-72 (methyl acrylate/ethyl methacrylate copolymer). The mixing and application method is described in Koob 1986 and Koob 2009. The glass transition temperature (T_g) is a crucial property for all adhesives used in conservation.

Fig. 1. Tang Dynasty model of a horse after treatment, H 76 x W 84 x D 28 cm, V&A C.50-1964, Mrs Robert Solomon Gift (Photo: © Victoria and Albert Museum, London).

Fig. 2. The 37 fragments of the model of a horse (Photo: Hanneke Ramakers © Victoria and Albert Museum, London).

It is defined as 'the temperature at which a material changes from a solid, "glassy" state to a softer, "rubbery" state' (Schilling 1989, p.110). In this study, the T_g is used as an indication of when an adhesive may start to flow, assuming that the higher the T_g, the less likely the adhesive is to flow at a given temperature. According to the manufacturer's information, the T_g for Paraloid B-72 is 40°C (Rohm and Haas 2007); this may pose the risk of joins softening and slumping at high temperatures (Nel and others 2011, p.132). In addition, Horie (2010, p. 24) points out that most T_g measurements are made over a timescale of around 1 minute; when measured over a longer period of time, the value of the T_g measurement can be lower (i.e. if the measurement time is increased to 10 minutes, the T_g can drop by 3°C). A lower value of the T_g over time would increase the risk of adhesive failure when the ambient temperature rises.

Paraloid B-44 with a T_g of 60°C offers an alternative. It is a slightly harder thermoplastic resin than Paraloid B-72. Both have similar solubility in acetone and are supplied as solid grade pellets (Rohm and Haas 2007).

A literature search did not reveal the extent of solubility of Paraloid B-44 after ageing. In this study, the ease of dismantling joins bonded with Paraloid B-44, before and after heat-ageing, is compared to joins bonded with Paraloid B-72 using simple tests that can be carried out in a conservation studio.

Adhesives Used for Elevated Ambient Temperatures

A number of adhesives with a T_g higher than that of Paraloid B-72 were considered for use on the Tang horse. Epoxy resins are not recommended to bond low-fired earthenware. Their cross-linking reaction can make them difficult to remove and the bond can be too strong, risking breaks to previously undamaged areas in the event of impact. However, there may be occasion to use them on earthenware objects, in combination with a Paraloid B-72 barrier layer (Oakley and Jain 2002, p. 70).

Conservators have used cellulose nitrate adhesives when a higher T_g is needed. The stability of cellulose nitrate adhesives in conservation applications, however, has been questioned for

several decades, with differences in opinion remaining (Koob 1982; Selwitz 1988; Shashoua, Bradley, and Daniels 1992; Nel 2007, p. 194; Nel and others 2011, p. 131).
Paraloid™ B-48N (methyl methacrylate/butyl methacrylate copolymer) and Paraloid™ B-66 (methyl methacrylate/butyl methacrylate copolymer) have a T_g of 50°C. A safety margin of 10°C was considered insufficient for use on the model of a horse. This was due mainly to the risk of damage to the object and nearby objects in the case of adhesive failure. A further disadvantage of Paraloid B-66 is that it has a considerably lower tensile strength than Paraloid B-44 (Down and others 1996, p. 34; Nisole 1997, p. 115).
Paraloid B-44 has a T_g of 60°C and has been used successfully on earthenware as an adhesive (Nisole 1997, p. 146; Marques 2007; Botha 2012; Tissier 2012). It has also been mixed with Paraloid B-72 to achieve an adhesive with a higher T_g (Vinçotte 2012). Paraloid B-44 has been mixed with glass microspheres and used in a filling material (Vétillard 2011, p. 17; Botha 2012) and applied as a retouching glaze (Vignier-Dupin 2012; Botha 2012).

Paraloid B-44: Comparison to Paraloid B-72

Adhesive testing published in 1996 by the Canadian Conservation Institute compared Paraloid B-44 with Paraloid B-72 in the laboratory and reported their flexibility after ageing to be similar (Down and others 1996, pp. 33–35). Cohesive tensile strength testing showed Paraloid B-44 and Paraloid B-72 were both medium to strong adhesives (Down and others 1996, pp. 33–34), the pH of the two adhesives remains similarly neutral after ageing (Down and others 1996, pp. 25–27), and they both displayed fair resistance to yellowing (Down and others 1996, p. 38). However, the elongation at break of Paraloid B-44 after ageing was significantly reduced compared to that of Paraloid B-72 (Down and others 1996, pp. 33–34), which could mean a join bonded with Paraloid B-44 would not stretch as far as Paraloid B-72. Unfortunately, in the research update of Down (2009), mechanical properties were not re-investigated.
Health and safety requirements, preparation, and bonding techniques for Paraloid B-44 are all comparable to Paraloid B-72. The main difference in application is a somewhat higher viscosity, which corresponds with a higher molecular weight and a higher T_g (Horie 2010, p. 109).
Koob (2009, p. 117) warns that Paraloid B-72 will not set well in high humidity environments and may develop a white bloom as a result of moisture being absorbed by the solvent. This issue may also affect Paraloid B-44. This does not generally present a problem in a museum environment in moderate climates, but it is a factor to consider in highly humid climates or working conditions.
No solvent-based adhesive should be used if temperatures in the workplace exceed 38°C, because it will prove difficult to apply without bubbling and stringiness (Koob 2006, p. 54).
Paraloid B-44 appears in many ways similar to Paraloid B-72 and, as such, could be a suitable alternative as an adhesive with a higher T_g for ceramic conservation applications. However, Down and others (1996) did not examine reversibility, and a literature search did not reveal previous testing on the extent of solubility of Paraloid B-44 after ageing.

Paraloid B-44: Potential Loss of Solubility

Paraloid B-44 is a main ingredient in Incralac, a commercially available lacquer formulated for the protection against corrosion of copper and copper alloys including bronze. Incralac also contains benzotriazole (BTA) as an ultraviolet stabiliser, epoxidised soybean oil as a levelling agent, toluene, and ethanol. BTA functions as a corrosion inhibitor for the copper in bronze (Bierwagen, Shedlosky, and Stanek 2003, p. 290). Erhardt and others (1984) found that Incralac applied to gold-plated bronze had cross-linked (and was difficult to remove) after 10 years of outdoor exposure. The composition of Incralac, the substrate, and the ageing conditions are different to those in this study. Nevertheless, it raises concern over the use of Paraloid B-44 as an adhesive on earthenware.
The use of a thin Paraloid B-72 barrier layer between the ceramic and the Paraloid B-44 adhesive was investigated as a suitable option to increase the reversibility of a bond without reducing its strength (Podany and others 2001). The thin Paraloid B-72 barrier layer between the earthenware and the Paraloid B-44 adhesive might lower the temperature at which the join can fail. This concern was raised with Peter Eastman (2008), Senior Scientist at Rohm and Haas Company, and his opinion was that this seemed unlikely. An adverse reaction between the Paraloid B-72 barrier layer and the Paraloid B-44 adhesive as a potential treatment for the horse seemed unlikely: Paraloid B-44 can be blended with Paraloid B-72 to adjust the resin to the balance of properties required for a particular application (Eastman 2008). Such a blend has been used by Vinçotte (2012) in

France for approximately 20 years. Blends were used by Vétillard (2011) in filling materials and by Vignier-Dupin (2012) in glazes for retouching.

Experiments Comparing the Reversibility of Joins: Paraloid B-44 and Paraloid B-72

Background

The study was carried out in a conservation studio by a conservator using a simple methodology that could easily be repeated by other ceramics conservators. Basic preliminary tests using a 50% weight/volume (w/v) solution of Paraloid B-44 in acetone were completed on broken plaster samples to assess the use of the adhesive on porous wares. The empirical information obtained from these tests was satisfactory, both in terms of workability and strength; however, doubts remained about the long-term reversibility of the joins. Further experiments were set up to test the solubility of the adhesive after ageing.

Sets of six replicates (identical samples) were made to give statistically significant results. Nine sets were prepared, including three sets that combine a Paraloid B-72 consolidation layer with a Paraloid B-44 adhesive in order to assess the effect of ageing on the solubility of this combination. Samples consolidated and bonded with Paraloid B-72 were prepared as a control for comparison (see table 1).

Sample Tile Preparation

A buff stoneware clay and firing temperature of 900°C were chosen to replicate the body of a Tang Dynasty model horse (Erickson 2012). After firing, sample tiles measuring H 103 x W 23 x D 14 mm were broken in half, before applying a consolidant and adhesive to the break edges in the combinations shown in table 1. Consolidation involved brushing two thin coats of a 12.5% w/v solution in acetone onto both break edges, which were left to cure for two days. The adhesive was prepared as a 50% w/v solution in acetone without fumed silica according to the method described by Koob (1986, p. 10). It was applied from an aluminium tube to one break edge of a sample, after which both break edges were pressed together. The bonded samples were then left to cure upright in a sand tray for two weeks. Adhesive residues on the surface were removed mechanically with a scalpel blade after curing.

Heat-ageing

The 54 sample tiles were divided in three batches. The first batch was left to age at room temperature for one month. The second batch was submitted to heat-ageing in an oven to a temperature of 75°C for 28 days. A rough estimation of what the heat-ageing may represent in years of natural ageing was calculated using the Arrhenius equation. Since the exact activation energy of Paraloid B-44 was not known at the time of testing, 100 kJ was used as an estimate. An activation energy of 100 kJ, which is average for organic materials in museum collections, equated to approximately 50 years of ageing at 20°C. It must be stressed that this assumption should be considered with caution since the equation has not always shown to represent natural ageing. Regardless of its limitations, the Arrhenius equation is frequently used in studies to estimate ageing behaviour. The third batch was kept for dismantling after longterm natural ageing at room temperature.

Dismantling

Podany and others (2001, p. 25) tested the reversibility of adhesive joins by suspending marble samples in a closed vessel containing a saturated acetone vapour environment. The method was adapted for this study in order to simulate a common practice in the V&A conservation studio using acetone as the most relevant solvent on cotton wool to dismantle the adhesive join.

On each sample, the join was wrapped in (0.5 g) of cotton wool and covered with aluminium foil to slow down the

Fig. 3. Sample preparation; the join is wrapped in cotton wool and covered with aluminium foil (Photo: Hanneke Ramakers © Victoria and Albert Museum, London).

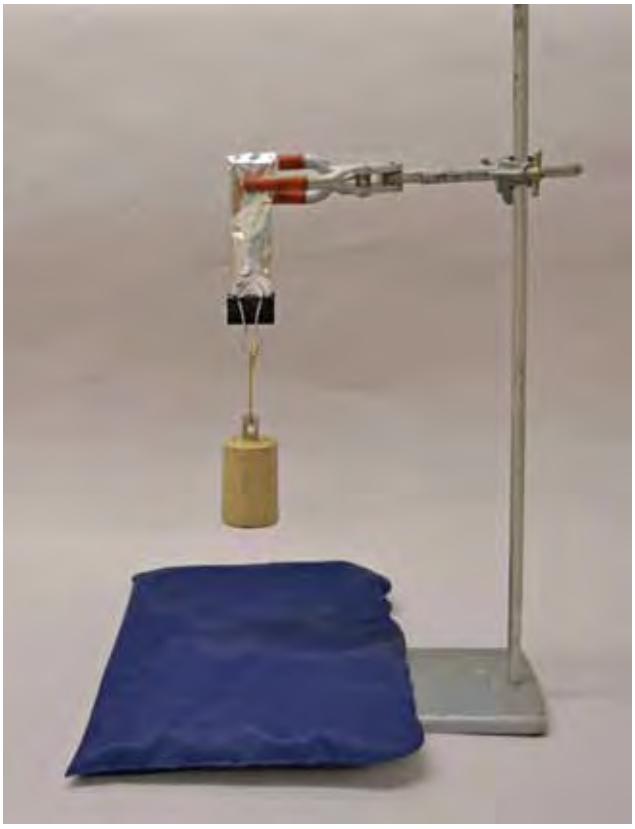

Fig. 4. The bonded sample is suspended from a retort stand with a weight attached (Photo: Hanneke Ramakers © Victoria and Albert Museum, London).

evaporation of the solvent (figure 3). To indicate a clear measurable point of separation (and solely for the purpose of the experiments), each sample was suspended vertically from a clamp in a retort stand. A small weight (302.7 g) was attached to the bottom of the samples to provide a tensile force on the adhesive join. Acetone (5 cm^3) was injected with a syringe through the aluminium foil into the cotton wool surrounding the join. The time taken for the join to separate under vertical load was measured (figure 4).
The use of weights or force in dismantling is not recommended as part of an object treatment because it can cause damage to the substrate.

Results

All joins separated easily even after ageing, with greater variation between the replicates than systematic differences between the adhesives (see table 1). The joins bonded with Paraloid B-44, regardless of the barrier layer, dismantled as easily as the Paraloid B-72 controls.

		Dismantling time (min:sec)						
	Consolidant (c) Adhesive (a)	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Average time with SD*
Aged at room temperature for 1 month **	B-72 (c) B-72 (a)	08:45	08:02	08:00	10:02	08:37	09:08	08:50 ±00:50
	B-72 (c) B-44 (a)	08:04	09:40	08:18	09:35	10:34	09:19	09:20 ±01:00
	B-44 (c) B-44 (a)	09:09	09:15	07:10	09:02	08:32	10:11	08:50 ±01:00
Heat-aged for 28 days at 75°C	B-72 (c) B-72 (a)	10:52	08:38	09:27	09:45	09:23	08:49	09:30 ±00:50
	B-72 (c) B-44 (a)	08:55	09:10	08:44	08:57	10:48	09:48	09:20 ±00:50
	B-44 (c) B-44 (a)	08:02	07:21	07:52	12:13	08:30	11:40	09:20 ±02:10

* SD = standard deviation. ** The first three batches of samples (shaded grey) were aged at room temperature for 1 month, while the last three batches were heat-aged for 28 days at 75°C.

Table 1. The time needed for the samples to separate before and after heat-ageing.

Discussion

The results suggest that joins on earthenware bonded with Paraloid B-44 remain reversible. The solubility of the adhesive after ageing is similar to that of Paraloid B-72 under the testing conditions applied in this study. It should be noted that the ageing conditions applied focused on thermal ageing, and many other parameters (including humidity fluctuations and light) were not taken into account, since they play a minor role in the museum environment foreseen for the Tang horse. Longer natural ageing periods at room temperature should give a clearer result on the long term solubility.

It should be noted that the heat-ageing of the samples was conducted at a temperature above the T_g of the adhesives. Ageing above the glass transition temperature may have an influence on the rates of deterioration reactions (Horie 2010, p. 4), which makes it more complicated to equate the results to room-temperature ageing. If more time had been available, it would have been worthwhile to repeat the heat-ageing at multiple temperatures above and below the T_g.

It must be stressed that adhesive joins on an object may not instantly fail when exposed to an ambient temperature close to the T_g of the adhesive. Failure depends on the load applied to the adhesive and the duration of that load. One should also take into account that the value given for the T_g can vary depending on how it is measured (Schilling 1989).

The study by Down and others (1996) used Paraloid B-44S, which is a 40% w/v solution of Paraloid B-44 in toluene. The results may have differed with a solution of Paraloid B-44 in acetone. There is some evidence that the tensile properties (and the T_g) of thermoplastic polymers can be affected by the type of solvent (Hansen and others 1991) and the extent to which it has evaporated from the set polymer (Schilling 1989, p. 111). Therefore, results obtained by Down and others (1996) may not be comparable to those obtained in this study.

Areas remaining for further work include assessing the extent and effect of embrittlement over time, the relevance of increased hardness compared to Paraloid B-72, and the exact point of failure in joins as a function of temperature and load. The use of Paraloid B-48N and mixtures of Paraloid B-72 and Paraloid B-44 would also be interesting to examine further. Other areas to be covered consist of adhesion to substrate, shrinkage, bond strength, and adhesive–substrate interactions.

Conclusion

Paraloid B-44 appears to be a promising alternative to Paraloid B-72 in conservation applications for bonding low-fired earthenware objects exposed to environments with risk of high temperatures.

Paraloid B-44 has several benefits. First, it has a Tg higher than that of Paraloid B-72, which reduces concerns with bonding heavy objects exposed to high ambient temperatures. Second, it has many properties that are comparable to Paraloid B-72. This includes the benefit of it having similar preparation and bonding techniques to Paraloid B-72. This familiarity is an advantage because it offers the conservator more control in its application (Pretzel 1997, p. 56).

The horse is currently on display in the World Ceramics gallery at the V&A. The time frame available meant that ageing tests were completed after the reconstruction of the horse. Whereas a reduction in solubility of Paraloid B-44 due to cross-linking behaviour was unknown, the reversibility of the joins was ensured with the use of a Paraloid B-72 barrier layer (12.5% w/v solution in acetone) on the break edges, before using Paraloid B-44 (50% w/v solution in acetone) as a primary bonding adhesive.

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Materials

Buff Stoneware 151-1117
Potclays Ltd.
Brickkiln Lane
Etruria
Stoke-on-Trent
ST4 7BP, UK
www.potclays.co.uk (accessed 20 October 2012)

Paraloid B-72 100% resin (Batch no. 6838240)
Rohm and Haas Company
100 Independence Mall West
Philadelphia, PA 19106-2399, USA
www.rohmhaas.com
Supplied by Conservation Resources UK Ltd.
www.conservation-resources.co.uk

Paraloid B-44 100% resin (Batch no. 0004185642)
Rohm and Haas Company
100 Independence Mall West
Philadelphia, PA 19106-2399, USA
Supplied by Rohm and Haas Company
www.rohmhaas.com

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Vacuum-formed PVC Moulds for Casting Epoxy Resin Fills in Glass Objects

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Keywords
glass; fills; epoxy; PVC; vacuum-forming

Abstract
This paper introduces a new method for casting epoxy resin fills in glass objects using vacuum-formed transparent polyvinyl chloride (PVC) foil for the mould walls. A review of the method of hand-forming PVC foil – from which this method evolved, including its advantages and limitations – is followed by a discussion of the process and advantages of vacuum-forming, as well as suitable equipment for its employ.

Introduction
Flawless transparent epoxy fills for glass objects can be difficult to achieve. They call for a level of finish surpassing that required for opaque fills, since the entire cross-section – both the interior and exterior surfaces as well as the body of the fill – remains visible in the finished product. Internal flaws that may have occurred during casting cannot be hidden by a layer of paint, and alterations to the fill, such as cutting or filing to re-shape it, may require hours of careful polishing to recreate a glass-like finish.
Materials that have typically been used for moulding epoxy fills are dental waxes, modelling clays, and silicone rubbers, each of which has limitations (Koob 2006). Dental wax sheets and modelling clays result in matte finishes. Silicone rubbers reproduce the surface of the glass faithfully, but they also pick up fine details from the area used to cast off that might not be appropriate for the fill. Silicone rubbers can also be too flexible and are therefore prone to distortion during the casting of larger fills due to the weight of the epoxy resin they must contain. Almost all of the materials with the exception of a few specialty silicone rubbers are opaque, or at best translucent, so it is difficult to see flaws that may occur during the filling process until after the fill material is set and the mould walls are removed.
Gorazd Lemajič of the National Museum of Slovenia introduced a novel material to glass conservation in 1997 when he began to use transparent polyvinyl chloride (PVC) foil as the mould walls for in situ fills (Lemajič 2006). This innovative moulding technique was inspired by commercial packaging often referred to as blister or clamshell packaging. As a mould material, PVC foil – with its thermoplastic, rigid, and transparent properties (European Council of Vinyl Manufacturers 2012) – offers a number of advantages over the more commonly used materials. The thermoplasticity of PVC allows it to assume the required contour through heating and placement over a positive plaster form with the same profile as the object. This precise shaping of the mould, coupled with the transparency, rigidity, and smoothness of the mould material, allows for the creation of colour-matched resin fills requiring little to no finishing after setting.
Shaping the PVC over the plaster form was initially done by hand. Lemajič spent several weeks in 2005 and 2009 at The

Metropolitan Museum of Art to introduce the PVC moulding method to conservators there and to explore its further evolution. This paper discusses the advantages of the PVC moulding method as initially practiced by hand-forming and subsequently using vacuum formers, the latter technique developed through the on-going collaboration between Lemajič and conservators at the Metropolitan Museum.

The PVC Hand-Forming Technique

The filling of a loss in a glass vessel using a hand-formed PVC mould begins with the creation of a plaster form with the same profile as the vessel in the area of the loss. This is generally accomplished by casting plaster in a silicone rubber mould taken from the object in an intact area with the same shape and surface decoration as the missing area. The PVC foil is heated with a hot air gun and then stretched by hand over the plaster form. The glass transition temperature of rigid PVC is approximately 80ºC and the working temperature for forming is approximately 120–140ºC (Reding, Walter, and Welch 1962; Perspex Distribution 2012). The foil must be continually and uniformly moved over the stream of hot air to ensure even heating. Once malleable, the foil is pulled tightly over the plaster form. The PVC cools and hardens almost immediately on contact with the plaster, resulting in a rigid and transparent mould wall in the shape of the vessel. The foil is cut so its outline extends just beyond the edges of the loss and is attached to the vessel with silicone rubber temporarily secured with custom-made wire clamps until set. The PVC foil can be used for one mould wall (usually the outer) in conjunction with a silicone rubber inner wall, or for both walls, in which case a second plaster form must be made. Epoxy resin is introduced by injection through a small hole in the PVC mould wall while the air escapes through a second exit hole. The key characteristics of PVC foil – thermoplasticity, rigidity, and transparency – make it an excellent choice for mould walls for epoxy fills.

The thermoplasticity of PVC foil allows for the formation of mould walls that fit tightly to the glass surface, thereby reducing irregularities in the fill. The foil takes the exact shape of the plaster form, which was cast in the silicone rubber mould taken directly from the object. Any flaws present in the silicone mould as a result of chips in the glass or joinlines in a repaired object can be removed from the plaster form by the addition of more plaster and/or smoothing with fine abrasives to create a perfect form on which the PVC foil can be stretched. The silicone rubber mould for the plaster form is usually taken from the object in an intact area with the same shape and surface decoration as the missing area; however, an even more efficacious fitting PVC mould wall can be created by taking the silicone rubber mould directly from the area of loss. In this case, the loss can be temporarily filled with modelling clay before moulding with the silicone; the plaster cast taken from the silicone mould also can be built up by hand with additional plaster in the area of loss. Either way, the resulting PVC mould wall will conform perfectly to the vessel around the loss since the initial silicone mould was taken directly from the area to be filled.

When the PVC mould wall is affixed in place over the loss using silicone rubber as an adhesive, a series of custom clamps hand-made of low-carbon steel welding wire keep the PVC pressed tightly to the glass. The close fit of the mould wall to the glass reduces the likelihood of leakage of the epoxy or of producing a step in the final cast. In addition, the rigidity and hardness of the PVC foil in contrast to the relative flexibility of sheet wax or silicone rubber makes it less likely to bulge out or become misshapen due to the weight of the resin in a large fill. Furthermore, the transparency and lack of colour of PVC foil allow for close visual control of the filling process. PVC mould walls provide a window through which the conservator has a clear view of the entire casting process, allowing for adjustments and corrections before the resin sets. Leakage can be avoided by checking for a continuous seal of silicone around the perimeter of the mould wall by viewing through the foil. Excess silicone in the fill area, which would affect the final shape of the fill, can also be seen through the foil. If excess silicone is present, the foil can be removed, the vessel cleaned, and the foil re-attached before introducing the resin. Once the resin has been introduced into the mould, any bubbles that form due to mixing or because of an acute angle in the outline of the loss can be seen and corrected by either of two methods: tapping the mould wall with a metal tool or introducing a small ball bearing through the air exit hole and manipulating it from outside with a strong magnet to push the bubble out through the hole (Mertik and Lemajič 2007). In addition, the inevitable shrinkage of the resin can be seen and corrected by topping up the fill with more resin before the previously added resin has fully set and the mould walls have been removed. Finally, the colour match of a tinted resin fill can be checked before setting.

If made correctly, the resulting epoxy resin fill has a glassy finish with no bubbles and is flush with the surrounding glass.

It requires little to no further finishing, which is significant since carving and sanding is not only labour intensive but can also put unnecessary stress on historic glass.

Limitations of Hand-Forming PVC

For simply curved shapes of modest size with shallow surface decoration, stretching the heated PVC by hand over the plaster form works well as long as the foil is heated uniformly and then quickly manipulated over the form at the proper angle. The technique can be mastered with experience, but difficulties can still arise with complexly curved fills or fills with pronounced relief. In these instances, additional strategies must be employed.

When heated, PVC foil is stretched by hand over a plaster form; the downward force is concentrated on the two opposite sides of the form. The foil can be easily stretched to achieve a strong curve in one direction with a more subtle curve in the crosswise direction. However, when the form curves strongly in two directions, it is very difficult to stretch the foil uniformly with only two hands. The foil will not conform closely in all areas and stretch marks can occur. This problem can be overcome by using a frame to which the PVC foil is attached around all four edges, resulting in a more uniform pressure when the frame is pulled over the form.

Plaster forms with concavities or deeply raised or recessed surface decoration pose an additional challenge, since the heated foil will catch on the raised areas without reaching into the recesses (figure 1). This problem can sometimes be addressed by using a second plaster form – a negative to slot into the positive – and a second conservator to manipulate it (figure 2; Mertik and Lemajič 2007). Besides the additional work to create the second form, this solution is also limited by the short time frame during which the heated PVC foil remains soft and malleable.

If these methods fail, the PVC mould can be made in discrete sections that can more easily pick up the curves; the mould then can be cut and fit together with tape (figure 3). In many cases, good results can be achieved with this approach. However, the process is labour intensive and leads to less than perfect fills since the seams allow some resin to leak through, resulting in raised ridges in the final cast. The fills must then be sanded and polished, instead of emerging from the mould with a glass-like surface that requires little or no finishing – which is the main advantage of the PVC moulding process.

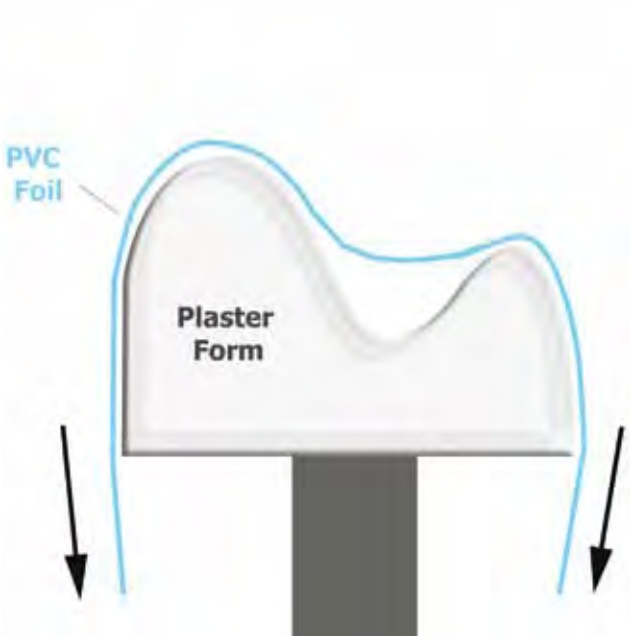

Fig. 1. Diagram showing the distribution of force (shown by black arrows) acting upon the PVC foil in the hand-forming method (Diagram: The Sherman Fairchild Center for Objects Conservation, The Metropolitan Museum of Art. Image © The Metropolitan Museum of Art).

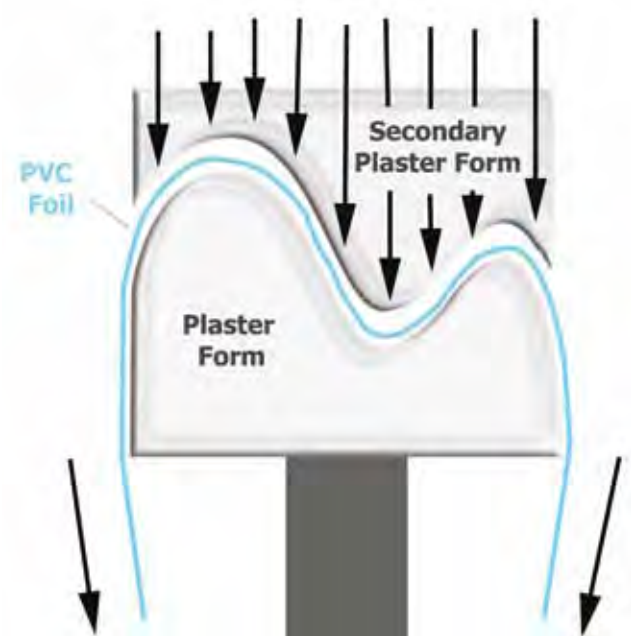

Fig. 2. Diagram showing the distribution of force acting upon the PVC foil in the hand-forming method using positive and negative plaster forms (Diagram: The Sherman Fairchild Center for Objects Conservation, The Metropolitan Museum of Art. Image © The Metropolitan Museum of Art).

For all these reasons, sole reliance on the hand-forming of PVC film for mould-making limits its potential. Commercial applications of thermoplastic PVC film, such as those used in packaging, employ vacuum-forming machines that can be adapted for use in the conservation laboratory.

Vacuum-Forming of PVC Foil

Vacuum-forming is the process by which vacuum suction pulls heated and softened plastic sheet onto a mould. Vacuums have been used since the early days of plastic-sheet manufacture, but, beginning in the 1950s, industrial machines combining a heating element with a vacuum platform began to be used in the manufacture of a wide range of products, from toys to car parts (Butzko 1958). Applications in dentistry were widely adopted in the 1960s (Escoe 1965). Today, several types of machines targeted for dentistry use are available at reasonable cost. In 2010, one of these machines was purchased for use by the Metropolitan Museum to shape rigid PVC foil for glass fills.

Using a Dental Vacuum Former

Since the vacuum formers used in dentistry serve a specific purpose, they are standard in size. They are designed to facilitate appliances for the human mouth; a five inch square (12.7 cm) of sheet plastic can create mouth guards and retainers, among other items (Pro-form 1992). This size is also suitable for the formation of moulds for a wide variety of small to medium fills for glass objects.

Fig. 3. Pieces of formed PVC cut and pieced together to make a conforming mould wall on a plaster cast (Height: 18.6 cm, Width: 13.1 cm, Depth: 6.5 cm) of a glass vessel (Photo: The Sherman Fairchild Center for Objects Conservation, The Metropolitan Museum of Art. Images © The Metropolitan Museum of Art).

Fig. 4. The Pro-form Dual Chamber Dental Vacuum Former, shown with a plaster form and heated PVC foil in the frame above (Photo: The Sherman Fairchild Center for Objects Conservation, The Metropolitan Museum of Art. Image © The Metropolitan Museum of Art).

Accordingly, a Pro-Form Dual Chamber Dental Vacuum Former (figure 4) was adopted for use in mould-making at the Metropolitan Museum.

The operation of the vacuum former is straightforward. The three most important parts of the machine are a heating element at the top, a perforated metal vacuum platform at the bottom, and a frame to hold a thermoplastic sheet that moves in between the two. Although other thermoplastic sheet materials can be used for the purposes of mould-making for glass objects, Metropolitan Museum conservators chose the same PVC foil used for hand-forming. A sheet of PVC cut to the appropriate size is placed in the frame, which is positioned just under the heating element. The plaster form is placed on the perforated platform. The heating element is switched on; when the PVC foil begins to sag enough to indicate that it is thoroughly and evenly heated, the vacuum is turned on and the frame is lowered. At that point the PVC foil is rapidly suctioned onto the form (figure 5). Following the vacuum process, the moulded PVC foil is removed and trimmed in the same manner as with the hand-forming method.

Since the suction pulls both through and around the semi-porous plaster form (figure 6), the resulting PVC mould wall conforms more closely to the form (figure 7)

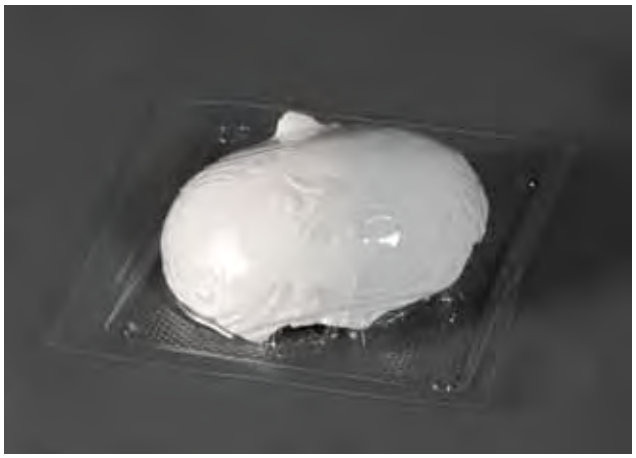

Fig. 5. Plaster form (Height: 7.1 cm, Width: 9.8 cm, Depth: 4.5 cm) with suctioned and cooled PVC foil (Photo: The Sherman Fairchild Center for Objects Conservation, The Metropolitan Museum of Art. Image © The Metropolitan Museum of Art).

Fig. 7. Plaster form (Height: 7.1 cm, Width: 9.8 cm, Depth: 4.5 cm) next to formed PVC mould wall showing good conformity (Photo: The Sherman Fairchild Center for Objects Conservation, The Metropolitan Museum of Art. Image © The Metropolitan Museum of Art).

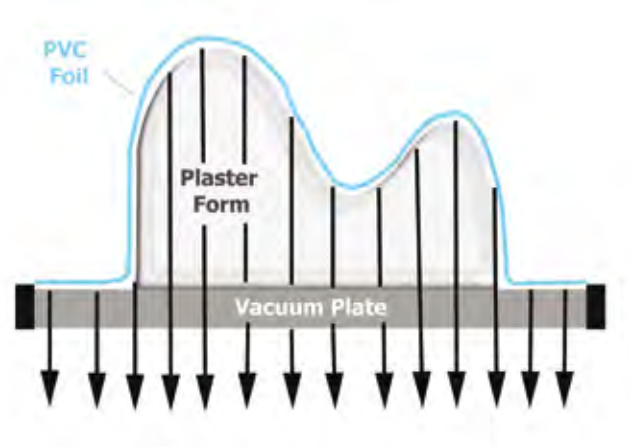

Fig. 6. Diagram showing the distribution of force acting upon the PVC foil in the vacuum-forming method (Diagram: The Sherman Fairchild Center for Objects Conservation, The Metropolitan Museum of Art. Image © The Metropolitan Museum of Art).

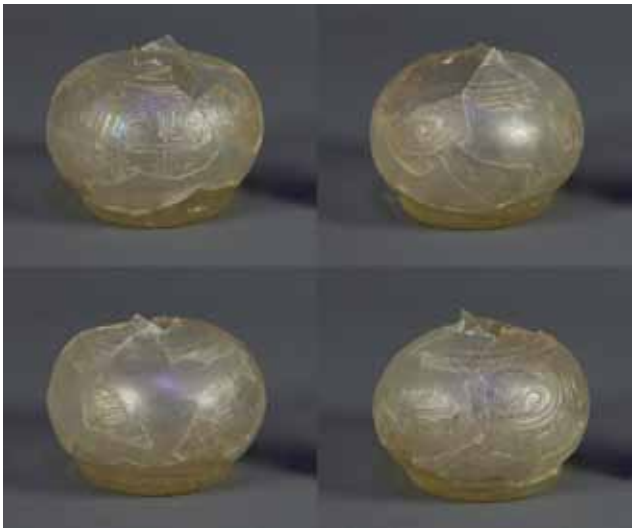

Fig. 8. Glass bottle (Height: 7.1 cm, Diameter: 10.0 cm) with epoxy fills made with vacuum-formed PVC technique. The Metropolitan Museum of Art, New York, Rogers Fund, 1940 (40.170.129) (Photo: The Sherman Fairchild Center for Objects Conservation, The Metropolitan Museum of Art. Image © The Metropolitan Museum of Art).

and, therefore, to the glass surface than one created by hand-forming with the same clarity and smoothness (figure 8). The machine is easy to use, leading to few failed attempts. The only limitation to mould-making using a dental vacuum former is one of size. The five inch square platform can be used with plaster forms no more than 3.5 inches (9.0 cm) in any direction and 2 inches (5 cm) in height. While this suffices for mould-making for fills in many glass objects, some types of fills exceed the capacity of these small machines, requiring a larger vacuum former.

Using a Table Top Vacuum Former

Most commercial vacuum formers designed for packaging are intended for large-scale production and are, therefore, too big and expensive for the typical conservation laboratory. The modest selection of smaller machines used for limited production can also be too expensive when the vacuums are built into the system. Machines designed to be used with an external household or shop vacuum and/or a vacuum pump are considerably less expensive and, consequently, more suitable for use in conservation. The household vacuum rapidly reduces the initial volume of air and the pump increases the power of the suction. One such machine, an EZFORM SV 1217 (Centroform 2009), was acquired for mould-making at the Metropolitan Museum. An existing household vacuum and vacuum pump were easily adapted for use with this vacuum former. Since these vacuum devices can be detached when not needed for use with the vacuum former, they remain available for other purposes in the laboratory.
The plastic sheet used in the larger vacuum former measures 12 inches (30.5 cm) by 17 inches (43.0 cm), which is suitable for the production of moulds for relatively large fills. Apart from the size difference and the necessity of an external vacuum, the operation of the machine is similar to that of the dental vacuum former. Having both machines available in the conservation laboratory ensures that moulds for epoxy resin fills in glass objects of all shapes and sizes can be made relatively easily and with the same degree of perfection as with the hand-forming process. Conservators faced with the task of restoring a large quantity of glass objects would find the expense of these machines reasonable, considering the many advantages they bring to the process.

Making a Custom Vacuum Former

Conservators with only an occasional need to make PVC moulds and who might not want to invest in a commercial machine can create a custom vacuum suction table for this purpose. This technique requires an otherwise sealed box with a perforated metal platform on which to place the plaster form and an attachment for a vacuum. A variety of materials can be used for the perforated platform, including a dismantled shower head (Escoe 1965). The volume of the box should be as small as possible to minimise the quantity of air that has to be evacuated during suctioning. A frame of the same dimension as or larger than the perforated platform is needed to hold the PVC foil. A simple picture frame to which the foil can be taped will suffice. The foil can be heated by hand with a hot air gun or by placing the frame in an oven. Once the PVC has softened, the vacuum can be turned on and the frame containing the PVC quickly placed over the form on the perforated platform; the suction will pull the foil tightly to create the mould wall. Although the preparation of the custom vacuum apparatus takes time and the suction process is somewhat less elegant than that achieved with a commercial machine, this technique will yield good results. Many instructional videos on making vacuum formers can be found on the internet.

Conclusion

The use of transparent thermoplastic PVC film for the casting of epoxy resin fills in glass objects represents a significant addition to the repertoire of glass-conservation techniques. Vacuum-forming machines streamline the process of shaping the foil, allowing for the creation of a wide range of complexly shaped PVC moulds more easily than can be achieved by hand. This expanded capability makes PVC moulding an even more attractive choice for the conservator. It is hoped that continued development of the method will reveal additional uses.

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Suitable Bonding Methods for the Conservation of Large Broken Plaster Casts of Ancient Sculptures

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Keywords:
plaster; bonding; adhesives; consolidation; strength

Abstract
This research addresses the difficulty of bonding broken plaster-cast sculptures. The cohesive and adhesive strength of different bonding systems is investigated using solvent-based adhesives (acrylic, polyvinyl acetate, and cellulose nitrate polymers) and epoxies applied to broken plaster samples. Bonding methods included a pre-consolidation of break surfaces. Tests were carried out on the bonded samples using a load-testing instrument with a three-point bend. The results of the mechanical load tests and visual assessment of the break edges after re-breaking gave important information about the bonding capacity of different adhesives for plaster. The strength of bonds with solvent-based adhesives came closer to the strength of the plaster itself, and those adhesives have the added advantage of possible reversibility compared to epoxy adhesives. Pre-consolidation of the break surface appears to influence the strength of the bond and the appearance after breaking.

Introduction
After a period of decline and disinterest, there has been a re-evaluation of collections of plaster casts of historical and antique sculptures in recent years. These plaster copies of original stone or bronze sculptures are now receiving growing attention because of their aesthetic, historical, and cultural value (Frederiksen and Marchand 2010). These collections and objects are now considered to have a value of their own, while at the same time providing information about the original stone or bronze sculptures the casts were taken from.

Changes in ideas on education and aesthetics in the first quarter of the twentieth century resulted in a growing disregard for plaster-cast sculptures. Copies were no longer deemed acceptable, and the casts were thrown away or became neglected. Poor storage and incorrect handling of the casts resulted in soiling and mechanical damage, plaster being fragile, porous, and hygroscopic.

Conservation of these objects has become a great challenge. Only limited research has been undertaken into the cleaning of plaster casts (Schulz 1992; Dooijes 2005; Anzani and others 2008; Badde 2009; Coon 2009), and there remains a lot to be learned about the problems of bonding heavy sections of broken plaster casts. This latter issue is the focus of this paper, contributing to a research project on plaster casts in the Netherlands by the Cultural Heritage Agency in cooperation with The National Museum of Antiquities in Leiden and the University of Amsterdam. Some of the results of this research relating to the composition and conservation techniques for plaster were presented during the 16th Triennial ICOM-CC Conference in Lisbon in 2011 (Megens and others 2011).

The aim of the investigation presented in this paper was to study the suitability of bonding methods for large broken plaster casts. Key issues are the fragility and porosity of the plaster and the difficulty of bonding heavy broken parts positioned at an angle, such as arms. The cohesive and adhesive strength of different materials and bonding systems were assessed, including their behaviour when placed under sufficient pressure to cause new fractures. Tests were carried out in order to simulate the sort of stresses encountered by restored plaster-cast sculptures.

The Making of Plaster-cast Sculptures

Plaster-cast sculptures are made by copying an original object by means of a plaster mould or, in the case of large sculptures with a complicated form, with multiple moulds. The surface of the plaster mould has to be treated with a releasing agent of gelatine or soap before a replica can be cast from plaster. Once the plaster has set, the separate sections of the mould are removed, and a copy of the original is obtained. To simulate the appearance of the original piece, the surface is often painted or patinated using oil paint or other materials.

Large plaster sculptures were occasionally made in several pieces, because of the weight of the casts. The pieces were fitted together using dowels, thereby reducing the stress of the weight at the point of contact. Often dowels or armatures, mostly made of wood or metal, were placed in the mould before casting in order to provide structural strength to the plaster cast.

Properties of Plaster Objects

Plaster is made by heating and grinding the mineral gypsum also known as hydrated calcium sulphate ($CaSO_4 \cdot 2H_2O$). By heating gypsum (120–150°C), water is driven off producing calcium sulphate hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$), known as 'plaster'. By mixing this powder with water, a chemical reaction then begins, resulting in hydrated calcium sulphate. The water molecules that do not bond to the calcium sulphate evaporate, leaving a gap or pore behind, which enables capillary movement of water into the plaster. Plaster is hygroscopic and attracts water. It is slightly soluble and will dissolve by 2.05 gram per litre at a temperature of 20°C. Plaster has a density of 2.31 g/cm^3 and a hardness of 2 on the Mohs scale. The working properties of plaster can be modified by adding other materials in order to obtain a longer working time or greater structural strength (Dubbers 2006).

Conservation of Plaster

The conservation of plaster casts is challenging, because of the specific properties of plaster, notably its vulnerability for physical damage and its high porosity. Plaster is affected by moisture and changes in humidity. Its hydroscopic nature results in the attraction of moisture and dust, which often leads to soiling of the pores at the surface.

Little is known about the effect of the different bonding methods used on plaster, and literature on the subject of bonding broken plaster sculptures is scarce, which is not surprising considering the lack of interest in these objects until recently. Interviewing conservators with experience in plaster conservation gave some insight into the bonding methods that have been used in recent years. Since plaster has comparable properties to low-fired ceramics, notably density and porosity, the same or similar conservation materials and techniques are often used in plaster conservation. Nevertheless, plaster has characteristics different to those of ceramics and, therefore, requires a different conservation approach.

In contrast with fired ceramics, plaster is slightly soluble in water. Aqueous cleaning can cause dissolution of the outer surface layer and transportation of water into the pore structure of the plaster by capillary action. This can lead to the corrosion of metal armatures near the surface. This corrosion can result in physical damage because of the expansion of corrosion products or staining at the surface of the object. These properties also influence the suitability of a bonding system.

Conservation ethics require that the bond between the adhesive (bonding material) and the object being bonded should be reversible and/or re-treatable (Bradley 1984). Because of the size, weight, and form of plaster-cast sculptures (often with extending parts), breaks in these sculptures generally require a strong bond. While a strong adhesive bond is desired, the adhesive strength of the bonding material used at the surface should not exceed the cohesive strength of the plaster. If this is the case, there is a risk that any new fractures that may occur will do so at a new point of weakness in the plaster instead of along the original bonded joint. The bonding method must be strong enough to hold the load, but should not be so strong that it carries the risk of further damage to the object in the future. The attempt to ensure sufficient strength can, therefore, be in conflict with ethical issues.

The use of dowels in the conservation of plaster-cast sculptures is currently considered to be acceptable, even though loss of original material will occur when holes are made for the dowels. The aim of this research was to provide greater insight into the effectiveness of bonding methods used on plaster to avoid having to resort to reinforcement with dowels.

Experimental work

Selection and Preparation of Plaster Blocks

To test the selection of bonding systems, plaster blocks were cast and then broken. The plaster brand chosen for casting the plaster test blocks was Molda 3 Normal™, which is used by renowned plaster casters in Brussels, Paris, and Berlin (Plaster Cast Workshop 2011). All test blocks were made from the same quantity of plaster and water (65:100 w/w). The test blocks were cast using a rectangular open-face mould 160 x 40 x 40 mm, constructed from wood strips that had been screwed together.

After casting, the blocks were placed in a warm environment at approximately 45°C (Clérin 1990; Dubbers 2006) for a period of two months to ensure that they were fully dried. The resulting plaster test blocks were then broken by means of a load-testing apparatus (Instron 8872 Fatigue Testing System) with a three-point bend to make them suitable for applying the selected bonding methods. The position and form of the breaks were made as uniform as possible, while still creating a naturally broken sample. All the breaks were perpendicular and without loss of material along the break edge. The breaks of the plaster test blocks were fairly uniform, with a few exceptions.

Selection and Application of the Bonding Materials and Methods

The selection of the bonding techniques to be tested was based on literature research, information gained from interviews with conservators, past conservation reports, and a study of the methods currently used in ceramic conservation. The bonding methods selected involved six different adhesives, divided into two groups: one group of solvent-based adhesives (acrylic, polyvinyl acetate, and nitrate polymers) and one group of epoxy adhesives. These were combined to produce ten different variants (table 1).

One of the adhesive used by many conservators is Paraloid B-72™, an ethyl methacrylate/methyl acrylate copolymer that is commonly used in the conservation of archaeological glass and ceramics (Buys and Oakley 1993; Koob 2009). Conservators generally use Paraloid B-72™ to conserve smaller plaster objects. Another material used in the conservation of plaster objects is Weldbond Universal™, a water emulsion of polyvinyl acetate (MacKay 1997). Another cellulose-nitrate-based adhesive, Mecosan L-TR™, is used by Belgian conservators at the Flemish Institute for Immovable Cultural Heritage (Vlaams Instituut voor het Onroerend Erfgoed).

Conservators commonly use epoxy adhesives in the conservation of glass and high-fired ceramics. However, these adhesives are also used in plaster conservation, as occurred during a restoration project of large plaster-cast sculptures for an exhibition at the National Museum of Antiquities in Leiden in 2008. In this case, Araldite 2020™ with the addition of fumed silica (Poly-service Aerosil thixotropic powder) was used. Other epoxy adhesive tested were Araldite 2012™ (a fast-curing epoxy that hardens in several minutes) and Araldite 2011™ (a viscous epoxy with a longer working time of 7 hours).

All the bonding methods involved pre-consolidation of the plaster surface in order to seal the break edges. This was done in an attempt to prevent the strong adhesives being absorbed into the plaster surface and to improve the reversibility of the bond (the ability to dismantle the bond without damage). Horie states that 'a two-stage process of a permanently soluble primer with a cross-linking adhesive may ensure reversibility for the process' (Horie 1987). In most cases, the consolidant used was Paraloid B-72™ diluted in acetone and ethanol (70:30 v/v). This material was chosen because of its known long-term stability, which is important since consolidation treatment itself is not reversible (Horie 1987). Ethanol was used in the Paraloid B-72™ solution to slow down the evaporation process and increase penetration into the pores in order to obtain deeper surface consolidation and therefore deeper structural strength through the surface layer of the plaster. Paraloid B-72™ is often used as a pre-consolidant in the conservation of porous ceramics to increase the reversibility of fills, as it is easy dissolved in acetone.

With other bonding systems researched, the consolidant used was a solution of the adhesive itself. This was tested to see if there was a difference in bond strength where one or two materials were used in the bonding system. When two different materials are used, the consolidant could reduce the bond strength as it creates an extra 'adhesive' interface between the adhesive and consolidant, which may be weaker than that between the consolidant and plaster.

The method of application used for the epoxy adhesives Araldite 2012™ and Araldite 2020™ differed. On some samples, they were partially applied on sections of the break surface as separate drops, while on others they were applied along on the entire break surface. The partial application of the epoxies was done in an attempt to improve reversibility, as it would enable better solvent penetration.

During application of the adhesives, a distance of approximately 5 mm was left between the adhesive and the edge of

Bonding methods

Adhesive	Consolidant	Load (kN)	Damage to break surface	Appearance after breaking
Solvent-based adhesives				
50 % Paraloid B-72™ in acetone	Three layers of Paraloid B-72 in acetone/ethanol (70:30): 5, 10, and 15%	0.6 ± 0.2; 1.4 ± 0.4 on plaster test blocks added borax	-	Few plaster pieces remain on break surface (1 – 8 mm thick)
Mecosan L-TR™	10% Mecosan L-TR diluted in Kiwosolv L72™ (commercial solvent based on ethyl acetate) (v/v)	0.8 ± 0.2; ~0.6 on plaster test blocks added borax	+	Few flakes pulled away from surface spots
Weldbond Universal™	10% Weldbond diluted in demiwater (v/v)	1.5 ± 0,3	-	Plaster remains on entire break surface (ca. 1.5 mm thick)
Epoxy adhesives				
Araldite 2011™, entire surface (pipette)	Three times with Paraloid B-72 in acetone/ethanol (70:30): 5, 10, and 15%	2.1 ± 0,1	--	Plaster remains on entire break surface (1–10 mm thick)
Araldite 2011™, entire surface (brush)	Three layers of Paraloid B-72 in acetone/ethanol (70:30): 5, 10, and 15%	1.1 ± 0.6	-	Plaster remains on entire break surface (1–5 mm thick)
Araldite 2012™, entire surface	Three layers of Paraloid B-72 in acetone/ethanol (70:30): 5, 10, and 15%	0.8 ± 0.1	-	Plaster remains on entire break surface (< 2 mm thick)
Araldite 2012™, drops on surface	Three layers of Paraloid B-72 in acetone/ethanol (70:30): 5, 10, and 15%	0.8 ± 0.1	-	Plaster remains on places where adhesive was applied (< 2 mm thick)
Araldite 2020™	Paraloid B-72 in acetone/ ethanol (70:30)	Joints broken before testing, due to insufficient strength	++	No damage
Araldite 2020™, drops on surface	Three layers of Paraloid B-72 in acetone/ethanol (70:30): 5, 10, and 15%	0.02	++	No damage
Araldite 2020™ with fumed silica (entire surface)	Diluted Araldite 2020 in acetone	1.4 ± 0.2; 1.2 ± 0.1 on plaster test blocks added borax	--	Plaster remains on entire break surface (< 2 mm thick)
Plaster blocks alone		1.8 ± 0.3; 1.6 ± 0.5 on plaster test blocks added borax		

Table 1. Test results of load testing on broken plaster test blocks bonded with different bonding methods. The load necessary (kN) to break the bonded plaster test blocks is listed and noted with a standard deviation of the three results from for each tested bonding method. The appearance of the break surface after breaking is described using heavy damage (--), medium (-), hardly (+) to no damage (++).

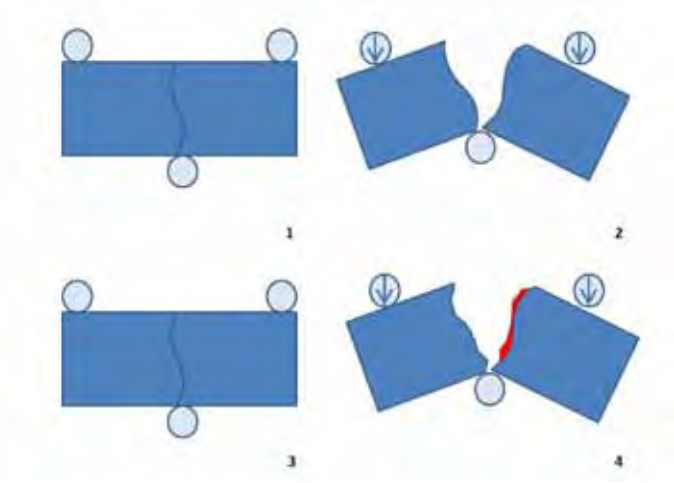

Fig. 1. Test procedure: preparation of broken samples and testing of adhesive in the three-point-bend test: 1. Plaster test blocks inside load-testing apparatus with a three point bend; 2. Plaster test block broken by means of vertical load; 3. Plaster test block after bonding in test machine; 4. Bonded plaster test block is placed under stress of a vertical load to induce a new fracture.

the break surface in order to prevent the adhesive squeezing out of the joint at the surface and becoming visible and/or staining the plaster surface when bringing the sections together.

Each bonding method was applied using the same technique on three plaster test blocks to obtain representative results. After the adhesives had set, the samples were inserted into the load-testing apparatus to measure the strength of the bond (figure 1).

Load Tests of the Bonds

The same load-testing instrument was used to test the bonds as had been used for breaking the plaster samples. This apparatus simulated the specific load that can occur on bonded plaster pieces (for example an extended arm). The instrument measured the load (expressed in kN) that was necessary to break a bonded plaster block and therefore provided information on the adhesive strength of the bond. These measurements were obtained through a connected computer system that regulates the speed (0.002 mm per second) and the vertical load that was placed on the blocks. After breaking, the blocks were examined visually to assess whether they broke at the original bond or elsewhere in the block.

Results and Discussion

There was a variation in the results regarding to both the force necessary to break the bond and the nature of the fracture. Some breaks occurred at the original bonded fracture, while others occurred next to the original bond within the plaster body (table 1).

The load (expressed in kN) necessary to break a bonded plaster block gives information on the adhesive strength of the bond. To break the plaster samples, an average load of 1.8 ± 0.3 kN was needed. This gives an indication of the strength of the plaster and could be compared to the strength necessary to break the bonded plaster.

The bonding system that supported the highest load was Araldite 2011™ with a Paraloid B-72™ pre-consolidation that had been applied with a pipette. This needed an average of 2.1 kN to break the bond, which was comparable to the intact plaster. With the same bonding method in which the consolidant was applied with a brush, 1.1 kN was needed to break the bond. The damage caused at the break edge when re-breaking these blocks was greater on the plaster blocks consolidated by means of a pipette than those where the consolidant was applied with a brush. An explanation for this could be that, when Paraloid B-72 is applied with a brush, a thicker layer is deposited at the surface; this creates an interface between the Paraloid B-72 and epoxy that is more susceptible to mechanical failure. In addition, application with a pipette 'flows' the consolidant over the surface, resulting in deeper penetration and deeper strengthening of the plaster surface

One method tested was with Araldite 2020™ mixed with fumed silica (mixed to a thin spreading consistency) that was pre-consolidated with Araldite 2020™ dissolved in acetone (70% v/v). This system proved to support a high load (1.4 kN) before breaking. However, when Araldite 2020™ was used without an additive and with a pre-consolidation of Paraloid B-72™, it had no bonding strength at all. The addition of fumed silica to Araldite 2020™ increased the bonding strength substantially because it reduces viscosity; therefore, it prevents the epoxy running out of the break or migrating into the porous surface (Byrne 1984). In addition, there was possibly poor adhesion between the two materials at the surface. The consolidation of the plaster with Araldite 2020™ diluted in acetone would also have resulted in more adhesive and strength, since this method produces a pure epoxy bond (the epoxy bonding well with itself). Test blocks bonded with Araldite 2011™ and Araldite 2020™ with fumed silica showed strong bonds but further damage to the plaster.

To break the bond of Araldite 2012™ (either covering the entire surface or with drops of adhesive), a lower load (0.8 kN) was needed. The resulting damage at the surface of the break edges was focused on the points where the adhesive had been applied. This was clearly visible on the break edges of the plaster test blocks where drops of adhesive had been applied. In this case, flakes of plaster had been pulled away from the surface spots (figure 2).

The test results from plaster test blocks bonded with solvent-based adhesives varied. Plaster blocks bonded with Weldbond™ needed a greater load (1.5 kN) to break the bond compared with Mecosan L-TR™, which broke at 0.8 kN, or Paraloid B-72™ at 0.6 kN. The plaster test blocks that had been bonded with Mecosan L-TR™ broke again very cleanly at the original break, with very few flakes of plaster attached to the break edges. Weldbond™ proved to have a high strength, but this did not necessarily result in more detachments of plaster at the break edges than seen in the test blocks bonded with Paraloid B-72™. With these adhesives, the plaster detached mostly at the areas of the break surface where the adhesive had been applied and did not break off the break edge up to a depth of 2 mm in depth. The angle of the breaks may also have been a factor influencing when flakes of plaster are detached from the break edges. Most breaks in the test blocks were not at a perfect 90° angle, possibly resulting in a slight variation of stress at the break surface.

Weldbond™ showed the highest bonding strength of the three solvent-based adhesives. That it is water based can be considered a problem. The application of water or water-based materials to plaster is considered undesirable, as this can (temporarily) weaken the strength of the plaster. Absorption of 2% volume of water can result in 50% reduction in structural strength (Coquard and Boistelle 1994). It could also possibly result in the corrosion of metal armatures (if close to the plaster surface). Although the test blocks bonded with Mecosan L-TR™ resulted in less new damage when re-broken, more research needs to be carried out on this adhesive. Cellulose-nitrate-based adhesives have been shown to be unstable, depending on the plasticisers used (Koob 1982; Shashoua, Bradley, and Daniels 1992). Mecosan L-TR™ contains camphor which, when used as a plasticiser,

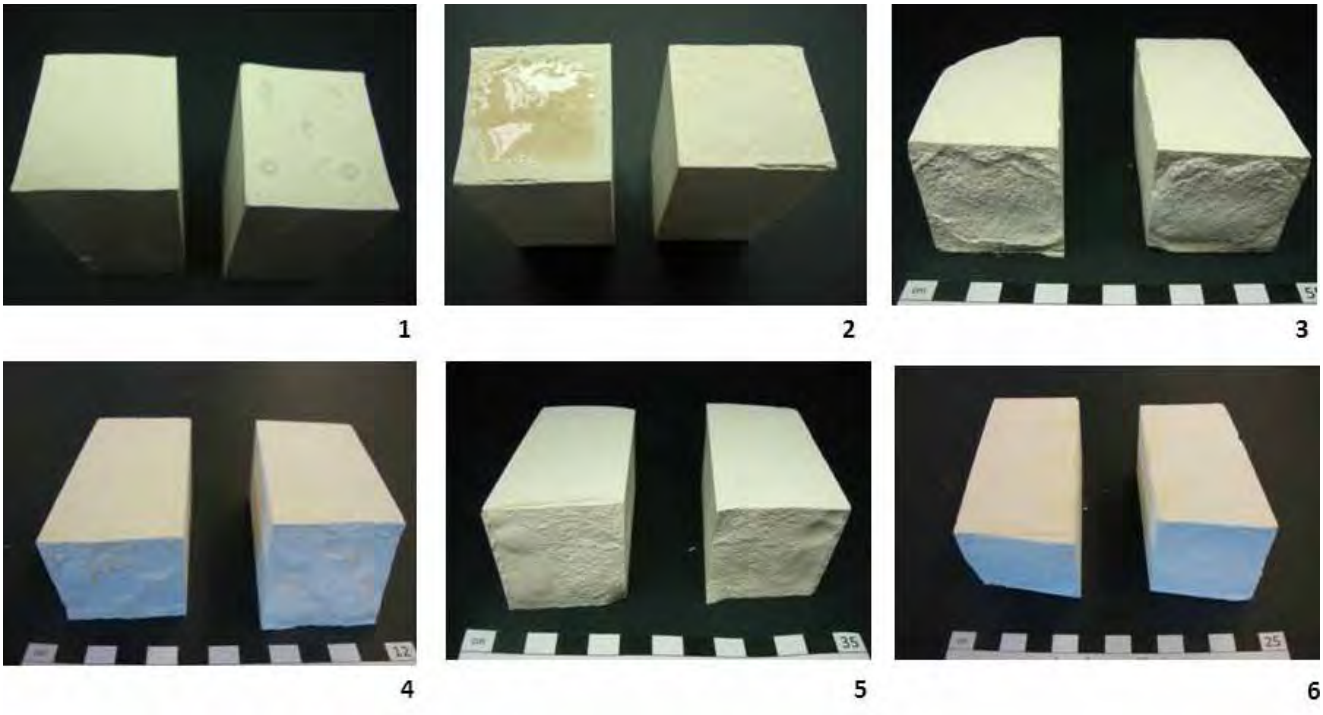

Fig. 2. Application method of adhesive on broken plaster test blocks (1, 2) and appearance of bonded test blocks after breakage: 1. Application with drops of adhesive 2. Application on entire surface with distance between adhesive and edge of break surface 3. Bonded plaster test block using Paraloid B-72 – after breakage 4. Bonded plaster test block using Araldite 2012 – after breakage 5. Bonded plaster test block using Araldite 2020 with fumed silica added – after breakage 6. Bonded plaster test block using Araldite 2011 (applied with brush) – after breakage.

is known to make an adhesive unstable over time.
Three bonding methods, using Araldite 2020™ with fumed silica, Mecosan L-TR™, and Paraloid B-72™, were also tested on plaster test blocks with added borax. There was no notable difference in the results of the load tests with blocks without borax added in the case of Araldite 2020™ and Mecosan L-TR™. However, such a difference was observed when Paraloid B-72™ was used, where a far greater load was needed to break the bond on the plaster test blocks with added borax compared to ordinary plaster (respectively 1.4 kN and 0.6 kN). The authors have as yet found no explanation for this difference.
Ethical codes in conservation (E.C.C.O. 2010) that state that the strength of an adhesive should not exceed the strength of the material to be bonded are in conflict with the reality of bonding large plaster pieces, since a strong bond is required to hold a heavy vertical load. The use of dowels allows the use of weaker bonding techniques, as the dowels absorb some of the stress at the join bit. This method has been rejected because of the loss of original material. However, stronger bonding methods can result in new damage when the break is put under enough pressure that it breaks.
Although conservators aim for reversibility, this is not likely to be achievable in plaster conservation. Because the break edges are broad and the plaster itself is very porous, it is assumed that solvents are not able to penetrate far enough into bonded fractures to dissolve or weaken the old adhesive without weakening the plaster itself or the finishes on the surface layer. This problem still needs testing. As a result of this concern, old restorations are generally removed mechanically.
When one considers the known properties of the selected adhesive materials, one can find evidence that some adhesives are known to have good aging properties. Some are not well tested, while others have been proven to become unstable over time. Yellowing of an adhesive is not a problem in plaster conservation if the adhesive otherwise remains stable. The Araldite epoxies are known to yellow but retain their adhesive strength. Mecosan L-TR™ contains cellulose nitrate, which is known not only to yellow over time, but also, depending on the plasticiser used, to become brittle (Koob 1982). Weldbond™ is a water-based adhesive that may temporarily weaken the plaster surface and also migrate into the pores of the plaster, causing possible corrosion of metal armatures near the surface. Further testing is needed to evaluate these concerns. Also, tests need to be made on actual plaster sculptures in order to see how far these results can be obtained in a real situation.

Conclusions

There was much variation in the results of load testing on broken plaster test blocks bonded with the chosen bonding methods. Broken plaster blocks that have been pre-consolidated with Paraloid B-72™ and bonded with Weldbond™, Araldite 2011™, and Araldite 2020™ with fumed silica had strong bonds that need a load to break the bond similar to that needed to break the plaster block itself.
Test blocks that had been consolidated and bonded with Paraloid B-72™, Mecosan L-TR™, and Araldite 2012™ broke when a lower load was applied. The strength of bonds with solvent-based adhesives, therefore, came closer to the strength of the plaster itself, and these adhesives have the added advantage of possible reversibility compared with epoxy adhesives.
Damage to the plaster break edges after re-breakage of the plaster test blocks varied depending on the bonding method. The degree of damage seems to be connected to the strength of the adhesives together with the amount and penetration of the consolidant, which reduces the ability of the adhesive to flow into the surface pores of the plaster. It appears that the strength of a bond can be related directly to the depth of consolidation, as the load can be spread further into the plaster and not just be concentrated at a thinly consolidated surface. This conclusion, however, raises ethical questions: is it more important to obtain a weaker bond that is likely to result in less damage by new breakage but may risk failure under stress, causing even more structural damage, or is it better to have a stronger bond that will not break until the load is very high, but is then likely to break in a new place?
The decision-making process relating to the conservation of plaster-cast sculptures has to take into consideration variations in the sculptures, such as the surface finish or the presence of armatures. No bonding technique is without risk, and the use of dowels, which was not tested in this study, could also be considered. Research into, and the monitoring of, plaster-cast sculptures that have been bonded with diverse bonding materials and techniques needs to be continued in order to provide more insight into these issues.

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Protection and Installation

The Effect of Climate and Particle Deposition on the Preservation of Historic Stained-glass Windows – In Situ Measurements and Laboratory Experiments

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Keywords
stained glass; protective glazing; climate measurement; particle deposition; environmental simulation

Abstract
A number of environmental monitoring projects were performed on historic stained-glass windows in Germany from 1994 to 2012. The quality of the protective glazing was assessed by recording environmental parameters in the interspace between the original and the protective glazing and on the inside of the original window. For this purpose, temperature, humidity and air velocity were measured. Particles were sampled with different methods and analysed by scanning electron microscopy combined with energy dispersive X-ray spectroscopy to determine their chemical composition. The effect of particles on model glass samples was investigated in climate chambers under accelerated weathering conditions. The results from in situ measurements and laboratory tests were combined to evaluate the potential effect of particulate matter on historic stained-glass windows.

Introduction
Stained-glass windows are nowadays frequently protected with glazing systems, involving the installation of a modern flat glass to shelter the stained-glass window from the outdoor environment. The interspace between the original and the protective glass is ventilated with air from the indoor or exterior environment. Protective glazings are generally recognised as being an effective preventive method in most countries, but the details of constructions vary considerably. The effectiveness of different types of protective glazing has been studied in many places in Europe, such as in the Cathedral of Cologne (Kontozova-Deutsch and others 2011), the Sainte-Chapelle in Paris (Godoi, Kontozova, and Van Grieken 2006), the Saint-Urban Basilica of Troyes (Bernadi and others 2013), as well as the St Lorenz and St Sebald churches in Nürnberg (Hör 2012). The basic technical and design requirements such as ventilation (with indoor or exterior air), size and location of openings, and sealing materials have been adjusted according to the results of scientific investigations (Oidtmann 1994). Climate measurements and levels of urban gaseous and particulate pollutants were investigated in the European VIDRIO project (Bernadi 2005). New installations of protective glazings have subsequently been frequently accompanied by monitoring campaigns such as in Frankfurt/Oder Marienkirche (Hahn 2008), in the Divi Blasii Church in Mühlhausen (Garrecht and others 2010, 2011) or in Erfurt Cathedral (Hahn 2011).

All studies evaluating the protective effect of glazings compare the potential corrosive impact of environmental conditions on three positions: outdoors, in the interspace, and indoors.

The most dangerous gaseous air pollutants for stained-glass windows are sulphur dioxide (SO_2), nitrogen dioxide (NO_2) and ozone (O_3), derived mostly from anthropogenic sources. Outdoor concentrations of SO_2 are generally higher than gaseous pollution levels inside the building. Indoor concentrations for NO_2, SO_2 and O_3 were found to be similar to the concentration in the interspace at the cathedrals of Troyes, Paris and Cologne (Bernadi and others 2013). The relative humidity (RH) inside a building and in the interspace is a key factor influencing the preservation of the original glazing. Studies on particle deposition on glass surfaces became available only in the last decade.

The types of particles collected on samples from outdoors, indoors and from the interspace at protective glazings in the Cathedral of Cologne seemed to be rather similar (Kontozova-Deutsch and others 2011). In the Basilica Saint-Urbain in Troyes, the composition of single particles was considered to be more aggressive inside the church than outside (Kontozova-Deutsch and others 2008). The fine fraction consisted mostly of soil dust, organic particles, ammonium nitrate and particles rich in calcium and carbon. The abundance of Ca compounds ($CaCO_3$ and $CaSO_4$) in Sainte-Chapelle in Paris in the interspace was reported as the highest, followed by the inside and outside levels (Godoi, Kontozova, and Van Grieken 2006). Scientists expressed their concern about the presence of particles deposited on the glass surface, since this significantly changes the dew point, i.e. the temperature at which water vapour condenses on the glass.
Protective glazings are installed primarily to protect the stained glass from water and high humidity. Protection from rain is easily achieved. Condensation of water on the inside of the glazing, however, may still occur, as was observed for example in Nürnberg (Hör 2012). Ongoing corrosion of paint layers and of the mediaeval glass was recorded there on stained-glass windows during a long-term project running for more than 10 years. The results were questioning the protective effect of the glazing.
The most effective way to avoid condensation on the glass is to provide sufficient ventilation. The distance between the original and exterior protective glazing (5 to 10 cm in general) as well as openings on top and bottom of the window are optimised to cause sufficient air movement in the gap. The air flow in the interspace determines the RH but also the particle transport and deposition in the gap between original and protective glazing. Individual particles can be removed from the glass surface when the air velocity is high or deposited on the glass surfaces at low air flows.
Previous studies indicated that particles deposited on sensitive glass surfaces have the potential to damage the glass. Atmospheric constituents such as gases and particulate pollutants have been identified as one of the main causes for weathering of mediaeval glass (Gysels and others 2004). Water-soluble salts and carbon-containing particles may accelerate glass weathering, because the former can maintain a high degree of humidity on the glass surface also during relatively dry periods and because the latter is a potential source of food for many biological species. In the VIDRIO-project (Bernardi 2005), the results of particle measurements show that the concentration of water-soluble salts was comparable in the interspace and inside, both in Troyes and in Cologne. The total carbon content was higher inside churches than in the interspace. In spite of the potential for damage by particles reported in the VIDRIO project, the general environmental impact measured on glass sensors indicated non-critical environmental conditions (see glass sensor values reported by Bernadi and others 2013). However, there is a considerable lack of information about the effect of particle deposition on the surface of different materials. This may be due to the complexity of the problem and the great variety of materials involved (Grau-Bové and Strlič 2013).
A goal of this project was to estimate the effect of particle deposition on glass surfaces. In our study, the effect of particles was investigated by experiments on model glasses of mediaeval composition in climate chambers. Testing was adjusted to conditions recorded at selected sites in Germany.
Whereas laboratory experiments and monitoring campaigns are necessary research tools, the long-term effect of glazing systems can be studied best by analysing the corrosion rate on the historic glass as such. A unique occasion for such a study presented itself during the project described here. For more than 20 years, our laboratory was involved in conservation and monitoring projects on stained-glass windows in Germany which accompanied the installation of protective glazings in churches, for example, in Halberstadt, Havelberg, Stendal and Quedlinburg (in 1993–1999) and at Marienstern in Panschwitz-Kuckau (in 1986) (Drachenberg 1999; Müller 2002).
Appropriate documentation of individual glass segments has been produced when the protective glazing was installed and was available now for this project. The same samples could be removed in 2009/10 from the panels to be investigated in precisely the same places by light microscopy and by environmental scanning electron microsopy (ESEM).
Combining long-term studies on original glass with laboratory experiments offers a unique chance to explore further how to rate the protective effect of glazing systems, especially considering particle deposition on glass.

Experimental Methods

Climate measurements were performed to characterise the current environmental condition of selected windows by using an ALMEMO® -2590-4S system with an FHAD 462 temperature and humidity sensor. Air velocity was measured with an ALMEMO® anemometer.[1]

Particles were collected using three methods: Inside the interspace, the particles were sampled on aluminium foil using 13 stages of a Dekati DLPI impactor,[2] with aerodynamic cut-off diameters between 0.03 and 10 µm, at a 10 L min^{-1} air flow. The sampling time was 240 minutes. Additionally, Si wafers of 25 x 20 mm exposed for 1 year were used as particle collectors. For comparison with the dust collected in the interspace, samples were taken from the reverse side of the stained-glass window by use of adhesive carbon tapes.

The combination of different methods of dust collection and energy dispersive X-ray spectroscopy (EDX) for elemental analysis of particles in our project provided a promising approach to characterise the major chemical compounds that can accumulate in the gap between the original stained glass and the protective glazing.

Chemical analysis of particles was performed with SEM/EDX on an FEI ESEM-XL30, EDX-EDAX. The EDX analysis was conducted within the high-vacuum setting of the microscope, for which samples needed to be coated with carbon. The images of the glass samples were acquired in the low-vacuum mode (purging with water vapour in the sample chamber).

For simulation experiments, a climate chamber (Weiss WK 11-180) was used. Based on the results of climate measurements in Panschwitz-Kuckau and Stendal Cathedral, the conditions in the climate chamber were chosen as follows: 50°C, 40% RH and 10°C, 90% RH for 2 hours (repeated four times between those two sets of parameters), followed by 4 hours at –10°C to simulate winter (RH was not defined at low temperature). The time between every change of parameters was 60 minutes. The total testing period ran for 4 weeks and represented an accelerated weathering regime.

Model glasses with chemical compositions similar to mediaeval glass (rich in potassium) were produced in slices and polished (Torge and others 2003; see also table 1). Glass samples were partially covered with particles, leaving reference areas for comparison. Seven compositions of dust were tested on three different model glass types. After weathering, the various surface areas of all glass samples were investigated by ESEM, and EDX spectra of characteristic elements were recorded in typical locations.

Climate Measurements

Climate measurements were carried out over a 12-month period from 2009 to 2010. Temperature and humidity have been measured on the inside (MS1) and the outside (MS2) of the original stained glass and the inside of the protective glazing (MS3). The results presented here as a typical example were recorded at the window in Panschwitz-Kuckau (information about the window: size: 2.00 x 8.00 m, gap size 8.0 cm, orientation in the building: east). Large temperature and humidity fluctuations are generated by both the seasonal cycle and the circadian rhythm (figure 1). The temperature and RH at the protective glazing (red) are always higher than at the original glass (blue). In the winter months, RH at the original glazing is between 80 and 90% for more than two-thirds of the measurement period. Often, condensation has been observed on the inside of the exterior protective glazing. When comparing the measurements from five different sites (figure 2), it can be concluded that glass installed in Panschwitz-Kuckau is exposed to the highest risk of corrosion (Torge, Bücker, and Feldmann 2011).

Investigations of Glass Segments After Long-term Exposure

According to Garrecht (Garrecht and others 2010), a high RH above 80% may have led to irreversible changes on the surface of mediaeval glass in Mühlhausen. To investigate whether this assumption also applies to churches in our study, samples were removed from selected panels to compare the surface conditions after decades of exposure. Surface changes have been observed locally only on the glass samples from Stendal and Havelberg. Due to their composition and dating (Müller 1999), those samples belong to the most corrosion-sensitive glasses included in this study. The climate conditions (characterised by about 2000 hours of RH at or above 80%) have caused corrosion progress within a period of 15 years that can be documented using light microscopy and SEM.

An example is shown in figure 3 (image taken in 1994) and figure 4 (image taken in 2009). Here it can be seen that cracks on the glass surface are more pronounced in the post-status analysis. Evidence of proceeding manganese browning and loss of paint layers has been found on other samples. Information from the surface is valuable, but even more important is the thickness of corrosion layers (and any growth in thickness), this being the best indicator for proceeding corrosion. However, examination of original glass segments in cross-section is challenging. It should be noted that the images shown below are not cross-sections as commonly found in

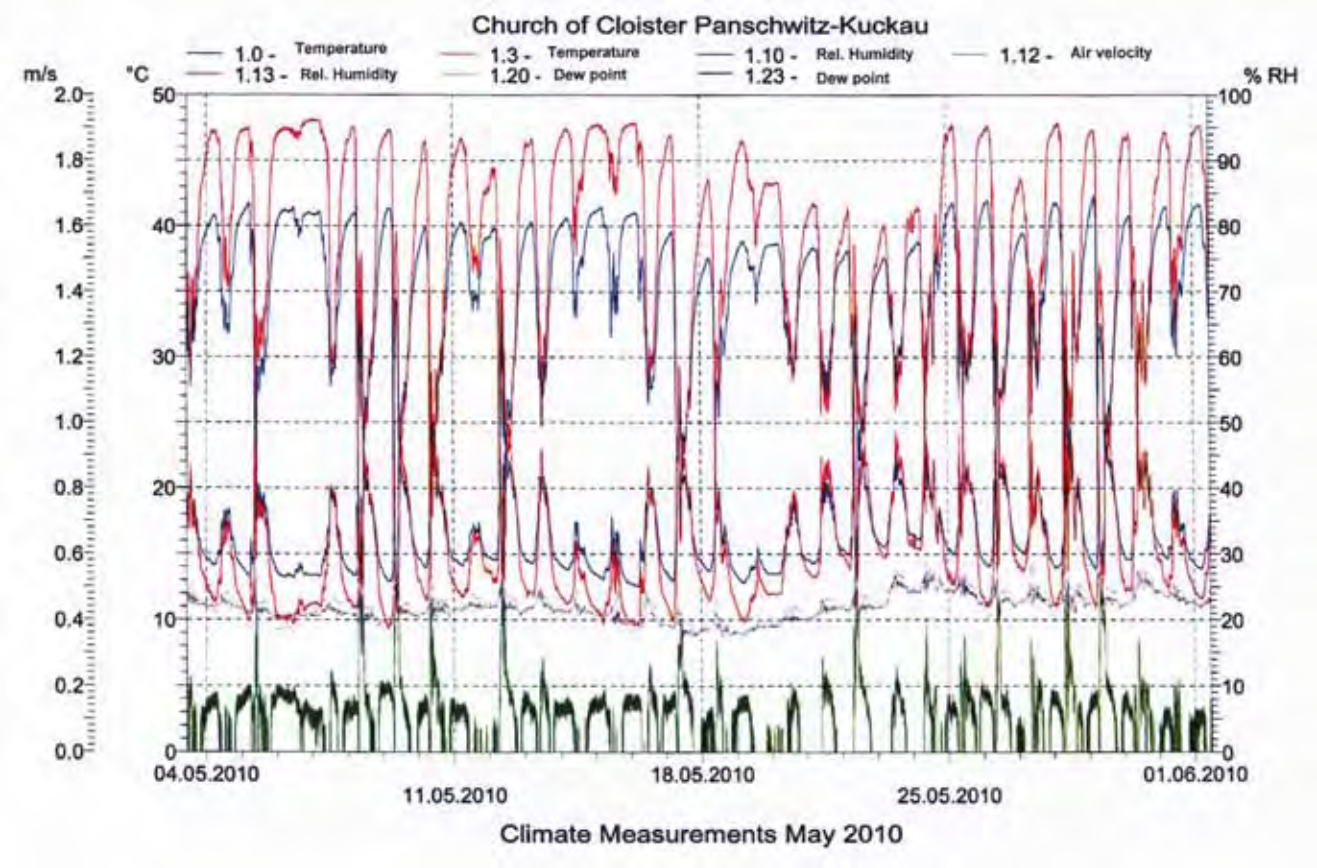

Fig. 1. Environmental monitoring (temperature, relative humidity, dew point and air velocity) in May 2010 in the Church of Panschwitz-Kuckau.

glass studies. The preparation of the samples was performed without embedding them in resin but by abrading and polishing a small area on the edge of the sample. Sputtering with carbon was done locally in order to enable conductivity for ESEM investigation. After analysis, the glass sample can be re-integrated in the stained-glass window and re-investigated after natural weathering.

Figures 5 and 6 provide a comparison of SEM and ESEM images of a sample from Havelberg. The old SEM image (taken in 1994, figure 5) indicates that the degradation layer (depicted in a darker shade of grey as compared to the bulk glass) varies in thickness and can reach up to 30 µm. The image of the same sample taken by ESEM in 2010 (figure 6) shows more detailed features of the degradation layer (due to higher resolution of the equipment). Exactly the same structure of the gel layer could not be found on this sample using ESEM. Therefore, we can conclude that some changes must have occurred. It can be assumed that, due to the weathering, the gel layer has altered and additional microcracks have formed, making the same spot non-recognisable. Ion-exchange processes between hydronium ions and alkali ions

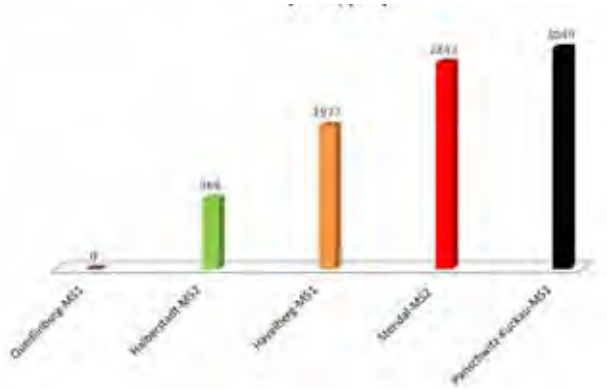

Fig. 2. Calculation of time in hours per year with relative humidity at or above 80% for the five objects.

from the glass due to high humidity can lead to variations in the gel layer and are a sign of progressive glass corrosion in the 16 years behind a protective glazing.

On other examples (such as Panschwitz-Kuckau), the same spot on samples could be found in new ESEM images, and it can be concluded that no changes have occurred. Previous investigations indicated that the glasses from Panschwitz-

Fig. 3. Microphotograph of the surface of a glass sample of Havelberg Cathedral (window sXI, panel 4c); condition in 1994 (Image: the authors).

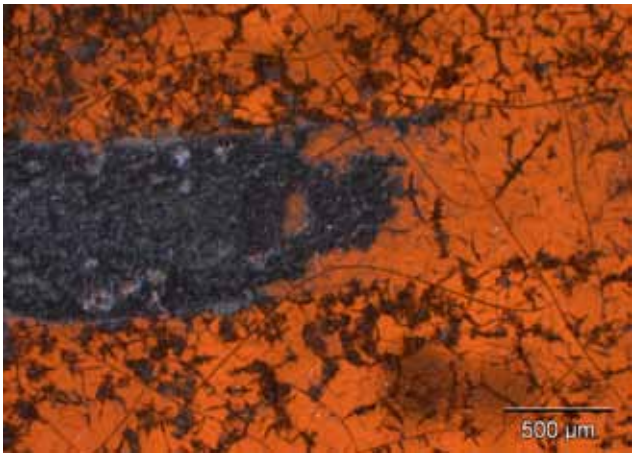

Fig. 4. Microphotograph of the surface of a glass sample of Havelberg Cathedral (window sXI, panel 4c, same sample as in figure 3); condition in 2009 (Image: the authors).

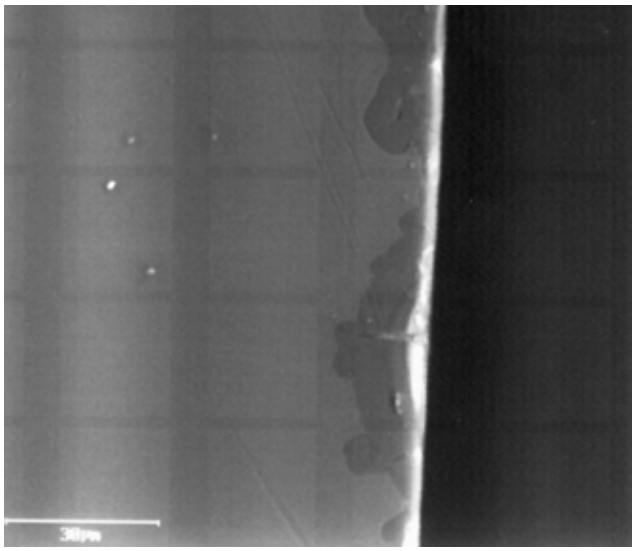

Fig. 5. SEM picture of the cross-section of a glass sample of Havelberg Cathedral (window nXI, panel 3a); condition in 1994 (Image: the authors).

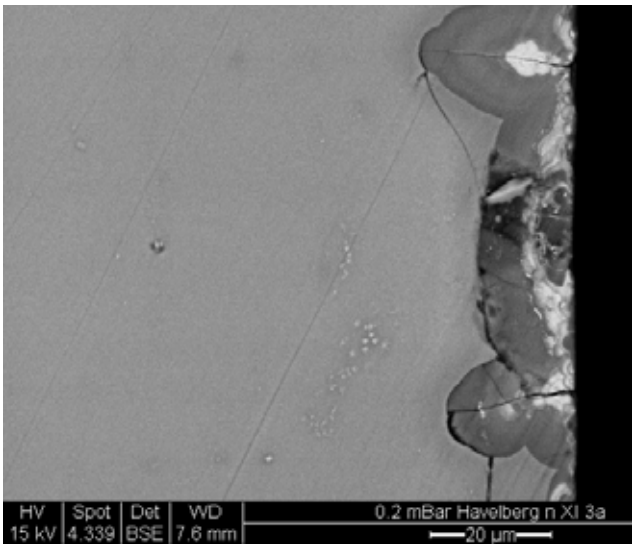

Fig. 6. ESEM picture of the cross-section of a glass sample of Havelberg Cathedral (window nXI, panel 3a, same sample as figure 5); condition in 2010 (Image: the authors).

Kuckau were heavily corroded, having built up a gel layer of up to 100 µm thickness during the centuries (Müller 2002). This may have provided protection from further weathering, even under particularly humid conditions behind the protective glazing in the church.

Dust Analysis

Light and scanning electron microscopic images were recorded to characterise the size and frequency of particles. The chemical compositions of particle deposits were analysed by SEM/EDX.

Dust particles were collected on all stages of the Dekati DLPI cascade impactor. The ESEM pictures show that the number of particles on each stage is object-specific and was, for example, higher at Stendal Cathedral than at Havelberg Cathedral. The recorded particle diameters were in both cases between 10 µm and 0.03 µm. Elements that were detected at all stages of the cascade impactor were calcium (Ca), potassium (K), sulphur (S), iron (Fe), lead (Pb) and aluminium (Al). Also, the elements silicon (Si), barium (Ba), sodium (Na) and magnesium (Mg) were frequently detected in these dust samples. Surprisingly, dust sampling in Stendal Cathedral and in

Havelberg produced crystals on stages 4, 5 and 6 of the cascade impactor that were much bigger than the permissible aerodynamic particle diameter of the corresponding stage. They must have been formed from the collected aerosol after the deposition on these stages. The size of the crystals was between 20 µm and 100 µm. EDX analysis of these crystals has indicated nitrogen (N) and oxygen (O), often in combination with sulphur (S) and potassium (K). Studies of air quality in churches in Denmark (Rasmussen and Skytte 2010) suggest that ammonium nitrate (NH_4NO_3) may be formed from ammonia (NH_3) released from agriculture and factory farming and nitrogen oxides (NO_x) resulting from car traffic. The formation of ammonium nitrate from components of the collected aerosol (NOx, NH_3) in the cascade impactor is conceivable on stages 4–6, considering that both Stendal and Havelberg Cathedrals are situated in areas with intensive agriculture and animal husbandry. If, as a result of climatic conditions, corresponding chemical reactions are possible inside the churches, nitric acid may be produced that may react with walls and glass surfaces.
In the long-term tests, dust accumulated on all Si wafers exposed in the interspace. The particle size ranged between 5 and 100 µm, or even up to about 400 µm at Quedlinburg, Nikolai Church. Differences in the composition of particles on the Si samplers compared to the impactor particles have not been ascertained, although the sample times differ (1 year as compared to 4 hours). The results of EDX analysis of the Si wafers can be divided into three groups, depending on their potential origin. In the first group, the elements potassium (K), calcium (Ca) and sulphur (S) have been found on all exposed silicon wafers. These are probably particles that were removed from corrosion layers on the back of the panels due to the air flow in the interspace. Metallic particles such as iron (Fe), lead (Pb), copper (Cu), aluminium (Al) and zinc (Zn) are probably corrosion products from the adjacent construction. The third group comprises the elements magnesium (Mg) and chlorine (Cl), which were only rarely found. Nitrogen (N) has been detected only on the Si wafers in Stendal, Havelberg and in Halberstadt, it may have originated from local agriculture or car traffic fumes.
Sampling of the back of the stained-glass windows using adhesive tapes suggests that dust particles may have come from both the surface of the corroded glass and from the adjacent construction and paint, thus being similar to the other two particle collection methods.

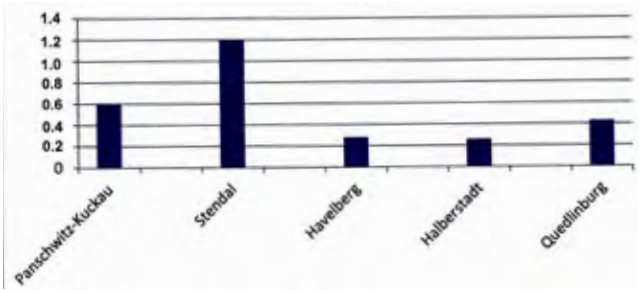

Fig. 7. Air velocity (v_{max}) in the interspace between original and protective glazing.

Dust Sampling and Air Velocity

The air flow in the interspace between original and protective glazing depends on the construction of the protective glazing, the height of the window and its orientation (north, south, east or west). Air velocity values for all five churches are compared in figure 7.
The window sV in Stendal Cathedral is a south window with a height of 14 m (v_{max} =1.2 m/s) and thus much larger than the north window nXI in Havelberg Cathedral with only 4.20 m height (v_{max} =0. 28 m/s). For comparison, air velocities measured in different other churches ranged between 0.11 m/s and 0.96 m/s (Oidtmann 1994). This indicates that the air velocity in Stendal is well above average.
Sampling using the cascade impactor in Stendal Cathedral recorded a larger number of particles at each stage than in Havelberg Cathedral. Thus, the higher air velocity in the larger window in Stendal Cathedral can be connected to a larger particle deposition,

	SiO_2	Na_2O	K_2O	CaO	MgO	Al_2O_3	P_2O_5	Fe_2O_3	MnO
Pk1a	45.0	0.5	31.0	16.0	4.0	1.0	1.5	0.5	0.5
Pk2	46.0	-	23.5	23.5	4.0	1.0	1.5	-	0.5
KS1	45.0	2.0	17.0	23.5	5.4	1.8	3.8	-	1.5

Table 1. Chemical composition of model glasses in wt% (synthesis)

Simulation of Particle Exposure

From the combination of different dust collection methods and the EDX elemental analysis of fine particles, conclusions can be drawn about the chemical compounds to be used as dust for simulation experiments. The effect of such deposits on model glass was tested in a climate chamber. The model glasses, with a chemical composition similar to mediaeval glass, were prepared at a laboratory scale. Like most mediaeval glasses, PK1a, PK2 and KS1 (see table 1) are very sensitive to corrosion due to their high content in potassium and low content in SiO_2. However, because of differences in their K_2O/CaO ratio, they exhibit different levels of sensitivity to environmental conditions in the following order Pk1a> Pk2> KS1 (Torge and others 1998).

