RECENT ADVANCES IN GLASS AND CERAMICS CONSERVATION 2016

International Council of Museums – Committee for Conservation (ICOM-CC)

EDITED BY
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Introduction

Nestled in the middle of the Silesian Lowland, Wrocław, the Polish city once described as “the holy blossom of Europe, a beautiful gem among cities” hosted the 2016 Interim Meeting of the ICOM-CC Glass and Ceramics Working Group. Wrocław’s internationally diverse history, paired with its current status as “the meeting place” and a “city of glass” that welcomes ceramics and glass artists from all over the world, made it a special place for the international glass and ceramics conservation community to converge, collaborate, exchange ideas, and inspire one another at this important triennial conference.

As with previous Interim Meetings, the organizers of the Wrocław 2016 conference aimed to provide a forum where professionals in the field could present interesting case studies in the conservation of glass and ceramics, and disseminate important research results to the international cultural heritage field. Additionally, the conference allowed individuals to promote innovative applications, new materials and technologies for conservation practice, as well as analytical and documentation tools. Another essential goal of this conference was to identify topics of current research and provide networking opportunities for future activities.

The target audience underlines the conference’s interdisciplinary nature and has included conservators (both in museum and private practice), scientists specialising in conservation, students from all conservation disciplines, curators, and other collections care specialists. With more than 140 attendees from 16 countries, the Wrocław 2016 Interim Meeting underscores the importance of an interdisciplinary approach and the shared passion of conservators and collections care specialists to collaborate more broadly.

Over the course of four days, the conference included 20 oral presentations, 29 poster presentations, private gallery and museum tours, excursion trips outside the city, and a student-organized forum, which included a day of student talks from a variety of international conservation programmes.

The conference was hosted by The Eugeniusz Geppert Academy of Art and Design. As Poland’s only institution to have a teaching faculty dedicated to the study, artistic production, and conservation of glass and ceramics, the Academy carries on the city’s longstanding tradition of glassmaking that began in the Middle Ages. With their newly erected (2014) building, the Ceramics and Glass department was excited to share its facilities for the conference. Guided tours of the National Museum in Wrocław helped round out participants’ experience of Polish culture, connecting a rich history with the current efforts of multicultural openness and dedication to advancement in the arts. It was an exciting time to be in the city of Wrocław, as it has been nominated the 2016 European Capital of Culture.

The dedicated members of the Local Organizing Committee included: Paweł Karaszkiewicz, Head of the Research and Development Centre for Renovation and Conservation in Nysa; Marta Sienkiewicz, Assistant Professor of Stained Glass Conservation at The Eugeniusz Geppert Academy of Art and Design; Henryk Stoksik, Professor of Ceramics Technology and Head of the Ceramics & Glass Conservation and Restoration Department at The Eugeniusz Geppert Academy of Art and Design; and Katarzyna Wautuch-Jarkiewicz, Assistant Professor of Glass Conservation at The Eugeniusz Geppert Academy of Art and Design.

The publication of colour preprints for this conference greatly enhances its impact on the conservation and cultural heritage communities at large, and we are grateful to continue this tradition of previous Interim Meetings and Forum Proceedings. 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 of glass and ceramics scholars.
All contributions were peer-reviewed by the editors, with tremendous support from the appointed conference editorial board, without whose expertise, this publication would not have come to fruition: Joost Caen, Professor of Glass Conservation Studies, Antwerp University Association, Belgium; Gerhard Eggert, Professor of Objects Conservation at the State Academy of Art and Design Stuttgart, Germany; Agnès Gall Ortlik, COREBARNA S.L., Conservation-restauration du Patrimoine, Barcelona, Spain; Astrid van Giffen, Associate Conservator at the Corning Museum of Glass, USA; Paweł Karaszkiewicz, Organising Committee coordinator, Head of the Research and Development Centre for Renovation and Conservation in Nysa, Poland; Kate van Lookeren Campagne, Senior lecturer in Ceramic and Glass Conservation at the University of Amsterdam, The Netherlands; Kazimierz Pawlak, Professor of Glass Art and Design at The Eugeniusz Geppert Academy of Art and Design in Wrocław, Ceramics & Glass Conservation and Restoration Department, Wrocław, Poland; Sebastian Strobl, Professor of Stained Glass Conservation at the Department of Conservation and Restoration, University of Applied Sciences, Erfurt, Germany; and Norman H. Tennent, Professor Emeritus of Conservation Science at the University of Amsterdam, The Netherlands.

We are deeply grateful to Janis Mandrus, Associate Conservator, Department of Objects Conservation, Metropolitan Museum of Art, New York, supported by New York University graduate students Emily Frank, Rebecca Gridley, Soon Kai Poh, and Chantal Stein, for their hard work in ensuring conformity and accuracy in the text.

Thanks to the hard work and dedication of all those mentioned above, we are certain that ‘Recent Advances in Glass and Ceramics Conservation 2016’ will serve to inform and inspire conservation professionals and those in allied fields for generations to come.