Prior to the weathering tests in a climate chamber, the model glasses were cleaned with alcohol in an ultrasonic bath and approximately one-quarter of the surface area was taped with adhesive tape, leaving about 1 cm^2 of the surface unexposed to weathering. For simulating particle deposits on the glass surface, the following chemical compounds were used: $CaSO_4 \cdot ½H_2O$, K_2CO_3, $CaCO_3$, $PbCO_3$, Fe_2O_3 (samples named 'dust 1' to 'dust 5', respectively). About half of the total surface of each model glass was covered with 0.02–0.04 g of the pure chemicals in powder form. An additional sample of each model glass type was coated with a mixture of all chemicals (dust 6), and one sample for each type was brought in contact with dust from Stendal Cathedral (dust 7) that originated from the cascade impactor experiments. Approximately one-quarter of total model glass surfaces were neither covered with adhesive tape nor exposed to dust. The taped surfaces represent references for the subsequent tests. All of these samples were weathered in the climate chamber. Even to the naked eye, it was clearly visible that the simulated dust behaved differently after exposure in the climatic chamber. Particularly noticeable changes were visible on all samples with potassium carbonate. After weathering, this compound was no longer a powder on the surface but was firmly bonded to it and distributed over a larger area. The same effect was observed on surfaces with a mixture of all the chemicals. Apparently, in high humidity, potassium carbonate reacts with water to form potassium hydroxide and potassium hydrogen carbonate. At room temperature, it crystallises from the solution as a hydrate of potassium. A chemical attack on the glass surface is very likely as a follow-up reaction. The original dust from the cascade impactor experiment that had been placed on the glass surface with aluminium foil at the beginning of the experiment induced a dust pattern on the glass surface after removal of the foil. On all other glass surfaces, the dust deposit remained inert and did not change during the course of the experiment.

Results From Laboratory Exposure of Model Glasses

The various surface areas of the glass samples were imaged in the ESEM, and EDX spectra were recorded in typical locations. The experiment showed that areas with dust deposits behave differently under changes of humidity and temperature, compared with the reference area. The damage potential of different dust compositions was determined by looking at different areas of the model glass with SEM/EDX after removal of the dust. The damage is manifested in the leaching of the surface that was covered with dust. Changes in the glass composition could be determined by EDX. The following rating is based on a comparison with the reference area that had been protected from dust. Potassium carbonate deposits, both by themselves (dust 2) as well as in combination with the other compounds (dust 6), have the highest damage potential. Severe damage was also observed on glasses covered with calcium sulphate (dust 1). This compound is normally found in corrosion crusts on historical glasses. Its damage potential may be related to the ability to absorb and store water so that extra moisture comes into direct contact with the glass surface, setting leaching processes in motion. Calcium carbonate (dust 3) appears to have a slightly lower damage potential. Leached areas were found directly beneath the dust (demonstrated by SEM surface pictures). A possible reason for this could be the formation of calcium hydrogen carbonate as a result of the reaction of calcium carbonate with water and carbon dioxide from the air. In contrast, lead carbonate (dust 4) and iron oxide particles (dust 5) showed no significant damage on the glass surface. On glass sample PK1, the most sensitive type of glass, surface damage from the original dust (dust 7) was detected in areas where dust crystals were in direct contact with the glass surface. On the more corrosion-resistant KS1 glass, no damage was visible.

Summary

Both the climatic measurements as well as the analysis of glass segments from five objects (Halberstadt, Havelberg and Stendal Cathedrals, Quedlinburg and Panschwitz-Kuckau) show that immediate steps to improve the protection of the stained-glass windows are not necessary. The examination of identical glass segments after about two decades of exposure in situ offered a unique chance to evaluate the progress of weathering. SEM images indicate that the corrosion progress is rather slow, although some progress in weathering was observed for the sensitive mediaeval glass from Havelberg. The original glass at Stendal, Halberstadt and Panschwitz-Kuckau was already heavily weathered and has formed a gel layer that protects it against further weathering. The gel layer acts as a diffusion barrier and must be conserved during restoration work. Glass from Panschwitz-Kuckau, for which the highest risk was expected based on environmental data, seems well protected by its thick gel layers, since no corrosion progress was detected. At the 19th century windows in Quedlinburg, no signs of damage could be observed because of the more resistant glass used in that period.

The investigation of particles suggests that the dust samples collected by both cascade impactor and by Si wafers yield practically the same composition. Aggressive particles, such as potassium hydroxide, potassium hydrogen carbonate or gypsum, can be expected to form, catalysing the reaction of humidity with mediaeval glass. This process has been shown in simulation tests on model glasses in the climatic chamber. The tests have also shown that loose corrosion products and particle deposits should always be carefully removed from mediaeval glass surfaces to avoid chemical reactions of the deposits with water from atmospheric humidity as well as to prevent damage to the glass.

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Notes

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Protective Glazing: The Conflict Between Energy-Saving and Conservation Requirements

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Keywords

stained glass; conservation; protective glazing; energy efficiency; heat loss

Abstract

Heating a historic church is expensive. To improve the energy efficiency of such churches, their windows are increasingly fitted with protective glazing using a double-glazed unit. This applies particularly to the great number of parish churches in Switzerland with post-mediaeval stained-glass windows. The added glazing is intended to protect the stained glass from weathering and to provide thermal insulation. In a collaborative research project, we are exploring whether, or to what extent, protective-glazing systems that are primarily fitted for insulation purposes fulfil energy-saving and conservation requirements. Among other issues, we are investigating the thermal efficiency and condensation behaviour of various protective-glazing systems. The aim of this study is to assist church authorities, architects, and monument conservators to evaluate energy-saving options.

Context and Aims of the Project

Switzerland has approximately 5,000 parish churches. About 80% of these churches were built before 1850 and have historic stained-glass windows that, with the exception of a comparatively small number of mediaeval windows, date mostly from the nineteenth and twentieth century. However, these churches also feature some restored Renaissance and Baroque glazing. Although originally constructed without heating systems, today the great majority of these buildings are heated (Giezendanner 2009, p. 24). Heating such large and mostly non-insulated buildings is usually very costly. The annual heating costs for a parish church in Switzerland lie between 5,000 and 40,000 CHF, depending on the heating system and the energy source used (Bickel and others 2009, p. 9). The average cost is 9,600 CHF (€ 8,000) per year. Two-thirds of the churches are heated electrically, with average annual heating costs of 7,200 CHF (€ 6,000) (Aufdereggen 2012). Because of rising energy costs, and encouraged by the current energy debate, church authorities are trying to lower the energy consumption of their buildings.

Numerous guidelines have been published that provide advice on how to improve the energy efficiency of churches (for example Dahm 2010). Measures to improve the windows are usually outlined among options to reduce heat loss in buildings and lower heating costs (Bickel and others 2009, p. 19). When considering energy-saving options, there is a tendency to assume that windows represent a determining factor in reducing energy consumption. This has already led church authorities to install protective glazing on a large scale. In the canton of Zurich alone, an estimated 50% of its nearly 300 churches have been fitted with protective glazing in the past 30 years, and the trend to install protective glazing for 'energy-saving' reasons continues. However, protective-glazing systems not only are intended to improve the thermal properties of churches, but also have to fulfil a number of other requirements: to protect the stained glass from environmental impact and vandalism, to reduce condensation on the historic windows and surrounding structures, to be aesthetically in keeping with the rest of the building, and to reduce the number of interventions (restoration, conservation, maintenance) on the stained glass.

The question as to whether thermally efficient protective glazing (e.g. protective-glazing systems glazed with a double-glazed unit) also represent an effective solution in terms of conservation has become fundamental to the preservation of the large body of post-mediaeval stained glass in Switzerland. The question becomes even more critical in the long-term if one considers the high cost of fitting protective glazing, the low durability of polymer materials often used in such glazing (e.g. silicone sealants), and the risk of subsequent damage to the stained glass and building structures adjacent to the windows (see, for example, Baumann, Zehnder, and Rüegg 1998).

In the process of planning for the renovation and thermal retrofitting of churches, architects and building owners in Switzerland are advised to follow the guidelines of the Swiss Federal Office of Energy and the Federal Commission of Monument Preservation, according to which the effects of measures to improve the thermal properties of a historic building have to be quantified (Furrer and others 2009). However, appropriate methods and techniques to quantify measures and evaluate requirements (conservation, aesthetic considerations, energy saving, comfort, etc.) have yet to be defined. There is a general lack of experience when it comes to understanding the effects of certain types of protective glazing on stained-glass windows; further, there is an inadequate understanding of the thermal losses and climatic impacts (condensation on the stained glass in particular). In order to close this gap, the Vitrocentre Romont initiated an interdisciplinary research project in 2012. The aims of the project are twofold:

1. To determine the overall heat transfer coefficient of historic windows fitted with protective glazing based on calculations and measurements in a climate chamber, the so-called 'hot box'.
2. To investigate the climatic effects of protective glazing, particularly condensation, on stained-glass windows, by initiating a survey in situ of post-mediaeval stained-glass windows with protective glazing, and by recording measurements in a weathering chamber.

The project has focused on two particular protective-glazing systems: (1) protective glazing fitted in a metal frame and glazed with a single glass sheet, and (2) protective glazing fitted in a metal frame and glazed with a double-glazed unit. Both systems have been evaluated with and without external ventilation. Despite being widespread in Swiss parish churches with stained glass from the nineteenth and twentieth century, these protective-glazing systems have hitherto received insufficient attention. Isothermal glazing, a system more commonly used in the preservation of mediaeval stained glass, has been excluded from this study.

The results of this investigation should enable the following questions to be answered. To what extent do the above-mentioned glazing systems improve the thermal efficiency of historic windows? Do they meet preservation requirements (by, for example, preventing condensation on the stained glass)? It is also hoped, that this study goes some way towards identifying appropriate solutions for the comprehensive, long-term preservation of post-mediaeval stained-glass windows in Switzerland.

Efficiency of Protective Glazing: Current State of Research

Condensation problems related to protective glazing have been reported from various places all over Europe (see, for example, Bacher 1988; Trümpler 1988; Berkenkopf 2005). The observations prompted research on the effectiveness of protective-glazing systems (see the overview in Oidtmann, Leissner, and Römich 2000; Römich 2004; Hör and Seele 2005). Among the first researchers to study systematically the effects of internally and externally ventilated as well as unventilated protective-glazing systems under variable climatic conditions was Stefan Oidtman, who carried out simulations in a hot box and compared them to in situ measurements (Oidtmann 1994). Many studies have followed since, including the European research project VIDRIO, which aimed to monitor the climatic conditions of stained-glass windows with internally ventilated protective-glazing systems, and to develop methods to detect condensation in the interspace between the historic window and the protective glazing (Bernardi and others 2012). Researchers from the Federal Institute for Materials Research and Testing in Berlin have looked at, among other things, the problem of dust deposition in the interspace in isothermal glazing (Torge and Müller 2011; Torge, Bücker, and Feldmann, 2013). To date, however, research has concentrated mostly on the conservation aspects of protective-glazing systems in general, and isothermal glazing in particular. To our knowledge, the only investigation focussing on the thermal effectiveness of protective glazing was published by researchers from Eindhoven Technical University (Neilen, Schellen, and van Aarle 2003).

Fig. 1. Unventilated protective glazing fitted in a metal or wood frame: 'Église des Capucins' in Romont, installed around 1950 (left); Parish church of Frauenfeld-Oberkirch, installed probably before or around 1900 (right). Photos: authors.

Those authors provide interesting insights into the energy efficiency of various insulation measures (including double glazing) in churches. They also point out that, among the various options to improve energy efficiency, the thermal insulation of a church's roof and floors, as well as well the replacement of old heating systems, usually provides much more potential for energy saving than the installation of protective glazing. Their conclusions draw on the evaluation (from a conservation as well as an energy perspective) of heating systems in churches (see, for example, Schellen 2004; Limpens-Neilen 2006). They also draw on the development of sustainable heating concepts such as 'friendly heating' (Camuffo and others 2010), which have found their way into various guidelines, textbooks, and standards on how to heat historic buildings appropriately (for example DIN EN 15757). Yet, despite these findings, church owners in Switzerland are reluctant to review the options to reduce heating costs (for example, by reducing temperature set points for heating). The fact that the Vitrocentre Romont continues to be consulted on the choice of thermally effective protective-glazing systems seems to justify further investigations into the efficiency of such systems, both in terms of energy and conservation.

Results

Efficiency of Protective Glazing in Swiss Parish Churches

One type of protective glazing with which the Vitrocentre Romont has been confronted in recent years (in connection with restoration and monitoring projects) is a system that was prevalent in the 1950s or even earlier. This type of protective glazing is fitted in a metal or wood frame to the window's reveal (i.e. the masonry adjoining the window) and is not connected structurally to the historic window (figure 1).

Fig. 2. 'Bonded' protective-glazing system: stained glass fitted in a metal frame together with the protective glazing, installed around 1970. Photo: authors.

It is usually unventilated, although such protective glazing is rarely perfectly airtight. The interspace between the stained-glass window and the protective glazing normally ranges between 10 and 30 cm, depending on the width of the window reveal. The framing is usually delicate. Occasionally, the drawn glass has been preserved, and the stained glass has remained untouched in its original place. Our observations show that this type of protective glazing is still effective in protecting the stained glass. Because of the limited extent of external ventilation, these systems have created very good climatic and conservation conditions for (at least certain types of) stained glass.

Another type of protective glazing became common in the second half of the twentieth century. Here, the stained glass is fitted in a metal frame together with the protective glazing to form a new type of 'bonded' glazing; the interspace between the stained glass and the protective glazing glazed with a single glass sheet is usually less than 4 cm and normally unventilated. This leads to condensation on cold surfaces in the interspace: in winter on the inner side of the protective glazing, and in summer on the outside of the stained glass and the lead cames (figure 2). Another problem associated with these 'bonded' systems is that structural changes have to be made to the historic windows. For example, the stained glass has to be trimmed to fit the new frame, and historic armouring usually has to be removed. Finally, a type of protective glazing that has found increasing use since the 1980s consists of unventilated systems that combine the stained glass with double-glazed units (figure 3). Practical experience shows that the fitting of such systems does not solve but only shifts the problem of condensation. Under certain climatic conditions, water condenses not on the glass surfaces but on the frames and cold wall surfaces adjacent to the windows. If the water is not properly drained, it can lead to damage and fungal growth (figure 3, bottom picture). In some cases, the double glazing creates quasi 'hermetic' conditions, which, in contrast to the originally permeable stained-glass windows (which often included little vent windows), can lead to climatic conditions that are detrimental to the interior of the church (affecting woodwork, wall paintings, organ, etc.). One variant of such a double-glazed protective glazing is the so-called 'sandwich glazing', which involves the stained glass being fitted between the two panes of a double-glazed unit (figure 4). The main problem with this system is the limited durability of the materials used in the double glazing.

Fig. 3. Protective glazing fitted with a double glazing unit: outside view (above) and inside view showing fungal growth on the walls surrounding the stained-glass window (below). Photos: authors.

Fig. 4. Type of double-glazed protective glazing known as 'sandwich glazing', installed around 1990. Photo: authors.

Over the years, the silicone sealing begins to leak, leading to condensation on the stained glass.

The durability of double-glazing systems has been shown to be relatively short compared with the lifetime of historic stained-glass windows with 'low-tech' protective glazing, which – if properly maintained – can span a century. The short lifespan of double glazing (with replacement likely to be necessary every 20 to 30 years) presents additional risks for the historic windows as well as additional costs, which are usually not included in the original cost calculations for improving the thermal efficiency of the church. Considering the risks and the costs of repair or replacement, double-glazing systems seem to be less sustainable than, for example, the 'simpler' protective-glazing systems that use a single glass sheet. One might also add that the possibilities of an aesthetic integration of a protective glazing using double-glazed units into church façades are limited in comparison with (to give an example) a frameless protective-glazing system or single-pane protective glazing framed in thin wooden or metallic frames.

Preliminary Experiments and Calculations

Preliminary measurements in a hot box, as well as thermal calculations, have been carried out in order to determine the overall heat transfer through various glazing systems in steady-state conditions (i.e. at constant internal and external air temperatures). The measurements provide the thermal transmission coefficients, called *U*-factor, for the tested glazing systems and allow verification of the thermal calculations. The *U*-factor is expressed in $W/m^2 K$ and represents the amount of heat transfer per square metre and per degree of temperature difference between the warm side and the cold side of the tested element. The rule is that the higher the *U*-factor, the higher the heat loss of the tested element. Three hot-box experiments have been carried out so far. In the first one, a stained-glass window (146 x 71.5 x 2.5 cm) fitted with a double-glazed protective glazing was tested. The stained glass was taken from Vitromusée Romont's depository and dates from around 1910. The dimensions of the unventilated interspace between the stained glass and the protective glazing were as follows: height 146 cm, length 71 cm, and width 0.39 cm. In the second experiment, the same assembly was used but was ventilated to the exterior and the interspace was slightly enlarged (gap width 0.44 cm) to allow for natural convection by four openings in the protective-element. A third experiment was conducted with the double glazing alone to get the precise *U*-factor of the unit. This last test also represents the reference measurement when comparing calculations to measurements. Figure 5 shows the stained-glass window and the double-glazed unit as well as a model cross-section of the tested glazing systems. In all three cases, the assembly was surrounded by insulating material with a known thermal conductivity in order to evaluate the thermal performance of the window only. The temperatures chosen in the measurements were 17°C for the room side and 2°C as the outdoor temperature. For the ventilated assembly, thermal conductivities of the air cavities were chosen according to the European standard EN ISO 10077-2. The *U*-factor of the stained-glass window alone and the sandstone wall were determined by calculation only, because they represent very simple cases and need not to be confirmed by hot-box measurements: for the existing stained-glass window, a *U*-factor of $U_{\text{stained glass}} = 5.78\ W/m^2 K$ was calculated; the *U*-factor of the sandstone wall with a thickness of 0.5 m was $U_{\text{wall}} = 2.38\ W/m^2 K$. The calculated and measured *U*-factors for the three different glazing systems range between 1.56 $W/m^2 K$ for the stained glass with unventilated double-glazed protective glazing and 2.1 $W/m^2 K$ for the double glazing alone. That the double-glazed unit is composed of three fields fitted in a metal frame explains its relatively high *U*-factor (which is usually found to be less than 1 $W/m^2 K$ for modern double glazing). The ventilation seems to have a negligible effect on the thermal conductivity of the window element: the *U*-factor for the unventilated system is 1.56 $W/m^2 K$, while that of the ventilated system is 1.68 $W/m^2 K$.

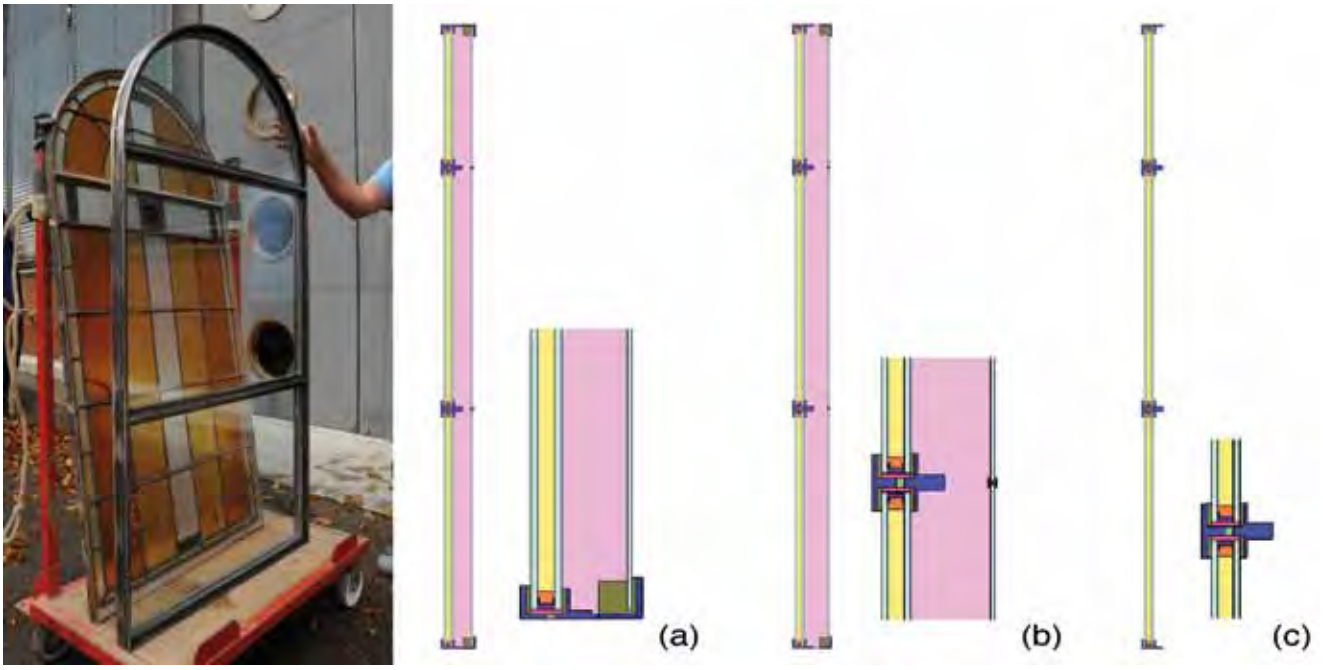

Fig. 5. Stained-glass window and double glazing used in the hot-box measurements (left) and model cross-section of the three window assemblies tested in the hot box (right): (a) unventilated assembly, (b) ventilated assembly, (c) double-glazed unit alone. Photo: authors.

In order to get an impression of the thermal efficiency of a stained-glass window protected with double glazing in an 'average' parish church, the following simple calculation was done using the calculated *U*-factors for the ventilated and the unventilated glazing systems as well as for the stained-glass window alone: $U_{total} = U_{window} \times A_{window}/A_{total} + U_{wall} \times A_{wall}/A_{total} + PSI \times P_{wall}$, where *U* is the thermal transmittance of the window or wall, respectively, *A* is their area, and P_{wall} is the circumference (perimeter) of the window. The total *U*-factor ranges between 2.6 $W/m^2 K$ (stained-glass window without protective glazing) and 2.4 $W/m^2 K$ (with double glazing). The results illustrate that, regardless of the type of glazing system present, the thermal loss through the windows, which in our example make up 5% of the total wall area, is very small compared with the loss through the walls. Figure 6 shows the calculated temperature distribution through a cross-section of each of the tested assemblies. The temperatures in the interspace are to be regarded as average temperatures, because the model does not include computational fluid dynamics to model real air flow. The calculated temperatures on the surfaces of the stained-glass window and the protective glazing will be relevant in our further investigations regarding condensation in the interspace between stained glass and protective glazing. In a further step to investigate condensation, water vapour transmission through

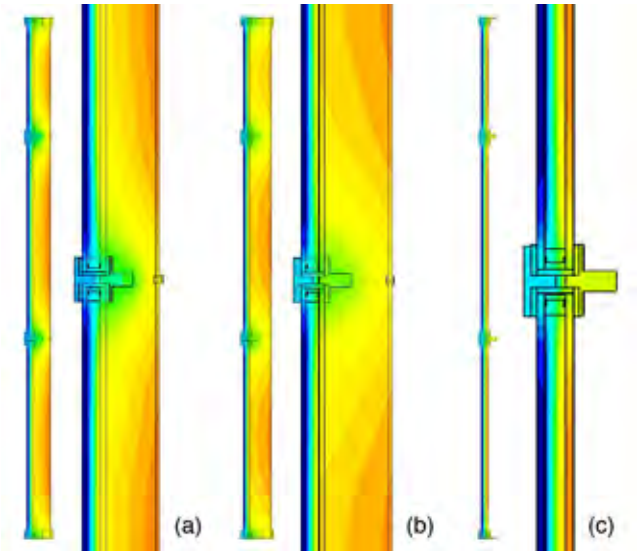

Fig. 6. Calculated temperature distribution in the three investigated assemblies for indoor temperature and external temperature of 17°C and 2°C, respectively. False colour images: the temperatures range between 0°C (dark blue) and 18°C (dark orange). Images: authors.

stained glass was measured. Two identical panes of stained glass measuring approximately 30 x 40 cm and dating from the mid-twentieth century were used in these tests: one test panel had naturally aged putty, while the other had freshly applied putty. The measurements were carried out according to the European Standard EN 12086. The test results show a clear reduction of water vapour transmission by a factor of approximately 1.6 for the stained glass with freshly applied putty. Additional measurements on older stained glass (nineteenth and early twentieth century) with naturally aged putty are planned. These supplementary measurements should provide an indication of the range of water vapour transmission values for stained glass in various states of preservation.

Summary and Conclusions

The calculations and measurements in this study represent preliminary results on the thermal efficiency of stained-glass windows protected by double-glazed units. The results have shown that the addition of protective glazing with a double-glazed unit improves the thermal conductivity of a stained-glass window by a factor of approximately 3 as compared to the stained-glass window alone. The experiments have also demonstrated that the *U*-factor for a double-glazed unit that is designed to protect stained glass and to fulfil aesthetic requirements does not achieve the thermal efficiency values of modern double glazing. Additional experiments on protective-glazing systems glazed with a single glass sheet will follow. They will include the thermal simulation of ventilated and unventilated systems with interspace widths varying between 3 and 12 cm. In a further step, the efficiency of the glazing systems investigated will also be compared under transient (i.e. varying) temperature conditions. These calculations will be verified by measurements in a weathering test chamber. The aim of the research is to compare the thermal performance of single-pane and double-glazed protective-glazing systems, while taking into consideration the specific characteristics of the different systems, for example the large insulating interspace of early protective-glazing systems and the divided metal frames in double-glazed protective glazing. The results of these experiments should enable us to discuss the pros and cons of the glazing systems studied, regarding both thermal loss and (more importantly in conservation terms) the frequency of condensation on the stained glass and in the interspace. They should also allow us to identify the systems that are most appropriate in terms of energy saving, stained-glass preservation, and aesthetic result. At this point in the study, the results already corroborate the hypothesis that, regardless of the glazing system chosen, the amount of heat loss through church windows is minimal compared to the loss through the walls. The effects of double-glazed units are negligible when considering that, in historic churches, the thermal loss through stained-glass windows without protective glazing is estimated to be less than 10% (Neilen, Schellen, and van Aarle 2003) and that the heat loss normally accounts for only between 10% and 20% of the total energy consumption (Baumann 2004).

With regard to appropriate solutions for the comprehensive and long-term protection of post-mediaeval stained-glass windows, our empirical survey has provided valuable information on the environmental impact (the risk of condensation on the stained glass in particular) of certain types of protective glazing. One major outcome of the study is the observation that the early protective-glazing systems dating from the first half of the twentieth century have created surprisingly good conditions for the conservation of at least some of the post-mediaeval stained glass in Switzerland. However, so far we only have a limited understanding of the efficiency of these systems, which is why they remain one of the focal points of the project. The aim of further research will be not only to establish whether there are additional arguments to preserve these early protective-glazing systems, but also to understand how these systems function and to apply the principles in the design of new protective-glazing systems. Notwithstanding the advantages of the systems outlined here (or any other protective-glazing system), alternative approaches to the conservation of stained glass should always be considered. Even from an energy-saving point of view, the conservation of stained glass without protective glazing must remain an option, at least for windows dating from the nineteenth and twentieth century.

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An Innovative Mounting System for Stained-Glass Window Panels at the Museum of Fine Arts, Boston

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Keywords
stained glass; mounts; exhibition; vibration damping; light box

Abstract
A stained-glass mounting system was developed for the newly constructed Art of the Americas Wing at the Museum of Fine Arts (MFA), Boston. Through the collaborative effort of MFA curators, exhibition designers, mount fabricators, and conservators, the design of the custom-made casework incorporated many (but not all) of the priorities and concerns involved, such as inert materials, environmental control, versatility, adequate illumination, overall display design within gallery context, and ease of operation of display method. The windows were installed into glass and steel cases and illuminated by LED light strips. New mounting frames with hinging capabilities attach to a tubular channel system inside the casework. The advantages and disadvantages of the design and how it relates to the handling and installation process are discussed.

Introduction
The Museum of Fine Arts (MFA), Boston broke ground in 2005 to erect a new Art of the Americas Wing. The plan first required demolition of the 1928 European and American Decorative Arts Wing to make way for the new glass and steel structure designed by Foster + Partners, London. The new wing opened to the public on 20 November 2010, and it displays more than 5,000 works of art from North, Central, and South America throughout 53 new galleries on four levels (Hatchfield and others 2012). The galleries have a modern design quite different from the earlier stone-dominated museum building. The new casework, designed by Foster + Partners working closely with MFA staff and case fabricators Goppion S.p.A. of Milan, Italy, echoes the sleek overall glass and steel of the architecture. The engineering and aesthetics of the casework resulted in a sophisticated display of the collection. The window panels are exhibited on Level 2 in galleries devoted to the American Renaissance (figure 1), the Arts and Crafts Movement (figure 2), and the Aesthetic Movement (figure 3). Five windows were installed within a closed casework system, while another group was instead installed along a vignette platform with a modified version of the same system. The design parameters were challenging to navigate while ensuring best practices and preservation of the windows. Could a light-box design be modified to incorporate seamless panels, new lighting technology, and case engineering, yet still allow for safe installation and long-term exhibition? The general care of stained-glass windows at the MFA falls under the responsibility of the Objects Conservation Department, which does not have a specialist in stained-glass conservation. The Department continues to re-visit the exhibition display more than two years after the opening of the Art of the Americas Wing in order to improve the display system.

Conservation Concerns Within the Design Parameters
The goal of conservation was to ensure that the re-installation provided an appropriate and safe display of the window panels. The conservation criteria included the following: ease of operation and minimal handling during installation process;

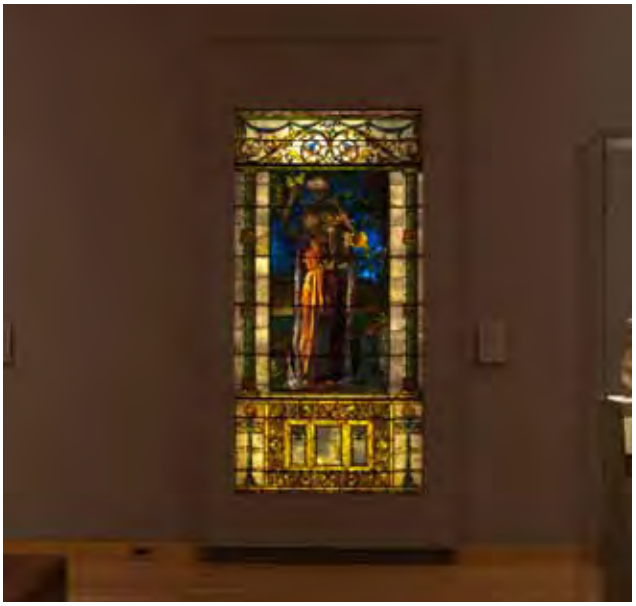

Fig. 1. Infant Bacchus, 23.249. Gift of Washington B. Thomas, 242.6 cm x 123.2 cm x 5.7 cm (Photo: Gerri Strickler © 2012 Museum of Fine Arts, Boston).

Fig. 2. Arts and Crafts Gallery featuring Morning Glories , 1974.498a-e. Gift of James F. and Jean Baer O'Gorman, 227.3 cm x 207.7 cm x 8.9 cm (Photo © 2012 Museum of Fine Arts, Boston).

Fig. 3. Robert P. and Carol T. Henderson Gallery (The Aesthetic Movement, 1870–1900). Left to right: Peonies Blown in the Wind, 1886, LaFarge, 13.2802, 164.5 cm x 116.4 cm x 3.3 cm; Parakeets and Gold Fish Bowl, Tiffany, 2008.1415, 202.6 cm x 111.8 cm x 5.7 cm; Butterflies and Foliage, 1889, La Farge, 38.954, 181.6 cm x 82.2 cm x 4.5 cm (Photo: Gerri Strickler © 2012 Museum of Fine Arts, Boston). The windows can be viewed at www.mfa.org (accessed April 2013).

rigid yet lightweight support for the panels within the framework of the display using archival and inert display materials; direct access to artwork and to separate components of the display requiring maintenance, such as electrical and monitoring devices; vented display to minimise and prevent heat build-up from internal lights; and protection of glass surfaces from direct public access in order to prevent damage and maintain visitor safety. The resulting designs met these criteria with compromises. The combination of display methods and materials described herein was used for the first time in the MFA.

The Window Panels

This paper discusses six late-nineteenth-century windows in the MFA collection. Four windows were made and designed by John La Farge: *Infant Bacchus* (figure 1), *Peonies Blown in the Wind* (figure 3), *Butterflies and Foliage* (figure 3), and *The Fish* or *The Fish and the Flowering Branch* (figure 4). A more recently acquired Louis Comfort Tiffany window, *Parakeets and Gold Fish Bowl* (figure 3), was made for exhibition at the 1893 World's Columbian Exposition in Chicago and is on display for the first time at the MFA. A multi-panelled window that was formerly attributed to La Farge but is now considered to have been designed by Daniel Cottier in 1877–78, *Morning Glories* (figure 2) needed special care for installation in order for each panel to be individually supported, levelled, and centred while hung as close as possible as they originally would have been. Like so many objects of the MFA's American collection, these are on display together for the first time in the new wing.

The display of windows by La Farge and Tiffany, with their dark and thick plated glass, is particularly challenging to achieve satisfactorily. Original architectural settings using natural light offers little control as the light changes throughout the day and year. Light intensity and colour rendering are major obstacles, especially for large panels.

The windows had been in storage crates for several years during demolition and construction. All have pre-existing physical damage and a certain level of prior repair, but are in generally good condition. They were re-examined by a specialist in stained-glass conservation and were found to be structurally stable for re-installation with very little or no deteriorated glass. Physical damage that is present on the La Farge *Infant Bacchus*, in particular, is more likely a result of heavy glass plating within the upper part of the panel, but internal stresses of the glass as a result of annealing at manufacture is also a possibility (Sloan 1993, pp. 87). Without existing documentation or disassembly, there is no visual indication that La Farge employed organic materials into the plating of this window that have been found in others (Sloan 1995). The Tiffany window similarly shows damage from internal stresses, mostly in the blue background and the fish bowl. Symptoms of chemical deterioration such as tiny fractures, iridescence, powdery pits, or flaking sometimes associated with windows made by these two artists (Sloan 1993, pp. 90–94) were not observed with normal visual examination.

Dialogue in the Planning Phase

The most important curatorial priorities for the window displays were to reduce visitors' distance from the window and integrate the displays into the context of each gallery. Additionally, providing adequate light for the darkest windows, *Peonies Blown in the Wind* and *Infant Bacchus,* was a major concern. The most important design priorities were to include invisible access panels around the windows and their integration into the surrounding display scheme of the gallery, such as flush mounting them to the wall. An open display framework using artificial or natural light did not fit into these criteria. A push to incorporate new lighting technology into the new galleries also added to the development of an improved light-box design. Incorporating the windows into the building architecture for natural illumination was never considered, in contrast to another stained-glass window reinstallation of a much grander scale, the Hampton Court Window, 'Window with Eight Apostles and Other Saints', which also occurred in 2010 as a result of the same master plan construction project (Rousseau 2010).

A conventional light box, which is the most common mounting and display method previously used by the MFA as well as by other institutions, was re-considered. This type is usually constructed of Medium Density Overlay (MDO), an exterior grade plywood panel with resin-saturated paper surfaces, and back lit with colour-corrected fluorescent tube fixtures evenly spaced behind a diffusing panel. Internal fans and vents along the top of these display boxes minimise heat build-up. A superior design of these boxes gives access along both sides and back, with an additional removable front cover to access the artwork. The design runs the risk of creating what some curators call the 'TV' look, and it was not an option the department desired.

Fig. 4. Recessed wall case containing The Fish, about 1890, La Farge, 69.1224. Edwin E. Jack Fund and Anonymous gift, 76.8 cm x 3.2 cm (Photo: Gerri Strickler © 2012 Museum of Fine Arts, Boston).

Another version previously used at the MFA was a false window box set into a gallery window well with the natural light blocked and artificial lighting installed. This gave some sense of architectural installation and allowed for flush-to-wall mounting but limited access around the artwork, often necessitating de-installation.

Once Goppion S.p.A. was contracted for the engineering, prototyping, production, and installation of the casework in the new wing, the stained-glass panel display options could be further developed. Benchmarking trips to other museums by an MFA team occurred with the goal of reviewing recent museum installations in London and Paris containing Goppion casework. The most influential visit for stained-glass display possibilities, in particular, was to the Victoria and Albert Museum, where a combination of display designs was employed for the newly installed British Galleries (Eatman 2008). Although the same display methods were not deemed appropriate for the American windows, given the MFA curatorial and design criteria, the team returned to Boston with a stronger overall vision.

As a result, variations on the 'Q', or quadrilateral, Goppion case model used throughout the new wing were also fabricated for the windows, with the exception of the Cottier panels: these were displayed outside of a case. The two different case types used are partially recessed wall cases (figure 4) and a free-standing floor case attached to a centre false wall (figure 3). Both types were designed to be 30 cm deep. The cases are made of stainless steel with a thermosetting powder coating. The exteriors were painted in-house according to the gallery wall colour. This was chosen over an earlier design of back-painted glass surrounding the windows, which is used frequently within the new galleries. The cases have an internal fan system to vent heat generated by the lamps. The hinged door contains shatterproof extra clear anti-glare glass. The idea of allowing the visitor closer access to see the revolutionary glasswork of Tiffany and La Farge was originally to be implemented without the use of physical barriers. The extra-clear non-glare glass[1] supplied by Goppion provides a very successful layer of protection without the resulting optical distortion that so often occurs when looking at glass through an additional protective glazing, while allowing the visitor to get inches away from the artwork.

Mounting and Display System

Frames

During the 1990s, loans and travel prompted two-part stainless steel frames to be added to most of the windows in the collection. Although the frames provided a removable but reinforced structure for the window sashes useful for display mounting, they also added a great deal of weight that complicated handling and travel.

New lightweight aluminium two-part mounting frames were manufactured for all the windows by American Metalcraft Co. Inc. using aluminium angle (Alloy 6061) following MFA specifications (figure 5). The window sash fits into the pan frame and is secured by a front frame with machine screws along the side. The two-part aluminium mounting frame is fully removable from the window and is isolated by thin strips of low density polyethylene sheet (LDPE).

The final gallery design did not permit visible access panels between or along the side of the window display. Since the backs of the cases were also inaccessible, the frames were

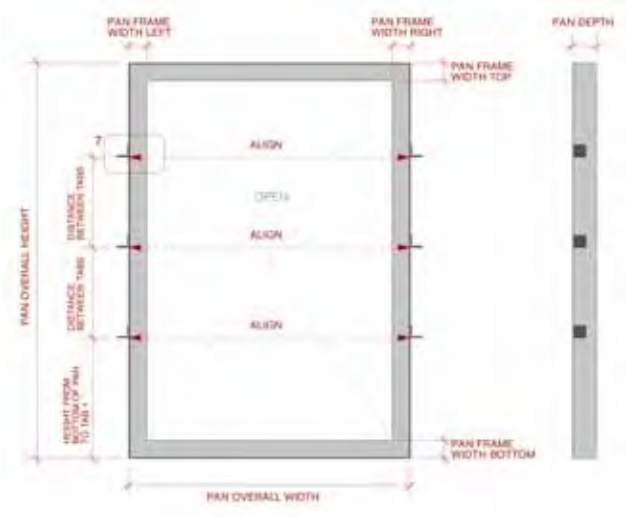

Fig. 5. Aluminium pan frame design (pdf design: Tomomi Itakura © 2012 Museum of Fine Arts, Boston).

hinged. Three horizontal welded tabs along each side of the pan frame mount the window to a channel frame work inside the display case (figure 6). Notches were cut along the sides of the front frame to accommodate these tabs.

Interior Casework and Lighting

A Unistrut® metal channel system inside the case receives the tabs along the verticals by means of sliding adjustable angle brackets (figure 6). A white acrylic diffusing panel is screwed into vertically aligned metal tabs along the inside of the Unistrut®. The channel system inside the case is adjustable; however, the case door window glass opening is not. It would need to be replaced if used with a larger-sized window panel.

In order to access the non-display side of the window and the light strips behind it, the window can pivot along one side using the three tab and bolt assemblies as a hinge mechanism (figure 6). Philips eW® Cove Powercore 2800K LED[2] lighting was chosen by the Design Department and used to light all the window panels based on the warm colour rendering and ease of use. These are dimmable low-profile twelve-inch linear fixtures that can be connected end to end with directional beam and housing rotation capabilities. The manufacturer's stated output for a one-foot section containing five lamps is 1238 lux at 21.34 cm.[3] Light strips are mounted horizontally onto a Marvelseal®360 lined MDO panel via wood screws which is hung on a separate

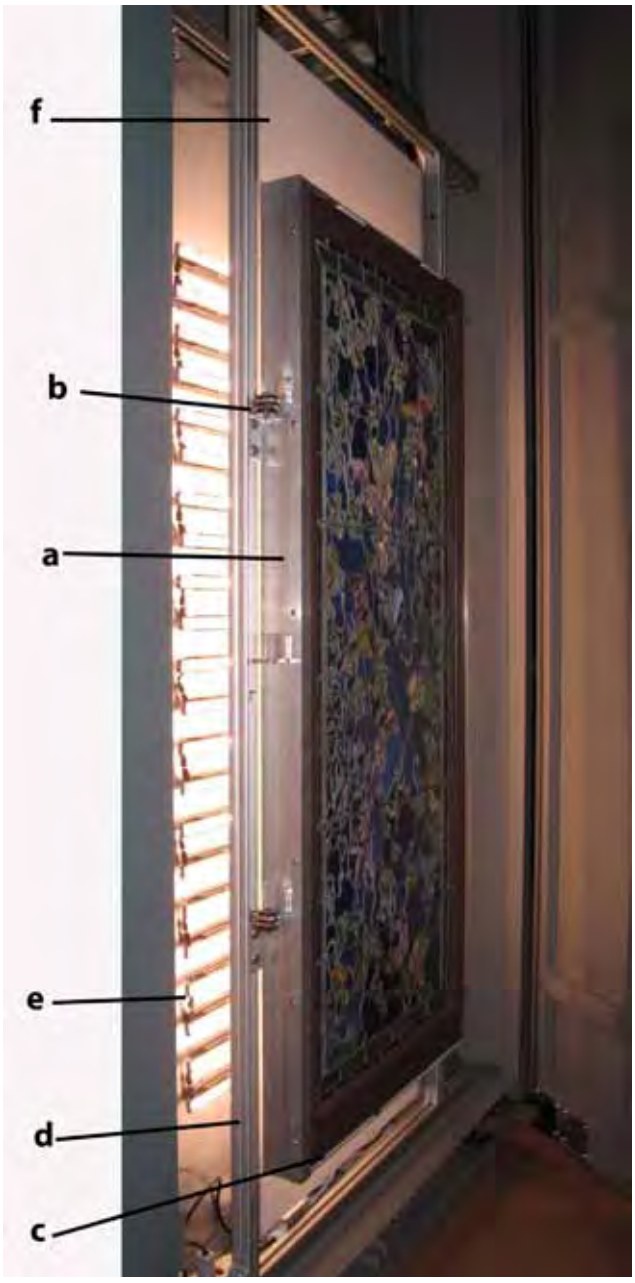

Fig. 6. Case interior during installation. (a) Aluminium frame; (b) tabs on brackets; (c) LDPE; (d) Unistrut®; (e) light strips; (f) diffusing panel (Photo: Gerri Strickler © 2012 Museum of Fine Arts, Boston).

track inside the case. The number and spacing of light strips vary with the needs of each window.

Fibre-optic lighting, although generally considered a safer lighting option to prevent heat build-up close to the surface of the glass, could not be successfully designed into the display. Additionally, LED light pads that efficiently combine lamps with a diffusing panel were not considered cost effective for these large displays. Overhead gallery lighting is angled away from the case, giving ambient light levels as

low as 22 lux on the face of the windows.

The John La Farge panels *Infant Bacchus* (figure 1) and *The Fish* (figure 4) are both installed into partially recessed wall cases. Both have fans along the top of the case that exhaust into the wall cavity behind. However, the amount and size of the fans correlate more with the number of lighting strips installed than the dimensions of the case. The larger window panel has more lamps in order to compensate for the more opaque centre imagery than the border design. Larger fans were therefore required to vent a greater amount of air per minute.

The large centre case with the two La Farge windows *Peonies Blown in the Wind* and *Butterflies and Foliage* flanking the Tiffany window *Parakeets and Gold Fish Bowl* is constructed as one large case with three separately hinged doors, three separate channel frames and lighting panels, and three exhaust systems above (figure 7). Warmer air inside the case exits through two vents at the top. Air enters into the centre vent where it is pulled into the fan housing below, through a micro-filter, and then pushed into aluminium tubing running along both sides of the back of the window panel. The air then moves along the back of the window and eventually rises to vent out the top in a forced updraft. The temperature probe above the window is connected to a thermostat that activates the fan at temperatures above the gallery environmental set points.

The Cottier window panels, *Morning Glories*, are not fully enclosed within a case (figure 2). Fans are installed along the top of the false wall. Light strips are dimmed due to the larger proportion of lighter-coloured and clear glass contained in these windows. The side panel of the false wall opens to access electrical connections and to remove the light-strip panels by means of a sliding track.

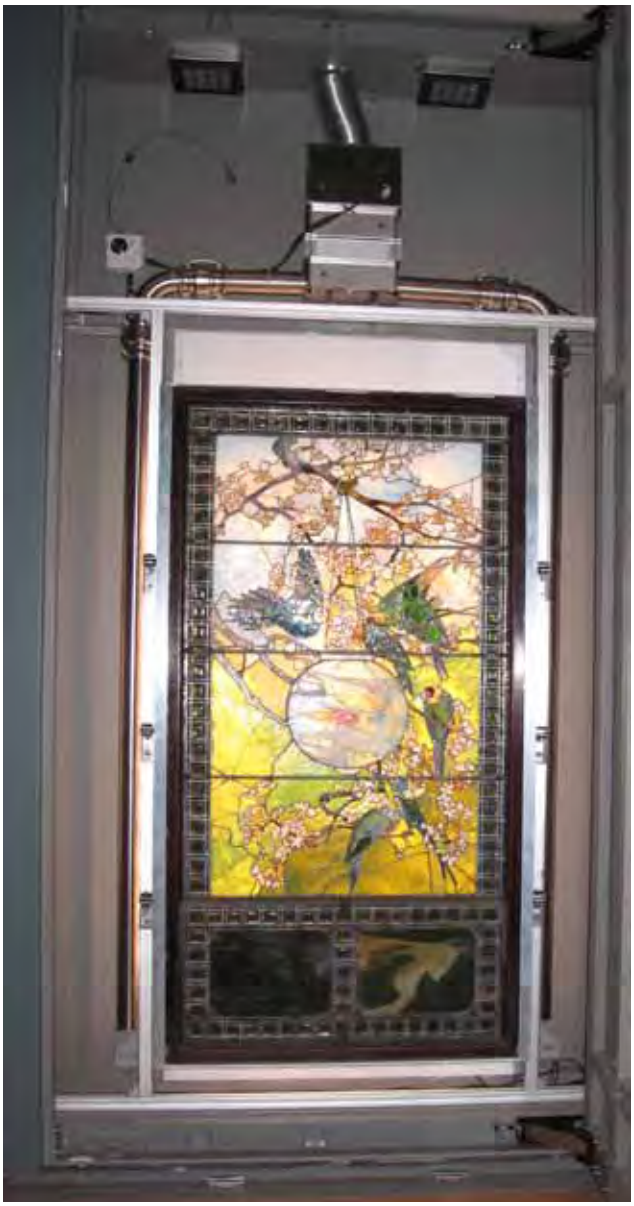

Fig. 7. Case interior showing exhaust system. Parakeets and Gold Fish Bowl. Gift of Barbara L. and Theodore B. Alfond in honour of Malcolm Rogers (Photo: Gerri Strickler © 2012 Museum of Fine Arts, Boston).

Vibration Damping

Concern over continuous or intermittent vibration, as well as stronger isolated shocks, led to the inclusion of vibration-damping material to the mounts. There are many sources of constant background vibration from visitor foot traffic, opening and closing the cases, lifts in the gallery, or even internal case fans, to name but a few. Incidentally, two earthquakes have occurred since the opening of the new wing, and the concern over seismic activity is increasing. Due to budgetary limitations and a compressed installation schedule, load per unit area calculations on the pads were not made for each individual window. Instead, the mounted

Fig. 8. Bolt assembly through tab and bracket showing Sorbothane® with stainless steel washers surrounding top, middle, and bottom pads (Photo: Gerri Strickler © 2012 Museum of Fine Arts, Boston).

windows were treated as a group with an average weight of 99.79 kg per frame. Using this as a conservative baseline, the load is spread along six points of each window onto 0.64 cm thick and 6.35 cm diameter doughnut-shaped Sorbothane® pads[4] with an average load calculated at 16.63 kg per cm^2. Pads were placed within the tab and bolt assemblies of mounting frames, as an assembled bushing, to buffer vibration along metal-to-metal connections (figure 8). This option was chosen over an earlier consideration of placing pads under and behind the casework. A medium soft range of 70 durometer[5] was chosen. Custom shapes were cut in-house by hand with a leather punch from commercially available larger pads according to tab hole and bolt diameters, 1.43 cm diameter and 0.635 cm diameter, respectively.

Installation and Access

A dedicated rack was fabricated in-house using galvanised stainless-steel perforated tubular channel to hang the windows by their new frames (figure 9). The windows could be hung one at a time while cleaning or while further minor treatment was performed. The rack was of welded and bolted construction with 20.32 cm diameter air ride or pneumatic wheels that gave smooth transport from the working space into the exhibition space. The rack was fully adjustable, corresponding to the dimensions of each window panel. The mobile rack and wheeled floor lamps made a versatile system for inspecting the panels in both transmitted and reflected light.

After all internal case work above and behind the windows was complete, including final cleaning, the panels were installed. Before mounting the windows into the new aluminium frames, the empty frames were hung into the cases to confirm the fit and approximate placement of the angle brackets that would bolt through the frame tabs. Some windows were hand lifted into the case. A fork lift was used to install the *Infant Bacchus* panel due to its size and weight, as well as its more confined case opening, and to install the *Morning Glories* panels due to the display height. The alternating frame tabs allowed for fine adjustment of the angle brackets during installation in order to centre the window panel opening within the case door window and compensate for sash corner angles.

Discussion and Conclusion

The exhibition of the stained-glass panels is generally considered successful and a welcome improvement to the previous light-box displays. The Goppion case design integrates the windows into the galleries well and offers new options for safe exhibition. The aluminium mounting frames provide appropriate rigid and lightweight support. The tab attachments act as hinges, making total restricted access to the space behind the artwork possible. The lighting strips are easily re-positioned and dimmable to increase or decrease illumination in certain areas of a window that have both dense and light areas. This was particularly problematic for the *Parakeets and Gold Fish Bowl* and *Infant Bacchus* panels. Although some components of the display system are versatile, the cases are truly custom fit.

As with many complex projects involving many constituents and tasks, staff faced considerable challenges. A continued problem during the design phase was the lack of access to the windows. Limited available collections storage space during construction required the windows to remain crated. As a result, handling was not minimised and window weights were only estimated. Additionally, it prevented a proper lighting study for each individual window to plan the light strip grid shape required and to further explore other LED strips and colour temperatures.

The new galleries have a well-controlled environment in which the stained-glass cases depend on fans for the provision of exhaust system make-up air.

Fig. 9. Rolling rack with Parakeets and Gold Fish Bowl pictured with MFA staff. Gift of Barbara L. and Theodore B. Alfond in honour of Malcolm Rogers (Photo © 2012 Museum of Fine Arts, Boston).

Although the window panels seem chemically stable, possible warm micro-environments continue to be a concern with all enclosed electrical components. Glass should not be considered inert, and therefore stable relative humidity and temperature is essential (Koob 2010, p. 131).

The *Infant Bacchus* window was the most problematic to install and remains the most vulnerable to environmental micro-climate problems. This window in particular would have greatly benefited from a focused lighting study of its own. The depth of the case is inadequate without enough space between the light strips and the object. The situation is made potentially worse by the concentrated amount of lighting strips in the centre where the glass is heavily plated and more opaque. Re-visiting LED lighting options that might offer greater intensity but fewer lamps may reduce the heat generated, since it is not the light itself, but the lamp electrics, that provides the heat (Druzik and Michalski 2011; Whitaker 2005). Additionally, increasing the flow of make-up air through the case could provide a lower internal temperature. Data recorded with an internal case logger over a seven month period in 2011 show the temperature to be consistently 1–3°C warmer inside the case than the ambient gallery temperature of 22°C. The fans are wired to operate with the lights; however, the data also show daily relative humidity spikes when the temperature drops 1–2°C at the end of a day when all electronics are turned off. Discussions are underway to allow the fans to operate separately from the case lights so they may continue to replenish the air after hours.

The beneficial properties of Sorbothane® are well known, and the material has been used in other projects at the MFA. However, like its application at other institutions (Fulton and Rossie-Wilcox 2008), it was not previously used for case interiors. In-house Oddy testing[6] gave visual results comparable to those of the accompanying controls, where the copper, sterling silver, and fine-silver coupons showed no discernible change, while the lead coupon darkened overall but lacked active spot corrosion. Although this would indicate that Sorbothane® is safe to use within cases for an extended period of time, the test is not conclusive and the polymer may not be a good long-term solution for the American windows, the lead cames of which are likely to be nearly 100% lead. Unused samples of the material from the same shipment have become soft and sticky. Available silicone bushing alternatives are yet to be sampled and compared, but none were chosen prior to installation.

Unlike conventional light boxes that can more easily be dismantled as a result of exhibition changes, these displays were built to be more permanent. Objects Conservation continues to monitor the internal case environments and ambient gallery climates. The results of these inspections and data collection will provide a more solid basis for recommended changes to better ensure stable conditions for the artwork over time.

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Materials and Suppliers

Exhibition casework, including interior components of channel, Diamant® glass, thermostat, fans Goppion S.p.A
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1. Diamant® is a float glass with very low iron oxide content made by Saint-Gobain-Glass. www.saint-gobain-glass.com (accessed March 2013).
2. Categorised as LED-HB (High Brightness) and warm white, 2800 K (+375/-300), Class 2 LED product. Philips Color Kinetics Product Literature, DAS-000002-02 R01 12-09.
3. Readings taken with a hand-held meter by MFA staff of an individual strip were found to be 1830 lux at 10 cm and 1184 lux at 15 cm from the housing.
4. Sorbothane® is a visco-elastic polyurethane-based material marketed for its shock- and vibration-absorbing properties, and it is used in the form of shoe insoles, ear plugs, and mounts in machinery. It is not foam and therefore is absent of a cell structure. According to the manufacturer, the energy absorbed dissipates as heat. www.sorbothane.com/faq.php (accessed October 2012).
5. Durometer is a measure of polymer hardness. Sorbothane® is measured using the Shore 00 hardness scale for soft materials. To see a comparison of different materials and hardness scales, go to www.plasticsintl.com/polyhardness.htm and www.cmrubber.com/pdf/durometer_latest.pdf (accessed March 2013).
6. Two separate tests were performed during the months of March 2009 and January 2013.

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The Re-installation of Stained-Glass Windows in Interior Architectural Settings in the Low Countries – Selected Case Studies

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Keywords

stained-glass windows; Pieter Hofman; re-installation; significance; integrative approach

Abstract

This paper is concerned with the re-installation of monumental stained-glass windows in an indoor architectural setting and how the ethical approach to this problem has developed in the Low Countries (the Netherlands and Belgium) in recent decades. Finding a suitable new place for monumental windows is often difficult. Prior to the decision to re-install, it is necessary to carry out research into a number of aspects, art-historical and cultural as well as practical, in order to inform the decision-making process. Collaboration between the various parties concerned with a re-installation is crucial. A new home for a glass window will never be as appropriate as the original location and concessions will have to be made. However, it is always (or almost always) to be preferred to a situation in which the window is left in storage, without the possibility for public access and display.

Introduction

Issues of re-use are relevant to all manner of architectural fragments and monumental mural art that have become movable. The Cultural Heritage Agency (Rijksdienst voor het Cultureel Erfgoed, RCE) is responsible for about three hundred stained-glass windows and desires them to be displayed.

The paper describes the re-installation of a stained-glass window in an indoor architectural setting, as opposed to a museum setting. Two other cases of indoor re-installations of glass windows have been added to broaden the perspective and allow for some degree of generalisation on the situation in the Low Countries.

To the author's knowledge, there is no appropriate literature available describing the approach to re-installation of stained-glass windows. In any case, there is no written material about similar cases published in the Low Countries. The aim of this paper is to encourage a broader discussion of these practices by describing some of the obstacles and restrictions encountered in the cases described below.

A Brief History of Re-installations

Re-installing glass windows is not specific to our times. Ever since glass windows were introduced in architectural history, long-lasting re-use of glass panels has taken place as a result of wars, demolition, and political regime changes. An example of the latter is the 1783 edict that Joseph II of Austria, sovereign of the Southern Netherlands, issued to abolish contemplative monastic orders. He considered these to be of no use to either religion or society.[1] As a consequence, certain cloisters were demolished, but the windows were taken out and re-used elsewhere. Many of them ended up in Great Britain, in castles, stately homes, and churches (figure 1). More often than not these re-installations were carried out with respect for the original piece. Decorative, often small, panels were made to fit by adding strips of glass that were transparent or had a pattern.

From the eighteenth, nineteenth, and the first part of the twentieth century, there are examples of re-installations within the tradition of Neo-Historic architecture and of the willingness of architects to integrate old elements into a new context.

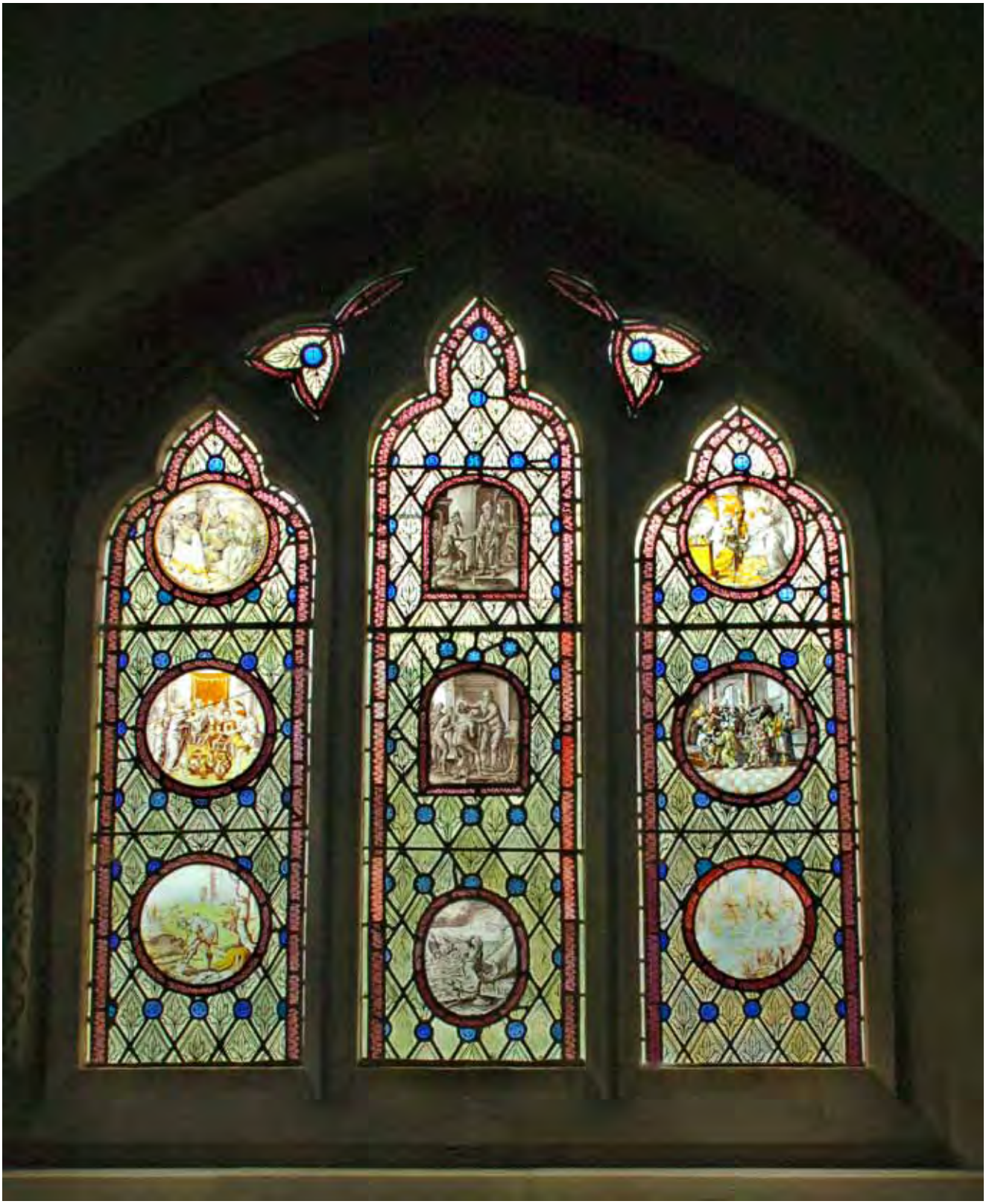

Fig. 1. Church of St Mary, relocation of 17th century Flemish panels Addington (Buckinghamshire, U.K.) (Photo: Kees Berserik).

However, in the 1960s, the situation changed with the arrival of a new school of architects. The new so-called 'archistars' (architect stars) did not tolerate old architectural elements, as they interfered with their designs. They emphasised their own creations and preferred to use the space available to make something totally new rather than to integrate elements from buildings that had stood there before.
In the past twenty years or so, there have been new developments in the approach to this issue in the Netherlands. A number of monumental buildings have been rebuilt, renovated, or extended. Changes of ownership or function can constitute a threat to buildings and the integrated architectural art. In this case, a number of the works of art have disappeared with (part of) the buildings; however, in some cases they have been saved and have become available as 'movables' for re-use.
The authorities in the Netherlands responsible for these windows are looking at ways to make the best of a bad situation and use these historical elements optimally in order to give them a new lease of life.

The Hofman Window

A stairwell window from the RCE collection designed by Pieter Hofman (1885–1965) found 'a new home' when the former PTT (Post Telegraph Telephone) building, now Nuffic building,[2] at Kortenaerkade 11 in The Hague was renovated (figures 2 and 3). The present owner is the Netherlands organisation for international cooperation in higher education (Nuffic). The relocation was triggered by a personal contact between the works coordinator and the RCE curator.
Initially, there was no exact information about the origin of the Hofman window. Research established that the window came from a stairwell in a wing that had been added to the PTT complex in the 1950s. The window was fabricated in 1958 by Glass Studio De Lint in Delft (Dam 1996, pp. 555–557).
The original window element had taken up some ninety square metres in total, within an extensive wall that probably was not straight but slightly curved.

Fig. 2. PTT window 'Mail traffic in the Middle Ages' Pieter Hofman (1885–1965), 1958 Den Haag (the Netherlands) (Photo: RCE).

Fig. 3. PTT window 'Traffic through the ether' Pieter Hofman (1885–1965), 1958, Den Haag (the Netherlands) (Photo: RCE).

This elongated wall was composed of rectangular clear glass panels, partly matted with grisaille. Two 'floating' figurative images, the one above the other, had been added. These were composed of pieces of coloured glass with lines and details in grisaille. Leadlines are used to create the contours of the figures and cross the rectangular lattice of the lead net. Against a background of roughly stippled and highlighted shading paint, powerful lines have been drawn of faces, hands, animals, clothing, jewellery, and folds. This grisaille has been applied with splendid effects of depth, relief, and fabric. Hofman's background as a draughtsman is evident from his handling of the grisaille details, and he was obviously well acquainted with the technique. He did not use grisaille in order to remove transparency, but to subtly vary light and colour, making expressive use of his skills as an illustrator. Below the images, Hofman inscribed the titles beautifully, alternately leaving the letters open in the grisaille and filling them in. The inscriptions express postal and telecommunication themes: *Mail traffic in the Middle Ages* and *Traffic through the ether* (see figures 2 and 3).
At the time it was common practice to depict the function and the use of a building, in this case 'messages between people'. The mission of Nuffic, the current owner of the building, fits in well with the subject of the windows.
Even though the thematical match was excellent, the size of the window was not. It did not fit in with the architecture of the building that was being renovated. Relocation at the original spot was not possible, as the extension in which the window was placed in 1958 had been demolished in the 1980s.

Finding a Place

The current stairwell in the building at Kortenaerkade 11 is composed entirely of square glass bricks, unfit to accommodate stained-glass windows. Therefore, two new walls were introduced, close to the entrance. The window with the theme '*Mail traffic in the Middle Ages*' (figure 2) was alloted a space in the hall, where a conference room on the left side could be fitted with glass walls. '*Traffic through the ether*' went to the right side of the entrance as part of a glass wall separating the hall from the reception (figure 3). Attention had to be paid to the dimensions. In the original situation, the stairwell had been fitted with a several-metres-high wall of transparent glass panels in which the two groups of figures were situated at the level of the first and second floors. In the new situation, the transparent glass panels on both sides had to be omitted, and the two groups of figures have to be seen as separate units. That resulted in the loss of the original spatial experience, since the figures were originally accessible from both upstairs and downstairs: in the new setting, there is much less room for the images.
The decision to change the function of the windows was preceded by art-historical research into Hofman's works. It turned out that Hofman used the layout of a figurative image within a blank field in the stairwells of several offices and government buildings in The Hague[3] (Nieuwe Haagsche Courant 1958; Haagsche Courant 1958; Hoogveld 1986, pp. 254–255; Dam 1996, pp 6–19) (figure 4). The themes that Hofman used were related to the setting of the windows and the function of the building or the company he made them for. Of overriding importance in the decision-making process concerning the re-installation was the fact that the communication theme of the windows matched so well with the Nuffic mission. All parties agreed that moving the Hofman windows to Kortenaerkade 11 was a second-best option.

Fig. 4. Hoge Raad window, Pieter Hofman (1885–1965), 1938, Den Haag (the Netherlands) (Photo: RCE).

Preservation and Conservation

A conservation plan was established in close consultation with a restorer. Since the windows would be placed inside the building, only minimal intervention was required. Complete re-leading was not necessary.

Restoration work on the window concentrated on cleaning of the reverse side, which was disfigured by house paint, cement, putty, bird droppings, and rust stains. In a number of places, lead cames, came joints, and glass panes were broken, and there were many badly damaged corner pieces, caused by taking the window out (see figure 5). Some glass panes were reversed during a previous intervention or were missing. The grisaille was in a good condition and did not require any treatment. Cracks have been bonded (using Araldite 2020) and retouched with coldpaint. However, in a few instances where breakage in the glass was disturbing, the glass was replaced and grisaille was applied to preserve the overall image. Missing panes have been replaced and their positions have not been marked on the glass, as the two groups of figures will be on view from both sides. However, those missing panes have been well documented on a lead-line drawing in the treatment report.

After conservation, the panels were fitted into individual metal frames that were screwed together, made after a design by the architect. The frames can be taken out individually if necessary.

Since the renovation was concluded in 2010, the two parts of the window can be viewed from both sides. On the hall side, a glass wall has been put up with lighting so as to facilitate the view from the other side.

Fig. 5. Damaged areas, PTT window (Photo: Henk van Kooy).

A New Home

The PTT windows have found a new home. Their visibility and the mission of Nuffic have given them a new meaning. Their original architectural function has been honoured, although in a different way, as their place is no longer in a stairwell. Also, the viewing distance to the windows has changed, as have the lighting and the way the light falls on and through the windows. This is not ideal, but is very functional and, in the circumstances, optimal.

Van Steenbergen Windows

In a similar way, modernist stained-glass windows by Eduard van Steenbergen (1889–1952), one of the major Belgian architects of the interbellum, were relocated in Antwerp. In addition to being an architect, Van Steenbergen also designed gardens, interiors, furniture, tapestries, and stained glass. For the 1930 World Exhibition in Antwerp, he designed the Sociale Werken (social affairs) stand, in which a number of abstract windows were incorporated (figure 6). After the exhibition, two of the windows were reinstalled in the bay of a small villa he also designed, in Heide (Kalmthout) (figure 7). In the 1990s, they were removed, as they were in poor condition and the owners opted for isothermal glazing.

The contact between Dr Joost Caen, professor for Glass Conservation at the Department of Conservation Studies, University College of Antwerp, and the Steenbergen family was instrumental in finding the windows a new home in the Institute for Conservation–Restoration in Antwerp. Van Steenbergen had been a professor of architecture at this academy for years, and his descendants appreciated that his work should thus remain linked to the academy.

Fig. 6. Window stand social affairs World Exhibition, Eduard Van Steenbergen (1889–1952), 1930, Antwerp (Belgium) (Photo: Brochure Wereldtentoonstelling Antwerpen 1930, Collectiviteit der hygieën en sociale voorzorg van de Federatie van Vakbonden).

Fig. 7. Window World Exhibition, Eduard Van Steenbergen (1889–1952), relocated at the Institute for Conservation–Restoration of the Royal Academy of Fine Arts Antwerp (Belgium) (Photo: Joost Caen).

After treatment, the windows were re-installed in 2002 in their new destination, the cloakroom of the Institute for Conservation–Restoration (Blindestraat 9, Antwerp, Belgium).

Again, in this case, re-installation was realised thanks to informal contacts. Several parties were involved in the re-installation itself: the owner and the users of the building, the regional council for the conservation of monuments and historic buildings, and the restoration architect. The windows were allotted a new place that does justice to the original setting, being fitted at the same height and in the same curved shape as during the World Exhibition. They are once again an eye-catching feature, in the passage between the buildings of the institute.

The treatment preceding the placement was carried out by students of the Institute for Conservation–Restoration under the direction of Caen. In addition to the conservation of the original steel frame, there was also much work to be done on the glass windows themselves. The curved stained-glass panels were treated in specially constructed curved moulds. The original lead net was preserved where

possible, but almost all the edge leads had to be renewed. In many places, the lead net had to be re-soldered. Missing glass panes were supplemented with matching glass, which was discreetly marked and dated with a diamond-tipped pen. These reconstructions were fairly easy to execute, as a major part of the composition is of a repetitive character. The broken glass panes were painstakingly removed and bonded with epoxy resin (Araldite 2020). After bonding, these pieces were integrated back into the lead net. In order to reinforce the structure, additional perpendicular iron support-rods were applied.

Berg Window

In 1953, Toon Berg (1877–1967) made a stained-glass window for the stairwell of the municipal hall of Numansdorp. This window symbolises the history of the shire. The former municipality of Numansdorp received the window during the construction of the municipal hall as a gift from the shire of Cromstrijen. It is composed of nine panels and depicts the issuing by the Emperor Maximilian of Austria of a perpetual hereditary tenure lease of accretions, mud flats, reed beds, a fishery, and birding rights. He gave this lease to his first secretary, Gerard Numan. If Numan and his heirs were to profit in any way from this gift, they had to make these wetlands productive and profitable. The gift led to the creation of the shire of Cromstrijen, of which Numansdorp formed a part. After the demolition of the former municipal hall, the window had been stored in the attic of the municipal workshop for twenty years. The municipality screened several locations to re-install the characteristic stained-glass window.
However, to place the window of 4.5 x 3 metres turned out to be no easy task. The Nationaal Landschapscentrum (NLC; national landscape centre), situated within the shire of Cromstrijen, was able to install the window in 2011 in the interior wall of a void. Considering the geographical location and the nature of its new host, this is a fitting place for the characteristic window, whose theme matches well with the educational character of the NLC.
The installation took place under the authority of Hoeksche Waards Landschap (HWL), the owner of the NLC, and was carried out by a construction training institute. In order to fit the window under the pitched roof, part of the window on both sides had to be cut off, resulting in the loss of part of the depicted wetland which is so characteristic of the theme (figure 8).

Discussion and Summary

The examples presented in this paper show that there is no such thing as an ideal re-installation for monumental stained-glass windows, as it is almost impossible to find a location as fitting as the original.
Finding a suitable new location for windows seems to a great extent a matter of chance. Informal contacts are a contributing factor, as well as the willingness of the parties concerned and the possibility of considering a variety of options. Apart from the importance of chance, it is possible to structuralise the process of re-installation to a certain degree. The basic steps of preservation, conservation, and ethical considerations are described in countless guidelines, including standards, specifications, the guidelines of the Corpus Vitrearum, the Burra Charter, and other charters.

Cultural Values

The fundamental consideration when planning interventions is the cultural value or significance of the original building and its glazing. All relevant factors will have to be considered. Often this happens implicitly, but a formalised explicit and interdisciplinary approach is to be preferred, as it creates transparency and opens up the possibility to develop more options and solutions. It is crucial to have a detailed picture of the cultural values attributed to windows and to decide which aspects – at a historical level as well as where the preservation is concerned – should be retained in a re-installation in order to do them as much justice as possible. This is where methods for cultural value assessment such as 'Significance 2.0: A Guide in Assessing the Significance of Collections' (Russell and Winkworth 2010) can be very useful.
In the Netherlands, the document *Op de museale weegschaal* ('On the museological balance') (2013) also concerns itself with cultural value assessment. This manual describes step by step the process of significance assessment and a set of criteria that may be used to describe the cultural values. It enables one to define a frame of reference enabling a comparison with other objects and collections. In addition, it can bring to light the future potential of the value of an item. For example, when more research is undertaken, the cultural value of an item may change the understanding or unlock its potential.
In the case of the Hofman window, the first step to assess the cultural value consisted in making an inventory of the knowledge available on the artist, his background, themes used, style, method of working, techniques used, patrons,

Fig. 8. Municipal hall window, 1953, Toon Berg (1877–1967), Numansdorp, 1953, relocated in the National Landscape Centre, Numansdorp (the Netherlands) (Photo: Ton Keijzers)

body of work, the place of the window within the oeuvre, and the original setting of the window. Aspects such as provenance, rarity, current cultural, and utility values were also relevant. On the basis of the most important characteristics, a cultural value assessment was made; at the time, this was done still in an informal and implicit rather than in a formal and explicit manner. Research on Hofman and the Hofman window in a wider historical and artistic context was helpful for the interpretation. It revealed how the window functioned and helped guide decisions about what to do next.

Finding a Suitable Place

In the case of the Hofman window, a statement of significance was not needed to develop the options to find a suitable building, as a potential re-installation presented itself out of the blue. The window had already been taken out of its original setting and had been in storage for many years. However, generally speaking, a statement of significance can certainly be helpful at this point. Additional information on cultural values allows for more re-installation options.
A useful strategy for finding a suitable location may be to begin with a narrow perspective and then broaden it.

The window may be relocated within the original building, integrated within a new building on the same site, or within an institution that has the same or a similar function as the original one, in the same town, region, or province.[4] Subsequently, aspects such as the viewing distance and incidence of light play a role, so the original situation should ideally be documented (preferably photographically) before the glass windows are taken out. To show the proportions, it is most useful to position a person in front of the windows. There should be images taken at different times of the day, to properly record the various perceptions of the light. The information thus gathered is very useful, but at the same time these aspects are among the most difficult to satisfactorily deal with in a re-installation.

Integrative Approach

Experience in the Low Countries has shown that informal contacts at an early stage may mobilise people and institutions to contemplate and facilitate the re-installation of stained-glass windows. In the best scenario, there is an integrative approach involving consultation between the building manager, cultural heritage representative, renovation architect, contractor, and conservator which may yield a realistic rescue plan.

Treating and Fitting in the Windows

The ideal treatment for windows obviously depends on several aspects, such as their condition, new function, orientation, and position on the inside or the outside of a building. In general, it can be said that conservation policies have radically changed over the years. Today, the minimalist approach to conservation is mostly favoured. The original work of art is to be respected as much as possible. This also implies that fitting in windows into their prospective new location must be done with great care. As a consequence, positioning the windows within a larger context (as in figure 1) may be acceptable, but down-sizing them usually is not. Also, when making decisions about treating and fitting in windows, a statement of significance is very useful for broadening the spectrum of options and favours the optimal 'use' of the works of art concerned.

Dealing With 'Originality' in Practice

The examples in this paper focus on windows replaced within a building, changing their original function as a 'window' to the outside. Consequently, the treatment and protective measures necessary in case of outside placement were not discussed.

The conservation of the Hofman window was very restrained, and to a large extent the original state of the window could be preserved. The other windows described were re-leaded for the most part, or even totally. If, on top of that, the original form is lost as often can be the case, how authentic can one call the result?

Seen in this light, the re-installation of the Van Steenbergen windows has retained most of the original features.

In the case of the Hofman window, down-sizing was involved; however, it was concluded that the advantages of the re-installment outweighed the disadvantages. The elements that were not used remain in storage, and the whole process was meticulously documented; thus, the windows can easily be returned to their original state. The new location of the Hofman window is thematically very fitting, but is much less successful concerning the 'lighting'.

It can be argued that the Numansdorp re-installation did not do enough justice to the theme of the window, as relevant corner pieces were left out. It is worth noting that, in the re-installations described, a special place or a wall had to be created to make them fit in.

Visibility

In the end,what ultimately prevails depends on a variety of circumstances. When creating an acceptable new ambiance, concessions are often inevitable; however, as long as the new setting resembles the original situation sufficiently, much will have been gained: the real meaning of a monumental work of art lies in its visibility and access for visitors.

It is a noble aspiration to keep relics close to their original context; however, if that fails, any serious alternative is to be preferred to having them stored or letting them go on the market.

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Notes

1. http://www.cartusiana.org/?q=node/1265 (accessed 15 March 2013).
2. This building was constructed based on designs worked out under the direction of government architect D.E.C. Knuttel (1857–1926) (Gulik 1993, pp. 5–8).
3. This research was carried out in 2010 as a training by Laura Plezier, student of Art History, University of Leiden.
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Creation and Degradation

Creation and Colouration of Stained-Glass Windows in Mediaeval Literary Sources: New Perspectives on Technical Treatises Dated Between the 12th and 16th Centuries

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Keywords
technical literature; glass; stained-glass window; Middle Ages; history

Abstract
This contribution presents the initial results of a study on technical treatises regarding stained glass (12th–16th centuries). A comparison of texts, both known and unpublished, allowed different typologies equivalent to various roles involved in stained glassmaking to be identified. The majority of treatises were likely written by or addressed to glaziers or glass painters, lacking in prescriptions on the production of glass and its colouration, which was entrusted to specialised glassmakers. Therefore, other literary sources have been observed, since only the whole spectrum of technical literature on glass opens the door to a full understanding of the technical procedures for stained-glass production.

Introduction
Despite its place as an object of varying interests and capability to provoke fascination for its handiwork, a systematic examination of the Ancient and Mediaeval technical literature relating to glass is still being awaited. New perspectives may be associated not only to the interpretation of literary sources, but also to the backdating of significant technical procedures, since those operations are documented in writing earlier than it is commonly believed.
Our starting point has been the observation of the whole spectrum of Mediaeval technical literature relating to stained-glass making. The texts have been addressed on the basis of their contents, identifying any distinction connected to their origins and use by the different specialists involved (glassmaker, glazier, and glass painter). The very frequent sharing of information and tasks between them requires therefore a thorough analysis not only of a restricted literature on stained glass, but also of a wider range of technical texts regarding glass and glassmaking.
Indeed, the processes of vitrification and glassmaking itself are at the base of numerous artistic techniques: similar processes govern the production of glass pastes as well as the creation of mosaics, glass (blown or in sheets), glass-covered ceramics, imitations of precious stones, and enamels. In order to fully understand, from a historical point of view, some of these technical procedures and their role and diffusion in the Mediaeval treatises, it is necessary to observe the literature on glass in its entirety. Only in this manner will it be possible to note those elements of continuity or novelty that are specifically evidenced by the treatises regarding the production of stained glass.

Methodology
This work is based on the belief that conservation should always have a confrontation with the history of materials, procedures, and artefacts, and that the historical knowledge was thereby strictly connected also to the technical literature. Our approach to the study of technical literature on glass, applicable even on other topics, hinges upon the observation of the original manuscripts, even when already published,

and upon the distinction between three phases:

1. Reading, i.e. textual analysis using every tool of philology (codicology, paleography, and linguistics);
2. Interpretation, i.e. textual comprehension by examining the contents from a technical point of view, inclusive of their practical feasibility;
3. Historic assessment, i.e. evaluation of the text, its reception and comparison with other coeval works.

Therefore, this work intends to address a continuing research by its authors. In addition to making a census of the literary sources, they endeavour to underline, on a phenomenological level, the principal arguments of interest within the ample Ancient and Mediaeval technical literature regarding the processes of vitrification.

In this first survey, it was possible to identify different characteristics of the literary sources, in particular, in those pertaining to the production of stained-glass windows. If one considers the entire line of production, it becomes evident that diverse categories of workers authored the various treatises, thus requiring the application of different interpretative principles. Obviously, it should be taken into account that these processes were likely not widely diffused, or at least not in written form.

State of the Art: Mediaeval Literary Sources on Stained-glass Windows

Currently there are five published Mediaeval texts, written between the 12th and 15th centuries, dedicated to stained-glass windows. Although this is not the appropriate circumstance in which to retrace the entire Mediaeval treatise and its ample bibliography (Boulanger and Hérold 2008; Boulanger 2008; Caen 2009), it seems that several references are necessary. First, it is obviously not possible to ascribe a single comparison among the various treatises, due to the geographic and chronological distance. As Karine Boulanger (2008) has rightly noted, none of these texts in and of themselves are exhaustive, but they should be read as a whole. Some texts bear resemblance to others, positioned in part on the wave of a similar tradition, but each brings its own original content as well.

The oldest and most complete Mediaeval treatise on stained glass is contained in the *De diversis artibus* (or *Schedula diversarum artium*), written at the beginning of the 12th century by a monk under the pseudonym Theophilus. The work has been the subject of numerous studies (Brepohl 1999); however, what is important to remark here is that the second book of the treatise, dedicated to the art of stained glass, contains an accurate description of the entire production process, uniting the expediency of each of the persons involved (glassmaker, glazier, and glass painter), although there are few references to pot-metal glass and to the substances that should be utilised for the painting of glass and the re-firing of painted glass. Further, the procedure of cold painting does not seem to be contemplated.

The second well-known text, also object of recent in-depth studies (Lautier and Sandron 2008), is the *Memoria del magisterio de fare fenestre de vetro*, dating back to the late 1300s and preserved in the ms. 692 of the Biblioteca del Sacro Convento in Assisi. The treatise, attributed to Antonio of Pisa, a master in the art of glass painting, is divided into forty-nine recipes, not always following a logical order. The work addresses the chromatic composition of the window, the colouration of glass (hot and cold processes), preparation of the kiln and the re-firing of painted glass, glass cutting, the production and soldering of came, the etching with acid, and the cleaning and polishing of stained glass. Contrary to Theophilus' text, this work does not address theory or the actual production of the glass, but focuses predominantly on the fabrication of artistic stained glass, presented as a purely practical text, even containing suggestions for the management of an *atelier*.

Another important work, untitled and anonymous, is preserved in the ms. L.XI.41 of the Biblioteca degli Intronati of Siena, and was written in the first half of the 1400s. The treatise demonstrates numerous affinities with the text of Antonio of Pisa, suggesting that one was derived from the other. The text addresses the production of *grisaille*, the arrangement of painted glass panels in the kiln and their re-firing, came soldering, engraving technique, and the cutting and cleaning of stained-glass windows. Compared to the previous texts, this treatise is certainly less complete and exhaustive. First, there is no mention regarding the production of glass and the processing of glass panels; second, there are no recipes for coloured glass (with the exception of a single recipe regarding *grisaille*), even if its use was evident, given the essay's particular concentration on the re-firing of painted glass. The incompleteness of the work and its lack of an incipit lead us to assume that only fragments of the original text were copied.

The last two known treatises remain anonymous as well and appear less complete than those written by Theophilus and Antonio of Pisa. The first was written by a monk in the Zagan Abbey, in Poland, during the second half of the

15th century and is preserved in the ms. rkps IV oct. 9 of the Biblioteka Uniwersytecka in Wrocław. The text, which paraphrases several chapters of the second and third books written by Theophilus, integrating original additions, describes the production of *grisaille* and silver stain, the preparation of the kiln and the firing of painted glass, the fabrication of came, and the decoration of glass using gem stones. The second work, also dating back to the mid 1400s, is found at the end of the so-called *Kunstbuch* in Nuremberg (Nuremberg, Stadtbibliothek, ms. Cent. VI, 89); it describes the production of *grisaille* and a table used to paint glass panels and compose stained-glass windows, the firing of painted glass, the production of a lozenge-shaped window, came soldering, the engraving technique, and the cleaning of old glass with lyes.

Another brief work has recently come to light, entitled *De fenestris* and conserved in the manuscript Canonici Misc. 128 of the Oxford Bodleian Library (Travaglio 2012). The treatise is part of a larger work entitled *Thesaurus pauperum*, drafted in the first half of the 15th century in northern Italy; it is composed of fifteen predominantly Latin texts regarding various artistic and artisan activities. It is credible to sustain that the treatise is not a true specialist text, but rather it is an easy-to-use practical manual, a 'treasure of the poor', in which simple and efficient procedures, deduced from various sources, can be found. The text, therefore, does not seem to be written for the author's private use, but instead represents a rich know-how to be shared. This expertise was intended to be dispersed among the artisan class or within the variety of orders composed of laymen and working class, such as those formed by Jesuati who, in fact, often defined themselves as pauperes, and who, especially in the 15th century, were specialised in artisan activities including the production of stained glass. Arranged in just over twenty recipes, *De fenestris* (ff. 108r–110v) describes the procedures of colouration in enamel and cold painting, the production of pot-metal glass, the firing of painted glass, the construction of windows utilising parchment or paper, glass cutting, and the production and soldering of metallic came used to connect glass sheets.

Who Writes What to Whom? An Analysis and Proposal

We can observe the disposition with which these treatises address the production processes involved in the construction of a stained-glass window, as exemplified in table 1.

What one notices on an initial analysis of this literature is the absence of references, with the exception of *De diversis artibus* and, in part, *De fenestris*, to the working of glass and colouring of glass sheets or to the coloured frits intended to colour the glass for subsequent enamelling. Evidently, these operations were delegated to a specialised master glassmaker, placing, therefore, the majority of these texts exclusively as manuals directed to the tasks of the glazier and glass painter, or rather those who handled the composition of the stained-glass window, the painting of individual pieces (hot and cold processes), and their assembly.

Upon observation of the actual activities of the glass painter in the literary sources, it becomes evident that the painting does not concern coloured glass-fusions on the sheet's surface, but rather exclusively the *grisaille* and silver stain. In reality, the glass painter *par excellence* seems only to arrange the design and cut the already coloured (or enamelled) glass, adding his pictorial contribution only in the drawing and shading. Everything regarding the glass and its colouring – pot metal, enamelled, or plated – seems to be outside of his realm.

An explanation seems to be found largely in the complex division and organisation of labour, characteristic of the artistic and artisan world of the most important European centres in the Late Middle Ages (Castelnuovo 1994). The role of the painter, via the supremacy of the drawing, simultaneously involves the design and finish of the work. Regarding the project, the painter handles, on one hand, the iconographical production of the image and, on the other, the arrangement and selection of glass and their cutting, obtaining supplies from specialised glass shops. In practice, he is responsible for the definition of outlines, lights, and shadows, conferring the image its finishing touches.

These considerations are confirmed in one of the most well known literary sources regarding artistic techniques. In Chapter CLXXI of his book *Libro dell'Arte,* Cennino Cennini writes: '*Tale arte* [that of stained glass] *pocho si praticha per l'arte nostra e pratichasi più per quelli che llavorano di ciò*' ('*It is true that this occupation is not much practiced by our profession, and is practiced more by those who make a business of it*'), further adding, in the description of the preparation of a stained-glass window, '*il tuo maestro de' vetri toglie questo disegno* […]. *Poi innanzi che leghi insieme l'un pezzo con l'altro secondo loro usanza, il chuocie temperatamente in chasse di ferro chon suo ciendere, che poi gli legha insieme*' (Frezzato 2003, pp. 191–192; '*your glass master takes this drawing* […]. *Then the master, before he fastens one piece to another, according to their practice, fires it moderately in iron cases with his ashes; and then he fastens them together*', Thompson [1933] 1960, p. 111).

At this point, it seems appropriate to consider that, already at the end of the 1300s, the activities of the painter, master glazier, and obviously the master glassmaker were considered different areas of expertise. Naturally, this does not exclude the possibility of persons able to assume multiple capabilities, as was likely the case of Antonio of Pisa. It is, however, plausible to believe that the literary sources have their origins in, or are generally directed to, each of these persons and that they should therefore also be interpreted from this point of view. Everything regarding colour and the composition of the single sheets of glass, including enamelling and plating, is the technological heritage of other workers. Treatises such as that of Theophilus, as part of an autonomous and isolated production context, confirm the necessity of a comprehensive discussion on the entire line of production for stained glass. Similarly, *De fenestris* presents the same problem, precisely because it belongs to the same 'isolated' context from a cultural and economic point of view. However, at the same time, this text shifts the attention to more diffused production techniques such as the *impannate,* windows made from parchment or paper, as well. The same discussion can be made, in reverse, for those that include cold painting: this can be utilised as a less expensive and relatively simple technique, as in the case of *De fenestris*, or to obtain particular effects by the painter, as in the treatise of Antonio of Pisa and the *Libro dell'arte* of Cennini, who writes, for example, '*tu puoi cholorire alchuni vestimenti e trattegiare di cholore ad olio*' (Frezzato 2003, p. 192; '*you may paint any costumes, and mark out with oil paint*', Thompson [1933] 1960, p. 112).

It does not seem to be a coincidence that, in these complex divisions of labour, precisely from the first half of the 1400s, a proliferation of increasingly more specialised texts is observed, at least in Italy. Thus, some texts have been dedicated exclusively to the painting on sheets of glass, apparently written by specialists of this technique, and others seem instead to be expressions of master glassmakers.

If in fact the series of aforementioned treatises can be qualified as literature pertaining to the technique of producing stained glass, certain distinctions must be made among these texts and other works. We can certainly define as 'literary sources on stained glass' all those works addressing the joining of different variously coloured sheets of glass in order to compose one single window with lead came or other metallic elements. These works, however, do not represent the whole of the literature that contributes, on various levels, to the transmission of the technical know-how of this art form: treatises exclusively addressing the painting on sheets of glass do indeed exist, but they do not mention their assembly in any way.

An example can be found in the *Tractato de modo de conponer li colori fini che si metano sopra li vetri et in che modo se ricosano* (*Treatise on making colours for glass painting and their re-firing*), preserved in the unpublished manuscript 2265 of the Biblioteca Casanatense in Rome (ff. 95r–98r; 16th century); this can be found within a collection of treatises, which, as in the case of *Thesaurus pauperum*, address various artistic and artisanal techniques (Precoma 2000). Within this text, only the methodologies used to paint glass panels using enamel or *grisaille* and the techniques of re-firing are described. Of all of these practices, particularly relevant is the description of the process of engraving an enamelled or plated glass panel using acid. The process consists of covering the panel with an acid-resistant wax, drawing on this wax with a sharp, pointed tool, and immersing the panel in an acid so that the area exposed by the engraving corrodes: '*Se tu poni l'aqua da partire sopra lo vitro rosso da quella parte del colore, lo rode ma in uno giorno et una nocte, et così coperdo lo vitro di cera et in quella designando ciò che voi con uno stilo et levando quella parte che sia per esser cavata, poi li meti de la dicta aqua forte et li cavara il colore che era scoperto; et per questo modo poi fare fiori e ogni designo*' ('*If you put the "aqua da partire" onto a red glass on the coloured side, it corrodes the glass in one day and one night; and hence cover the glass with wax and draw whatever you wish using a stylus, and remove that part to be carved out. Then put the "aqua forte" and it will corrode the colour that was uncovered. In this way you can make flowers and any drawing*').

The process described here is very similar to the modern technique using hydrofluoric acid and potassium bifluoride, although these acids capable of etching glass were not known in that period. We can suppose that the *aqua da partire* indicated in the text was essentially nitric acid, principally acting on the colouring agents of the most superficial layer. In fact, the text adds '*Nota che la soprascripta aqua messa in lo vitro azuro lo fa verde et lo verde fa azuro*' ('*Note that the water mentioned above when put on a blue glass turns that green, and makes the green one blue*'). Probably the text set forth how to make drawings on flashed glass, namely a double-layered glass. The first example refers to a clear glass with a red layer applied. By etching this first coloured layer with acid, drawings in transparency on a red background are obtained. This engraving using acid for a red glass is already mentioned by Antonio of Pisa. However, the second part of the recipe seems to allude to a blue–green glass, a compound of two layers of glass, one green and the other blue. Using a similar procedure, one could obtain a green or a blue drawing on a blue–green background, depending on the side exposed to the acid.

Similar recipes have recently been published as part of recipe books that gather a series of procedures based on other literary sources. Within these collections, one can discover actual texts dedicated to the painting on glass, often not easily identifiable within the erratic surrounding literary materials. Such is the case of *Colori diversi per colorire vetri da finestre et altri lavori* (*Different colours for colouring glass windows and other works*) preserved in the well-known manuscript It.III.10 of the Biblioteca Marciana of Venice (16th century; ff. 154r–155v) (Frezzato and Seccaroni 2010). This text explains the method of painting with *grisaille,* using iron or iron and lead–tin calcined, and the technique using silver stain; every other colour is applied using oil as a binder.

A similar case can be found in a brief, untitled text contained in the manuscript 99 of the Biblioteca Comunale in Fermo (15th century; ff. 47v–48r) (Laskaris 2008), where one can find *A far colore da pengere finestre de vitro* (*Making colours to paint glass windows)* and *A far vitro dipento* (*Making painted glass*). Here, the *grisaille* is used with ground copper, recalling the practice of painting with (coloured?) glass; the subsequent procedure of re-firing is then described, as well as the execution of the stained glass, combining the various panes, painting them, and then setting up with lead cames. After that, a recipe to make enamels in any colour and another regarding a 'glue' for glass is given.

Once again, in the noted manuscript 2861 of the Biblioteca Universitaria in Bologna (15th century, f. 168) (Muzio 2012), we find *A dipengiare li vetri cum li smalti de omne collore che tu voli* (*To paint glass with enamels in every colour you desire*), discussing the grinding of enamels and, although concisely, the re-firing of glass.

Several of these examples appear to indicate clearly how the overall responsibility of the colouration of glass was attributed to the master glassmakers, who produced coloured glass (glass lumps or panes) or frits and also beads and *paternostri* that were able to be pulverised and ground by the painters.

Therefore, in order to understand and compare the treatises to the current works, they must be distinguished among themselves, as they address different techniques and procedures. They are, in fact, a very 'dispersed' body of literary sources that, on the one hand, reveal unexpected details and, on the other hand, provoke us to observe categories of literary sources for which relatively little research has been done: those related to the colouring of glass.

A Backwards Overview: From Antiquity to the Middle Ages

Regarding the subject of glass and vitrification, it is not yet clear what, and through which texts, actually arrived in the Latin Middle Ages from Antiquity. It has been revealed (Tolaini 2004) that fragments of Hellenistic alchemistic texts and technical collections regarding glass had indeed been variously translated in Latin, between the 4th and 5th centuries.

From the translations of the first historic alchemic writings, and in particular from an epitome of works tied to the intellectual circles of the alchemist Zosimos of Panopolis, translated from Greek into Latin probably in the 4th–5th centuries and known today as *Mappae clavicula*, we can observe procedures regarding glassmaking and the production of artificial gems, indicated in the index of the work, but today not preserved in its entirety. The titles themselves of *Mappae clavicula* indicate the practice of tracing designs and painting on glass surfaces, which had already been thoroughly explained in the writings of the first historical alchemistic texts (Halleux and Meyvaert 1987; Baroni, Pizzigoni, and Travaglio 2013).

Within this literary genre lies an ample, although not yet sufficiently deepened, text, an incredibly important piece for the history of glass and its colouration, which is now the subject of a study. The work is made up of three books, two of which address the preparation and the use of glass-colouring substances and the other composed of a *tabula* summarising the effect of the single substances in the colouration of glass (*De corporum efficacia quae igne convalescente, vitro habent commisceri*). The text, which we can refer to as *De vitri coloribus*, could also be entitled with the name of the translator and with the title with which it was known in the southern part of Italy, in a version adapted to the glazing of ceramic bowls: *Flos de coloribus istius libri quos Rusticus transtulit*. The text is displayed in two versions, leading us to assume that at least two distinct traditions and translations did indeed exist: one, adapted to ceramic vases, is tied to the name of the translator, Rusticus, and held in the Biblioteca Nazionale in Turin (ms. 1195) and in the Biblioteca Nazionale Centrale in Florence (ms. Pal. 951); the other, regarding glass, is in Paris, in the Bibliothèque Nationale (ms. Lat. 6714), already published by Marcelin Berthelot (1893, I). Other codices can be identified via the catalogue of incipits by Thorndike and Kibre (1963): *Aurum itaque aureum generat colorem* (167), *Ex antiquorum scientia philosophorum percipitur quod omne genus colorum* (530), *Ut antiquorum*

scientia philosophorum percipitur (1613), *Ut ex antiquorum* […] (1618), and via the *Database of Alchemical Manuscripts*, nn. 1445, 2525, 3713 (DAM). In the various manuscripts, the text is attributed to different authors including Alcuin, Alquindus, Alkindi, Arnaldus de Villa Nova, Morienus, Johannes, and others, with different titles among which *Liber sacerdotum, Liber coniunctionum–Liber de naturis colorum–Liber administrationum, Flos de coloribus*, and others.

This text brings to light the monumental principle of the ancient technical knowledge regarding glass and the importance of this treatise at the base of the re-workings of mediaeval glazed ceramic and glass itself (pot-metal glass or sheets) painted using *grisaille* or lustre: in fact, this same text is over time adapted to both processes. At this point in the research on this work, its origins are still not entirely clear; *De vitri coloribus* was, however, widely circulated in the Latin world between the 12th and 13th centuries.

What is of most interest, however, is that, after a table explaining the efficacy of roughly thirty substances utilisable in the colouring of glass, single methods for the preparation of the materials are described. In the various accounts, numerous erratic fragments of hermetic or alchemic literature follow, recipes that will be equally important in the history of glass painting and the colouring of stained glass, as well as in the decoration of ceramic vases: '[Paris, BNF, Lat. 6714, f. 46vb] […] *vitrum cuislibet coloris subtiliter pulverizantur distempera cum aqua nitri/vitri et recoque in fornace. Item si in vitreo vase vel scutello Ispanie operari volueris, argentum runcinum, vel cuius sit dimidia pars argenti vel plus, accipies et fundes ipsum in vase aliquo cum sulphure, donec redigatur in pulverem, et adiunge fecis vini pars quinnariam et distempera cum aceto et pinge, et coque; et si diu coxeris, diversos colores videbis*' ('*Pulverise finely glass of any colour, distemper it with "aqua nitri/vitri" and re-fire in the kiln. If you wish to work on a glass vase or Spanish bowl, take plane silver or made at least largely by silver, and melt it with sulphur in a vase, until it is powdered. Add a fifth part of wine dregs, distemper it with vinegar, paint it, and fire. Firing it little by little, you will see different colours*').

Here we observe the technique of glass enamelling, obtained by fusing the glass of another coloured paste: the flux utilised is *nitrum*, the antique *natron*, essentially sodium carbonate. Instructions for a yellow–brown silver-based painting follow. Consecutive recipes address *grisaille* and different processes for obtaining iridescent glass painting (*rubinizzazione*), which is none other than lustre painting in ceramics.

We can therefore affirm that *De vitri coloribus* contains all the strategic techniques utilised to colour, paint, and draw on glass; these are procedures that we find once again in the most sophisticated material accounts pertaining to vitrification and, in part, in the literature and treatises specifically dedicated to stained glass.

The wealth of knowledge obtained from the late Latin world, both through diffusions within the Latin world and following translations from Middle Eastern or Greek languages, profoundly and ceaselessly influenced the mediaeval techniques of producing and working with glass. White pot-metal glass and many glazes were well known in the Middle Ages from time immemorial, at least throughout literary transmission. The manuscript 490 of the Biblioteca Capitolare in Lucca (8th century) (Baroni 2013) offers, therefore, a proper example, since it contains a recipe for a white glass made with tin (*De alia tinctione lactis coloris*, f. 217r); it can be found within a more extensive collection of works called, in recent studies, *Corpus artium*, which has its first attestation right in the *Compositiones ad tingenda musiva* of Lucca's manuscript (Brun 2011). These texts, originating from Antiquity, although with a disorderly tradition, were present and handed down in the Western world through several manuscripts, which carry the understanding of these procedures uninterruptedly down through the late Middle Ages (Baroni, Caprotti, and Pizzigoni 2007).

Conclusion

A systematic analysis of the technical literature on stained glass and more generally on glassmaking should be connected to several aspects that have not yet been largely considered. This work allows some fallacies to be rectified in the light of a critical and comparative review of literary sources. For instance, although the studies report the use of silver stain only from the 14th century, it is now clear that this technique is already described, gathered from the Hellenistic treatises, in *De vitri coloribus*, in manuscripts dated to the 12th–13th century.

Again, *grisaille* and enamelled glass, iridescent glass, and aventurine glass were already well known in the Hellenistic literature of the Middle Ages (*Mappae clavicula* and *De vitri coloribus*). Regarding stained-glass windows, it seems limiting, therefore, at least in relation to the techniques of glass colouration (enamelling, plating, and painting), to rely wholly on the texts that also mention the joining of the panels. There are texts regarding the painting on glass, addressed specifically to the glass painters. These same painters could utilise materials and glass sheets produced by specialists, who in turn consulted

❖ one recipe	Theophilus	Antonio of Pisa	Ms. L.XI.41 Siena	De fenestris	Ms. rkps IV oct. 9 Zagan Abbey	Kunstbuch
Glass production	❖❖					
Glass-blowing (panes)	❖					
Construction of the kiln	❖❖❖					
Glass colouring (pot-metal glass)	❖❖	❖		❖❖❖❖❖❖❖❖		
Enamel paintings	❖	❖❖❖❖❖❖		❖❖❖		
Stained-glass design	❖	❖❖❖❖❖❖❖❖				❖
Glass cutting	❖	❖❖❖❖❖❖❖❖❖❖	❖❖❖	❖		
Glass finishing	❖			❖		
Grisaille	❖❖	❖❖❖	❖	❖	❖	❖
Silver stain		❖			❖❖	
Painted glass re-firing	❖❖	❖❖❖❖❖❖	❖❖❖❖❖❖❖❖ ❖❖❖❖❖❖❖❖	❖	❖❖	❖
Cold painting		❖❖❖		❖❖		
Came	❖❖❖	❖❖❖❖❖❖❖❖	❖❖	❖	❖	❖
Etching with acid		❖				
Engraving technique			❖			❖
Decoration with gems	❖				❖	
Stained-glass washing or polishing		❖❖❖❖❖❖❖❖❖ ❖❖❖❖❖❖❖❖	❖❖			❖
Parchment/paper made glass				❖		

Table 1. Contents of mediaeval treatises on stained glass.

other specific literature aimed at master glassmakers. Furthermore, there are other sources that mention the use of different types of metals, in addition to lead, such as brass, copper, and iron for the production of came, as well as particular instruments for cutting, finishing, and etching glass panes (*De fenestris*).

Looking forward to new more in-depth studies, we must therefore be satisfied with a varied, dispersed, and uneven literature, still largely unpublished, but full of surprises and able to question each of our certainties regarding glass and stained glass.

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‘Luce Floreo’, an Historic Technique for Creating Glass Windows

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Keywords
Luce Floreo; compensation; glass etching

Abstract
‘Luce Floreo’, is the term for an unusual technique for creating glass windows that was invented by the Munich painter Otto Dillmann in 1890. This special form of glass painting creates pictures using different thick overlays of etched coloured glass, through which light passes and causes the colours to blend. The re-creation of missing parts during the restoration of such works presents unique challenges.
Many techniques have been used to compensate for losses due to the fact that suitable flashed-glass panes are no longer available and the complex etching technique used has been forgotten.
This article presents selected case studies to show the different approaches that have been tried to restore and reconstruct these extraordinary windows.

The History of ‘Luce Floreo’
‘Luce Floreo’, or in English ‘Blossom through Light’, is the term for the unusual technique for creating glass windows invented by the Munich painter Otto Dillmann (Korn 2007, p. 416). He patented his ‘procedure for the manufacture of multicoloured stained glass pictures’ on May 28,1890 (Kaiserliches Patentamt 1891, p. 1). Only a few companies opted to use the method, most prominent among them being the ‘Gesellschaft Luce Floreo’ (‘Luce Floreo Society’) located in the town of Barmen in Germany’s Ruhr district. However, the technique failed to catch on and was forgotten after a few decades.

The ‘Luce Floreo’ Technique
The technique of Luce Floreo is quite distinct from stained glass in the conventional sense. Luce Floreo windows create pictures using different thick overlays of etched coloured glass, through which light passes and causes the colours to blend (Kleine 2007, p. 151). The Luce Floreo picture is composed using three panes of flashed glass with overlays in red, yellow, and blue, which are placed one behind the other (figure 1). By means of a complex etching technique, it is possible to remove the overlay completely or partially on each single pane of glass. Depending on the thickness of the remaining overlay, different shades of colour appear when light is transmitted through the combined panes. In this sense, the technique is similar to multicolour printing (Korn 2007, pp. 416–417). Indeed, by combining etched overlays of subtly different thicknesses, it was possible to achieve as many as 4,000 distinct shades of colour.
To create Luce Floreo windows, particularly large and evenly coloured panes of flashed glass were used. At the turn of the twentieth century, it was possible to manufacture panes measuring from 1 to 1.5 m² in size (Geiger 1901, p. 179). The window panels were not separated by lead cames, as is the case for stained-glass windows (Korn 2007, p. 416). An example of Luce Floreo is shown in figure 2.
The etching of the glass panes is accomplished using hydrofluoric acid (Randau 1905, pp. 249–250). All parts of the surface of the panes that are not to be etched must be

carefully protected against the effect of the acid (Jaennicke 1890, p. 242). For this, a protective varnish is used that is resistant to the acid (Randau 1905, p. 263). One method is to apply the protective varnish with a brush (Stahl 1912, p. 200) and to scratch the varnish off the parts that are to be etched (Jaennicke 1890, p. 242). Filigree ornamentation can also be drawn with a fine brush or a pen.

In order to achieve different shades of colour through the etching process, it is necessary to begin with the lightest shade, i.e. with the parts of the glass from which the overlay has to be removed completely. After this stage is complete, the next lightest shades are etched, until every desired nuance is achieved.

The book '*Glaserkunst, Glasmalerei und moderne Kunstverglasung*', by C. J. Stahl (Stahl 1912), describes in detail the technique of manufacturing this type of glass windows. The designs used for Luce Floreo are usually based on an original image such as a painting.

The original picture is photographed three times using different colour filters; the use of a halftone screen results in different shades of colour. Reprints from the negative images are then made using the technique of lithography and are transferred onto the corresponding pane of coloured glass. Treatment with colophony and asphalt makes the print resistant to the acid. In the next step, the panes are etched (Stahl 1912, pp. 201–210).

This description of the procedure accounts only for the overall reference image in each of the three colour categories; however, multilevel etching requires separate, individual prints that display each required shade. Exactly how late-nineteenth century manufacturers separated the overall reference image into these individual prints remains unclear. The difficulty of the method lies in the generation of the individual prints that complement each other to create the complete picture, and must be transferred with a high degree of accuracy (Randau 1905, p. 283).

The difficulty and complexity of the technique makes it doubtful that it was used in all Luce Floreo windows. The manufacture of as many as three lithographs for just one glass picture was also very expensive. Only in the case of frequently recurring ornaments would a method like this have been worth the effort.

In the case of complex works with figurative motifs, a printing technique would not be used. Such windows were normally unique, one-off products that were customised for the client, and the use of lithographs in their production would not have been profitable. It seems more likely that a colour-separated reference image was created on paper or a similar medium, and then placed behind the pane of flashed glass so that it showed through, as through a piece of tracing paper. The protective varnish was then applied by hand to the appropriate areas of the glass surface. The analysis of surviving fragments of the Luce Floreo windows created for Berlin Cathedral between 1904 and 1906 supports this hypothesis. When viewed under an optical microscope, traces of fine structures appear that are consistent with the application of a protective varnish using a brush (figure 3) (Siebe 2012, pp. 96–97).

Once the etching process is complete, the finished panes of a Luce Floreo window are arranged one behind the other and are sealed with a bitumen-like substance; the edges are then covered with a thin metal foil (Keller 2000, p. 1).

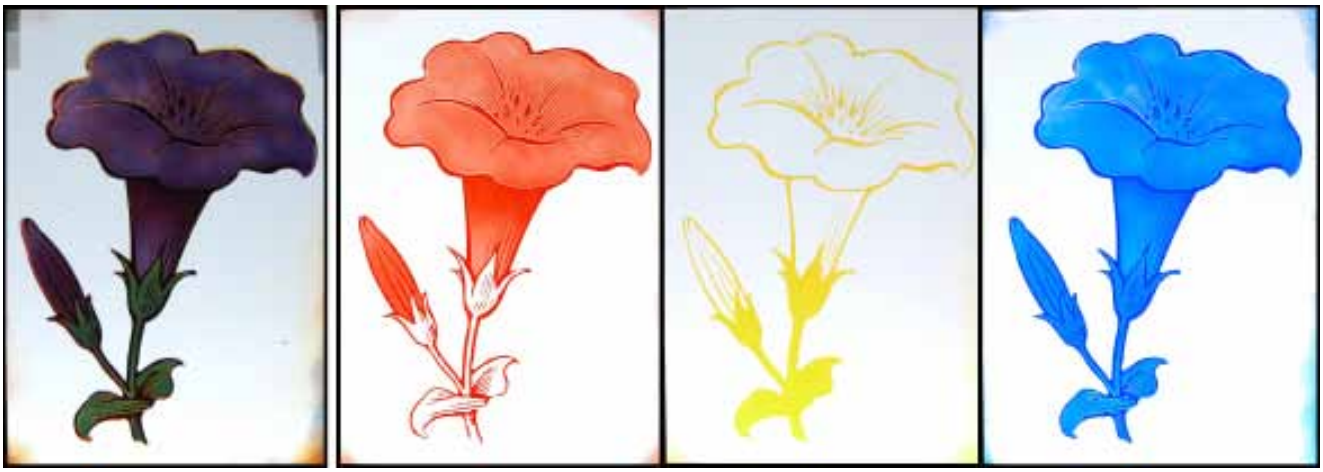

Fig. 1. Concept of a Luce Floreo window. Left: complete window; right: single panes (Photo: Glasmalerei Peters 2012).

As the result of the stacking of three panes, a Luce Floreo window takes on a certain three-dimensionality. This effect is reinforced by the barely-noticeable edges and recesses that result from the etching of the glass surfaces. These produce additional light refractions and further minute gradations in the shades of the colours (Kleine 2007, p. 151).

Difficulties Involved in Restoration and Reconstruction

The compensation of losses during the restoration of Luce Floreo windows presents two specific difficulties. The first is that the technique used to etch the panes has largely been forgotten. It is still not quite clear how the original reference picture was separated into the three primary colours, or how the individual images corresponding to the different shades were created. The answer to these questions must be sought in the realm of photography and printing, which were enjoying a boom at the time when Dillmann patented his method. Today, we can use computer technology to divide the reference image into the primary colours and easily create the different shades. Self-adhesive foils, which can be cut exactly to a single pattern by a plotter, can be used to replace the protective varnish. In this way, the major difficulties in producing Luce Floreo can be readily overcome using modern technology.

A second, more intractable problem when restoring Luce Floreo windows is the difficulty of getting suitable panes of flashed glass. Even though subsequent processes are easier to carry out, the base material is difficult to obtain.

Flashed-glass Panes

The panes of flashed glass used around the turn of the twentieth century were larger (up to 1.5 m²) and had a more homogeneous overlay than the ones that are produced today. The mouth-blown panes available today do not display the same quality and, as a result, loss compensation during restoration or reconstruction is difficult. Not only the technical equipment but also the knowledge and experience necessary for manufacturing such large panes have been lost. Any attempt to do so would require a great deal of costly experimentation (Hartl 2012).

In addition, a comparison between fragments of the historical windows of Berlin Cathedral and modern flashed glass reveals some important differences, especially concerning the relative thickness of the glass and its overlay. At its thickest part, the blue flashed glass from Berlin Cathedral is approximately 1.61 mm thick and has an overlay of 0.22 mm, while the yellow is 1.47 mm thick with an overlay of 0.08 mm and the red is 2.15 mm thick with an overlay of 0.08 mm.[1] In contrast, a sample of modern flashed glass shows thicknesses of 3.44 mm / 0.44 mm (blue), 3.20 mm / 0.15 mm (yellow), and 3.87 mm / 0.11 mm (red). This analysis shows that flashed-glass panes, as well as their overlays, were far thinner a century ago than their modern counterparts are today. This would have made them easier to etch. Moreover, the historical overlays tended to be more consistent than the modern ones, which are uneven and have many small cracks.

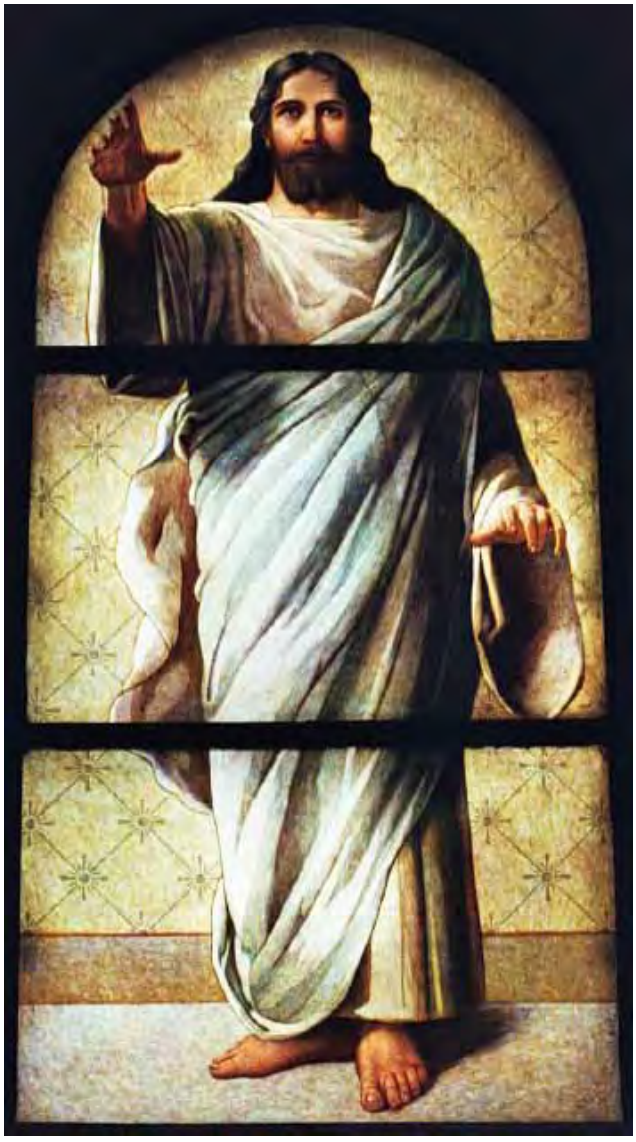

Fig. 2. Luce Floreo window of a church in Döbern (Photo: Siebe 2012).

Together, these two factors suggest that producing Luce Floreo using modern flashed glass could prove to be difficult and result in a product of inferior quality.

Restoring and Reconstructing 'Luce Floreo' Windows

Because the technique of Luce Floreo as practised around 1900 is no longer known, some difficulties inevitably arise when it comes to restoring and/or reconstructing these windows. As mentioned above, the acquisition of suitable flashed-glass panes presents a problem. To resolve it, different basic approaches have been chosen in the past.

The first priority in the conservation of historic stained-glass windows is the protection of authentic material, not restoration to a mint or 'original' condition. It is not the purpose of heritage conservation to 'make the old new again' or to replace original components and, by doing so, 'falsify' the historic work. That said, the reconstruction of missing parts can be necessary, especially in the case of pictorial stained glass. Such interventions can be limited to reconstructing small, individual gaps or blemishes or can encompass larger parts of an ensemble. The restorer must consider the overall effect as the decisive factor. If the reconstruction of lost elements is genuinely necessary, they should not follow a pseudo-historical design or be the product of individual taste. Completely different approaches may be acceptable in special cases, such as loss compensation with freely-invented ornaments (Van Treeck 1993, pp. 43–44).

The following case studies were chosen to illustrate the implementation of the approaches described above.

Windows of a Mansion in Witten-Bommern

The addition of a layer of protective glazing, as was done during the restoration of the Luce Floreo windows of a villa at Witten-Bommern in Germany's Ruhr region (1913; restored in the late 1990s), is one of the simplest but most effective methods of saving and protecting these unusual works of art. However, it should be noted that this method involves extensive modifications to the window frame, which is itself an essential part of the historical window and should be preserved as a document of the manufacturing technology.

In Witten-Bommern, an effort was made to save the maximum amount of original glass during the restoration. It was possible to limit the interventions to gluing a few breaks and cracks. This presented some difficulties, because the individual panes had been fused tightly on top of one another and the areas of relief on some of the etched panes had resulted in a build-up of tensions within the fused block (Pohl 2012).

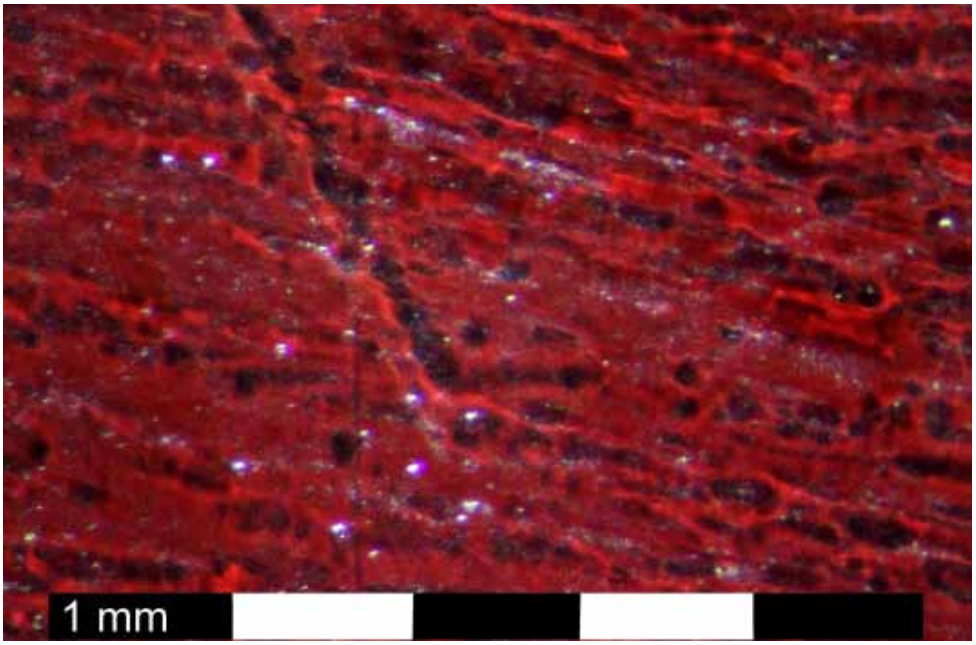

Fig. 3. Traces of fine structures on glass due to the application of a protective varnish using a brush (Photo: Siebe 2012).

Windows of a Church in Kopitzsch

Conserving authenticity becomes particularly difficult when parts of a glass window have been lost entirely. At the church in Kopitzsch (State of Thuringia, Germany), for example, the lower area of the southern window (dating from 1897) was lost and reconstructed. As no documentation concerning the original window was available, a new design was made, based on another window in the same church that had a similar theme. The reconstruction was supposed to be executed as far as possible with gradually-etched flashed glass, which would come closest to the historical model. Because it was impossible to obtain a single pane of blue flashed glass of the required size and quality, the decision was made to use several panes attached together by means of lead cames. However, these lead cames increased the space between the layered panes. As a result of this experience, it was decided not to make the red and yellow panes in the same way. Instead, the red and yellow elements were applied to a thin pane of float glass using an airbrush technique (Besser 2008, p. 64).

The use of this method unquestionably compromised the authenticity of the window. However, the fact that an etched flashed-glass pane was used for at least part of the addition can be seen as extremely positive. It represents the only attempt to date to perform a reconstruction using the historical technique. That only one of the three panes could be made in this way is again because no suitable panes were available. Nevertheless, it was possible to come quite close to the original technique by retaining the structure of the three panes layered on top of one another. The result is a glass window that can be experienced in its full complexity, without straying too far from the original.

Windows of a Church in Hornow

Unfortunately, there exist other examples that are not as successful. From 1992 to 1996, for example, the windows of the church in Hornow (dated to 1902) in the German State of Brandenburg were restored after having been heavily damaged by vandals. Many cracks were glued, but attempts to fill in missing parts of the windows using etched flashed glass failed (Flügge 1998, p. 144); for this reason, these areas were repaired using the conventional technique of painting on clear glass (Konrad 1999, p. 88). These repairs are immediately noticeable due to the fact that the enamel colour used does not have the same transparency as the partially-etched panes of flashed glass.

As in Kopitzsch, the originality of the window in Hornow was compromised because the technique chosen to compensate the lost areas was completely different to that used in the original window. The lack of transparency in the additions profoundly affects the real impression of the glass picture, appearing as it does like a foreign material.
Furthermore, the painted additions carry something of the personal signature of the artist who performed them, thus transforming the window from an historical into a contemporary work of art.

Winter Garden Windows of a Mansion in Wuppertal-Unterbahmen

A very similar treatment was given to a skylight window in a villa in the Ruhr town of Wuppertal-Unterbarmen. It is composed of 24 small rectangular Luce Floreo panes.
Only one of these panes had been broken in the past and replaced by a copy, created using traditional glass painting (figure 4). As in Hornow, the appearance of this pane differs from that of the others. Because the paint used was opaque, the copy appears pale and dull and has none of the colour intensity of the other panes. Direct comparison of the documented original and the copy reinforces this contrast.

Winter Garden Windows of a Mansion in Lüdenscheid

A slightly more restrained approach was chosen for the restoration of the glazing in the winter garden of a villa at Lüdenscheid, in North Rhine-Westfalia. The option of producing a correct reconstruction of the original was eliminated from the start, as there was no documentation showing the complete original design. Instead, the missing parts were

Fig. 4. Skylight window in a villa in Wuppertal-Unterbarmen, reconstruction with traditional glass painting (Photo: Siebe 2012).

filled-in with float glass, and fixed in place with silicone. Filling the gaps using clear material has the disadvantage of being immediately visible, although in this way the complex structure of such a window can still be understood. Cracks in the original glass were glued using colourless epoxy resin[2] (Korn 2007, pp. 419–420). Careful attention was paid to ensuring the reversibility of the adhesive. By using this method, as much as possible of the original glazing at Lüdenscheid was retained. A falsification, as would have resulted from the use of painted glass, was avoided.

Windows of a Funerary Chapel in Osnabrück

A much more radical approach is the complete replacement of damaged windows. The windows of a funerary chapel (1900) in Osnabrück, for example, were replaced with copies in 1987 and 1992, for conservational reasons, and the originals were removed to the protected environment of a museum. The replicas are made of clear glass coated with imprinted film. In such a case, the question of authenticity becomes more ambiguous: the originals are not lost, but they are no longer in their original context. Moreover, the copies do not display the same intense brightness and colour of the originals, as they have been bleached over the years.

Windows of the Cathedral in Berlin

A different approach was taken in the re-creation of the windows of Berlin Cathedral, which were completely destroyed in World War II. The basis for the reconstruction of the windows was the original designs that survived, as well as a wide range of photographs (Kleine 2007, p. 153). Because knowledge of the technique had been lost and flashed-glass panes were unavailable, it was decided to carry out the reconstruction using tricoloured halftone printing on three different clear-glass panes. The original draft images were separated into the three basic colours, as is traditional with Luce Floreo. What was different in this case was that no overlay was removed from the panes by etching; rather, the colours were imprinted onto the glass panes using a serigraph technique. The raster chosen was not too fine in order to avoid the impression that these are the original Luce Floreo windows. Likewise, the raster was not made too coarse to avoid a result that could disturb the overall effect. Viewed as a whole, the windows now appear intact, while on closer inspection they are easily recognisable as reconstructions (Kleine 2007, pp. 153–154).

In this case, the question of the extent to which a recreation of the windows is justified must be addressed. An attempt was made to keep as close as possible to the historical technique; however, because it was impossible to acquire suitable flashed-glass panes, the decision was made to use printed glass instead of etched glass. Since the original design and good documentation was available, the new windows are very similar in appearance to the originals. At the same time, the active choice of using the raw serigraph shows a commitment to the principle of avoiding falsification by pretending that these are the original windows.

Evaluation of Approaches to Restoration and Reconstruction

To date, a variety of techniques have been used for the restoration and reconstruction of Luce Floreo windows. However, completing missing parts by using etched glass, the original material of which these windows were made, has rarely been used. The reasons for this are twofold: on the one hand, panes of flashed glass of a size suitable for repairing large gaps are unavailable. On the other hand, reproducing the complex etching technique with its multiple shades requires a great deal of experience, which is no longer found today.

As shown in this publication, a variety of approaches can be applied, with varying degrees of success. Gluing of breaks and cracks is perhaps the simplest and most straightforward method of repair. Saving the window by using the original material is of course preferable, as this respects current conservation guidelines.

However, if parts of the original glass have been lost, they should be replaced. Two possible approaches have been developed: the first is to fill the gaps with clear glass, which leaves the replacements visible but also has the didactic advantage of revealing the complex structure of these windows.

Furthermore, this method preserves the original to the greatest extent possible while also retaining traces of the passage of time. The second approach involves the compensation of lost parts by using painted glass. This method can also be useful, so long as it is applied with caution. Smaller additions in less prominent areas can be retouched so that they no longer catch the eye. Larger additions, however, must be approached more carefully. Because the paint used is often opaque, it can attract attention to the repairs. The painted areas do not display the brightness and colourfulness that is characteristic of Luce Floreo. It should be noted that such additions always distort

the original to a certain extent. Newly created loss compensation will always bear the hallmark of the restorer, which inevitably deviates from the original.
The use of protective glazing has the advantage of shielding these rare windows, but is often accompanied by extensive changes to the original window frame.
The complete reconstruction of a window, as was done at Berlin Cathedral, is quite another matter. On the one hand, the question arises regarding the extent to which such a radical intervention makes sense and is acceptable from the viewpoint of heritage conservation. In this case, the reconstruction was undertaken because the original designs provided a solid foundation for the work. At the same time, it was decided not to use the historical technique but to employ an innovative serigraph technique instead. This had the advantage of approximating the effect of the three coloured panes produced by the original Luce Floreo windows. Furthermore, this technique made it possible to show, by means of the raster used, that these were not the historic windows, but new creations. At the same time, this approach implies that the original windows are preserved in safe storage or will be placed on prominent display in a museum.

Summary

One of the most impressive techniques for creating stained glass around 1900 was the Luce Floreo process. This technique made use of the contemporary development of printing technology and connected it with the special characteristics of coloured glass. The result was glass paintings that outshone conventional windows in terms of their brightness and range of colour.
Luce Floreo was manufactured for only a few decades, however, and today very few of these windows survive. The historic literature gives some indication of the technology, but the exact method of production is still unclear. In any case, it is certain that the printing technology of the time played a determining role in the invention of the method by Otto Dillmann. It provided the conceptual basis for the Luce Floreo technique, which involves separating a reference image into its component 'primary' colours and using these to generate further nuances in shade.
The major difficulty in compensating lost parts during restoration campaigns of such windows is the unavailability of flashed-glass panes of the required size and quality.
The panes that were made around 1900 were considerably larger than those produced today. Due to a lack of demand, such large panes went out of production and the technique of Luce Floreo stopped being used. Today only very few of these windows remain; for this reason alone, they demand our special attention.

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Notes

1. Because the historical fragments represent the final product of the Luceo Floreo process, it is possible that the overlay on the unprocessed glass was somewhat thicker. Because the shade on the fragments is very intense, it can be assumed that the overlay was removed only minimally, or not at all. Nevertheless, some reduction in the thickness of the overlay cannot be ruled out entirely. See Siebe 2012, pp. 98–102.
2. Araldite 2020.

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On the Production and Firing of 7th Century Chinese Reinforced Ceramic Horses and Camels

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Keywords
tomb figures; China; terracotta; metal core; firing technology

Abstract
In 2010, the Rijksmuseum began research on a group of tomb figures presumably made in central China between A.D. 7th and 9th century. During a previous treatment, an iron armature had been discovered inside one of the horses. The other figures were examined to find out if they also have a metal armature and to confirm the date of production. The main goal of this study was to investigate how the figures were produced. Based on research and observations on the objects, a hypothesis for the production process was formulated, and replica figures were modelled with an iron armature and fired. The combination of technical research with practical experimentation has resulted in a better understanding of how and when the figures were produced.

Introduction
An important place has been given to a group of six terracotta horses and camels made in central China between A.D. 7th and 9th century in the renewed exhibition of the Asian Pavilion in the Rijksmuseum (see figure 1).
During treatment of one of the horses in 1993, some intriguing technical questions were raised. It was discovered that missing parts of the animal had been re-made of fired clay; however, even more remarkable was the discovery of a metal armature in the original part of the horse that had been fired together with the clay. The firing of earthenware with a core of metal is considered to be technically impossible: because the expansion of both materials at high temperatures is different, this causes the ceramic to break apart. Some of the figures show cracks possibly caused by internal tension. The belief that these cracks could have been caused by the degradation of an internal iron armature needed to be investigated. The renovation of the Rijksmuseum provided the perfect opportunity for extensive research prior to conservation and the preparation of this exceptional group of burial objects for exhibition.

From Tomb Figure to Museum Object
The group consists of two camels with riders, two horses with riders, and two horses with saddles. The riders and saddles are made of separate parts (see figure 1). All the figures are made of fired earthenware and are about 50 cm high. The remains of cold painting are visible.
Burial figures from China were originally placed in a tomb to accompany the highborn deceased in their journey to the hereafter. During the Tang dynasty (A.D. 618–907), the use of tomb figures was at a high point. Although some tombs were robbed during the following centuries, others remained undisturbed until the construction of the railways in China in the early 20th century. From that time onwards, the interest of western collectors developed. In the 20th century, the trade in tomb figures and other archaeological objects resulted in the large-scale production of fake objects that flooded the market.
The 'Society of Friends of Asian Art'[1] bought the group of tomb figures in 1966 from the Dutch diplomat Reijnier Flaes (1902–1981), better known as the writer F.C. Terborgh.

Fig. 1. The group of six tomb figures: AK-MAK-68-A and B, AK-MAK-65 A and B, AK-MAK-69 A and B, AK-MAK-67 A and B, AK-MAK-66 A and B, AK-MAK-70 A and B. The riders and saddles have suffix –B, while the six animals have suffix –A. Height of the figures: around 50 cm (Photo: Rijksmuseum, Amsterdam).

Flaes collected and wrote about art, and he purchased these figures while posted in Beijing between 1939 and 1942 (Fontein 1966; Ruitenbeek 1989). In a register of his purchases, Flaes recorded that the group had come from an excavation in Luoyang in 1937. He purchased it in 1939 from the Hungarian Art dealer Mathias Komor, who at that time resided in Beijing and in 1941 moved to New York (Flaes 2012).

The analysis of a tiny sample of black paint on the hair of one of the riders revealed that the object had been underground for an extensive period of time. What is remarkable is the strong oxidine reduction in the tar of pine wood that is typical for archaeological finds.[2] This confirmed that the objects originate from an excavation.

Discovery

In 1993, one of the horses was broken while on loan and needed to be restored. This unfortunate accident allowed us to make interesting observations during the process of cleaning and mending of the broken parts. Parts of the legs and the footplate of the horse are clearly made of a fine grey ceramic that is different than that used for the original parts.

Dating of one of these additions using thermoluminescence showed that it had been fired in the first half of the 20th century.[3] Another interesting discovery was made during the treatment, notably that heavily corroded metal rods were visible in the original parts. At that time, the assumption was that this was an earlier restoration.

An X-ray photograph of that horse revealed the presence of a metal structure in the front legs and a separate one in the hind legs. The metal is fully embedded in the ceramic, making its addition as part of a restoration almost impossible. However, there was no alternative explanation, and further research was not possible at the time because of the permanent exhibition of the figures in the museum.

Production Process of Chinese Tomb Figures

From literary sources, it can be concluded that terracotta burial figures were generally mass-produced using moulds (Strahan and Boulton 1988). The 'Terracotta Army' in Xi'an is the most famous example of the large-scale production of clay figures using moulds during the Qin dynasty (221–206 B.C). The production of tomb figures made of grey earthenware continued during the Han dynasty and on into later periods. Nine centuries later, during the Tang dynasty, the large-scale production of white-bodied clay tomb figures with the so-called *Sancai* glazing is well known (Needham, Kerr, and Wood 2004).

Some rare examples of statues made of grey–brown fired clay with a metal skeleton are known in the collections of Western museums. The discovery of metal structures in Chinese tomb figures has been reported by the British Museum, the Brooklyn Museum of Art in New York, and the Royal Ontario Museum in Toronto (Jayne 1930; Fernald 1950; Todd 1952; Strahan and Boulton 1988; Smith and others 1995). The Brooklyn Museum of Art possesses two horses that are quite similar to the figures in the Rijksmuseum. They are also made of grey ceramic with a metal skeleton. In this case, the metal armature was discovered during the treatment of damage that was directly related to the metal structure. The croup of one of the horses had split exactly along the U-shaped metal rod (Bruno 1997).

Another example, found in the Ontario museum, is a damaged terracotta figure of a female figure that was treated in the 1950s. The corrosion of the metal structure had caused the figure to crack, and the metal was removed to prevent further damage. As a result of this invasive action, the imprint of vegetable fibres on the fired clay that had been in direct contact with the metal structure was revealed (Fernald 1950).

Dating with Optically Stimulated Luminescence (OSL) and Radiocarbon Dating (C–14)

Finally, in 2010, the opportunity arose to begin extensive research on our group of tomb figures. That the Rijksmuseum possesses a group of six figures with separate riders and saddles, in total twelve parts, makes the relevance of a technical study even higher.

The dating given by thermoluminescence in 1985 indicated that one of the riders had been fired in A.D. 535 ± 300 years.[4] The dating of the other parts of the group (two saddles, three riders, three horses, and two camels) using OSL was undertaken at the Netherlands Centre of Luminescence Dating in Delft in 2010 and 2011.[5] This confirmed that these ten parts had also been produced in the same period. The average production date is estimated to be A.D. 750 ± 175 years. The results obtained on the individual samples range from A.D. 483 ± 116 to A.D. 985 ± 85 years. More research is needed to determine the reason for this spread in results.

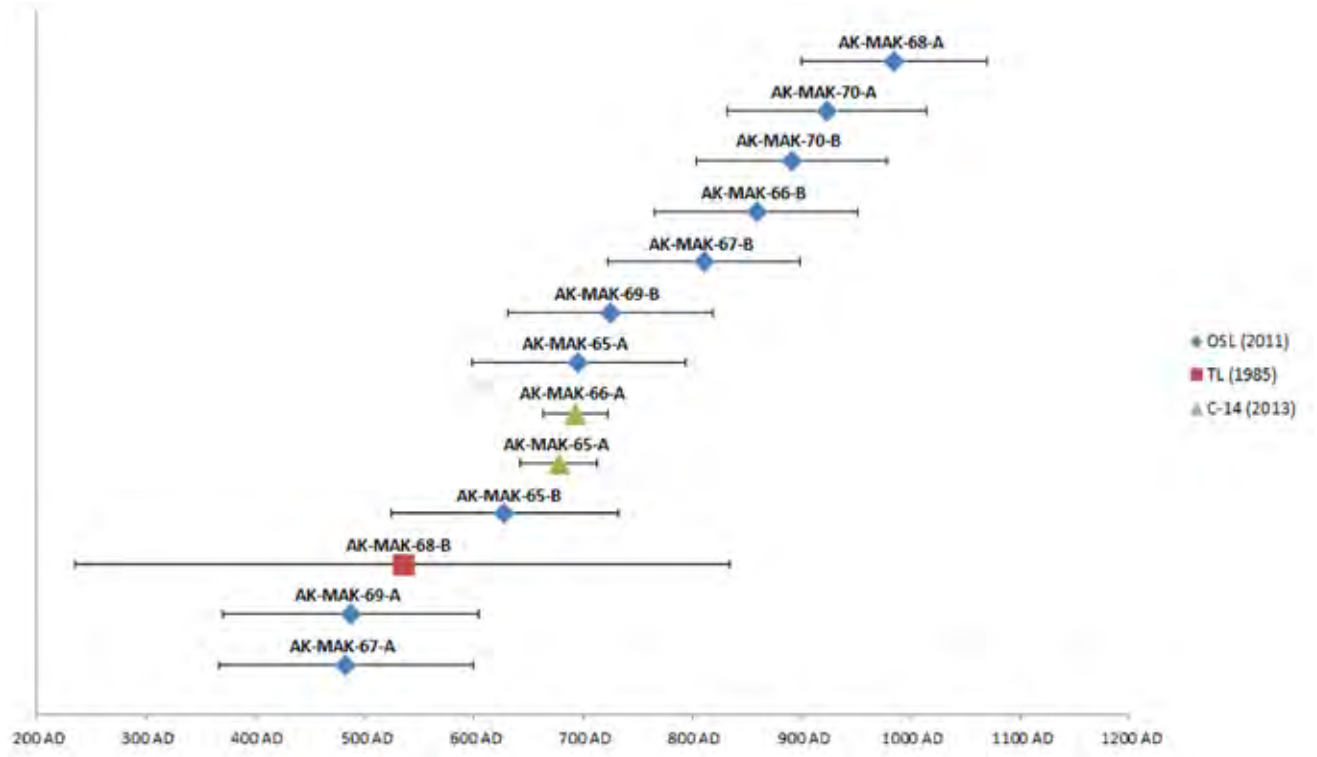

Fig. 2. Dating of 12 parts of the figures with different analytical methods (Graphic: Guus Verhaar, Rijksmuseum, Amsterdam). OSL, optically stimulated luminescence; TL, thermoluminescence; C–14, radiocarbon dating.

Two horses contained enough organic material for a C–14 dating, providing the opportunity to cross-check the values obtained by luminescence dating. [6] C–14 results indicate a production date of A.D. 685 ± 33 years. Figure 2 shows a comparison of dates obtained by various methods.

An Intriguing Metallic Skeleton

The figures were studied with the naked eye as well as with light microscopy and endoscopy. The production techniques were further visualised with computer tomography (CT) scans and X-ray imaging.

X-ray photographs[7] and CT scans[8] revealed that all six animals contain a metal structure. In the horses, this is in the form of U-shaped metal rods embedded in the front and hind quarters of the animals. In the camels, the metal structure consists of a more or less straight metal rod in each of the four legs ending in the shoulder and croup of the animals. Figure 3 shows the CT scan of a camel where the metal rods clearly appear as white stripes. The straight rods are not connected through the body as with the horses and it was not possible to determine if they had originally been so. One of the metal rods extends into the hoof of the camel and even a little beyond.

None of the riders or saddles has a metal structure.

The X-ray photographs show that some parts of the metal structure are corroded while other parts are broken or missing. Figure 4 features an X-ray photograph of the lower part of a horse where the iron rods embedded in the ceramic of the original parts of the legs appear as light stripes. Uneven grey areas at the interface between the metal and the ceramic reveal the presence of hollow spaces. This could indicate that organic material was placed around the metal rods to form a buffer, which would have burned away during firing.

Condition and Additions

X-ray photography and CT scanning were also very helpful in deciding which parts of the figures are original. Figure 3 shows a CT scan where the difference in density between the

ceramic of the original parts and of the modern additions is clearly visible. The original parts are made of fired clay containing inclusions appearing as white dots on the scan. The ceramic of the modern additions is more homogeneous.
After examination, it is clear that many of the lower and most fragile parts of the legs of the quadrupeds had been completed with new legs made of a grey ceramic. The exceptions are two camels, each of which has one original front leg. All footplates and most of the protruding parts, such as the ears and tails of the animals, appear to be modern additions made of the same grey ceramic. The riders and saddles have no additions.
The non-original parts had been joined to the original with adhesives and the joins were levelled, filled with plaster-like materials, and masked with paint.
Aside from the additions of non-original pieces, many structural damages appear on the CT scans and X-ray photographs. Internal cracks in the core of the animals that occurred during the drying process were revealed as well as original parts of the animals that had been repaired. Both camels have repaired breaks around the neck, and many glued joins and large loss-compensations were detected on the bodies of both the horses and camels.

Fig. 3. Computer tomography image of camel AK-MAK-68-A (Photo: Rock and Fluid Science Technology, Shell International Ltd.).

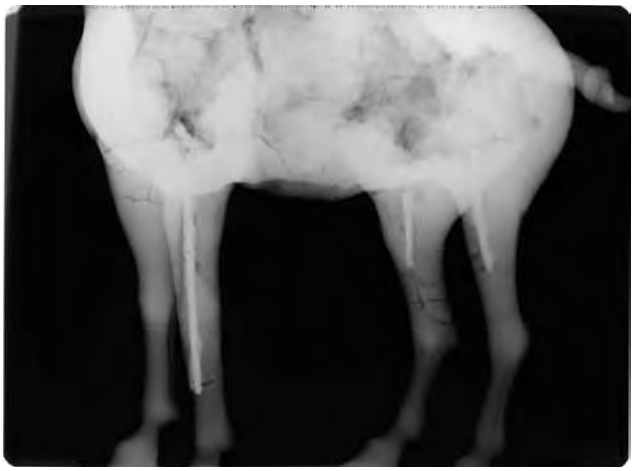

Fig. 4. X-ray photograph of horse AK-MAK-69-A (Photo: Arie Wallert, Rijksmuseum, Amsterdam).

Previous and New Treatments

The research also shed some light on the complex restoration history of the figures. From archival sources, we knew that they had been restored more than once in the past.
The earliest restoration probably took place in China before the animals were sold in Beijing in 1939. It is very likely that, between the excavation and the sale to Flaes, the missing parts were reconstructed with fired clay and that many of the structural damages in the original parts were restored.
A second restoration took place in the Netherlands in the 1950s. From the correspondence between Flaes and H.F.E. Visser, [9] we know that the figures were damaged on arrival. It seems that they remained packed during their long journey by train, boat, and plane from Beijing to Amsterdam. When Visser opened the crates in 1950, he was disappointed to have to report to the owner that the figures had been improperly packed standing-up and that the legs and footplates were broken. In 1952, the private restorer F.A.J. Smoorenburg, who often restored objects for the 'Society of Friends of Asian Art', was commissioned to repair the broken figures. Unfortunately, as was common practice in those days, no conservation records were kept. We assume that, during the journey, previously restored joins collapsed and that some new breaks occurred on original and non-original parts. For example, three of the footplates that had been newly fired and added in the 1930s also have repaired breaks that are very likely to be the result of the poor packing and handling during the transport to Europe. Later, in 1985, the broken arm of one of the riders was restored and an initial dating test was carried out using thermoluminescence.[10]

Finally, the restoration of one of the horses in 1993 led to the fortuitous discovery of the metal armature.
Between 2010 and 2012, the condition of the entire group was assessed. Instability caused by the corrosion of the metal was not found to be a problem. Many of the existing cracks were located in restored areas and had more to do with the ageing of previous conservation materials than with internal tension.
Each animal had been previously restored in many places and was covered with various retouching materials. In order to imitate the unglazed dark grey–brown surface of the original tomb figures, which had characteristic deposits of earth from the burial ground, the damaged areas had been re-touched with a mixture imitating the structure and the colour of the ceramic.
For the animals, the treatment consisted of cleaning the surface that had been obscured by dust and the muddy layer of re-touching. The animals were mechanically cleaned by carefully dusting the surface with a soft brush. It was sufficient to clear the original surface of dust and part of the excessively powdery re-touches.
Considering the fragility of the original clay body and of the poorly adhering remains of cold paint and earth, it was decided that there was no advantage in dismantling the previous repairs. Cracks that were audibly loose were impregnated with a 14% solution (by weight) of Paraloid B-72 in acetone. Some repairs that excessively covered the original surface were replaced by less conspicuous fills and re-touches. During the treatment, a variety of previous adhesives, re-touching, and fill materials were discovered, and samples were retained for later research.

Characterisation of Clay and Metal

Further analysis was performed to characterise the various materials. It can be assumed that, for the production of tomb figures, local readily available materials were used. Chinese loess is an iron-rich clay that is readily available in northern China. It is deposited after transport by wind or (sometimes) water and consists of minute grains of quartz, feldspars, and mica with small amounts of kaolinite, illite, and calcium carbonate. The iron oxide content is about 6 wt %. The typical low true-clay content of loess means its shrinkage is minimal (Needham, Kerr, and Wood 2004). Chemical analysis of the ceramic of the tomb figures shows the characteristic composition of loess with an amount of iron oxide between 5 and 7 wt %.[11] The thin section of a sample of the ceramic reveals its fine structure in which larger mineral grains of quartz, manganese, magnetite, and hematite are recognisable (see figure 5).
Analysis of the trace elements present in the clay body of the tomb figures was also performed.[12] This might be useful to trace the place of origin of the clay more precisely and is still an on-going research project.
Another focus of the research was to find out if some material had been added in order to reduce the shrinkage of the clay during drying and firing or to improve the plasticity of the loess. Examination of the animals and riders with CT scanning showed the presence of many small round inclusions in the fired clay. The nature of these inclusions is still under investigation (see figure 3).

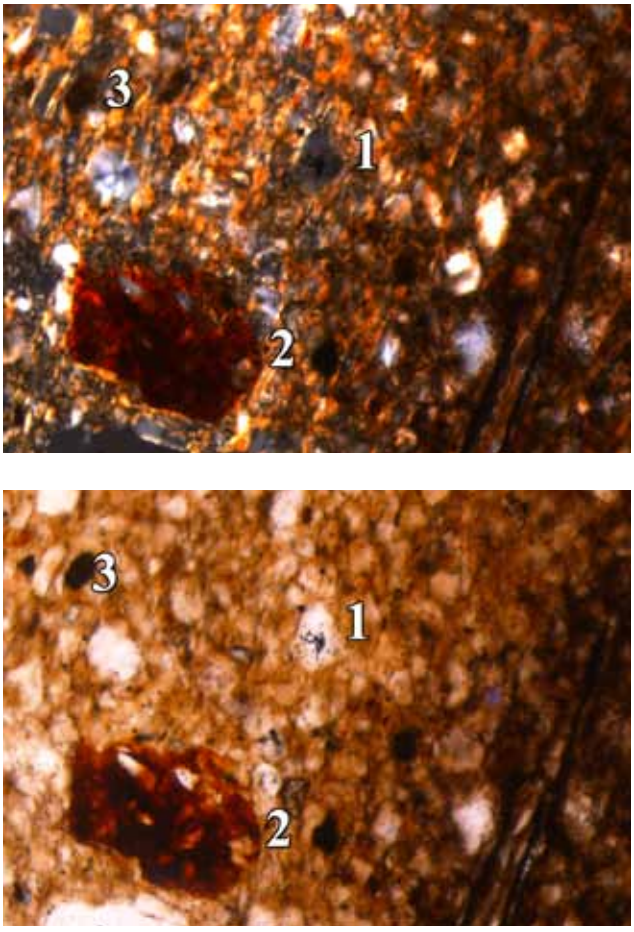

Fig. 5. Thin section of a clay sample (magnification 500X) in direct transmitted light (bottom) and crossed polarised light (top) showing particles of: 1 manganese surrounded by quartz; 2 hematite; 3 magnetite (Photo: Arie Wallert, Rijksmuseum, Amsterdam).

The analysis of the metal was more straightforward. On the leg of one of the horses, the metal core was visible because of a small loss of the ceramic, and a tiny sample was taken and analysed. X-ray fluorescence analysis confirmed the metal is fairly pure iron.[13] The microscopic image of an embedded cross-section of the iron showed some black inclusions that point to forged iron (see figure 6).[14] Scanning electron microscopy (SEM) revealed the presence of slag in the cross-section, an indicator that the iron was forged.[15]

Production Process

Many publications on Chinese ceramic figures propose that the figures were made in moulds. A description with illustration of the use of moulds is given in Strahan and Boulton (1988). The different parts were joined together with slip and the combination of parts enables a variation of figures. If this had been the case, one would expect to find traces of the moulds and of the seams where the parts were joined. Another characteristic of the mould production method is relatively thin and regular ceramic walls.

Our group of figures presents other characteristics showing they were hand-formed individually. The ceramic walls vary considerably in thickness and are very uneven.

Although all the animals in the group have similarities, they differ from one another; for example, the heads are all different in form and size. This variation applies to all parts of the animals, and the size and posture of each animal is unique.

All the animals have an opening under the belly and are partially hollow. Inside the animals, traces of charcoal remains and partly burned fibres are visible. Microscopic examination of the fibres using SEM shows various grass species. A kind of sedge (*carex*) and pith rush (*juncus effusus*) were identified. The SEM microphotograph shows the characteristic structure of the cells in the stem of pith rush (see figure 7).

The charcoal remains in the hollow belly suggest a particular production method: a bundle of straw was formed and then the metal rods were placed through the bundle to support the legs. This rudimentary form was used as a basis to build a hand-formed clay animal. The straw also functions as a regulator during the drying of the clay, partly preventing the occurrence of cracks. During the firing process, the straw burns away, leaving some residue. That the straw remains are not fully burned and that the clay inside the belly is poorly fired indicate a relatively low firing temperature. Further research is needed to assess the firing temperature and firing conditions. After firing, the figures were cold painted with pigments.

We decided to partly reconstruct a horse in order to test our hypothesis of the production process. The form, size, and weight of the original horses were followed as closely as possible. During the drying period, cracks appeared in several places through the clay, especially around the metal armature (see figure 8). Over a two-week period there was a 20% weight loss, and the shrinkage of the horse was considerable.

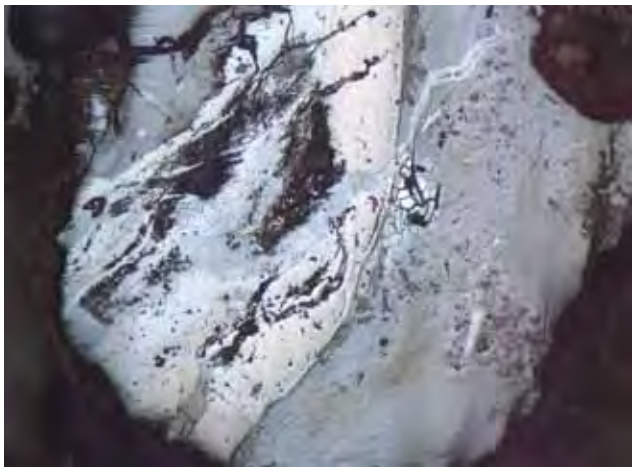

Fig. 6. Microphotograph (magnification 200X) of highly corroded forged iron from AK-MAK-66-A (Photo: Arie Wallert, Rijksmuseum, Amsterdam).

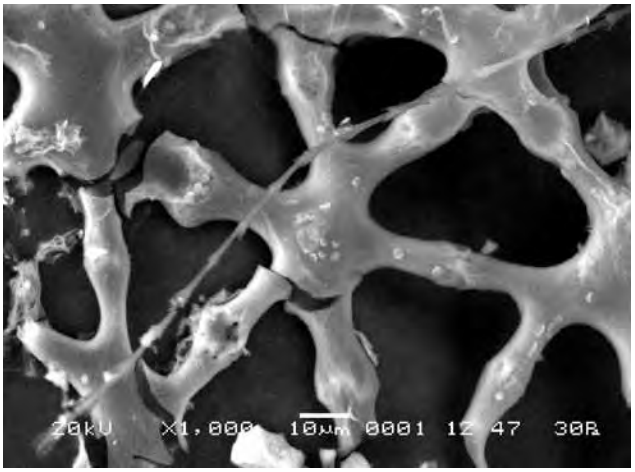

Fig. 7. SEM microphotograph (magnification 1000X) showing the structure of the cells in the stem of juncus effusus, found in AK-MAK-65-A (Photo: Ineke Joosten, RCE).

Fig. 8. Unfired clay dummy of part of a horse showing shrinkage cracks along the internal metal core; height: 28 cm (Photo: Conservation Department, Rijksmuseum, Amsterdam).

Fig. 9. Fired dummy made of clay with fibres and internal forged iron armature; height: 38 cm (Photo: Loe Jacobs).

Experimental Firing

The Ceramics Laboratory at Leiden University conducted further experiments to test the proposed production process, and several figures were modelled and fired.

The first experiment consisted of making a human figure to test the shrinkage process. Serious cracks appeared during the drying phase but not during firing. This also occurred when extra tempers, such as sand or crushed pottery shards (grog), were added to the clay. Although adding such materials will obviously reduce shrinkage, it will not prevent cracking. Although the cracks can be repaired, preventing them would be a better option.

Further tests focused on preparing the clay to strengthen its cohesion and diminish cracking during the shrinkage process. It is possible to reinforce the clay with fine fibres such as hair, coconut fibre, bamboo, and reed fluff such as 'Typha Latifolia'. Most of such fine fibres will disappear during the firing process. The carbon content will specifically increase in the thicker parts of the clay body. This would be visible as dark grey or black colouring, which would not be seen in the oxidised areas of the fired clay.

Winding fibres around the metal structure can improve the cohesion and flexibility of the clay mass and prevent cracks during the drying phase. A thin layer of fibres must remain to accommodate the expansion of the iron rod during the firing. Expansion of the iron is a minor problem compared with the problem caused by the shrinkage of the clay during the drying phase.

Finally, a second horse was modelled using clay mixed with fibres of 'Typha Latifolia' on an armature of forged iron rods wrapped in fibres. The firing of this dummy was successful (see figure 9). Further tests with Chinese materials will be the next step of the research.

Conclusion

This research provided answers to some of the questions as to how and when the objects were made. The dating of the tomb figures using various methods have confirmed that the presumed production date is around A.D. 700. The combination of technical research with practical experimentation was extremely useful to better understand how the figures could have been produced. These experiments have provided proof that firing clay with iron reinforcement is technically possible.

Examination of the animals showed that the metal armature was not found to be a cause of instability, and no connection could be made between corroding iron and internal tension. The conservation treatment of the figures consisted mainly of the consolidation of superficial cracks and improving conspicuous previous repairs.

This research is one part of a larger project that is still ongoing and, as usual, the preliminary results bring more questions. No Chinese publication has yet been found describing comparable objects. Private communications with Chinese specialists have confirmed these types of metal structures are sometimes present in Tang tomb figures.

The next step of the project will be to look for similar excavated burial figures in China for comparison in order to refine the dating and geographical origin of this important group of burial objects.

Acknowledgements

The authors thank Luc Megens from the Cultural Heritage Agency of the Netherlands (RCE); Candice Johns from the Netherlands Centre for Luminescence Dating; Jolanda van Iperen from the Conservation Department of the Rijksmuseum; and Fons Marcelis, John Coenen, and Axel Makurat from Rock and Fluid Science by Shell International Ltd.

Notes

1. Vereniging Vrienden der Aziatische Kunst (VVAK).
2. Henk van Keulen 2012, Cultural Heritage Agency of the Netherlands (RCE). Method: thermally assisted hydrolysis and methylation gas chromatography-mass spectrometry (THM-GC-MS) in combination with pyrolysis. The pyrolysis unit used was a Frontier Lab 3030D pyrolyser mounted on a Thermo Scientific Focus GC/ISQ mass spectrometer combination.
3. Doreen Stoneham 1994, Research Laboratory for Archaeology and the History of Art, Oxford University.
4. Doreen Stoneham 1985, Research Laboratory for Archaeology and the History of Art, Oxford University.
5. Jakob Wallinga, reports NCL-7909b and 7211, Netherlands Centre for Luminescence Dating, Wageningen University.
6. Johannes van der Plicht 2013, Centrum voor Isotopenonderzoek, Rijksuniversiteit Groningen. Methods: Carbon is pre-treated with the AAA method (acid/alkali/acid) to clear possible contamination and provide a clear datable fraction. This fraction is burned to pure CO_2 gas, which is reduced to graphite. In the graphite, the ^{14}C concentration is measured with the accelerator mass spectrometry method. The result is reported in BP (conventional ^{14}C years). These are calibrated to calendar years relative to a standard curve of dendrochronology.
7. Arie Wallert, Rijksmuseum, Amsterdam. X-ray photographs were performed with General Electrics, Eresco MF3. 83 kV, 3.3 mA, 20 seconds and 30 seconds, 90 cm. Film: Agfa Structurix D7.
8. Fons Marcelis, Rock and Fluid Science by Shell International Ltd. CT scans were performed with Siemens Somatom. 140 kV, mA 50 for 99.6 seconds, 512 images.
9. H.F.E.Visser was chairman of 'Society of Friends of Asian Art'.
10. Stoneham 1985, op. cit. (note 4).
11. Pieter Vroon 2012, Faculty of Earth Science, Vrije Universiteit Amsterdam (VU). Analysis performed by inductively coupled plasma optical emission spectrometry.
12. Pieter Vroon 2012, Faculty of Earth Science, Vrije Universiteit Amsterdam (VU). Inductively coupled plasma mass spectrometry.
13. Arie Wallert 2012, Rijksmuseum, Amsterdam. Elemental analyses with energy dispersive X-ray fluorescence spectrometry were done with an ARTAX µ-XRF spectrometer, 50 kV, 600 µA, Mo-anode, using a 0.060 µm capillary lens. Measurements usually took 120 seconds. To increase detection of low Z elements, a He-flush (1.7 L/m) was applied.
14. Arie Wallert 2012, Rijksmuseum, Amsterdam. Observations of metallographic sections were made with a Leica DMLM microscope (magnifications 50X, 100X, 200X, 500X, and 1000X). Micrograph images in direct light (bright field, with crossed and uncrossed polars) and ultraviolet light (filter cube BL/VIO C105) were recorded with a digital Leica DFC 420 C camera. For etching, a conventional Nital solution was applied.
15. Ineke Joosten 2013, Cultural Heritage Agency of the Netherlands (RCE), Amsterdam,the Netherlands. Analysis was performed with a JEOL JSM-5910LV variable pressure scanning electron microscope, which was equipped with an energy dispersive X-ray spectroscopy detector (EDS, Silicon Drift Detector, Noran System Seven software, Thermo Fisher Scientific). The analysis was conducted at a voltage of 20 kV for 60 seconds at 30 Pa.

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17th Century Dutch Tiles in the Tropics: the Importance of State and Trait on the Deterioration Process

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Keywords
tiles; salt damage; tin glaze; tropical climate

Abstract
Glaze damage as a result of the crystallisation of soluble salts is a well-known phenomenon in historic tin-glazed tiles. However, it has been noted that not all tiles in the same context are affected in the same way. This paper documents an unusual case study of a group of 17th century Dutch tile panels that have been integrated for 300 years in an outside wall in a Brazilian Franciscan monastery. A condition survey recorded the influence of this unusual tropical environment and made it possible to evaluate in a new light the significance of the production process of 17th century Dutch tiles on their susceptibility to damage. This research project was part of a fact-finding mission set up by the Foundation for the Exploration and Conservation of Monuments of the Dutch West India Company (MoWIC) to advise Brazilian conservators and administrators on the historical context and conservation priorities of these historically significant Dutch tile panels. A comparison with Portuguese tiles in the same building led to suggestions that the clay composition, in particular the calcium content of imported clays, plays an important role in the specific problem of glaze loss.

An Unusual Discovery
In 1957, 26 panels made up of 924 17th century Dutch tin-glazed tiles were discovered under a layer of whitewash on the external balcony wall of a 17th century Franciscan monastery. What made this unusual was the fact that the monastery was situated in Recife, in the state of Pernambuco on the Brazilian east coast, in a building that has been in permanent use since the 17th century. The tiles are known to have been in place there since the early 18th century, meaning that the tiles have been exposed to an outdoor climate for approximately 300 years.

In 2010, a fact-finding mission (including the author) was organised by MoWIC (the Foundation for Exploration and Conservation of Monuments of the Dutch West India Company) to study the historical background and condition of these significant Dutch tiles, in order to contribute to a plan for their future conservation. The conservation will be undertaken by Brazilian conservators, and the aim of the mission was to advise local administrators and conservators on the specific issues relating to Dutch tiles from this period. At the time of the visit, the many 18th century Portuguese tile pictures situated in the monastery were in the process of conservation. This enabled a comparison to be made between the deterioration patterns of Dutch and Portuguese tin-glaze tiles (albeit produced in different centuries) as well as giving an insight into local conservation methods. The Brazilian conservators working on the Portuguese tiles in the monastery will probably undertake the conservation of the Dutch tile panels, and the mission provided the opportunity to discuss the issues that came to light with both the conservators and monastery administrators.

The History of the Monastery
Saint Anthony's Monastery in Recife (Convento de Santo Antônio do Recife) was built between 1606 and 1613 by the Portuguese colonisers. In 1621, the Dutch West India Company (Geoctroyeerde West-Indische Compagnie or (G) WIC) was founded following the tradition of the VOC (Vereenigde Oost-Indische Compagnie), which had been set up in 1602. The WIC was a chartered company of Dutch merchants who were given a trade monopoly in the West

Fig. 1. Map of Phernambucq harbour, the city of Mauritsstad, and the village of Recife, Brazil, circa 1644 in Vinghoon's Atlas, 1617–1670 (Photo: National Archive, the Hague, acc. number: 619.74).

Indies by the Republic of the Seven United Netherlands and had jurisdiction over the African slave trade, Brazil, the Caribbean, and North America. In February 1630, they drove the Portuguese out of Olinda, Recife, and the island of Antônio Vaz, and established the colony of New Holland, the capital of which was *Mauritsstad* (present-day Recife), which remained in Dutch hands for 24 years (figure 1). Building began on the island of Antônio Vaz, and in 1631 the residence of the commander of the Dutch troops, Fort Ernestus, was built incorporating the then convent of Saint Anthony. Between 1636 and 1644, the port was developed under the governorship of Johan Maurits, Prince of Nassau-Siegen, who built parks, markets, hospitals, and churches. Soon Mauritsstad was a maze of bridges and canals in true Dutch style. The period of Dutch rule ended in 1654 when the Portuguese took back the colony.

The Origin and Placing of the Dutch Tiles

After 1654, Dutch colonial buildings in Recife were slowly demolished. The convent underwent a period of rebuilding from 1696 and on into the 18th century, and it was at this time that the tiles must have been installed. It is probable that the tiles originated from Dutch colonial buildings demolished nearby, having been stored as useful building material, possibly in the convent itself. There is no reason to believe that 17th century tiles would have been imported at such a late date. It is not known when the tiles were painted over with whitewash, but it is presumed that this took place sometime in the middle of the 20th century.

The tiles are positioned in niches in the upper walls of the inner courtyard (figure 2). The size of the panels varies. There are 18 panels containing 42 tiles each (14 x 3 tiles) and eight smaller panels containing 21 tiles (7 x 3). In total, there are 923 tiles (one having fallen out since the tiles were first revealed in 1957). They are of a classic size for

Fig. 2. The position of the tile panels in the inner courtyard (Photo: Kate van Lookeren Campagne).

17th century Dutch tin-glaze tiles, being between 12.8 and 13 cm in diameter and approximately 1 cm thick (where they could be measured). The tiles are covered on one side with a tin glaze and are predominately decorated with cobalt blue, and in a few cases with iron-oxide additions. It was not possible to ascertain if some or all of the tiles have a second lead glaze layer ('coperta' or 'kwaart'). The panels are arranged in themes, including soldiers, sea scenes, animals, playing children, and vases of flowers (figure 3). The niches in the stone walls appear to have been designed to fit Portuguese tiles, which are larger than Dutch tiles from this period (being approximately 15 x 15 cm). This would explain the lower row of cut-down tiles (figure 4), which were necessary to fill the gap left over by the use of the smaller Dutch tiles.

In the past, there was some discussion as to the origins of the Dutch tiles' manufacture (Dos Santos 1959; van Nederveen Meerkerk 2008; de Jager and Schadee 2009); however, during the 2010 fact-finding mission, art historians Ingrid de Jager and Nora Schadee became convinced that the tiles originated from various Rotterdam factories and were made between 1625 and 1645. This conviction was based on stylistic aspects of the tile decoration as well as historical evidence of export routes (van Nederveen Meerkerk and others 2010).

Tin-glaze tiles were first manufactured in Rotterdam in 1609 and the industry then quickly developed. By the second half of the 17th century, Rotterdam was a major production centre. Commissions from abroad began to arrive in about 1630 and a flourishing export market soon developed. It is not known who ordered the Recife tiles or how they were transported to the colony. In 1634, a tile maker from Rotterdam, Nicolaes van de Hoeve, emigrated from Rotterdam to Mauritsstad and it is possible that he brought the tiles with him (van Nederveen Meerkerk and others 2010).

Fig. 3. Detail of one of the tile panels containing tiles depicting soldiers (Photo: Kate van Lookeren Campagne).

Fig. 4. Tiles 'cut down' to fit the remaining space in the niche (Photo: Kate van Lookeren Campagne).

The monastery also contains thousands of 18th century Portuguese tin-glaze tiles. These tiles can be found in the church, sacristy, and cloister and depict panels with scenes from the Old Testament framed in Baroque-style cartouches. These tiles are also decorated in cobalt blue on a tin glaze and show the stylistic influence of Dutch tiles on Portuguese tile decoration.

Conservation History

The poor condition of the tiles came to the attention of Hannedea van Nederveen Meerkerk on a visit in 1965. A second visit made in 2004 lead to concern about their further deterioration. In 2006, a survey of all the tiles in the monastery was carried out by IPHAN (Instituto do Patrimônio Histórico e Artístico Nacional). This survey clearly documented the condition of the tiles and proved to be very useful as a comparison with the situation in 2010. As far as is known, no repair or conservation work has been carried out since the removal of the whitewash layer in 1957. It is not known how the whitewash was removed, but it is assumed that the paint would most likely have been removed with water and brushes. The cement and plaster repairs and fills must have been done sometime between 1957 and 2006.

During the 2010 fact-finding mission, a full survey of the condition of the 923 tiles was undertaken. The condition of the glaze and ceramic body and evidence of salt damage was recorded, as well as the bonding of the tiles to the mortar. In addition, the condition and use of the building were assessed, paying special attention to water transport and possible sources of soluble salts. One central question was how these tiles could have survived in an outside environment for at least 250 and probably 300 years. It is possible that the whitewash layer may have provided some protection from the elements.

Condition of the Dutch Tiles

The ceramic body of the Dutch tiles appeared to vary quite considerably from harder, red iron-containing pottery to a softer, calcium-rich, buff-coloured body. There is evidence of the 'dry' mixing of local and imported clays that was common during the early 17th century and that resulted in a layered structure particularly susceptible to salt damage (van Dam 1999).

The tiles are set slightly apart from each other and are grouted. This is contrary to the traditional setting of Dutch tiles (which were always set with the edges close); however, this has probably been advantageous for the preservation of the tiles, as it will have enabled the evaporation of water and the growth of salt crystals to occur through the porous grouting as opposed to through defects in the glaze layer. Various materials have been used for the grouting: mortar, plaster, and, in some places, cement. Cement was also used to fill missing areas of tile, and it is evident how cement has prevented water evaporation: this has led to the build-up of salts and resulted in extreme damage in one area. Old cement repairs have also caused problems in the stone facade, resulting in irregular erosion patterns and problems with drainage.

About 80 of the tiles are broken. The percentage of broken tiles varies from panel to panel. These damages appear to have occurred before the tiles were placed in the monastery. Thus, one can assume that the damage occurred when the tiles were removed from the previous locations, although it is possible that some may have fallen off the wall at some time in the past and then have been re-installed. The tiles have clearly been fixed into the mortar in their broken state, as mortar is visible in the breaks. In some cases, these breaks have loosened and the tiles are in danger of becoming detached.

Possibly the greatest problem is the poor attachment of the tiles due to the failure of the mortar. The tiles are embedded in lime mortar, although the precise composition and structure of the mortar layer has not yet been analysed. The niches are approximately 9 cm deep and appear to be filled with rubble behind the mortar. Where a loose tile has been removed, it is evident that the mortar is very inconsistent and weak. Lime-plaster mortars are easily damaged by long-term exposure to high humidity and water filtration. By tapping the tiles gently, a hollow sound could be heard where the mortar has failed.

Salt Damage

Physical damage due to the growth of soluble salt crystals at the surface of the porous ceramic body is one of the major factors of damage to tin-glazed tiles in general (Buys and Oakley 1996; van der Veen-Slager 1996; Durbin 2005; Letizia and Ruffinelli 2009; Mimoso and others 2009). Soluble salts (predominately nitrates and chlorides) are transported into the porous body with water. When the

humidity level falls below the point of deliquescence of a particular salt (this is the point of dissolution of the salt as a result of the absorbance of moisture from the air), the salt (re-)crystallises, resulting in damage. Depending on the evaporation opportunities and the strength of the glaze bond, glaze and/or ceramic material can be pushed away from the surface due to the pressure of the crystals that grow at the ceramic/glaze interface and/or through glaze faults such as pin holes.

The source of the salts can vary, but they generally originate from the mortar, ground water, or other external sources. Taking the geographical position of Recife into account, salt-rich precipitation or marine aerosols are an obvious source of chlorides, which has been investigated (Meira and others 2007). Simple spot tests for the presence of chlorides, nitrates, and sulphates were carried out on loose pointing and mortar samples, although the results were not definitive. The (semi-quantitative) spot tests recorded the salt levels as being low (around 500 mg/l of chlorides and nitrates); however the results could have been influenced by the heavy rainfall and particularly high relative humidity (around 95%) in the period when the tests were made. These factors would have caused the removal of dissolution of the salts at the tile surface. The presence of soluble salts in the tiles is evident in the visible salt damage found in many places.

Trait: Specific Problems Related to the Manufacture of the Dutch Tiles

From 1625, local red iron-containing clays were mixed with imported calcium-rich buff-coloured clay in an attempt to improve the quality of the fired product. Up until around 1640, the clays were mixed while in a plastic state, resulting in a 'layered' ceramic body. Tiles made by this method are particularly susceptible to salt damage due to differences in the porosity and coefficient of expansion of the different clay types (van Dam 1999). This form of damage can be seen in some of the tiles (figure 5). From around 1640, the clays were mixed in a 'liquid' form (a suspension in water), enabling a solution to this problem.

With certain Dutch tin-glazed tiles, the type of damage as a result of salt crystal growth is clearly directly related to poor attachment of the tin-glaze to the pottery body. This can result in the partial or total loss of the glaze layer with little apparent damage to the ceramic body (figure 6). This form of damage is found on many of the tiles. Poor glaze attachment is primarily related to the composition of the clay and glaze, which have to be well matched in order to ensure a good 'glaze fit' (Green 1975; Fraser 1995; Hamer and Hamer 2004). The match relates to the linear expansion coefficient or shrinkage of the materials on cooling after firing. A greater shrinkage of the glaze leads to 'crazing' or 'craquelé', while a greater shrinkage of the ceramic body leads to glaze detachment in the form of 'shivering' or 'peeling'. Crazing can also occur long after firing if a pottery body absorbs moisture, resulting in an expansion of the ceramic body. Firing conditions (notably rapid cooling) also influence the development of

Fig. 5. Salt damage resulting in the delamination of a ceramic body where different clays were mixed in the plastic state. The different clay types (red iron-rich clay and a buff-coloured, calcium-rich clay) are clearly visible (Photo: Kate van Lookeren Campagne).

Fig. 6. An example of salt damage resulting in 'shivering' of the glaze (Photo: Kate van Lookeren Campagne).

glaze loss or crazing; however, when this is the case, the problem tends to be evident directly after firing. One could assume that the tiles have suffered from water saturation in their long history in an outside environment; nevertheless, crazing of the glaze is not prevalent, apart from the tiles lower down in the panels where water has been more likely to collect. More common is the evidence of poor glaze attachment linked to shivering. As can be seen in figure 6, the glaze layer has come away from the ceramic surface in some areas. In other examples, the complete glaze layer has lifted from the surface but is not yet detached. Interestingly, remains of the pre-1957 whitewash layer are still visible in areas of glaze loss in figure 6, suggesting that much of the glaze damage must have been from before that date.

The time in which these tiles were produced (1625–1640) was a period of change in clay use and preparation (Tichelaar 1965; Lins 1984; Tichelaar 2001). Calcium-rich clays were imported from abroad, and there was little understanding of the results that could be expected from the clay mixtures used. It was a time of trial and error. The changes in clay preparation and use in the Dutch tile industry during the 17th and 18th centuries and the effect it had on susceptibility to glaze deterioration is the subject of a PhD research project at the University of Amsterdam.

Damage Patterns Observed on the Portuguese Tiles in the Monastery

The Portuguese tin-glaze tiles in the monastery presented a quite different deterioration pattern. These tiles are situated around the courtyard on the back wall under the balconies as well as inside the building and are therefore protected from the weather. Before conservation, they had suffered from serious salt damage due to rising damp and significant mould contamination. However, in this case, the ceramic body itself had been damaged rather than only the glaze; this suggested that the glaze was well bonded to the ceramic body. In figure 7, one can clearly see that the ceramic body had been damaged by the salts to quite a deep level.

Although not particularly of high quality, the (18th century) Portuguese tiles showed no apparent evidence of either crazing or shivering. Interestingly, the ceramic body is seen to be red in colour, suggesting an iron-rich/low-calcium clay composition. A recent analytical study of Portuguese tiles dating from the 17th to 18th century and suffering from poor glaze adhesion has suggested that the problem is related to tiles where the ceramic body has a high calcium content (Mimoso and others 2009; Mimoso, Salta, and Gonçalves 2011).

Fig. 7. Glaze damage on Portuguese tiles situated within the convent (Photo: Perside Omeda).

State: the Influence of the Environment

The condition of the Dutch tiles has been influenced by a number of factors, but the environment has obviously had a major influence on their condition. These tiles were made for interior use: the fact that they have survived so long in an outdoor environment is exceptional.

The monastery is built primarily of lime-sandstone. This material degrades in humid environments, and there is evidence that sand that has come loose from the stone has deposited on the tile surface, giving the tiles a discoloured appearance. A particular problem for the tiles is the poor state of the grouting in the stone facade and the floor inside the balcony (figure 8). There are many gaps in the stone, and water (from the daily watering of plants in pots without drip-trays, or from the cleaning of the upper balcony) is able to seep through the gaps in the stone where pointing has been lost into the mortar behind the tiles. There appeared to be a clear correlation between these gaps in the stone balcony and the mortar failure. Figure 9 is a schematic diagram of two panels on the south side of the balcony. The arrows show the position of cracks in stone and the orange areas are where the mortar is failing. The 'south side' faces north, which could explain the salt damage as water will evaporate more slowly enabling salt crystal growth.

The extended section of the roof provides some protection from the rain, although it is also not clear in how far the

rain contains salts. The deposit of chlorides by marine aerosols (the salt-laden Maresia wind) is evident and is a known source of chloride pollution in the area (Van Grieken and others 2003; Meira and others 2007). The climate in Recife is fairly consistent with warm temperatures that never drop under 18°C and a relative humidity (RH) between 60 and 90 % (figure 10). Considering that the RH fluctuates permanently above and below 75%, one would theoretically expect more salt damage from chlorides than is now visible, as the point of deliquescence for pure sodium chloride is 75% RH (although where chlorides are combined with other salts, levels can be quite different and are often below the point of the pure salt). An alternative reason for the lack of salt damage could be that salts at the surface are regularly washed away by the rain. Furthermore, the ambient conditions are never dry enough to encourage the growth of salt crystals.
The consistent high and relatively stable temperature and RH mean that the tiles do not suffer from frost damage as they would in Northern Europe. On the other hand, the constant high humidity has a damaging effect on the mortar and aids the transport of salts into the tiles. In general, it is the lower row of half-tiles that show visible salt damage. Salt-containing water drains to the bottom of the panels, where the salts then crystallise.

Fig. 8. The poor state of the grouting in the stone facade (Photo: Kate van Lookeren Campagne).

Future Conservation Plans

The mission in 2010 resulted in a report (van Nederveen Meekerk and others 2010) on the origin and condition as well as the conservation strategy suitable for the Dutch tiles. Certain treatments used successfully on the Portuguese tiles, such as slow freezing to kill bacterial growth, were considered unsuitable for Dutch tiles due to the poor glaze attachment and fragile body. The advice emphasised that the first priority relates to problems of water transport in the building. Once funding has been secured, the conservation work on the tiles will probably be carried out by the same Brazilian conservators who conserved the Portuguese tiles in the monastery, working with conservation and mortar specialists from university departments and conservation institutes in the region. Further research will be necessary to gain more knowledge about the salt contamination and the composition of the original mortar. The tiles will have to be stabilised with a facing, then removed and desalinated.
The major challenge for the conservators if and when the tiles are treated and returned to their original position will be how the space in the niches should be filled and what

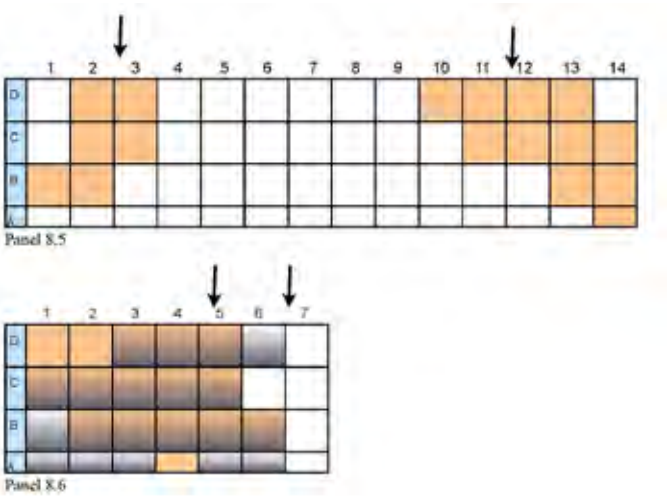

Fig. 9. Schematic diagram of two panels on the south side of the balcony. The arrows show the position of gaps in the balcony stonework and the orange areas are where the mortar is failing. The 'south side' faces north, which explains the high level of visible salt damage (grey).

mortar would be suitable to re-fix the tiles. Concerning the conservation of the tiles themselves, it is unclear what material is suitable for consolidating the loose glaze in an environment where temperatures (out of the sun) can rise to 35°C or more and the average RH is 75%. At present, there is an on-going research project at LNEC in Lisbon into materials suitable for the conservation of tiles in an outdoor environment. As part of this project, testing of mortars for filling missing areas in tiles in an architectural context is being undertaken by a Masters student at the University of Amsterdam.

Conclusion

The study of 17th century Dutch tiles in such an unusual environmental setting is not only historically fascinating but has provided greater insight into the physical nature of Dutch tiles from this period and how the production process can affect susceptibility to deterioration. This was more evident when the type of damage was compared with Portuguese tin-glaze tiles. The findings of the condition survey and comparison of the damage patterns observed suggest that the composition of the clay, notably the calcium content, is a significant factor in the deterioration pattern of tin-glazed tiles subjected to salt damage. Future research on tiles in the Netherlands will look at the relationship between glaze damage on 17th and 18th century Dutch tiles and the percentage of calcium in the ceramic body. Tiles from different production centres will be compared and the significance of other factors such as firing variations assessed. Attention will also be paid to what happens at the glaze–body interface.

This case study has made it possible to observe the specific deterioration patterns of 17th century Dutch tin-glaze tiles in a very unusual environment and to assess in how far damage patterns are primarily related to the materials and methods of production (state) or the environment (trait). Although the climatic conditions that these tiles have experienced are importantly different from tiles situated in 17th and 18th century Dutch interiors, the damage patterns are primarily the same.

The Dutch tiles in Saint Anthony's Monastery in Recife represent one of the few visible traces of the Dutch presence in Brazil during the first half of the 17th century; they have great historical value, which must be preserved. While the tropical climate of Recife provides an unusual environment for these tiles, the stability of the climate may well have proved their salvation. Although there is reason to be concerned about their deterioration, the fact that they have managed to survive in an outdoor environment for around 300 years is a miracle.

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Manufacturing Techniques and Production Defects of 16th–17th Century Majolica Tiles from Antwerp (Belgium)

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majolica; crazing; intermediate layer; ceramic tiles; Antwerp

Abstract

The analytical study of majolica gives us information about raw materials, technological skills of the potter, and the related production defects. Those production defects often represent the fragile zones in the object, which may be important for conservation. In this study, 30 majolica tile fragments from the 16th–17th century from Antwerp (Belgium) were investigated. The results show that, over a period of eight decades, various manufacturing techniques were applied. Tiles from the 16th century show reddish bodies with a higher amount of silica and better-preserved glazes with a good glaze bonding. Tiles from the 17th century contain a higher amount of calcium in the body and often show a weaker glaze bonding. Specific choices during manufacturing can be related to production defects, which influence the stability of majolica tiles and future conservation.

Introduction

From the beginning of the 16th century until around 1630, Antwerp (Belgium) was an important production centre for majolica, as well as for Façon de Venise glass. Hence, it is not surprising that Antwerp majolica was the subject of several art historical and archaeometrical studies (Hughes and Gaimster 1999; Dumortier 2002; Oost and Veeckman 2002; Veeckman 2002). Until now, most chemical analysis of majolica concentrated on provenance studies, using neutron activation analysis and inductively coupled plasma analysis for the study of the chemical composition of the ceramic body (Hughes 1991; Hughes and Gaimster 2002; Hughes 2007; Hughes 2008). X-ray fluorescence (XRF), a non-destructive approach, was used by Padilla and others (2005), performing analysis on the glaze. Until today, Antwerp majolica has not yet been studied in detail. The combined information, i.e. the chemical composition of the body and glaze, contains invaluable information concerning: (1) the technology used in a specific period, (2) technological changes, and (3) specific production defects. The main focus of our investigation was the study of tiles from archaeological sites. The advantage of this approach is that there is sufficient material to analyse and that sampling is allowed in many cases. The drawback of the chosen methodology is that defects incurred during production interfere with the deterioration occurring during the burial period and lifetime of the object. We believe not only that time and external influences are the main causes of decay, but also that specific intrinsic features of the material play an important role. This study aims to study the technological features of Antwerp majolica and its relationship with the fabrication defects, more specifically the problem of crazing and glaze adhesion.

Background Information

Majolica refers to earthenware covered with a layer of white opaque tin glaze. Different metal oxides are applied to the surface of the white glaze in order to create appealing decorations. The artists had only a limited palette of colours at their disposal: blue (Co^{2+}), yellow ($Pb_3(SbO_4)_2$), orange/brown (Fe_2O_3), green (Cu^{2+}), and purple (Mn^{3+}). To opacify

the glaze, cassiterite was added (SnO_2) (Viti and others 2003; Padilla and others 2005; Guilherme and others 2011).

Written historical sources concerning material preparation of majolica are rare. There are no known records of recipes and manufacturing techniques associated with the production of 16th–17th century Antwerp majolica. An important manuscript relating to the Italian majolica production is that of Cipriano Piccolpasso, '*Li tre Libri Dell'Arte Del Vasaio*' written in 1557. This work was translated in English by Lightbown and Caiger-Smith (1980) as '*The Three Books of the Potter's Art*'. The first majolica artists in Antwerp were Italian, so it is plausible that they used the same methods as described by Piccolpasso.

The fabrication of majolica is a complex technique combining several types of materials, where a porous earthenware body is decorated with a glassy substance. First, the clay was moulded in a form. Afterwards, it was fired for the first time at about 1000°C to obtain the 'biscuit' or unglazed fired object (Rackham and Van de Put 1934). Second, the glaze was applied. Piccolpasso describes the different steps to prepare the glaze: a *marzacotto*, or transparant fusible glass frit containing fused lead, soda, or potash and silica. To make tin glaze, tin and lead ash were added to the basis *marzacotto* and the entire mixture was calcined and pulverised. To enhance the brilliance and brighten up the colours, a layer of colourless glaze could be applied on top of the decoration. This layer is known in Italian as '*coperta*' (Caiger-Smith 1973) or as '*kwaart*' in Dutch (De Jonge 1971). The multilayer system of the biscuit, the white tin glaze, coloured decoration, and coperta was fired for the second time at about 950°C.