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Notes:


Conservation of Stained Glass
The Assessment, Conservation, and Restoration of Stained-Glass Windows in the Chapel of the Salesian Sisters of Saint John Bosco, Dzierżoniów, Lower Silesia, Poland

Marta Sienkiewicz

Abstract
The Salesian Sisters are a religious community in Dzierżoniów, Lower Silesia, Poland. Their building includes a chapel with two stained-glass windows that were made in two different German studios around 1900. The other two of the four windows were glazed with poorly crafted simple lead-lights, installed in the 1980s. All of the double-framed windows were removed during restoration of the building. The two historic stained-glass panels required conservation before being transferred to new frames. There were some broken glass elements, and the lead profile was partly damaged at the panels’ peripheries. Despite having been installed relatively recently, the diamond patterned lead-lights in the other two windows were in poor condition as a result of poor craftsmanship. These modern windows were removed and replaced with new stained glass. Two new panels were made using stained-glass ornamental patterns to give the chapel a coherent appearance. One of the new windows was made with figurative stained glass depicting Saint Maria Domenica Mazzarello, the patron of the order, as requested by the Sisters. The reinstallation and restoration provided a new context for the historic panels that emphasized their historical and artistic values.

Introduction
"Conservatio est aeterna creatio"
A monument, a fundamental historical source for a researcher [of architecture] … [is] of a complex character. It comprises information on all the spheres of life it has served, and the list of the material and intellectual or spiritual spheres is long. Therefore, a monument can be examined from different points of view: as a work of building technique, as a material object, as an amenity building and as a ‘vehicle of messages’ or a material product comprising some ideological problems reflecting socio-economic, ideological and political conditions which led to its creation and determined its shape. One must not forget that only all the aspects put together will create a relatively full picture” (Tomaszewski 2012, p. 19).

Dzierżoniów is a historic town with a population of 35,000, situated in the south-western region of Lower Silesia, Poland. Before World War II, it was known as Reichenbach im Eulengebirge or "Reichenbach in the Owl Mountains.” In the period immediately following the war, the town was known by different names: Rychbach (its traditional Polish name), Reichenbach, Rychonek and Drobniszew. In 1946, the town was renamed Dzierżoniów, after the apiarist Jan Dzierżoń. In a sense, this fragmented nomenclature can be read as a microcosm of the history of the region, which was subsumed in great upheavals of borders, population, and culture in the mid-twentieth century (Dzierżoniów 1998, p. 248).

The order of Saint Francis de Sales deals with the education of children and teenagers and was established for this purpose by St John de Bosco. The Daughters of Mary Help of Christians, also called The Salesian Sisters of Saint John Bosco, are based in a religious community in Dzierżoniów. The community occupies a building at No. 2 Spacerowa Street, which houses both the convent and classrooms for the kindergarten run by the Salesian Sisters (Kaczmarek
and Brzeziński 2010, pp. 38-39). The building includes a chapel that is used every day by the nuns and children in their care. The chapel has four windows, two with figurative stained glass with great historic value. The exact origins of these windows (here referred to as Window 1 and Window 2, see figures 1 and 2) are unclear, although it is known that they were produced by two German studios at the turn of 19th and 20th centuries. It is likely that
Fig. 2. Window 2 before conservation and restoration (photo credit: Marta Sienkiewicz).
they were brought from two different places and moved to the chapel after 1945. The other two windows (Window 3 and Window 4) were glazed with poorly-crafted, simple lead-lights, most likely installed in the mid-1980s.

**Assessment and Context**

Because the old double-framed windows (Windows 1, 2, 3 and 4) had become warped and were leaking, it was determined that the joinery in the chapel on the first floor should be changed to ensure the safety of the children who were using this space.

A joiner specializing in window manufacture was commissioned to dismantle the old frames and sashes, and to fabricate and install new ones. However, while on site he realized that all of the windows in the chapel included either stained glass or lead-lights. This required new joinery because the size of the modern frame openings and sashes would be different than the original ones. The only task that the craftsman refused to undertake was the transfer of the stained-glass panels from the old frames to the new ones. It was at this stage that a professional conservator was brought in to assess the panels and advise on the project.

Based on research and observations, it was determined that the historic stained-glass windows in the Dzierżoniów chapel were made between 1890 and 1900. Window 1 is not dated but contains the reference: ‘Ostermann & Hartwein, Kgl. Hofglasm, München,’ indicating that it was produced in the Königlich Bayerische Hofglasmaleri von F. X. Zettler, München (Franz Xaver Zettler’s Royal Bavarian Stained-Glass Workshop in Munich). Executed in a Neo-Baroque style, it shows a central scene of Jesus with children and consists of three horizontally-oriented panels interconnected in one frame. The remainder of the window is comprised of panels with a simple rectangular lattice, which are adorned with painted borders and silver stained ornamental motifs, including architectonic or metal frames and flower garlands (figure 1). The window is similar to the stained-glass windows by the same workshop from the Sanctuary of Our Lady of the Snows, Igliczna Mountain near Międzygórze, about 70 km from Dzierżoniów. The Międzygórze windows are well documented and date to 1897. It is likely that the Dzierżoniów windows are from the same period.