Throughout history, majolica potters made specific technological choices in order to facilitate the production process and enhance the quality of the final product (Tite 2009). Traditionally, majolica was made from chalky clay, which turns yellowish/whitish after firing. This high-lime clay was chosen because of the favourable properties of the raw material (Dingeman Korf 1968; Caiger-Smith 1973; Van Dam 1999), including:

- Better glaze fit: adequate expansion rates between glaze and body
- Fusibility: hardens at lower temperatures due to the natural fluxes in the clay
- Whiteness of the ceramic body
- Chipped edges did not contrast with the white glaze as red clays would have done
- Lighter in weight
- Less tin glaze needed.

The production of Antwerp majolica was entirely empiric and therefore went hand in hand with trial and error. In the Antwerp region, the local clay was plastic, tended to deform and fired red under oxidative conditions. In the 16th–17th century, several active potters, such as François Frans, Guido Andries, and Otto Van Mierop, owned red-firing clay mines in a radius of about 10 km around the city of Antwerp (Dumortier 2002). In Antwerp, lime clays and chalky deposits were not locally available. The potters had to blend their local red clays with lime clays known as '*marne de Tournai*' (Belgium). Dumortier mentions the change in colour of the ceramic bodies of Antwerp majolica over time: from intense red–brown (beginning of the 16th century) to pinkish and later to whitish (17th century) (Dumortier 2002). Other '*marls*' were found in Boyton on the Suffolk coast (England) and Carrickfergus (Northern Ireland) (Caiger-Smith 1973; Gaimster 1999).

The limited access for raw materials probably had consequences for the quality of the final product. The changes in manufacturing techniques for tiles and the relation with quality have been mentioned by Dingeman Korf (1968). He suggested that the earliest tiles from the 16th century were thick (14–20 mm) with a coarse structure and a glaze that was well attached to the body. Tiles that were made in a later period, the first half of the 17th century, became thinner (12–8 mm) and more fragile (Dingeman Korf 1968).

One of the principal concerns and difficulties in firing majolica is fit: the dimensional adjustment of a glaze to a clay body. This is related particularly to thermal expansion and shrinkage rates of the two materials: body and glaze. Unequal contraction during cooling can cause a variety of defects, e.g. crazing. Crazing occurs when the glaze contracts more than the body and develops a fine network of microcracks in the glaze (Liebscher and Willert 1955; Rice 1987). The opposite effect of crazing is known as 'shivering'. This phenomenon occurs when the glaze contracts less, or more slowly, and separates from the body (Rice 1987). This problem occurs more often when the intermediate – the part where the glaze meets the body – is weak.

Experimental

A set of 30 representative majolica tiles were selected from the vast amount of excavated artefacts found in Antwerp (Veeckman 1991; Veeckman 1992). The tiles cover a period of eight decades (1550–1630) of active majolica production and originate from archaeological local production centres in Antwerp. The dating is based on the style of decoration and archaeological records. These representative tiles are named after the streets or archaeological sites where they were found: *Aalmoezenierstraat* (two fragments), *Schoytestraat* (eight fragments), *Steenhouwersvest* (thirteen fragments), and *Sint-Jansvliet* (seven fragments). From the selected tiles, small fragments of the glaze and body from already damaged areas of a few mm in size were removed using a diamond saw or scalpel. The fragments were embedded in epoxy resin. The orientation of the samples in the resin was such that a cross-section, perpendicular to the original glaze surface, could be studied. The surface was ground flat with silicon carbide papers and polished with diamond pastes with a grain size down to 3 µm. Optical light microscopy was used for a first visual screening and to document the clay structure, colour, inclusions, stratigraphy, and glaze defects. Micro X-ray fluorescence (µ-XRF) was used for the compositional characterisation of the material. An EDAX Eagle-III micro-XRF spectrometer was used for this purpose. The instrument consists of an Rh X-ray tube, a polycapillary lens Si(Li) detector. Measurements were performed in vacuum using a beam size of around 25 µm. The X-ray tube was operated at 40 kV and spectra were accumulated for typical 1000 s. This technique is suitable for the detection of major, minor, and trace elements down to atomic number 11 (Na). The embedded sample was placed in the vacuum chamber, and three line scans were collected through the body, glaze, and pigment layer. The line scans consist of point measurements with a step size of 25 µm. An XRF spectrum was collected at each point. The use of the scanning methodology is important because majolica is a very heterogeneous material with many inclusions. From the XRF spectra, the chemical composition (in wt% of oxides) was calculated and normalised to 100%. All measurements were standardised with glass samples of known composition. The line scan data were divided into sub-sets corresponding to glaze and body, based on the lead (Pb) signal, because this element is typical for the glaze. The average composition of the different layers was determined as the mean composition of the corresponding layer. Due to the heterogeneous nature of the material and uncertainties concerning the low Z-matrix ($Z < 11$), the results are considered semi-quantitative.

Scanning electron microscopy (SEM) coupled with an energy-dispersive X-ray detection system (EDS) was used for the microstructural characterisation. This approach was also used to document the inclusions, fabrication defects of the glaze and intermediate layer. A JEOL 6300 scanning electron microscope equipped with an energy dispersive Si(Li) detector and digital acquisition electronics from Princeton Gamma Tech. was used. Elemental X-ray maps were collected using an electron beam with a current between15 and 20 nA. Elemental maps of 100x100 µm areas were acquired in about 3600 s. A carbon coating was applied on the embedded and polished samples in order to make the samples conductive. Using SEM-EDS, it was possible to detect the light elements (Na, Mg, Al) in the glaze and body with an improved sensitivity.

Results

Figure 1 shows a well-preserved tile (dated 1556–1562) from the Aalmoezenierstraat site. The backscattered image shown in figure 2 shows the cross-section of the tile with four layers. Because of the wavy character of the pigment line and depth of the pigment grains in the glaze (about 100–120 µm), it is plausible that a coperta layer was applied using a stiff brush and sprinkled on the glaze, a method described to be used in Italy and the Netherlands from the 16th until the 18th century (Paape 1794; Lightbown and Caiger-Smith 1980).

Optical microscopy investigation of the body of all majolica fragments reveals a few interesting characteristics. There are different overall colours (reddish or whitish) varying from more reddish in the 16th century and more whitish in 17th century. Also, there are different types of inclusions of various colours (brownish, reddish, or whitish). Most bodies of 16th century tiles contain intense red inclusions and/or red coloured veins. An example is given in figure 3(A): a tile dated 1556–1562 from Steenhouwersvest site. In figure 3(B), clear inclusions and clay veins are observed. These observations prove that potters mixed white firing clay with small amounts of local red firing clay and that different fill materials were added to the clay body. Dingeman Korf mentioned several fillers to the clay body, including quartz, feldspar, and chalk (Dingeman Korf 1968). These components were also found in our samples as proven by XRF. The practice of clay mixing was reported in the literature for 18th century Delft production in the Netherlands (Paape 1794; Hoynck van Papendrecht 1920). Our study demonstrates that

this method was also used in the 16th century majolica production in Antwerp. Bodies of 17th century tiles show a more homogeneous texture and a whitish colour. This can be observed in figure 4: a tile dated 1590–1613 from Schoytestraat site.

µ-XRF imaging reveals the chemical composition of the body and the distribution of elements in the material. Two examples of the Ca map are shown in figure 5 and figure 6, illustrating the heterogeneous distribution of Ca in the body of two distinct samples. In some cases, Ca is present mainly in the inclusions (figure 5), while in other cases the entire body is richer in Ca (figure 6).

Fig. 1. Wall tile fragment of sample number A187/1/T1 (Aalmoezenierstraat, 1556–1562), with stylistic and geometrical patterns in blue and yellow (Photo: F. Caignie).

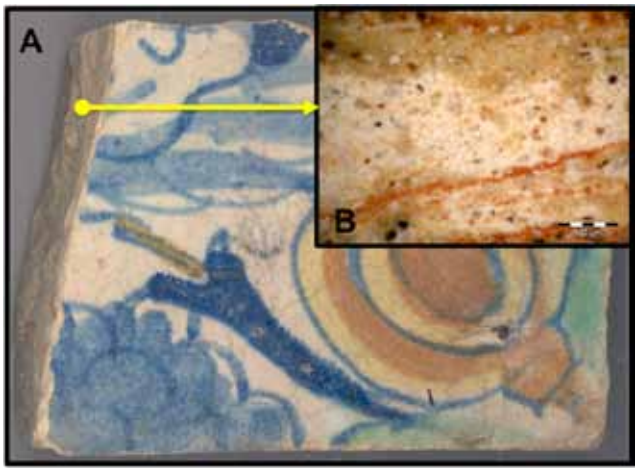

Fig. 3. Tile fragment of sample number A117/7/T6 (Steenhouwersvest, 1556–1562) (A), with optical microscope images showing clay veins and inclusions (B) (Photo: M. Vandevijvere).

Semi-quantitative µ-XRF results show interesting trends between the composition of the body , namely its SiO_2 and the CaO content, and the production date of the ceramic tile (figure 7). Two extreme cases can be identified.

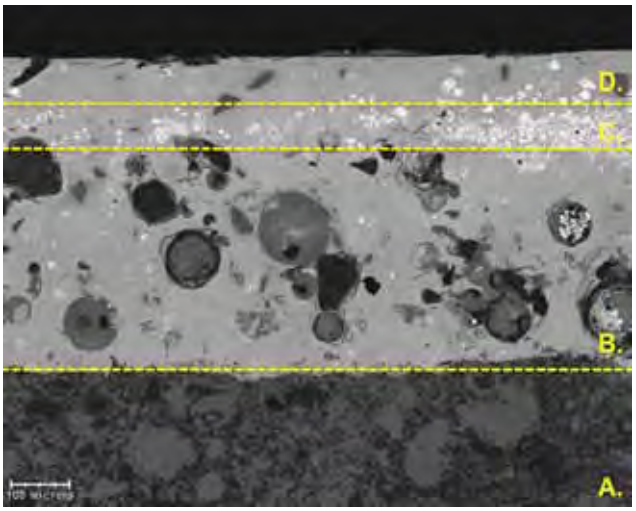

Fig. 2. Backscattered scanning electron microscope image of the cross-section of sample number A187/1/T1 (Aalmoezenierstraat, 1556–1562), showing a clear layered structure. (Photo: M. Vandevijvere). (A) Body, (B) primary white glaze with gas bubbles (round shapes) and inclusions (greyish shapes), (C) pigment layer, and (D) a coperta layer.

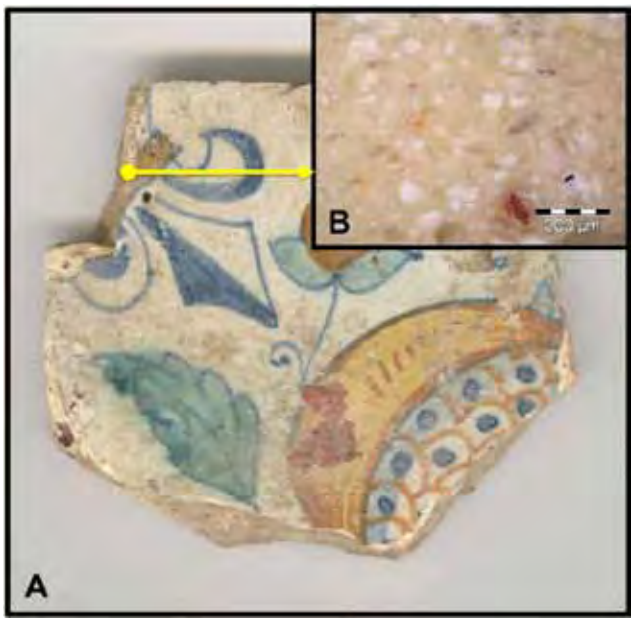

Fig. 4. Tile fragment of sample number A152/6/M7 (Schoytestraat, 1590–1613) (A), with optical microscope image showing a white well-blended clay (B) (Photo: M. Vandevijvere).

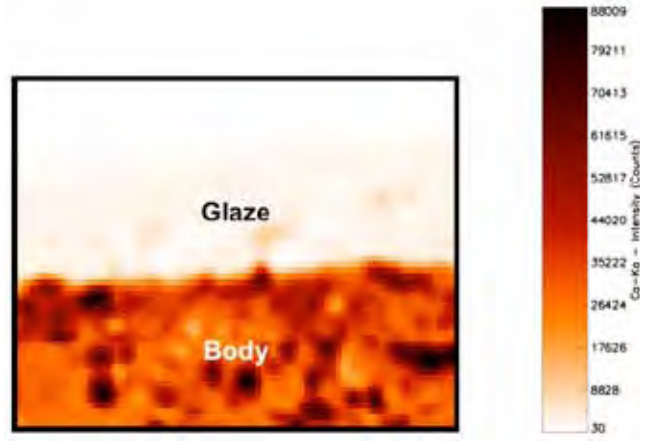

Fig. 5. Scanning micro-XRF image: elemental distribution of Ca in a cross-section of sample number A187/1/T1 (Aalmoezenierstraat, 1556–1562) with Ca enriched in inclusions. Width of microphotograph: 1620 µm x 1220 µm (Photo: XMI-group, UGent).

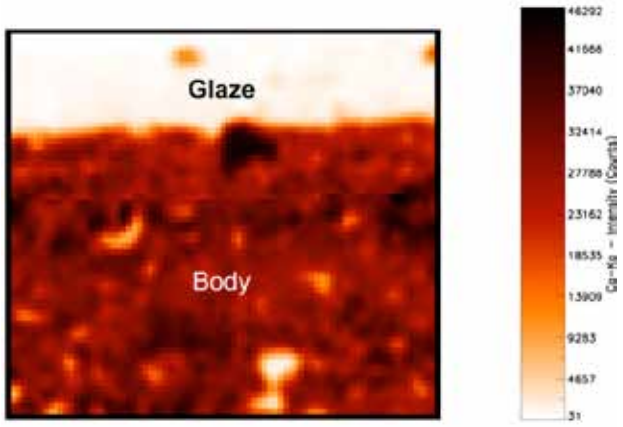

Fig. 6. Scanning micro-XRF image: elemental distribution of Ca in a cross-section of sample number A218/0/M6 (Steenhouwersvest, 1577–1613) with Ca enriched in the clay body. Width of microphotograph: 1620 µm x 1380 µm (Photo: XMI-group, UGent).

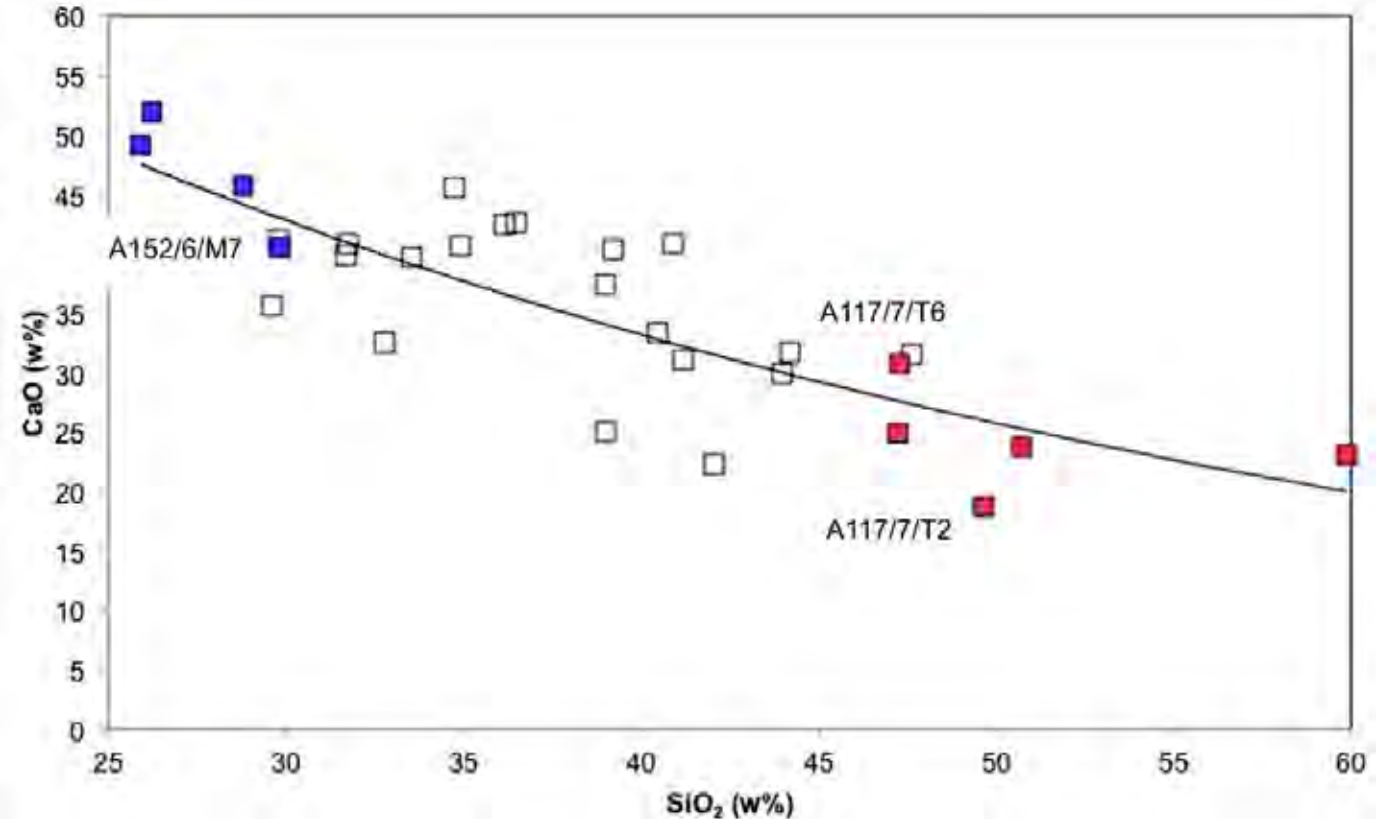

Fig. 7. Scatter plot of SiO_2 versus CaO in wt% illustrating the different composition (Graph: M. Vandevijvere). Red squares: tiles dating from the 16th century. Blue squares: tiles dating from the 17th century. Open squares: samples with varying composition/workshop and period.

A first group of tiles date from the 16th century (red squares in figure 7). The first group (red squares in figure 7) are chemically characterised by a higher content of Si and a lower content of Ca. The body of these tiles have a reddish colour with prominent clay veins. Although crazing is not always visible with the naked eye, it was observed in all of these fragments using light microscopy. However, the bonding between the clay and the glaze layer is still good in all these fragments dated from thew 16th century. This can be observed in the backscattered SEM image of the cross-section of a fragment from Steenhouwersvest site (1556–1562) An intrusion of the glaze into the body is observed, indicating a good fusion between both layers (figure 8).

A second group of tiles (blue squares in figure 7) are characterised by a higher lime content (Ca). These tiles show whitish coloured bodies and are quite homogeneously blended. The backscattered SEM of the cross-section of a typical sample of this group is shown in figure 9. Although a similar wavy intermediate line is observed as seen in figure 8, it is clear that there is almost no fusion between the two layers. Although there are almost nearly no cracks in the glaze in these samples, the inferior glaze/body bonding causes higher risk of flaking off. This problem is more often observed on tiles from the 17th century.

Apart from those two extreme cases, a large number of samples exist with varying composition/workshop and period. This is indicated in figure 7 (open squares). All the samples show also variable quality and demonstrate the experimental approach used in Antwerp for tile production. However, it is clear that all samples with a good preserved glaze have a high Si and low Ca content.

Conclusion

This investigation reveals differences in manufacturing of ceramic tiles originating from a relatively short period of active majolica production in Antwerp during the 16th and 17th century. The adoption of different recipes suggests the presence of several majolica workshops in Antwerp that preferred different manufacturing methods and worked rather experimental. It has been proven that, during the 17th century, potters tried to modify the composition and preparation of the ceramic body, probably in order to improve the quality of the final product. Nevertheless, our observations and analysis indicate that this practice did not always lead to a more durable product. This conclusion is based on the study of the intermediate layer. This study is the first assessment of the relationship between manufacturing and production defects of majolica tiles, which is of concern for conservation. Essentially two types of points for attention were identified on these tiles: crazing and loss of glaze. Crazing results in channels from the surface through the glaze down to the body. It is necessary to be careful with those tiles during cleaning. This defect is observed mainly on 16th century tiles. The other point for attention is loss of glaze and is seen

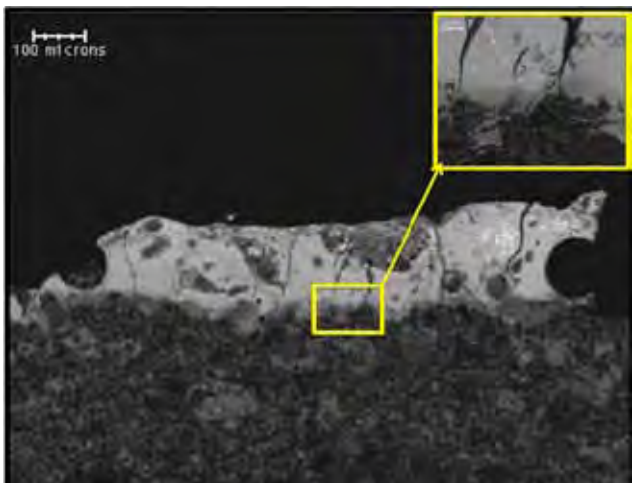

Fig. 8. Backscattered scanning electron microscope image of the cross-section of sample number A117/7/T2 (Steenhouwersvest, 1556–1562), showing crazing throughout the entire glaze layer (about 200 µm). In the right corner, a detail is shown from the lower region of the cracks and a well-fused glaze (Photo: M. Vandevijvere).

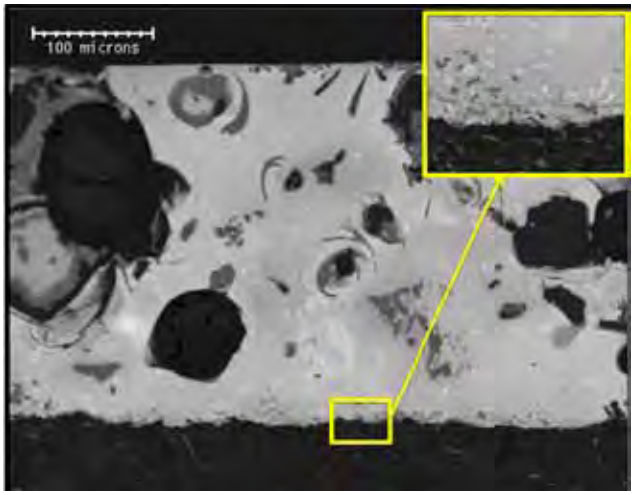

Fig. 9. Backscattered scanning electron microscope image of the cross-section of sample number A152/6/M7 (Schoyestraat, 1590–1613), showing a lot of inclusions in the glaze layer and a sharp transition to the intermediate layer (Photo: M. Vandevijvere).

only on 17th century tiles with a whitish and high-lime body. This group of tiles need more attention and demand controlled environment conditions and consolidation. It has been observed that majolica tiles from the later period are more fragile and prone to deterioration. Since the glaze is the pictorial layer of the ceramic object, it is important both stylistically and with regards to the art historical interpretation. This research has proven that μ-XRF and SEM-EDS analyses represent a valuable approach in characterising degradation and manufacturing features of majolica.

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Richly Decorated Pottery from Apollonia Pontica (4th Century B.C.) – Technical Study, Damage Phenomena, and Approach to Conservation

Daniela Cherneva

Keywords:
polychrome ceramics; archaeological ceramics; conservation strategy

Abstract

The richly decorated pottery found during the archaeological excavations of the ancient necropolis of Apollonia Pontica dates from the 4th century B.C. and can be classified as red-figure ceramics with polychromatic decoration and gilding. By determining a number of physical and chemical parameters of the materials, data could be obtained on the technological characteristics of the pottery. The conservation problems that needed to be solved were a result of the manufacturing technology, as well as the damage that resulted from long-term burial. Of central importance to the susceptibility for damage were the different clay types used for the ceramic body and decoration, as well as the techniques used for in-fired decoration. A conservation strategy was developed based on the results of the analyses. The conservation methods were defined respecting the original materials and involved minimum treatment with chemical agents.

Introduction

During archaeological excavations of the necropolis of Apollonia Pontica at Sozopol on the Bulgarian Black Sea coast (Hermary and others 2010), pottery was excavated that suffered various conservation problems that were difficult to solve due to a lack of archaeometric and technological information. The artefacts included different ancient vessels of utilitarian function and were dated to the 4th century B.C. These were mainly vessels intended for storing liquids such as *oinochoai*, *pelikai*, and *hydriai*, the most numerous objects being *lekythoi*. The diameter of the base of the vessels ranged from 6 to 14 cm, the height from 8 to 40 cm, and the thickness of the wall from 0.15 to 0.8 cm. These vessels were used as grave gifts in burial rituals and were characteristic in their diversity of style. Most of the vessels were decorated with embossed ornaments. Some types of decoration were added with clay before firing. The vessels were then partially coloured and gilded (figure 1). Stylistically, this pottery was considered to have developed from the ancient red-figure vase, enriched with polychromatic decoration and gilding, belonging to the Kerch style (Blavatskij 1953).

Approximately 95 artefacts of this type were found during the last stage of the excavations (1996–2008), many of which have as yet not been published.

The aim of this study was to create a strategy for the conservation of the richly decorated ancient pottery. In order to achieve this, a detailed examination was made of its

Fig. 1. Decorated surface of lekythos No. 5518, Grave 65, 2007, before conservation (Photo: A. Vatov).

production technology, chemical composition, and structure. The technological preconditions for deterioration and the influence of the soil on the pottery were also studied.

Analytical Methods

The condition of each object was assessed immediately after arrival at the laboratory. Non-destructive testing techniques were applied in order to preserve the original material; where samples were taken, these were kept to a minimum where possible.

Initially each object was observed under ultraviolet and infrared light. This method enabled the localisation of the colour coatings, the drawings, and the heterogeneous deposits on the surface of the vessel, as well as some organic substances.

Microscopic observations (MO) were made using an optical microscope (Stemi 2000; Carl Zeiss®), as well as a digital optical microscope (VHX-100; Keyence®). For the study of technological features, microscopic images of polished cross-sections were obtained using an oil immersion objective.

Qualitative chemical analysis of the pottery and decoration was achieved using X-ray fluorescence analysis (XRF) and an energy dispersive X-ray fluorescence spectrometer (EDX 720). X-ray diffraction (XRD) was used to determine the phase composition of the ceramic material and the polychrome decoration, and was performed with a TUR-M62 model providing Bragg–Brentano geometry and computer control of the goniometer HZG-3 and Co-K radiation. For the analysis, fragments were selected that were not significant for the restoration of the vessels.

Scanning electron microscopy (SEM) was performed with a scanning electron microscope (Philips 515) to study the surface structure. An X-ray micro-analyser (SEM-ERMA) was applied to test the chemical and physical nature of the various materials included in the ceramics: ceramic materials, pigments, and metal decoration data were acquired with a JEOL JSM 35 CF, equipped with a Tracor Northern TN/2000 energy dispersive X-ray analyser.

For the analysis of organic compounds, micro-analytical chemical methods and thin layer chromatography (TLC) were applied.

The morphology of the surfaces was investigated using atomic force microscopy (AFM) using a Nanosurf® Easyscan 2, with a Budgetsensors® Tap 190 Al G working needle with a working surface of 49x49 µm and image resolution of 256 dots per line. This method provided information on the degree of erosion of the ceramic surface. As the method could be destructive, fragments were chosen for analysis.

In order to determine the technological properties of the ceramic (the physical properties of the thermally treated ceramic body), the degree of sintered density and porosity as well as other measurements, analyses were performed at the University of Chemical Technology and Metallurgy in Sofia.

The study of the environmental influence on the finds included the analysis of heterogeneous deposits on the surface. To do this, soil deposits were mechanically removed from the ceramic surface using wooden spatulas and soft brushes. In order to determine the type of the salts present in the water extracted from the soil deposits, semi-quantitative analyses were performed using colorimetric test strips (Merck®). In some cases, samples of the soil deposits as water suspensions were also analysed using inductively coupled plasma optic emission spectroscopy (ICP-OES). In addition, an optic emission spectrometer (Varian Vista MPX CCD Simultaneous) was used. The ionic strength of the soil solutions and the pH of the soil environment were determined using a Hanna® combined pH and conductivity meter.

Technological Characteristics of the Ceramics

The data collected from the analyses allowed us to characterise certain specific features of the polychrome pottery.

Characterisation of the Ceramic Body

Potteries from the necropolis were prepared using low-firing red clay. The clay most probably underwent special pre-treatment and fractionation by washing and sedimentation. Red-firing clay rich in Fe_2O_3 was used, which was evident from the increased content in the studied specimens. The average Fe_2O_3 content in usual types of clay is 5–8 mass% (Bachvarov and others 2003), while XRF data showed that Fe_2O_3 in the studied objects was from 23 to 36 mass%. Phase differences in individual samples established by XRD suggested different origins of the pottery – being either imported or locally produced (Pavlova, Cherneva, and Velinov 2013).

The degree of sintering was assessed by measuring the density, including water absorption, apparent density, and porosity. To determine these parameters, fragments without decoration were selected from various artefacts. In order to remove the heterogeneous deposits from the pores in the ceramics, these fragments were pre-treated with solutions of

chelating agents (ethylenediaminetetraacetic acid [EDTA] and sodium hexametaphosphate) and de-ionised water. Samples that were thought to be from imported ceramics displayed water absorption from 23.2 to 26.7 wt%, their apparent density ranged from 1.4 to 1.6 g/cm^3, and their apparent porosity from 43 to 36%. In samples of domestic ceramics, water absorption ranged from 32.7 to 34.7 wt%, apparent density from 1.3 to 1.4 g/cm^3, and apparent porosity from 47.1 to 45.8%. All investigated ceramic samples showed high water absorption and a low degree of sintering, which suggests firing at a low temperature at about 900°C. The samples of imported ceramics were more sintered than those considered to be manufactured in Apollonia.

Decoration of the Pottery in Red, Black, and White

According to known ancient technology, the black gloss (sintered slip) was made from the same initial clay as the ceramic body, while the white surface decorative layer was made from kaolin (slip). The red figures on the surface are enclosed by a clay slip that becomes black and glossy during firing. These surface layers were analysed to clarify the differences between them using XRF, XRD, and SEM.
Although the red and black glosses were produced from the same initial clay source, differences were detected in their chemical composition and structure. The difference in colour is due to the technological features of their production: the selection of clay of a certain mineral composition, the specific treatment of the clay, and the change in furnace environment during firing. The clay slip used for the black gloss was produced from the fine fraction with a particle size < 5 µm, to which basic compounds were added containing Na^+ or K^+ ions, which contributed to the dense sintering of the applied slurry layer in reduction atmosphere at 850–900°C (Noble 1988). SEM revealed that the black gloss featured a smooth homogenous surface of a high density. In some areas, single crystal inclusions were registered (figure 2(A)). The structure of the red surface was homogeneous, having few pores and no obvious crystals (figure 2(B)).
Compared to the black gloss, the white kaolin coating was not homogeneous; it was coarser and its surface was not smooth (figure 2(C)). Different qualities of the kaolin coating were observed in the individual objects. In some cases, the kaolin layer was smooth, consisting of small colloidal particles, while in other cases the white coating was uneven and contained larger particles. Occasionally, a pink colour was seen, which was a result of adding hematite to the kaolin.
The clay used to produce the red decoration had a high Fe_2O_3 content, confirmed by XRF analysis. To give an example, the content of Fe_2O_3 in the red coating of an *oinochoe* (Field Inventory No. 50, 1995) was 35 mass%, while its content in the ceramic body was 24 mass%. Pigments based on iron oxides were added later to the diluted clay suspensions. Such coatings, which result in an intense red colour on the ceramic surface, are known as '*velaturas*' (or diffusion layers). Decoration with the clay coatings was completed before firing, as each colour component was produced by special processing of the raw material.

Embossed Decoration

The most popular relief decoration found on the Apollonian red-figure pottery was made using the *barbotine* technique. In order to obtain embossed ornaments, dense clay slip (highly concentrated homogeneous suspension of clay) derived from the ceramic body was applied. The ornaments were created before firing by dropping or repeatedly brushing the slip on pre-made contour drawings. This type of decoration is only loosely adhered to the surface of pottery, especially on the black gloss surface, and it could be easily separated.

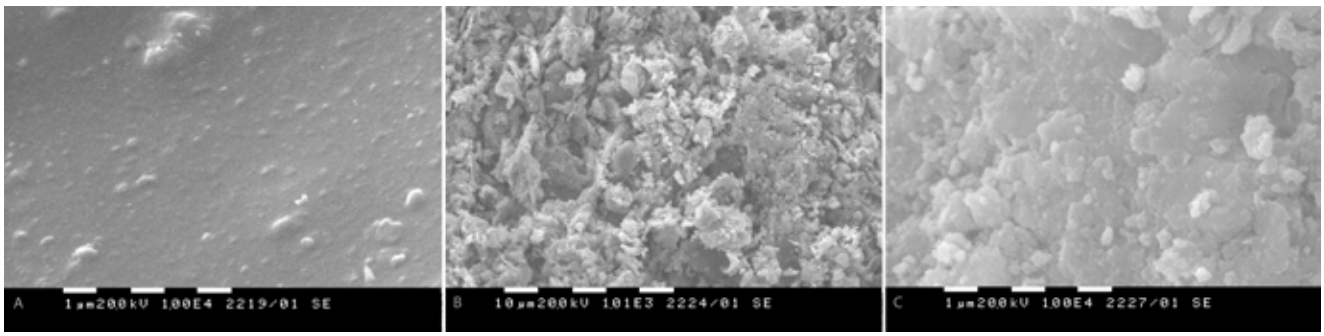

Fig. 2. SEM images (x5000): (A: left) black gloss; (B: middle) ceramic body; (C: right) white kaolin layer (Photo: G. Maleshkova).

On almost all clay vessels with colourful decoration, the gilded relief reproduced attributes of clothing on the figures, as was the case on the decorative ornaments of the friezes.
A relatively less common technique was to create a relief image in a matrix applied on the surface of the vessels, mostly *lekythoi*. In earlier archaeological studies of Apollonia Pontica, they found eight *lekythoi* decorated with embossed figurative compositions.
Colour coatings (using pigments) were applied after firing and gilding. All such vessels were used as part of funerary practice, and the decorations and figurative compositions had special meaning or conveyed particular messages. Technological features determining this type of ceramic included polychrome painting and partial gilding after firing, also called 'cold painting'. Such colourants were prepared from pigments with organic binders. Ancient authors indicated that various rubber plant extracts, honey, and glair were used for this purpose (Sharenkov 1988). In our study, it was not possible to determine which organic material had been used as a binder.

Colouration and Gilding

The palette of pigments used was rich, containing red, yellow, blue, and green in different hues and intensities. The red colouration was achieved using cinnabar (HgS) and hematite (Fe_2O_3). Yellow was obtained with ochre (Fe_2O_3) and orpiment (As_4S_6). The blue coating contained Egyptian blue (cuprorivaite $CaCuSi_4O_{10}$), and lighter nuances of blue were achieved by whitening the Egyptian blue with kaolin $Al_4[Si_4O_{10}](OH)_8$. The green colour was attained using malachite ($Cu_2CO_3(OH)_2$) or some iron-containing minerals, or created optically by mixing ochre with Egyptian blue. These pigments were identified on the samples by using XRF and XRD. It was also established that there were differences in the quality of the colour coatings that had different grit sizes, thickness, uniformity, and colour intensity. Most of the coatings had a granular powder-like structure, and their uneven density led in many cases to dissociation between the coloured layer and the ceramic surface, as revealed by microscopic examination.
Studies of the gold decoration found four different techniques of application. Thin metal foil from 1.5 to 8 µm of approximately 22 carat gold was used for gilding. In one case, the use of glair as an adhesive was determined by micro-chemical analysis and TLC. Gold was laid without heat treatment on the selected ornaments on top of the pre-applied layer of red clay suspension. In another case, the use of an organic dye (alizarin) as colouring agent was defined (Nikolova 2010). In a few vessels, gold foil was laid on a kaolin layer or colour pigment (ochre) under-layer. Most commonly, the gold foil was cut in advance into desired shapes and was then applied directly onto the ceramic surface. According to literature sources, glair, animal glue, isinglass, and rubber plant extract were used as adhesives (Lapatin and others 2008). During this study, the presence of such organic material used as a glue was not detected.

Technological Pre-conditions for Deterioration

Each ceramic vessel presents a complex multi-component system of materials with different physical and chemical parameters. As a whole, this structure may not have high mechanical strength or a good adhesion between the individual layers. The tensile strength, compressive strength, and other mechanical stresses depend on the production technology.
Vessels for which the degree of sintering was lower (temperature range between 850 and 900°C) or products with higher volume and thin walls are characterised by lower mechanical resistance. Manufacturing defects cause stress and microcracks in the structure, which reduces its strength. Most ceramics from archaeological excavations were found with a significant degree of fragmentation.
In the fragments of artefacts with an apparent average degree of surface degradation, the morphology of the red ceramic surface and the black gloss was studied using AFM. An irregular structure of the surface was revealed (figure 3). The red ceramic surfaces were more uneven and rougher. Surface roughness increases the contact area, which is a prerequisite for an increase in influence of environmental factors. On the artefacts themselves, the soil deposits attached most firmly on the red sections. The black surface is less rough. Furthermore, the more highly sintered black layer increases the structural strength of the objects due to the fact that it fills the micro-cracks and open pores in the ceramic material. The red clay surface is porous and, compared to black surfaces, it absorbs much more water, which makes it vulnerable to physical and chemical attack when buried.
The red ceramic body showed good resistance to the environmental conditions compared with the white kaolin layer (figure 4). With vessels that were of lower quality of production, the kaolin layer was incomplete and there were more

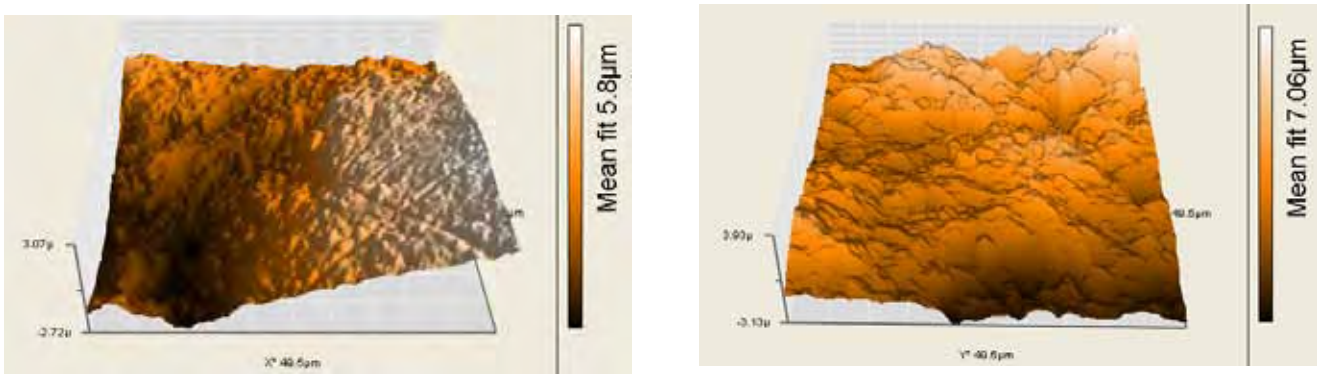

Fig. 3. AFM, 3D-images: (left) black gloss surface; (right) red ceramic surface (Photo: S. Kogucharov).

cracks and lacunas in it. This can be explained by differences in mineral composition and the different properties of iron-rich and kaolinite clays that influence the level of sintering at different temperatures.

The embossed decoration on the kaolin layer demonstrates better cohesion as well as adhesion to the ceramic body as compared with the coloured coating pigments. The pigments in the painted decoration have been reduced to powder due to the loss of the organic binder that dissolved in the buried environment. In the gilded artefacts, the gold foil remained fixed in place by electrostatic forces and heterogeneous deposits (figure 1).

Because the process of manufacturing of antique ceramics was so refined, the quality of the finished product was determined largely by the individual skill of the potter. Since the ceramic of the Kerch style was a complex combination of different materials (ceramic body, black slip layer, decoration with mineral paints and gilding), their stability was determined by the strength of the weakest component. In this case, the weakest components were the painted layers and gilding that had been applied after firing. Each product was therefore characterised by the individual technological parameters that existed within the specified type of ceramic.

Fig. 4. Degradation of white kaolin layer (photomicrograph x25) (Photo: P. Bonev).

The Influence of the Soil

There are numerous factors that influence the degradation of ceramic materials in a buried environment. In the case of pottery from Apollonia, it is necessary to consider the coastal location of the ancient necropolis, resulting in problems with salt solutions, water, and biological factors. The condition of each object depends on the properties of the surrounding environment.

The heterogeneous soil deposits on the surfaces of certain objects were analysed. A representative sample was taken of deposits at different spots on the surface of each vessel. Water extractions were prepared from each sample of 10 g soil in 50 ml de-ionised water. The ICP-AES results were obtained individually for each artefact. As an example, the analyses of samples from two separate finds are given in table 1.

Concentrations of chlorides and sulphates were lower than the average for this type of soil (Kauricheva 1973). The results obtained with Merck® colorimetric test strips indicated the presence of chlorine, sulphate, carbonates, and traces of nitrate ions. The measured pH ranged from 6.2 to 8. The environment influenced individually each finding, and revealing this influence was necessary for effective conservation treatment. For example, the study of heterogeneous deposits in a polychromatic *lekythos* (field inventory No. 5518, Grave 65 from 2007; figure 5) revealed the

	Ca	K	Mg	Na	SO_4	Cl
lekythos No. 5518 (Grave 65 from 2007)	435	55	41	177	143	161
lekythos No. 4269 (from 2006)	1249	44	88	700	708	136

Table 1. Composition of soil from two finds (mg/l of soil suspension); data obtained by ICP-OES.

Fig. 5. Fragmentation of the ceramic body of lekythos No. 5518, Grave 65, 2007, before conservation (Photo: A. Vatov).

presence of sulphates in quantities less than 200 mg/l, the presence of chloride in a quantity less than 500 mg/l, and carbonates. The soil environment is slightly acidic with pH value of 6.2. This knowledge influenced the considered approaches to cleaning aimed at reducing the harmful action of salts in the ceramic structure.

Damage Classification

The damages on excavated ceramics were assessed both visually and under a microscope and could be classified into five groups: (1) a significant degree of fragmentation of the ceramics with formation of many macro- and micro-cracks in the structure resulting in reduced strength of the ceramic body; (2) delamination and disintegration of the ceramic due to crystallisation of salts in pores and spaces between the layers as a result of how the clay was worked; this could also cause disintegration of ceramic body (figure 6); (3) uneven deposition of heterogeneous products and salt crystals within the ceramic body and different decoration layers; this led to splitting, separation and loss of black gloss and red ceramic surface material, often resulting in peeled spots (figure 7); (4) disintegration (at micro and macro level) and significant losses in the painted layers (figure 1); and (5) deformation and fragmentation of gold leaf, separation from the substrate, and material losses.

The damages listed above were caused by the particular character of the soil environment. The archaeological site is very near to the sea, with sandy soil that is very permeable and well drained. Each find reacted differently to the environment, resulting in a variation in types and degrees of damage on different areas of the objects.

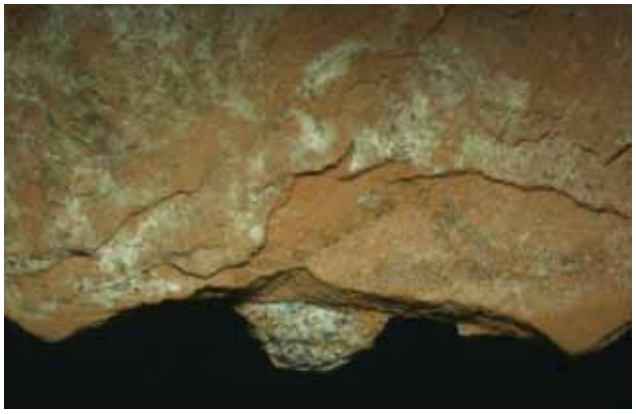

Fig. 6. Characteristic degradation of the ceramic shard, caused by salts (photomicrograph x25) (Photo: Pl. Bonev).

Fig. 7. Characteristic damages of red-figure surface (Photo: D. Cherneva).

Conservation Strategy

The results of the research were used to develop a conservation strategy. The aim was to enhance the strength of the materials (both their cohesion and adhesion) and to reveal the polychromatic decoration as far as possible with limited use of chemical agents.

The conservation methods and the materials to be used were selected according to the type and the condition of the various materials found in an object, as well as its condition. The choice of materials and techniques was also in conformance with the requirements of best conservation practice (Buys and Oakley 1993).

Preventative measures for the preservation of the artefacts should be taken immediately on discovery. A method for 'safe lifting' of finds has been developed during the joint field work of archaeologists and conservators. The decorated vessels are packed in situ together with the adjacent soil and are transported to the laboratory in appropriate protective containers.

In the laboratory, an initial visual inspection is undertaken, and a diagnosis of the condition is made and documentation completed. At this point it is decided if and which kind of samples need to be taken.

Priority is given to the preservation of the decoration – the various colour coatings and the gilt, which are the most susceptible elements of the object. For this reason, the initial treatments are aimed at removing the soil deposits from the outer surface of the vessel or of each fragment. The application of chelating agents is limited to the deposits, and the action of the chemicals is restricted by applying them as water solutions in gels.

The use of sequestering agents for treatment of the ceramic objects is avoided. The aqueous solutions of chelating agents could react vigorously with salt deposits in the porous structure of the ceramics, possibly resulting in new damage. This is especially valid for the decorations in which such reactions may lead to severe losses.

Semi-dry and mechanical cleaning methods are applied for the removal of heterogeneous deposits from the painted decoration layers after careful assessment of risk for individual parts of the object.

The next important step was to improve the adhesion of the decorative layers to the ceramic surface. Solutions of Paraloid B-72 (3–4 wt% in acetone) were applied in most cases, as recommended in conservation practice (Koob 1991). The deformation of the gold foil was treated by a dry soft brush and adhered with the same solution.

Cotton swab compresses with de-ionised water were found to be the most appropriate for salts extraction from ceramic vessels. This treatment was limited to the parts without colour decoration. The rate of de-salination could be calculated using conductivity meters (Ellis, Derrick, and Newman 2007).

The consolidation of the ceramic body (or fragments) was carefully controlled, sometimes starting on the inner ceramic surface, and being limited locally to the spots that required treatment. Solutions of 3–5 wt% Paraloid B-72 in organic solvents were applied.

The extent and the method of reconstruction of a vessel in cases of fragmented finds depend on the preservation of the original material. Paraloid B-72 dissolved in acetone in concentration of 45–50 wt% was used as an adhesive.

Choices concerning the reconstruction of missing parts were made individually for each object. A plastic paste was prepared from an 8% solution of polyvinyl alcohol in de-ionised water mixed with a filling material (limestone). The mixture could be coloured by adding iron oxide pigment.

When determining the conservation strategy for the finds from Apollonia Pontica, their original appearance was taken

Fig. 8. Lekythos No. 5518, Grave 65, 2007, after treatment (Photo: K. Georgiev).

into consideration and emphasis was placed on preserving the colour decoration. In order to show the finest detail as well as the composition as a whole, the colours of the restored areas were adjusted. Retouching was carried out using acrylic paint in the same colour as the black gloss or a shade that was slightly lighter than the ceramic object. The final result of this work is shown in figure 8.

Conclusion

The investigation into the technological characteristics of these objects made it possible to define the typology and manufacturing type of the red-figured ceramics with polychromatic decoration and gilding that were produced from the 4th century B.C. and found in Apollonia Pontica.

It should be stressed that any conservation strategy must consider the technological specifications of the ceramic and the type of damages found on the objects. In our study, the nature of the decoration influenced the selection of the conservation methods, since conventional treatment was inapplicable. A principle of minimal chemical intervention was observed in order to preserve the original material when choosing conservation materials and methods.

Each ceramic vessel was assessed and treated as a unique complex of different materials, and the sequence of treatments was determined after a detailed investigation of the technology used for making of the object and the extent and type of damage it had undergone. The aesthetic integrity, the authentic decoration, and the condition of the objects were preserved by using only semi-dry and mechanical cleaning methods and by limiting the consolidation of the ceramic body to the inner surface. The coloured decoration and the gilding underwent exclusively micro-scale treatment.

The conserved and restored objects are now on display in the galleries of the Archaeological Museum in Sozopol and the National Museum of History in Sofia, Bulgaria.

Note

Various terms are used for the sintered slip layer that forms the red and black decoration on this type of pottery. The most common terms are gloss, glaze, and slip. The author has chosen to use the term 'gloss' as found in the following references: Noble 1998; Boardman 1997; Cohen and others 2006.

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Degradation and Treatment

The Browning Phenomenon on Stained-Glass Windows: Characterisation of the Degradation Layer and Evaluation of Selected Treatments

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Keywords

stained-glass windows; browning; manganese; treatment

Abstract

Mediaeval glasses usually contain a small amount of manganese that is considered to be involved in a deterioration process leading to the formation of brown stains. As a consequence, stained-glass windows lose their transparency. In the past, various chemical agents for the treatment of historical glasses have been proposed that have proved to be more or less successful. They were tested independently on different glasses and with different protocols, which lead to inconsistent results. This study focused on visual and chemical characterisations of degradation layers with an aim to optimise the diagnosis of darkened glasses. Furthermore, selected treatments and protocols were evaluated on small fragments of original glass. Two reducing agents (hydroxylamine hydrochloride and sodium hydrogen sulphite) performed the best in the tests and are currently being tested on limited areas of stained-glass windows.

Introduction

The main parameters determining glass deterioration involve the composition of the glass (intrinsic factor) and the exposure conditions (extrinsic factors). Mediaeval potash–lime silica glass is very sensitive to environmental conditions and is considered to be a low durable material. The weathering processes lead to the formation of a hydrated leached layer (depleted in alkali and alkaline-earth elements). Additional reactions, such as the formation of crusts, can occur and increase the opacity of windows. Even though the general degradation mechanism of stained-glass windows is known (Sterpenich 1998), questions still remain concerning the structure of opaque layers and the role played by specific elements such as manganese.

Manganese is assumed to play a key role in the darkening of historical glass (López and others 2002; Weber, Eggert, and Watkinson 2007). Glass may contain manganese, either as an impurity or as a deliberate addition into the glass batch. In the latter case, Mn is used either to colour the glass (colours ranging from brown–reddish to violet–purple) or in an attempt to obtain truly uncoloured glass by neutralising the greenish hue caused by the presence of iron (Geilmann and Bruckbauer 1954; Newton 1978; Davison 2001, p. 186). Glassmakers could obtain a wide range of colours by modifying the Mn/Fe ratio and controlling the amount of oxygen in the furnace (Mirti, Davit, and Gulmini 2002).

The darkening, which occurs in the gel layer of the glass, is generally assumed to be linked to Mn enrichment, but the formation process of the different stain features is still unclear. It is commonly suggested that Mn(II), present in the bulk glass, may be extracted from the silica network during the weathering process. Manganese is then oxidised and may precipitate as a dark insoluble compound (Mn(III), Mn(IV)) (Barbey, Sterpenich, and Libourel 1997; Watkinson, Anheuser, and Weber 2005; Weber, Eggert, and Watkinson 2007; Cagno and others 2011a and b; Schalm and others 2011). In specific examples of archaeological glasses, the browning was explained by an enrichment of iron (Weber, Eggert, and Watkinson 2007, p. 39). In one particular case, orange–brown spots occur beneath an apparently undamaged surface of glass. The content of manganese is depleted, disturbing the Mn/Fe equilibrium and thus suggesting that the

brown colour may be due to excess Fe_2O_3 (López and others 2002). In all these cases, the affected glass appears to be either brown or (in severe cases) black, causing a strong light absorption and affecting the legibility and the aesthetic quality of the windows.

Glass conservators and curators have requested a solution to this problem, and thus the diagnosis and the assessments of treatments of such artworks have become essential. The limited number of studies on treatments in the literature have proposed the application of reducing solutions to reverse the browning process by converting the oxidised manganese into a lower (colourless) state of oxidation (Pinto 1991; Cagno and others 2011a and b). Up to now, research had involved some glass samples and windows being treated with different reducing agents (for a review, see Venault de Bourleuf 2012). The agents most commonly used for stained-glass windows were hydrazine or BDG 86 Azzurro® (a commercially available hydrazine-containing mixture) (Fitz 1981; Müller and others 1986; Pinto 1991; Pinto 1997; Müller 1999; Pivet 2000; Müller 2002; Küpper 2003; Vincent-Petit 2006), sodium hydrogen sulphite (Bettembourg and Pivet 1992; Pinto 1997; Pivet 2000; Vincent-Petit 2006), oxalic acid (Bettembourg and Pivet 1992; Pinto 1997), and potassium iodide (Pinto 1991; Bettembourg and Pivet 1992; Pinto 1997). Hydroxylamine hydrochloride and hydroquinone were used on archaeological glasses (Cagno and others 2011a and b).

Despite the research referenced above, no satisfactory treatments have been found. The results are inconsistent, depending on several parameters (the glass type used for testing, protocols of application, pH values, or concentration of the solutions). Moreover, questions remain concerning the risk of immediate or long-term degradation of the glass. In some studies, the risk of damage of the glass has been highlighted (Cagno and others 2011a and b) and it was reported that the browning occurred again after some years (Müller 2002). The present work aims to investigate the effect of chemicals that can reduce the oxidised state of manganese. The study was performed on a set of window fragments. In a preparatory phase of the project, the six aforesaid chemicals described in the literature except hydrazine were tested. The three most effective chemicals (hydroxylamine hydrochloride, sodium hydrogen sulphite, and BDG 86 Azzurro®) were selected for further evaluation, as presented below.

Material and Methods

Sampling

This project benefited from sampling authorisation on ancient glasses selected among a set of twenty-two glass pieces spanning from the 13th to the 16th century. The samples were provided by various French and English workshops. Results from two colourless samples will be highlighted in this paper:

- Notre-Dame church of Kernascléden (KERN, 16th century);
- Saint-Thurien church of Plogonnec (PLOG, 15th century).

Experimental Techniques

Each glass was submitted to microscopic observation (in transmitted and reflected light). Small samples were subsequently taken, embedded in epoxy resin (Hardclear H59, SODEMI), cut, and polished. A multi-analytical approach was used in order to obtain information on the distribution, the morphology, the colour, and the composition of the darkened layer, before and after treatment. Samples were first observed with an optical microscope (Leica DM-RM). Further, backscattered electron images (BEI) were collected with a scanning electron microscope (SEM, type JEOL JSM 5600 LV). The electron beam was generated by a tungsten filament with an accelerating voltage of 15 kV. X-ray semi-quantitative maps were recorded by energy dispersive X-ray spectrometry (EDX, equipment type Oxford 6587) under low vacuum (17 Pa). Cross-sections were carbon coated (to increase conductivity), enabling quantitative analyses with a microbeam electron microprobe at the CAMPARIS analytical facility of the Universities of Paris VI with a CAMECA SX 100. The column conditions were set to 30 kV and 5 nA. The samples were analysed for 5 seconds/element in order to increase the probed volume and to minimise possible alkali evaporation. The X-ray intensities were corrected for dead-time background and matrix effects using the Pouchou and Pichoir (1984) routine. The composition of the bulk glass is normally given in wt% of oxides. However, in order to better compare the content of the different elements in the bulk glass, the gel layer, and brown areas whose total masses changed due to leaching and hydration, atomic percentages are calculated. For the weathered layer (with and without browning), the conversion has been done assuming that water was the missing oxide to reach 100 wt%. Ten measurements were averaged for the bulk glass. Several measurements are reported for the gel layer; but cannot be averaged due to the heterogeneity of this area.

Methods and Materials Selected for Treatment

Three chemicals, rated as appropriate in previous tests, were investigated:

- hydroxylamine hydrochloride (CHHY)
- sodium hydrogen sulphite (HS)
- BDG 86 Azzurro® (BDG).

For each chemical, two concentrations were tested (5 wt% and 10 wt% of reagent in water) with two different pH values. To minimise damage on the glass, a neutral pH would be best. For comparison, a pH value of 5 was also chosen: this is theoretically more effective and it was often tested during previous studies with satisfactory results (Bettembourg and Pivet 1992; Pivet 2000). The initially acidic pH of two solutions (CHHY: pH = 2 and HS: pH = 3.5) was adjusted with NaOH.

In conservation practice, chemicals may be applied using different methods: total immersion of an object in a given solution (considered to be a drastic intervention), vapour exposure, and applications of a gel or poultice soaked with the solutions. From a practical point of view, the last two options seem to be the most suitable, enabling the restriction of the application to a small area. The immersion of samples makes treatment difficult to control and may result in the leaching of various other elements together with manganese (Cagno and others 2011a and b). For this reason, soaked poultices were chosen for all tests and prepared with three layers of absorbent paper (cellulose base). The poultices were covered with a cling film (polyethylene) to slow down the evaporation process. Treatments were performed for 3 hours. Every hour, the poultices were changed after the pH value was checked. An intermediate and thorough rinsing was carried out using de-ionised water and then ethanol soaked cotton wool swabs were rolled over the glass surface. Treatments were performed on representative pieces providing sufficient surface area (about 6 cm²) to compare the results. Digital photographs and photomicrographs were taken every hour in transmitted and reflected light. At the end of the treatment, cross-sections of treated glass were prepared in order to observe in depth the colour and the chemical changes of the brown areas. In parallel, poultices were directly applied on cross-sections made of untreated glass so that the same area could be compared before and after treatment.

Results and Discussion

Morphology of the Degradation Layer

Small dark spots, localised or wide spread, interspersed both surfaces of the fragments. Two categories of patterns have been distinguished and are described as type I (figure 1) and type II (figure 2). These types (especially type II) have been previously reported for archaeological glasses (Geilmann 1956; Sterpenich 1998; Watkinson, Anheuser, and Weber 2005; Weber, Eggert, and Watkinson 2007; Cagno and others 2011a and b; Schalm and others 2011).

Type I is the most commonly found for stained-glass windows, and all our samples (except PLOG) have been classified in this category. A weathered glass, without browning, is usually whitish (left side of the surface in figure 1(b)). At a microscopic scale, it can be seen to consist of lamellae in which brown areas are visible (right side of the surface in figure 1(b) and figure 1(c)).

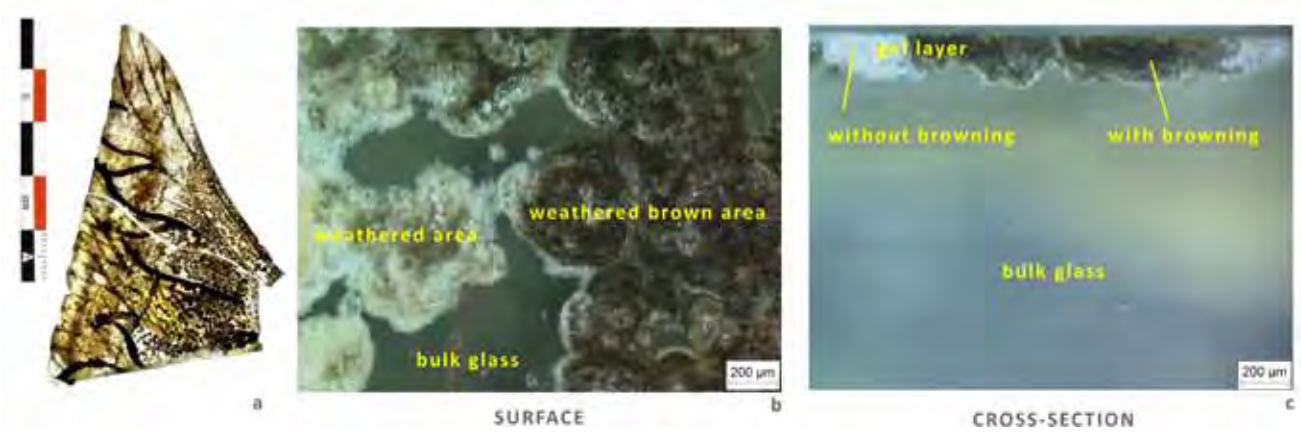


Fig. 1. KERN sample, type I (a). Photomicrographs (reflected light) showing the surface (b) and the corresponding cross-section (c) before treatment (Photos: © LRMH).

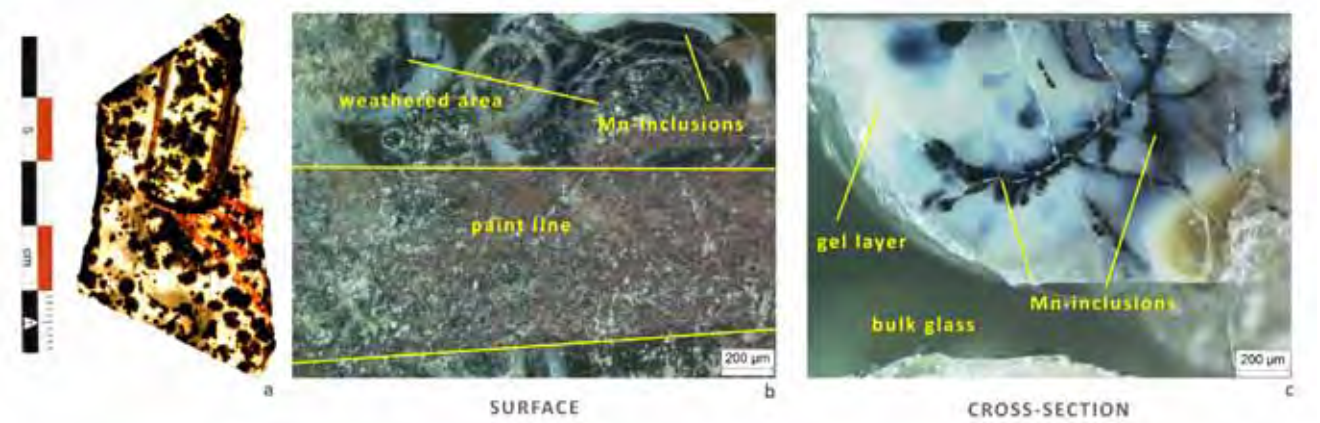


Fig. 2. PLOG sample, type II (a). Photomicrographs (reflected light) showing the surface (b) and the corresponding cross-section (c) before treatment (Photos: © LRMH).

Stains can be shaped as more or less concentric rings. Each ring may show slightly distinctive hues. The browning can range from very dense and dark brown to nearly black. In transmitted light, the brown stains are sometimes quite well defined, but can also be more 'fuzzy' in appearance. The size of the dark-brown spots ranges usually between a few tens of microns to a few hundred microns.

Some rare examples of in situ stained-glass windows are described as type II (Loisel and François 2005). In our batch of samples, only the PLOG sample can be classified in this category. Circular black lines or feathered-shapes are visible on the glass surface (figure 2(b)). Separate stain features develop through lamellar structures of the weathered glass. The cross-sectional image (figure 2(c)) suggests that the brown inclusions have a tree-like appearance (called dendrites), spreading out into the whitish laminated layers.

On all of the samples studied, the browning phenomenon was always restricted to the leached layer itself where the distribution of dark structures was heterogeneous. The bulk glass was not affected.

Chemical Characterisation

Seventeen samples were analysed and proved to be silica–lime–potash glasses (table 1). The MnO content ranged between 0.7 and 1.5 wt%, except for the coloured glasses (about 2.3 wt%). The compositions of the un-corroded glass, the leached layer, and the brown areas have been compared (table 2). The weathered layer was confirmed through the compositional changes such as a decrease of the glass modifiers (K^+, Na^+, Ca^{2+}, Mg^{2+}) as a result of the leaching process.

The bulk glass of PLOG sample contained, on average, a small amount of Mn (0.24 at.%) (table 2). In the whitish deteriorated area, the concentration was 0.02 at.%, while it is 1.97 at.% in the dark features. Manganese is thus seen to be completely depleted near the black spots, which, in contrast, are highly concentrated in Mn. While internal and external sources of manganese were mentioned to explain the browning phenomenon in archaeological glass, only internal accumulations can explain the browning observed on the present sample. The backscattered electron image (figure 3(f)) and EDX-mapping (figure 3(e)) allowed us to identify without doubt the Mn inclusions (bright area) in the leached layer (dark area). Only calcium and phosphorus were identified to have a correlation to manganese in the alteration layer.

The sound area of the KERN sample, which had been chosen to represent the type I group, displays a concentration of 0.30 at.% Mn (table 2). No dendritic structure could be distinguished in the dark-coloured zone using optical microscopy (figure 3(a)) or using SEM (figure 3(b) and (c)). Despite the dark colour of the gel layer, no enriched Mn inclusions could be observed. The chemical analyses (table 2) showed that the concentration of Mn in this area (about 0.3 at.%) is similar to the one measured in the bulk glass. The amount of Fe in KERN was also similar in the bulk glass and in the leached layer.

These results could suggest that the browning phenomenon is not always associated with a significant enrichment of manganese, as seen in the PLOG sample. In the case of the type I sample, it is most probable that microprobe analyses were not directly performed in a Mn-rich zone due to the difficulty to locate such small areas.

SAMPLES	Na_2O	MgO	SiO_2	Al_2O_3	P_2O_5	K_2O	CaO	TiO_2	Cr_2O_3	MnO	FeO	Cl	SO_2	F	TOTAL
FDAT1/ FOND D'ATELIER	4.5 ± 0.1	8.8 ± 0.1	53.6 ± 0.7	0.79 ± 0.07	2.9 ± 0.1	12.7 ± 0.1	12.3 ± 0.1	0.06 ± 0.06	0.03 ± 0.03	1.5 ± 0.1	0.31 ± 0.05	0.54 ± 0.04	0.07 ± 0.05	0.06 ± 0.05	98.1 ± 0.9
FDAT3/ OND D'ATELIER	3.7 ± 0.2	7.6 ± 0.1	55.6 ± 0.4	1.52 ± 0.05	3.7 ± 0.1	10.5 ± 0.2	14.5 ± 0.2	0.12 ± 0.06	0.03 ± 0.04	0.8 ± 0.1	0.52 ± 0.03	0.51 ± 0.04	0.15 ± 0.05	0.02 ± 0.03	99.4 ± 0.5
FDAT4/ FOND D'ATELIER	3.6 ± 0.2	7.4 ± 0.1	55.1 ± 0.4	1.47 ± 0.03	3.8 ± 0.1	10.3 ± 0.1	14.9 ± 0.2	0.15 ± 0.05	0.01 ± 0.02	0.8 ± 0.1	0.55 ± 0.07	0.57 ± 0.06	0.13 ± 0.05	0.04 ± 0.03	98.8 ± 0.5
FDAT5/ FOND D'ATELIER	4.7 ± 0.1	8.2 ± 0.1	53.5 ± 0.5	1.35 ± 0.04	4.3 ± 0.1	10.8 ± 0.1	13.7 ± 0.1	0.15 ± 0.09	0.02 ± 0.03	0.7 ± 0.1	0.5 ± 0.1	0.56 ± 0.03	0.16 ± 0.04	0.08 ± 0.06	98.8 ± 0.8
GUEN/ GUENGAT	3.3 ± 0.1	7.1 ± 0.1	53.5 ± 0.4	1.09 ± 0.08	3.7 ± 0.1	14.6 ± 0.2	12.9 ± 0.2	0.12 ± 0.07	0.01 ± 0.02	1.1 ± 0.1	0.60 ± 0.06	0.47 ± 0.04	0.12 ± 0.06	0.13 ± 0.06	98.9 ± 0.7
INCO1/ INCONNU	3.9 ± 0.1	4.1 ± 0.1	55.3 ± 0.6	3.02 ± 0.06	3.2 ± 0.1	5.0 ± 0.1	20.6 ± 0.3	0.23 ± 0.08	0.04 ± 0.06	0.9 ± 0.1	0.92 ± 0.09	0.60 ± 0.06	0.17 ± 0.04	0.08 ± 0.09	98.0 ± 0.9
KERN1/ KERNASCLÉDEN	6.4 ± 0.1	9.6 ± 0.2	53.0 ± 0.5	1.36 ± 0.04	2.4 ± 0.1	11.5 ± 0.1	12.0 ± 0.2	0.11 ± 0.06	0.02 ± 0.06	1.2 ± 0.1	0.46 ± 0.09	0.44 ± 0.03	0.07 ± 0.03	0.09 ± 0.06	98.7 ± 0.6
KERN2/ KERNASCLÉDEN	4.8 ± 0.1	8.2 ± 0.1	52.9 ± 0.3	1.3 ± 0.1	2.8 ± 0.1	14.4 ± 0.2	12.5 ± 0.2	0.12 ± 0.08	0.02 ± 0.03	1.3 ± 0.1	0.41 ± 0.06	0.41 ± 0.06	0.07 ± 0.03	0.08 ± 0.06	99.4 ± 0.3
KERN3/ KERNASCLÉDEN	6.7 ± 0.1	9.6 ± 0.2	48.8 ± 1.1	1.16 ± 0.07	2.3 ± 0.1	11.4 ± 0.2	11.8 ± 0.2	0.13 ± 0.09	0.01 ± 0.01	1.1 ± 0.1	0.37 ± 0.07	0.39 ± 0.05	0.09 ± 0.04	0.10 ± 0.07	94.1 ± 1.5
KERN4/ KERNASCLÉDEN	6.8 ± 0.1	9.4 ± 0.1	53.4 ± 0.4	1.21 ± 0.06	2.7 ± 0.1	11.5 ± 0.2	12.3 ± 0.1	0.08 ± 0.08	0.02 ± 0.02	1.1 ± 0.1	0.35 ± 0.06	0.36 ± 0.04	0.13 ± 0.04	0.09 ± 0.05	99.6 ± 0.6
LANN/ LANNÉLEC	3.8 ± 0.1	7.4 ± 0.1	52.7 ± 0.3	1.09 ± 0.06	4.0 ± 0.1	14.7 ± 0.1	13.0 ± 0.2	0.14 ± 0.06	0.03 ± 0.05	1.1 ± 0.1	0.6 ± 0.1	0.51 ± 0.06	0.13 ± 0.05	0.1 ± 0.1	99.2 ± 0.4
LINC/ LINCOLN	6.6 ± 0.2	9.6 ± 0.1	49.8 ± 0.3	1.07 ± 0.05	4.9 ± 0.1	10.7 ± 0.3	14.2 ± 0.2	0.05 ± 0.05	0.02 ± 0.02	1.4 ± 0.1	0.41 ± 0.05	0.50 ± 0.02	0.10 ± 0.06	0.02 ± 0.02	99.5 ± 0.6
PENI/ PÉNITY	2.4 ± 0.1	7.1 ± 0.1	55.1 ± 0.5	0.75 ± 0.04	2.6 ± 0.1	14.6 ± 0.1	12.1 ± 0.2	0.09 ± 0.05	0.04 ± 0.03	1.3 ± 0.1	0.35 ± 0.06	0.53 ± 0.04	0.09 ± 0.04	0.10 ± 0.04	97.3 ± 0.6
PERG1/ PERGUET	1.5 ± 0.1	4.3 ± 0.1	56.9 ± 0.5	3.1 ± 0.1	2.9 ± 0.1	7.3 ± 0.1	20.0 ± 0.2	0.25 ± 0.09	0.03 ± 0.04	1.0 ± 0.1	0.9 ± 0.1	0.24 ± 0.04	0.13 ± 0.06	0.10 ± 0.08	98.7 ± 0.6
PLOG/ PLOGONNEC	3.2 ± 0.1	7.5 ± 0.1	55.6 ± 0.5	1.27 ± 0.07	3.8 ± 0.1	10.6 ± 0.3	15.9 ± 0.2	0.11 ± 0.09	0.01 ± 0.03	0.8 ± 0.1	0.50 ± 0.09	0.47 ± 0.02	0.11 ± 0.04	0.03 ± 0.03	99.8 ± 0.4
ROSC/ ROSCUDON	3.8 ± 0.2	7.6 ± 0.3	52.5 ± 1.0	1.18 ± 0.05	4.1 ± 0.1	12.4 ± 0.5	13.8 ± 0.4	0.11 ± 0.08	0.03 ± 0.04	2.6 ± 1.6	0.6 ± 0.2	0.48 ± 0.08	0.09 ± 0.03	0.03 ± 0.04	99.3 ± 0.8
TOUR/ TOURCH	0.32 ± 0.04	3.7 ± 0.1	56.5 ± 0.5	3.14 ± 0.06	1.3 ± 0.1	10.0 ± 0.2	18.8 ± 0.4	0.20 ± 0.07	0.02 ± 0.02	2.1 ± 0.1	0.4 ± 0.1	0.02 ± 0.01	0.20 ± 0.05	0.11 ± 0.09	96.9 ± 1.0

Table 1. Composition of the bulk glass (oxides, wt%) measured by electron microprobe. For each sample, an average from 10 measurements is given.

	Na	Mg	Si	Al	P	K	Ca	Ti	Cr	Mn	Fe	Cl	S	H	O	TOTAL
PLOG																
Bulk glass (1)	2.3 ± 0.1	4.1 ± 0.1	20.3 ± 0.4	0.55 ± 0.03	1.17 ± 0.03	5.0 ± 0.2	6.2 ± 0.1	0.03 ± 0.02	0.00 ± 0.01	0.24 ± 0.03	0.15 ± 0.03	0.29 ± 0.02	0.04 ±0.01	0.6 ± 1.0	59.1 ± 0.4	100.00
Gel layer (2)	0.14 ± 0.01	0.30 ± 0.02	15.3 ± 0.3	0.82 ± 0.04	1.33 ± 0.03	0.21 ± 0.02	3.13 ± 0.00	0.05 ± 0.01	0.00 ± 0.00	0.02 ± 0.01	0.16 ± 0.1	0.02 ± 0.01	0.06 ± 0.00	26.13 ± 0.2	52.30 ± 0.2	100.00
	0.16 ± 0.01	0.28 ± 0.02	14.9 ± 0.3	0.88 ± 0.04	1.38 ± 0.03	0.23 ± 0.02	3.14 ± 0.00	0.06 ± 0.01	0.01 ± 0.00	0.01 ± 0.01	0.28 ± 0.1	0.03 ± 0.01	0.06 ± 0.00	26.48 ± 0.2	52.05 ± 0.2	100.00
Brown inclusion (3)	0.03 ± 0.01	0.30 ± 0.03	9.9 ± 0.4	0.51 ± 0.01	1.7 ± 0.2	0.10 ± 0.00	3.9 ± 0.4	0.05 ± 0.00	0.00 ± 0.00	2.0 ± 0.1	0.14 ± 0.00	0.01 ± 0.01	0.05 ± 0.00	33.1 ± 0.3	48.13 ± 0.02	100.00
	0.05 ± 0.01	0.25 ± 0.03	10.5 ± 0.4	0.52 ± 0.01	1.4 ± 0.2	0.10 ± 0.00	3.4 ± 0.4	0.05 ± 0.00	0.00 ± 0.00	1.8 ± 0.1	0.14 ± 0.00	0.02 ± 0.01	0.04 ± 0.00	33.5 ± 0.3	48.10 ± 0.02	100.00
KERN3																
Bulk glass (1)	4.1 ± 0.2	4.6 ± 0.2	15.5 ± 0.9	0.43 ± 0.03	0.61 ± 0.05	4.6 ± 0.2	4.00 ± 0.2	0.03 ± 0.02	0.00 ± 0.00	0.30 ± 0.03	0.10 ± 0.02	0.21 ± 0.03	0.03 ± 0.01	12.6 ± 2.8	52.9 ± 1.1	100.00
Brown gel layer (2)	0.1 ± 2.5	0.4 ± 2.6	11.7 ± 3.8	0.41 ± 0.04	0.1 ± 0.3	0.3 ± 2.6	0.2 ± 2.1	0.03 ± 0.01	0.00 ± 0.00	0.4 ± 0.2	0.10 ± 0.01	0.1 ± 0.1	0.03 ± 0.02	40.3 ± 19.3	45.9 ± 5.6	100.00
	4.5 ± 2.5	4.9 ± 2.6	16.3 ± 3.8	0.44 ± 0.04	0.7 ± 0.3	4.7 ± 2.6	4.1 ± 2.1	0.02 ± 0.01	0.01 ± 0.00	0.3 ± 0.2	0.13 ± 0.01	0.2 ± 0.1	0.06 ± 0.02	9.6 ± 19.3	54.7 ± 5.6	100.00
	0.1 ± 2.5	0.4 ± 2.6	8.9 ± 3,8	0.36 ± 0.04	0.3 ± 0.3	0.2 ± 2.6	0.7 ± 2.1	0.01 ± 0.01	0.00 ± 0.00	0.1 ± 0.2	0.11 ± 0.01	0.05 ± 0.1	0.03 ± 0.02	45.2 ± 19.3	43.4 ± 5.6	100.00

Table 2. Chemical composition of the bulk glass and the deteriorated layer of PLOG and KERN samples measured by electronic microprobe in wt%. The values have been converted in atomic percentage of elements (at.%).

Analysis with higher resolution techniques (microbeam electron microprobe type JEOL JxA-8500F, column conditions set to 15 kV and 4nA) on similar samples have indeed shown that there is evidence of Mn enrichment in type I stained-glass windows (Ferrand 2012).

Results of the Treatments

Hydroxylamine hydrochloride and sodium hydrogen sulphite were tested on the PLOG sample (type II), and both performed very well. Treatments on several pieces of type I (KERN 2 and 4) (figure 4) show that some areas gradually regain transparency (figure 4(b) and (d)). Through observations in transmitted light, the best and quickest results were provided by using hydroxylamine hydrochloride (lightening after 20/30 min) followed by sodium hydrogen sulphite (lightening after 30/60 min). The BDG 86 Azzurro® turned out to be disappointing, considering the promising results that had been found in earlier research (Pivet 2000; Vincent-Petit 2006). The pH value was constant during the treatment, and its initial value had no influence on the effectiveness except in the case of the sodium hydrogen sulphite which was more effective with pH = 5. The concentration did not seem to be a decisive parameter. As the visual result observed on the treated pieces was equally satisfactory with the different chemical solutions (5% and 10%), the less concentrated solutions are preferred. The cross-sections of a treated piece show that the browning within the leached layer disappears (figure 5). The whitish aspect obtained after treatment (figure 5) is similar to the gel layer without browning (figure 1(c)). The treated surfaces appear to be whitish in reflected light revealing the weathered glass. However, this does not affect the aesthetic improvement in transmitted light. Visual observations in transmitted light showed clearly that the treatment was satisfactory. It should also be noted that the painted areas do not seem to have changed visually during and after treatment. Future studies should include more tests to evaluate the effect of treatments on the glass paint. The observations with SEM-BEI of the treated cross-sections (KERN 3 and 4) show that no significant physical damage such as microcracks was detected on the glass. The amount of manganese and other elements was quantified before and after treatment to ascertain whether any damage had been caused to the gel layer. The results obtained by electron microprobe analysis are difficult to interpret.

The heterogeneity of this area and the micrometric size of the dark structure did not allow for exact monitoring before

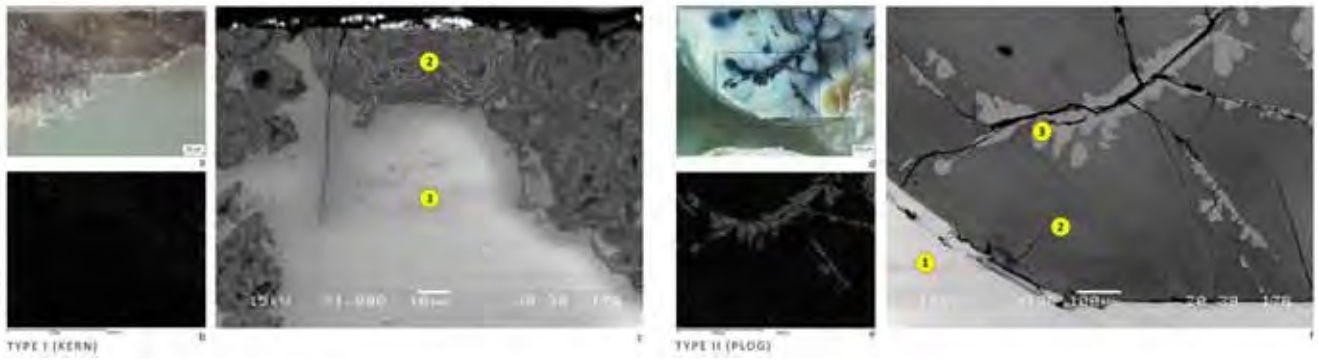
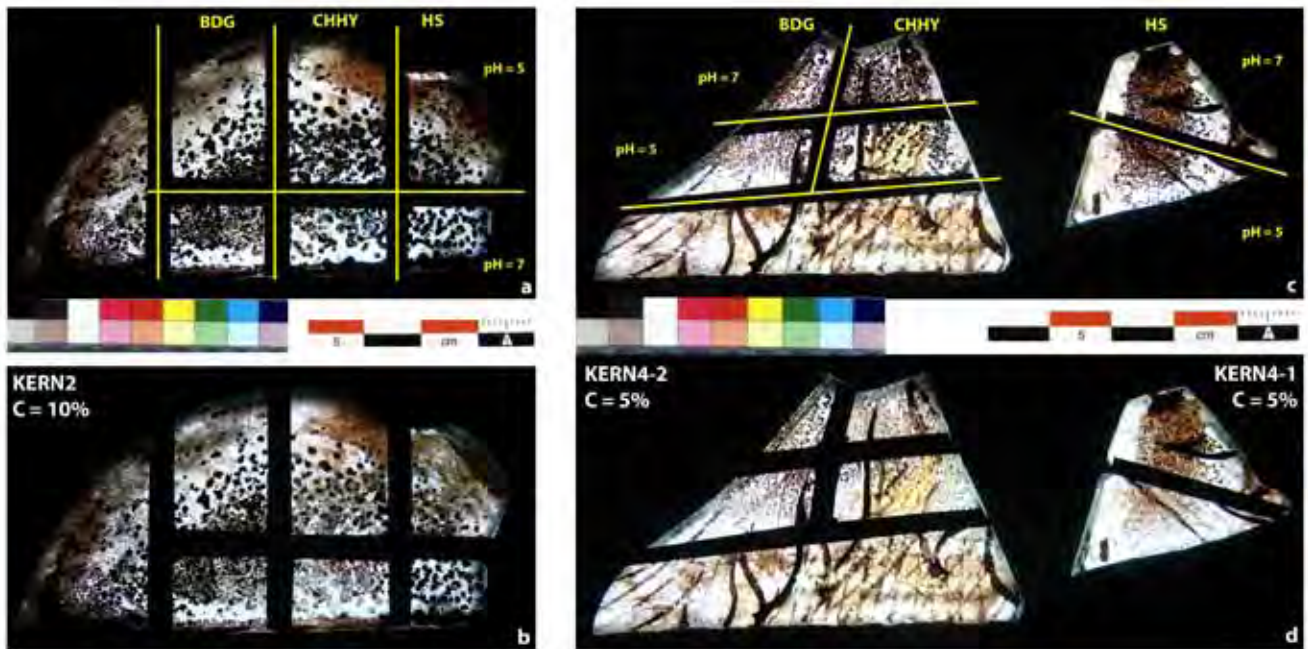


Fig. 3. Cross-sections of KERN (type I) and PLOG (type II) documented with optical microscopy (a, d), SEM-BEI (c, f) and EDX for Mn mapping (b, e). The numbering (c, f) refers to the areas where measurements were performed with electron microprobe (table 2) (Photos: © LRMH).



	BDG	CHHY	HS	BDG	CHHY	HS
pH = 5	+	++++	++	++	++++	+++
pH = 7	+	++++	+	+	++++	++

Fig. 4. Fragments of KERN2, KERN4-1 and KERN4-2 before (a, c) and after 3 hours of treatment (b, d) with BDG 86 Azzurro®, hydroxylamine hydrochloride, and sodium hydrogen sulphite. Selected parameters: C = 5 wt% and C = 10 wt%, pH = 5 and pH = 7.
In the table: not very efficient + → ++++ very efficient (Photos: © LRMH).

and after treatment. Nevertheless, measurements still detected manganese after treatment, implying that it had not been fully extracted from the leached layer. Further, no traces of the salt solutions (sulphur or chloride) were detected after treatment, suggesting that the rinsing stage had been effective.
It is planned to evaluate the long-term effects of the treatment as a next step. The treated samples are currently being stored at ambient conditions (20 ± 2°C, 42 ± 3% RH). In a parallel project, selected areas of windows from Les Junies and Pont-Sainte-Marie Church (France) were treated and re-installed in situ with a protective glazing system. These historical glasses will be inspected at regular intervals.

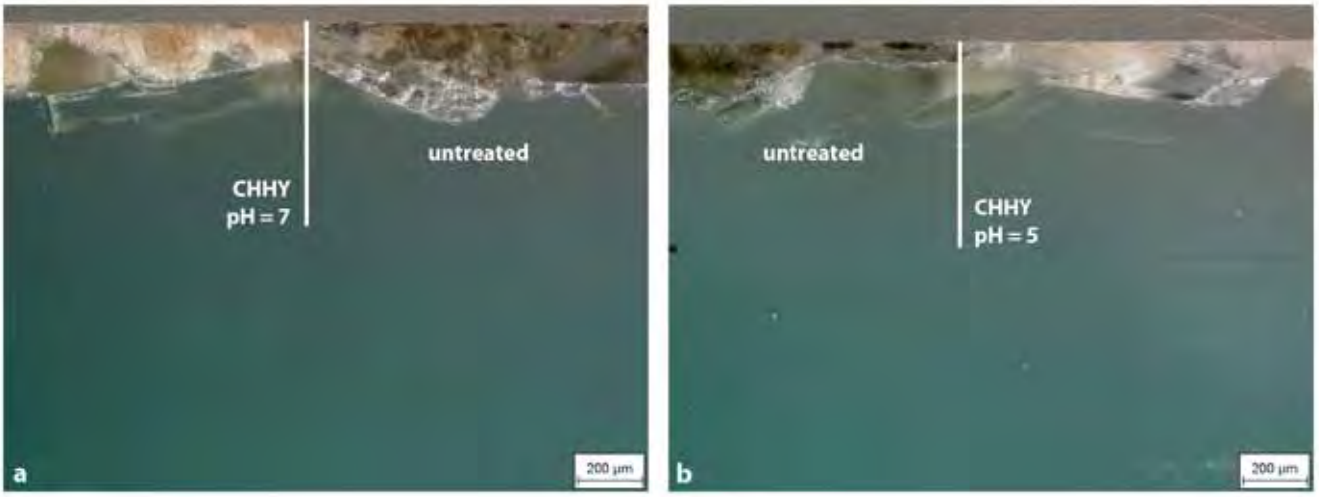


Fig. 5. Photomicrograph of a cross-section of KERN4-2 treated with hydroxylamine hydrochloride (5 wt%), at pH = 7 (a) and pH = 5 (b). For both images, the untreated area is indicated (Photos: © LRMH).

The panel at Pont-Sainte-Marie can be easily removed from the exposure site to assess the progress of browning and to document any potential darkening by standardised photography in the studio.

Conclusions

This study has highlighted two types of browning patterns. In both cases, the deterioration seems to combine the damage by weathering (leading to the formation of a leached layer) with the darkening of the glass as the result of a chemical reaction involving manganese, as has been suggested in the literature (Cagno and others 2011a and b). Type II is characterised by brown inclusions enriched in Mn. In contrast, type I, most typical for in situ stained-glass windows, presents a staining within the corrosion layer without any evident enrichment of Mn. It is possible that the small size of the Mn-rich areas made detection difficult using the analytical techniques available for this study. While type II is easily attributed to the so-called 'manganese staining', in the case of type I, the diagnosis is more difficult.

To make a complete diagnosis of the presence of manganese staining, the measurement of the oxidation state of Mn is required. This point is the main topic under investigation in a PhD thesis that is currently in progress. As part of that research, the samples are being studied using X-ray absorption spectroscopy.

Even though the diagnosis of browning needs to be refined, the visual observations clearly show that the treatments were efficient on both the KERN (type I) and the PLOG (type II) samples. The transparency of the treated areas is significantly increased compared with untreated parts of the same sample. These first results are encouraging even though questions still exist about the use and the long-term effects of such chemicals on ancient glass and especially on painted areas, an aspect that was not studied in this project. Further research is necessary in order to help conservators to develop ethical, aesthetic, and long-term solutions.

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Materials:

Sodium hydrogen sulphite and hydroxylamine hydrochloride:
Sigma Aldrich Chemie S.a.r.l.
80 rue de Luzais
B.P. 701 l'Isle d'Abeau Chesnes
38297 St. Quentin Fallavier Cedex, France
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Fax: +33-800 03 10 52
E-mail: FRACS@sial.com
sigma-aldrich.com

BDG 86 Azzurro®:
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Tel.: +33-1 43 55 60 44
Fax: +33-1 43 55 66 87
E-mail: ctsparis@gmail.com
ctseurope.com

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High-resolution Desktop Microcomputed Tomography for the Evaluation of Reducing Treatments on Historical Glass Suffering From Manganese Browning

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manganese browning; manganese intrusion; desktop microcomputed tomography; reducing treatment

Abstract
Historical glass, especially non-durable mediaeval glass, can undergo corrosion. This sometimes results in the formation of dark-coloured manganese-rich inclusions or stains that reduce the transparency of the glass. A conservation treatment with reducing or chelating agents may be considered with the aim of improving the transparency. In this paper, high-resolution desktop microcomputed tomography (μCT) is used in combination with element-specific two-dimensional imaging methods for in situ monitoring of manganese removal by hydroxylamine hydrochloride from an archaeological stained-glass sample suffering from manganese browning and from artificially corroded model glass samples. μCT also proved itself useful for the study of the (re-)penetration of manganese into the gel layer during artificial corrosion of a model glass.

Introduction
Glass, including window panes from existing stained-glass windows or fragments encountered in an archaeological context (e.g. at excavations of church sites, monastery sites), is often affected by so-called darkening or browning caused by the development of dark-coloured Mn/Fe-rich zones in the alteration layer; sometimes this can lead to a reduced or total loss of transparency of the glass. This phenomenon has been reported in the literature for archaeological glass excavated from different northern European sites situated in, for example, Belgium, Spain and the U.K. and dating from the 11th to the 16th century (Newton and Davison 1989; Schreiner 1991; Müller, Torge, and Adam 1994; Müller, Torge, and Adam 1995; Watkinson, Weber, and Anheuser 2005; Doménech-Carbó and others 2006; Cagno and others 2011; Schalm and others 2011; Wouters 2013). In this paper, the focus of attention is on the darkening caused by Mn-rich zones or plugs (Roemich and others 2003), henceforth referred to as Mn inclusions (Doménéch-Carbó, Doménéch-Carbó, and Osete-Cortina 2001), and how high-resolution microcomputed tomography (μCT) can be used to explore their formation and treatment.

While this study deals with both the removal and artificial intrusion of Mn staining, it is important to point out that the main objective of a glass conservator (based upon internationally accepted guidelines) is the conservation of original (glass) material and the prevention of further decay with minimal intervention. This objective would generally not include the recovery of the transparency of Mn-darkened glass fragments through the removal of corrosion products and deposits. Corrosion products are considered to be a part of the material history of a sample and thus a part of its cultural value (Corpus Vitrearum, Guidelines for the Conservation and Restoration of Stained Glass 1.3, 2nd edition, Nuremberg, 2004). To appreciate the highly fragmented state of archaeological glass collections, it is important to understand their lifespan through the interpretation of signs of production, design, use, re-use, repair and deposition of such fragments in relation to their specific context (Wouters 2013). For glass, any loss of the corrosion layers results in a

loss of technological traces and, therefore, a loss of information (Wouters 2013). Any intervention should be reversible and non-destructive. However, a non-reversible treatment method may be considered in a limited number of cases, e.g. in extreme cases of darkening where the original colour of the glass and other signs of its history such as applied paint or design on the surface can no longer be appreciated.

Two different strategies are known to conservators for removing the darkening effect induced by manganese: one is based on the reduction of the highly oxidised black/brown compounds, and the other focuses more on the extraction of this element from the inclusions by means of the application of chelating agents (Fitz 1981; Newton and Davison 1989). The heterogeneity of degraded historical glass (Newton and Davison 1989) makes it difficult to compare different methods of treatment, since historical glass exhibits a large range of weathering phenomena (Newton and Davison 1989) and has a variable composition, while its corrosion history is in many cases unknown. Samples with identical initial properties are rarely available. This can be circumvented by testing treatments on model glass samples, which may be artificially corroded to simulate phenomena encountered on original glass fragments; this allows full control over the composition of the glass and the parameters of the artificial corrosion process in order to ensure the reproducibility of such experiments. Additional reasons for preparing synthetically corroded glass are (a) that it is ethically appropriate to use such material in order to avoid damaging historical glass fragments during comparative tests and (b) that a systematic study of the phenomena taking place during glass corrosion and/or its treatment may expand our knowledge on the manganese browning phenomenon and the factors that govern it.

In some cases, evaluation of conservation measures requires high-resolution analytical techniques appropriate to detect the degradation phenomena and the subtle changes that may occur to the glass during treatment. µCT has already proven its usefulness for the characterisation of degraded glass (Lopez and others 2002; Roemich and others 2003; Mees and others 2009; Schalm and others 2011). By employing the local density contrast, a 3D image can be obtained in which not only the position and volume of (internal) cracks and voids in the glass may be visualised but also the size and shape of the Mn inclusions may be determined. Schalm and others (2011) describe the presence of dendrites and of planar- and tubular-shaped enrichments inside the gel layer. These findings allowed them to formulate the hypothesis that such inclusions are formed by migration of Mn(II) towards the inclusions, followed by in situ oxidation.

In order to assess the effect of a reducing treatment on existing Mn stains or of a treatment intended to induce the artificial formation of such stains, the glass material in which these transformations take place needs to be compared before and after treatment. While µCT is very useful to determine the 3D morphology of the Mn inclusions, it suffers from the limitation of being not element-specific. In what follows, we therefore use µCT either in combination with scanning electron microscopy-energy dispersive X-ray spectrometry (SEM-EDX), a conventional analytical method frequently employed to study glass degradation (Janssens and Van Grieken 2004), or together with microscopic X-ray fluorescence analysis (µXRF), a more sensitive equivalent of SEM-EDX. These methods require polished cross-sections to be prepared from the samples, making it more difficult to study changes before, during and after treatment.

In a previous study on manganese browning, microscopic high-resolution synchrotron-radiation-based CT (µSR-CT) was used to evaluate the effect of a hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) treatment of glass. Glass fragments with a comparable provenance as the materials employed here were immersed in a 2–5 wt% $NH_2OH{\cdot}HCl$ solution. At a spatial resolution level of 0.7 µm, it could be demonstrated that not only was Mn in inclusions (assumed to be present as MnO_2) reduced to the water soluble Mn(II) form (Cagno and others 2011), but also the enhanced mobility (Watkinson, Weber, and Anheuser 2005) of the Mn allowed it to diffuse into the treatment solution, thus removing it from the gel layer (Cagno and others 2011). While µSR-CT allows one to distinguish between the original glass, the gel layer and the Mn inclusions, another advantage of the SR variant is its speed: by exploiting a total scan time of approximately 10 minutes, it was possible to monitor the gradual removal of the Mn resulting from a series of short exposures to the treatment solution (Cagno and others 2011). An important restriction of µSR-CT, on the other hand, is the limited availability of experimental time at large-scale synchrotron facilities. A relevant question in this context is, therefore, to what extent a high-resolution desktop mCT apparatus may be used for the above-mentioned type of investigations.

Accordingly, in this paper, we first describe the results of a comparative study between desktop and SR-based mCT conducted on an expendable historical glass fragment showing manganese staining; SEM-EDX was employed to map the presence of this element. The sample was characterised in 3D

before and after treatment with a 5 wt% $NH_2OH{\cdot}HCl$ solution, intended to reduce and remove the Mn from the glass. Second, in combination with µXRF, high-resolution desktop µCT was used to study the phenomenon of Mn intrusion from a solution into the glass gel layer during artificial degradation. More specifically, these methods were used to verify whether Mn intrusion and precipitation occurs only in the microscopic cracks of a pre-corroded non-durable glass fragment or whether Mn(II) effectively penetrates into the gel layer, as suggested by Schalm and others (2011).

Background on Manganese Browning

Glass Corrosion

In general, corrosion of historical silicate glass (Roemich and others 2003) is induced by the presence of water: molecular water penetrates into the glass via diffusion and/or reversible hydrolysis/condensation reactions. As a result, the silica network will undergo structural transformations (Bunker 1994). Simultaneously, an ion-exchange process will take place, mainly at low pH values, between protons from the environment and cations present within the glass network (Scholze 1982; Janssens and others 1996; Adams and others 1997; Melcher and Schreiner 2004). This results in leaching out of most mobile cations (i.e., monovalent Na^+ and K^+), during which the density of the gel layer will decrease, since heavier metal cations are being replaced by lighter protons and water. If the surface of the glass is subject to dry/wet cycles, microcracks can occur, leading to the formation of very thin (< 1 µm) lamellae (Schalm and others 2011). In addition, weathering products (such as sulfates and chlorides of Mg or Ca) can be formed on the glass surface (Roemich and others 2003; Doménech-Carbó and others 2006). If the original glass contains Mn, this element can also become depleted in the gel layer (Janssens and others 1996).

Manganese Browning

As described elsewhere in more detail (Schalm and others 2011), when an internal or external manganese source is available, Mn inclusions can be formed within the leached layer. Historical glass often contains a small amount of manganese (typically 0.5–1 wt%) with Mn(II) being the predominant species. Manganese can be present in the glass as an impurity of the starting materials or can have been added deliberately as pyrolusite (MnO_2), a de-colourising agent (Newton and Davison 1989). Alternatively, manganese may be introduced into archaeological glass from the soil in which the glass was buried (Cox and Ford 1993; Doménech-Carbó, Doménech-Carbó, and Osete-Cortina 2001). Previous experiments have indicated the presence of MnO_2 in the Mn inclusions (Schalm and others 2011), and a hypothesis for its formation was proposed: in the presence of water and oxygen, Mn(II) and/or Mn(III) ions can be oxidised to higher oxidation states, giving rise to, for example, insoluble MnO_2 from which the Mn inclusions are formed (Doménech-Carbó, Doménech-Carbó, and Osete-Cortina 2001; Cagno and others 2011; Schalm and others 2011). Manganese inclusions are sometimes referred to as 'corrosion bodies' (Cagno and others 2011; Schalm and others 2011).

Experimental

Microcomputed Tomography

X-ray absorption tomography is a non-destructive technique that allows 3D visualisation of the linear attenuation coefficient, which is equal to the product of the local mass absorption coefficient and density (Sasov and Van Dyck 1998). The 3D images generated by µCT consist of slices, where each slice corresponds to a virtual cross-section of the sample. In each slice, the grey value represents the linear attenuation in that specific location.

Two different lab µCT scanners were used to image the corroded glass fragments, namely a Skyscan 1172 high-resolution micro-CT and an Xradia MicroXCT-400 instrument. The first is equipped with a Hamamatsu 100 kV tungsten X-ray source and an 11 Mp Skyscan CCD camera. The Xradia has a Hamamatsu 150 kV X-ray source and a 2 K x 2 K Andor CCD camera. In addition to the geometric magnification, the Xradia also includes a set of scintillator-coated objective lenses with an optical magnification of 0.5x, 4x, 10x, 20x and 40x, which allow better resolution than the Skyscan 1172. All measurements using the Skyscan 1172 were carried out with an operating acceleration voltage of 70 kV and a source current of 139 µA. A 0.5 mm Al filter was inserted in the incoming beam in order to remove the soft X-rays. These cannot pass through the sample and do not contribute to the acquired radiograph, but their scattering can still induce noise and unnecessary sample heating. Only one glass fragment was measured using the high-resolution

Sample	Scanner	Treatment	μCT parameters				
			Exposure time/ angle	Rotation step (°)	Total rotation angle	Image pixel size (μm)	Total scan duration (hours)
Sample A	Skyscan 1172	30 min 5 wt% $NH_2OH{\cdot}HCl$	300 ms	0.150	360	4.2	± 4.5
Sample B Fraunhofer M1.0	Skyscan 1172	2 h 1 M HCl	500 ms	0.4	360	3.05	± 2
Sample C Fraunhofer M1.0	Skyscan 1172	2 h 1 M HCl + 24 h 0.5 M $MnCl_2$	780 ms	0.3	192	2.4	± 2
Sample D Fraunhofer M1.0	Xradia XCT-400	2 h 1 M HCl + 24 h 0.5 M $MnCl_2$	10 s	0.072	180	1.1	± 17 h

Table 1. Summary of the treatments applied to the glass samples and the instrumental parameters used during μCT acquisition.

Xradia instrument employing a 50 kV acceleration voltage and a 200 μA current. Reconstructions were performed using an algorithm based on cone beam filtered back projection, including ring-artefact and beam-hardening corrections. The latter is required since a polychromatic primary beam is used. Other experimental parameters are unique for every measured glass fragment and are summarised in table 1; this table also summarises all the chemical treatments employed.

Reducing Treatment of Historical Glass

Sample A, used to compare SR-CT with desktop μCT, is part of a series of glass fragments that originate from an excavation at a former Franciscan friary and are dated to the 14th century. Since the context data of the excavation were lost, the heritage value of this fragment is limited (Hind, Marsden, and Evans 1994). The major components (wt%) of the original glass in sample A were determined by SEM-EDX analysis:[1] MgO 5.2%; Al_2O_3 2.0%; SiO_2 46.8%; K_2O 18.4%; CaO 23.6%; and MnO 1.6%. The relatively large size (around 1 mm depth and around 2 mm width) of the dark Mn-enriched zone at the original glass surface makes this sample very suitable for the μCT comparison study. In order to obtain optical microscopy images from this sample before and after $NH_2OH{\cdot}HCl$ treatment, the glass sample was embedded in Versocit-2 acrylic resin and consecutively cut and polished. Embedding also helped to preserve sample integrity during diamond saw cutting.

The reducing treatment involved immersing the embedded glass sample for 30 min in a 5 wt% $NH_2OH{\cdot}HCl$ aqueous solution. The same concentration as employed in the SR-CT study was used; there, this relatively high concentration was chosen in order to accelerate the treatment effect and to allow for a series of short exposures to the $NH_2OH{\cdot}HCl$ alternated with SR-CT data acquisition (Cagno and others 2011). Also in this case, immersion in this solution results in consecutive Mn reduction and removal. An important difference between these experiment and 'real' treatments performed by glass conservators can be noted with respect to the contact surface of the glass fragment with the treatment solution. In the present experiment, a cross-sectional plane of the sample (figure 1(c)) was exposed to the reducing solution, while the original (naturally corroded) surface of the glass fragment was shielded by the embedding resin; during an actual conservation treatment, the solution would be in contact with the original surface.

Artificial Degradation

Fraunhofer type M1.0 sensor glass (54.2 wt% SiO_2, 28.8 wt% K_2O, 17.0 wt% CaO) (Fuchs, Roemich, and Schmidt 1991) was used as starting material for the artificial alteration. A two-step treatment was employed to realise a rapid weathering/staining process. Fragments of type M1.0 glass were immersed consecutively in 1 M HCl (2 hours) and 0.5 M $MnCl_2$ solutions (24 hours). The immersion in acid leads to the creation of a leached/hydrated layer, while immersion in the $MnCl_2$ solution introduces Mn into the gel layer.

Results and Discussion

Desktop μCT Imaging of a Reducing Treatment

A schematic overview of the orientation of original bulk glass, gel layer and Mn inclusions of sample A is shown in figure 1(a). Figure 1(b) shows a Mn elemental distribution map of part of the area obtained by SEM-EDX,[2] indicating

that Mn-rich inclusions of lateral dimension 10–20 µm are present. On the optical microscope image prior to treatment (figure 1(c)), a gel layer (in grey) can be observed on both outer surfaces of the glass fragment with black Mn inclusions inside. (The purple regions that can be observed on the left side of the sample in figure 1(c) are a flashed glass layer.) Figure 1(d) shows a microphotograph of sample A after the treatment. In figure 2, tomograms of the left Mn stain of figure 1(c) are shown, obtained by µCT before (figures 2(a) and (c)) and after (figures 2(b) and (d)) the reducing treatment. The large dimensions of the Mn inclusions (figure 1(b)) allowed the lower resolution settings (4.2 µm) of the Skyscan 1172 system to be used, making it possible to visualise a larger volume (see table 1 for a summary of all operating parameters).

A comparison of the images in figures 1(c) and (d) shows that, already after 30 min of exposure, the damage to the bulk glass caused by the treatment can be observed; the surface has developed a crack pattern, resulting in increased light scattering. A second observation is that the browning effect has partially disappeared; this indicates that some manganese, originally present in the +IV state of oxidation, was reduced in accordance with the results obtained by Cagno and others (2011). However, some residual bluish-grey coloured zones can still be observed inside the gel layer, suggesting that not all oxidised Mn has been removed.

While one tomographic scan using SR-CT required approximately 10 minutes, by means of the desktop µCT, a total of 4.5 hours of measurement time was needed. Thus, it was only possible to evaluate the reducing treatment in a before/after fashion without recording of 3D data at the intermediate stages. The tomograms shown in figures 2(a) and (b) correspond to the contact surface, while the slices in figures 2(c) and (d) are situated around 40 µm below the surface. More dense areas are represented by lighter grey values, and less dense areas are represented by by darker values. Accordingly, the less dense gel layer appears darker grey in the CT image than the bulk glass. Due to a higher local density, Mn inclusions show up brighter than the surrounding gel layer. At the surface (figures 2(a) and (b)), a significant fraction of the Mn has disappeared during the 30-minute exposure to the reducing solution; however, at 40 µm below the surface (figures 2(c) and (d)), this is far less the case.

When comparing SR-CT and desktop CT, it can be noted that the desktop CT employed here has sufficient resolution and contrast to make the distinction between the various phases in the corroded glass and to observe relevant changes inside the material when it is exposed to the reducing solution. The long data acquisition time required by the desktop instruments, however, makes it not practical to record many intermediate stages during a treatment of this kind. From the images shown in figure 2, it can be concluded that, after 30 minutes of exposure, the influence of the $NH_2OH{\cdot}HCl$ solution is fairly superficial only.

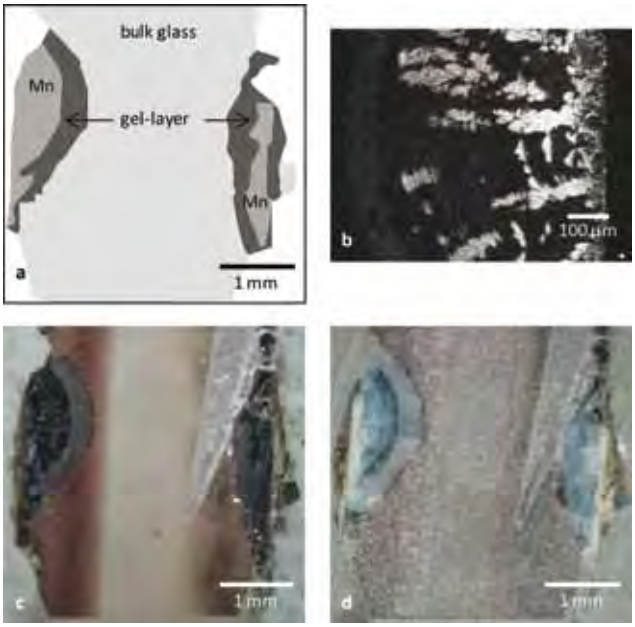

Fig. 1. Sample A prepared as cross-section: schematic overview (a); elemental distribution map of Mn, obtained with SEM-EDX (b); optical microscopy image, before treatment (c); optical microscopy image, after 30-minute treatment with 5 wt% $NH_2OH{\cdot}HCl$ solution (d) (Images: the authors).

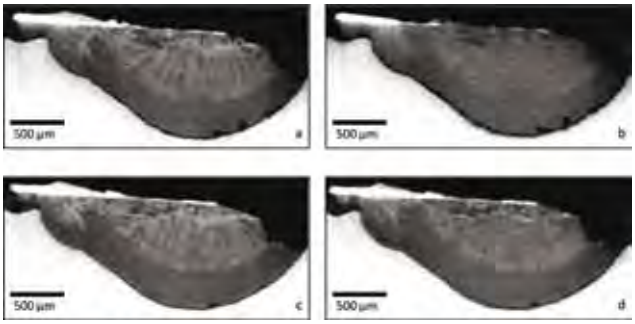

Fig. 2. Virtual slices of sample A obtained by means of desktop µCT: at the surface of the cross-section of the embedded fragment, before (a) and after 30 min treatment with 5 wt% $NH_2OH{\cdot}HCl$ solution (b); parallel slice at around 40 µm below the surface, before (c) and after treatment (d) (Images: the authors).

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Microcomputed Tomography on Model Glasses: Detecting Artificial Corrosion Layers

The optical photographs shown in figures 1(c) and (d) underline that chemical treatment methods for glass can induce unwanted damage; this makes it questionable to use historical glass fragments in optimisation experiments for conservation methods, especially considering the art-historical value of most fragments.

During previous experiments on artificial glass alteration, it was already demonstrated that Mn intrudes into the gel layer (Nuyts and others 2013). Figure 3(a), obtained by μXRF[3] from a cross-sectioned sample of Fraunhofer M1.0 glass treated with HCl and $MnCl_2$, shows that this preferentially takes place via microscopic cracks that have formed during the exposure to HCl (figure 3(b)). It was previously shown that Mn_3O_4 is the dominant Mn species (Nuyts and others 2013), without any significant spatial variation or any variation with treatment time, causing the typical brownish-black colour (Hao and others 2011). The specific advantage of μCT here is that glass fragments can be studied at and below the exposed surface without the necessity to prepare exposed, polished cross-sections of the sample and thus without the risk of removing intruded Mn during such preparation.

Figures 3(c) and (d) show virtual cross-sections of the gel layer, 14–15 μm below the original glass surface, after treatment of M1.0 sensor glass with both the HCl and $MnCl_2$ solutions (sample C). The dark grey colour visible in almost the entire slice corresponds to the gel layer, having a density lower than that of the original bulk glass. When sample C was analysed using the Skyscan 1172 instrument (using the conditions given in table 1), a series of virtual slices with around 2.4 μm resolution were obtained. At the top of the tomographic slice shown in figure 3(c), which is not perfectly parallel to the outer surface of the fragment, the denser bulk glass is visible. Inside the gel layer, some brighter areas/lines, corresponding to a higher density material, can be observed. These areas correspond to the cracks visible in figure 3(a), where a local enrichment and the higher density is caused by local precipitation of Mn. Without the $MnCl_2$ treatment (sample B), the cracks are also visible in the tomograms, but then as areas of lower density (dark lines in figure 3(b)). Thus, the combined μXRF and μCT images suggest that Mn has indeed penetrated the cracks created by the HCl treatment.

In order to ascertain whether the Mn only filled up the cracks or actually penetrated the gel layer, glass sample D (a duplicate of sample C) was analysed at higher resolution by using the Xradia instrument (resolution of around 1 μm; see table 1 for the data-acquisition parameters). A virtual cross-section parallel to the original glass surface within the gel layer is shown in figure 3(d). Similar to the image shown in figure 3(c), Mn enrichments can be observed as brighter areas in the grey-coloured gel layer. In this image (figure 3(d)), also some unfilled cracks (dark lines across the gel layer) are present. More importantly, however, inside the bright areas, a slightly darker core can be observed, representing the original, physical cracks in the material. From this observation, we tentatively deduce that Mn effectively enters the material via the cracks previously created by the HCl treatment and, from there, diffuses into the silicon–oxygen network of the gel layer. The μXRF elemental distribution maps (figure 3(a)) do not provide enough resolution to visualise this effect.

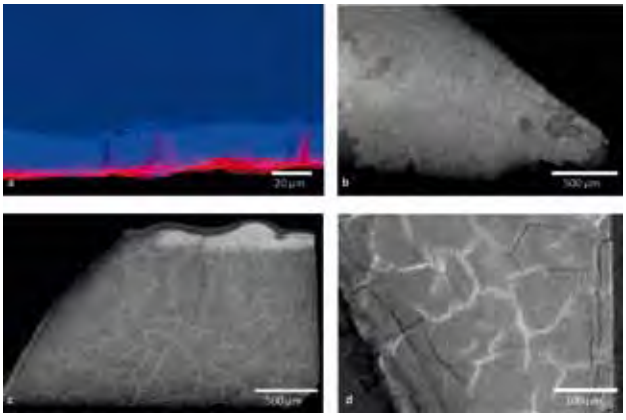

Fig. 3. (a) Si (blue) and Mn (red) elemental distribution maps of a cross-section of an artificially altered model glass sample, obtained with μXRF; (b) virtual slices of model glass samples obtained with μCT, around 10 μm below the original glass surface after a 2-hour HCl treatment (sample B, medium resolution Skyscan 1172 data); (c) around 14 μm below the original glass surface after consecutive HCl and $MnCl_2$ treatment (sample C, medium resolution Skyscan 1172 data); and (d) around 15 μm below the original glass surface (sample D, higher resolution Xradia XCT-400 data) (Images: the authors).

Conclusions

In the first part of this paper, the treatment of historical glass suffering from manganese browning with $NH_2O{\cdot}HCl$ was investigated: the applicability of desktop μCT for in situ monitoring of chemical changes was compared to that of the synchrotron-radiation-based equivalent.

Using a medium resolution desktop µCT instrument (Skyscan 1172), a behaviour in accordance with the results previously obtained by Cagno and others (2011) using µSR-CT was observed, where consecutive Mn reduction and removal was demonstrated. However, the relatively long scan times of the desktop system did not allow quasi-continuous monitoring of the treatment effects. On the positive side, the desktop variant does not suffer from the limited availability of SR-CT facilities and could therefore be used for in situ monitoring of slower-acting, and therefore more realistic, conservation procedures of this type, albeit with a coarser time resolution (i.e. of the order of days rather than of hours).

In the second part of the paper, desktop µCT was proven to be useful for determining how Mn may be introduced into the gel layer formed during artificial corrosion of glass samples of low durability (Fraunhofer M1.0). Previous experiments associated visual browning of the altered glass with the precipitation of Mn in the gel layer as brownish-black Mn_3O_4. This could also be observed by medium-resolution desktop CT. In high-resolution scans (1.1 µm), indications suggesting the diffusion of Mn from the microcracks into the surrounding gel layer could be observed. This will need to be investigated in greater detail by means of an element specific method such as high-resolution XRF tomography or transmission electron microscopy coupled to EDX.

The two-step artificial corrosion, described in this paper, was performed to induce manganese browning in a relatively short time period (around 26 hours), making it possible to evaluate the applicability of desktop µCT. However, gel layers produced by immersion in acidic solutions are different compared to degradation layers of glass fragments buried in the soil. Thus, in a next step, a less aggressive form of artificial corrosion will be evaluated. Another parameter to change is the composition of the substrate. In this study, highly sensitive M1.0 Fraunhofer glass without Mn was used together with an external Mn source. To better match realistic conditions in future experiments, the artificial corrosion will be performed on Mn-containing glass, allowing browning on glass with an internal Mn source to be simulated, as described by Roemich and others (2003). In both cases, high-resolution desktop µCT in combination with an element-specific imaging method will be used to visualise the Mn distribution before and after treatment in order to compare different methods applicable to conservation practice.

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Notes

1. Quantitative analysis was performed using a JEOL 6300 scanning electron microscope equipped with an energy dispersive X-ray detector. Spectra were collected for 200 seconds using a 2 nA electron beam current, an accelerating voltage of 20 kV and a microscope magnification of 500. The net intensities were calculated with the program AXIL (Analysis of X-rays by Iterative Least squares) and quantified by means of a standardless ZAF program.
2. The X-ray map was recorded using a JEOL JSM 5510 scanning electron microscope equipped with an Inca X-ray microanalysis unit and applying an accelerating voltage of 20 kV.
3. µXRF maps were recorded at beamline 21, ESRF (Grenoble), using a primary beam energy of 6.57 keV, and the sample was positioned at 45° with respect to the incoming beam (0.3 x 0.8 μm^2). The fluorescence yield was recorded using a silicon drift detector at an angle of 45° with respect to the sample. A step size of 5 x 5 μm^2 was applied with a measuring time of 500 ms/pt, and all recorded spectra were evaluated using the PyMCA software package.

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Re-thinking the Approach: Techniques Explored at Winterthur for the Stain Reduction of Ceramics

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Keywords
stain reduction; ceramics; cleaning; chelating agents

Abstract
Stain reduction is often required during conservation treatment of ceramics. Although the historical relevance of the stain must first be considered, stains are often disfiguring enough that they limit full aesthetic appreciation of an object. This is particularly true within fine arts collections. For the past several years, the authors have delved deeper into this topic, evaluating current materials and methodologies and applying these concepts during the treatment of dozens of ceramics in the Winterthur collection. In the process, they go beyond what is mentioned in the conservation literature by considering new options and developing a sequence of steps for stain reduction that has provided excellent results. In this paper, the authors discuss cleaning theories and present new techniques and materials, proposing a re-thinking of the approach to stain reduction on ceramics.

Introduction
Knowing the nature of ceramic bodies and how stains are held within them is essential to designing procedures for the reduction of those stains. Ceramics vary in mineral composition, particle size, and ionic exchange potential; also, stains are often mixtures of organic and inorganic constituents. Although the stains are held by a number of forces, including hydrophobic/hydrophilic interaction and specific bonding, electrostatic forces represent a key reason stains are held within ceramic bodies. This paper focuses on how we can control our cleaning systems by adjusting the pH and ionic environment and by targeting (chelating) specific metal ions. Understanding the crucial role that ions play in binding stains to a ceramic structure goes a long way in determining how to desorb them. This can then be followed by (or used in concert with) other standard methods, such as oxidative bleaching, to further affect organic staining materials.

Ceramic Cleaning Theory
The electrostatic net charge on a mineral surface such as a silicate, and the type of ions held or 'sorbed' there, is fundamentally a function of pH. Ion-binding sites are amphoteric: they take on an extra H^+ or lose one to develop either a net positive or negative charge:

$$\equiv Si\text{-}O^- + H^+ \leftrightarrow \equiv Si\text{-}OH \quad (1)$$

$$\equiv Si\text{-}OH + H^+ \leftrightarrow \equiv Si\text{-}OH_2^+ \quad (2)$$

At high pH values, the species on the left of equation (1) predominates, and the silicate attracts positively-charged ions from solutions; in an acidic environment, equation (2) predominates, and a silicate surface is positively charged, attracting negatively-charged ions. The 'zero-point' pH (pH_{zpc}) is the pH where positive sites are minimal and equal to the number of negative sites, and the net surface charge is zero. With clay structures such as kaolinite, the pH_{zpc} is 4.6; the $pH_{zpc\ for}$ montmorillonite is 2.5, for feldspathic minerals it is 2–2.4, and for many silicates it is 2.0 or slightly above. At the pH_{zpc}, interactions between solute ions and the mineral surface are minimised.

When silicates are predominantly negatively charged, polyvalent cations held at the surface can bind other ionic material to them, thus retaining staining compounds, such as weakly acidic organic materials. Particle size contributes to the availability of these charged sites, and most clay minerals have high surface area-to-weight ratios. Because of this, small particles can bind significant amounts of adsorbed molecules at their surface as hydrated species. These are often described as 'outer sphere' complexes where the ion remains bound to the hydration shell, not directly to the surface, and attraction is purely electrostatic. The charges at these binding sites are often significantly higher than in the ceramic itself.

Outer-sphere species are held in a manner where they are easily exchanged with ions of a similar charge. Ions adsorbed by outer-sphere complexation in particular diffuse and are readily exchangeable with similar ions in solution.

Generally, for minerals such as silicates or aluminates, whose surface charge is pH-dependent, the amount of sorbed cations increases with increasing pH. Again, this is due to positively-charged surfaces that repel cations at low pH values, while at high pH values, negatively-charged surfaces attract them. Each cation exhibits a relatively narrow range of pH (about 2 units) over which its sorption increases from near 0% to near 100%; this further emphasises the need for careful control of pH during stain reduction.

While stain retention through ionic means is clearly a function of ion type, pH, and binding site availability, other factors influencing solution dynamics are equally important. These include the porosity of the ceramic itself and capillary movement of liquids through the structure, as well as diffusion of active cleaning agents into the ceramic and the movement of staining materials outward. This is where choosing the right materials to apply the solution is important.

Ceramic Stain Reduction in Practice

Keeping these properties in mind, the authors recommend a protocol: first, use a chelator; second, use an oxidising bleach; and, finally, rinse thoroughly. Throughout the process, it is critical to choose materials that provide careful control, minimising negative reactions and the risk of leaving residues behind. The choice of materials for each treatment presents its own challenges, yet the suggested approach proved successful at safely reducing stains on a variety of ceramics.

Step 1: Choosing a Chelator

Because electrostatic forces largely hold stains to a ceramic body, utilising a chelator to target specific metallic components is often the best place to start. A 'chelate' is any material with an affinity to bind a divalent metal ion and stay in solution without precipitating.

It is essential to understand that the functionality of any chelator is dependent on the pH of its surrounding solution. Most of the common chelators contain 'ligands' or functional groups that are ionisable acid groups. The acid dissociation constant (pK_a) of each acid group present in the chelator structure determines the pH where these groups will be fully charged (usually one pH unit above the group pK_a). Chelation is most effective when at least three groups of the chelator are ionised (pK_3), and the pH value is closer to the pH_{zpc} of the ceramic. Stain removal from ceramics is probably most efficient at pH values close to the pH_{zpc}. Common chelators and their range of pK_a values are listed in table 1. For example, citric acid is already triply ionised at pH 6.4 and is efficient chelator above that pH.

	Citric acid[1]	EDTA[2]	DTPA[3]	Tiron[4]	HBED[5]
pK1	3.13	1.99	1.80	-	4
pK2	4.76	2.67	2.55	-	8
pK3	6.40	6.16	4.33	7.66(-2)	
pK4		10.26	8.60	12.60(-3)	
pK5			10.58		

1. (Dean 1973); 2. Disodium ethylenediaminetetraacetic acid (Dean 1973); 3. Diethylene triamine pentaacetic acid (Dean 1973); 4. 4,5-Dihydroxy-m-benzenedisulfonic acid (Dean 1973); 5. N,N'-Di(2-hydroxybenzyl) ethylenediamine-N,N'-diaceticacid monohydrochloride hydrate (http://pubchem.ncbi.nlm.nih.gov/summary/summary.cgi?cid=124920 accessed 11/30/2012)

Table 1. Selected acid dissociation constants (pK_a) of various chelators.

A common way to determine the relative strength of a chelating material is to compare the formation constant (pK_f) of the chelator–metal complex to the solubility product (pK_{sp}) of a metallic species. In general, complexation will occur when the pK_f of the complex is greater than the pK_{sp} of a given species. Table 2 demonstrates that, in order to dislodge components of a stain being held (adsorbed) by ceramic bodies, certain chelators will be more effective than others, depending on the metal ions being targeted.

Citric acid, for instance, can effectively desorb organic material being held to a magnesium silicate by outer shell adsorption, as described above. However, if rust is the staining culprit, the pK_{sp} for $Fe(OH)_3$ is 38.5; only a chelator with a pK_f greater than this number will preferentially bind Fe^{+3} ions in

Mineral	pK_d/pK_{sp}	Metal ion	pK_f citric acid[3]	pK_f EDTA	pK_f DTPA[4]	pK_f Tiron	pK_f HBED[5,6,7]
Stain Components							
$Ca(OH)_2$	5.2	Ca^{+2}	4.7	11.0	10.9	5.8	9.3
$CaSO_4$ $2H_2O$	4.5						
$CaCO_3$	8.5						
$Mg(OH)_2$	11.2	Mg^{+2}	3.3	8.7	9.0	6.9	
$MgCO_3$	5.2						
$Al(OH)_3$	32.9	Al^{+3}	14.7	16.1	18.6	31.1	24.8
		Pb^{+2}	6.5	18.0	18.9	18.3	18.2
$Fe(OH)_2$	15.1	Fe^{+2}	3.1	14.3	16		
$Fe(OH)_3$	38.5	Fe^{+3}	12.5	25.1	27.9	35.9	39.6
$Cu(OH)_2$	19.6	Cu^{+2}	4.3	18.8	21.5	23.7	21.4
CuCO3	9.86						
Silicates							
CaO $nSiO_2$[1]	7.9						
MgO $nSiO_2$[1]	4.6						
Clay Components							
Pyrophillites/Talc							
$Al_2Si_4O_{10}$ $(OH)_2$[2]	1.0						
$Fe(III)_2Si_4O_{10}$ $(OH)_2$[2]	-13.7						
$Fe(II)_3Si_4O_{10}$ $(OH)_2$[2]	7.2						
$Mg_3Si_4O_{10}$ $(OH)_2$[2]	25.1						
Micas							
$KAl_2AlSi_3O_{10}$ $(OH)_2$[2]	16.2						
$KFe(III)_2AlSi_3O_{10}$ $(OH)_2$[2]	1.0						
$KFe(II)_3AlSi_3O_{10}$ $(OH)_2$[2]	23.4						
$KMg_3AlSi_3O_{10}$ $(OH)_2$[2]	42.0						
Celadonites							
$KAl_{1.66}Si_4O_{10}(OH)_2$[2]	6.3						
$KFe(III)_{1.66}Si_4O_{10}(OH)_2$[2]	-6.9						
$KFe(II)_{2.5}Si_4O_{10}(OH)_2$[2]	11.7						
$KAl_{2.5}Si_4O_{10}(OH)_2$[2]	26.9						

1. At 25°C (You and others 2007); 2. (Rodriguez-Clemente and Tardy, eds. 1987); 3. (Ohman and Martin 1994); 4. http://www.akzonobel.com/dissolvine/functions/the_right_chelate/ accessed 11/30/2012; 5. (Taliaferro and Martell 1984); 6. (Martell 1978); 7. (Krokhin and others 2000).

Table 2. Selected solubility products (pK_{sp}) of stain and clay components vs formation constants (pK_f) of chelator–metal complexes (pH 7, 20°C).

the presence of OH^- ions. From table 2, it is clear that only HBED will work to complex Fe^{+3} directly from rust (pK_f 39.6 for Fe^{+3}).

Another important consideration is that some of the chelators have higher pK_f values than the pK_{sp} values of metal-containing components normally present in a ceramic. For example, if $Fe(OH)_3$ in a ceramic that inherently contained significant amounts of Fe-containing pyrophyllitic structures was treated with HBED, Fe^{+3} would also be removed from the ceramic body (the pK_{sp} for Fe^{+3} in these structures is –13.7). On the other hand, a rust-stained pyrophyllite of the generic form $Al_2Si_4O_{10}\cdot(OH)_2$, although free of Fe in the body, may contain soluble Al^{+3} with a low pK_{sp} of 1.0. However, any Al^{+3} bound to HBED would quickly be replaced by Fe^{+3} from the rust, with a higher pK_f than Al^{+3} for the chelator (24.8 vs 39.6). As with any cleaning system, a balance must be struck between targeting staining materials without disrupting the clay bodies themselves. If the ceramic in question suffers condition issues such as particularly low firing or unstable glazes and enamels, then the use of chelators may not be recommended, and water alone may be successful at reducing a stain, particularly if the right poultice material is used. While knowing the composition of the materials present in the object is ideal, analysis is not always possible, and therefore spot tests prior to choosing a chelator are of paramount importance.

The final factor to consider when creating a chelating solution is its ionic strength. Too high a concentration of chelating material in solution (hypertonic to the ceramic) or too low (hypotonic) means that unnecessary physical pressures are brought to the ceramic surface. Hypertonic solutions also flood the ceramic with salts and increase the risk that salts will diffuse deep into the surface, thus disrupting the ceramic body and becoming more challenging to subsequently rinse. The goal of a chelating solution is to be isotonic with the surface, theoretically matching the conductivity of the ceramic (this can be estimated through a simple conductivity measurement).

Because chelate formation is an equilibrium reaction, once a chelator is completely saturated with a metal ion, and at its equilibrium point with dissociated ions, it cannot bind additional ions (Wolbers 2000, pp. 117–118). Therefore, more will be needed to deplete additional ions in a stained ceramic. A better cleaning strategy would be to work with multiple applications of a low isotonic amount of chelator in solution and simply replenish it as needed, rather than work at initially high concentrations of a chelator.

Step 2: Choosing an Oxidising Bleach

As most stains also include organic components, bleaching often becomes a necessary second step in the stain reduction process. Oxidising bleaches function in two ways: chemically altering organic residues (making them more polar on oxidation and therefore more water-soluble), and de-colourising them. In contrast to reducing bleaches, their effect on these residues is permanent. Preliminary testing is essential, as all oxidising bleaches can potentially oxidise metallic components, particularly within low-fired bodies, or cause adverse reactions with unstable enamels, metallic glazes and gilding (Hogan 1998; Buys and Oakley 1993).

The most cited oxidising bleach in ceramic stain reduction is hydrogen peroxide (Olive and Pearson 1975; Buys and Oakley 1993; Navarro 1997; Hogan 1998; Oakley and Jain 2002; Williams 2002). Its oxidation potential is 1.8, higher than chlorine, yet weaker than ozone. Made to a slightly alkaline pH, the bleach is more effective while maintaining a safe range for most ceramic glazes. While hydrogen peroxide is stored at cool temperatures to ensure the reactivity of the solution, it is best applied under warm conditions, as the bleaching potential of the given solution increases with elevated temperatures.

Hydrogen peroxide performs well, either used at lower concentrations (~5% v/v) for general applications, or progressively at higher concentrations (10–15%) for more stubborn or specific stains. The material is quite reactive and breaks down quickly into water and hydrogen, especially in contact with organic residues. Therefore, its use in controlled poultices to limit penetration is recommended. Otherwise, tidelines may form as the hydrogen peroxide breaks down to simple water, carrying organic residues with it, re-depositing stains at the surface upon drying. Rinsing with water afterwards can be done only superficially, controlling the amount of time the bleach is active in the ceramic body.

An oxidising bleach that the authors prefer is carbamide peroxide, which is a stabilised form of hydrogen peroxide, made by adding an equal molar amount of urea. Its main advantage is its uniformity and increased efficiency at reducing organic stains (Norquest 2008). With carbamide peroxide, bleaching takes longer to occur, since it first breaks down into hydrogen peroxide, then to water and oxygen; the urea component breaks down into carbamic acid, which quickly volatilises into ammonia and carbon dioxide. This allows for a more progressive action, no residues, and better results, as demonstrated by its use in the teeth-whitening industry (Tam 1999).

Concentrations recommended are 3%, 5%, 10%, or exceptionally 20%, although proper precautions must be followed when using higher concentrations.
A group of other oxidising bleaches being tested include perborates and percarbonates, which are also more stable than hydrogen peroxide. Their main advantage is functionality at neutral pHs, but as of now more testing is required before they can be recommended.

Step 3: The Critical Rinsing Phase

Rinsing is crucially important whenever materials from a treatment could remain behind in the ceramic body. Rinsing also becomes critical, yet more difficult, with porous bodies; also, as of now, no easy method exists to evaluate the effectiveness of the rinsing phase.
The most important consideration is what happens to the reagent once it has penetrated into the ceramic body. For instance, is the reagent a stable product? Does it break down over time, and into what?
One example is the difference between ammonium and sodium citrate: both of these deliver a citric acid chelator, yet react differently within the ceramic body if not adequately rinsed. Ammonium citrate breaks down into volatile ammonia and citrate ions, which may be left behind, potentially exposing the body to the pH of citric acid (2.5–3) with future introduction of moisture. Sodium citrate, however, is more stable, and potential residues are stable salts that do not deliquesce into more acidic components. Hydrogen peroxide and carbamide peroxide, especially when used at lower concentrations, will quickly break down, causing no long-term impact. In contrast, most acids and alkalis easily form salts with materials in the ceramic body; these materials could then migrate to the surface and cause significant salt and stability issues. Stability aside, it is essential to minimise any risk of residues by using the lowest concentration of chosen solution possible. If multiple applications, larger volumes of solution, or deep penetration into the ceramic body are required, rinsing becomes even more critical. In a nutshell, best practice is to use lower concentrations, minimise the amount used, and act at the surface as much as possible.
In the chelator–bleach sequence, the latter serves already to rinse chelator residue. This is followed by a final rinse with de-ionised water. If low concentrations of chelator and bleach are utilised, the final rinse need not flood the ceramic and deeply penetrate; rather, smaller quantities of water are effective. Tests show that excessive rinsing with water is risky, as residual staining materials now affected by the chosen cleaning solutions can be more readily mobilised by water, creating the potential for tidelines and re-deposition of stains.
Another rinsing technique tested is using a DEAE (diethylaminoethyl) cellulose poultice to deliver the rinse water. This material has increased affinity for the ions one hopes to rinse, for instance to draw out remaining citrate anions. Finally, rinsing with a solvent or a solvent/water mixture (e.g. denatured alcohol/water) is being tested. Theoretically, this system can be more effective at clearing remaining citrate ions.

Step 4: Choosing a Poultice System

The most successful technique for stain reduction is through the use of a poultice material, allowing for control of the various parameters under which stain reduction is carried out. This section summarises various poultice materials tested, presenting ways in which they can be used, treatments they may be suitable for, and their limitations. Every case is different, and these will vary with each treatment. Table 3 presents recommendations for each type of poultice material discussed, including product information and application tips.
The class of materials based on cellulose includes paper pulp, cellulose powder, wet-strength tissue, and cellulose ethers. Being the polysaccharides that make up primary cell walls of green plants, cellulose is extremely hydrophilic, and its products readily absorb aqueous solutions. Its ease of use and inertness make it an extremely useful poulticing material. Paper pulp and cellulose powder poultices generally maintain good contact with the substrate through complete drying. As with any poultice application for stain reduction, allowing the poultice to dry completely is essential to ensure the stain is pulled into the poultice; if the poultice is removed before evaporation is complete, a concentrated amount of stain can redeposit on or just below the ceramic surface, often becoming more visible and disfiguring. Wet-strength tissue, while the easiest poultice to apply, does not always maintain contact as it dries. While cellulose ethers are a viable option, other gels have been found to be more effective as poultice materials.
One such gel is made from agarose. Like cellulose, agarose is a linear polysaccharide from plants, specifically species of Asian seaweed. It is soluble only in hot water (T>85°C) and gels upon cooling to a semi-flexible film within a few hours. Studies show that little to no residues are left behind, even without a barrier tissue (Warda and others 2007).

Material	Product Information	Application Technique	Pros	Cons
Paper pulp	• Acid-free, ash-free pulps (Filter Flockenmasse, formerly supplied by Mike Schafers at Custom Machine and Design) • DEAE (diethylaminoethyl) paper pulp (Sigma-Aldrich)	• Mix into damp slurry with chosen solution. Allow complete drying before removal. • Can make own pulp by blending paper sheets in blender with deionized water and letting dry.	• Conforms to smooth and uneven surfaces. Easy to apply and remove when dry. • DEAE paper pulp ideal for rinsing phase.	• If not shredded fine, tends to clump and may result in uneven stain reduction. • Danger in applying slurry too wet and causing tidelines.
Cellulose powder	• Alpha cellulose (Sigma-Aldrich, Whatman)	• Mix into damp slurry with chosen solution. Allow complete drying before removal.	• Conforms to smooth and uneven surfaces. Easy to remove when dry (brushes off).	• More difficult to apply than paper pulp due to finer particle size. Not very absorbent, meaning that repeated application may be necessary.
Wet-strength tissue	• Kaydry EX-L (Kimberly-Clark)	• Dampen sheets with chosen solution and lay on (smooth) surfaces. Allow complete drying before removal.	• Easy to apply, with fast drying time allows for speedy results. • Ideal for application where limited moisture is desired or for follow-up rinsing.	• Often does not maintain contact throughout drying, especially on concave surfaces.
Agarose gel	• Agarose powder (Universal Medical)	• Make gel of desired concentration and mix with chosen solution. Functions at pH 4.5-10. Can mix with paper pulp for added adsorption. Cast in thin sheets or blocks and cut gel to desired shape to lay onto ceramic. Allow complete drying, or remove after short time to replace with adsorbent material such as Kaydry.	• Easy to make and apply. • Easy to remove with no residues left behind. • Can control degree of penetration. • Use with water, chelator, solvent, or bleach.	• Need gravity to keep gel in contact with substrate. • Not highly adsorbent so requires addition of paper pulp to hold stain in poultice on drying.
Laponite gel	• Laponite® RD (conservation suppliers)	• Make into thick gel with warm water and chosen solution. Applied over (recommended) barrier of gampi usuyo paper and allowed to dry completely.	• Affinity for ceramic surface creates good adhesion and strong pulling power of poultice. • Ideal for pulling stains out of cracks.	• If allowed to dry directly on surface, hard film is tenacious to remove. Residues left behind may alter surface of ceramic.

Table 3. Poultice materials: product information and application tips.

Agarose gel can be made with chelating solutions, oxidising bleaches, or organic solvents, and is easy to make: a gel made with de-ionised water alone can be placed into a solution of chosen reagent and, within a few hours, the gel will equilibrate with the solution.

Perhaps the most useful quality of an agarose gel poultice for ceramic-stain reduction is the ability to control its pore size and thus its permeation into a ceramic body. When a heated agarose gel cools, the randomly-coiled polymer chains become double helixes, creating a three-dimensional network with even pores. Varying the gel concentration (possible range between 0.5 and 5%) determines the pore size. Lower concentrations have larger pores (hypertonic with the ceramic), yielding greater penetration and permeability into a ceramic. Conversely, higher concentrations yield a lesser-penetrating poultice. Practically speaking, agarose gels can be adequately used for a variety of stains, depending on how the gel is constructed.

Clay-based gels are another poultice option. The authors use Laponite RD, a synthetic silicate clay, but other options include Sepiolite (hydrated trisilicate) and Attapulgite (hydrated magnesium–aluminium silicate). All have associated health risks, and many have been found to leave residues behind or present difficulty during removal if allowed to completely dry on porous surfaces, such as ceramic and stone (Lee and others 1997; Vergès-Belmin and Siedel 2005; Warda and others 2007).

Category of Stain	Characteristics	Approach suggested
The more straightforward ones	• Stain is mostly near surface, readily accessible through loss or crazing/cracks in glaze • No sensitive components adjacent to stained area • Often the case for porcelain and higher-fired bodies	• Use poulticing material that allows ample access of reagent to the stain e.g. paper pulp, cellulose powder, 1-2 % agarose gel • Follow standard approach, using chelator, then bleach; rinse superficially afterwards with deionized water and with material that has a strong affinity for the reagent used, e.g. DEAE paper for citrate ions
The ones on rather delicate ceramics	• Access to stain is made more difficult with vulnerable/sensitive adjacent components • Often the case for ceramics with unstable enamels (particularly early ones) and gilding • For ceramics that have either a wood, ivory, metal component	• Use poulticing material that allows for careful control of the amount of reagent to the stain e.g. KayDry tissue, 3-5% agarose gels, Laponite RD • Test carefully first whether water alone or low concentration bleach; use chelators only if no contact with sensitive components can be guaranteed • Only superficially rinse afterwards
The extensive, deeper ones	• Stain has permeated throughout the body and is abundant • Stain is localized, but intense, related for instance to a specific loss or crack in an otherwise non-crazed glaze • Often the case for earthenwares that have been extensively used	• Determine goal of treatment as to whether a surface application could achieve the desired aesthetic improvement or whether entire stain must be reduced • Ideally a surface application of the reagent (chelator and bleach respectively) is desired, using a poulticing material that will carefully control the amount in contact with the ceramic e.g. agarose gel • If entire stain needs to be reduced, use poulticing material that allows for abundant application of reagent e.g. paper pulp, along with relatively high concentration of reagent (chelator and bleach respectively). Apply poultice slightly beyond area of stain to counteract formation of tidelines. Rinse carefully afterwards so as not to bring to surface remaining staining materials
The stubborn ones	• Stain is resistant to standard chelators/bleach • Often the case for ceramics that have been exposed to the elements, and the stain has become "weathered" through exposure to the outdoors, burial, or particularly harsh previous treatments • Stain has been set, possibly "cooked" in place through usage • Stain is compounded by oily or greasy component • For archaeological ceramics or those associated with cooking	• Use chelators, testing at different pHs, e.g. citrates, EDTA or careful application of acids (wet surface pre-treatment if acids used) or still solvents that are also weak chelators, e.g. acetylacetone • Use poulticing material that allows for careful control of the amount of reagent to the stain e.g. Kaydry tissue, gels, or with strong ability to retain staining material e.g. clays, agarose gels/ cellulose powder mix • Remain aware that approach may need to be modified after initial application of reagent, as stain is broken down and now more mobile and readily absorbed by poultice

Table 4. General classification of different types of stain on ceramics and approach suggested for their reduction.

If used with a barrier tissue, Laponite gels can be effective at strongly pulling stains from a body, especially those held within cracks, without presenting challenges in the removal of the dried poultice.

Case Studies

Although it is not possible to present all the ceramics treated as part of this multi-year study, four general categories emerged that capture the range of problems one may encounter. Table 4 outlines each group, as well as the suggested approach for stain reduction. Presented below is one case study from each category, demonstrating the protocol in action. One important point is that our knowledge of stain-reduction principles keeps evolving, and, in some cases, our approach would be slightly modified if faced with the same problem. Furthermore, these tests relate exclusively to objects in the Winterthur Museum collection, which holds mostly European, American, and Chinese export ceramics from the 17th to the 19th centuries.

The first category represents a standard approach with a straightforward stain on a mochaware tea bowl with a stable ceramic body void of any sensitive components (table 5). After a bleach poultice, the interior remained stained and patchy, and this reaffirmed the need to begin with a chelator to address ionic interactions holding the stain. Subsequent chelator–bleach poultices successfully reduced the stain.

The second category characterises cases where a particular component of the ceramic may be affected during stain reduction, for instance a creamware teapot with a historic pewter repair (table 6). The goal was to reduce the stain on the exterior, while preserving evidence of use on the interior and not affecting the pewter. The approach consisted of applying first a protection to the sensitive component, then targeting the stain with appropriate poulticing materials and oxidising bleach, allowing for application at the surface and locally.
The third category presents a suggested approach for porous ceramics with deeply-penetrating stains overall localised due to specific glaze losses. A pearlware pitcher with staining that penetrated through an interior glaze loss demonstrates this (table 7). The protocol of chelator–bleach–rinse was carried out successfully, the goal being to reduce staining on the exterior surface only, using a low-porosity agarose gel.
The fourth category, illustrated by a slipware dish, represents those cases where stains prove particularly stubborn. Tests with chelators and bleaches showed how the stain could be reduced, but irregularly, creating areas that appeared overcleaned. The approach consisted first in using agarose gel, with acetylacetone to break down greasy residues, and bulked with cellulose powder to absorb them. After a few applications, the procedure for stain reduction returned to a standard approach, applying a low-porosity agarose gel with a chelator, followed by an agarose gel rinse with water/denatured alcohol (table 8).

Mochaware tea bowl and saucer (Staffordshire, late 18th century, Acc. #2008.0053.002.1a,b, H4.2cm D10.7cm)

- Staining clearly associated with use; extensive overall in tea bowl obscuring pale earthenware body and giving impression glaze is tinted yellow

Before treatment:

Treatment

1. Oxidizing bleach in paper pulp poultice (15% H_2O_2, pH 8.5 with NH_4OH) applied only on interior, with incandescent lamp to aid in heating and polyethylene sheeting to control evaporation
2. Chelator in paper pulp poultice (5% ammonium citrate, pH 8.5 with NH_4OH)
3. Repeat step #1

After treatment:

Rationale

- For total stain reduction to take place, the chelator needed to be applied first; this could have been a two-step treatment only
- Sodium citrate would have been just as effective as chelator, without posing risk of acidic residues

During treatment: after first bleach poultice showing still-stained interior

Table 5. Case Study #1: straightforward stain reduction treatment (Photos: Winterthur Museum).

Creamware teapot with enamel decoration and historical pewter repair (Staffordshire, 1770, Acc. # L2007.1031.1a,b, H13cm W19.1cm)

- Staining overall, yet particularly accentuated in crazed glaze, at losses and along crack; clearly associated with use (tea)
- Treatment aims to improve overall appearance, yet leaving stains within the interior, and not affecting historical pewter repair at spout

Before stain reduction:

Treatment

1. Pewter collar protected with microcrystalline wax and Parafilm® M
2. Bleach in Kaydry tissue poultice (first 10%, then 15% hydrogen peroxide made to pH 8.5 with NH_4OH) to reduce overall stain
3. Localized bleaching of crack in Laponite RD poultices (20% carbamide peroxide at pH 8.2), applied with and then without barrier tissue
4. Deionized water/denatured alcohol rinse in Kaydry tissue poultice

After treatment:

Rationale

- Use of chelator not desired because of metallic component; two applications of low-penetrating bleach ideal for reducing staining just at surface
- Effect of bleach accentuated by covering poultice with polyethylene film and under warm incandescent light for a few hours before air drying
- Use poultice with stronger pulling power, e.g. Laponite RD, only where necessary

During treatment: dry Kaydry tissue poultice prior to removal; as it dries, it conforms and stays in better contact with convex surfaces

Table 6. Case Study #2: stain reduction on a delicate ceramic (Photos: Winterthur Museum).

Pearlware pitcher with enamel and lustre decoration (Staffordshire, mid-19th century, Acc. # 1959.1354, H 17.4 cm, W 21.9 cm)

- Heavy brown staining – heaviest throughout interior, but also evident on exterior and in concentrated patches around design elements
- Stain entered through glaze crazing and area of exposed body on bottom interior of pitcher
- Inorganic components of stain, likely migrated from hard water that was carried in this vessel

Before treatment:

Treatment

1. Chelator in agarose gel poultice (4.5% agarose saturated with 2.5% sodium citrate, pH 8.5 with NH_4OH) applied in thin strips on undecorated areas the exterior. After 10 minutes to 1 hour, stain visibly broke down, and gel strips were replaced with squares of Kaydry tissue dampened with citrate solution to adsorb remaining materials
2. Bleach in Kaydry tissue poultice (20% carbamide peroxide, pH 8.5 with NH_4OH) to remove remaining stain
3. Deionized water rinse in Kaydry tissue poultice for final rinse

After treatment:

Lessons learned

- Multiple applications of low-penetrating, low percentage of chelator were ideal for reducing staining just at surface
- If agarose gel poultice was left to dry on surface, not all staining material was pulled into it and stain deposited at the surface, just under the glaze; replacing gel with Kaydry tissue after a period of time served to avoid this problem

During treatment: strips of agarose-citrate poultice visibly breaking down stain, replaced with squares of Kaydry tissue at edges

Table 7. Case Study #3: stain reduction of an extensive, deep stain (Photos: Winterthur Museum).

Earthenware (slipware) dish with colored slips and lead glaze (Samuel Malkin, Burslem, Staffordshire, 1726, Acc. # 2010.0004.001, D 35.1 cm)

- Localized, irregular stains that masked the cream color of the slip, reducing the contrast between the background and the most important decorative elements (also composed of slightly raised brown/orange slips)
- Tests showed how application of low concentration chelator or bleach tended to specifically clean some areas, while leaving the darker stains unaffected; likely because stain includes greasy or oily components, possibly cooked into place (related to use)

Before treatment:

Treatment

1. Initial overall cleaning in zeolite/enzymatic bath to ensure even penetration of aqueous reagents and to reduce risk of pushing deeply ingrained dirt into ceramic body
2. Agarose gel chosen as it allows careful control of solvent (in this case acetylacetone, also a mild chelator, within a water phase); poultice left an hour under polyethylene film, then allowed to air-dry; four applications made
3. After fourth application, tidelines formed indicating how stain had now broken down; further testing determined that 2% agarose gel with sodium citrate, followed by rinsing with agarose gel in 80/20 deionized water/denatured alcohol now could evenly reduce stains without causing tidelines

During treatment: after surface cleaning and two applications of Agarose/cellulose powder gel blocks in 20% acetyl acetone

Rationale

- With stubborn stains, be ready to adapt approach and choice of materials as treatment progresses, since early phases of treatment may disrupt stain, allowing it later on to be effected by materials to which it was impervious at first
- Use of solvents in an aqueous phase can be effective when aqueous reagents fail, both in terms of chelating stain and rinsing residues
- Note that this treatment is still underway at time of publication; overall brighter appearance of buff-colored background already contrasts better with the decoration, but improvement still desired by curator

During treatment: with the agarose gel blocks still wet on the surface; these can be cut to exactly match the area where the stain is present, serving also to minimize the impact of the reagent on other component of the ceramic

Table 8. Case Study #4: reduction of a stubborn stain (Photos: Winterthur Museum).

Conclusion

Where do we go from here? It is hoped that many conservators will consider the proposed sequence of steps for stain reduction on ceramics and begin to test it, using the methods and materials presented here. It is clear that each stained ceramic requires careful consideration and its own treatment protocol, based on localised testing and observations. This approach allows for a logical and controlled selection of materials and methods, offering a good likelihood for a successful outcome, while minimising the risks for unwanted results.

Our main goal now is to have conservators try the techniques, materials, and sequence proposed, and later contribute their observations to the conservation community. This could be through tests done with a specific chelator, bleach, or poulticing material, or related to a specific kind of ceramic body. To this effect, we have thus far presented two day-long advanced seminars to select groups of conservators at the Metropolitan Museum of Art (May 2012) and the Walters Art Museum in Baltimore (January 2013). The participants are provided a series of chelators in agarose gel blocks with which they can safely conduct tests on a broad range of ceramics, and they are encouraged to share their results with us and the conservation community.

Similar to the changes in approach that occurred following Richard Wolbers' work on the gel cleaning of decorative surfaces (Wolbers 2000), we believe stain reduction on ceramics can be achieved safely and successfully with a strong understanding of the properties of ceramic bodies, chelators, bleaches, and poulticing materials. This will not be achieved without a few setbacks, and the discovery yet to come of new or modified materials that will work better in specific cases. However, we feel confident in providing an approach that will contribute to the continued advancement of our field. We plan to steadily continue our work, and welcome comments and ideas.

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The Bacteriological Contamination of Archaeological Ceramics: an Example from Pachacamac (Peru)

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Keywords
ceramics; archaeological objects; bacteria; biodeterioration; biocide

Abstract
This paper concerns the efflorescence of bacteria on ceramics from archaeological excavations. Biodegradation was due to Streptomyces Sp., a bacterium of the Actinomycetale order. After analysis of each contaminated object, its location in the storeroom, and our conservation materials, it is suggested that the origin of the bacteria is in the soil of the archaeological site. Microclimatic conditions and organic nutrients from the soil create a favourable atmosphere for the development of bacteria inside the storeroom. With regard to conservation treatment, the desalination process does not prevent the emergence of bacteria but appears to restrict it considerably. The application of the biocide Biotin R at 2%, diluted in ethanol, has been successful: there has been no recurrence of the bacteria.

Fig. 1. Excavations of Cemetery 1 at Pachacamac (Photo: P. Eeckhout).

Introduction

Pachacamac is a monumental coastal site in the Central Andes that reached its apogee after being incorporated into the Inca Empire (figure 1). It is situated half a kilometre from the Pacific Ocean, near the mouth of the Lurín River. It covers about 600 hectares (2.31 square miles), of which one third is occupied by the monumental sector.

The U58' section of the Cemetery 1 excavated by the Ychsma Project was heavily utilised for interments from the 10th to the end of the 14th century A.D. (i.e. the Late Intermediate Period or LIP), leading to disturbance of earlier layers. In terms of stylistic/relative dating, we have funeral contexts displaying cultural markers that span the Middle Horizon (ca A.D. 700–1000) and part of the LIP, the latter corresponding to the Epigonal and Early/Middle Ychsma (Feltham and Eeckhout 2004; Vallejo 2004).

The Ychsma ceramic style includes several successive phases. Our typological classification is based on form, ware, and decoration. We distinguish three main local ware categories: Orange, Brown, and Black.

The surface of **Orange ware** has a few-mm-wide, moderate orange-pink (10R 7/4 on the Geological Society of America rock-colour chart [GRCC 2009]) paste next to a few-mm-wide, pale-red (10R 6/2) outer paste. Microscopical examination shows that the temper is polylithic with granite and fine-grained volcanics. A pale-coloured, very clean clay carries abundant, rounded to sub-rounded single grains of quartz, as well as zoned plagioclase, potassium feldspar including perthite, together with lesser amounts of zoned brown amphibole and clinopyroxene and trace amounts of sphene. The ware carries clasts from a medium-grained granite including quartz-plagioclase, potassium feldspar-plagioclase intergrowths. Internally fine-grained altered/weathered volcanics include much chert (some with quartz or feldspar microphenocrysts), 'trachyte', and felted feldspathic rocks, as well as rare sandstone. Voids in the clay are partially infilled with micritic carbonate.

The surface of **Brown ware** is a moderate brown (5YR 5/4) within a 1-mm-wide, discontinuous black (N1) rim. Microscopical examination shows that the temper is almost monolithic in its non-plastics. A dirty clay carries abundant, sub-rounded to sub-angular single grains of quartz, plagioclase (some altering to fine-grained white mica), and potassium feldspar, together with minor amounts of green and green-brown pleochroic amphibole and trace amounts of sphene and epidote. Other rock clasts are rare but include spherulitic rhyolite.

The surface of **Black ware** is a uniform medium-grey (N 5), with a darker rim that is less than 1 mm wide. The raw materials are similar to Orange ware, but black ware pots are made either of a fired untempered dirty clay or a polylithic sand temper added to a poorly cleaned/uncleaned clay.

Since 2005, the Ychsma Project's conservation team has been handling the treatment and preventive conservation of archaeological objects removed from the excavation. These are mainly ceramics, gourd, wood, metal, bone, and textiles. The team's tasks are to help on the excavation with the extraction of fragile pieces, to work in the laboratory on conservation and restoration treatment, and to make the storeroom at the Pachacamac Site Museum (MSPACH) fit for the long-term storage of objects. The conservation season lasts between one and three months.

Sampling

The selected group of samples includes 215 complete pottery vessels. These belong to the set of 254 archaeological objects that received conservation treatment between 2005 and 2011. 92.5% of the samples come from Unit 58'. The collection has been kept in the Ychsma Storeroom at the MSPACH.

After excavation, the archaeological material is taken to the registration area, where ceramic vessels (whole or fragmented) are separated from the remaining potsherds. The vessels pass to the conservation laboratory where they receive treatment; this consists in most cases of mechanical cleaning, desalination with deionised water, and the reassembling of

Fig. 2. Vessel storage in a cardboard box, Ychsma Storeroom 2010 (Photo: K. Colonna-Preti).

fragments. The remaining potsherds are washed with tap water, and then the diagnostic sherds are selected and receive a desalination treatment.
The vessels are kept on polyethylene foam stands and protected with bubble wrap; potsherds are stored in polyethylene bags (figure 2). All the pieces are placed in cardboard boxes, which are then arranged on the shelves of the storeroom with the rest of the archaeological material. Until 2011, the pieces were stored in 36 boxes. In that year, the ULB handed over the archaeological material to the MSPACH. At that time, the vessels were removed from the boxes, placed on shelves, and displayed in the same way as the rest of the pieces in the museum storerooms.

Biodeterioration

Description and Progression of Biodeterioration

It was in 2008 that we first observed an alteration to the surface of ceramic material; this consisted of small, white, round floccose spots, between 1 and 2 mm in diameter (figure 3). Despite the whitish colour, the spots can be distinguished from a saline efflorescence, which forms a more uniform veil whose crystals can be recognized. In that year, three vessels seemed to be affected. All of them came from the same archaeological unit (U58'), excavated in 2004 and 2005. They had been kept in individual bags and stored in two different boxes. None of the vessels had been desalinated. We carried out a desalination treatment and subsequent cleaning with ethanol (see table 1).
There was no conservation season in 2009, but an assistant monitored our collection. Six vessels were found to have been affected by the spots (figure 4), one of which had already been affected previously and been given treatment. All came from U58' and were excavated during the 2005 and 2008 field seasons. The vessels had been kept in three different boxes, one of which had already contained contaminated vessels. Five of the vessels had been desalinated. At that point, our investigations commenced with a view to identifying the micro-organisms responsible for the spots and to decide on the appropriate treatment.
The number of contaminated objects had already increased to 35 by the time we were able to start work on them in the following season. The vessels came from three units: U58', U89, and U94, excavated in 2004, 2005, and 2008. They had been kept in 11 different boxes, four of which already contained affected vessels. Two vessels had been desalinated. We washed the objects with tap water, desalinated them, and treated them with the selected biocide product.
In 2011, five new objects were affected: four came from U58', which had been excavated in 2004, 2005, and 2008. The vessels were kept in four different boxes, one of which

Fig. 3. Small white spots on ceramic observed in 2008 (Photo: K. Colonna-Preti).

Fig. 4. White spots observed on pottery in 2009 (Photo: K. Colonna-Preti).

had already been affected; none had been desalinated. We treated the affected vessels with the biocide as well as treating those that had been stored in the affected boxes.
In 2012, after monitoring the entire group of samples, it was observed that any vessel from the Ychsma Storeroom showed spots. Although the pottery of the 2012 season does not belong to the samples previously analysed, it is relevant to note that we found a bag with some diagnostic sherds with white spots (figure 5). These had not been previously analysed; however, they are very similar to the identified bacteria. The sherds come from U58', and they had only been washed with tap water. Following desalination, the fragments were treated with biocide. It is noteworthy that this 2012 material had never been in contact with the sample analysed previously, because in that year we installed our laboratory in Puente de Lurín, 5 km from MSPACH.

	2008	2009	2010	2011
Affected objects	3	6	35 (+6 already affected in 2009)	5
Boxes whose contents have been affected	2	3	8 (+3 already affected in 2009)	4
Desalinated objects	0	5	2	0
Treatment	ethanol	none (no conservation season)	Biotin R 2%	Biotin R 2%
Recurrence	-	1 (treated with ethanol)	1 (treated with ethanol)	0
Archaeological Unit	U58': 3	U58':6	U58':33, U89:1 U94:1	U58':4 A2:1
Field Season	2004, 2005	2005, 2008	1999, 2004, 2005, 2008	2004, 2005, 2008

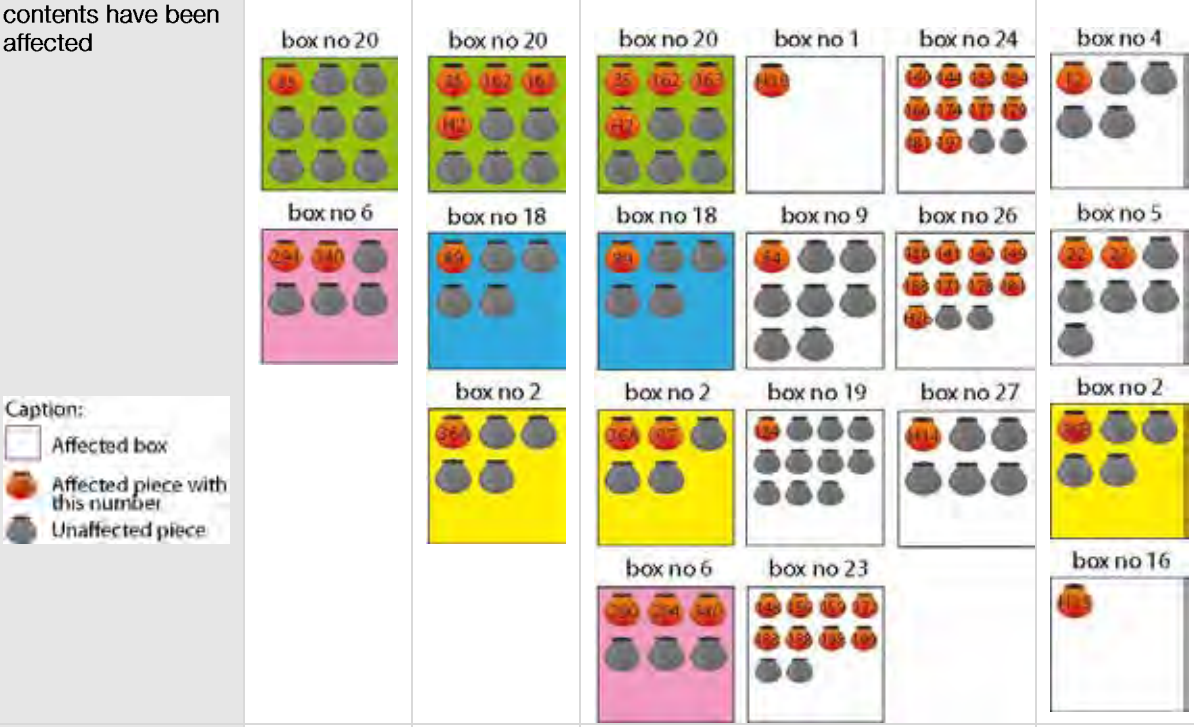

Table 1. Summary of the provenance of objects and biodeterioration progression.

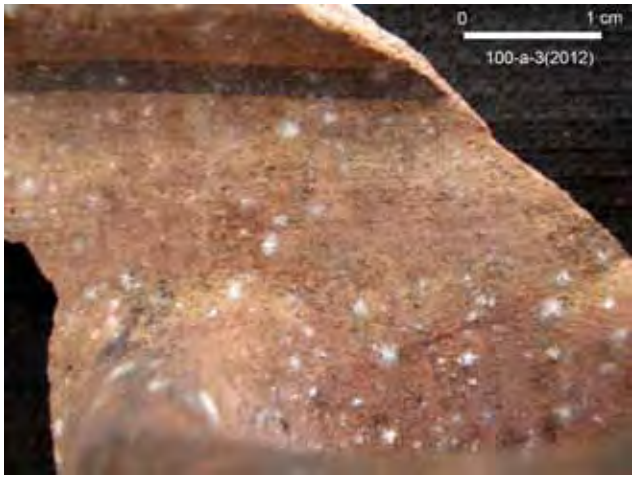

Fig. 5. Small white spots on ceramic observed in 2012 (Photo: K. Colonna-Preti).

Identification of Micro-organisms

Initially the appearance of the micro-organisms made us think of a fungal contamination. The microscopic observation of the samples in the Mycothèque of the Université Catholique de Louvain (MUCL), in 2009, determined that the colonies were not created by fungi, but exhibited the typical morphology of actinomycetes.

The Microbiology Laboratory at Ghent University (LMG) isolated five dominant colony types using the following method. The material was placed in an LMG medium no. 185 – TSA – and incubated aerobically at 28°C for several days. For the initial analysis, a fatty acid gas chromatography was used. The profiles were identified with the Microbial Identification System (MIDI Inc., Newark, DE, USA), using the TSBA50 database. The results indicate that three colonies, whose colour ranges from pale to dark beige, belong to the genus *Bacillus*, and one yellow colony belongs to the *Microbacteriaceae* family. The fifth type, a white colony similar to the spots observed on the original material, was identified in a second analysis after being isolated in actinomycetes isolation agar (AIA) and incubated at 30°C for several days. The results obtained with a partial 16S rDNA sequence analysis for the two strains indicate that they belong to the genus *Streptomyces*, of the Actinomycetale order of bacteria.

According to M. Pennincks (Unit of Microbial Physiology and Ecology – ULB), the principal biodeterioration is caused by those actinomycetes (personal communication 23/9/2009).

Biocide Treatment

With these results in mind, we carried out an investigation to determine the most appropriate treatment. Several practical limitations restricted our research: first, the difficulty of accessing the collection because of the short duration of our field seasons, which prevents us from making regular observations, from sampling at will, and from carrying out in situ research. Furthermore, because the next field season was almost upon us, it was urgent to find a speedy solution since we feared an uncontrolled contagion. Hence we concentrated on finding a biocide treatment to eliminate micro-organisms while making an in-depth study of contamination.

Searching through relevant literature, we found several biocides whose action is effective against bacteria (Borgioli, De Comelli, and Pressi 2006; Borgioli, Pressi, and Secondin 2003; Gabrielli and Zander 2007). Biotin S, a biocide from C.T.S. brand, seemed to be a good option because of its antibacterial properties, its broad spectrum of action and its resistance over time. This tin-derived compound contains heavy metals and is likely to be banned in the future because of its toxicity for the environment (Borgioli, De Comelli, and Pressi 2006). Upon the acquisition of the product, the supplier (C.T.S.) ceased to market it. They proposed a substitute: Biotin R, an iodopropynyl butylcarbamate (IPBC) and octylisothiazolinone (OIT)-based compound. The active ingredients of IPBC and OIT are known for their antibacterial and fungicidal efficacy and are used as preservatives for many products such as varnishes, plastics and wood. In conservation and restoration, they have been used against bacteria and other types of biodeterioration with good results (Bartolini, Pietrini, and Ricci 2007). The concentrated product is a thick yellowish liquid, not self-flammable, insoluble in water, and soluble in alcohol, ether, and aromatic and aliphatic hydrocarbons; it has been applied in a diluted form on numerous monuments (C.T.S. 2009).

In 2010 and 2011, after removing the white spots with water and a brush, and desalinating the pieces, we applied Biotin R at 2% in ethanol with a brush. So far we have not observed a recurrence of bacteria on the objects treated in that way.

Results and Discussion

After four years of study, we herewith propose an initial hypothesis about the origin of micro-organisms, the factors leading to their development, and the treatment that should be applied.

Origin

We have identified four possible sources of micro-organisms: the archaeological soil, the water used for washing and desalination, the cardboard boxes, and the air in the MSPACH storeroom.

With regard to the archaeological soil, it has been noted that the first three vessels with bacteria come from U58', as do 93.9% of the contaminated pieces. This high percentage is not surprising considering that 92.5% of the sample comes from this unit. In 2012, four years after the last excavation, we are still finding affected sherds from that same unit. Hence, an analysis of the soil in the unit U58' will be a priority for the next season.

With regard to the water, it has been noted that bacteria first appeared in three vessels that had been washed with tap water, but not desalinated. However, a minority (30.6%) of the affected vessels were washed with tap water in different seasons. If the contamination source comes from the water distribution system, it would mean that the water has been contaminated for several years and affects the MSPACH and Puente de Lurín. Yet it is unlikely that bacteria come from deionised water (coming from an external laboratory), since the first affected vessels and those from 2012 had not been desalinated. Interestingly, biodeterioration tends to appear on undesalinated vessels (81.6%). Ongoing water analysis will allow us to test these hypotheses.

With regard to the boxes, they were made to measure from re-used cardboard, as it is common in the Peruvian archaeological field. Until recently, we did not consider the boxes as a contamination source, which is why we did not replace them. In 2011, with the new display of the objects, the boxes were removed. As biodeterioration appeared in the material excavated in 2012 that was never stored in boxes, we think that the containers are not a source of contamination. Nevertheless, this hypothesis will have to be confirmed by the analysis of the remaining boxes.

In 2011 and 2012, we examined another storeroom within MSPACH, located in the same building as the contaminated Ychsma Storeroom. We did not observe any biodeterioration similar to the kind found in our collection. The fact that we find the same biodeterioration in material excavated in 2012, which has never been stored in the MSPACH, makes us think that the contamination does not come from the museum storerooms themselves, because it seems to be limited to the Ychsma Storeroom.

An examination of the literature reveals that actinomycetes, especially *Streptomyces*, have been identified in other items that are part of cultural heritage, such as wall paintings (Karbowska-Berent 2003; Karpovich-Tate and Rebrikova 1990) and stone (Abdulla and others 2008; May and others 2000). They often occur in a subterranean environment (Akatova, Gonzalez, and Saiz-Jiménez 2007; Groth and others 1999). However, up to now we have not found instances where they have been identified on ceramics.

The actinomycetes are a successful group of bacteria found in a multiplicity of natural and man-made environments. They are an important component of the microbial population in most soils. Among the genera, isolated *Streptomyces* are the most numerous. Regarding its presence in soil, Goodfellow and Williams (1983, p.195) mention: 'Streptomycetes spores can be dispersed above the soil when soil aggregates are disturbed by wind or rain, whereas dispersal within soil is assisted by water movement and arthropods'. Actinomycetes are also found in aquatic environments: 'There is little to suggest that any actinomycete has become specifically adapted to living in the freshwater ecosystem. However, there is some evidence that they can become active in such habitats in the presence of suitable substrates and favourable conditions for growth. Actinomycetes have also been detected in water distribution systems, where organic debris and well-oxygenated water can allow growth and production of taints' (Goodfellow and Williams 1983, p. 201).

At the present stage of our analysis, our conclusions suggest that the *Streptomyces* responsible for the biodeterioration come from the soil of U58', which has been excavated from 2004 onwards. This unit contains a cemetery with numerous organic remains. Its underground environment is conducive to bacterial growth, as has been observed in other cultural hypogea. However, at present we cannot rule out contamination from tap water, until we have made further analysis.

Growth Factors

Observations on the occurrence of micro-organisms in the Ychsma Storeroom indicate two possible methods for its transmission: either objects within the same box become contaminated and then the contamination is transferred from one box to another, or bacteria occur in a latent state in all the ceramic remains. Both possibilities might occur in tandem.

With regard to the reproduction and nutrition of actinomycetes, Goodfellow and Williams (1983, p. 195) indicate: 'It appears that streptomycetes exist for extended periods as resting arthrospores that germinate in the occasional

presence of exogenous nutrients. Particulate organic substrates, such as root fragments and dead fungal hyphae, are rapidly colonized by mycelium, which soon produces spores above the substrate; several different strains may grow together in a restricted area'. Studies done on actinomycetes in decayed stone indicate that 'since the nutrients available in decayed stone are likely to be complex organic remains, the actinomycetes may dominate this environment as they have remarkable abilities to utilise a wide range of more complex and recalcitrant polymers such as proteins, polysaccharides and lignocellulose' (Abdulla and others 2008, p. 218).

An essential aspect for the growth of micro-organisms is the availability of water, which varies depending on the composition of the substrate and the environment. Bacteria are very demanding of water and can only be developed on substrates with high water availability (Cahagnier 2002).

Besides nutrition, several environmental factors influence the activity of actinomycetes in the soil. Studies conducted in the laboratory have shown that the optimum temperature for growth is between 25 and 30°C. Most grow with a pH between 5.0 and 9.0, with an optimum value around neutrality. However, there are acidophilic streptomycetes growing between pH 3.5 and 6.5 (Goodfellow and Williams 1983).

In the present case, the MSPACH is 3 km away from the sea, in an arid environment, which is deficient in rainfall throughout the year. The climate is semi-hot and humid (SENAMHI 2012). The MSPACH weather station indicates that moisture levels at the site are high, ranging from 65% relative humidity (RH) in the hottest months (January and February) to 100% in the coldest months (July and August). The average minimum temperature is 12°C during August; the average maximum temperature is 40°C in February (Pacheco and Uceda 2011).

Microclimatic conditions in the Ychsma Storeroom are conducive to the development of bacteria because of the warm temperature and high relative humidity outside. The fact that bacteria developed in 81.6% of cases in undesalinated vessels leads us to believe that the organic residue present on ceramics, even after they have received a preliminary washing with tap water, provides sufficient nutrients for the development of bacteria. Moreover, the presence of hygroscopic salts favours the availability of water (which the bacteria need for their growth). Further studies are needed to define better what values of temperature and relative humidity cause the growth of bacteria. For the moment, we cannot see if there is contagion from one piece to another, even though the growth of bacteria inside the boxes suggests it.

Alteration and Treatment

So far, examination of the objects was limited to visual observations of the surface with the naked eye. The alteration caused by the bacteria on ceramic sample that we observed is aesthetic in nature. The white spots on the surface hinder our appreciation of the ceramic paste and the surface finish.

Apart from the aesthetically disturbing effect, micro-organisms may cause further damage. Some bacteria can create discolouration and staining (Karbowska-Berent 2003; Portillo and González 2011). The chemical alteration produced by micro-organisms was initially disregarded, but some studies show that it has an effect on the substrate. Studies carried out by May and others (2000) indicate that the weight loss produced by actinomycetes in decayed stones is negligible. However, as seen under the scanning electron microscope, there was evidence of pitting and erosion troughs around the margins of colonies of bacteria.

With regard to the biocide treatment, if the bacteria have not recurred after a lapse of two years when Biotin R has been applied, it would be an indication of the product's efficacy. As a preventive measure against contamination, we applied the biocide on vessels stored in affected boxes. However, not all the objects have been treated, as we do not know how the product evolves in the long term. For this reason, and because chemical treatments may affect future analysis on ceramic, we limited ourselves to a minimal intervention. We are carrying out analysis to check chromatic variations of the ceramic after biocide application. Further investigation is necessary to check the chemical stability of the product, whether it is harmless for treated surfaces, and its long-term efficacy.

Although direct methods are one of the options, and sometimes the only option, for limiting the agents of biodeterioration, indirect means are to be recommended because their results are definitive. Limiting the source of nutrients and controlling the environmental conditions (i.e. humidity, light, temperature, and pH) are the best strategies for controlling the development of micro-organisms (Portillo and González 2011; Nugari and Salvadori 2003). Warscheid (2000) recommends keeping artefacts already contaminated at humidity levels lower than 55% of RH; non-contaminated objects will tolerate up to 65% RH, depending on the type of material. Because of its proximity to the sea and its structural features, the Ychsma Storeroom does not offer ideal conditions for controlling the microclimate. We have limited the supply of light and tried to promote better

ventilation; however, a long-term solution has to be found in collaboration with the MSPACH to control and maintain stable environmental conditions at low RH values. In addition, a periodic control and a simple maintenance work are essential to prevent biological growth.

Conclusions

Micro-organisms that appeared on archaeological ceramics from the Ychsma collection have been identified as bacteria from the genus *Streptomyces Sp.* and *Bacillus Sp.* It is the former that seem to be responsible for the macroscopic small white spots visible on the objects. The rapid development of these micro-organisms within the storage boxes has been impeded by the application of biocide Biotin R at 2% in ethanol.

Our own observations, as well as the analysis of the bacteria, have led us to conclude that the source of the micro-organisms lies in the excavation soil, particularly in U58' where many mummies and organic remains have been found. *Streptomyces* are common in soil and have been identified in other items of cultural heritage, such as mural paintings and stones, particularly in subterranean environments. Moreover, the tap water used to give a preliminary wash to the vessels is a source of possible contamination. Ongoing analysis will verify these hypotheses.

With regard to the factors that promote the growth of bacteria, we think that the organic residue already present on ceramics provides sufficient nutrients, even after a preliminary bath and desalination treatment. The presence of water within ceramics is essential for the development of bacteria, and the environment outside contributes to this development with its high humidity levels and microclimatic variations; the presence of hygroscopic salts inside the ceramics also participates. For this reason, desalination treatment appears to be an essential factor in limiting the supply of nutrients. At present, we are unable to determine if there is a contamination of micro-organisms within the boxes, and eventually from one box to another.

Biocide treatment has been successful in the short term. This direct method of eliminating biodeterioration must be combined with control of the microclimate within the Ychsma Storeroom in order to prevent bacterial growth. However, the reduced resources available locally for adapting rooms to the storage of archaeological material and climatic characteristics of this area is a real challenge for conservators. Further studies are needed to define better the chemical alteration produced by bacteria, to detect potential damage on the substrates, and to monitor the efficiency and stability of the biocide treatment.

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Public Art – Developing a Roadmap for Management and Conservation

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Keywords
public art; outdoor ceramics; outdoor sculptures

Abstract
The project 'Public Art' was part of a broader research programme of the Movable Heritage Division of the RCE (Rijksdienst voor Cultureel Erfgoed or Cultural Heritage Agency of the Netherlands) that was active from 2010 to 2013. The target group for the project were the caretakers of public art in the Netherlands, and the objective was to improve the preservation of public art by developing a roadmap to be used as a guideline for both management and conservation. Public art was defined as: all artworks permanently situated in the public space, such as outdoor sculptures, or attached to public buildings (monumental art). The roadmap will soon be available on the RCE website (www.cultureelerfgoed.nl), and an English version is in preparation.

Introduction
Public art forms a significant part of a society's cultural heritage. It is also the most accessible part of this heritage, being located in the public domain: in parks, squares, streets, and buildings. However, the management and conservation of public art in the Netherlands is still in its infancy, and practical preservation strategies have not yet been developed. Interventions relating to conservation or maintenance are often made ad hoc without a clear structure or focus. Further, no overview of the specialised expertise available exists in the Netherlands, and there is no targeted training for the caretakers (employees responsible for managing a collection) of public art. The fate of public art is different from that of artworks in a museum environment where such structures and strategies do exist.
The management problems related to public art are increasingly in the spotlight, both in the Netherlands and abroad. The need for more knowledge and clear guidelines on both the conservation and the management of public art is evident, as is shown by the number of questions on this subject that are asked of the Rijksdienst voor Cultureel Erfgoed (RCE, Cultural Heritage Agency of the Netherlands). Such questions come mainly from the individual caretakers, but also from maintenance companies. Defining the roles of the caretaker, maintenance employee, and conservator has proved to be difficult, largely due to the lack of clear procedures or guidelines.
A project group within the RCE was set up to deal with this issue. During the initial phase, the members studied the existing knowledge and experience in the field from publications (Morelissen 2007, De Wal 2009) and related projects abroad. One such project was the 'Save Outdoor Sculpture' (SOS) in the U.S.A. (http://www.heritagepreservation.org/programs/sos/ index.html). The SOS project was very inspiring, especially in its work on public participation in caring for public art, and it was helpful in the process of creating simple and structured guidelines. In Germany, a working group, 'Aussenskulpturen', was set up within the German Society of Restorers (VDR: Vereinigung Deutscher Restauratoren) (Breder and others 2011).
Further, relevant museum procedures and guidelines were studied to see if they could be adapted to the issues of public

art (Luger, van Leijen, and de Rijke 2008). Such guidelines included SPECTRUM, the UK museum documentation standard (McKenna and Patsatzi 2009) and LAMO (Bergevoet, Kok, and de Wit 2006). However, the specific problems and risks relating to public art, such as weathering and vandalism, are hardly mentioned in the existing museum guidelines as they are generally aimed at artworks in an indoor environment. The aim of this project was not only to produce a practical roadmap specifically relevant to the management and conservation of public art but also to combine this with an educational programme to stimulate and teach its application.

The Structure of the Project

The project was planned in phases. After the initial literature research was completed, an expert meeting was organised to shape the project structure. The following step was the setting up of an online survey to obtain information about the size and composition of municipal collections. Three case studies were chosen, each focusing on a different aspect that represented typical problems related to Dutch public art that had come to light as a result of the survey: vandalism, biological growth, and location-related issues. With the experience gained from the preliminary research together with the case studies, it was possible to draw up a roadmap.

Survey of Public Art

The online survey involved 25 municipalities in the Netherlands (both large and small) and aimed to obtain data on the then current situation. The results showed that the municipalities surveyed owned an average of 158 works of public art (varying between 34 and 600 items). Most municipalities were responsible for approximately 100 works of art, with the larger municipalities owning significantly more. Art in public spaces is made from a wide variety of materials, although metal was found to be the most common. The average composition of the collections was as follows:

1. metal = 47%
2. stone and stone-like material = 22%
3. composite materials = 13%
4. glass and ceramics = 6%
5. plastic = 4%
6. wood = 3%
7. other materials (for instance interactive artworks) = 3%
8. painted surfaces (mainly wall paintings) = 2%

Because municipal collections of public art involve a wide variety of materials, there is inevitably much diversity in the damage and problems encountered. The types of damage most frequently mentioned were: vandalism, biological growth, location-related issues, and damage relating to the outdoor environment. It was further discovered that, although some collection documentation exists in most municipalities, it is generally very limited in both its detail and scope.

The Approach to the Case Studies

As a result of the findings of the survey, three case studies were chosen that represented common issues. The case studies involved three different materials (ceramics, steel, and stone), and the problems they posed were considered to represent typical issues that caretakers encounter on a daily basis. By examining these case studies, it was possible to map out the processes needed to deal with the problems and thereby to build up the structure of a practical roadmap. The project team was multi-disciplinary, including scientists, art historians, museum curators, and conservators. A number of focus areas were defined and placed within a working framework that could be tested on the case studies and then be adjusted and improved. Apart from examining the artworks themselves, their cultural context (the collection to which the work belonged and their place in the oeuvre of the artist), the physical context (location and environment), the objects' history, and the function of the artwork were also documented. The aim of the roadmap was to provide a system that involved low-tech techniques that could be applied by caretakers or their staff. However, in order to assess the relevance of a low-tech approach (does it tell us enough?), a limited number of high-tech analytical techniques were applied to the case studies in order to verify certain results.

Case Study 1: 'Ripped Archive Box' (1985), by Kees van Renssen (1941–present)

The artwork 'Ripped Archive Box' is situated in the Town Hall Square of the town of Emmen (figure 1) and serves as a general war memorial for the municipality. The title and the shape of the artwork refer to the municipal archives formerly situated at this location. Every year on 4 May, a Remembrance Day event is held.

It is a large work (254 x 331 x 80 cm) consisting of two masonry elements that are covered with glazed tiles.

The glazed tiles are made of light-coloured high-fired earthenware, and are all different in shape, thickness, and size (approximately 35 x 35 cm and 15 x 20 cm). The work depicts a cardboard archive box, ripped into two parts, showing fragments of the documents that it contains. These fragments relate to archive records of the municipality of Emmen from the period 1940–1945, the duration of the Second World War in the Netherlands.

The research question posed by the municipality of Emmen was: 'The memorial continues to deteriorate, and it seems that the cause is water. How can we preserve the artwork and develop a viable and affordable restoration and maintenance plan?'

The documentation of the object supplied by the municipality of Emmen was fairly complete and consisted of a brief description of the object, its history, photographs from different periods, two reports of previous research, and an outline sketch of the construction. Unfortunately, no images of the original situation after installation, information on the materials used to make the artwork, or drawings of its internal structure were available. Maintenance data either had not been recorded or were lost. The available details and dates of past damage and vandalism were incomplete. Although the research reports were useful, the data given were often very brief. Through an interview with the caretaker and a former employee, it was possible to obtain additional information.

The artwork was measured and photographed from all sides, and details were recorded, notably of the damages, old restorations, and biological growth (figure 2). The vegetation growth, degradation of the surface, and damage spots were studied further using a USB microscope (Dinolite) at magnification 30 and 200x.

The different forms of damage and past treatments were defined and documented and later recorded on a digital damage map. Simple spot tests were carried out (using Quantofix semi-quantitative test strips) to provide an indication of the presence of soluble salts. Small samples of mortar and loose tile fragments were taken to enable analysis of their composition and to investigate salt content further. In addition, the physical context was assessed. The work is situated in a wooded park, and the trees influence both the length of precipitation contact (overhanging trees that drip) and the drying process (lack of direct sun). A heavy rainstorm during the investigation clarified the problem of water drainage when rainwater was seen to collect on the top of the work (figure 3).

Fig. 1. General view of the work 'Ripped Archive Box' in Emmen by Kees van Renssen (Photo: R. Morelissen).

Fig. 2. Detail of 'Ripped Archive Box' showing the damage to the ceramic (Photo: R. Morelissen).

Fig. 3. Detail of the war memorial: Water 'pooling' on top of the artwork in the rain (Photo: R. Morelissen).

The collected data were processed and recorded on a digital map using Metigo mapping software (figure 4). This helped the working group to visualise the damage zones and to analyse and understand the causes of the damage.
A risk analysis was carried out together with the caretaker in order to determine which factors were significant for the deterioration of the work. Damage caused by water (primarily through precipitation) and human actions (notably unsuitable conservation and maintenance treatments) were considered to be central factors, while vandalism (which had initially been seen as a major concern) was shown to be of minor significance.
Much useful information was gained from an interview held with the artist regarding the materials used as well as the process, design, concept, and meaning of the work. In addition, the location and the choices (materials and procedures) made by the artist were discussed. The artist explained that, due to deadline restrictions, the tiles were fired for a shorter time than is desirable for an outdoor environment; this could have played a role in the present poor condition of the ceramic. He also could tell us that the original mortar was cement-based and that the tiles had been glued to the inner brick elements with a commercial tile adhesive (the name of which he had forgotten). The artist later sent additional documentation, including recipes of the clay and glazes and photographs of the creative process. It then became clear that the tiles were hollow with approximately 4 cm thick walls.
In order to gain a better idea of the composition of the mortar and the presence of soluble salts, samples were analysed, using spot tests (Quantofix chloride test strips) as well as scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDX) (figure 5) and X-ray diffraction. SEM-EDX analysis showed the mortar to consist of quartz or silica–alumina particles bound together with a calcium-based material. The mortar is quite hard and most probably cement-based. Spot tests proved negative for the presence of soluble chlorides or sulphates, but SEM-EDX showed sulphur to be present, which is typical for Portland cement. Under the SEM, the degradation of the ceramic surface as a result of salt crystallisation was evident.
The main problems found on this work were loss of the mortar (figure 6) and active flaking of the tile surface. The problems with the mortar probably stem from the fact that it lacked porosity, resulting in water being trapped and causing damage by extreme temperatures (during freeze–thaw cycles).
The flaking of the glaze was first recorded in 2007, when restoration work took place that involved retouching of the lost fragments rather than tackling the cause of the deterioration. The most severe damage of glaze loss was on the top of the sculpture where water could enter through the porous joints between the tiles (the glaze being non-porous). This was most problematic on the top of the sculpture, which, due to its contoured shape, collects water, causing it to pool and then penetrate down into the sculpture. It is possible that this water contains salts from the mortar. The drainage pipes in the base of the sculpture (which are meant to drain water from the interior) were probably obstructed by dirt, thus trapping water inside the structure.

Fig. 4. Damage mapping of the east side of 'Ripped Archive Box' (green = biological growth; light blue = cracks; dark blue = glaze loss; red = old repairs; yellow = mortar loss) (Photo: R. Morelissen, damage mapping by E. Moody).

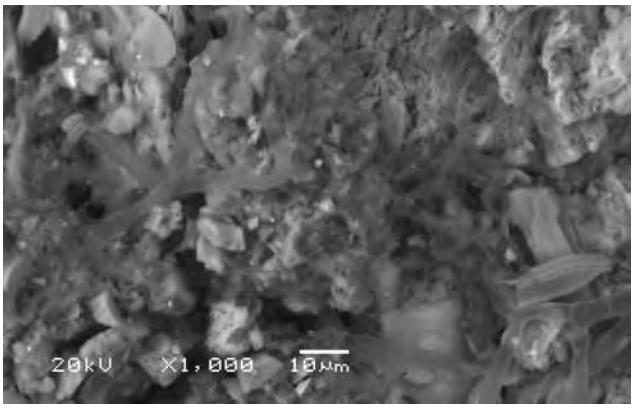

Fig. 5. SEM image (1000x) showing unidentified roots (probably a fungus) penetrating and damaging the ceramic structure (Photo: I. Joosten).

Biological growth was found primarily on the mortar, the interior wall of the northern element, and exposed areas of earthenware where there was glaze loss. Plant organisms can cause damage to a ceramic by increasing water absorption, secreting chemicals that selectively dissolve minerals, or mechanically breaking up the surface with their roots. Photographs of four different species of lichen (figure 7) found on the artwork were shown to a lichen expert, who identified three of them, although he could not say whether any of these different types could damage the ceramic.
The treatment proposal (Moody, Morelissen, and Huisman 2012) formulated following the condition report focused on reducing the transport of water through the monument, by taking measures to adapt both the artwork itself as well as its surroundings (reducing vegetation).
The lesson learned from this case study was the importance of knowing as much as possible about the materials and techniques used by the artist as well as any previous treatments. Another aspect that became clear was that, before commissioning an artwork, pre-conditions such as the durability of the materials are seldom defined or discussed with the artist.

Case Study 2: Steel Sculpture (Untitled, 1971), by Arie Berkulin (1939–present)

The second case study was a galvanised steel sculpture created in 1971 by Arie Berkulin. The sculpture is part of the national collection of the Netherlands, which is managed by the RCE. In 1971, the sculpture was given on loan to the municipality of Emmen. The main problem in this case was the corrosion that affected mainly the lower part of the sculpture. The research question was: 'How serious is this corrosion?' Research showed that there were some minor traces of vandalism (scratching and a dent). Further, it was discovered that the sculpture had an insufficient foundation, making it unstable.
Research of the corrosion showed that this was caused by the rough way the sculpture had been galvanised (an effect intended by the artist, as he explained during our interview). The corrosion proved to be superficial and could be removed quite easily.
This case study brought to light the difficulty for caretakers with limited knowledge of materials and deterioration to assess a complicated problem such as metal corrosion. It also showed the advantages of damage mappings to clarify the different problems and zones of damage.

Case Study 3: War Memorial (1958), by Jaap Kaas (1898–1972)

The third case study was a war memorial in French limestone by Jaap Kaas situated in De Bilt and dating from 1958. Here, the main problem was the formation of cracks in the lower part of the sculpture. The caretaker feared there was a problem with the structure (foundation) of the artwork. Also, a graffiti attack and the consequent removal of the graffiti using unsuitable methods had resulted in a disfiguring stain. The Euville limestone is known to be porous and susceptible to the wet climate of the Netherlands,

Fig. 6. Mortar-loss on top of the war memorial (Photo: R. Morelissen).

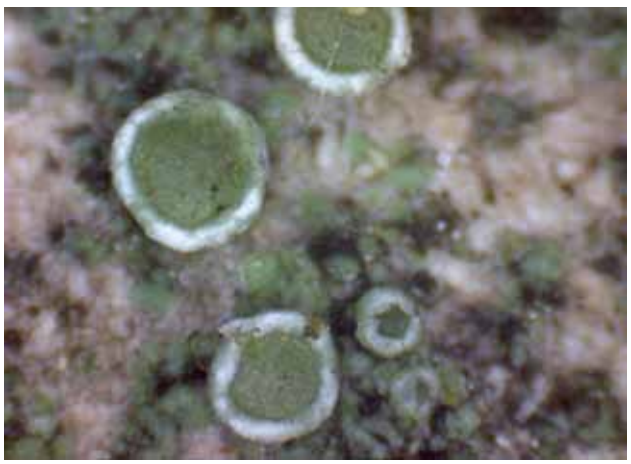

Fig. 7. Microphotograph of the lichen Lecanora hageni on 'Ripped Archive Box' (200x) (Photo: R. Morelissen).

although this sculpture did not show much weathering damage. Damage was observed mainly on the higher section of the sculpture, whereas the lower section was still in good condition and retained evidence of chisel marks. An anti-graffiti coating based on beeswax (Supral) had been used on the sculpture in the past and had apparently obstructed the drying of the stone, causing it to retain water. The research team concluded that the cracks had been caused by moisture retention in combination with freeze–thaw cycles rather than by a structural problem. Improving the drying of the stone should reduce the chance of new cracks forming.
This case study proved that it is difficult for caretakers to decide whether a specific treatment or conservation product that had been used in the past is still providing protection to the surface. This could help to decide if such a product could be used in the future – if it is still available on the market.

Conclusions from the Case Studies

The case studies provided practical insights into the problems of the management and conservation of public art in Dutch municipalities and helped the project group to shape the roadmap.
Although documentation is often substantial, it is generally limited with regards to the initial situation (materials used, inner construction, foundations, and physical context of the object). Previous condition reports were usually made only after an incident (such as a vandal attack), and documentation of treatments and maintenance was usually incomplete.
Although there is often information about the products used for maintenance and conservation, essential details are missing (such as product fact sheets). Changes in the surroundings of the object were hardly documented.
Interviewing the caretakers and present and former maintenance workers about existing procedures and practice concerning management and maintenance proved to be very valuable and enabled the researchers to obtain the missing information needed. It became evident how the caretakers' lack of knowledge seriously affects decision-making.
Interviewing the artists was shown to be invaluable, and this provides essential information about the materials and methods used to create the artwork. Information could also be gained regarding the intentions of the artist and the artist's view on the present situation, the conservation problems, and the importance of the artwork within their oeuvre.
The danger of 'ad hoc' treatments that often focus only on symptoms rather than causes became evident. The products used are often not suitable, such as the beeswax-based anti-graffiti coating on the Kaas sculpture. Risk analysis and risk management was shown to be an essential tool that can enable the prevention of future damage.
Maintenance is frequently focused on making an artwork look clean (especially war memorials are supposed to look clean on the day of the commemoration ceremony). The same treatments are often repeated without considering the necessity or the effect. It became clear that a shift to a focus on regular monitoring before deciding if and what kind of maintenance is needed would benefit the artworks and may save money.
Condition reports are often unstructured, inconsistent, and lack vital information about past treatments and damage, and mapping of damage was hardly ever used. Further, the use of a collection plan was rare, and regular evaluation of a collection was unusual. Structured procedures, such as those used in museums, are virtually absent in the management of municipal collections. Caretakers often find it difficult to decide when and what type of expert is needed. Also, it is not easy for them to find a qualified expert.
Another aspect that came to light was the advantage of assessing an object with a team (as opposed to a single expert), while working together with the caretaker. The opportunity for group discussion of a problem should be encouraged.

The Roadmap

These findings and the discussions with caretakers and colleagues formed the basis for developing the roadmap. Some colleagues are developing methodologies for valuing cultural heritage (Tessa Luger and Stephen Hartog, RCE researchers) and risk management (Agnes Brokerhof and Bart Ankersmit, RCE researchers).
An earlier roadmap for monumental art (van den Bulk, Vermaat, and Morelissen 2008) was used. After evaluating the survey and the case studies, the essential and/or typical aspects of management and conservation were defined. Then, a flow chart was created that provided an overview of the main procedures. The next step was to work out each of these aspects, which would then form the chapters of the roadmap:

- Adding a new artwork to the collection
- Monitoring the collection
- Risk management
- Maintenance
- Damage and Conservation

- Vandalism
- Transport
- Storage.

The building up and augmentation of collection documentation forms a key element in the roadmap and is part of every chapter.
Existing guidelines (Burkom and others 2003; Weitkamp and others 2008) often consist of large amounts of text from which caretakers have to distil the steps that need to be taken. This system did not appear to work in practice for our target group, and we therefore decided to keep the information brief and provide it as a flow chart. The guidelines have been reduced to clear, defined actions; this makes the steps to be taken easy to follow and provides structure in the decision-making process. The flowchart indicates clearly the responsibilities of all experts involved in the process.
The roadmap is not material-specific. It is meant to be used as a tool and not as an encyclopaedia that provides a strict set of rules. The aim is to develop a structured approach and the creation of an awareness of the effects of decision-making and how risks and problems can be prevented.
Context and environment are both central aspects of an artwork that are usually overlooked. Some of the other key elements are: defining preconditions before commissioning or buying a work of art, structuring the contact with the artist (after an initial interview, arranging to contact them in the case of damage or changes in location), clarifying copyright, and improving public participation. In the long term, this should help to save both time and money.
The roadmap focuses on the target group, the caretakers of public art, but may also prove to be useful to anyone involved in the management or conservation of public art.
As the roadmap is an e-publication, it will be relatively easy to make additions or updates if necessary. It will soon be possible to download a digital version of the roadmap from the RCE website (www.cultureelerfgoed.nl). An English version is in preparation.

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Examination and Analysis

The Stained-Glass Panel Depicting The Anointing at Bethany – Art Historical Research, Technical Analysis, and Treatment

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Keywords
stained glass; glass conservation; Charterhouse; Louvain

Abstract
In 2008, Museum M in Louvain (Flanders, Belgium) acquired a panel depicting 'The Anointing at Bethany' that is believed once to have adorned the city's former Charterhouse. The panel required conservation treatment, which was preceded by a thorough art-historical and technical examination.
It emerged that comparable panels are kept at the Metropolitan Museum of Art and the Riverside Church in New York. Chemical analyses show most of the glass in the panel to have a typical 16th century high-lime–low-alkali composition. The conservation treatment was based on the evaluation of these findings and focused very strongly on enhancing the aesthetic balance for an improved reading of the panel.

Introduction
When Joseph II, Holy Roman Emperor and sovereign of the Southern Netherlands from1765 to 1790, ordered the closure of all contemplative monasteries in 1783, their estates were put up for sale. While former donors, often from aristocratic circles, were given an opportunity to reacquire their donations, few did so in the case of stained-glass windows. Stained glass had gone out of fashion by the late 18th century, and production was largely restricted to heraldic images. Concurrently in England, the rise of a Romantic movement found expression in an insatiable appetite for antiquities from Continental Europe, including stained-glass windows. Such pieces were snapped up by dealers at public auctions and sold on in Britain to those who sought to convert their Palladian villas into Gothic castles. What little ecclesiastical possessions remained after this sell-off would subsequently be confiscated and sold during the French Revolution. Consequently, by the beginning of the 19th century, there were hardly any stained-glass windows left in the monasteries of the Southern Netherlands (Berserik and Caen 2007, pp. XVII–XXV).

The stained-glass panel depicting 'The Anointing at Bethany' most likely ended up abroad in this manner. Many similar medium-sized panels now reside in churches and collections in the United Kingdom, and some are found in collections in the United States. As for Flemish museum holdings, this is the first panel of its type to have returned recently to its region of origin.

Art historical research
The previous owner, a British antiques dealer, bought the panel in 2006.[1] He inserted into it a number of newly stained pieces of glass, as well as some salvaged pieces (figure 1). In 2008, he sold the panel to the City of Louvain, who purchased it on behalf of Museum M (Inv. no.: B/III/259).[2]
The main scene represents Jesus' anointment at Bethany. In the foreground, Christ and three other men (Peter, Judas, and Lazarus *or* Simon?) are sitting at a laid table. To Christ's right, a standing woman pours balm from a vessel onto his head.

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Fig. 1. Panel depicting 'The Anointing at Bethany', before conservation treatment (2008) (Photo: J. Caen).

The scene is described in the Gospels of Mark (Mk 14, 3-9) and Matthew (Mt 26, 6-13). The secondary scene in the background also features a group at a table. Presumably it depicts the Old Testament story of Esther accusing Haman before Ahasverus (Est. 10, 1-10), which is traditionally represented as a banquet scene.[3]

Almost all studies concerning stained-glass windows of this type and size (59.2 x 45.1 cm) identify the former Charterhouse of Louvain as place of origin. Starting from the assumption that the panel indeed originated there, this article searches for indications regarding its authorship.

Numerous stained-glass windows were manufactured for the Charterhouse over a relatively short period of time due to a succession of donations; therefore, the windows cannot possibly have been the product of a single hand. Several stained-glass artists are known to have been involved, but the sources mention just two, namely Hendrik and Jan Van Diependale, who were commissioned with the production of windows for the monastery church.[4] The other windows that may have originated there – many of which are still disseminated across mostly foreign collections – can be attributed to specific workshops only on the basis of stylistic comparison. Some of these windows almost certainly hail from the Louvain Charterhouse, including the so-called Nicholas series, now spread over the collections of the Victoria & Albert Museum (V&A) in London as well as other museums (Engels 1999, pp. 208–218).

Recent research by Dr Yvette Bruijnen (Bruijnen 2011) into the Louvain-based painter Jan Rombouts the Elder suggests that he worked as a designer and possibly also as a glass painter, and may have been involved in the sizeable stained-glass window project of the Carthusians. However, identifying a single workshop as the production site of a window by no means implies that the Master of the shop produced the window single-handedly. Quite often, several glass painters would have worked side by side, while the Master performed a more managerial role. This explains why a single panel or series of stained-glass windows may contain evidence of several 'hands' (Caen 2009, pp. 174–175 and p. 351). It should also be pointed out that the designer of a stained-glass window need not have been the same person as the actual glass painter. For the production of, for instance, small panels (very often roundels), there were drawn designs (models or 'modellos'). This was a 'mother design' drawn by the 'Master'.[5] If the Master or his journeymen used that model, it resulted in a stained-glass panel that was showing (nearly) no difference with the 'modello'. Sometimes the 'modello' was copied or 'stencilled' on paper by hand (called a 'workshop drawing'). These workshop drawings were frequently sold to other workshops to serve as 'models' for stained glass, small paintings, engravings, etc. Very popular themes were also 'translated' into prints (woodcuts and copper engravings) and spread to numerous craftsmen on even a larger scale. This proves that the initial hand of the Master designer can be far away from the stained-glass panel itself (Berserik and Caen 2007; Berserik and Caen 2011). The archives contain numerous small-scale design drawings for monumental stained-glass windows. These 'vidimusses' were almost always the work of a Master. A commission to design a monumental window was, after all, prestigious and lucrative. Full-sized 'cartoons' are rarer, and research has revealed (Caen 2009) that these were not always executed by the Masters themselves. Especially in the larger production centres of the 16th century, such as Antwerp, this part of the process was often outsourced to a cartoonist (Caen 2009, pp. 215–225 and especially 222–223). Strikingly, not a single surviving full-scale drawing is known that was designed for certain for a window in the Carthusian monasteries. The most likely explanation is that a different production method was used.

If a visual programme was worked out prior to the glazing campaign, as was customary in such projects (Bleyerveld 2009, pp. 44–77), we may assume that full-scale drawings of individual iconographic series were made beforehand with a view to attracting sponsorship.[6] In this way, donors could select scenes and have their names and possibly their coats of arms incorporated into the composition. Such designs were most likely kept at the monastery until enough donors had subscribed to that particular part of the glazing programme. Once the donations had been arranged, the designs could be presented to a glass painter of the monastery's or donor's choice. It is not clear what would have happened to the design subsequently. Would it have remained with the glass painter or was it customary for it to be returned to the monastery? In any event, no such drawings are known to us today.

The panel discussed in this article may, on the basis of similarities in terms of size, style, and technique, be associated with a number of stained-glass windows kept at The Metropolitan Museum of Art and at The Riverside Church in New York. We refer to the following panels at the Metropolitan: Healing the Paralytic at Capernaum; Jesus and the Woman Taken in Adultery; The Parable of the Workers in the Vineyard; The Multiplication of Bread and Fish; The Parable of the Wise and the Foolish Virgins; Jesus

Calms the Storm; and Jesus and the Daughter of Jairus.[7] The Riverside Church possesses a similar series of panels that may also have originated in the Charterhouse in Louvain. What follows is a brief comparison of characteristics.

To begin with, the cutting of the glass pieces is remarkably jagged, as if the glazier painstakingly tried to follow the design. This would seem to suggest that the glass painter and the designer of the panels were not one and the same person. However, visual observation quickly reveals that other series have a much more 'fluent' matrix and hence were probably the work of a designer who also worked as a glazier and glass painter. Hence, he would have been aware of the technical difficulties involved in glass-cutting and may therefore have chosen not to overcomplicate the design. The edges of most glass pieces were painted black, presumably to camouflage any irregularities in the lead profile. This technique is commonly encountered in 16th century glass painting (Caen 2009, p. 267).

The rather busy compositions are executed in a limited range of colours, primarily brownish-black grisaille, two hues of silver stain, and the occasional dash of transparent sanguine. Each of the compositions has just a few colour accents, realised by means of brightly coloured glass (dark blue, red, brownish-pink, and, in some panels, green and light blue).

The silhouettes are loosely modelled, with finely painted shading and sketchy highlights. They are tightly arranged and divided into groups across the image plane. Their hands generally appear unwieldy and bulky. The draping is characterised by a fairly simple fold. In almost all of the images, Christ's aureole appears in the form of a broad-armed yellow cross inscribed in a circle.

As regards the decor, the patterning of natural stone in floors and walls is similar. A number of architectural borders are adorned with similar decorative motifs.

The panel depicting 'The Anointing at Bethany' may, on the basis of art-historical research findings and the technical analysis (see below), be attributed to a Brabantine workshop from the second quarter or middle of the 16th century. As has been suggested above, the panel may have originated in the Carthusian monastery at Louvain, where it would have been part of a New Testament cycle. Among other indications, the dimensions of the panel (59.2 x 45.1 cm, without the accompanying caption) would appear to point in that direction (Maes 1987, pp. 42–43). Still, one cannot rule out that it originally adorned another house of prayer, e.g. the Celestine monastery. This was, after all, a period of extensive glazing activity in Louvain. Nor can one exclude the possibility that the panel hailed from another Brabantine Carthusian monastery, such as the flourishing monastery of Scheut (Anderlecht),[8] the monastery at Kiel in Antwerp, or the foundation in Lier.

The hypothesis that the panel originated in Louvain is not implausible though. The 16th century up to around 1570 is, after all, regarded as the 'golden age' of the city's stained-glass industry. Moreover, the fact that Louvain's Carthusian monastery was adorned with prominent stained-glass windows is confirmed in archival sources, including documents in the General State Archives in Brussels under the title 'Comité voor de religiekas'.[9] These documents were drawn up in consequence of the decree issued by Joseph II, whereby the Carthusian monasteries, among others, were suppressed. The estates of the monasteries were usually listed in great detail. Not so, though, in the case of the stained-glass windows of the Louvain Charterhouse. The only mention that is found specifies that, in 1786, a number of stained-glass windows were returned to the Teutonic Order in Alden Biesen and that the scheduled sale of the windows did not go ahead, as apparently just two damaged roundels remained.

The panel in question was most likely a donation. Donating stained-glass to a Carthusian monastery was a sure way of acceding to society's elite. Donators commonly had their names, portraits, or coats of arms incorporated into the compositions, as this would guarantee their inclusion in the prayers of the monks (Damen 2009, p. 103). A chronicle (Reusens 1877, pp. 228–299) mentions several glass donations, as well as the name of the stained-glass artist who created the church windows. It states that, in 1501, Hendrik Van Diependale produced three choir windows for the account of merchant Gilbertus Gillis, followed the next year by a stained-glass window representing Saint Anne. This window was a gift from Gillis's mother-in-law, W. Zonneberch from Deventer. Canon Regular Jan Fabri from Liège also donated a window. In 1507, Nicolas Ruterius, Bishop of Arras and founder of the Arras College at Louvain University, commissioned the construction of a cell at the monastery. He also financed four stained-glass windows (probably consisting of several scenes), which he had fitted near this cell. They represented the history of St Nicolas, his patron saint. The series of windows also included some panels featuring Ruterius's arms and motto (Maes 1987, p. 41). Some parts of this ensemble still exist today and are spread

out over museums in London, Glasgow, New York, and Toronto. One of the panels in the V&A carries the monogram N R (= Nicolas Ruterius) and the coat of arms of the bishop (Williamson 2003, p. 86). Another panel, now in the Royal Ontario Museum, likewise carries the monogram and arms (Maes 1987, p. 42).

It is by no means certain that all of these stained-glass windows were made by Hendrik Van Diependale: after his death in 1509, his son Jan after all continued the work on the Charterhouse particularly in its ambulatory. In 1518, he signed a contract for two windows donated by a Mr Van den Berghe. The following year, he committed himself to concluding a commission by Candlemass. Under the terms of the contract, if he failed, the monks could reclaim the cartoons they had provided and entrust the assignment to another artist. This provides further evidence that drawings and cartoons by one designer could be used in other workshops, by other glass painters. It also shows that the Carthusians could assign commissions to other glass painters if they so wished. Nonetheless, Jan Van Diependale was still making windows for the Charterhouse in 1534. They had been commissioned by the procurator Johannes van Heemstede from Haarlem. Indeed, the stained-glass artist enjoyed a highly productive career. He also realised large ensembles for the Celestine monastery at Heverlee, St Peter's Church, the Augustian monastery, the Abbey of St Gertrude, and the Refugium of Averbode at Louvain (Maes 1987, p. 41; Bruijnen 2011, pp. 133–134).

Another prominent dynasty of glass painters from Louvain to be associated with numerous realisations in the city is the Rombouts family. Nicolaes Rombouts the Elder was born to a well-to-do family in the mid-15th century. He is mentioned in archival sources as glassmaker and native burgher to the city. He started out in the workshop run by Nicolaes van Goethem, also known as Yenen. Later, he would marry the sister of glass painter Hendrik Van Diependale.[10] He resided in Louvain until moving to Brussels around 1485. His son Nicolaes Rombouts the Younger, born in 1491, was also very active as a glass painter (Maes 1987, pp. 41–47; Caen 2009, p. 52). In her recent study of Jan Rombouts the Elder and Jan Rombouts the Younger (circa 1505–1559), Bruijnen (Bruijnen 2011) presents findings regarding their activities as designers and glass painters. According to her data, Jan Rombouts the Elder was born after 1475, the child of another Jan Rombouts, who was a nephew to glass painter Hendrik Van Diependale and Elizabeth Roelofs. He married Barbele van Compenrode circa 1505 and died in 1535. Jan Rombouts the Younger married in 1526 Lysbetten Van Montenaken. He held a prominent position on the Louvain city council alongside his relatives Jan and Adriaen Van Diependale. Bruijnen demonstrates in her research that he supplied stained glass in, for example 1534. He died in 1559. According to our dating of the stained-glass panel under discussion, it may have been the work of the aforementioned Jan Rombouts the Younger. It is moreover quite possible that, in executing this commission, he relied on designs by another artist, most likely his father.

Quite recently, a manuscript was identified in the archives of the Belgian Ministry of Foreign Affairs that, alongside an obituary, contains a description of some ninety stained-glass windows intended for the 16th century ambulatory of the Carthusian monastery Scheut in Anderlecht.[11]

This particularly interesting source has been studied meticulously. As previously pointed out, our research suggests that such a visual programme was also developed for other charterhouses. The scenes in the windows were not distributed randomly across the various monastery buildings, but constituted a thematic ensemble. This manuscript was most likely a working document preceding the actual production stage of the windows. The visual programme for Scheut is, moreover, iconographically interesting, because each window encompasses several scenes (usually nine) and the design indicates very precisely where each scene was to be realised (Bleyerveld 2009, p. 45). The document also contains some technical details, but mentions no particular artist. This makes sense, as the visual programme was developed prior to the execution.

In all likelihood, the monastery in Louvain also relied on a previously outlined iconographic programme. As we have seen, mention is made in the contract with Jan Van Diependale of pre-existing designs. Thus far, no such visual programme for the Louvain Charterhouse has been found. Some images and the surviving stained-glass windows refer to coherent iconographies. Except in the case of the Nicholas series, these data are too disparate to allow a reconstruction of thematic units. The panel studied by us and the related panels in New York do, however, clearly constitute a series with various scenes from the life of Christ.

Technical examination

Before starting the conservation treatment, we ascertained that the stained-glass panel had been executed in brownish-black grisaille. In addition, it incorporated two hues of silver stain and a transparent sanguine. All original glass pieces had been cut from small sheets of blown glass. It is likely that primarily cylinder glass was used, with some coloured crown glass. Because of the small size of the glass pieces, it was impossible to identify the latter group visually. None of the transparent glass pieces cut from cylinder glass was larger than the customary size of glass sheets at the time, i.e. approximately 26–27 by 22–23 cm.[12]

The glass pieces had been set in non-original lead and the panel had been fitted into a non-original metal profile. This re-leading and framing was carried out by the previous owner. Some of the glass pieces could not be identified beyond doubt as original, while some were clearly not original. This was the result of several prior interventions. For example, there was a discordant 'insertion' in the face of the woman holding the balm vase as well as various stopgaps in the drapery and background. Some of these interventions had not been integrated, to the detriment of the aesthetic appeal of the panel.

The panel displayed some problematic breaks and mending leads that prevented a normal reading of the piece. The re-leading had been carelessly executed, and many solder joints had been applied injudiciously. The metal frame was of inferior quality, and the panel had not been set at right angles. The original glass was in fairly good condition with hardly any sign of corrosion. Some pieces exhibited slight weathering on the exterior in the form of iridescence. Glass-paint deterioration was observed on the interior side of the glass pieces in the side scene at the top, along the left and the right borders of the panel and at some of the breaks. The panel had also become soiled by excess putty along the lead cames and in the corners at the solder joints.

In the initial phase, the glass pieces were analysed for their chemical composition. The glass composition reflects the nature and the quantities of the raw materials (sand, lime, plant ash…) used in its production. It varies according to the production period and location. Many compositions are documented in the literature, and thus it is possible to verify historical and stylistic observations through chemical analyses. During the treatment of the window, small samples (1–2 mm) were taken from some of the glass pieces (see figure 2). All sampling locations were situated under the lead matrix to ensure invisibility after treatment. The glass splinters were set in an acrylic resin and subsequently polished to a perfectly flat surface to ensure the analysis was being conducted on original, non-deteriorated bulk glass.

Two analysis techniques were applied: scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM–EDX) and laser ablation–inductively coupled plasma–mass spectrometry (LA–ICP–MS) were conducted at the University of Antwerp. SEM–EDX allows one to determine the main components of the glass, while LA–ICP–MS is used to determine the concentrations of trace elements.

The results of the two analyses (table 1) show that the panel contains two types of glass: potash–lime (PL) glass and high-lime–low-alkali (HLLA) glass.

The first group encompasses the purple and the pink glass (figure 2: nos. 12, 13, 25, and 26). Glass of this composition was commonly used in the Netherlands from the late 14th to the mid-16th centuries, peaking in the 15th century.

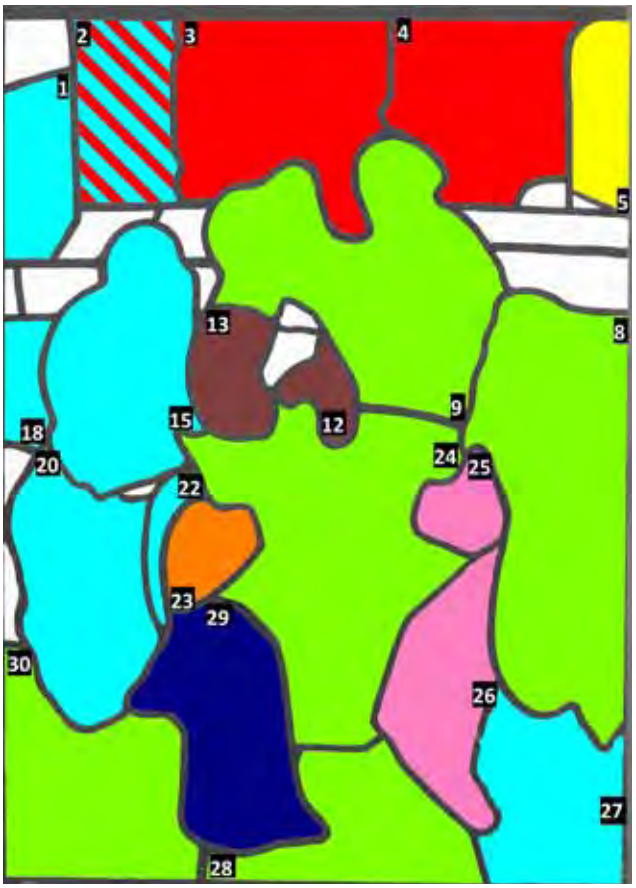

Fig. 2. Location of samples for glass analysis and glass types (colour codes explained in the text and in table 1) (Diagram: S. Cagno).

#	colour	group	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	MnO	Fe_2O_3	TiO_2	CoO	CuO	SrO	BaO	PbO
1	colourless	HLLA3	2.4	4.0	2.8	59.2	1.8	6.2	21.3	0.7	0.7	2363	46	71	1059	1781	30
2	colourless	HLLA3-4	2.2	3.5	2.7	60.0	1.7	5.9	21.4	0.8	0.8	2641	19	93	1335	2299	27
3	colourless	HLLA4	2.4	3.4	2.5	61.7	1.9	5.5	20.1	0.7	0.9	2010	36	257	769	2019	20
4	colourless	HLLA4	2.0	3.0	2.6	61.5	1.7	5.3	21.4	0.8	0.8	2317	13	140	859	2573	35
5	colourless	HLLA5	3.3	3.4	2.4	61.6	1.8	4.3	21.0	0.7	0.5	1905	15	61	1404	1721	27
8	colourless	HLLA2	2.1	3.5	3.1	58.9	2.2	7.2	20.6	1.0	0.6	2105	50	144	814	3003	36
9	colourless	HLLA2	2.4	3.4	3.0	58.5	2.0	7.3	20.6	1.0	0.7	2285	50	144	864	3145	31
12	purple	PL1	0.8	4.4	2.8	55.6	1.0	13.8	17.7	2.4	0.6	1835	40	106	858	7659	26
13	purple	PL1	0.6	4.3	2.8	56.0	1.1	13.8	17.7	2.4	0.5	1612	33	100	745	6892	23
15	colourless	HLLA3	2.3	3.9	2.7	59.6	1.8	6.0	21.3	0.8	0.7	1864	33	69	980	1760	26
18	colourless	HLLA3	2.5	4.0	2.8	59.5	1.7	6.0	21.1	0.8	0.7	1703	33	69	976	1742	26
20	colourless	HLLA3	2.4	3.9	2.7	59.4	1.8	6.2	21.3	0.7	0.7	1780	42	69	933	1582	48
22	colourless	HLLA3	2.7	3.9	2.8	59.3	1.8	6.1	21.1	0.7	0.7	1492	45	69	796	1638	37
23	colourless	HLLA1	0.5	3.9	3.6	54.4	1.9	9.4	23.2	1.3	1.0	2313	59	188	898	4777	60
24	colourless	HLLA2	2.0	3.6	3.2	58.7	2.1	7.2	20.7	1.0	0.6	1741	46	138	764	2928	27
25	pink	PL2	0.7	3.5	2.3	56.6	0.9	17.0	15.6	2.1	0.5	1363	13	218	967	4309	435
26	pink	PL2	0.7	3.7	2.4	56.8	0.9	16.8	15.4	2.0	0.5	1559	14	461	1088	4393	24
27	colourless	HLLA3	2.2	3.8	2.7	59.6	2.0	6.1	21.3	0.7	0.7	-	-	-	-	-	-
28	colourless	HLLA2	2.2	3.6	3.1	58.3	2.1	7.3	20.8	1.0	0.6	1658	50	145	729	2988	44
29	blue	HLLA3b	2.1	3.7	2.7	60.1	2.0	6.3	20.4	0.9	0.8	1639	1817	360	620	2194	91
30	colourless	HLLA2	2.1	3.6	3.2	58.7	2.0	7.3	20.7	1.0	0.6	2014	49	138	787	2957	26

Table 1. Results of the analysis. Results are given in wt% (Na_2O to Fe_2O_3) and µg/g (TiO_2 to PbO). HLLA= high-lime–low-alkali glass; PL= potash–lime glass (Table: S. Cagno).

This expensive high-quality glass, often referred to in the Low Countries as 'French' glass, originated in Normandy and was usually produced as crown glass. From around 1490, this type was increasingly pushed out of the market by HLLA glass (Caen 2009, pp. 119–129 and pp. 226–242). This second group encompasses the clear, colourless glass and the blue glass in the panel (figure 2: dark blue, light blue, green, yellow, orange, and red zones). HLLA glass was cheaper, blown according to the cylinder technique in Alsace-Lorraine. It was known in the Low Countries as 'Borgoens' (Burgundian) glass. In the first half of the 16th century, it was not uncommon for the two types to appear side by side: the valuable stocks of old glass would continue to be used after the new, cheaper alternative had become available. After 1550, potash–lime glass was rarely used in stained-glass windows in the Netherlands (Caen 2009, pp. 119–129 and 226–242). The composition of the panel studied here situates it in the first half of the 16th century.

Within the HLLA group, one can distinguish between a number of subgroups (table 1 and figure 2). The glass in the green and light-blue zones was almost certainly produced in the same glassworks, possibly originating in the same crucible and melt. The glass pieces in the red zone, however, are quite different from the other clear glass. This indicates that they were probably not part of the original panel and originated from another 16th century stained-glass window.

Piece no. 29 is a dark-blue glass of a basic composition that corresponds almost perfectly with the clear glass in the light-blue zone. We may assume that it was produced from the same crucible and melt, and was coloured with cobalt to create the deep-blue effect.

The analysis further shows that the chemical composition of the glass from the side scene at the top is different from that of the other clear glass, although these pieces too have a typical 16th century composition. This suggests that the side scene is a later addition to the panel. A further indication that this is the case lies in the fact that the glass paint in the background scene was in far worse condition than that in the main scene. Moreover, the other panels of this group do not combine New and Old Testament scenes, let alone scenes that are iconographically incongruent, as in this instance. All this confirms the hypothesis that the side scene does not belong to the original window.

Fig. 3. Panel depicting 'The Anointing at Bethany', after conservation treatment (2010) (Photo: J. Caen).

Treatment

The treatment[13] was conducted in accordance with the Conservation Guidelines of Corpus Vitrearum.[14]

Broken glass pieces were provisionally fixed with transparent tape on the unpainted zones of the back. The panel was packed for transportation in polyethylene blister padding with additional hardboard protection. It was kept and treated at an always-dry, well-ventilated, and dust-free location at a constant temperature (20°C) and relative humidity (55% RH).

The documentation at the workshop encompassed photographic imaging of the panel prior to, during, and after treatment, drawings, and cleaning tests. The drawings, prior to and after treatment, contain full notes on the workshop examination, including the dating of the various pieces of glass and an overview of the damage sustained and previous restorations with breaks, mending leads, etc. The lead matrix of the panel, which was very recent (2006–2008), was dismantled because it had been poorly executed. This operation was performed mechanically by means of adapted tongs.

The cleaning tests revealed that cleaning with a water/ethanol mixture (50/50%) would generally yield a good result. Cleaning was undertaken with cotton swabs that were frequently replaced during the process. After treatment with water/ethanol, the glass pieces were always 'post-dried' with ethanol. Cleaning proceeded step by step, focusing on small surfaces at a time. Excess putty and/or glue were removed using a combined mechanical and chemical procedure. In the first instance, a scalpel was used at an appropriate angle to avoid scratching. After most of the putty or glue had been removed in this manner, residual patches were treated with dimethylformamide. Final cleaning also proceeded as described above. Some spatters of paint were removed with acetone. These delicate operations were carried out under a microscope.

After cleaning, the pieces for gluing were kept in a dry environment at a constant temperature (about 40% RH and 20°C) They were subsequently glued by using epoxy resin (Araldite 2020®) according to the infiltration method. The environmental factors were also kept constant during the polymerisation process of the glue. Care was taken not to leave glue residues on the painted side of the glass. After 24 hours of drying, tape and residual glue were carefully removed.

After a workshop meeting, it was decided that a number of discordant previous stopgaps should be removed and replaced with new stained-glass pieces. These larger replacements were produced by means of traditional stained-glass techniques on new glass. Most of the new pieces were subsequently inserted by gluing. The reconstructions with figurative or decorative elements were executed on the basis of visual documentation. The reconstruction of the female face was based on a study of the faces in the panels kept in New York. Preparatory drawings were made with a view to some of these interventions. A few further additions, for which there was no relevant documentation, were executed on a tint/tone basis to ensure optical integration into the panel. All new pieces were clearly yet discretely marked on the exterior side with the monogram of the conservator. On one piece, the monogram was clarified with the full name of the conservator and the year of restoration: 'Rest. J. Caen 2010'.

Re-leading was performed with semi-hard lead in accordance with the findings of the preliminary examination. Any changes to the matrix were discussed with the museum staff. The new lead matrix is quite different from that resulting from the previous intervention in England and almost identical to the original. The shape and breadth of the cames approximate to those in the original panel, as they were based on traces at the borders of the glass pieces. The pieces were reset 'core to core' in the lead. Core-to-core soldering was applied using a solder consisting of 40% lead and 60% tin. Cleaning after leading-up was performed with ethanol-drenched cotton swabs.

The panel was not systematically cemented, only where there were small openings between the glass and the lead. In those places, a linseed/whiting putty was carefully rubbed into the aperture. The panel no longer needed to be watertight and windproof; thus, more comprehensive cementing was unnecessary and would have posed an undue risk. The mechanical strength of the panel is guaranteed by the new matrix and frame.

After cementing in selected places, the lead flanges were pressed down using a wooden spatula. This procedure was followed on both sides of the panel, beginning at the back, so that the pieces would sit plane parallel at the front.

The panel was carefully cleaned with cotton cloths. Any minor residue of putty in the corners was removed with a wood pick.

Small lacunas, grozed edges, and breaks were subsequently retouched with colour fast pigments and using a stable high-quality acrylate (Paraloid B72®) as a binding agent. Any loose paint in the upper glass pieces was affixed beforehand using the same acrylate. Transparent retouches (silver stain) were performed with a commercial durable and colourfast cold paint.

The panel was set in a frame of tin-plated brass that was soldered at the corners and fixed to the matrix.
Finally, the panel was carefully packed and returned to the museum in Louvain.

Conclusion

The final result of our research and treatment is a balancing act between the 'layered' material history of the stained-glass panel and the restoration of the readability and aesthetic appeal of the image (see figure 3). The historical research showed that other panels of these series do not show any side scenes, and the chemical analysis of the glass has confirmed that this scene may not be original to the panel. In spite of this 'mutilation', the panel was conserved with respect for its 'layered' history according to the 'Guidelines' of the Corpus Vitrearum.
Our treatment was conducted with a view to the sustainable conservation of this unique panel in a museum environment. During this process, we took on the challenge of making a number of technical and aesthetic choices. Hopefully this inter-disciplinary approach will become more and more common practice for all who care for stained-glass windows.

Acknowledgment

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Notes

1. Christie's Amsterdam, 20–21 December 2006 – lot no. 257.
2. Sotheby's London, 9 July 2008 – lot no. 52.
3. With thanks to Professor Dr Jan Vanderstock (K.U. Leuven).
4. A.R.A.B., Comité van de religiekas, Louvain Charterhouse, no. 214, 430.
5. Also referred to as 'pourtraict', 'protractorium', or 'petit patron'.
6. There was no point in drawing to scale, since the difference in size between a small unipartite (= undivided) glass pane (ca. 20–30 cm in diameter) and a Carthusian panel (ca. 45 by 60 cm) was minor.
7. Healing the Paralytic at Capernaum (inv. no: 44.114.7), Jesus and the Woman Taken in Adultery (inv. no.: 44.114.4), The Parable of the Workers in the Vineyard (inv. no.: 44.114.3), The Multiplication of Bread and Fish (inv. no.: 44.114.5), The Parable of the Wise and the Foolish Virgins (inv. no.: 44.114.8), Jesus Calms the Storm (inv. no.: 44.114.1), Jesus and the Daughter of Jairus (inv. no.: 41.170.72).
8. This monastery was set alight and largely demolished during the political and religious troubles of 1578–1580. It is conceivable that some glass panels were preserved and given a new purpose after the calamities.

9. A.R.A.B.: Comité voor de religiekas, Louvain Charterhouse, no. 214, 430.
10. For genealogical information on the Keldermans, Van Diependale and Rombouts families, see "Jan Van Damme, Nicolaes Rombouts y las vidrieras de la Cartuja de Miraflores," in La Cartuja de Miraflores III. Las Vidrieras, Burgos: Fundación Iberdrola, 2007, pp. 46–47.
11. Belgian Ministry of Foreign Affairs, Archival Department, dossier 245.
12. Inferrable from the dimensions of square roundels where the selvedge of the glass is still present and from the size of a pane from a batch of flat glass for exportation that was recovered from a shipwreck (J. Caen Collection, Schoten, Belgium).
13. The conservation treatment of this panel was performed by the author in deliberation with the late Véronique Vandekerchove and Marjan Debaene (Museum M, Louvain).
14. Corpus Vitrearum. Guidelines for the Conservation of Stained Glass (Nuremberg 2004). See: Madeleine Manderyck, "Conservatie en restauratie van glasramen," in Monumenten & Landschappen. Binnenkrant, vol. 24, no. 3, May–June 2005, pp. 13–16.

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The Stained-glass Collection of King Ferdinand II of Portugal: Concept, Conservation, and Chemical Analysis of Two Panels

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Keywords

stained-glass panels; historic glass composition; conservation; deterioration; exhibition

Abstract

King Ferdinand II of Portugal (1816–1885), an avid art collector, created a unique collection of stained glass with works from as early as the fourteenth century through to the nineteenth century. In 2011, a recently restored set of stained-glass panels originally installed in the King's Palace in Lisbon was presented to the public for the first time. This paper describes the condition of the panels as they were found in storage, the conservation approach, and the results of the analytical characterisation of two panels, one thought to date from the fifteenth century from Germany and the other from the seventeenth century from Switzerland. Evidence of glass deterioration was documented and surface deposits were analysed.

Introduction

During his lifetime (1816–1885), King Ferdinand II's stained-glass collection was divided between his two principal residences: the Palace of Pena (Sintra) and the Palace of Necessidades (Lisbon). In the Palace of Necessidades, the king had the majority of his collection of stained-glass panels mounted together into the windows of the dining room. He had a further assemblage from his collection installed in the great hall of National Palace of Pena (Teixeira 1986; Martinho and Vilarigues 2011). Unlike the windows in the great hall at the Palace of Pena, the collection from the Palace of Necessidades had been in storage since 1947 and was known only to a small number of people. In 2011, this set was presented to the general public for the first time in the National Palace of Pena (the exhibition was entitled 'Glass and Stained Glass – Ferdinand II's Passion') (Martinho and Vilarigues 2011). The objective of this exhibition was not only to present the collection but also to illustrate for the public its process of restoration.

The collection consists of 37 panels produced between the fourteenth and the nineteenth centuries, in the territories corresponding to modern-day Switzerland, Germany, and the Netherlands (see examples in figure 1). It also includes *Bierscheiben* panes, giving a total of ninety pieces.

The collection contains pieces of great quality with rich designs including both religious and secular imagery. Among the religious works are scenes inspired by the New Testament, including images of the Virgin of the Apocalypse and of the Virgin and Child. Representations of the Holy Church Fathers, an iconographic motif commonly found in fifteenth century German stained-glass panels, are prominent. Scenes from the Old Testament (Book of Judith) and of the Christian Martyrs (Martyrs of Morocco) are also part of the collection. Secular pieces include panels representing patrons and their coats of arms, as well as episodes related to the history and/or legends of their respective regions. A highlight is the depiction of the famous incident of William Tell and the apple, and romantic scenes such as a young noble playing the lute to his lady (Martinho and Vilarigues 2011). Two engravings have been identified that were used for the drawing of two of the panels (figure 2(a) and (b)): *Flight into Egypt* by Jean Baptiste Barbé (engraving dated 1593–1598)

Fig. 1. Windows originally mounted in the dining room of the Palace of Necessidades after the most recent restoration (200 cm x 75 cm each) (Photo: Parques de Sintra Monte da Lua – Luís Pavão).

('Die Flucht nach Ägypten' 2012) and *The Good Samaritan tending the Jew*, after Maarten van Heemskerck, Southern Netherlands, sixteenth century ('The good Samaritan tending the wounds of the traveller' 2013). The collection also contains a set of three panels that were likely produced in Germany in the fifteenth century, based on the work of the engraver, Meister E. S. (Höfler 2007), attribution and dating proposed by Daniel Hess in 1998 (Hess 1998).

Due to the wide range of themes within the collection, a complete iconographic analysis must embrace very different areas, from the heraldry, to the garments, and, specifically, the military dress of the knights, in order to establish where the individual works fit within the German, Swiss, and Dutch territories. In the same way, an analysis of the architectural elements and representations of interiors will permit a chronological framework to be established (for example, to relate these images to other historical pieces with similar architecture). The study of the landscape could be used to draw parallels with the development of landscapes in seventeenth century Dutch paintings. To date, this extensive art historical study remains to be undertaken.

In 2009, a project was initiated by Parques de Sintra – Monte da Lua (the organisation entrusted with the management of the king's summer residence), the National Palace of Pena (where the collection now resides), and the Research Unit VICARTE – Glass and Ceramics for the Arts and the Department of Conservation and Restoration, Universidade Nova de Lisboa.

The goal of this project is: (i) to make this collection known to the public and (ii) to characterise the glass and painting materials in order to support art historical interpretation of the panels. This paper discusses the first results on dating based on analysis of two of the panels.

Fig. 2. Examples from the collection: (a) Flight into Egypt (PNP2856), after the engraving (1593–1598) by Jean Baptiste Barbé (ca. 32.5 cm x 42 cm) and (b) The Good Samaritan tending the Jew (PNP2871), after Maarten van Heemskerck, Southern Netherlands, sixteenth century (ca. 18 cm x 13 cm) (Photo: Parques de Sintra Monte da Lua – Luís Pavão).

The State of Preservation

In the Palace of Necessidades, the stained-glass panels were mounted in five windows and in three transom windows. The windows were removed from their original position when the Palace of Necessidades became the property of the Portuguese government in 1910; they were sent to the National Palace of Ajuda, where they remained in storage for several decades. In 1948, the complete collection arrived at Palace of Pena with the aim of being installed in the windows of the Stag Room (Teixeira 1986). This plan was never implemented, and the windows were kept in storage at the Palace of Pena for the next six decades.

Over the years, parts of the collection had been dismantled. When the current restoration project began in 2009, some of the panels were missing their wooden window frames, and fragments from others were discovered mixed together in paper envelopes. A large section, originally mounted in the central window of the dining room at the Palace of Necessidades, had signs of attack by xylophages insects on the window frames. Due to the poor condition of the remaining wooden structure, it was decided to present this grouping (which could be reconstructed with archival photographs) as individual panes. With other fragments, it was not always possible to assign them to their original mounting systems.

In spite of the poor conditions in which these stained-glass panels had been stored for some six decades, the damage and deterioration found was mainly due to inadequate handling (likely occurring during transport to the palace); extensive corrosion products were not found on the glass surfaces (see the 'Analytical Studies' section below), and little significant corrosion was observed on the lead cames.

The panels were covered with thick layers of dust and in some cases with splatters or brush strokes from house paint (occurring when the wooden frames had been painted). A number of glass pieces had been broken and were held in place with the extensive use of paper adhesive tape (masking tape). Removing the residual adhesive from this relatively recent attempt to stabilise the glass pieces was one of the most time-consuming aspects of the conservation treatment.

In some of the panels, the paint was powdery and partially detached from the glass support. Finally, several panels exhibited evidence of previous restoration, which included

the introduction of new glass to compensate missing parts. This was probably carried out in the nineteenth century when the windows were assembled.

Conservation Treatment

The conservation strategy adopted for the panels was based on the 'Guidelines for the Conservation and Restoration of Stained Glass' issued from the *Corpus Vitrearum Medii Aevi* (CVMA 2004).

The state of preservation for each individual panel was evaluated and documented. Based on this information, the overall conservation plan was then designed.

The surfaces of the glass were first cleaned of dust and loose dirt using soft brushes. Afterwards, the glue from the paper adhesive tape was removed with a combination of solvents (ethanol and/or acetone) and mechanical action using surgical scalpels. Further cleaning was performed using a solution of ethanol and distilled water in a 1:1 ratio. Fragments were joined with an acrylic co-polymer of ethyl methacrylate and methyl methacrylate (Paraloid B-72^{TM}) dissolved in acetone (40 wt%). Missing areas were filled with colourless glass, either transparent or frosted. The choice between frosted or transparent glass depended on the intended luminosity and final transparency, in relation to the adjacent glass fragments. No colour was introduced in the infill materials to ensure that the losses remained obvious. Local consolidation of paint was carried out with Paraloid B-72 dissolved in acetone (5 wt%). Fractures in the lead cames were mended by soldering with a lead/tin solder. Where possible, the stained-glass panels were maintained in their nineteenth century wooden structures.

Exhibition

The exhibition 'Glass and Stained Glass – Ferdinand II's Passion' opened on 21 September 2011. It was comprised of all the stained-glass panels that belonged to the windows of the dining room in King Ferdinand's Palace of Necessidades in Lisbon. It took place in the Stag Room in the Pena Palace (where full decoration with stained-glass windows and glass objects had been planned in the nineteenth century, but was never carried out).

Showcases were purpose built, to meet the needs of both conservation and exhibition of the pieces and to create a large open space for the public. Panels of stained glass were installed with artificial illumination from behind and with enough space for air circulation. Four of the original wood structures were kept, and the overall organisation of the panels respected, where possible, the original design of King Ferdinand for his dining room in the Palace of Necessidades. When the wooden structure was lost, some exceptions were made to display a selection of panels as individual pieces. Also included in the exhibition were a variety of glass objects such as goblets and jars, which were housed in showcases alongside the panels. The exhibition was designed by Mariano Piçarra and carried out by the architectural firm Atelier Afonso Carvalho. A particular feature of the exhibition was the inclusion of didactic material on the restoration itself in the form of a video showing details of the restoration procedures and laminated cards for visitors with more information on the conservation of the glass collection. The didactic materials proved to be very popular.

Analytical Studies

Two panels created some centuries apart were chosen for an in-depth study with reference to the composition of their glass and paint materials: a panel thought to be German from the fifteenth century (Saint Ambrose) and a Swiss panel (Ioannes Heinricvs Fleischlin Parochvs in Kriens) with inscribed date 1688 (figure 3). For the production of the German panel, several coloured glass pieces had been used with the image painted with grisaille, while the Swiss panel consisted of colourless glass painted with grisaille, silver stain, and blue, purple, and red enamels.

Analytical Techniques

The glass composition was analysed by micro energy dispersive X-ray fluorescence (EDXRF), using an ArtTAX spectrometer (Bruker) operating with a molybdenum X-ray source, focusing polycapillary lens, and XFlash (Si drift) detector with 170 eV resolution. The accurate positioning system and polycapillary optics enabled the primary radiation to be restricted to a small area (diameter ~70 μm) of the sample. Elemental composition was obtained from an average of three independent spots, using a tube voltage of 40 kV, a current intensity of 600 μA, and a live time of 360 s. Quantitative analyses were carried out with the WinAXIL program, making use of spectra obtained from glass standards (B, C, and D from Corning Museum of Glass,

Corning, NY, USA). To establish the limits of sensitivity of this analytical method, the standard glasses were analysed under the same experimental conditions as the samples, and the concentration values of the certified samples were calculated. The calculated error associated with the analysis of SiO_2, K_2O, BaO, and CoO is below 5%. For CaO, Fe_2O_3, MnO, and SrO, it is below 10%. For the remaining elements or oxides (Al_2O_3, CuO, PbO, Sb_2O_5, SnO_2, TiO_2), the error is below 25%. These errors are valid assuming that the glass surface was not significantly corroded. More accurate data can be obtained only by destructive analysis of cross-sections, when the pristine bulk glass below the surface is accessible for analysis. The analytical capability of the equipment is limited to elements with atomic numbers $Z \geq 13$; thus, it was not possible to detect sodium and magnesium. Therefore, their concentration was calculated with the 'matrix by difference' method (Canberra 2003). The disadvantage of this procedure is that it is not possible to separate both of these elements from other light elements that may also exist in the glass. For the identification of corrosion products, infrared and Raman spectroscopy were performed on micro-samples, which were taken from the glass and painted surfaces.

Raman microscopy was carried out using a Labram 300 Jobin Yvon spectrometer, equipped with a 17 mW HeNe laser operating at 632.8 nm. The laser beam was focused with a 50x Olympus objective lens. The laser power at the surface of the samples was controlled using a set of neutral density filters varying between 0.1 and 1.7 mW. Infrared spectra were acquired using a Nicolet Nexus spectrophotometer coupled to a Continuμm microscope (15x objective) with a MCT-A detector cooled by liquid nitrogen. The spectra were collected in transmission mode, in 50–100 μm areas, after sample compression with a Thermo diamond anvil compression cell. The spectral resolution setting was 4 cm^{-1} using 128 scans.

Glass Composition

Table 1 summarises the results obtained for the composition of the glass and painting materials of the two panels. The small circles in figure 3 indicate the locations of analysis, performed on both sides of the glass fragments with no detectable differences in the glass composition of the two sides.

SA panel original glass	SiO_2	Al_2O_3	P_2O_5	CaO	K_2O	MnO	Fe_2O_3	CoO	CuO	PbO	Na_2O+MgO
Colourless	57	2.8	1.6	23.0	4.7	1.3	0.5	n.d.	t.	t.	7.6
Red	58	3.3	2.0	23.0	5.3	1.0	0.6	n.d.	0.4	t.	7.1
Brown	58	2.5	1.1	18.2	10.1	0.5	0.6	n.d.	t.	0.2	7.7
Purple	59	2.8	1.0	17.3	12.8	1.3	0.3	n.d.	t.	t.	7.2
Blue	58	2.9	1.4	20.5	5.8	1.0	0.8	0.3	t.	t.	7.7
Grisaille	12–30	1.2	0.5	8–12	0.8–1.6	0.2	0.6	n.d.	10–18	23–30	n.d.
SA panel added glass	SiO_2	Al_2O_3	P_2O_5	CaO	K_2O	MnO	Fe_2O_3	CoO	CuO	PbO	Na_2O+MgO
Turquoise blue	65	1.0	n.d.	8.4	12.8	0.1	0.2	t.	4.0	0.2	n.d.
Blue	73	0.6	n.d.	7.6	17.0	t.	0.3	0.2	t.	0.1	n.d
Dark purple	68	1.1	n.d.	7.0	11.2	4.5	0.2	t.	t.	0.3	n.d
Orange	72	0.6	n.d.	11.1	16.3	t.	t.	t.	t.	t.	n.d
Light green	65	1.0	n.d.	6.8	15.1	t.	0.2	t.	5.2	t.	n.d
JHF panel	SiO_2	Al_2O_3	P_2O_5	CaO	K_2O	MnO	Fe_2O_3	CoO	CuO	PbO	Na_2O+MgO
Colourless	56	3.9	1.1	20.3	5.8	0.8	0.9	n.d	t.	0.2	10.3
Grisaille	50	6.1	3.9	13.0	3.3	0.6	8.3	n.d.	0.5	2.4	10.3
Blue enamel	60	1.0	0.7	2.4	9.2	0.5	1.9	1.3	n.d.	0.6	15.5
Purple enamel	61	1.0	0.9	0.8	7.9	6.6	1.5	0.3	0.1	0.9	11.8
Sanguine red	26	1.6	1.0	13.8	4.0	0.6	8.0	n.d.	n.d.	0.6	41.2

n.d. – not detected; t. – trace element

Table 1. Average chemical composition of the glass of the Saint Ambrose panel (SA) and the Ioannes Heinricvs Fleischlin panel (JHF) obtained by μ-EDXRF analysis on three points per glass fragment and three different fragments of the same colour, expressed in wt% of the corresponding most common oxides.

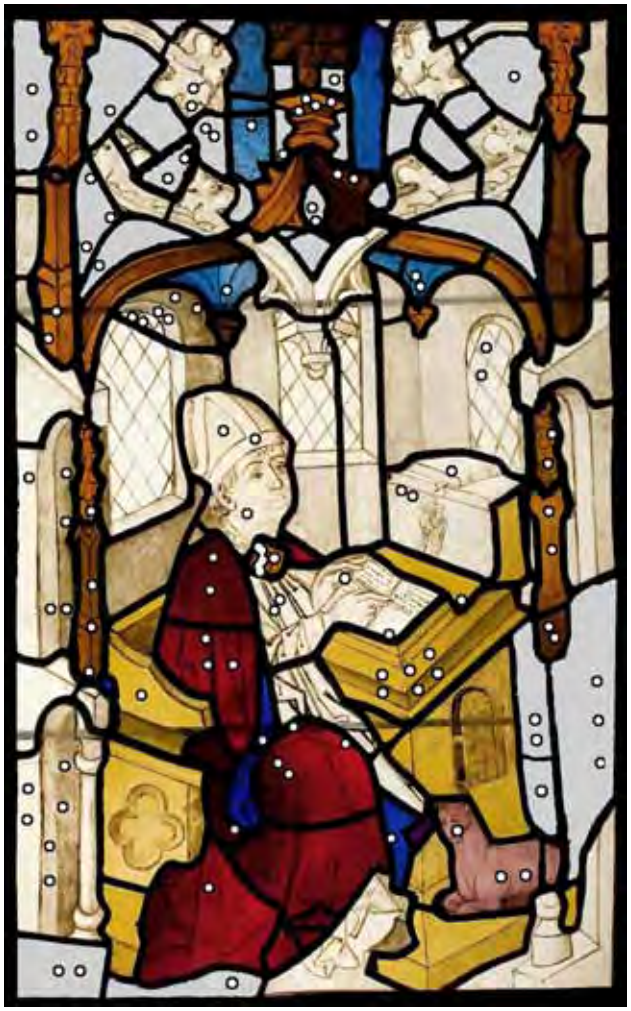

Fig. 3. Mapping of points analysed by μ-EDXRF: (a) Saint Ambrose (PNP2821) (ca. 46 cm x 73 cm) with replacement glass in light gray and (b) Ioannes Heinricvs Fleischlin (PNP2820) (ca. 60 cm x 51 cm) (Photo: Parques de Sintra Monte da Lua – Luis Pavao).

In the *Saint Ambrose* panel, it was possible to differentiate potentially original and non-original glass. The presumably original fragments are recognisable visually by their thickness and by the presence of fine design work in the grisaille painting (see figure 3(a): non-original glass is depicted in light grey). Also, by observation of the characteristic production defects (e.g. bubbles), we can conclude that the glass sheets were produced from blown glass: the bubbles in the glass tended to be elongated due to the extension of the original sphere into a cylinder (Martlew 2008). These production marks are not visible in the presumably non-original glass.

Analysis shows that the original colourless, red, and blue glass can be classified as high-lime low-alkali (HLLA) glass; following Schalm and others (2007), the ratio between K_2O and CaO is below 0.5. For these glasses, the Na_2O content is lower than 6 wt%, with an amount of MgO between 3 wt% and 4 wt%, associated with the chlorophyll, as expected in wood-ash glass (Wedepohl and Simon 2010). The purple and brown glasses are classified as potash glass with their characteristic high contents of K_2O and a ratio between K_2O and CaO higher than 0.5 (Schalm and others 2007). Finally, the concentration of P_2O_5 between 1 wt% and 2 wt% points to the use of unpurified wood ash (Wedepohl and Simon 2010).

The composition of the replacement glass within this panel is significantly different: the content of K_2O is higher and the content of CaO is lower as compared to the original glass; also to be noticed is that no P_2O_5 was detected, indicating the use of purified wood ashes.

According to the literature, HLLA and potash glasses were both produced in Central Europe between the twelfth and seventeenth century, with the predominance of HLLA glass after the fifteenth century (e.g. Brill 1999; Schalm and others 2007; Caen 2009; Wedepohl and Simon 2010). By the end of the fifteenth century and mainly during the first half of the sixteenth century, potash and HLLA glass pieces could be found in the same panel; this supports the assigned dating for the *Saint Ambrose* panel, but leaves open the possibility of a later production (sixteenth century). In the seventeenth century, potash glass started to be produced with purified wood ashes, with very low contents of P_2O_5 (Caen 2009). Published data on potash glass (Schalm and others 2007) indicate that this was produced as late as the eighteenth century, which may allow one to conclude that the replacements may have been introduced between the seventeenth and eighteenth centuries and not when the windows

were mounted in the Palace of Necessidades in the nineteenth century, as originally thought.
Different shades of brown were used: a lighter brown for the Saint's table and a darker hue for the architectural decor. Purple appears in the figure of the bull, and red was used for the Saint's coat. These colours are known to be obtained with transition metal oxides as colourants, such as iron for brown and manganese for purple (Weyl 1999). In the glass pieces analysed in this study, manganese oxide is present in concentrations of ca. 0.5–1.3 wt% and iron oxide of 0.5–0.8 wt%. Batch composition and melting conditions are the key parameters controlling the oxidation state of both manganese and iron in the glass matrix with implications in the final colour. In the case of light-purple glass, we believe that this oxide was added as a colourant, and the glass was produced in a kiln with an oxidant environment, since Mn^{3+} is usually the ion responsible for purple colour in glass. The brown colours in glass could be obtained in more reducing atmosphere. In glass from the *Saint Ambrose* panel, cobalt was detected in dark-blue glass and copper was identified in turquoise blue, red, and green glass, which is in line with published literature on glass colourants (Weyl 1999).
The seventeenth century colourless glass from the Ioannes Heinricvs Fleischlin Parochvs in Kriens panel may be classified as mixed-alkali glass because of its high content of CaO (about 20 wt%) and alkaline oxides (about 15 wt%). To the best of our knowledge, no previous studies on the composition of seventeenth century Swiss glass have been published, so further comparisons were not yet possible.

Grisaille, Silver Stain, and Enamels

The black grisaille in the *Saint Ambrose* panel was very heterogeneous; therefore, only a range of values can be given in table 1. The most significant characteristic of this grisaille is the fact that the pigment used was not iron but copper. Iron oxide is normally responsible for the colour of black grisaille (Veritá 1996; Lautier and Sandron 2008); however, in this panel, instead of iron oxide we find copper oxide, present in a concentration varying from 10 wt% to 18 wt%. This type of grisaille was reported, for example, in the stained-glass panels in the church of Saint Catherine of Oppenheim on the Upper Rhine in Germany (Marschner 1996) and from Batalha Monastery in Portugal (Vilarigues and da Silva 2004).
The grisaille in the *Ioannes Heinricvs Fleischlin* **panel** was much more homogeneous. The paint was rich in iron, similar to most glass paints described in the literature (Veritá 1996; Lautier and Sandron 2008). This panel does have yellow silver stain: the amount of silver detected on the glass surface varies between 1.5 wt% Ag_2O for the lighter colours and 3.2 wt% Ag_2O for the darker colours.
The blue and purple enamel colours have approximately the same average composition. Less than 1 wt% of both calcium and lead were detected. Normally, lead compounds were added to lower the melting point of glass to which the colourants were added (Snickt and others 2006). Although recipes for an enamel composition with extremely low Pb content may be found in some seventeenth century treatises, such as Dossie (1758) and Le Vieil (1774), to date this has not been reported for historical panels. Further studies with other, potentially destructive analytical techniques are needed to fully understand the composition of these enamels.
The red and carnation colours were obtained with sanguine red as a colourant (iron oxide within a glass with very low silica content and a very high content of sodium oxide acting as a flux). Results obtained on the *Fleischlin* panel are typical for sanguine red according to other studies (Caen 2009; Schalm and others 2009).

Corrosion Products

On the surface of both panels, crystals were observed and analysed. Infrared and Raman results indicated compounds normally associated with glass corrosion: $CaCO_3$, $CaSO_4$, and K_2SO_4 (Clark and Zoitos 1992; Römich 1999; Vilarigues and da Silva 2006). Oxalates were also detected on the surface of the Swiss panel. This compound is typically associated with the presence of microorganisms (Perez y Jorba and others 1980).

Conclusions

In this work, the glass, painting materials, and corrosion products from two panels of the collection of King Ferdinand II, presently on exhibition at National Palace of Pena, were analysed. We were able to successfully establish the composition of the different glasses, grisailles, and enamels and to characterise the corrosion products formed at their surfaces.
The glass from the two panels may be classified as HLLA glass, potash glass, or mixed-alkali silica type, which is typical for the glass produced between the fifteenth and the seventeenth century in Central Europe.

The replacement glass in the *Saint Ambrose* panel is probably from the eighteenth century, since its composition is typical for potash glass produced with purified wood ash. The different colours of the glass may be associated with the usual colourants such us iron, manganese, copper, and cobalt oxides. The panels are painted with grisailles, silver stain, and enamels (blue and sanguine red). The grisaille on the *Saint Ambrose* panel contains copper as a colourant instead of iron, which is unusual for grisaille produced in the fifteenth–sixteenth century in central Europe. Further research will concentrate on the study of the production techniques, by comparing the results of chemical characterisation with historical treatises.
A non-invasive analytical technique was chosen to characterise the glass in this study. EDXRF offers the advantage of quick analysis on very small areas, which is ideal for mapping the composition of numerous spots of a panel. However, errors due to surface degradation cannot be excluded and, especially when analysing thin layers of paint, the information depth of the method becomes a critical feature. Further studies have to include analysis of selected samples with destructive methods, providing information on the precise composition of major and trace elements as well as on the degradation of the surface.
This results of the detailed study of these two panels also indicated that corrosion products and fissures from microorganisms caused a clearly visible effect on the glass surfaces. Further research on the biodeterioration of glass is underway, and is based on these examples.
The study of the iconography of King Ferdinand's stained glass collection, which was only done for the *Saint Ambrose* panel, is absolutely essential, since the identification of the themes, figures, and their relationships will establish parallels with other works of stained glass of the same period.

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Stained-Glass Windows of St Jacobs Church, Antwerp, Belgium: An Interdisciplinary Investigation

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Keywords

stained-glass windows; St Jacobs Church Antwerp; sixteenth and seventeenth century; conservation; chemical analysis

Abstract

Five out of 11 sixteenth–seventeenth century stained-glass windows of St Jacobs Church, Antwerp, were investigated within the scope of an ongoing conservation campaign. The updated historical study and an assessment of the actual condition of the panels and the conservation treatment are outlined in this paper. The glass composition was determined non-destructively using proton-induced X-ray emission/proton-induced gamma-ray emission and by studying cross-sections with scanning electron microscopy coupled with energy dispersive X-ray spectroscopy, as well as by laser ablation inductively coupled plasma spectrometry. The original glass could be determined as being different types of high-lime low-alkali glass. The inserts resulting from various nineteenth and twentieth century restorations could be identified as soda–lime–silica glass. The analytical study of a re-discovered window containing heads, apparently replaced during the nineteenth century, reveals important evidence concerning the type of glass used for the different windows.

Introduction

Belgium has a well-defined and rich stained-glass heritage (Manderyck 2005). However, historically acquired knowledge regarding window-glass composition in combination with how glass material was supplied in Belgium is rather poor. This knowledge is based mostly on single application studies (Wouters 2005; Schalm and others 2007; Baert and others 2011). The inaccessibility of the monumental glass, (namely its high position within the churches) is a major reason for the general lack of detailed information. Opportunities to examine this heritage (even in a non-destructive manner) are scarce and exceptional.

The Collegiate Church of St Jacobs, Antwerp, underwent a preparatory phase of interior restoration during the past decade. It was during this intervention that five of 11 sixteenth and seventeenth century stained-glass windows were removed from their locations, for safety reasons (see figure 1). This made it possible to undertake crucial treatment to the windows to secure future protection (i.e. placement of isothermal glazing) and created a unique opportunity to investigate, document, and perform analytical investigation.

The proposed extensive and interdisciplinary research aims to achieve different objectives and attempts to formulate answers to questions such as: 'who was the client that gave the commission to realise the window?', 'what factors determined the iconographical program?', 'can chronological changes in the use of the window glass be established?', and, finally, 'what is the degree of authenticity in 2013?'. The scientific analysis of the composition of the glass and glass paint supplement the data already available regarding the glass windows. Throughout the entire project, the synergetic approach between art history, documentation, and chemical analysis was kept as a central thread.

The aim to characterise chronological changes in the window glass used has resulted in the unusual opportunity to investigate a re-discovered stand-alone stained-glass panel preserved for years in the St Jacobs Church. This exceptional window was assembled with the remains of 18 highly probable authentic pieces showing human heads, which seem to be the leftovers of nineteenth century restoration campaigns. For this study, these recoveries were of inestimable value since they presented important opportunities for dating.

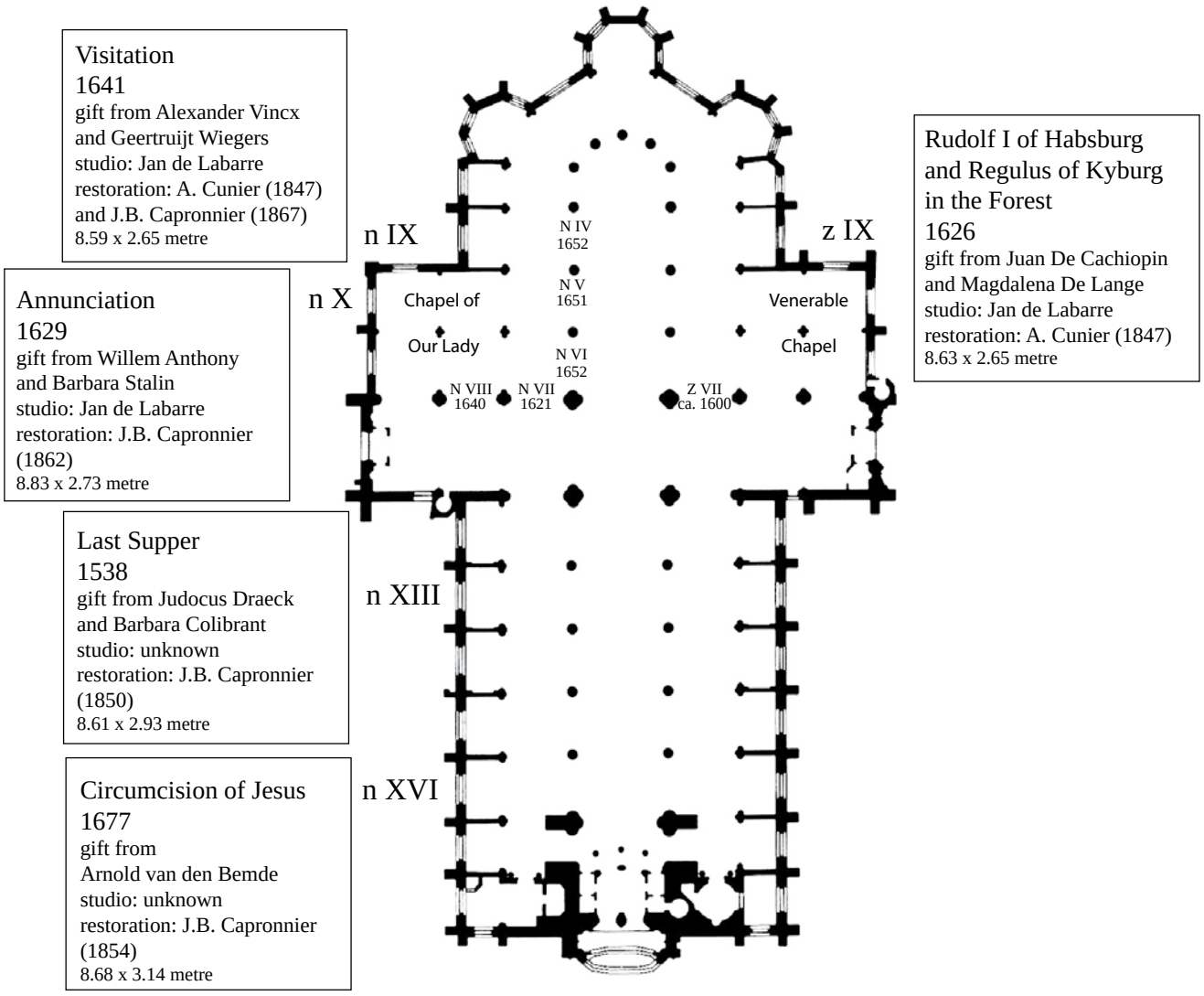

Fig. 1. Plan of the St Jacobs Church and indication of the five windows under investigation.

This paper presents the updated historical study of the St Jacobs Church stained-glass ensemble. A description of the actual state of the de-installed windows is given, as well as an outline of the emergency interventions executed. The preliminary outcome of the chemical analysis for the five stained-glass windows under treatment is explained and the findings relating to changes in glass compositions are discussed. Since the project is still ongoing, additional considerations for future research are proposed.

Historical Context

After the turbulent period of the Reformation (mid-sixteenth century), a considerable amount of the glass patrimony in Belgium was damaged or completely destroyed. Under the impulse of Archduke Albrecht and Archduchess Isabelle, there followed the dawning of a short period of prosperity for the religious visual arts. During the Counter-Reformation, many of the existing churches were restored and often decorated with 'new' baroque styles. It was within this context that private individuals from the region of Antwerp and its fraternities began to order new stained-glass windows for several religious buildings. Examples of these commissions are St Elisabeth Gasthuis chapel, Onze-Lieve-Vrouwe Cathedral, and St Jacobs Church.

The gothic St Jacobs Church still contains 11 monumental stained-glass windows. In their publications, the authors Lévy (and Capronnier) (Lévy 1860) and Helbig (Helbig

Fig. 2. 'Last supper' (1538) (Photo: KIK-IRPA, neg. no. Z003683).

1943 and 1951) show how the seventeenth century glass heritage of this church remained preserved until the nineteenth and twentieth centuries. In 1939, under the threat of war, in Belgium, the Royal Commission for Monuments and Sites commissioned the cataloguing of all historically valuable stained glass. This was an important initiative to safeguard against any future damage. Local governments were obliged to de-install their valuable glass windows and store them safely. Jean Helbig, art historian and glass specialist (conservator of the Royal Museums for Art and History, Brussels), seized the opportunity to study the dis-assembled glass from St Jacobs, panel by panel. The panels were photographed; this action proved to be extremely important, since the fragmentary preserved stained glass that stayed in situ was lost in the bombing of World War II.

Today, seventeenth century stained-glass ensembles have been preserved in only a few places in Belgium. One example is St Michiels-St Goedele Cathedral in Brussels (Vanden Bemden, Fontaine-Hodiamont, and Balis 1994). Within the cathedral's Chapel of Our Lady, the four monumental glass windows (a gift from the archduke and archduchess and their successors) were protected. Of these four windows, the south side (glass SVI [1656], SVII [1658], SVIII [1663], SIX [1663]) dates between 1654 and 1663. Theodoor Van Thulden delivered the cartoons for three of the glass windows, and master glazier Jan de Labarre was responsible for the execution. The fourth window was realised completely by de Labarre.

Regarding Antwerp's Onze-Lieve-Vrouwe Cathedral, Archduke Albrecht and Archduchess Isabelle commissioned J.B. Van der Veken to supply the design for the glass for the northern transept window (nVII). The workshop of Cornelius Cusser was responsible for its execution in 1616. It should be noted that, during this process, the northern transept was consequently glazed with four stained-glass windows (nIII–nVI).

The Antwerp St Jacobs Church contains 11 historic glass windows. The oldest window represents 'The Last Supper' (nXIII), but the studio is unknown (see figure 2). This window falls within the scope of this project.

The remaining 10 seventeenth century windows are scattered across the church. Four of them were subject of this investigation. The oldest seventeenth century stained glass dates from 1626 (zIX) and represents 'Rudolf I of Habsburg and Regulus of Kyburg in the Forest'. The 'Annunciation' (nX) and the 'Visitation' (nIX) windows were installed in 1629 and 1641, respectively. These two windows are, according to inventories of the church archive (mid-nine-

teenth century), attributed to Jan de Labarre.
Finally, in 1677 the 'Chapel without a name' was enriched with a stained glass depicting 'The Circumcision of Jesus' (nXVI). The 12 lower panels underwent reconstruction in the nineteenth century.
Further, until the first half of the twentieth century, several windows in the clerestory of the nave of the church were filled with fragments of stained-glass windows.

Documentation and Conservation Treatment

In preparation for the research project, the iconography of the windows was investigated using archive records.[1] Consequently, data were collected on the origins of the windows and their restoration history. The majority of historical information was found within the church archives. Attempts were made to gain insight into the initial contracts with designer Jan de Labarre, who is listed in the nineteenth century inventory of the church archives. These appeared to be untraceable. However, the contents of the various nineteenth century restoration campaigns are reconstructed through the use of various archive records. In 1847, a Brussels-based workshop A. Cunier restored two of these stained-glass windows (nIX and zIX). In 1867, the famous Brussels glazier workshop of Jean-Baptiste Capronnier again undertook restoration works on nIX. Why work was commissioned initially to Cunier instead of Capronnier, who had good relations with the Royal Commission of Monuments, is not clear.
In addition to the written sources in the Royal Museums of Art and History for three of the five windows, restoration cartoons have been preserved. After arriving in the workshop, Capronnier made detailed drawings in real size (see an example in figure 3). He indicated the condition of the glass with glass cracks (red lines) and lacunae (pencil). The cracks are marked now with red dashed lines. During that intervention, some broken heads were taken out of the lead and replaced by copies. The original pieces were kept, and afterwards they were worked into an individual stained-glass panel (see figure 4).
As is shown in figure 5, the drawing for panel 5b from the nXVI window shows a broken head of a woman. The different cracks correspond to the old painted head. The glass pieces are numbered and signed on the drawing with an 'x' (re-use) or 'o' (new pieces to be painted). The sum of the pieces that needed to be replaced or were recuperated are also mentioned at the borders of the drawing. The head of the woman was replaced by a copy.

Fig. 3. Restoration cartoon (real size) (Capronnier), Royal Museums of Art and History (Brussels) (Photo: Aletta Rambaut).

Fig. 4. Panel (size 160 cm x 64.5 cm) with original heads recuperated from windows which were restored by Capronnier (Photo: KIK-IRPA, neg. no. X009262)

The pictures taken in 1942 following the de-installation of 1939 provide valuable information. The impact of the recent restoration treatment (preceding the re-installation post World War II) was evaluated. After comparing these photos with the current situation, the dating diagrams can be drafted.
After de-installation and transfer to the studio, the stained-glass windows were photographed from the interior side (with reflective and transmitting light) and with reflective light from the exterior side. Visual information (in combination with microscopic examination) was listed in a graphic data system documenting the condition of the glass (glass breakage and gaps), weathering of glass and glass paint, surface deposits (dust and rust), cold paint retouching, types of inscriptions, etc.

Fig. 5. Original head of a woman (from panel 5b of the 'Circumcision window') (Photo: KIK-IRPA, neg. no. X009263), restoration drawing by Capronnier (ca. 1865), Royal Museum of Art and History (Brussels) (Photo: Aletta Rambaut), and the replaced head painted by Capronnier (photograph taken in 2011) (Photo: KIK-IRPA).

After documentation, the panels underwent a minimal conservation treatment. The surface of the stained glass showed slight corrosion and was therefore cleaned with a dry cleaning method using 'akawipe'.[2] However, some of the seventeenth century panels indicated problems with regard to the paint layers. It is possible that some of the panels had been 'patched up' during the twentieth century, using cold painting.
The interior side of the glass was cleaned with a soft brush and akawipe eraser powder so that the powder particles could be gently rolled over the surface. Where the paint was fragile, cleaning was not undertaken. The exterior side was cleaned with de-mineralised water and ethanol (50/50). In those cases where broken glass pieces risked falling out of the panel, it was decided to adhere the breaks with Araldite 2020 (an epoxy resin). The panel was stabilised with a reinforcing frame before re-installation.
Authenticity diagrams of the stained-glass windows were drafted based on a comparison of the observed actual state of the panels (glass breaks, lacunae, paint loss, corrosion of the glass, etc.) with the archival data. An example of such a diagram is explained in the different stages seen in figures 6 and 7: figure 6 shows the complete window with an indication of panel 3a, which is presented in detail in figure 7. This, in turn, includes the various outlines relating to the actual condition and the assembled information about the historical technology marks, derived from Capronnier's restoration drawings, the photographs taken in 1942, and those pictures made from the actual condition of the panel.

Fig. 6. 'The Annunciation' (nX), St Jacobs Church (Antwerp) (Photo: KIK-IRPA, neg. no. Z003648).

Analytical Approach: Materials and Methodology

Although we recognised from the beginning that the best way to conduct the required analytical investigation would involve taking glass samples from representative positions in the panels, a balance between gaining information and respecting the integrity of the artwork had to be found. As a result, both invasive and non-invasive analysis techniques were deployed.
Non-invasive analysis by proton-induced X-ray emission/proton-induced gamma-ray emission (PIXE/PIGE) was performed at Accélérateur Grand Louvre d'Analyse Elémentaire (AGLAE), France. The AGLAE facility of the Centre de Recherche et de Restauration des Musées de France provides access to a 2 MV tandem accelerator (Pelletron 6SDH-2). Since this technique could be operated in an open-air envi-

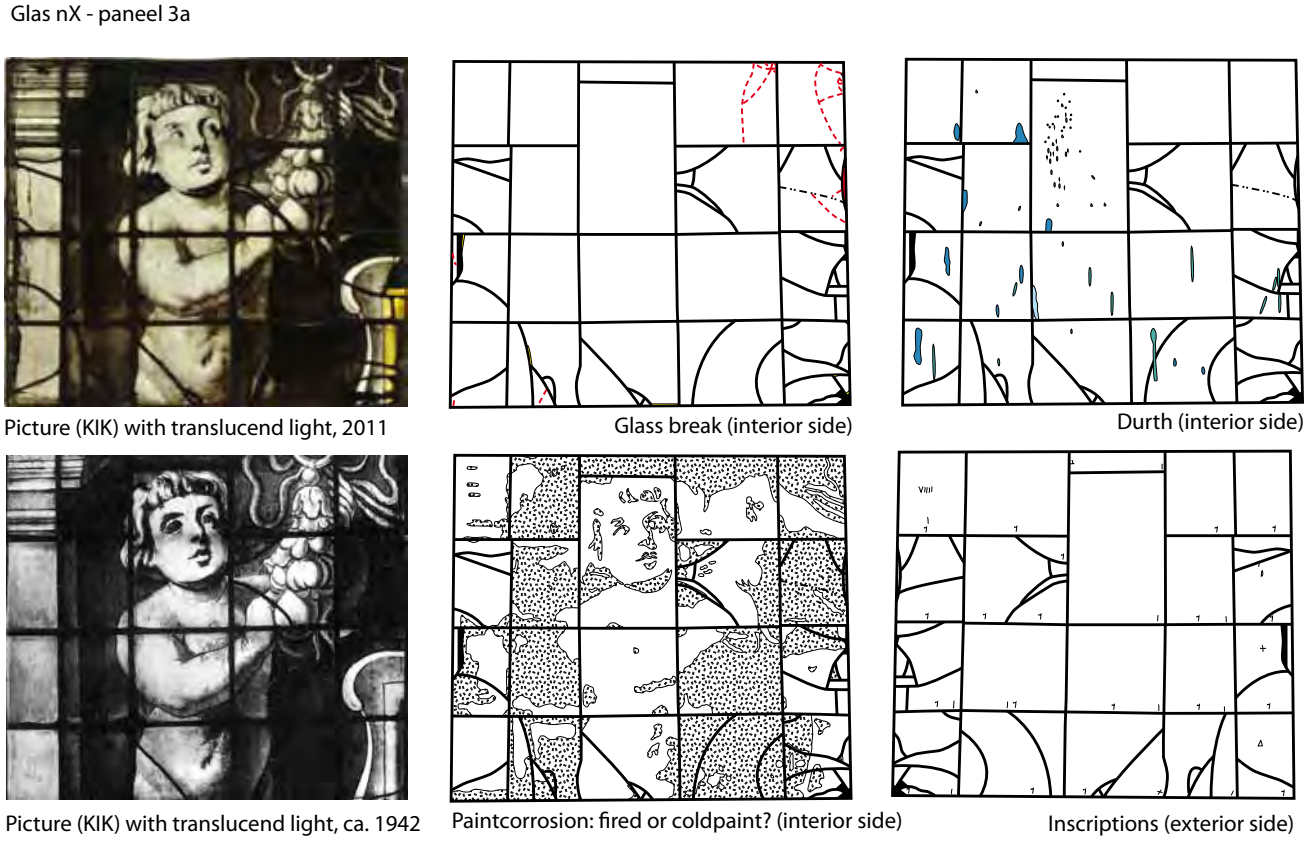

Fig. 7. Examples for the documentation of panel 3a (window nX): picture from ca. 1942 (Photo: KIK-IRPA, neg. no. a22416) and from 2011 (Photo: KIK-IRPA).

ronment, no sampling is required. Complete glass pieces from the windows (dismantled from their lead cames) could therefore be analysed. After the study is completed, these parts will be returned to their original position in the respective panels.

PIXE/PIGE analysis was carried out along recent fractures of 47 selected glass pieces. In order to minimise contamination errors, the fractures were cleaned softly with diluted ethanol just before measurement. A proton beam of 3 MeV with a spot size of 50 µm and a current of 2 nA was used. For each glass, three different areas were analysed, and an average value was calculated from a 500x500 µm beam scan taken in steps of 10 µm within 3 minutes. Quantification was done from X-ray spectra using the GUPIX software combined with the TRAUPIXE software developed at the AGLAE facility (Pichon and others 2010).

The study was enlarged by analysing 70 tiny samples (about 1 mm^2) prepared as cross-sections. The major and minor elements of the glass were determined using a scanning electron microscope (SEM; JEOL, JSM 6300) coupled with an energy dispersive X-ray spectrometer (EDX), equipped with an Si(Li) detector (Oxford Instruments, INCA II). The operating conditions were 20 kV accelerating potential and 0.1 nA beam current, a working distance of 15 mm, and counting time of 100 seconds. Throughout the entire analytical procedure, the results were normalised to 100%. On each sample, at least five different areas along the cross-section were analysed, and an average value was calculated.

In order to complement the SEM-EDX data with information concerning the trace elements, laser ablation inductively coupled plasma spectrometry (LA-ICP-MS) was carried out at the Department of Analytical Chemistry of Ghent University on some of the cross-sections prepared for SEM-EDX. LA-ICP-MS provides element detection down to the ppm level (Resano, García-Ruiz, and Vanhaecke 2010). Sample analysis was achieved by an ArF*-Excimer laser ablation system (New Wave Research UP193HE) and a quadrupole-based inductively coupled plasma mass spectrometry instrument (Thermo Scientific XSeries II).

Analytical Approach: Results and Interpretation

The analysis results reported here focus on transparent white glasses and their various tones from greyish, bluish, greenish, and yellowish to almost perfectly clear glass, as well as a few coloured glasses, especially the violet ones.

The results of the PIXE/PIGE analysis reveal important differences in glass composition. Figures 8(a)–(d) show binary correlation diagrams of potash (K_2O) versus soda (Na_2O) concentrations, K_2O versus lime (CaO), P_2O_5 versus magnesia (MgO), and Zr versus Sr concentrations, respectively. The graphs allow differentiation of some distinct clusters. A first consistent group, indicated by a dashed line circle in the diagrams, represents the high-lime low-alkali (HLLA) glass. The majority, except one, has a glass composition characterised by a low amount of alkali (6–8 wt% K_2O and less than 1 wt% Na_2O) and a high CaO content (> 17 wt%). This group of HLLA glass is also characterised by a concentration of MgO and P_2O_5 of around 3%. Several selected pieces of three seventeenth century windows (zIX, nIX, and nX) could be allocated to this group.

Additionally, all the selected heads corresponding to all four seventeenth century windows are belonging to this group. Attention must be drawn to the fact that none of the pieces selected from the nXVI window for PIXE/PIGE analysis seem to be of HLLA glass, whereas the corresponding original heads clearly are. A closer look at those diagrams also suggests a slight differentiation in glass composition in those pieces belonging to the nIX window (including the respective heads) compared to the rest of the cluster.

Except for the trace elements Sr and Zr, one glass piece (highlighted in the diagrams of figure 8 with a square) appears clearly separated from the other analysed HLLA glass. It has a comparable CaO and P_2O_5 content, but is distinct due a much higher MgO value. Above all, although the same total alkali content is found, the proportion of K_2O (4 wt%) and Na_2O (3 wt%) is different. This piece represents the presumably original head (the one found in the assembled panel) and is assumed to come originally from panel 4d of the sixteenth century stained-glass window (nXIII). Based on data of English, French, and German historic window glass (Barrera and Velde 1989; Wedepohl 2003; Torge, Adam, and Müller 2004; Freestone and others 2010; Lagabrielle, Pivet, and Velde 2010; Dungworth 2011), this piece corresponds to other sixteenth century glass compositions and can be categorised as mixed-alkali glass. The rather low potassium value is also noticed for some of the colourless and yellow glasses of the 'süd IV, V, and VI' windows of the Erfurter Dom (Torge, Adam, and Müller 2004). The ratio of the potassium content to sodium, the higher MgO, and a sufficient amount of P_2O_5 suggest the use of fern as alkali source. Apparently no other original glass segments from this sixteenth century window (nXIII) have been analysed up to now. These findings suggest extending the number of analyses in order to confirm these distinct sixteenth century glass compositions as well as to explore the possible reasons for this.

As can be seen in figure 8(a), the second large group of glasses has a substantial proportion of Na_2O (6–15 wt%) while having less than 1.5 wt% K_2O; hence, these glasses are categorised as soda–lime–silica glass. A first sub-cluster is found having around 6 wt% Na_2O, just above 1 wt% K_2O and MgO, 15–18 wt% CaO, and still around 0.5% P_2O_5. The corresponding glass pieces from all the studied windows, except for window nX, fall within this group. The dating of this glass is unclear and needs further investigation.

Within this large soda–lime–silica glass group, another subgroup can be observed and is characterised by its very low P_2O_5, MgO, and K_2O content, each below 0.2 wt% . Such very low levels of impurities, together with traces of less than 0.1 wt% of Cl, MnO, and Fe_2O_3, may suggest the use of synthetic soda (Dungworth 2011). In 1787, the French chemist Leblanc invented a process to produce alkali from common salt (sodium chloride, NaCl); later, from 1863 on, the process was superseded almost completely by the Belgian Solvay procedure to produce soda from sodium chloride and limestone by using ammonia (Lauriks and others 2012). Consequently, the glasses belonging to this sub-group, characterised by the use of synthetic soda, can be allocated to the nineteenth and twentieth century replacements.

Data derived from the SEM-EDX results were used to compile similar diagrams, confirming the distinction of HLLA and soda–lime glass. Due to the extended number of samples, some additional comments can be made. Concerning the sixteenth century window (nXIII), some of the glass samples were found to be HLLA glass with comparable K_2O and Na_2O proportions as detected for the presumably authentic head piece. Unfortunately, the P_2O_5 content (around 3 wt%) is much lower than that found for the head-glass, which does not allow a firm dating of the original glass of the window. Possible reasons for the distinct composition need to be explored.

None of the samples from window nXVI present the composition expected for seventeenth century potash–lime–silica glass (Schalm and others 2007).

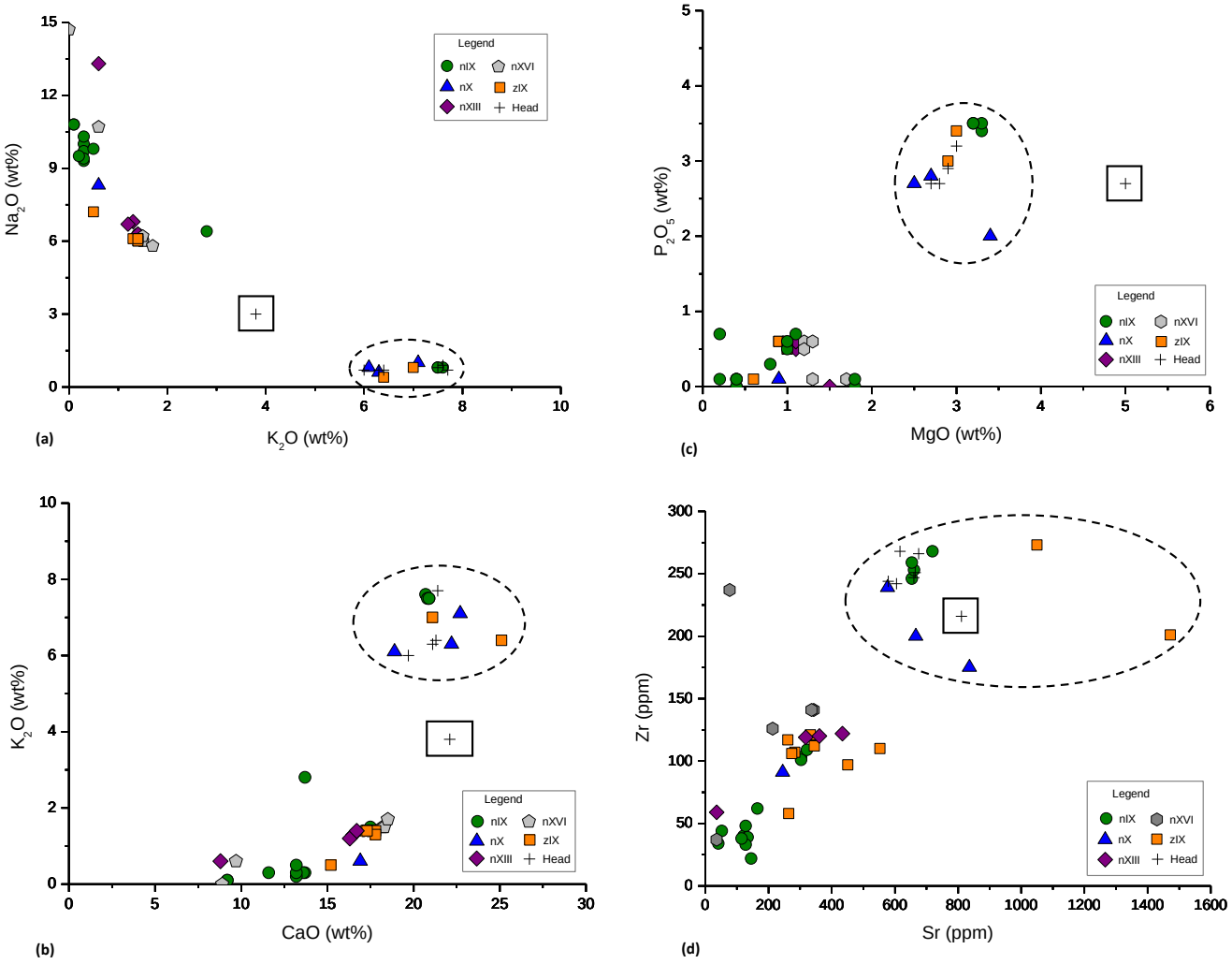

Fig. 8. Binary correlation diagrams for the glass pieces analysed by PIXE/PIGE. (a) K_2O vs Na_2O; (b) K_2O vs CaO; (c) P_2O_5 vs MgO; (d) Zr vs Sr.

All of them have a substantially high Na_2O content, which characterises them as soda–lime–silica glass. For some of the glasses analysed from window nXVI, the clear presence of K_2O, MgO, and P_2O_5 suggests the use of plant ash. Other glasses analysed from this window are, due to the absence of impurities, concluded as being made with synthetic soda. Information about trace elements derived from the LA-ICP-MS analysis allows the conclusion that, for both groups, the provenance of the sand is completely different. The rather high value of Hf, Zr, and Ti measured in the plant-ash soda glass indicate the use of unpurified sand. The presence of those elements in the synthetic soda glass is very low and, therefore, the sand may have been purified.

Concluding Remarks and Future Research

Research in various archives yielded information about the origin and restoration history of five out of eleven sixteenth–seventeenth century stained-glass windows of St Jacobs Church, Antwerp.

Valuable information concerning the dating of the historic windows was gained from the PIXE/PIGE analysis. The original glass from the seventeenth century windows (nIX, nX, and zIX) reveals an HLLA glass type. For the presumably original 'head' from the sixteenth century window (nXIII), a typical mixed alkali glass composition was found. Within the limited dataset, no definite conclusion can be drawn yet as to whether the glass from the window and that of the head are from the same period. Further research is planned to investigate the dating of various parts of this window.

The glasses for window nXVI are all characterised as soda–lime–silica glass, having a plant-ash soda source, whereas the three presumably original 'heads' were all made with HLLA glass. The observed difference in the glass composition raises doubts and questions the art historical information gathered so far for this window, and that information will be very valuable in the proceeding interpretations.

The ongoing research aims to expand the current sampling in order to explore further questions about dating. The application of LA-ICP-MS will be exploited to gain trace element information, which is necessary to understand fully the different types of glasses used and the purification of their raw materials.

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Notes

1. The archival and iconographic research was performed in the context of the DWTC (Diensten voor Wetenschappelijke, Technische en Culturele Aangelegenheden) project (KIK 2003–2007) in the preparation of a doctoral thesis on monumental stained glass in Antwerp. Consulted archives: St Jacobs Church (Archive UFSIA, Antwerp); Royal Commission of Monuments and Sites (KCML, Ruimte en Erfgoed, Antwerp); the Royal Institute for Cultural Heritage Photo Library (KIK-IRPA, Brussels); Royal Museums of Art and History (RMAH, Brussels).
2. Eraser powder produced by Akachemie GmbH (Hamburg, Germany).

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Polychrome Decoration on Staffordshire Figures: Identification of a New Enamel Colourant and Underglaze Oxide

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Keywords
Staffordshire; enamel; underglaze; earthenware polychromy

Abstract
Thanks to a generous donation in 2002, Winterthur's collection of Staffordshire figures is now the largest of its kind in an American museum, with about 270 earthenware sculptures that represent the full range of manufacture and decoration techniques known to English potters at the time. Dating from 1740 to 1900, they span the rise and fall of figure production in Staffordshire. Research, survey, and analysis were conducted to identify manufacture technologies and chemical compositions of the polychrome decoration. Underglaze and overglaze techniques are discussed. Several analytical techniques (X-ray fluorescence spectroscopy, Raman spectroscopy, and scanning electron microscopy equipped with energy-dispersive X-ray microanalysis) were employed, making important discoveries, including the identification of an orange enamel colourant unique to Staffordshire earthenwares, new compositional information on high-temperature underglaze oxides, and the technology of a mysterious blue overglaze colour.

Introduction
The Staffordshire figure, produced in Staffordshire (West Midlands, England), was a popular collectible in eighteenth and nineteenth century England and in the colonial and new United States (Grigsby 1990, p. 271; Halfpenny 1991; Schkolne 2006); the figures represented subjects from characters of allegory, poetry, and mythology, to contemporary English royalty and politicians. Figures in lead-glazed earthenware (pearlware) afforded middle classes the chance to showcase luxury items in their homes, upon mantelpieces and dining tables. In many ways, English factories were capitalising on the public esteem held for Chinese and Continental European porcelain prototypes, producing strikingly similar replications in a more affordable material (Sandon 2009, p. 33).
Highly decorative, Staffordshire figures exhibited a range of painting techniques, including coloured slips, glazes, underglaze oxides, and overglaze enamels. The decorating techniques examined in-depth in this paper focus on those under and over the glaze, including high-temperature underglaze oxides (Pratt colours), overglaze enamels, and a second blue overglaze.

Staffordshire Figures at Winterthur
Winterthur has a representative collection of over 270 Staffordshire figures, the largest of its kind in an American museum. A detailed survey carried out as part of this research identified three distinct time periods: Early (1780–1820), Middle (1820–1860), and Late (1860–1900); as well as all decoration techniques listed above. Table 1 provides a breakdown of the figures in each category.

Underglaze and Overglaze
Known as Pratt colours, high temperature underglazes were developed in Staffordshire in the 1790s to expand the decorating colour palette; the 'new' colours could withstand high gloss-firing temperatures (Lewis and Lewis 2006, p. 18). Although the Pratt factory is known to have made only a few ceramics with this type of decoration, contemporary collectors now refer to this class of pottery as Pratt ware (Halfpenny 1991, p. 100).

Period	Date range	Total # recorded	Slips	Coloured glazes	Underglaze oxides	Enamels	Second blue overglaze
Early	1780–1820	97	12	34	12	58	0
Middle	1820–1860	100	1	1	0	99	23
Late	1860–1900	35	1	0	4	35	3
Totals		*232*	*14*	*35*	*16*	*192*	*26*

Table 1. Breakdown of figures surveyed by date range and type of decoration present.

Technique, with example at Winterthur	Application	Visual	Chemical
Underglaze Pratt colours  Shepherd with lost sheep, c.1795–1810 (02.30.14) H 22 cm W 8.25 cm	• Concentrated metal oxides ground with a medium (oil or water) • Applied to a bisque body by brush • Painted figure dipped in lead glaze and glost-fired at 1050°C	• Glossy surfaces • Mixtures of colour particles often visible under the glaze • Total glaze coverage from dipping • Palette contains blue, olive greens and browns, muted oranges and yellows	• Mixtures of concentrated pigments create colour • Pigments are dispersed colour compounds (not dissolved)
Overglaze enamels  Shepherd and shepherdess bocage group c.1800–1820 (02.30.57.1) H 29 cm W 18.6 cm	• Low-fired coloured glasses consisting of metal oxides ground with fluxes in a medium • Applied to an already glost-fired ceramic • Fired again in smaller kilns at successive firings between 700-and 900°C	• Textures vary from matte to glossy • Bubbling from firing is common • Always occurs over the glaze • More susceptible to surface abrasions, delamination, and flaking • Great variety of colours including brilliant pinks, reds, turquoise, oranges	• Mixtures of metal oxides and lead or borax fluxes • Pigments can be dissolved or dispersed
Second blue overglaze  John Brown and the Prince of Wales, c. 1850–1860 (02.30.130) H 20 cm W 10.6 cm	• Hypothesis: painted on a glazed ceramic (like an enamel) but then 'passed a second time through the glost oven, when the colour combines and sinks into the glaze, producing a magnificent effect' (Sandeman 1901, p. 318)	• Glossy, rich blue colour that appears to be in glaze matrix	• Colourant is cobalt (Co^{2+})

Table 2. Key characteristics of underglaze and overglaze decoration (Photos: Winterthur Museum).

Overglaze enamels, developed slightly later, allowed for an even greater colour variety by lowering the required firing temperature, and thus the range of colourants on English ceramic figures expanded throughout the nineteenth century. A second type of blue overglaze decoration, deep and rich in colour, appears in the mid-nineteenth century, and is primarily used to decorate the jackets on figures. These three decorating techniques are defined in more detail in table 2. Colour recipes were often highly guarded, leaving enamelling shops to explore their own colour-making chemistry and most painters to purchase enamels from independent vendors. This culture of secrecy yielded a wide variety of materials and much experimentation to achieve the brightest and best colours. Potters and craftsmen searched for new colours to keep up with consumer demands (Lowengard 2002, p. 102; Keefe 2000, p. 10).

Dossie's *Handmaid to the Arts* (1758) discusses enamel production with listed enamel recipes, and a workbook of Mr Thomas Lakin (of Lakin & Poole, then Lakin, Poole & Shrigley of Burslem, 1795) was published posthumously by his wife in 1824 that contains recipes for enamels, coloured glazes, and underglazes (Baines 1824).

Until now, knowledge of Staffordshire colour recipes has come from these limited sources. While Chinese, Continental European, and a few select English porcelain glazes and enamels have been characterised chemically, this study is the first to systematically analyse Staffordshire earthenware decoration. This study establishes a database of enamel and glaze compositions present on Staffordshire earthenware figures, determining how they evolved over time and providing a baseline of information that can be used for future research.

Technical Study

A representative group of 32 figures was selected for technical study of the polychrome decoration (table 3).

Elemental analysis with X-ray fluorescence spectroscopy (XRF) established colourants and fluxes present in the glazes, underglazes, and enamels. A laboratory-based spectrometer with ~70 μm beam size was used for finely painted areas. Although XRF is a surface analysis technique, it penetrates several layers of ceramic decoration, presenting challenges for distinguishing between elements detected from different layers. Where possible, spectra were compared to those of glaze and body (or body alone) to determine which elements belong to coloured decorations and which belong to underlying layers. Elements located in underlying layers could also be identified by detecting the inversion of high-energy and low-energy X-ray line intensities (for example, the ratios of the Lα and Lβ lines), since the lower energy lines are more highly attenuated for buried elements.

Four figures were selected for microsampling and were analysed with scanning electron microscopy equipped with energy-dispersive X-ray microanalysis to help understand body–glaze and glaze–enamel interaction zones and changes in compositions as a function of depth. These samples were also studied with micro-Raman spectroscopy. When pigments or opacifying agents such as cassiterite (SnO_2) are dispersed within the glass matrix, identification of these oxides is possible by micro-Raman spectroscopy. Appendix I details all experimental methodologies.

The authors are unaware of previous comprehensive technical studies of decoration techniques on eighteenth and nineteenth century Staffordshire ceramics, but studies of Meissen, Sèvres, and Du Paquier polychrome porcelain are numerous. For a summary of comparable analytical studies, see Fair and Mass (*Ars Ceramica* publication forthcoming).

Results and Discussion

All analysis data are in table 4, Appendix II. Further discussion below is organised by colour.

Blues

Cobalt is the main colourant for most blue decoration on Staffordshire figures and is the only blue underglaze colourant. When present, cobalt is detected along with varying degrees of nickel and arsenic, suggesting that Staffordshire craftsmen used cobalt minerals from Erzgebirge mines in Saxony, which also supplied Meissen and Du Paquier (Gratuze and others 1995; Bezur and Casadio 2009, p. 1189).

Blue enamel shades are light blue, dark blue, turquoise, and blue–green. Light and dark blues contain cobalt, and occasionally have copper, tin, manganese, and iron. Turquoise enamel consists primarily of copper and arsenic; four figures with turquoise enamel in the Early Period also contain cobalt, along with arsenic, tin, and antimony. Arsenic could be present as opacifying lead arsenate or as a residual component of the cobalt ore. Blue–green enamel is unique to the Middle and Late Periods and consists primarily of cobalt and chromium.

AL number	Accession number	Description	Decoration type	Date range
5411	2002.30.5	Faith	coloured glaze and slip	1780–1820
5414	2002.30.14	Man with lost sheep	underglaze oxide	1780–1820
5415	2002.30.79.1	Dick Turpin on Black Bess (equestrian)	blue overglaze and enamel	1860–1900
5426	2002.30.11	Iphigenia	coloured glaze and underglaze oxide	1780–1820
5427	2002.30.20	Falconer or sight or air	enamel and slip	1780–1820
5433	2002.30.96	Nicholas Ridley and Hugh Latimer	enamel	1820–1860
5434	2002.30.57.1	Shepherd and shepherdess or Sound	enamel	1780–1820
5436	2002.30.25	Demosthenes	enamel	1780–1820
5437	2002.30.26	Jupiter	underglaze oxide	1780–1820
5438	2002.30.78	Bull baiting dogs and man	enamel	1820–1860
5439	2002.30.139	Lighthouse with boaters (Grace Darling)	enamel	1820–1860
5440	2002.30.80	Guiseppe Garibaldi and horse (equestrian)	enamel	1860–1900
5441	2002.30.101	Tam O'Shanter and Sooter Johnny	enamel	1860–1900
5442	2002.30.82.1	Prince of Wales (equestrian)	enamel	1860–1900
5444	1959.579	George Washington	enamel	1780–1820
5445	1960.517	Benjamin Franklin	enamel	1780–1820
5447	2002.30.97	Purity	enamel	1780–1820
5452	2002.30.172	Vase or spill vase (the Rival)	enamel	1860–1900
5453	1960.518	Benjamin Franklin	enamel	1780–1820
5457	1958.3103	Shepherd and Shepherdess	coloured glaze and slip	1780–1820
5458	2002.30.15.2	Sportsman's companion	coloured glaze and underglaze oxide	1780–1820
5461	2003.13.63	St George and the Dragon (equestrian)	coloured glaze	1780–1820
5463	2003.13.63.1	Vase (male gardener)	coloured glaze and enamel	1780–1820
5464	2003.13.64	Tithe (Tythe) Pig Group	enamel	1780–1820
5466	1967.900.1	Lion	enamel	1820–1860
5467	2002.30.42	Stuff Taker or Smell	underglaze oxide	1820–1860
5470	2002.30.142	Queen and King of Sardinia	enamel	1820–1860
5475	2002.30.47.1	Uncle Tom	enamel	1820–1860
5476	2002.30.68	Shepherd and dog	enamel	1820–1860
5478	2002.30.73.1	Tailor's Wife (on goat)	enamel	1820–1860
5479	2002.30.151	Highland Jessie (Jessie and Corporal Brown)	blue overglaze and enamel	1820–1860
5483	2002.30.129	Vase or spill vase (dog and child)	enamel	1860–1900

Table 3. List of 32 figures in Winterthur collection analysed in this study. Museum accession numbers with corresponding Analytical Lab (AL) numbers.

The data suggest that zinc as a flux with cobalt oxide was popular in Staffordshire significantly later than the 1760s date attributed to Meissen. No Early Period blue enamels contain zinc as a major component; however, after 1820, zinc is often a major component, with roughly equivalent concentrations in the Middle and Late Periods. Zinc may also be intentionally added to enhance the colour; at Meissen, Höroldt noted that adding zinc to cobalt blue precipitate softened the harsh blue tone (Casadio and others 2012, p. 62).

In both the Middle and Late Periods, the other blue overglaze technology contains cobalt as the colourant. A similar dark blue/black in the Late Period was found to contain cobalt and iron, as well as copper, chromium, manganese, and arsenic as minor components. Zinc is not detected with cobalt on areas with this particular overglaze technique.

Greens

Green underglaze Pratt colours contain cobalt, tin, and antimony, achieving the colour by mixing blue and yellow pigments. This confirms that the high-temperature underglaze oxides are mixtures of concentrated pigments, and proves a different colouring technology from polychrome glazes or early underglazes, a fact not always well understood in the literature.

All of the Early Period green enamels are copper-based. Chromium green enamels first appear on Winterthur's figures in the Middle Period, nearly 20 years after the introduction of chromium green at Sèvres in 1802 (Préud 1997, pp. 57–58). At both Staffordshire and Meissen, copper as a green colourant does not cease once chromium is introduced. In the Middle Period, there are two enamel greens: one with chromium, and one with copper. Chromium and copper were used together to make green enamels in the Late Period. Lakin's recipe book lists two green enamel recipes: one Grass Green based on 'Blue Vitrol [sic]' (copper (II) sulfate) mixed with Naples yellow; and another Pomona Green based on 'Oxide of Green Chroma' (chromium (III) oxide). Lakin's Grass Green formulation is the same recipe for 'grass green' documented by Höroldt at Meissen (Casadio and others 2012, p. 67; Domoney, Shortland, and Kuhn 2012). Darker greens come from mixing cobalt with copper or chromium, and sometimes manganese and iron. This is similar to Du Paquier dark greens; however, 'subtractive colour mixing' using Naples yellow and cobalt blue was also found there and at Meissen (Bezur and Casadio 2006, p. 1192).

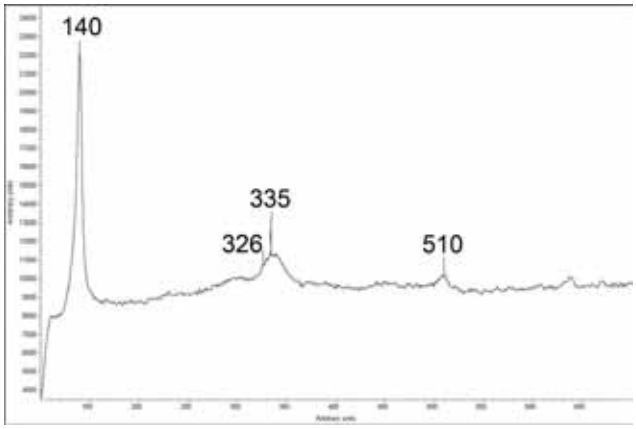

Fig. 1. (top) Lion, c. 1825–1840 (1967.900.1) H 21.4 cm W 13.3 cm (Photo: Winterthur Museum), with sample location starred; (bottom) Raman spectrum from yellow enamel indicating peaks for Naples yellow and lead–tin yellow type II.

Yellow

Yellow enamels and underglazes contain lead, tin, and antimony. Antimony comes from lead antimonate (Naples yellow, $Pb_2Sb_2O_7$), but tin can be present as the opacifier cassiterite (tin oxide, SnO_2) or as the yellow pigment, lead–tin yellow (type I, Pb_2SnO_4 or type II, $Pb(Sn,Si)O_3$). Historic recipes suggest tin oxide is added for opacity: Lakin includes 'oxide of tin' in recipes for orange, yellow, and green underglaze colours (Baines 1824). Dossie mentions using tin compounds for pigmentation of yellow and green enamels, but where transparency is desired, the tin is omitted (Dossie 1758, pp. 291–296). Research from Meissen, Sèvres, and Du Paquier explain the presence of tin by cassiterite (Colomban, Sagan, and Faurel 2001, p. 356; Casadio 2004, p. 181; Bezur and Casadio 2006, p. 1186), and small amounts of tin oxide have been found in English porcelain glazes (Owen and Hillis 2003, p. 867; Owen 2001, pp. 112–113).

As yet, cassiterite is absent in all Raman spectra of Staffordshire enamels. Raman spectroscopy of yellow enamel on the base of the Lion (figure 1) clearly identified lead–tin yellow type II (silicon-substituted lead (II) stannate, $PbSn_{1-x}Si_xO_3$) with two peaks (140, 326 cm^{-1}). Naples yellow was also confirmed with three peaks (140, 335, 510 cm^{-1}). There is evidence that lead–tin yellow was adapted for use in enamelling on Chinese porcelain in the eighteenth century (Kerr and Wood 2004, p. 634; Miao, Yang, and Mu 2010). Raman spectroscopy investigation of an olive brown underglaze sample from the Sportsman's Companion (figure 2) also identified a mixture of Naples yellow and two peaks to confirm lead–tin yellow type I (123, 303 cm^{-1}). The cross-section of this sample shows clearly that underglaze Pratt

Fig. 2. (left) Sportsman's Companion, c. 1790–1820 (2002.30.15.2) H 18.4 cm W 7.6 cm (Photo: Winterthur Museum), with sample location indicated; (right) cross-section image of underglaze brown.

colours consist of mixtures of pigments that remain undissolved in the overlying glaze.

Zinc as a flux in green and yellow enamels was used at Meissen after 1800 (with the exception of one *hausmaler* ware), but at Du Paquier there are documented cases of zinc-fluxed green and yellow enamels as early as 1725 (Page and Chilton 2001, p. 234; Bezur and Casadio 2009, p. 1187). Only one Staffordshire figure from the Early Period contains zinc as a minor component, while in the Middle and Late Periods, zinc is present as a major component in green enamel compositions only.

Orange

In the Early Period, orange enamel was achieved mostly with dissolved iron oxide (Fe_2O_3), while orange underglaze colours contain Naples yellow and iron oxide. In the Late Period, copper and antimony are added to these iron-based orange enamels.

In the Middle Period, a bright, vibrant orange that seems entirely unique to Staffordshire decoration was added to the enamel palette, observable in the figure of the Queen (Victoria) and the King (Victor Emmanuel II) of Sardinia (figure 3). Raman spectroscopy confirmed the presence of lead (II) chromate, as mixtures of chrome yellow ($PbCrO_4$, peaks at 340, 407, 842 cm^{-1}) and chrome yellow–orange ($PbCrO_4 \cdot PbO$, peaks at 355, 378, 825, 832 cm^{-1}). Massicot (lead (II) oxide, PbO) is also detected, with peaks at 143 and 289 cm^{-1}.

Lead chromate as an orange enamel colourant has, to our knowledge, no precedent in Continental European or Chinese enamelled porcelain wares from the nineteenth century. At Sèvres, lead uranate ($PbUO_4$) was used for golden-yellow enamels enamels (Colomban, Sagon, and Faurel 2001), but uranium was not identified here. Furthermore, chromium in orange enamel recipes is discussed by neither Lakin nor Dossie.

Red, Pink, and Purple

Red, pink, and purple enamels can be divided into three groups: (1) deep rustic reds and brownish-pink shades where iron oxide is the colourant; (2) deep reds and brownish-pinks where iron, but also iron chromate and colloidal gold (with tin) are the colourants; and finally, (3) pink, magenta, and purple colours that contain mainly gold and tin.

The use of gold and tin (purple of Cassius) as a red, pink, and purple enamel colourant was common practice in Staffordshire from the Early Period onward, and was documented by both Dossie and Lakin (Dossie 1758, pp. 284–285, 298; Baines 1824, pp. 55–57).

In addition to gold, Staffordshire purple and magenta colours contain instances of cobalt and manganese in both the Middle and Late Periods. Cobalt, and also copper, were added to gold-based purple enamels at Du Paquier to create deeper tones; while at Meissen, the purple shade is dependent on the colloidal size of the gold (ratio of gold-to-tin) (Domoney, Shortland, and Kuhn 2012, p. 468).

Dossie describes how to obtain a 'cheaper' red colour with iron oxide, which can be 'enlivened by mixing one part of glass of antimony…' (Dossie 1758, p. 286). Iron oxide-based reds were found on seventeenth century English porcelain jars at the British Museum (Spataro and others 2009). The Early Period Staffordshire figures analysed contain instances of both gold-based reds and iron oxide-based reds. Antimony is detected, along with iron and gold, on pink enamel from the Early Period and red enamel from the Late Period.

Lakin's recipe lists 'chromate of iron' as a colourant for Cornelian Red enamel (Baines 1824, pp. 50–51). Chromium in red and purple enamel is identified only on one figure from the Middle Period.

Browns

Brown underglaze colours contain mixtures of cobalt and/or manganese, with Naples yellow, lead–tin yellow, and iron

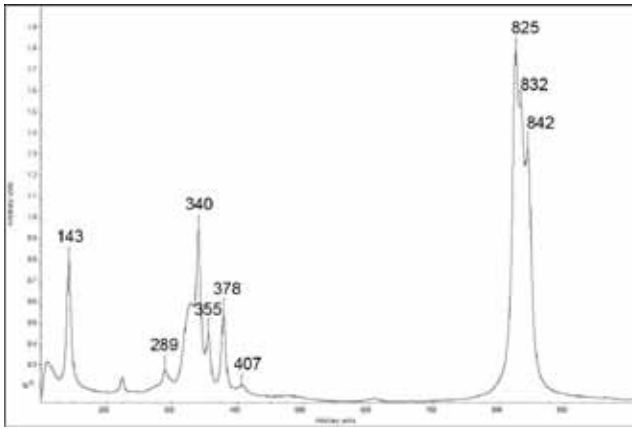

Fig. 3. (top) Queen and King of Sardinia, c. 1855 (2002.30.142) H 34.3 cm W 21.3 cm (Photo: Winterthur Museum), with sample location starred; (bottom) Raman spectrum from orange enamel indicating peaks for massicot, chrome yellow, and chrome yellow–orange.

oxide. Brown enamels are based primarily on iron oxide, with varying additional components including copper, manganese, cobalt, and occasionally gold, tin, antimony, and chromium. Gold and tin are detected together, suggesting that the pigmentation involves colloidal gold reduced with tin chlorides. Du Paquier brown enamels also contain gold and tin (Bezur and Casadio 2006, p. 1200). In the Middle Period, colloidal gold as a brown colourant is replaced by chromium.
In the Late Period, chromium and iron are the major colourants in the brown enamels. Chromium is present either as dispersed lead (II) chromate or as an iron chromate compound. At Meissen, a nineteenth century brown enamel was found to contain iron and manganese, but also chromium, cobalt, and nickel (Casadio and others 2012, p. 70). Colomban found black/brown enamels at Sèvres to contain mixtures of magnesium oxide, iron oxide, and iron (II) dichromate (Colomban, Sagon, and Faurel 2001, p. 354).

Grey and Black

Grey enamels and black underglazes are coloured with iron, manganese, and cobalt.
In the Early Period, two black enamels are detected: one with iron, manganese, copper, and cobalt with nickel; and the other with copper and cobalt with nickel and arsenic.
In the Middle and Late Periods, black enamels contain chromium, in addition to iron, cobalt (with varying degrees of nickel and arsenic), and manganese. In the Middle Period, copper is also detected.

At Meissen, nineteenth century black enamels were found to contain chromium (Casadio and others 2012, p. 70), and, as stated above, Colomban found that black/brown enamels at Sèvres contained a mixture of manganese oxide, iron oxide, and iron (II) dichromate.

Conclusions

This study has shed new light on polychrome decoration of Staffordshire earthenware figures. In many cases, the techniques closely follow trends established at the leading European porcelain production centres. However, several significant differences are noted, demonstrating the scientific progress made at Staffordshire during the period 1780–1900. Previously, scholars believed underglaze colourants were the same metal oxides used in glaze technologies. Instead, Pratt

colours are made by mixtures of concentrated metal oxides. For example, where copper is the sole colouring oxide in green glazes, Pratt green underglaze consists of concentrated mixtures of cobalt blue and Naples yellow/lead–tin yellow pigments.

Detection of nickel and arsenic with cobalt in both underglaze and overglaze technology suggests that a Saxony cobalt ore source was used at Staffordshire.

While exact application methods of the second blue overglaze could not be definitively determined with non-destructive analytical techniques, the results of this study suggest that the deep blue colour was applied in a second process of overglaze enamelling. This contradicts the hitherto-accepted idea that this impressive deep blue used to colour coats and jackets of many mid-nineteenth century Staffordshire figures was applied under the glaze.

Use of a zinc flux with blue, yellow, and green enamels appears to be a post-1820 technology in Staffordshire, later than at porcelain factories in Continental Europe.

An apparently new orange enamel colour based on dispersed lead chromate was used in Staffordshire that has not been documented elsewhere, either in Asian or European enamel recipes. Chromium was also detected in brown, black, red, and purple enamels. Further investigation is needed to determine if iron chromate or lead chromate is the colourant in those cases.

Yellow underglaze and overglaze in Staffordshire contain tin and antimony colourants. Based on Raman spectroscropic findings, tin is most likely present not as cassiterite, as is documented at other European porcelain factories, but rather as lead–tin yellow, mixtures of which type I and II have been identified. This is in conjunction with Naples yellow, perhaps to prepare a cooler, less orange yellow.

The survey and analysis of Winterthur's Staffordshire figure collection has amassed a body of knowledge that contributes to the understanding and appreciation of Staffordshire ceramic glaze and enamel technology and of these important, yet understudied figures.

Appendix I. Analysis Details

X-ray Fluorescence Spectroscopy (XRF)

An ArtTAX μXRF spectrometer with Si PIN diode detector and both molybdenum (Mo) tube and tungsten (W) tube was employed for qualitative and semi-quantitative elemental analysis of glaze, slip, underglaze, and enamel compositions. Both the Mo and W tube operate at 600 μA current and 50 kV, detecting elements with energies as low as potassium ($Z \geq 19$) and as high as uranium ($Z = 92$) (Bronk and others 2001). With Mo tube, collection time averaged 100 seconds (no filter); with W tube, collection time averaged 300 seconds (Ni 50 μm filter).

A W tube was used for the majority of XRF analyses. The primary excitation for molybdenum (Mo $K\alpha_1$, 17.480 keV) renders this tube most efficient at exciting elements with X-ray lines of 17 to ~5 keV. This is highly useful for ceramic bodies, glazes, and enamels because pigments and glaze colourants are typically transition metals with K lines in this energy range. The primary excitation line for tungsten (W $L\alpha_1$, 8.396 keV) renders this tube most efficient at exciting lighter elements with X-ray lines below this energy; the W $K\alpha_1$ occurs at 59.318 keV and, for this reason, W tubes are also efficient at exciting heavier elements with X-ray lines between ~20 and 30 keV. This enables the W tube to have high sensitivity detecting elements such as tin, antimony, and barium, often seen in glazes and enamels. Disadvantages to using the W tube are that the $L\alpha_1$ line often interferes with the detection of copper (Cu $K\alpha_1$, 8.048 keV) or gold (Au $L\alpha_1$, 9.713 keV), two common enamel colourants. A nickel filter effectively absorbs the W $L\alpha_1$ lines, however, and allows for improved identification of elements with X-ray lines in this region.

Scanning Electron Microscopy With Energy-dispersive X-ray Microanalysis

Samples were removed from edges of prior loss using SPI Supplies diamond scribe or #15 scalpels. Samples analysed with SEM were prepared in one of two ways: powder samples were mounted directly onto SPI Supplies 10X15 mm carbon stub using double-sided carbon tape. Intact fragments were prepared as cross-sections by casting in Epo-Kwick epoxy resin (Buehler) and polishing with series of silicon carbide papers (240-, 400-, and 1200-grit) and Buehler diamond suspensions (6-, 1-, and ¼-µm) on Texmet 2000 polishing cloths. Once polished, cross-sections were mounted onto carbon stubs with carbon tape adhesive.

Samples were examined using a Topcon ABT-60 scanning electron microscope with an accelerating voltage of 20 kV, a working distance of 24.0 mm, varying magnifications between 300 and 2000X, and 20° sample tilt. EDS data were analysed with Bruker XFlash detector and Quantax model 200 EDS detector with Esprit 1.8 software.

Micro-Raman Spectroscopy

A Renishaw inVia dispersive Raman microscope with 785 nm laser was the source used for qualitative phase identification. The laser operates in 3200–100 cm^{-1} spectral range with 3 cm^{-1} resolution and 30-second scan time at varying powers from 1 to 5% laser power. Generated spectra were interpreted with Galactic Grams and OMNIC software and compared to reference spectra published in the literature and available online (Burgio and Clark 2000; Colomban, Sagon, and Faurel 2001; Casadio 2004; Colomban and Milande 2006; Casadio and others 2012; RRUFF Project and online database of Raman spectroscopy, http://rruff.info; UCL Raman Spectroscopic Library of Natural and Synthetic Pigments, www.chem.ucl.ac.uk/resources/raman/index.html).

Appendix II.

XRF Data of Underglaze and Overglaze

Colour	Time period	#	Major elements	Minor elements	Possible colourants
Underglaze Pratt Colours					
Medium green	Early	2	Pb, Co	Sn, Sb, Ni, As*	Ground cobalt oxide; lead antimonate; lead stannate**
Olive green	Early	2	Pb, Co, Sn, Sb	Ni, As*, Zn(tr)*	Ground lead antimonate; cobalt oxide; lead stannate**
Blue	Early	2	Pb, Co	Ni, As	Ground cobalt oxide
Medium brown	Early	1	Pb, Co, Mn	Ni	Ground cobalt oxide and manganese oxide
Dark brown	Early	1	Pb, Mn	Sb, Sn, Fe	Ground manganese oxide; iron oxide; lead antimonate; lead stannate**
Olive brown	Early	1	Pb, Co, Sb, Mn	Sn*, Ni(tr)*, As(tr)*	Ground cobalt oxide; lead antimonate; manganese oxide; also with lead stannate
Orange	Early	4	Pb, Sb, Fe	Sn	Ground iron oxide; lead antimonate; lead stannate**
Yellow orange	Early	1	Pb, Sb, Sn	Co, Zn*	Ground lead antimonate; lead stannate**; cobalt oxide
Yellow	Early	3	Pb, Sb, Sn	Cu(tr)*	Ground lead antimonate and lead stannate**
Black	Early	1	Pb, Mn, Co, Ni, Fe*	Cu(tr)	Ground manganese oxide; cobalt oxide; copper oxide; also with iron oxide

Colour	Time period	#	Major elements	Minor elements	Possible colourants
Overglaze Enamels					
Medium green 1	Early	1	Pb, Cu	As, Sn, Sb, Ba(tr)*	Dissolved copper; dispersed lead stannate**; lead antimonate
	Middle	2	Pb, Cu	Sn(tr)	Dissolved copper; dispersed lead stannate**
Medium green 2	Middle	3	Pb, Co, Cr, Zn	Sn, Cu, Ni*	Dissolved cobalt; chromium; also with dissolved copper
	Late	2	Pb, Cr, Zn	Co, Cu*, Sn, Ni*, Sb*	Dissolved chromium; cobalt; dissolved copper, dispersed lead stannate**; or lead antimonate

Colour	Time period	#	Major elements	Minor elements	Possible colourants
Overglaze Enamels					
Yellow green 1	Early	4	Pb, Cu	Sn, Sb, Zn, Co, Fe*, Ni*, As*	Dissolved copper; dispersed lead stannate** and/or lead antimonate; and/or dissolved cobalt, iron
	Middle	3	Pb, Cu	Sn, Sb, Co, Mn	Dissolved copper; dispersed lead stannate**; lead antimonate; dissolved cobalt; manganese
Yellow green 2	Middle	2	Pb	Co, Cr, Sn, Sb, Zn	Dissolved cobalt; chromium; dispersed lead stannate**; lead antimonate
Lime green	Early	2	Pb, Sn	Cu	Dispersed lead stannate**; dissolved copper
	Middle	1	Pb	Sb	Dispersed lead antimonate
Olive green	Early	2	Pb, Cu, Fe*	Sn, Sb*, As*	Dissolved copper; dispersed lead stannate**; dissolved iron or dispersed lead antimonate
	Middle	1	Pb, Cu, Co, Mn	Sn, Sb(tr)*, Ni*	Dissolved copper; cobalt; manganese; dispersed lead stannate**; dispersed lead antimonate
Blue green	Middle	3	Pb, Zn, Cr	Co, Sb, Sn, Ni(tr)*, Mn(tr)*	Dissolved chromium; cobalt; dispersed lead stannate** and/or lead antimonate; dissolved manganese
	Late	3	Pb, Cr, Zn	Co, Cu, Sn(tr)*	Dissolved chromium; cobalt; dissolved copper
Blue 1 (lighter)	Early	1	Pb, Cu	Co, Sn, Fe*	Dissolved copper; cobalt; dispersed lead stannate**; dissolved iron
Blue 2 (darker)	Early	2	Pb, Co	Ni, As, Cu(tr)*	Dissolved cobalt; also with dissolved copper
	Middle	7	Pb, Co, Zn	Ni, As	Dissolved cobalt
	Late	2	Pb, Zn, Co	Ni, As*	Dissolved cobalt
Dark blue	Early	1	Pb, Co	Ni, As, Sn(tr)*	Dissolved cobalt
	Middle	1	Pb, Co	Mn, K, Ba?, Ni(tr)*	Dissolved cobalt; manganese
	Late	1	Pb, Zn, Co		Dissolved cobalt
Turquoise	Early	7	Pb, Cu	As, Sn, Sb, Co, Zn(tr)*	Dissolved copper; dispersed lead stannate**, calcium antimonate and/or antimony oxide, and/or dissolved cobalt
	Middle	1	Pb, Cu	As	Dissolved copper
	Late	1	Pb, Cu	As, Sn*	Dissolved copper; dispersed lead stannate**
Brown	Early	5	Pb, Fe, Cu	Mn, Au(tr), Sn(tr), As, Co(tr)*, Zn(tr)*	Dissolved iron, manganese, and/or copper; mixture of other trace elements
	Middle	6	Pb, Fe	Mn, Cr, Ni, Co, Cu, Ca*	Dissolved iron; dissolved manganese, chromium, cobalt, copper
	Late	1	Pb, Fe	Zn, Cr, Co, Mn*	Dissolved iron, chromium, cobalt; dissolved manganese
Red brown	Early	4	Pb, Fe	Cu*, As*, Mn*, Sn(tr)*, Au?*	Dissolved iron; mixture of other trace elements
	Middle	5	Pb, Fe, Cu, Co, Mn	Zn, Cr, Ni*, Sn(tr)*, Ca*	Dissolved iron; dissolved copper, cobalt, manganese, chromium
	Late	5	Pb, Fe, Co*	Zn, Cr, Mn, Sn(tr), Sb(tr), Cu*, Ni*, As(tr)*	Dissolved iron; chromium, manganese, dispersed lead stannate**, and/or lead antimonate, dissolved copper
Grey brown	Early	2	Pb, Fe	Mn, Cu, Co*, Sn(tr)*	Dissolved iron, manganese, copper; dissolved cobalt
	Middle	3	Pb, Fe, Mn	Co, Ni, Zn	Dissolved iron, manganese, cobalt
	Late	1	Pb, Cu	Zn, Mn, Co, Cr*, Fe*, Ni*	Dissolved copper, cobalt, manganese; also with chromium and iron
Red	Early	4	Pb, Fe	Au, Sn(tr)	Dissolved iron; colloidal gold
	Middle	6	Pb, Fe	Cr*, Zn(tr), Au?, Ca(tr)*	Dissolved iron; possibly dissolved chromium and/or colloidal gold
	Late	5	Pb, Fe	Sn(tr), Sb(tr), Cu, Zn, Au(tr)*	Dissolved iron; also with dispersed lead stanate** and lead antimonate, dissolved copper and colloidal gold?
Red orange	Early	2	Pb, Fe		Dissolved iron
	Middle	6	Pb, Fe	Ca, Cu(tr)*, As(tr)*	Dissolved iron; dissolved copper, calcium (for bleaching effect?)
	Late	1	Pb, Cr*, Fe*		Dissolved chromium and/or iron
Orange	Middle	5	Pb, Cr, Fe*	Cu, Sn(tr), Sb(tr)*	Dissolved chromium, copper; dispersed lead stannate**, lead antimonate and/or dissolved iron
	Late	5	Pb, Cr	Sn, Fe, Sb(tr), Cu*, Ca*, Au?*	Dissolved chromium; also with dispersed lead stannate** and/or lead antimonate, dissolved iron, calcium and colloidal gold?

Colour	Time period	#	Major elements	Minor elements	Possible colourants
Overglaze Enamels					
Peach	Early	8	Pb, Fe	Au(tr)?, Ca	Dissolved iron and/or colloidal gold; calcium as bleaching agent?
	Middle	8	Pb, Fe, Ca	Cr(tr)*, Mn(tr)*, Cu(tr)*, Hg(tr)*	Dissolved iron with calcium as bleaching agent? And trace other elements
	Late	6	Pb	Fe, Ca, Zn, As(tr), Au?, Cu*	Dissolved iron; also with dissolved calcium, colloidal gold?
Pink 1	Early	2	Pb	Au, Sn(tr), Fe*, Sb*	Colloidal gold; dissolved iron or lead antimonate
	Middle	2	Pb, Au	Sn, Co, Ag(tr), Cu(tr)*	Colloidal gold; dissolved cobalt
	Late	3	Pb	Au(tr), Sn(tr), Zn(tr)*, Co(tr)*	Colloidal gold; also with dissolved cobalt
Brown pink 1 (darker)	Early	4	Pb, Fe, Cu*	Hg*, Zn*, Sb*	Dissolved iron; dissolved copper, lead antimonate
Brown pink 2 (lighter)	Early	1	Pb	Au(tr), Sn, Cu	Colloidal gold
	Middle	1	Pb, Fe*	Ca, Au(tr), Zn*	Colloidal gold; dissolved iron
	Late	2	Pb, Fe	Au(tr), Ni, Cu(tr)	Dissolved iron; also with colloidal gold and/or dissolved copper
Magenta	Early	1	Pb	Au, Sn(tr)	Colloidal gold
	Middle	3	Pb, Au	Sn, Co*, Mn*, Cu*	Colloidal gold; dissoved cobalt, manganese, copper
Purple	Early	4	Pb	Au, Sn, Sb(tr)	Colloidal gold; dispersed lead antimonate, and/or calcium antimonate
	Middle	1	Pb, Au, Co	Sn, Cr	Colloidal gold, dissolved cobalt, chromium
	Late	1	Pb, Co	Au, Sn, Zn(tr)*, Ni(tr)*	Dissolved cobalt, colloidal gold
Yellow	Early	7	Pb, Fe	Sb, Sn, Ni, As, Cu, Zn, Ba?*	Dispersed lead antimonate, and/or lead stannate**; dissolved iron and copper
	Middle	6	Pb, Zn*	Sn, Sb, Cr*, Cu(tr)*	Dispersed lead stannate, lead antimonate; dissolved chromium or copper
	Late	5	Pb	Fe, Sn, Sb, Zn, Cr	Dissolved iron, dispersed lead stannate**, lead antimonate; dissolved chromium
Yellow orange	Early	4	Pb	Fe, Sb, Mn, Cu, Ba, Sn, As*, Au(tr)?*	Dissolved iron, dispersed lead antimonate
	Middle	3	Pb	Fe, Sb, Cu*, Sn*	Dissolved iron, dispersed lead antimonate; dissolved copper, dispersed lead stannate**
	Late	1	Pb, Sb, Sn		Dispersed lead stannate**, lead antimonate
Grey	Early	1	Pb	Fe, Co, Mn, Ni, Ca, As	Dissolved iron, cobalt, manganese
	Middle	1	Pb	Fe, Co, Mn, Ni*, As*	Dissolved iron, cobalt, manganese
	Late	2	Pb	Co, Fe, Mn, Ca	Dissolved cobalt; dissolved iron and manganese
Black 1	Early	5	Pb, Fe	Mn, Co, Ni, Cu	Dissolved iron, manganese, cobalt; dissolved copper
	Middle	9	Pb, Fe, Co, Cu, Mn	Ni, As, Cr, Ca, Ba	Dissolved iron, cobalt, copper, manganese; dissolved chromium
	Late	6	Pb, Fe, Co	Mn, Zn, Ni, Cr	Dissolved iron, cobalt, manganese; dissolved chromium
Black 2	Early	2	Pb, Cu	Co, Ni*, As*, Sn(tr)*	Dissolved copper, cobalt
Second Blue Overglaze					
Blue	Middle	1	Co		Dissolved cobalt
	Late	1	Co		Dissolved cobalt
Dark blue/black	Late	1	Co, Fe	Cu, Cr, Mn, As	Dissolved cobalt; dissolved iron, copper, chromium, manganese

*Table 4. XRF data of underglaze and overglaze decoration on Winterthur figures. * Detected only once. ** Presence of tin may indicate tin oxide opacifier, rather than lead–tin yellow pigment.*

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Does Lead Enamel Corrode Metal? Evidence From the Examination of 18th Century Snuff Boxes

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Keywords
glass corrosion; copper alloys; sodium copper formate acetate; historic conservation treatments

Abstract
Historic glasses and enamels made from unstable glass and metal pose particular problems. Acid emissions from wood (for example) together with alkaline liquid films from glass hydration induce metal corrosion in the contact area. The most common corrosion product, sodium copper formate acetate, was found where metal contacted white opaque enamel on 18th century snuff boxes. Sixty-two boxes from the Landesmuseum Württemberg and 20 boxes from four other collections were visually examined before samples of corrosion products were analysed using Raman spectroscopy. Sodium copper formate acetate was found on five of the snuff boxes. Since the results of enamel analyses by electron-probe microanalyses did not suggest deterioration problems, alternative sources of sodium in corrosion products were taken into consideration in order to explain the degradation of the snuff boxes.

Introduction
In recent years, an unusual and previously unknown metal corrosion phenomenon has increasingly been detected on enamel objects. Alkaline surface films, formed by the hydration of the glass, cause special forms of metal corrosion in the contact area between the glass and metal. This form of corrosion has been reported for historic glass and enamel objects in contact with copper alloys (Eggert and others 2008, 2010). So far, two different copper formates have been identified as corrosion products. The most common copper/glass corrosion product is a sodium copper formate acetate compound also known from treated archaeological bronzes (Trentelman and others 2002). More recently, another compound, copper trihydroxyformate, was also identified (Eggert and others 2011). Carbonyl pollutants, emitted by wood, glues, or cleaning agents, are the major source of the formation of both formates and acetates in corrosion products (Grzywacz and Tennent 1994).
In Stuttgart, the GIMME (Glass Induced Metal-corrosion on Museum Exhibits) Project has been set up to investigate in detail this corrosion phenomenon and its causes. How common is this phenomenon in collections and in what context does it appear? The identification of the corrosion products is important, as their composition contains a great deal of information about the object and its history. The nature and quantity of the corrosion products are a measure of an object's exposure to adverse environmental influences, particularly factors that have a cumulative impact over long periods of time.
The survey of 18th century enamel boxes in the Landesmuseum Württemberg reported in this paper demonstrates the approach and the objectives of the GIMME Project. This group of objects contained two items with conspicuous turquoise corrosion. In both instances, the corrosion occurred in the area of contact between the white opaque enamel and the copper.
The analyses of corrosion products have been hitherto mainly carried out by X-ray diffraction (XRD). In this study, micro-Raman spectroscopy was used for identification. The ability of this technique to focus on individual crystals under the microscope seemed most promising, as only small quantities of corrosion products were required for sampling.

Andrea Fischer, Gerhard Eggert

The Collection

Most of the enamel boxes in the collection of the Landesmuseum Württemberg were probably used to store snuff. In the 18th century, snuff boxes were very popular and were valuable accessories, often having a personal character. Many of these boxes were rich in detail and made from a variety of materials such as gold, gems, and painted enamels. In Germany, enamelled snuff boxes first appeared in the first half of the 18th century. They can be seen as an imitation of the increasingly popular Chinese porcelain. At the beginning of the porcelain manufacture in Meissen, their products were still expensive. However, the production of enamelled boxes was considerably cheaper, and the boxes could be produced in greater quantity (Le Corbeiller 1966, p. 72).

The museum owns a large collection of these small decorative boxes, 62 of which are enamelled. The majority are square, but oval or round shapes are also found. Particularly remarkable are the sculpturally formed boxes in the shape of animal heads. Enamel lids and bases are mounted onto gilded brass frames, which are joined with hinges. Copper has been used as a substrate for the opaque white enamel. In some instances, the white enamel is overlaid with coloured enamels. The lids are often adorned with portraits, classical vignettes, or floral ornaments. One of the boxes was decorated by the well-known enamel painter Johann Andreas Bechdolff, who worked in Ellwangen (Germany) around 1760.

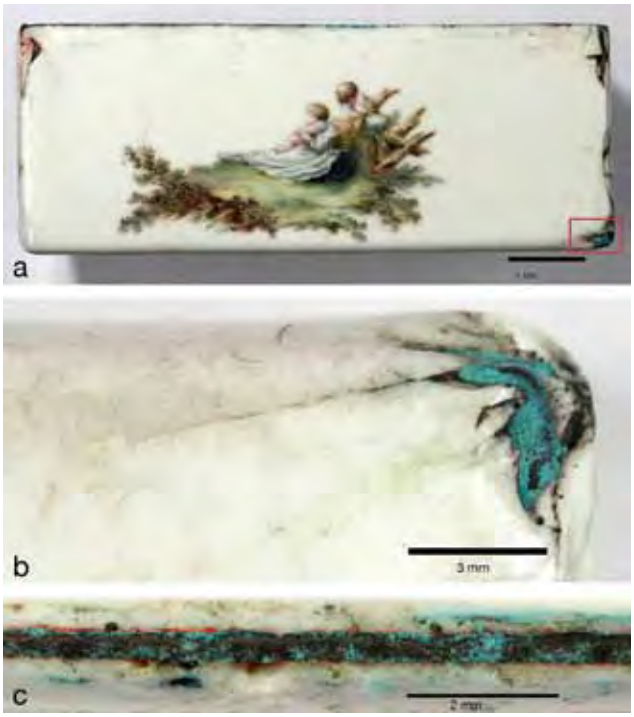

Fig. 1. (a) Box no. G 8,360, rear outer side. (b) Corrosion products on the base. (c) Edge of the two-sided enamelled copper plate (Photos: Andrea Fischer).

Visual Examination

The survey was carried out in the storage area of the museum. Basic equipment was available notably a camera and a microscope (x10). Corrosion phenomena were detected in 11 out of 62 boxes. The corrosion was observed where spalling of the enamel occurred, on exposed edges of the copper plate and on the gilded brass frames. The surface of most of the opaque white enamel appears semi-glossy. A few of the boxes show localised areas with a dull appearance. Several enamels have suffered damage by fractures, probably caused by mechanical stress. Some boxes have been repaired in the past.

Corrosion at the Spalled Areas in the Enamel

Most notable is the damage on the snuff box illustrated in figure 1 (no. G 8,360). One outer side shows several spots of spalled enamel with turquoise corrosion products. They appear crystalline, loosely adhering to the copper plate. Similar corrosion products can be observed on a tiny spalled area on the lid of another box (no. 5433). However, this kind of damage is rarely observed, since most of the snuff boxes with spalling on the outside do not show any evidence of corrosion.

Corrosion on Exposed Edges of the Copper Plate

On three of the boxes under investigation (nos. G 8,360, 5735, and 1309), the gilded metal frame has become detached from the base (box no. 1309 is shown as an example in figure 2). This offers a most interesting insight. The two-sided enamelled copper plates exhibit layers of red, green, and turquoise corrosion products. In the contact area, the white enamel has changed to a red or turquoise hue (example no. G 8,360, see figure 1(c)). Turquoise corrosion products can be found in the gaps where there are small losses of enamel or damage to the copper plate. In this context, it is important to mention adhesive residues that are localised at the edges of the copper plate and in the fold of the metal frame.

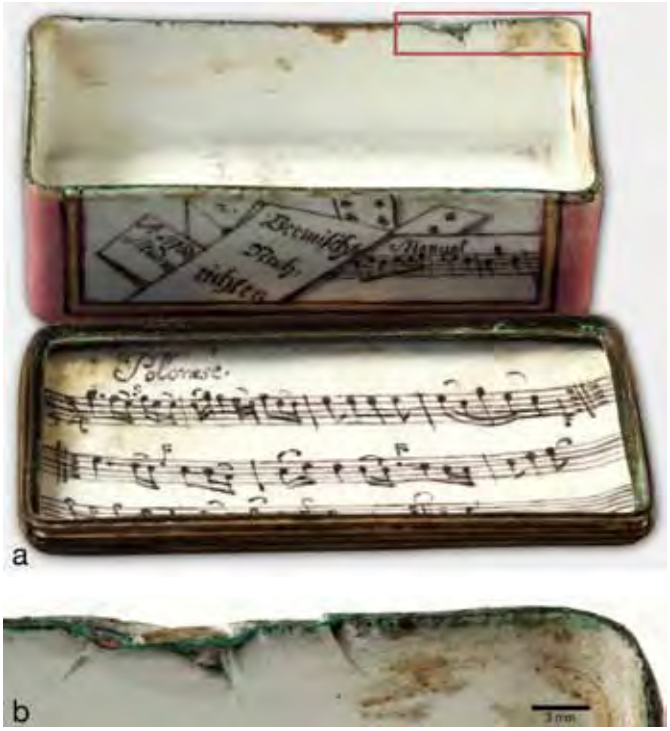

Fig. 2. (a) Box no. 1309, gilded metal frame detached from the base. (b) Damage to the copper plate and loss of enamel (Photos: Andrea Fischer).

Fig. 3. (a) Box no. 5744. (b) Corrosion products on the metal surface of the hinges and on the enamelled copper plate (Photos: Andrea Fischer).

Corrosion on the Gilded Brass Frames

All the frames on the inside of the boxes (figure 3) are corroded, but none on the outside. In some instances (nos. 1973-32, E 1280, G 8.24, 5433, and G 10.200), the corrosion layers appear homogeneous, even, and dense; they are obviously not related to 'glass-induced metal corrosion', which has quite a different appearance. In other instances, the corrosion lies loosely on the surface.

Corrosion Products

When analysing corrosion products, the size of samples is a challenging factor, as it is often limited to a few crystals on the surface of the object. For this reason, the use of conventional XRD was not considered suitable. Micro-XRD could be an option, but this is not readily accessible for most laboratories. As an alternative, micro-Raman spectroscopy seemed the most promising approach for our study. This technique is becoming increasingly available in conservation science and has proved to be an appropriate method for examination of pigments, minerals, binding media, or varnishes. The instrument used was a Renishaw inVia Raman spectrometer with a Leica DMLM microscope and a RenCam CCD detector. The spectrometer was equipped with a He–Ne laser operating at 632.8 nm, with power kept below 800 µW on the sample surface. Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) was used as a complementary technique to characterise the corrosion products. The investigation was undertaken with a Zeiss EVO 60 operating at 20 kV in high vacuum.

Sodium copper formate acetate was identified as the most significant corrosion product. It was detected on four snuff boxes and was found in all the turquoise corrosion products on box no. G 8,360; in the corrosion products on the gilded brass frame in the inside of box no. 5744; in the corrosion on the copper plate of box no. 1309; and on the lid of box 5433. The Raman spectra of all samples showed almost identical Raman shifts and relative intensities, corresponding to those published by Trentelman and others (2002, p. 221) and Robinet and Thickett (2005, p. 331). The homogeneity of the samples varied: some appeared pure and others contained crystals that have not yet been identified.

According to the X-ray photoelectron spectroscopy and Raman spectroscopy data of Trentelman and others (2002), this corrosion product is a mixed sodium copper (1:1)

formate acetate, with the formate/acetate ratio estimated between 1:2 and 2:1. However, further research is needed to determine the exact composition of the corrosion product. The Raman spectrum clearly shows peaks for formate, while there is little evidence for the presence of acetate assumed by Trentelman and others (2002) in the spectrum. The peak at 941 cm^{-1}, interpreted as C-C stretching vibration, is weak. Most of the samples gathered from the gilded brass frames of the snuff boxes have been determined as chloride, sulphate, and carbonate-containing corrosion products. SEM-EDX and Raman spectroscopy have been applied for identification.

The residues of the old adhesive were identified using Fourier transform infrared spectroscopy with attenuated total reflection (ATR-FTIR; Perkin Elmer Spectrum One). Animal glue was used to attach the gilded metal frame to the enamel base. It is likely that the hygroscopic properties of the glue have encouraged the corrosion process, since the areas exhibited increased the occurrence of turquoise corrosion products.

Enamel Composition

To gain some information about the enamel composition, two spalled opaque white splinters of about 1 mm^2 were examined: one from box G 8,360 (on this box, the evidence of sodium copper acetate formate had been detected with Raman) and the second from box 12920 (where evidence of copper chloride was found). Only these two detached splinters were available for investigation. There was neither the possibility of additional samples being taken nor the possibility of using non-destructive analysis techniques such as micro X-ray fluorescence or particle-induced X-ray emission. The samples were embedded in acrylic resin, polished and carbon-coated before being analysed using SEM-EDX. The opaque white enamel samples were found to be a sodium–lead–silica glass, with tin as an opacifier.

Additionally, quantitative measurements were carried out by electron-probe microanalyses (EPMA) using a Joel JXA 8200 Superprobe. The glass matrix of the sample of box G 8,360 contains 46.8% (± 0.7) SiO_2, 12.2% (± 0.5) Na_2O, 3.3% (± 0.2) K_2O, 6.1% (± 1.7) SnO_2, 1.1% (± 0.3) CaO, and 25.8% (± 1.5) PbO (average of multiple EPMA analyses; values given in wt%).[1] The measured values for box 12920 are comparable. This composition does not indicate that the opaque white enamel is likely to be subject to deterioration. According to a number of studies on the degradation of painted enamels, opaque white lead–silica enamels with comparable high lead oxide percentages (here 25.8 wt%) are always described as stable (Smith, Carlson, and Newman 1987; Perez y Jorba, Rommeluere, and Bahezre 1991; Biron 1999). Lead oxide can function as a stabiliser and causes a high hydrolytic stability. In contrast, a number of coloured translucent alkaline silicate enamels are particularly susceptible to deterioration (Smith, Carlson, and Newman 1987).

Sources of Ions

The evidence of sodium copper formate acetate suggested that the exposure to organic pollutant gases, containing carbonyl groups, is involved in the deterioration of the snuff boxes. Since the boxes are kept in wooden cabinets, wood is the obvious source of the pollutants. Conservation materials such as polyvinyl acetate adhesives, which emit organic acids during deterioration, were not found.

First, it seemed most probable that the enamel has provided the sodium ions for the formation of sodium copper formate acetate, since all turquoise corrosion products are located near the interface between the enamel and the metal. In only one instance (box no. 5744) are the corrosion products positioned at the junction of enamel and metal, as well as on the metal surface of the hinges.

However, only four out of 62 boxes are affected by this corrosion phenomenon. This raises the question as to whether this explanatory approach is appropriate.

The white opaque enamels of the snuff boxes have suffered damage by fractures and spalling, but show no obvious signs of glass deterioration such as a fine crazing or a moist surface film. Further, the results of the enamel analysis do not indicate a composition sensitive to degradation. This is different from all other combined glass/metal objects with metal corrosion positioned next to glass: here the glass always showed clear evidence of corrosion.

Are there alternative sources for the sodium found in the corrosion products?

The snuff boxes were prestigious objects that were most likely frequently cleaned. Most of the corrosion products were detected in comparatively inaccessible parts of the boxes, in gaps between the enamel and metal. Residues of a cleaning agent can accumulate here. The influence of cleaning with alkaline solutions in the past has not been considered in the previously published instances of metal/glass corrosion on

historic objects, as the instability of the glass due to its composition was generally obvious and the corrosion always occurred at the interface between glass and metal. Many objects under investigation, such as the Black Forest Schäppel (Eggert and others 2010), were complex in design and contained various textile components, which made it seem unlikely that they were treated using alkaline solutions.

Trentelman and others (2002), Robinet and Thickett (2005) as well as Paterakis (2007) observed sodium copper formate acetate on archaeological copper artefacts. In the case of archaeological finds, there are two possible sources for sodium. First, an arid soil can be quite rich in soda and therefore can contribute to the formation of the corrosion. The conservation materials used are a second possible source. Paterakis (2007, p. 95) refers to the use of sodium sesquicarbonate. This material has been used to stabilise archaeological copper alloys since the 1920s (Scott 1926, p. 36).

Traditional Cleaning Treatments

Several traditional cleaning agents contain acetic or other organic acids as well as alkaline components. It is conceivable that these materials provide the source of the ions that make sodium copper formate acetate. In the past, objects in decorative arts and design collections had to represent the splendour of bygone times. In the case of the snuff boxes, this meant that the painted enamels had to present their full colour, and the gilded metal had to appear shiny. During the time of use, it was also important to look after the small hinges of the box in order to keep the lid movable.

There are no specific manuals available about how to care for enamels or enamel boxes. In sources from the late 18th century ('Hausväterliteratur') and the first half of the 19th century, several recommendations were made concerning the cleaning of glass, brass, and gilded ware.

For the cleaning of brass, instructions specify wood ash or a strong potash-lye as an alkaline component of the cleaning agent (Löffler 1801, p. 242). Ash is recommended even for the cleaning of glass (Grebitz 1826, p. 275). For more delicate items, such as gilded chains, soap is listed. Occasionally the use of 'Venezianische Seife' (similar to Marseille soap, made with soda ash) is explicitly stated. Summing up, it can be said that most of the early cleaning agents in theory contain potassium ions, but rarely sodium ions, in the recipe.

In Germany, soda, processed with diluted citric acid and ground lime, was introduced for the cleaning of silver in the first half of the 19th century (Anonymous 1834, p. 683). Soda was also recommended for the cleaning of stained glass (Chevreul 1864, p. 353). Since the industrial production of soda became more important in the course of the 19th century, it is consistent that various applications of related reagents are recommended in the early conservation literature. Rathgen advises using soap and soda for the cleaning of very soiled stained glass (1924, p. 108) and a solution of caustic soda for various applications related to bronze conservation, including electrolytic reduction (Rathgen 1898, pp. 104, 121). For copper and bronze, Scott (1921, p. 12) recommends the application of an alkaline solution which is made by dissolving Rochelle salt and caustic soda in water. Scott (1926, p. 36) also describes the use of sodium sesquicarbonate (mentioned above) for the treatment of 'bronze disease', but it seems unlikely that this method was applied on non-archaeological metals. Another material used in early times of conservation, which may provide a source for sodium ions, is Calgon, formerly a sodium polyphosphate. It has been suggested by Plenderleith (1956, p. 247) for the removal of calcareous deposits from bronze. Emmerling (1965) recommends the use of the di-sodium salt of EDTA for the cleaning of bronze. As early as 1921 (pp. 8, 12), Scott suggests formic acid for silver and formic or acetic acid for bronze. The application of all of the above-mentioned stripping reagents was recommended for archaeological rather than for decorative arts objects. However, over time, the applications have been modified by the means of inhibitors, and the use of cotton swabs or poultices has enabled localised usage.

Since a document describing the treatment of the snuff boxes was not available in the archive of the Landesmuseum Württemberg, internal reports of comparable objects treated in the 1970s were studied. Gilded copper alloys and silver as part of composite objects were usually cleaned by the means of a solution containing soap and ammonia, applied with cotton swabs or cloth. The treatment was completed by a polish, using jewellers' cloth. The use of ammonia solution is widely recommended, even in the early conservation literature (Petrie 1904, p. 98).

In most instances, gilded silver was cleaned employing commercial chemical dips, applied locally. According to the conservation reports, these chemical dips were frequently used for various gilded metal objects as well, including copper alloys. The main constituents of reagents in silver dips are usually thiourea and sodium thiosulphate, dissolved in

diluted acids. Other cleaning dips contain potassium or sodium cyanide. Petrie names potassium cyanide for silver cleaning (Petrie 1904, p. 98).
In 1970, the conservators at the Landesmuseum Württemberg established a list of materials and methods that were used as specific codes for their treatment reports. A note refers to the conservation manual published by Mazanetz in 1960. Various materials, already mentioned above, are included. This might be of interest concerning the formation of sodium copper formate acetate: solutions of caustic soda (electrolysis), sodium acetate (electrolysis), sodium sulphite, sodium thiosulphate, several commercial silver dips, di-sodium salt of EDTA, and soap were recommended for cleaning.

Snuff Boxes in Other Collections

The museum of local history in Ellwangen (Germany) dedicates one exhibition room to the above-mentioned enamel painter Johann Andreas Bechdolff. Nine enamel snuff boxes made by the painter are included, which are on permanent loan from various major collections in the south of Germany. All the boxes are in a good state of preservation and do not show obvious fractures or spalling. Five are affected by corrosion at the hinges on the inside of the box.
The investigation of the corrosion products using Raman microscopy revealed that sodium copper formate acetate is evident on one box (no. 10777; figure 4) only. This particular box is of special importance for the exhibition due to the depiction of the townscape of Ellwangen on the lid. For the current study, this box could be one key to understanding the origin of sodium ions and possibly also organic acid residues. The box was placed at the Ellwangen museum's disposal for exhibition only in 1994, originally having belonged to the Landesmuseum Württemberg. It seems very likely that this box was treated in Stuttgart, together with the four boxes mentioned above, resulting in the occurrence of sodium copper formate acetate. This evidence is therefore an important indication that all five boxes were cleaned with the same agent. Unfortunately, there are no records available to prove this theory.
Further investigations included six boxes belonging to a private collector, three boxes from the collection of the Museumslandschaft Hessen Kassel, and another two from the Museum für Hamburgische Geschichte.

Fig. 4. (a) Box no. 10777. (b) Corrosion products on the metal surface of the hinges (Photos: Andrea Fischer).

All these boxes show no occurrence of sodium copper formate acetate or any other corrosion products related to 'glass-induced metal corrosion'.

Conclusion and Prospects

The present case study is part of the recently started GIMME Project. It shows that copper corrosion products containing formate and acetate ions can frequently be detected on historic enamel objects. However, the first assumption, that the conspicuous turquoise corrosion products on the snuff boxes in the Landesmuseum Württemberg are caused by 'glass-induced metal corrosion', cannot be confirmed.
The opaque white enamel samples were found to be a sodium–lead–silica glass with a high lead oxide content. The overall composition proves the stability of the enamel, and it seems unlikely that the enamel has provided the sodium ions for the formation of sodium copper formate acetate.
Another important indicator for the fact that residues of a cleaning agent have caused the corrosion is supplied by the

evidence of sodium copper formate acetate on one snuff box in a museum of local history. As this box was provided by the Landesmuseum Württemberg, it is safe to assume that all affected boxes were treated in the museum's conservation laboratory with the same cleaning agent.

However, it is not possible to give a clear statement concerning the contents of the cleaning agent. The application of alkaline reagents is as likely as the application of formic acid and commercial silver dips. Further, the occurrence of carbonyl pollutants from wooden cabinets and shelves has to be considered, as it may influence the formation of the corrosion products.

The use of micro-Raman microscopy for the analysis of copper corrosion products has proved to be very successful. Most of the samples generate strong Raman signals. Since the beginning of the project, various case studies have provided a strong basis for the interpretation of the analyses. Several copper corrosion products have been detected in addition to sodium copper formate acetate.

The case study of the snuff boxes occupies a special place in the GIMME project, since the composition of the enamel suggested that this glass, with high lead and low sodium content, is not likely to be involved in their degradation. Alternative sources of sodium in corrosion products have to be determined.

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Notes

1. Other components: 0.51% (± 0.13) Al_2O_3, 2.84% (± 0.55) CuO, 0.4% (± 0.2) MgO, 0.97% (±0.09) P_2O_5, and 0.28% (±0.30) FeO.

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The Development of an Ion Chromatography Protocol for Detecting the Early Stages of Glass Degradation

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Keywords:
Rijksmuseum; unstable glass; glass sickness; condition survey; ion chromatography

Abstract
In conjunction with the re-display of the collections of the Rijksmuseum, Amsterdam, a condition survey of the vessel glass holdings revealed that approximately 10% displayed changes of appearance, ranging from surface haze to advanced crizzling. Ion chromatography analysis of samples taken from the glass surface by moist cotton swabs has the potential to pinpoint unstable glasses. Thus, difficulties in identifying objects that were indubitably in the early stages of glass deterioration led to investigation of ion chromatography to quantify surface residues of sodium, potassium, calcium, and magnesium ions, symptomatic of only those items undergoing breakdown of the glass matrix. Results are reported for the development and optimisation of a straightforward analytical protocol. Good recovery and reproducibility were achieved for extraction of all four cations from cotton swabs in a laboratory validation, prior to full implementation for the examination of historic glass.

Introduction
'Glass sickness' is the evocative term coined, and still commonly in use, to describe the propensity of vessel glass with unstable composition to undergo surface changes primarily referred to as 'weeping' and 'crizzling'. Most studies of glass sickness have been devoted to understanding its causes and to controlling the environment in order to prevent the onset of glass weeping and crizzling in museum collections (see, for example: Organ 1957; Brill 1972; Brill 1975; Hogg and others 1999; Römich 1999; Koob 2006; Kunincki-Goldfinger 2008). Less attention has been focused on identifying the early stages in the deterioration process and, in particular, the difficulty of distinguishing the first signs of true glass sickness from other surface effects. This paper concerns the visual categorisation of a range of surface changes displayed by vessel glass in the Rijksmuseum, Amsterdam, and the initial phase of the development of a straightforward analytical approach to pinpoint those glasses actually undergoing breakdown of the glass matrix.

This research was motivated by a condition survey of vessel glass in the Rijksmuseum. The conclusions had urgency because the survey was being carried out in preparation for re-display of the collection for the re-opening of the museum, in 2013, after several years of refurbishment. Priorities had to be set for conservation treatments, and recommendations were required for optimal parameters for the display and storage environment. A clear-cut specification of vulnerable glasses with unstable compositions was necessary in order to identify items where special measures should be put in place to minimise deterioration of the glass. Prior to initiating the survey, discussions took place with conservators in other museums. Account was also taken of the methodology and conclusions of similar assessments, notably in the United Kingdom (Cobo del Arco 1999; Oakley 1999). The stages of glass deterioration proposed by Koob for specifying the advancement of crizzling (Koob 2006) provided a very useful framework to categorise unstable glass, but it soon became apparent that many Rijksmuseum items could not be classified with certainty as unstable. Particularly problematic were those glasses where the surface changes were minor; were those effects due to glass deterioration or less worrisome causes that could broadly be described as soiling?

This led to the development of five descriptive categories covering the full range of deterioration (table 1) but focusing on the numerous examples of minor surface effects (denoted by terms such as 'loss of brilliance', 'surface haze', 'greasy appearance', etc). For many glasses, it was realised that, without relevant scientific analysis, no conclusions could be made about whether they were exhibiting the initial stages of glass sickness or what the prognosis for these items would be, on display or in storage, without special environmental control. However, as a support for the visual analysis, no suitable analytical technique and protocol had been reported by other museums confronted by this question.

The ability of instrumental means of analysis to determine glass stability is clearly of benefit to those charged with the conservation of ancient and historic glass. Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy have been used to categorise glass stability (Earl 1999; Robinet and others 2006). While the potential of these spectroscopic non-invasive techniques has been demonstrated, as yet they are unable to provide conservators with a sufficiently clear-cut assessment of glass stability. Accordingly, the research described in this paper was initiated to explore the scope of ion chromatography, a technique that has the potential to detect minute quantities of glass breakdown products on the surface of objects and thus pinpoint the onset of glass sickness.

Rijksmuseum Glass Categories

The objects in the Rijksmuseum glass collection were divided into the categories fully described in table 1. Examples are depicted in figures 1–3. Category A consists of items that are in perfect condition and no treatment is necessary. Category B glasses show very minor surface changes, possibly indicative of degradation, such as loss of brilliance or mild haziness. Category C consists of objects that show very probable signs of glass degradation denoted by, for example, a distinctly 'oily' surface (figure 1). Category D contains objects that show undisputed symptoms of degradation such as clear crizzling or the formation of small droplets on the surface (figures 2 and 3). Finally, Category E contains objects that are beyond restoration; these objects are no longer fit for display. This paper is primarily concerned with the need to categorise more precisely the dubious effects represented in Categories B and C. It is anticipated that the positioning of items within these categories may well be revised once more information becomes available.

Fig. 1. (top) Ornate Dutch glass, height 25.6 cm, ca 1550–1600 (Rijksmuseum Amsterdam, Reg. No. BK-NM-776).
(bottom) Detail showing surface deterioration, assigned to category C (Photo: © Rijksmuseum).

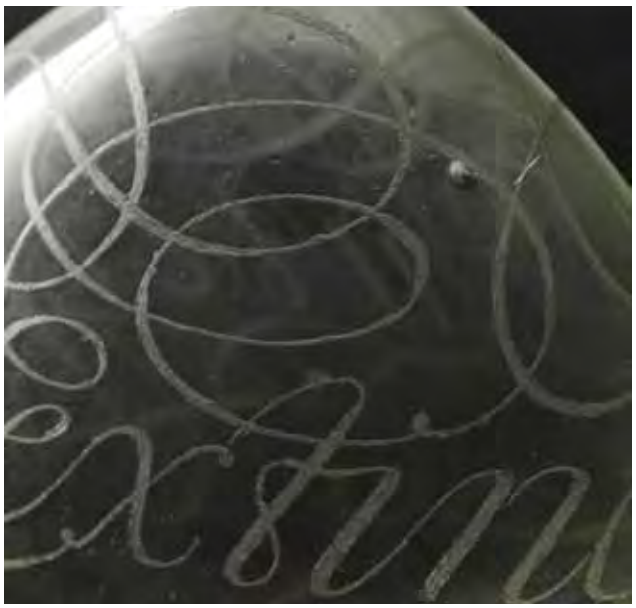

Fig. 2. (top) Dutch engraved glass flask, height 17.6 cm, ca. 1675–1692 (Rijksmuseum Amsterdam, Reg. No. BK-NM-754). (bottom) Detail showing surface deterioration, assigned to category D (Photo: © Rijksmuseum).

Fig. 3. (top) Venetian clear glass vase, decorated with blue dots, height 14.1 cm, ca 1900–1910 (Rijksmuseum Amsterdam, Reg. No. BK-1978-111). (bottom) Detail showing surface deterioration, assigned to category D (Photo: © Rijksmuseum).

Ion Chromatography

Ion chromatography is a form of high performance liquid chromatography for quantification of low concentrations of cations or anions in aqueous solutions. In this technique, ion exchange mechanisms are used to separate ionic species in a solution that is pumped at high pressure through a column containing small spherical beads with ion-exchange sites. Various procedures, but most commonly conductivity detection (as used in the experiments described below), can be used to monitor the elution of the separated ions from the column. The first commercial instrument was produced by Dionex almost 40 years ago following pioneering work by Small, Stevens, and Bauman (1975). Since then, ion chromatography has become an important technique in analytical chemistry. Several textbooks are available; that by Fritz, Gjerde, and Pohlandt (1982) covers the subject well. A description of the technique and some applications to the examination of surface changes occurring on historical artefacts has been reported (Tennent and others 1992). Of importance to the present study is the power of ion chromatography to detect the presence of 'incipient efflorescence'; it was demonstrated that ionic species could be detected on the surface of artefacts, even when invisible to the naked eye (Tennent and others 1992).

The research reported in the present paper explored the potential of ion chromatography to detect cations that are liberated from the glass structure by ion exchange (Römich 1999) and easily removable from the glass surface by swabbing with moist cotton buds. The research, the first stage of a continuing project, focused on the identification and quantification of sodium, potassium, calcium, and magnesium, the principal glass components whose presence on the surface, associated with barely discernible visual changes, is likely to signify breakdown of the glass. Consequently, this approach offers the potential for a direct and clear-cut categorisation of unstable glass. Changes in the glass itself as represented by modification of the Si–O bonding arrangements can be probed by FTIR and Raman spectroscopy (Earl 1999; Robinet and others 2006; Robinet and others 2008); however, as yet, neither has the ability to discern, unambiguously, the early stages of glass sickness.

Experiments were undertaken to develop a protocol to quantify cations on the glass surface, indicative of the inherent instability of the glass composition and the susceptibility of these glasses to progressive decay. As with all new applications of analytical techniques, it was necessary to establish a straightforward methodology and to verify that it produces reliable results. The validation of this protocol, prior to implementation for the examination of historic glasses, is the focus of the research reported below.

Experimental

Instrumental Set-up

The set-up used in this research is illustrated schematically in figure 4.

Sample injection was performed using a Waters 717 Autosampler that enabled multiple samples to be analysed consecutively from a carousel with 1 mL vials. The eluent used in this study was 20 mM methane sulfonic acid, filtered using a 0.22 µm filter. A Waters 616 Pump was used with a flow rate of 0.5 mL min^{-1}. A Waters 6005 Controller gave connection between the pump, autosampler, and conductivity detector. A Dionex IonPac CG12A-5 µm 3 x 30 mm Guard Column and 3 x 150 mm Analytical Column, designed specifically for the analysis of alkali and alkaline earth metals, was used in conjunction with a Dionex CSRS300 2 mm self-regenerating suppressor and a Dionex CD20 conductivity detector in combination with a Dionex DS3 detection stabiliser. A Waters CHM column heater was set at 30°C to give maximum peak resolution. Waters Empower chromatography software controlled the analytical set-up features.

A typical cation chromatogram is shown in figure 5. The peak surface area is a measure of the concentration of a species in solution.

Extraction Experiments

This paragraph describes the experimental set-up and the protocols developed for the extraction experiments. The first experiments focused on extracting given amounts of cations from cotton swabs as simply as possible. As the research proceeded, more complex methods of extraction were investigated in order to achieve consistent and reliable results. The goal of these experiments was to improve the extraction of ions from the swabs into solution with good recovery and reproducibility.

Basic Extraction Method

An amount between 50 and 100 µL of a stock solution containing the four cations under investigation (hereafter referred to as the test solution) was applied to a cotton swab

using a micro-pipette. After application of the test solution to the swabs, they were left to dry until all the water evaporated; this was done to simulate a real-life sampling procedure (namely, when a conservator takes a sample from a glass surface and lets the sample dry before sending it for scientific analysis). After drying, the swab was placed in 1 mL of de-ionised water and left for 90 minutes. After extraction, the swab was removed from the tube, and the extraction fluid was centrifuged for 10 minutes, in order to avoid possible contamination by particles or fibres released from the swab. 800 µL of the extraction fluid was removed from the tube using a pipette and inserted in a vial. The solutions obtained were analysed to assess recovery and reproducibility of the extraction method.

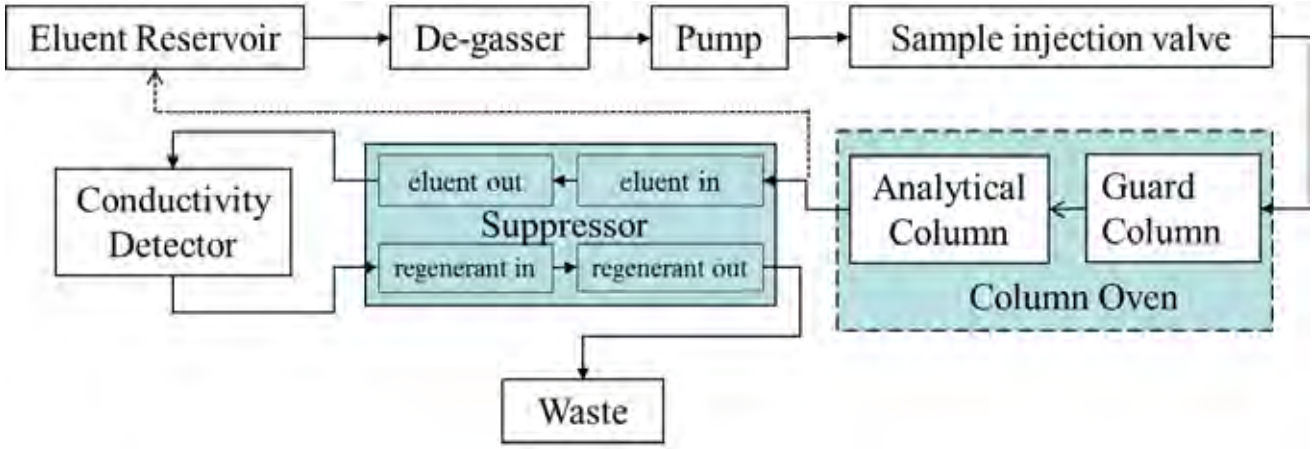

Fig. 4. Schematic overview of the set-up of the ion chromatography system used for the experiments.

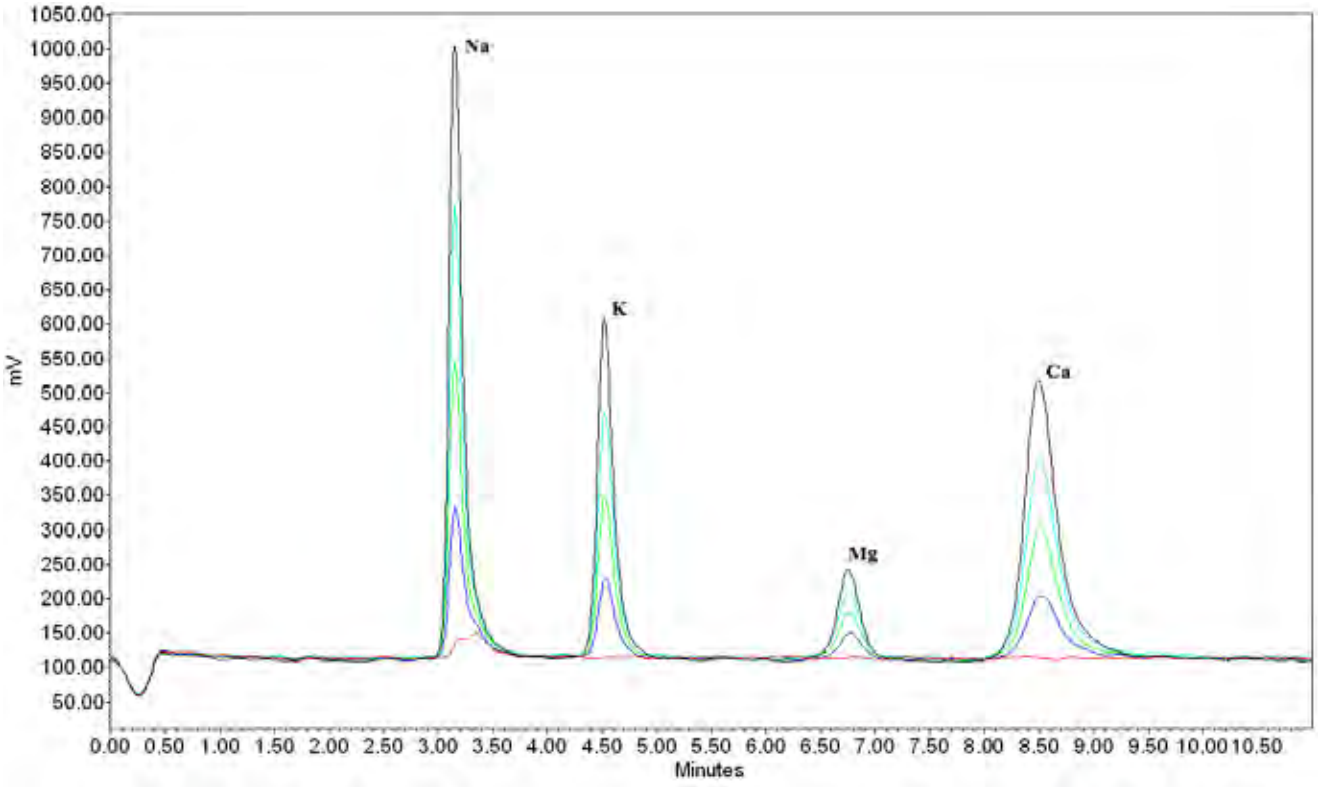

Fig. 5. A typical chromatogram for sodium, potassium, magnesium, and calcium; ion calibration solutions with analyte concentrations of 100 ppm (black), 75 ppm (light blue), 50 ppm (green) and 25 ppm (dark blue) and a blank sample (red).

Reference Samples

In parallel to the extraction experiments, reference samples were also analysed. These samples were prepared by making a solution similar to that of the extraction solutions. The same volume as applied to the cotton swabs was pipetted directly into a vial and diluted to a total volume of 1 mL. Ideally, this would yield a solution with the same concentration of ions as the extracted solution. In this way the analytical results of the extracted solutions can be compared with the reference samples, and the recovery – the degree to which the ions applied on the cotton swabs are brought into solution during extraction – can be determined.

Variants of the Extraction Procedure

Extraction in an Ultrasonic Bath

This experiment was performed to investigate if extraction in an ultrasonic bath provided more reproducible analytical results and increased recovery. The application of the test solution to the swab, drying procedures, centrifugation, and sample analysis were the same as during basic extraction. During extraction, however, the samples were placed in a Styrofoam tube holder and extracted for 90 minutes in an ultrasonic bath.

Extraction With and Without Drying

Drying samples is time-consuming and can be avoided if the conservator places a sample directly into a tube filled with de-ionised water after sampling. In order to assess the influence of drying the cotton buds, identical volumes of concentrated solutions were applied to a series of cotton swabs. One set of swabs was left to dry overnight in a fume hood, the other set was placed immediately into a tube for extraction. The dried swabs were placed in a tube for extraction the following morning when the water had evaporated. For both sets of swabs, the extraction time was 90 minutes. Since the volume applied to the swab also contributes to the extraction volume if the swabs are not left to dry, the volume of de-ionised water in the extraction tube was adjusted so that the total extraction volume added up to 1 mL.

Extraction in Eluent

The water used for extraction of the swabs has an influence on the chromatogram obtained. The water causes a change in conductivity compared to the eluent and is, therefore, a possible cause of irreproducible results. Thus, extraction was performed with the eluent as the extraction fluid. Application of the test solution to the swab was followed by extraction in the eluent for 90 minutes. The sample was centrifuged and the extraction fluid was transferred into a vial.

Swab Removed from its Plastic Support

The manner in which a cotton swab is wrapped around the support can be a cause of decreased recovery during extraction, especially if swabs produced industrially are wrapped tightly around the support. In order to decrease their compactness, the cotton swabs were removed from the plastic holder by cutting them open. After removal of the swabs, the test solution was applied and the swabs were then placed in a tube for extraction.

Tissue Extraction

Tissue paper was used as an alternative carrier for the test solution. The advantage of using tissue paper for extraction is that the surface is larger and the material is thinner and more homogeneous than a cotton bud. A disadvantage of using tissue paper for sampling is that the handling of a piece of tissue paper is less convenient than handling a cotton swab on a stick. To perform the tissue-extraction experiment, a sheet of tissue paper was cut into as small a square as possible, so that the paper could just hold the volume of test solution applied without it being saturated. The test solution was applied by holding the small piece of tissue paper in a pair of tweezers.

Double Extraction

The possibility was investigated that, by repeating the extraction step, more ions could be brought into solution than with a single extraction. After application of the test solution to the swab, the swab was placed in a plastic tube for a 90-minute period of extraction. Thereafter, the swab was removed from the first tube and placed in a second tube for a further 90-minute extraction.

Extraction from Melinex as a Simulation of Ions on a Glass Surface

Extraction from the Melinex surface was done by applying the same amount of test solution to a small piece of Melinex and letting it dry overnight, so that salts were present on the surface. After drying, the small pieces of Melinex were placed in an extraction tube containing 1 mL of de-ionised water for a period of 90 minutes. The centrifugation and analysis steps were the same as the basic extraction experiment.

Sampling of Surface Material from Vessel Glass Using a Swab
Several objects showing various surface effects were selected for sampling. Sampling was done by swabbing 1 cm^2 area of the glass surface ten times back and forth. The samples were stored in a tube, and extraction was subsequently performed in the laboratory using de-ionised water. The extraction volume was 1.1 mL, so that the solution could be filtered; the filters absorbed approximately 0.1 mL of the solution that is being filtered. Prior to filtering, the cotton swabs were removed from the tubes, and the extraction fluid was centrifuged for 10 minutes.

Results and Discussion

The results achieved in this study represent the conclusion of the first phase of the development and implementation of a regime for chemical analysis as a tool to aid conservators in identifying unstable glasses. A protocol has been developed whereby ion chromatography can reliably quantify low concentrations of ionic species absorbed by cotton swabs.
Validation of this protocol was necessary prior to the second phase of the project, namely ion chromatography of the ionic species extracted from swabs used to sample the surface of historic glasses displaying a range of stability. Unexpectedly, much experimentation was required to ensure that this protocol gave good recovery and reliable reproducibility.
Initial experiments focused on the ion chromatography analytical errors. Relative standard deviations for analysis of 50 ppm standard solutions of Na^+ and K^+ were 3% in both cases. For analysis of pipetted samples of 50 µL of 1000 ppm Na^+ solutions added to two 475 µL pipetted aliquots of water, a relative standard deviation (in this case somewhat less than 3%) indicated that the error in sample preparation can be neglected compared to the error in the determination of peak surface area from chromatograms.
Less straightforward was the extraction and quantification of ions applied to cotton swabs, the key factor that had to be optimised prior to the use of cotton swabs for sampling from the surface of historic glasses. The basic extraction of a standard solution of the four analyte ions applied to a commercially prepared cotton swab gave poor total recovery and too wide a spread of results, i.e. the reproducibility of the extraction step was inadequate. In order to give superior results, extraction was carried out in an ultrasonic bath in an attempt to free the ions from the cotton swabs; however, this experiment did not increase recovery or reproducibility. The effect of drying the samples before extraction was evaluated by performing experiments in which the extracts of dried samples were compared to those where the swabs were placed directly in the extraction fluid after application of the test solution. This demonstrated that drying the samples had no effect on the analytical results. Thus, for sampling by conservators, the swab may be either dried or placed directly in a vial with extraction liquid prior to analysis. For simplicity, the drying step is now omitted from our sampling protocol. Experiments to investigate extraction in the acidic eluent, as opposed to distilled water, increased the recovery somewhat but did not improve the reproducibility – the recovery was generally below 70%, and the relative standard deviation was still above 10%.
Finally, satisfactory results for both recovery and reproducibility were obtained by removal of the cotton swab from its plastic holder prior to application of the test solution and extraction. This achieved recovery of more than 90%, with a reproducibility comparable to the internal error of the ion chromatography system. It is concluded that the compactness of the commercially prepared cotton swabs was such that extraction of the applied salts was inhibited. Loosening of the swab from its plastic holder enabled satisfactory extraction. The same results were obtained for analysis with tissue paper extraction.
As a further refinement, a double extraction was also performed. This showed that, during a second extraction, more ions were extracted from the swab; however, because of the complexity of determining ion concentrations in the second extraction, combined with the high level of recovery in a single extraction, this does not form part of the recommended sampling protocol.
With this thorough validation in place, implementation of the protocol for historic glasses has become possible. The preliminary results, first for a simulation with salts on the surface of Melinex and then using the swab protocol for sampling a small set of unstable historic glasses, confirm the usefulness of this approach. These results will be reported in full at a later date.

Conclusions

This investigation had its impetus in the glass condition survey carried out at the Rijksmuseum in preparation for its re-opening after 10 years of refurbishment. The survey resulted in the establishment of five overall categories of deterioration, representing approximately 10% of the museum's glass collection, in order to assist in prioritisation of items for display and storage.

It transpired that the numerous items where the visual signs of possible glass deterioration were minor were most problematic for the conservation decision-making process. It was concluded, therefore, that non-invasive analysis of the glass was necessary to supplement conservators' visual observations in order to identify which glasses were actually of unstable composition. Since no appropriate methods had been reported to do this, ion chromatography was identified as the most promising analytical method. The development of a protocol to extract sodium, potassium, calcium, and magnesium ions from cotton swabs was the essential first step in an overall strategy to sample surface deposits from vessel glass as indicators of glass deterioration. The successful validation of this protocol is the focus of the results presented above. Accordingly, the research can now enter the implementation phase, already trialled with a small number of items in this initial phase, involving optimisation of the procedure for sampling and analysis of surface deposits from a range of historic glass displaying different degrees of degradation.

Acknowledgements

The authors wish to thank Robert van Langh and Isabelle Garachon for support and encouragement for studies of the Rijksmuseum glass collection. Associated with this investigation, Frederike Burghout, Mandy Slager, Christel van Hees, and Barbara Schoonhoven made possible comparative assessments, engaged in extensive discussions on the categorisation of glass degradation, and enabled sampling of vessel glass surfaces at the Museum Boijmans van Beuningen, which will be reported in due course. The interest and advice of Lorraine Gibson, University of Strathclyde, is warmly acknowledged.

	Description
Category A	*Glasses in this category are in a perfect condition* No conservation treatment is necessary.
Category B	*Symptoms B1–B4 may concern glass degradation* This category contains glasses showing very slight surface changes. It is desirable to clean the glass – after cleaning most of the glasses should have the same appearance as those in category A. Glasses in this category should be monitored after cleaning to see if new surface changes have occurred.
B1	Very slight 'oily' appearance which may be an early stage of glass degradation, but can also be unrelated to degradation (grease, etc.)
B2	Very light haze, clearly visible in raking light.
B3	Fingerprints are visible on the surface.
B4	Combination of B1–B3.
Category C	*Symptoms C1–C9 may concern glass degradation* This category contains glasses that show probable early stages of glass degradation. Glasses that were treated previously for glass degradation and now appear stable are placed in this category. After cleaning, most glasses (except C7 and C10) should have the same appearance as those in category A. Monitoring is essential in order to detect new surface changes or other symptoms of degradation.
C1	Slight or incipient crizzling; tiny localised cracks on the surface.
C2	Slight discolouration of the glass; suspicion that a colour change has occurred over the years.
C3	Oily surface which may also be localised, manifesting itself as a spotted appearance. This can be an early stage of glass degradation or the presence of external deposits, such as grease.
C4	Harder deposits or haze (which can be scratched away using a finger nail). They may also be localised, giving a spotted appearance.
C6	A cavity in the glass (from the manufacturing process) in which a fine powder or light haze is visible.
C7	Archaeological glass that shows iridescence.
C8	A combination of symptoms C1–C6.
C9	A combination of symptoms C1–C6 and symptons from category B.
C10	Results from earlier treatments and restoration such as glued cracks or fractures and fills.
Category D	*Symptoms D1–D6 concern glass degradation* This category includes glasses with clear symptoms of degradation. Glasses with very unstable or severely aged restoration(s) are also included in this group. It is desirable to clean the glasses (but not D5 and D8). Monitoring is essential in order to detect new surface changes or other degradation symptoms.
D1	Clear crizzling; tiny cracks on large areas of the glass surface.
D2	Clear discolouration of the glass; especially a shift towards purple or pink.
D3	Clear symptoms of weeping glass; small droplets forming on the surface which may appear oily.
D4	Very hard deposits or haze which are difficult to remove.
D5	Archaeological glass with pronounced iridescence.
D6	A combination of the symptoms in category D.
D7	A combination of the symptoms in categories in B, C, and D.
D8	Unstable or severely aged restorations.
Category E	*Symptoms E1–E3 concern glass degradation* This category contains glasses with crizzling that is so advanced that restoration is hardly possible. Glasses in this category can be kept only in storage – the current state is too fragile for display.
E1	Severe crizzling; cracks on large areas of the surface so that the structure of the object is severely affected. Possible flaking.
E2	A combination of different factors; crizzling, discolouration, weeping glass, possibly combined with a surface haze (irremovable) and/or an oily surface appearance.
E3	Severe deterioration such as fractures, complex cracks, and/or missing parts.

Table1. Description of glass degradation categories developed prior to re-display of the Rijksmuseum vessel glass collection.

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Extended Abstracts

The Department of Glass and Ceramics Conservation at the ENSAV La Cambre in Brussels

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Keywords:
education; conservation; glass; ceramics

History and school organisation

The Conservation–Restoration Department at the ENSAV La Cambre (École Nationale Supérieure des Arts Visuels de La Cambre) was founded more than 30 years ago (Boitel and others 2009). In this abstract, we wish to present an overview of the school and of the glass and ceramics department in particular.

The Institut Supérieur des Arts Décoratifs was founded in 1926 by the architect and designer Henry van de Velde. The school's philosophy stemmed from the Bauhaus movement and the principle of the interdisciplinarity of arts. The institution became the 'École Nationale Supérieure d'Architecture et des Arts Visuels' in 1978. Architecture has not been taught in La Cambre since 1980.

Fig. 1. The abbey/school park with the Conservation–Restoration Department building in the background (Photo: J.-A. Glatigny).

Fig. 2. The Conservation–Restoration Department occupies three floors of the Louise Avenue building (Photo: S. Benrubi).

The main building is located near Brussels city centre, on the exceptional site of the Cistercian Abbey of La Cambre (figure 1). The Conservation–Restoration Department is situated in a modern building very close to the abbey (figure 2).
At the moment, the institution consists of 17 departments including painting, sculpture, fashion design, photography, industrial design, ceramics, book binding, and conservation–restoration, and has in total 700 students. The studies are organised in a five-year programme (a three-year Bachelor and a two-year Master). Besides the specific department courses, all students follow both theoretical and practical classes. The courses cover general knowledge in art history (architecture, photography, music, and cinema), literature, philosophy, semiology, aesthetics, and copyright law. All students attend a number of practical courses such as drawing, colour science, and perspective drawing.
The Conservation–Restoration Department was created in 1981 under the auspices of the Royal Institute of Cultural Heritage, the Université Libre de Bruxelles, and La Cambre. Currently, 70 students are distributed over four specialisations: painting (panel/canvas), sculpture (wood, stone, plaster), paper or book, and ceramics and glass (figure 3).
Specific conservation classes cover topics as diverse as the history of conservation and ethics, specific art history, and chemistry, as well as applied conservation techniques (adhesives, solvents, gels, varnishes, pigments). There are also classes in scientific methods of analysis, climatology, photography applied to works of art, and materials technology (wood, canvas, paper and ceramics). The scientific courses are given mainly by specialists and professionals from the above-mentioned institutions.

Seven instructors and four assistants teach the practical conservation courses. They all work as private conservators and are active in their respective fields.

Practical Conservation Course Organisation

After successfully passing an admission exam, the students dedicate their first two years to learning about ancient techniques: painting (copies), gilding techniques, and ceramics technology (pottery and modelling). They also spend a few days working in each of the four specialisations to have a more precise idea of each area. Further, exercises in active and preventive conservation are carried out.
The students choose to follow courses in two departments during the second year. He/she is progressively responsible for the different steps of treatment: preliminary examination, composing a treatment proposal, treatment, graphic and photographic documentation, historical research, simple scientific analysis, and, finally, the production of a complete conservation report.
In the ceramics and glass section, the students begin by working on archaeological objects from Belgian sites. Then another simple treatment is carried out on European earthenware objects.
In the third year, the student must specialise in only one department. If the specialisation 'ceramics and glass' is chosen, he/she will be responsible for the treatment of a few objects, and will begin to learn about porcelain and glass conservation (figure 4) and the use of conservation materials and techniques.

Fig. 3. The laboratory of glass and ceramics conservation (Photo: S. Benrubi).

Fig. 4. Presentation to the jury of the third year's work (June 2012) (Photo: S. Benrubi).

During the fourth year, different objects are treated, one of them featuring distinctive and extensive conservation problems. The student will begin to deal with a more complex conservation project, which will test his/her proficiency with the research literature and his/her ability to find solutions and to select a correct treatment.
The programme's final year is dedicated to writing a thesis, which is a comprehensive research project. Subjects are chosen from a variety of fields including the theoretical and ethical aspects of conservation, the historical and technical features of particular objects or groups of objects, and the evaluation of conservation products and techniques.
The school profits from extensive collaboration with museums as well as with public and private institutions. As a result, every student in the ceramics and glass laboratory has the opportunity to work on various types of assignments. They experience a wide range of ceramic and glass materials and treat archaeological as well as modern objects.
Our department benefits from academic and cultural education partnerships at both national and international levels (universities, the Royal Institute of Cultural Heritage, European school[1]).
From the first year, our ambition is to empower and prepare our students for each dimension of their future profession. As a result of the good balance between theory and practice, they are able to take complete charge of treatments. Specific features of the school (including permanent contact with artists, temporary exhibitions, and collections management of the school art collection and the Henry van de Velde archive) give the students a broader view of conservation. For this reason, the proximity to, and collaboration with, other creative departments in the school is an asset. Interdisciplinary placements and external internships are strongly encouraged in the last two years, and we are always open to new contacts and exchange of knowledge.

Notes

1. Université Libre de Bruxelles and Université de Liège (Belgium), Artesis Hogeschool Antwerpen (Belgium), Fachhochschule Köln (Germany), Academy of Fine Arts Split (Croatia).

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Silicone as a Moulding Material for Loss Compensation: How to Choose the Right One?

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Keywords:
silicone rubber; mould; loss compensation; glass; ceramic

Silicone rubbers are commonly used to reproduce all or part of an object. They are used mostly on objects in good condition made of low- or non-porous materials, such as high-fired earthenware, stoneware, porcelain, and glass. They are made for the art-moulding market but also for the dental industry, which offers a wider range and specific properties. The silicone rubber commonly used for making moulds to enable loss compensation in conservation is a room temperature vulcanising (RTV) rubber silicone, which is a two-component system: the synthetic rubber and a catalyst. Two major types of RTV rubber silicone are available: the condensation reaction, or tin-catalysed, rubber, and the addition reaction, or platinum-catalysed, rubber.

Although condensation silicone has a shrinkage (0.1–1 vol.%) slightly higher than the addition-reaction-type silicone (0.01–0.1 vol.%) due to its volatile components, both types can be used to reproduce very precise details of an object. Condensation silicone, with a tin-based catalyst, can sometimes adhere to glass or silica surfaces, such as porcelain or enamel ceramics, due to the similarity in composition (containing Si–OH). Even though this problem is not often experienced, the use of a release agent can be helpful. Condensation silicone rubbers are also more sensitive to epoxy resins. Epoxy resin should not be poured into a tin-catalysed rubber mould before the volatile components have evaporated, a process that usually takes 72 hours or 24 hours in an incubator (Koob 2006). If this precaution is not taken, the epoxy resin may react and bond to the surface; this results in damage to the mould or a reaction between the epoxy resin and the mould. This can also occur if a fast catalyst is used, probably because the faster setting time does not allow the volatile components to evaporate sufficiently. The addition reaction silicone rubbers are less reactive to epoxy resins; thus, they are more suitable for epoxy casting. However, the platinum-based catalyst can be very reactive, for instance to sulphur, which can inhibit curing (Morgos, Nagy, and Palossy 1984). Sulphur is found in some plaster and ceramic substrates or in certain modelling pastes that are used during the moulding process (the manufacturers usually mention their compatibility with an addition silicone rubber). In general, every container, spatula, or surface in contact with an un-cured addition silicone rubber, should be very clean to avoid inhibition of curing.

RTV silicone rubbers are available in three main consistencies: viscous liquid, soft paste (which has the consistency of a toothpaste), or putty paste. The choice of consistency and/or hardness is dependent on the location of the surface and the shape and the profile to be reproduced. In order to choose the right silicone, the conservator should consider several questions:

How precise are the details to be reproduced? The viscous liquid and most of the soft paste silicones, such as Exaflex Regular®, give more precision than putty paste silicones because they can flow into small undercuts and reproduce fine details and textures (figure 1).

Where is the shape to be moulded? If the area is located on the object itself, it can be useful to employ a soft paste or a putty paste silicone, such as Elite HD Putty Soft®, because they will not flow down a sloping surface and their fast setting time will allow the conservator to complete treatment on the object in a shorter time. Moreover, a silicone with a thick consistency and a short setting time will have less

opportunity to react with the surface, either leaving a residue or adhering to it (Maish 1994). However, if the shape to be moulded is a detachable fill or fragment, viscous liquid silicones, for instance MM903® (very flexible) or MM922® (more rigid), can be used to create one-part moulds; the silicone is poured into a container in which the object is fixed (figure 2).

Does the surface have deep undercuts? If the shape is complex, a very flexible silicone with low hardness should be used (for example MM903®). Conservators need to keep in mind that it is the silicone mould that has to be removed from the object, and not the object that has to be removed from the silicone mould (figure 3).

Which fill materials will be poured into the mould? If epoxy resins are to be used, it is preferable to make a one-part mould (figure 2). Epoxy resins with very low viscosity may otherwise flow between the join of a two-part mould. If the fills are of plaster, the cast will be more fragile, making it preferable either to make a two-part mould, for instance with a fast-setting viscous silicone such as Elite Double 22®, or to use a very flexible silicone (figure 4).

The choice of a suitable silicone rubber can also be influenced by other criteria, such as the size of the area to be moulded (Blanpain 2011). Another consideration is cost. Some silicones are very expensive, and the cost of making a mould can be prohibitive.

To conclude, taking care to consider the choice of a silicone rubber can result in fewer risks for an object and gaining time. In order to choose the most appropriate silicone and moulding technique, the conservator should therefore first carefully examine the particular features of the object, the shape to be moulded, as well as its composition and condition. Having the choice of two or three different silicone rubber moulding systems considerably enlarges the possibilities of casting and enables the conservator to adapt to each specific situation.

Fig. 1. One-part mould made with the fast-setting silicone Exaflex Regular® (Photo: S. Benrubi).

Fig. 2. One-part mould made with the viscous liquid silicone MM903® to cast a detachable fill and the final fill in epoxy resin (Photo: H. Blanpain).

Fig. 3. Open mould with MM903®, a very flexible silicone (Photo: S. Benrubi).

Fig. 4. Two-part mould made with the fast-setting viscous liquid silicone Elite Double 22®, to cast a plaster fill with a fragile and complex shape (Photo: S. Benrubi).

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Materials and suppliers

MM903, MM922 (ACC silicones)
Mida composite
Avenue de Stalingrad 106
1000 Brussels, Belgium
Tel. +32-25 124566
www.finres-sa.com (accessed on 12 May 2013)

Elite Double 22, Elite HD Putty Soft (Zermack),
Exaflex Regular (GC America Inc.)
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Synchrotron Radiation as a Probe for Copper Oxidation States in Glass

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Keywords

historical glass; decay; non-destructive; synchrotron radiation

Abstract

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

Introduction

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

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

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

Experimental Section

Samples

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

Analytical Techniques

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

Results and Discussion

The red samples exhibit different degrees of deterioration: sample Mi-3 is heavily corroded with an iridescent surface and abundant interconnected craters; sample To-5 is lightly degraded with some pits homogeneously distributed on the surface; sample Vi-2 shows an almost unaltered surface. XANES spectra of the three fragments (Mi_3, To_5, and Vi_2, figure 1(b)) show important differences when they are compared to those of the reference compounds (figure 1(a)). Sample Vi_2 shows a XANES spectrum similar to the Cu foil reference, indicating the presence of metal (Cu^0) nanoparticles, while the Mi_3 and To_5 spectra exhibit the characteristic edge resonance of Cu^{1+} in Cu_2O.

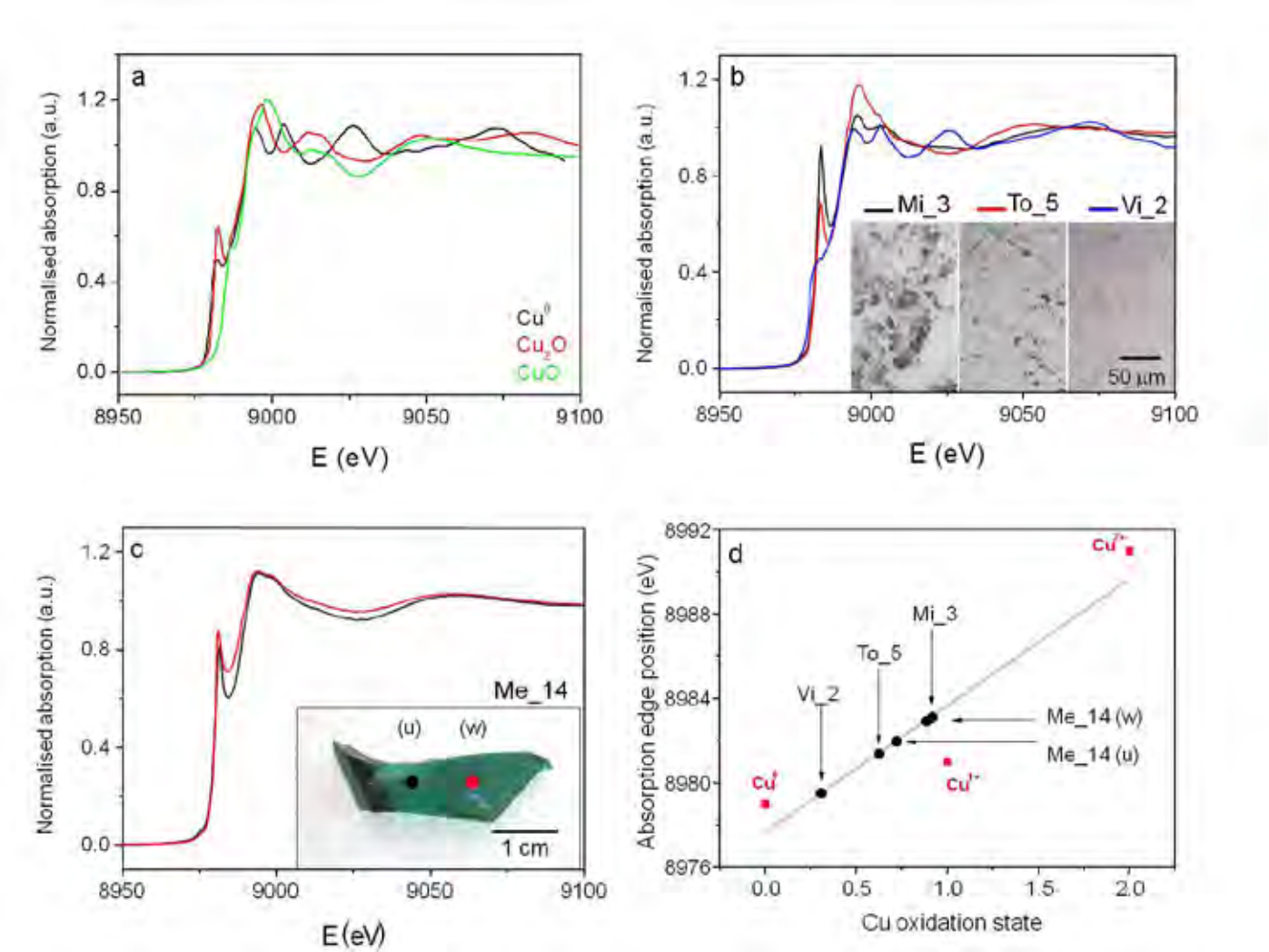

Fig. 1. Normalised Cu K-edge XANES spectra of: (a) reference compounds: metallic Cu, Cu_2O and CuO; (b) historical red glasses: Mi_3, To_5 and Vi_2 (spectra combined with light microscopy images); (c) comparison of two areas of sample Me_14 (u – unweathered and w – weathered; spectra combined with overview image of the sample); and (d) relationship between the Cu K-edge absorption edge energy and Cu oxidation state of all samples (black points) and reference compounds (red squares).

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

Table 1. Sample description.

Sample Me_14 shows an intense green colour characteristic of Cu^{2+} ions (figure 1(c)). Partial flaking on one side allowed the measurement of a non-degraded surface (point named u – unweathered) compared to a degraded part (gel layer with an iridescent surface, point named w – weathered). In order to evaluate differences in Cu oxidation state because of weathering, XANES spectra were recorded. Both show an intense peak at the edge, characteristic of Cu^{+} in Cu_2O as well as a single oscillation spectral shape, indicative of highly disordered systems. The observed modification of the edge position indicates that the local order around Cu is higher in the non-corroded area, while it shifts towards higher energies in the other area, indicating the increasing presence of Cu ions in a higher OS in the degraded areas of the glass surface (point w).

Finally, the relation between the absorption edge position and the Cu OS may indicate the degree of degradation on the glass surfaces. Figure 1(d) shows that sample Vi_2 is located near the Cu^{0} point, indicating an abundance of Cu^{0} colloids and almost no degradation; corroded red glasses To_5 and Mi_3 points are located near the Cu^{+} point, indicating the presence of this ion as +1 OS and an intermediate superficial degradation; and the green glass Me_14 points are near Cu^{+} and Cu^{2+} ions points, indicating the presence of both Cu ions in OS +1 and +2 and higher degradation.

Conclusions

Through study of the Cu K-edge absorption energy of three red glasses (Vi_2, To_5 and Mi_3), it was possible to establish a correlation between the OS and the surface decay, from non-weathered to middle and heavily corroded glasses. On different areas of the same green sample (Me_14), it was possible to distinguish the non-corroded from the corroded areas.

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

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Cloudy Patches and Misty Glass: Early Signs of Glass Disease?

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Keywords
glass; deterioration; survey; thesaurus

Introduction
In recent years, several internationally renowned museums have carried out various surveys to study the condition of glass collections (Oakley 1990; Cobo del Arco 1999; Oakley 1999; Kunicki-Goldfinger 2008). In 2008, a large project to survey the condition of the glass collection of the Museum Boijmans van Beuningen (MBvB) in Rotterdam, the Netherlands, was set up. The glass collection of the MBvB contains a wide variety of glass objects from very diverse origins and historical periods. Modern glass is particularly well represented. The collection was surveyed in a specially designed glass laboratory (see figure 1) that was set up near the storage rooms in the museum. While the condition survey was carried out, for which an inspection checklist was designed, the object documentation in The Museum System (TMS 2013) was also carefully checked. This made it possible to link information about techniques of manufacture, period of manufacture, and artist or glass factory involved with features of various forms of glass deterioration detected during the survey. The glass project in the MBvB paid special attention to the phenomena that might be related to early signs of glass deterioration.

Course of the Project
In identifying the different stages of glass disease, several methods of standardisation of vocabulary were studied, and previous surveys in other museums and research outcomes (Oakley 1990; Cobo del Arco 1999; Oakley 1999; Koob 2006) were incorporated in the project. The main purpose was to arrive at a set of 'best practices' and develop a working method that would contribute to an international method of communicating and documenting glass sickness and its very diverse symptoms. Condition checks were carried out, and material characteristics, such as alteration in appearance, sensitivity to finger imprints, and surface depositions, were studied. Several methods of cleaning were applied depending on the condition of the glass. Various stages of glass disease were encountered such as cloudy appearances, slippery surfaces, weeping glass, and 'crizzled' objects. The conditions in the glass depot were subjected to re-inspection; wooden cabinets were replaced.

Fig.1. Glass laboratory in Museum Boijmans van Beuningen (Photo: Restauratieatelier Mandy Slager).

In order to investigate in more detail whether and how symptoms of early glass disease will develop within the next years, very-high-resolution photographs with a Nikon D3X 24 MP camera were made of a representative selection of objects before and after cleaning (see figures 2(a) and (b) and 3(a) and (b)). In addition, the condition of these objects was described in detail.

Results and Discussion

The glass collection of the MBvB comprises over 5000 objects. 4005 objects were documented, checked on condition, and cleaned during the glass project of 2008–2011 (see figure 4).

The group with possible signs of glass disease was difficult to define and describe, since not much is known of early manifestations of glass disease. Especially the description and classification of features within this presumptive group of possible sick glasses encountered some difficulties. Questions were raised such as: To what extent can one visually distinguish between different types of cloudiness? Do all forms of cloudiness evolve in the same manner? In what patterns does cloudiness evolve over time? For example, within one range of modern glass tableware, beside objects in perfect condition, two types of cloudiness were observed: patchy and overall. This group of objects is also susceptible to finger imprints. These objects are now categorised as 'possible glass disease' and will be accurately monitored.

Fig. 2. Anna green wine glass: part of the Romanda Tableware, Andries Dirk Copier 1924 (V 119 c5 (KN&V)). (left) Before cleaning. Cloudy patches and finger imprint. (right) After cleaning (Photo: Cees de Jonge Visual Art Box).

Fig. 3. Part of sculpture 'Enlightenment with Measure' 2000 (2061 a (KN&V)). (left) Before cleaning. Overall cloudy appearance and finger imprints. (right) After cleaning (Photo: Cees de Jonge Visual Art Box).

Conclusion

The glass survey gave a good insight into the general condition of the glass collection of Museum Boijmans van Beuningen with respect to possible degradation. 83% of glass objects were found to be in good condition. Further, various stages of glass sickness were encountered within this unique glass collection. The system of documentation used makes it possible to examine correlations between art historical information and vulnerability to glass sickness. Photographs of glass degradation will help to examine possible changes in the glass condition over time.

Within this survey, it became evident that a standardisation of vocabulary and the development of an international thesaurus for the description of the different phenomena of glass deterioration are essential and need to be developed

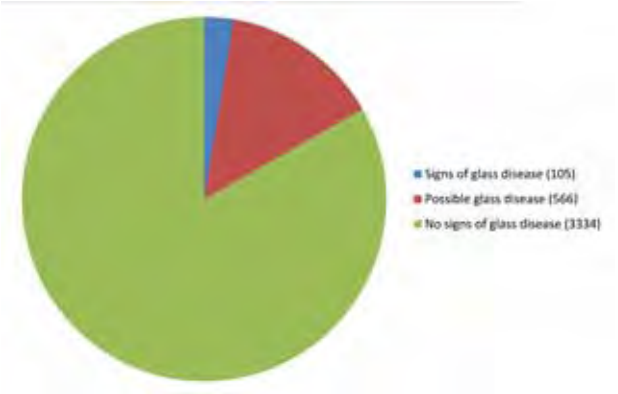

Fig. 4. Pie chart showing the condition of the glass at Museum Boijmans van Beuningen.

further in the future. Cooperation between international parties is fundamental. Additionally, we hope the project will contribute to a better understanding of the early symptoms of glass disease.

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Restoration and Conservation of Glass Objects from the Great Necropolis of Russian Princesses and Queens at the Ascension Monastery of the Kremlin in Moscow

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Keywords:
Moscow Kremlin; glass corrosion; conservation; necropolis

The museums of the Kremlin in Moscow are in the process of conducting a large-scale study of the great necropolis of Russian princesses and queens at the Ascension Monastery at the Kremlin in Moscow. The necropolis was opened in 1929 for the first time since the Middle Ages.

The construction of the necropolis in the Ascension (Voznesensky) Monastery was begun in 1407 by Prince Dmitry Donskoy's wife, Princess Eudoxia, and was finished in 1468. Since the sixteenth century, this necropolis became a tomb for female members of Moscow's ruling dynasty, while men were buried in the Cathedral of Archangel, located nearby.

In 1929, the Ascension Monastery was demolished. The Soviet government gave a month for archaeologists to remove the sarcophagi and gravestones. These were dug up and moved into the underground chamber of the Archangel Cathedral, along with partially excavated coffins and burial items. The study of these remains began only in 2000.

This paper presents some of the recent restorations of archaeological glass that had been found in the necropolis. These objects are attributed to the households of Russian princesses and queens.

Work on the reconstruction and conservation of glass vessels was part of the research project into the Ascension Monastery necropolis. The results are published in a number of volumes (Panova 2009).

This paper describes the methods used to conserve and reconstruct three glass vessels from the Princesses' burial sites.

The first vessel is a Venetian goblet dated 1558 (figure 1), excavated from the tomb of Princess Eudoxia, daughter of the Grand Duchess Anastasia Romanovna and Ivan IV (the Terrible). It is a wine glass made from clear glass, decorated with glass trails. The vessel was kept at the Department of Archaeology but was not numbered. It consists of 32 fragments. The surfaces of the fragments were very dirty. Some fragments had greatly deteriorated, and others were covered with a crust as the result of local corrosion. In this condition, the vessel could not be documented or exhibited. Some fragments have been joined together to reconstruct one part of the vessel, but many pieces have been lost.

The composition of the glass and its deterioration layer was determined in the laboratory. Using time-of-flight secondary ion mass spectrometry (TOF-SIMS)[1], it was possible to explore the gradual transformation of the glass from the

Fig. 1. Venetian goblet (dated 1558), excavated from the tomb of the Princess Eudoxia (Photos: Ekaterina Sharkova).

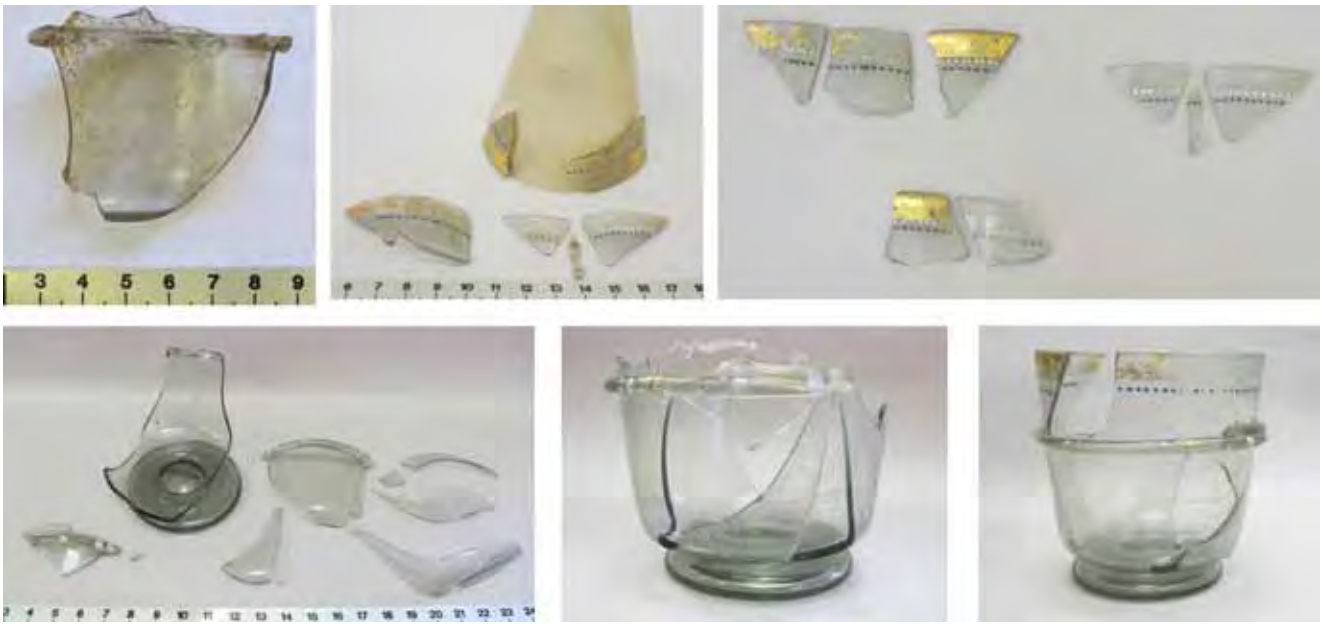

Fig. 2. Venetian vessel (dating from the mid-sixteenth century) from the tomb of the Princess Irina Godunova (height 8.1 cm; diameter 7.5 cm) (Photos: Ekaterina Sharkova).

surface to the bulk. Table 1 shows, for example, that the sodium and potassium content are lower near the surface of the glass as compared to deeper layers. These changes in chemical composition had occurred due to corrosion, leading to selective leaching of mobile ions, as described by Davison (2003).
The second vessel (figure 2) is from the tomb of the Princess Irina Godunova (#2959. sob. F-1765). It is a Venetian vessel dating to the mid-sixteenth century (height 8.1 cm; diameter 7.5 cm) with gilding and white and blue enamels. The vessel has been in the possession of the museum since 1929. Many fragments have been lost, and it took over a year to find the other fragments belonging to the vessel that were stored in the museum collection. Five pieces were without inventory numbers because they had been found in the sarcophagus only in 2000. The other three fragments were discovered on the plastic support of another vessel (no. Arch-408), to which fragments had been attached by mistake in 1929.
These past treatments left the restorer with the problem of how to add new fragments and re-create the entire shape of the vessel. All the fragments had suffered from surface contamination (grease and dust), as well as traces of the previous restoration and yellowing of the adhesive. The glue joints were rough and darkened, and both iridescence and external deposits were visible. The glass had become partially cloudy because of the degradation of its upper layers. All the fragments required cleaning, the removal of traces of previous restorations including adhesive, and filling of the missing parts.
The third vessel is a glass goblet made in Germany in the mid-sixteenth century (height 23.1 cm; diameter 11.3 cm; figure 3). It was excavated from the tomb of the Grand Duchess Anastasia Romanova, wife of Tsar Ivan IV (#2964 sob, F-1728). Prior to the restoration, there were 23 fragments (42 fragments after cleaning).
The vessel had a great deal of surface contamination, and many of the fragments were affected by corrosion (70%) and partial loss of the top layer of the glass.

Fig. 3. Wine glass (German, dating from the mid-sixteenth century) from the tomb of the Grand Duchess Anastasia Romanova (height 23.1 cm; diameter 11.3 cm) (Photos: Ekaterina Sharkova).

	SiO_2	Na_2O	K_2O	CaO	MgO	Al_2O_3	Fe_2O_3	MnO	H_2O
5 µm	90.31	0.03	0.03	1.87	<0.03	0.08	<0.03	N.D.	6.01
950 µm	77.81	0.74	17.45	1.57	<0.03	0.07	<0.05	N.D.	0.75

Table 1. Chemical composition of the Venetian goblet dated 1558: a glass fragment was analysed in different depth from the surface (5 and 950 µm) by time-of-flight secondary ion mass spectrometry TOF-SIMS to explore the change of composition due to surface corrosion; all numbers are given in wt%.

The glass had become cloudy. It was possible to form a single vessel with the remaining fragments, but much had been lost. The sherds of the vessel required cleaning and bonding, and the missing fragments had to be filled.

The conservation process can be divided into three main stages: cleaning; bonding of fragments; and reconstruction. All stages were comprehensively photographed.

The process started with the preliminary assembly of all fragments; this was followed by the removal of the traces of previous restoration and the removal of old adhesive and any other residue from the surface of the fragments. That was done by submerging the vessel in ethanol until the glue had softened.

The appropriate method for chemical cleaning of the glass surface was chosen following tests that were conducted in advance. The final complete cleaning was done by alternately dipping the vessel in acetic acid (4%) and NaOH (5%) sodium hydroxide to soften carbonate deposits and to remove iridescence (the method known as acid–alkali washing). Then the vessel fragments were washed in distilled water and dried in ethanol.

The second stage involved the consecutive bonding of the fragments. These were assembled using BMK-5 (copolymer of butyl methacrylate with 5% *methacrylic acid*) and Araldite 2020 (Davison 2003, pp. 242–345).

At the third stage of the reconstruction, for the bigger fragments involving complex shapes, plaster moulding was used. The missing areas were filled by making plaster moulds and then casting them in epoxy resin. The casts were then attached to the object using Araldite 2020 (Koob 2006, pp. 81–110).

In our work, we made an effort to integrate and conserve all suitable fragments. The corrosion on the upper layers of the glass and traces of the previous restoration were removed, the fragments were joined, and missing areas were filled. It is now possible to study the reconstructed vessel and appreciate the object as a significant artefact related to the history of the families of the Russian Tsars.

Acknowledgments

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Notes

1. A polished cross-section of the sample of glass was prepared using a polyester resin matrix. This cross-section was examined directly after preparation with a TOF-SIMS 5, ION TOF (Germany) in the static mode. The surface of the sample was scanned with a 15 keV primary ion beam with a Cs^+ metal ion gun. The scanned sample area was 256 x 256 pixels (500 x 500 µm).

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Advanced Scientific Methods Applied to Investigate the Results of Laser Cleaning of Glass Samples

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Keywords

laser cleaning of historical glass; AFM; OCT; SEM-EDX

Introduction

Historic glass objects and especially stained-glass windows require an individual, careful treatment when corrosion or external surface deposits are cleaned. The laser cleaning of historic stained-glass windows has been proposed as an alternative for conventional chemical and mechanical methods (Leißner and others 1995; Römich and others 2003). In particular, the possibilities to remove corrosion crusts, biolayers, and aged coatings have been investigated. However, the effectiveness of this treatment and the possible alterations that could occur to the glass are still the subject of controversial discussions between conservators and scientists. This paper presents the application of modern scientific techniques such as atomic force microscopy (AFM), optical coherence tomography (OCT), and scanning electron microscopy coupled with energy dispersive spectrometry (SEM-EDX) to verify the effects of laser cleaning on glass.

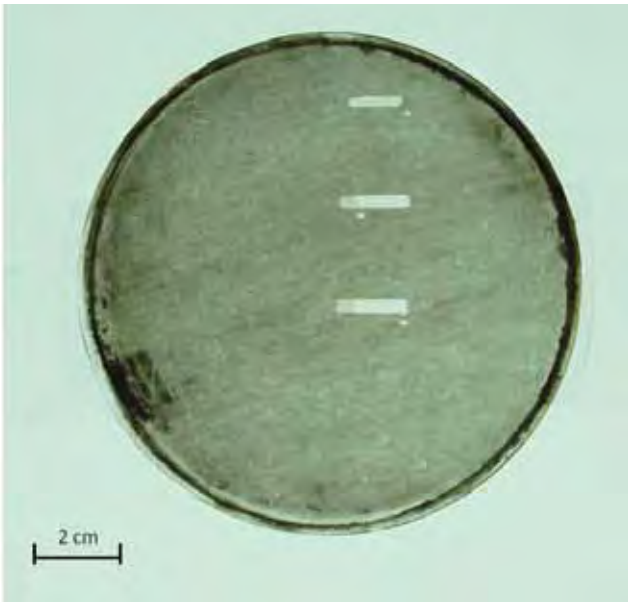

Fig. 1. Colourless glass piece taken from a 19th century stained-glass window (St Catherine Church, Krakow, Poland). The three cleaned areas were irradiated with fluences of 0.13, 0.21, and 0.46 J cm^{-2}, respectively (from the top to bottom) (Photo: authors).

Experimental

In order to study in detail the effects of laser cleaning, 19th century colourless glasses dismantled from the stained-glass windows of the St Catherine Church in Krakow (Poland) were chosen for testing (figure 1). Each piece was 10 cm in diameter. The exterior of the glass was covered by a superficial layer of dark soiling. Removal of this layer was performed by irradiation with one pulse of Nd:YAG laser (Big Sky Laser Technologies; 1064 nm, 6 ns), at fluences from 0.1 to 1 J cm^{-2}. The total area treated was 1.5 x 0.5 cm^2.

Atomic force microscopy (JPK Nanowizard III, working in contact mode, in air) was employed for topographic observations. To exclude any side effects caused by thermal and/or mechanical stress due to the laser irradiation, the OCT tomograms of the cleaned areas were recorded. The OCT technique is based on interferometric analysis of IR light dispersed on internal features of an object (Kunicki-Goldfinger and others 2009). This method can provide information on possible microcracks or other internal stresses that may have occurred as a result of the laser operation. The OCT instrument used here has been constructed in the Nicolaus Copernicus University (for construction details, see Targowski and others 2010).

Additionally, samples were studied by SEM (JEOL JSM-5500 LV), while the elemental composition of the bulk glass, the soiling layer, and the irradiated (cleaned) area was determined by EDX (IXRF Systems). Imaging was performed with a 20 keV electron beam (the size of the spot was in the range of 20 nm). Prior to the SEM imaging, all the samples were covered with a thin carbon layer to avoid the charging of sample surface. For EDX analysis, X-ray photons with energies up to 20 keV were used.

Results

The surface morphology of soiled and laser cleaned areas was observed by AFM (figure 2). The untreated areas present a scattered distribution of particles including large agglomerates. The average surface roughness (R_a) was detected to be 282 ± 71 µm. After the removal of the soiling layer, the surface roughness reduces to 51 ± 6 µm. This applies to a laser treatment at 0.21 J cm^{-2}. The SEM images of the surface demonstrate the effect of cleaning: the irradiated areas exhibit greater smoothness and apparently reduced soiling compared to those with a dirt layer. Also, the OCT tomogram shows no possibly damaged structures within the bulk glass that could have been formed as a result of laser ablation. The results listed above prove that no damage to glass, at least none traceable by the methods used, has been found. To check the efficiency of laser treatment, the composition of the outer layer before and after cleaning has been compared. Comparison of EDX spectra (figure 3) proves that the dirt layer was completely removed, as elements found in it did not occur on the cleaned surface.

Conclusions

In this study, areas cleaned with a nanosecond laser (1064 nm) were compared to non-cleaned areas on a non-painted and chemically stable glass from the 19th century.
This work shows the potential to use advanced scientific techniques such as AFM, OCT, and SEM-EDX to control the progress of glass cleaning. The data gathered deliver important information concerning the changes in surface roughness and the chemical composition of the superficial layer. This result needs to be verified on more complex surfaces before recommending the possibility of using lasers as a cleaning tool for historic glass. It is necessary to strictly control laser parameters and to adapt them for each object to be treated. Further, a direct comparison of lasers and conventional cleaning techniques is essential in order to select the appropriate treatment based on a cost-benefit analysis.

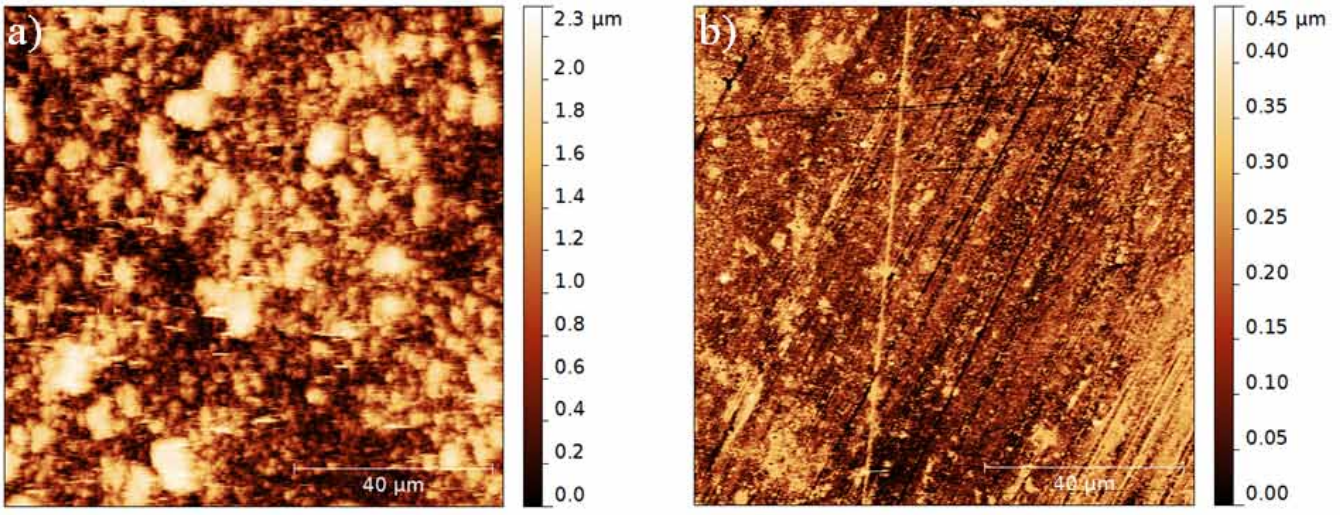

Fig. 2. AFM topographical images of (left) area with superficial soiling layer and (right) cleaned area (window of 100 x 100 µm) (Photos: authors).

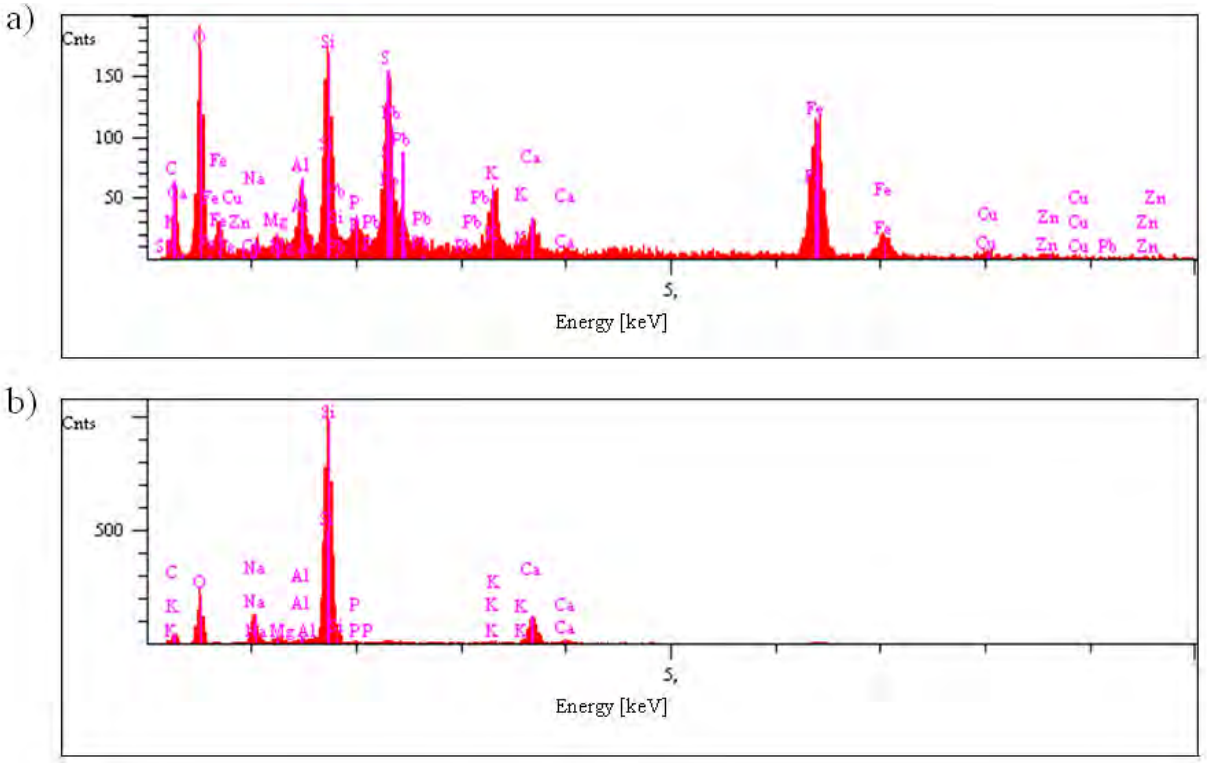

Fig. 3. EDX spectra of (a) superficial soiling layer and (b) cleaned area on the glass piece shown in figure 1 (Graphs: authors).

Acknowledgments

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Window with Apostles, the Pietá, and other Saints: Re-installation and Environmental Monitoring

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Keywords:

stained glass; protective glazing; installation; environmental monitoring

This publication discusses the re-installation of the early 15th century *Window with Eight Apostles, the Pietá, and other Saints* at the Museum of Fine Arts, Boston (MFA; figure 1). The monumental window, 5.63 metres tall by 2.63 metres wide, was first installed at MFA in 1927 facing northward over a courtyard in a gallery designed to mimic its historic setting in the chapel of Hampton Court House, Herefordshire, England. In 2003, the window was removed due to major construction, providing opportunities for examination and study (Caviness 2011) along with analysis, cleaning, repairs, partial re-leading, and framing prior to re-installation in 2010 (Rousseau 2010; figure 2). The complex nature of this project involved input and decision making by conservators, art historians, architects, structural and environmental engineers, masons, and glazing contractors.

The key goal of the re-installation was to return the window to its stone tracery in the dedicated gallery with the best possible environmental protection. Challenges included the harsh New England climate, preparing for the addition of climate control to the gallery, and a new building closely facing the exterior of the stained glass. A climate-modelling study commissioned by the MFA concluded that an insulated glass unit (IGU) would be required to reduce the risk of condensation, particularly at the stone perimeter during severe cold temperatures. However, an overall IGU on its own would not allow adequate air movement on the reverse of the glass without the addition of mechanical systems. Ultimately, the window was covered with three layers of protection: a single pane isothermal glazing with an additional overall double pane IGU.

Fig. 1. Window with Apostles, the Pietá, and other Saints in 2011 after treatment and re-installation. MFA 25.213.1-.21, Maria Antoinette Evans Fund. A wire at the sill connects a datalogger probe in the interspace; glass sensors for monitoring are circled in green (Photo © Museum of Fine Arts, Boston, 2013).

Fig. 2. Detail of the Pietá: before 1927 (left); before de-installation in 2003 (centre); and after treatment in 2010 (right). Leaded repairs at the neck of the Virgin were present prior to acquisition; additional lead mends in the Christ figure date to World War II. In the current treatment, these key areas were repaired with epoxy adhesive, while repairs in the drapery were made with copper foil. The support bar has been moved to the back of the glass (Photo © Museum of Fine Arts, Boston, 2013).

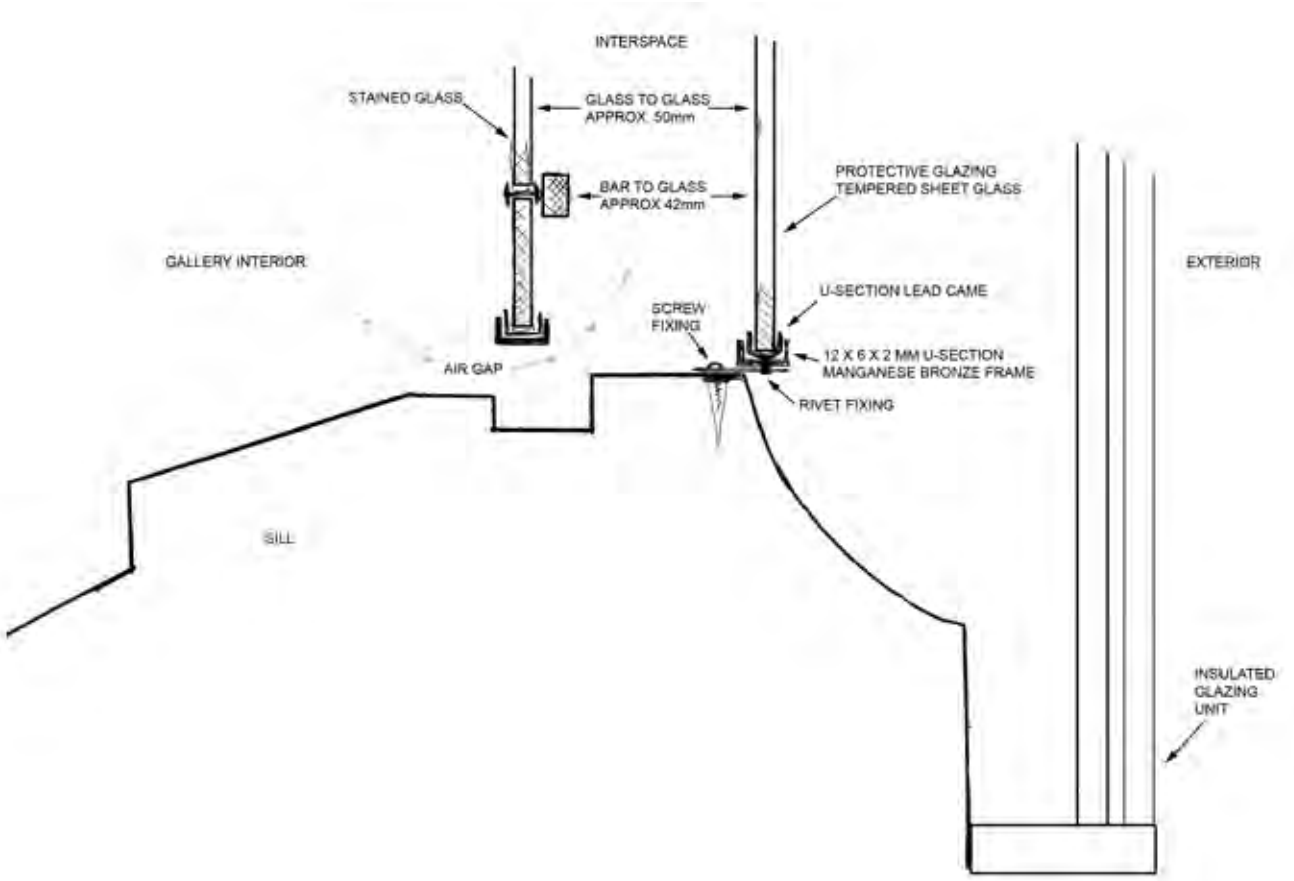

Fig. 3. Cross-section of the installation at the sill. The stained glass is in the original groove with ventilation slots at bottom and top while the protective glazing is set to the exterior of the openings. An overall insulated glazing unit covers the entire exterior. Not to scale (Diagram © Museum of Fine Arts, Boston, 2013).

Manganese bronze frames were used for the stained glass, set in its original position in the stone tracery, and for the protective glazing, which is set 4.2 cm to the exterior (figure 3; Barley 2010). The new framing also allowed a readily reversible installation system. Vents above and below the stained glass allow air exchange to create equal environmental conditions on both faces of the mediaeval glass. The IGU echoes the glass curtain wall used in the adjacent new construction and serves to effectively bring the window indoors after six centuries of exposure (figure 4).

Since the installation, environmental data have been gathered with dataloggers tracking temperature and relative humidity both in the gallery and, with a remote probe, in the interspace between the stained glass and the isothermal glazing. Comparison of the climate outdoors, in the gallery, and within the interspace shows that temperatures at the interspace have remained above the dew point even during extremely low winter temperatures and with the addition of humidity control.

Fig. 4. Exterior view with IGU covering (Photo © Museum of Fine Arts, Boston, 2013).

In order to assess the effectiveness of this unusual installation, glass-sensor monitoring was carried out for one year following installation (Fuchs, Roemich, and Schmidt 1991; Roemich 2004). Six sensors were placed on opposite faces of the original glass at three heights and a seventh was placed outdoors; their corrosion rate was measured with infrared spectroscopy after exposure. The sensors attached at the outer side of the stained glass were only slightly corroded, similar to the ones attached on the inside of the stained glass, and both sets were significantly less corroded than the exterior sensor. Thus, the glass sensors confirmed that the protective glazing provides a significant improvement for the window compared to the exterior exposure. Environmental monitoring shows that this unusual installation, an internally vented isothermal glazing in combination with the overall IGU, provides effective protection for the window while preserving its mediaeval character when viewed from the gallery interior.

Acknowledgments

We are grateful to the Class of the Museum of the Fine Arts and to the Museum of Fine Arts Associates for funding this project. We also thank many people for their advice, contributions, and collaboration, including Tracey Albainy, Drew Andrews, John Bachman, Elizabeth Byrne, Marietta Cambareri, Madeline Caviness, Jeffry J. Ceruti, Michele Derrick, Danko Davidovic, Mike DiBlasio, Pamela Hatchfield, Dawn Kimbrell, Richard Newman, Michael Patrican, Lisa Pilosi, and Peter Quigley.

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Broken Crockery Brings Luck – The Limits of a Proverb: A Disaster Management Case Study

Franziska Schillinger Joseph

Keywords:
porcelain; disaster-management; object extrication

The Museum of History in Basel, Switzerland, is currently in the process of re-organising its main storage facilities. During the setting-up of a new drawer cubus for flags and textiles in November 2010, the enormous cubus shell (2.9 x 3.2 x 3.1 m) collapsed and 'shot' sideways into a row of metal cupboards that store ceramic, porcelain, and glass. This lead to a domino effect involving two cupboard rows, 10.5 m long, 2.5 m high, and 0.5 m deep each, falling into a third and fourth one. Luckily the last two were set up back to back, which gave them more stability. The fallen cupboards had doors that faced downwards, which meant that the objects fell out onto the floor, where the doors became unhinged; within the cupboards, the objects were jumbled about. After the accident, everything was poised in a fragile balance and the extrication of the objects promised to be complex. The damage could not be assessed since only one of the four rows of cupboards was accessible.

It was decided to extricate the objects from the back of the cupboards because there was no other means of access (the cupboards were too damaged to just be set upright). It was essential to secure the cupboards in position. Any further movement would endanger both people and objects. For this reason, an industrial logistics firm was hired to secure the fallen cupboards. This was done with the aid of long beams that were suspended from the ceiling to which straps were lashed and further attached to the cupboards' partition walls with screw clamps (figure 1). The construction was stable but not strong enough to sustain strong vibration or dynamic load. Fortunately, it was possible to loosen the screws that held the cupboard back walls from the outside even though the nuts

Fig. 1. Conservator Helena Fuertes extricating objects from the suspended cupboards (Photo: HMB-Museum of History/Barfüsserkirche)

were trapped inside. We were thus spared the usage of a kind of 'tin opener' tool with which we would have had to cut open the back walls. Safe access was now provided thanks to a small lifting platform onto which a long board was attached. It meant that the work had to be done while lying face-down on the board, which was exhausting even though we placed two old camping mats on top for comfort (figure 1).

Starting from the cupboard lying on top, the objects and shards were taken out one by one and shelf by shelf and were placed in the same order on long tables. Keeping them in 'shelf order' made assembling the loose shards easier. With the cupboards lying down, the objects were now resting on the inside of the front doors, which acted as slides. As long as the shelves were still in position, that did not cause big problems. However, many of the shelves were unhinged, and the objects had consequently slid down. Quite often they were still in position but had to be propped-up using polyethylene foam and long-term masking tape, so that they would not move when objects or shards next to them were removed. It was like a gigantic Mikado game. A special anti-slide barrier was cut out of polyethylene foam, and this barrier could be wedged underneath the shelf that we were about to clear. This prevented small shards from sliding down and therefore made it easier to allocate them. For picking up small fragments and tiny shards, several types and sizes of rubbish pickers, a vacuum cleaner with a piece of fabric tied over the nozzle, and sometimes simple masking tape proved very useful; the last was particularly helpful to pick up very small fragments that were sometimes almost invisible.

Parallel to the extrication, an assessment of the nature and the degree of damage on every object was made. The most efficient way to proceed was in teams of two people. First, all objects of one shelf were extricated and assembled. Second, the damage assessment was made and photographs taken. All the information was gathered in an Excel chart, based on the accession number of the objects. The damage was classified in five categories:

- no damage,
- old damage (before the event),
- light damage, such as a small crack or a small chip,
- medium degree of damage, such as several small breaks or chips,
- severe damage.

It proved to be difficult to always apply the same criteria. Continuity was easier if the same person kept making the assessments. The chart records the old location, the number of the packing container, the new (temporary) location, the date extricated, and the people involved. The data were then imported into the Museum's accession system.

The objects were packed in polypropylene boxes. The broken objects were first wrapped in transparent bags to keep the fragments together. The objects in each box were photographed and a small inventory was made for each container. Both the inventory and photos were stuck on the outside of the container for easier location of the objects. In all, there were 2727 accession numbers affected (many of which include several objects). Surprisingly, only (approximately) one fifth of them were damaged in one way or another. The entire project was carried out in three months, with two conservators working fulltime and more people helping selectively.

The incident is a third-party insurance case. The two main companies involved are arguing over the liability, and the museum now has to go through the courts; the result is that the conservation of the objects has not even begun two years after the event. Despite this, the conservators still had to make a rough estimation of the conservation costs. This was done on the basis of the assessment chart and the photographs. The full conservation of all the objects will not be possible. Certain particularly important groups of objects were therefore singled out. The estimate for the work was about 1350 hours for 360 objects. This involves consolidation and bonding all of the objects, but re-touching of only selected ones. The main criterion for selection was the importance of a certain object within the museum collection and the likelihood of it going on display.

The accident happened because the subcontractor did not follow the instructions of the construction firm 'to the book'. Considering the situation, it was very lucky that no people were harmed! To prevent an incident such as this, a strict supervision of the external contractors is necessary. This has to be done by someone with a technical understanding of the construction plan and with enough courage and authority to intervene when necessary. It would of course be best to have the entire storage cleared of objects during a period of construction. However, we all know that, in reality, this is impossible, because there is neither time nor space to ship objects around. The objects might have been less damaged had they been packed or embedded within the cupboards. However, in storage, they can never be

packed to a shockproof standard. It would make the objects completely inaccessible. In future, they will be stored in a mobile shelving system with pull-out-drawers. The objects will be packed and padded more densely, while still remaining visible and accessible. With hindsight, it would have been advisable to pack the extricated objects straight away with sufficient padding for transport. Even though this was not the initial plan, they have had to be moved twice since the event and will have to be moved at least twice more.
The Excel chart has proved very useful for keeping record of the different old and new locations.
There are no national guidelines or rules about dealing with disasters in Switzerland. However, dealing with this disaster enabled us to benefit from two meetings organised by the Swiss Conservators Association, both held in 2005 shortly after a major flood disaster had affected various parts of central Switzerland. The first meeting, under the title '…Screw loose? Responsible dealing with technical cultural objects', was held in Lucerne, where the Museum of Transport allowed us to visit the warehouse where the objects that had been affected in the disaster were stored, and the firm in charge of the extrication ('Die Schmiede', Duisburg, Germany) enabled us to see work in progress. The second meeting was held in Schaffhausen, in the Museum zu Allerheiligen, on the general subject of 'storage'. The presentations in Thun about the flood damage in Sarnen (Frauenkloster St. Andreas), given by Karin von Lerber (Prevart GmbH), and about the flood damage in the storage of the Historical Museum Bern, given by Susanne Stadler, helped us to set up our own strategy.
When dealing with a disaster such as this, one is confronted with enormous pressure to clear up as quickly as possible. However, frantic action tends to cause more damage. It is most important to remain calm and insist on a systematic and coherent approach.

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A Helpful Support for Bonding a Large Delft Plaque

Margot van Schinkel

Keywords
Delft; earthenware; plaque; bonding; support

For the re-opening of the Rijksmuseum in April 2013, many objects needed to be restored. One of them was a late 17th century blue and white plaque made of Delft earthenware painted by Frederik van Frytom. The Rijksmuseum glass and ceramic conservation department had restored large plaques and tiles in the past. Most of these had broken into two pieces and were adhered to each other using a vertical support fabricated on a cart used to transport paintings. However, this Delftware plaque posed a challenge, as it was larger than any of those previously treated (64 cm by 105.5 cm) and was broken in six pieces. The thickness of the plaque varied between 1.0 and 1.8 cm. Restoration was necessary because of the many discoloured old fills and overpainting. Further, it had been mounted with an excess of plaster in a rusty iron frame, which had to be removed because it had caused staining. After dismantling, the excess plaster was mechanically removed and the pieces were cleaned using a steam cleaner.

Although the plaque appeared to be flat, it was not. During drying and firing, the clay had shrunk, causing the plaque to warp. One of the warped corners was broken. When this corner was held in position with tape, it 'floated', meaning it did not make any contact with the surface of the table underneath; thus, all the weight rested on the joint, which itself did not fit well. The previous restorer(s) must have had problems with assembling this object, and had resorted to filing down the edges of this joint (figure 1). Many pieces of this object had suffered this mechanical damage, and some broken edges were very thin. An attempt to bond them in a horizontal position failed because the pieces could not be manoeuvred into the correct position. The best position to hold them in place to enable bonding appeared to be vertically, so that the gravitational forces would help to keep the pieces in position. During bonding, it was necessary to work from both the front and the back of the plaque. Because the sections were large, fragile, and difficult to handle, it was not possible to adhere all the pieces to each other in a one-step process. For this reason, none of the existing methods for supporting the object during restoration was appropriate. A solution to the problem was found after discussion with

Fig. 1. The first stage of bonding with two pieces vertically secured on the frame in the correct position. When the corner piece was aligned at the front, a crack remained at the back due to the filing-down of the break edges (Photo: author).

Fig 2. Frame with slats. Wooden strips on these slats held the large piece in the correct vertical position during the first stage of bonding (Photo: author).

Fig 3. The second stage of the bonding process. Below left is the corner piece that had been bonded during the first stage. It was then possible to change the position of this piece to a position suitable for bonding the rest of the section (Photo: author).

colleagues from the Rijksmuseum furniture department: it involved an adjustable system consisting of a frame with wooden slats (figure 2) and a rack. The frame could be put vertically in the rack, in different positions, so that the angle could be adapted. This was important because, by adjustment of the angle, a proper alignment of the sections could be achieved. The frame and rack were made of red cedar wood. The choice was coincidental and was because there was a large stock of this wood. It turned out to be a good choice, as cedar wood is not heavy and is easy to work. The frame had three removable wooden strips that could be placed anywhere in the frame, so that the best position could be chosen to provide access to the break at the back. The slats were recessed in the frame and fixed in place with screws. The stand was a simple but stable support to hold the frame in a vertical position and at the correct angle.

The bonding of the broken sections of the Delft plaque took place in two stages. The 'floating' corner was adhered initially to one of the two largest sections. To do so, an extra profile slat that followed the line of the break was fixed at the bottom of the frame to support the irregular shape. Now the corner piece could be placed on top and glued. It was reinforced at the back with plaster of Paris and acid-free Japanese paper. When the adhesive (Paraloid™ B72, used in a solution of 40 wt% in acetone) had set, the frame supporting the two sections was removed as one unit from the stand and carefully placed horizontally on a table. On the table, the section was turned and fixed. Then it was put back in the stand again. Now the rest of the pieces could be adhered in one go (figure 3) and reinforced at the back in the same way. Although the back had been reinforced, the joints were still too weak to handle the plaque. A strong backing

material such as Alucore aluminium honeycomb sandwich panel was needed. In order to back the plaque, it was necessary to place it horizontally, face down, on a table so that the Alucore could be attached. In order to put the plaque safely on the table, a firm cardboard plate with a foam layer was placed at the front side to make a 'sandwich' support. The cardboard, object, and wooden frame were secured together with straps. This sandwich construction was placed horizontally, face down, on the table and the frame was removed from the back. Once the plaque was adhered securely to the Alucore, it was turned face up, and the filling and retouching of the front side was done.

The wooden stand turned out to be a very convenient and easy-to-make support for the bonding of large, warped, flat objects that are broken in several sections. It is a very flexible system because every element can be adjusted and made to measure. For smaller objects, an easel could be used as a rack. The wooden strips can be made in different shapes to fit any break edge. The main advantage of the system is that it provides the possibility to access both the front and back of the object at the same time, while the object is continuously and securely supported. After bonding, the object can be safely supported in any orientation, so that the final backing can be applied to give the object optimal support.

Materials and suppliers

Paraloid™ B72: www.kremer-pigmente.com (accessed May 2013).

Alucore™ (aluminium honeycomb sandwich panel): www.almet.nl (accessed May 2013).

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The Treatment of Blackened Archaeological Delftware from Anaerobic Sites

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Keywords:
Delftware; blackened glazes; lead sulfide; light exposure; photo-oxidation

Abstract

This investigation explores the potential of photo-bleaching compared to chemical treatments for the reversal of blackening of Delftware glazes from cesspits and canals. Outdoor exposure to strong summer sunlight in Lisbon proved an effective means of recovery of the original glaze appearance, but photo-bleaching using an accelerated light aging set-up was considerably slower. Photo-reversal has the advantage of no deleterious side effects.

Introduction

In the Netherlands, much potentially interesting tin-glazed earthenware is recovered during excavations in cesspits and canals. In these anaerobic sites, centuries of burial gives rise to a blackened appearance as the result of the chemical transformation of the glaze in these majolica items, often referred to as Delftware but also produced in other centres such as Amsterdam, Haarlem, and Dordrecht. A previous investigation of this phenomenon established that the blackening is due to lead sulfide produced by microbially induced conversion of lead in the glaze (Tennent, Baird, and Gibson 1996). This is consistent with the action of sulfate-reducing bacteria that are responsible for the formation of lead sulfide on lead artefacts buried in similar wet, anaerobic sites (Duncan and Ganiaris 1987). Because the glaze design of these Delftware objects is no longer discernible, an effective treatment with no harmful side effects is much needed to restore the original glaze appearance.

Since blackening is caused by chemical reaction of the glaze during burial, simple cleaning in the sense of removal of extraneous material will not be effective. For successful recovery of the glaze appearance, transformation of the black lead sulfide is necessary; however, there is the likelihood that chemical methods that have a beneficial effect on the appearance will also have deleterious consequences for the structural integrity of the glaze or ceramic body. This inherent dichotomy has been observed in practice: strong mineral acids, often used for treatment of these blackened archaeological finds, bring about a satisfactory visual improvement to the glaze but at the expense of the ceramic body. Calcite in the clay matrix reacts with the acid, and the coherence of the earthenware body is lost (Tennent, Baird, and Gibson 1996). Nor is hydrogen peroxide an effective, milder alternative. With this treatment, oxidation of the sulfide to sulfate is likely to be occurring, as with works of art on paper where lead sulfide blackening is rectified by the use of hydrogen peroxide to form white lead sulfate. For blackened Delftware glazes, the extent of the recuperation is mostly unsatisfactory, possibly as a result of the inaccessibility of the lead sulfide within the glaze to the reagent. Likewise, for other possible chemical treatments investigated (Tennent, Baird, and Gibson 1996), some of which showed promise, the beneficial effects are counterbalanced by negative side effects. This is also true of the experiments involving

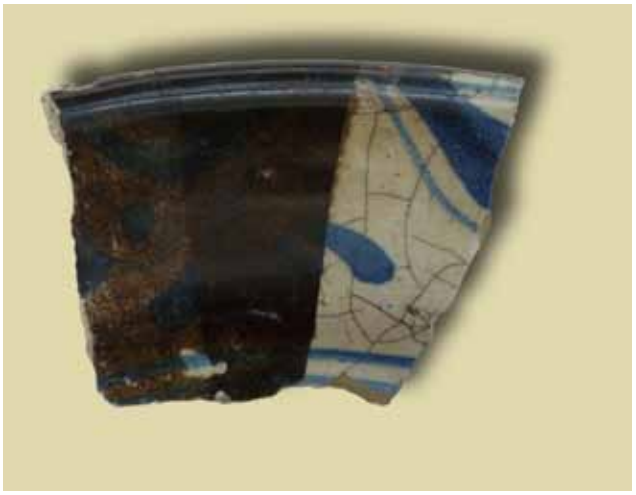

Fig. 1. Fragment of blackened Delftware (ca1660–1680, found in Amsterdam) illustrating recovery of the original glaze design in the right-hand portion that was exposed to Lisbon summer sun for 12 weeks (Photo: Norman Tennent).

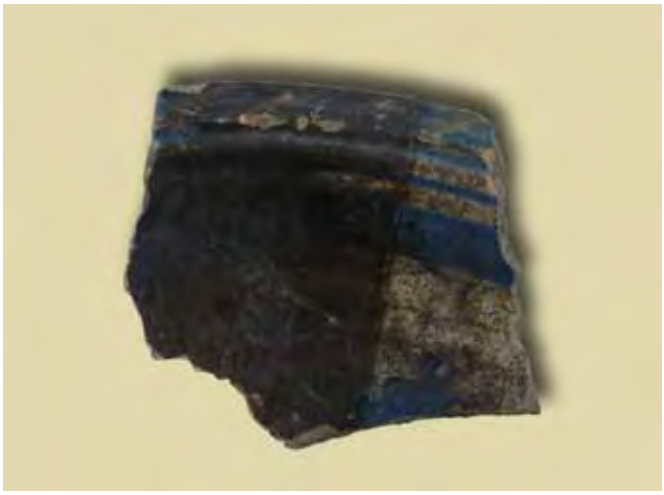

Fig. 2. Fragment of blackened Delftware (ca1620–1640, found in Amsterdam) illustrating partial recovery of the original glaze appearance in the right-hand portion after constant exposure to a xenon light source for 12 weeks (Photo: Norman Tennent).

re-firing. Very appealing glaze colours and gloss resulted from kiln re-firing at approximately 920ºC, but the ethical legitimacy of a conservation treatment that re-forms the glaze at high temperature is questionable.

To overcome these difficulties, the present study examined the use of light bleaching as a milder method to reduce the blackening.

Results and Discussion

This research was undertaken on the basis of anecdotal evidence followed by further unpublished tests by the author, which indicated that some reduction in the degree of blackening can occur in sunlight. The opportunity to undertake an evaluation of outdoor roof exposure to strong sunlight at the National Laboratory for Civil Engineering in Lisbon led to the results presented below.

The left-hand portion of the Delftware fragment illustrated in figure 1 was covered by aluminium foil during a 12-week period of exposure to summer sun in Lisbon. Complete recovery of the blue and white glaze design was accomplished in the half exposed to light. In addition, the surface gloss was in no way diminished by the treatment, in contrast to the use of strong chemical reagents. The remarkable success of sunlight reversal of the lead sulfide blackening suggests a photo-oxidative process, similar to the formation of sulfate with hydrogen peroxide. There may well be an additional thermal factor in the process, leading to the satisfactory recovery of the design in an acceptable timescale. Subsequently, the possibilities of effecting a similar change using an accelerated light aging apparatus were explored. A second Delftware fragment was exposed to a xenon light source adjacent to the Delftware shard successfully bleached by sun. These samples were exposed accompanied by ISO Blue Wool Standards for light fading. The rate of transformation of the blackened glaze zones in both fragments was slow, approximately equal to the rate of colour change exhibited by ISO Standard 4 and 3 for the previously exposed and new sample, respectively. The change is illustrated for the latter sample in figure 2. The change in the xenon light set-up is so slow compared to Lisbon outdoor exposure that artificial light is unlikely to be a satisfactory treatment method. It is estimated that it would take approximately two years to bring about the reversal of blackening accomplished in less than three months' outdoor exposure in Lisbon.

In a bid to find support for a mechanism involving photo-oxidation of lead sulfide within the glaze, documentary evidence was sought in the scientific literature. Somewhat surprisingly, very little has been published on the photo-oxidation of lead sulfide in any circumstances. A single pertinent but obscure report does exist and, remarkably, it pertains to lead sulfide bleaching in the context of cultural heritage (Price 1865). In this 1865 publication, Price reported observations on lead white paint in the showcases of the Technological Museum at the Crystal Palace in London.

He noted that blackening of the lead white paint occurred when items within the showcases emitted sulfur-containing gases, but only when the paint was protected from light, for example by the descriptive cards for the specimens. These observations led Price to conduct laboratory experiments to explore this process. He prepared paint samples of lead white in linseed oil, converted the pigment to lead sulfide by the action of hydrogen sulfide, and investigated the effect of daylight. Price ascribed the bleaching that occurred in what was, quite literally, a 'case study' to the photo-chemical oxidation of lead sulfide but did not carry out any experiments to identify the end product of this reaction. Unfortunately, there is little associated documentary evidence from the analyses of oil paintings. One exception is the report (Carlyle and Townsend 1990) of a superficial thin layer of lead sulfate in the backing canvas of a painting (by Turner) in which lead sulfide had initially formed by the reaction of lead white with atmospheric hydrogen sulfide. Although lead sulfide within a Delftware glaze is a very different situation to that in oil paint, it is proposed that, in sunlight, recovery of the original glaze appearance is also brought about by photo-chemical oxidation to sulfate and that this process is enhanced by the higher temperature of summer exposure outdoors. Experiments are planned to establish the chemical transformations taking place.

Conclusions

The results illustrate, for the first time, the full potential of light exposure for the restoration of the original appearance of blackened Delftware glazes from anaerobic archaeological sites. Compared to chemical treatments, the light bleaching has no harmful side effects. Strong natural sunlight is significantly more rapid than the use of accelerated aging with a xenon light source. Total reversal of the blackening can be accomplished within 12 weeks' exposure to Lisbon summer sun. Further, the quality of the glaze remains unimpaired and the surface gloss undiminished by the light treatment.

Acknowledgements

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Conservation of a Lidded Double-Gourd-Shaped Celadon Ewer from *Taean Mado* Shipwreck No. 1, South Korea

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Keywords

celadon ewer; *Taean Mado* Shipwreck No. 1; underwater ceramic; *bingryeol*

Abstract

A lidded double-gourd-shaped celadon ewer from Taean Mado Shipwreck No. 1 was excavated in 2009 in Chungnam Province, South Korea. The object was broken and a part from the spout was missing when it was recovered from the seawater. The spout was bonded together temporarily with Loctite® 401™ (superglue, polycyanoacrylate) without a fill. Conservation was then completed in April 2012. This paper describes the conservation process of the ewer and gives a brief background of Korean conservation of underwater ceramics.

The *Taean Mado* was a ship that was originally heading to Geagyoung (the capital of Goryeo Dynasty) in 1208 carrying tributary payments from Jeonnam province (southern area of South Korea). Unfortunately, the ship was wrecked in the open sea of Taean, in an area of the ocean called 'Anheungryang'. In this area, the sea is very deep and the conditions are extreme, with high waves, heavy fog, uncharted reefs, and complicated geographical features on the ocean floor; all of these have resulted in many shipwrecks in the area (Cultural Heritage Administration Korea 2010).

There have been approximately 250 discoveries and reports of underwater cultural heritage in South Korea since 1971. At present, 11 shipwrecks, about 95,000 ceramics, and countless other objects have been excavated from 18 different sites. The Underwater Excavation and Conservation Division of the National Research Institute of Maritime Cultural Heritage Korea is the only institute that specialises in the study and conservation of underwater excavated objects in South Korea.

In 2009, a lidded double-gourd-shaped celadon ewer from *Taean Mado* Shipwreck No. 1 was excavated in Chungnam Province, South Korea. This celadon ewer is made up of two oval gourd shapes, with a smaller gourd form sitting above a larger one. The ewer is decorated with a green and greenish-yellow glaze. The height of the ewer with the lid attached is 25.9 cm, with the diameters of the neck and the foot rim measuring 2.4 and 8.9 cm, respectively. In addition, it has a twisted vine handle, a hexagon-angled spout, and a small lid. The small rings on the lid and the handle would have been tied together with a string. *Bingryeols* (cracks on glaze that appear during the firing process) can be seen all over the glaze surface. Furthermore, peony and lotus patterns are in the circle, and inlayed in black and white clay on the body, with cloud patterns engraved near the circle (figure 1). The celadon ewer was in quite good condition, without marine encrustations or organisms on the surface when it was excavated from the sea (it actually came from mud on the sea floor). The spout of the celadon ewer was broken and some areas around the body of the ewer were missing. Further, there were several unstable cracks on the lid and the body (figure 2).

Directly after excavation in 2009, the gourd was de-salinated in tap water for four weeks, with the water being

changed every morning. The general period for de-salination in the laboratory is 4 weeks, and we check the concentration of chloride ions twice a week with a chloride meter (Thermo electron, US/ORION 5-star), before deciding when to finish the treatment. The water was heated at 60°C for 8 hours a day, and the quantity of water used was approximately ten times the weight of the ewer (John and Pearson 1975). The last measurement of the chloride level was similar to tap water, but unfortunately the change in the level of chloride was not recorded. After de-salination, the broken spout was temporarily adhered with superglue by the exhibition team. The choice of the adhesive was related more to convenience than to elaborate research. The object was on exhibition for about 2 years.

Fig. 1. Lidded double-gourd-shaped celadon ewer from Taean Mado Shipwreck No. 1, South Korea (Mado-1-56, 1-56-1, 1-57/ lid, body, bowl). Before treatment (Photo: National Research Institute of Maritime Cultural Heritage).

At the curator's request, the ewer was re-treated in 2012. The most common filling material used for celadon ewer restoration in South Korea is an epoxy resin paste such as CDK 520A (520B) and Araldite SV427-2 (HV427-1) which is then retouched with acryl colour using a brush or air brush (Cultural Heritage Administration Korea 2011). In this case, it was decided to make a fill-in paste using a low-viscosity epoxy that was mixed with other additives in order to control the viscosity. The celadon glaze colour was then replicated using a tinted transparent epoxy resin rather than retouching with acrylics.

The missing part was filled with a mixture of Epo-tek 301-2 (epoxy resin), fumed silica (silicon dioxide), and dry powder pigment. Dental wax (paraffin and microcrystalline wax blend) was used to support the inner side, and a removable fill was made. It took approximately 1 week for the fill to harden and dry completely. In order to add the glaze layer, the base fill was made lower than the surface level, which was sanded with micromesh. To reproduce the celadon glaze, epoxy was mixed with dry powder pigments (cadmium green, gold ochre, and green earth) (figure 3). To adjust the celadon colour, several thin coats of epoxy and pigments were needed. In order to simulate the *bingryeol*, several scratches were made with a scalpel and filled by dry power pigment (lamp black). Epoxy resin was then fed into the cracks by capillary action for stabilisation. After several hours, the excess adhesive was removed using a scalpel, and the area was cleaned with acetone on cotton wool swabs.

Fig. 2. Lidded double-gourd-shaped celadon ewer from Taean Mado Shipwreck No. 1, South Korea (Mado-1-56, 1-56-1, 1-57/ lid, body, bowl). During treatment: the process of making a fill (Photo: author).

Fig. 3. Lidded double-gourd-shaped celadon ewer from Taean Mado Shipwreck No. 1, South Korea (Mado-1-56, 1-56-1, 1-57/ lid, body, bowl). After treatment (Photo: National Research Institute of Maritime Cultural Heritage).

To summarise, this celadon ewer was conserved by de-salination, cleaning, adhering, filling, and retouching. For the first time in South Korea, coloured fills using Epo-tek 301-2 were used to fill and retouch ceramics. In order to achieve a more accurate de-salination and to address potential problems in the future, the periodical change of chloride level should be checked and recorded twice a week. In addition, it is necessary to study the nature of *bingryeol* if it has to be reproduced on a fill. This object is now on the permanent exhibition in the Goryeo shipwreck gallery of the National Research Institute of Maritime Cultural Heritage.

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Henkel Ireland Ltd., Dublin/Tallaght
Business Park, Withestown, Tallaght, Dublin 24, Ireland, Tel: +353-1 404 6444.

CDK 520A (520B)
Nagese ChemteX Corporation
1-1-17, Shinmachi Nishi-ku Osaka, Japan, Tel: +81-6 6535 2542.

SV427-2 (HV427-1)
Huntsman Advanced Materials
Klybeckstrasse 200, CH-4057 Basel, Switzerland, Tel: +41-61 966 3333.

Epo-tek 301-2
Epoxy Technology, Inc.
14 Fortune Drive, Billerica MA 01821, USA, Tel: +1-978 667 3805.

Fumed silica (silicon dioxide)
Sigma-Aldrich Korea. Ltd
698-84 Maeng-ri, Wonsam-myun, Cheoin-gu, Youngin-si, Kyunggi-do, South Korea 449-871, Tel: +82-31 329 9000, sakr@sial.com

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Minimal Intervention for Maximum Impact: Treating Fragile Surfaces

Fi Jordan

Keywords

reverse-painted glass; enamel on metal; consolidation

Introduction

Conservators routinely consider the ethical and practical consequences of their actions when introducing materials to stabilise an object. Reverse-painted glass with fragile surface decoration and inherently unstable enamel on metal present particular dilemmas. The conservator has to acknowledge that the total reversal of consolidation treatments will not be possible. Environmental controls may not provide sufficient protection. If the object is left untreated, increasing vulnerability to damage may lead to total loss. This study illustrates a minimal interventive approach undertaken within a short timeframe to stabilise objects and allow them to regain their aesthetic value for public display.

Flaking Surface Decoration: Border Panel for a Chinese Reverse Painting on Glass

Active flaking of the unfired gold leaf and paint layers (V&A:P.11:1-1936) made intervention necessary for museum display (figure 1). The glass substrate is the most stable component but provides poor support to the reverse-applied layers in terms of adhesion (Baumer and others 2012). Approximately 35% of the decoration on the border panel was lost or detached as fragments (the size of a grain of sand to a few millimetres in diameter). Areas of the remaining decoration were barely adhered (cleavage between glass/paint), and they lifted at the slightest touch.

Intervention was restricted to stabilising active de-lamination and re-attaching flakes. To make efficient use of time and prevent risk to the object, lost decoration was replicated on backing sheets. Tests on paint/gold leaf flakes were carried out to evaluate consolidation criteria, solubility in solvents, suitability of resin/solvent combinations, and application methods.

Fig. 1. Glass panel (9 x 8 cm): (top) before and (bottom) after treatment (V&A:P.11:1-1936 Bequeathed by Amy and John Hall) (Photo: Fi Jordan ©Victoria and Albert Museum, London).

Tested materials included:

- Aquazol® 500 (poly(2-ethyl-2-oxazoline)) ≤ 20% solution w/v in de-ionised water/industrial methylated spirits (IMS) (95:5 v/v) (or ≤ 20% solution w/v in IMS);
- Regalrez™ 1094 (hydrogenated hydrocarbon resin) 10% solution w/v in ShellSol® D40 (mineral spirits);
- Gelatin (collagen-based) or Isinglass dissolved in de-ionised water (≤ 5% w/v);
- Paraloid™ B-72 (ethyl methacrylate and methyl acrylate copolymer) ≤ 20% solution w/v in acetone (or ≤ 10% solution w/v in methyl proxitol (1-methoxy-2-propanol)).

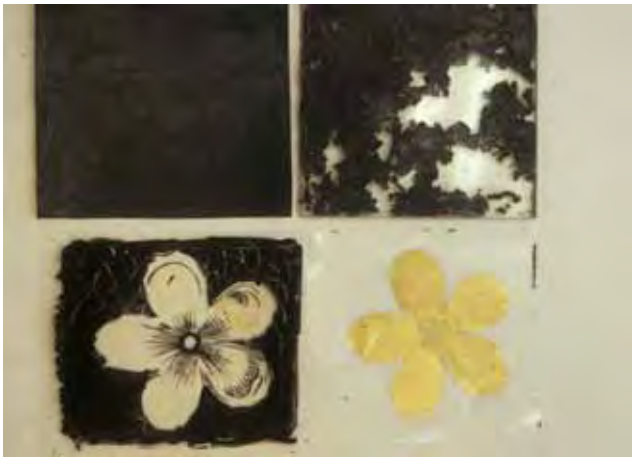

Fig. 2. Reverse view of original panel and new layers before sealing. Top left: painted backing card. Bottom left: painted reproduction on Melinex®. Bottom right: gold leaf on Melinex®. Top right: original glass with consolidated paint (Photo: Fi Jordan ©Victoria and Albert Museum, London).

In summary, the Regalrez™ 1094 solution gave good results but required too long a drying time for this application. The Aquazol® 500 combinations proved to be the most successful. The paint layer softened too readily in all IMS concentrations, but the Aquazol® aqueous/IMS 20% solution w/v (95:5 v/v) secured fragments without complete softening. The properties of Aquazol® (50, 500) and its use on porous and non-porous materials are discussed in Wolbers, McGinn, and Durbeck (1998).

Under magnification, treatment included removal of some loose dirt with a dry sable brush. Aquazol® 500, 10% solution w/v in de-ionised water/IMS (95:5 v/v) was applied by brush to provide local penetration only at the edges and in cracks of lifted decoration. Complete relaxation of the paint and the filling of cleaved areas were not carried out. Once dry, further removal of dirt and excess consolidant was achieved without paint disturbance. A 20% solution re-attached fragments in their original positions. A tracing taken from an identical panel enabled replication of the missing pattern on backing sheets (figure 2).

Deteriorated Enamel on Metal

Treatment of a fifteenth century altar cross (V&A: M.580-1910) with 22 basse-taille translucent enamel plaques on a silver substrate was prompted by degradation obscuring decorative content. The principal of minimal intervention required a judgement on prioritising individual plaques for immediate or future treatment.

Fig. 3. Plaque, translucent enamel on silver (diameter approximately 4.5 cm): before treatment; salts trapped between coating and enamel (V&A: M.580-1910 Salting Bequest) (Photo: Fi Jordan ©Victoria and Albert Museum, London).

Fig. 4. Plaque, translucent enamel on silver: after treatment (V&A: M.580-1910 Salting Bequest) (Photo: Fi Jordan ©Victoria and Albert Museum, London).

In 1971, the entire cross had been coated in a polyurethane lacquer obscuring the surface. It created a microclimate promoting alkaline salts under the lacquer detrimental to the enamel (figure 3). Trapped deliquescing salts caused the coating to lift, pulling off enamel flakes with it (Jordan 2009). Treatment of the enamel was confined to surface cleaning and local consolidation. A high percentage of treatment time was allocated to removal of degraded coatings and crystallised salts; if the enamel or previous restoration appeared in fair condition, the coating was left in place (figure 4). Consolidation was restricted to the most severely deteriorated areas of enamel and re-attachment of lifted flakes (Paraloid™ B-72, 2% solution w/v in acetone, brush application).

Conclusion

An appropriate interventive approach to composite objects with deterioration caused by their construction or environmental history remains a cautious one. The increase in published technical studies on the different types of reverse paintings on glass and the continuing research on glass deterioration informed the treatment decisions. The priority was to prevent the immediate loss of paint, gold, or translucent enamel from the substrate and to limit further deterioration. Compromises were made in regard to the appearance of both objects. Minimal intervention may also demand additional time to be spent monitoring degraded objects in the medium to long term. Collaborations between glass, paintings, stained glass, and metals conservators/scientists continue to expand our knowledge on the materials' interactions with environmental conditions and on innovative uses of consolidation materials.

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