Window 2 was almost certainly made by a different artist or workshop, but may also date to the turn of the 19th to the 20th century. There is no reference on the existing panels to the circumstances of their production. The artistic value of the window is not as great as that of Window 1. Designed in a somewhat eclectic fashion, it shows the enthroned Madonna with Child, flanked by Saint Joseph to her left and Saint John the Baptist to her right. The figures are set against a colourful architectural background, decorated with natural elements such as fruits and flowers (figure 2).

It is unknown whether the windows were specifically designed for their current location. Based on the variation in size and shape of three of the window spaces (two are slightly larger, and one is considerably larger), it is possible that these openings were originally intended to house stained glass from a previous building on the site, which
has been occupied by an orphanage run by the Order of the Hospital of Saint John of Jerusalem since 1364 (Chabros 2003, pp. 45-53) (figure 3).

While the glass in Window 1 appears to have been designed for this particular location—evident in the composition and details of the window armature construction—Window 2 seems to have been adapted at a later stage. As the majority of the chapel windows are in three sections, intersected by astragals, they each appear to consist of six panels. In Window 1, the main scene is shown at the center panel and is enclosed on all sides with decorative panels. In Window 2, the scene is shown in the three bottom frames, while the top three panels are glazed with a carpet pattern, each with centrally placed, symbolic motifs. These three top panels do not have great artistic value, and there exists a noticeable discrepancy in technical skill and craftsmanship between the top and bottom window panels.

Fig. 4. Window 3 before refurbishment (photo credit: Marta Sienkiewicz).

Fig. 5. Window 4 before refurbishment (photo credit: Marta Sienkiewicz).
Also the colour schemes for the top and bottom portions of the window are not in harmony with one another. In the 1980s the remaining two windows were glazed with an intense yellow–golden diamond lattice surrounded by a crimson border (Windows 3 and 4, see figures 4 and 5). At the time of the author’s assessment, the condition of the new glazing on these windows was much worse than the historic windows because of the poor quality craftsmanship. The artistic value of these was assessed as low, and inconsistent with the historic windows.

**Historical Overview**
Conservators encounter a great number of undocumented monuments in their work. Often, it is only possible to classify and describe these monuments based on the residual remains of their original imagery. In the case of the Dzierżoniów windows, the conservator looked to local history to understand the original context and current condition of these historic windows.

Lower Silesia is a classic example of a region full of monuments, which has been until recently described as “heritage without homeland” (*le patrimoine expatrié*). Stages of European integration over the past few decades, along with the passing of generations, make it possible to look objectively and respectfully, without resentment, at the cultural legacy of the region’s previous inhabitants (*PWN* 2004, pp. 117-118).

Ruled nearly for 200 years by the Kingdom of Prussia and then by the German Empire, Lower Silesia was an important region through many periods of history, especially in the Second Reich. Historicism, a national style appropriate to the 19th-century Germany, comprises artistic styles that draw inspiration from and seek to recreate historic styles (Lucie-Smith 1988, p. 100). The tremendous development of art during this period is manifested in churches with Neo-Gothic or Neo-Baroque stained glass. Polish migrants displaced from Eastern Borderlands, the majority of whom were practicing Catholics, became involved with Post-War destruction of historical objects. While they rarely destroyed paintings or figures of saints on stained-glass windows, they often removed reference numbers from the stained glass windows as evidence of their origins. Art historians, therefore, continually face a challenge in determining the provenance of stained glass. The research related to the Dzierżoniów windows is still in progress, but this history helps to explain the condition of the inscriptions found on Windows 1 and 2. As has been noted, the inscription in Window 1 was preserved and ascribed to Ostermann & Hartwein, from Zettler’s workshop in Munich. On the top panel at the center, an angel’s face is depicted above an ornamental banner with the German inscription: ‘Lasset die Kleinen zu mir Kommen’ (Let the little children come to me), taken from Saint Mark’s Gospel. At some point, the inscription on the banner was covered with oil paint because the wording is in German.

On the right panel of Window 2, St. John the Baptist holds a banded staff with the inscription ‘Ecce Agnus Dei’ (Behold the Lamb of God), from Saint John’s Gospel. As this was recognized as a Latin maxim, the Catholic migrants displaced to the Regained Territories did not associate it with the former enemy and left it intact.

**Restoration History**
The windows in the Dzierżoniów chapel had been restored on at least one previous occasion. The condition of the figurative panels indicated that they had been cleaned and repaired, and the puttying of lead profiles had been supplemented. The ornamental panels had also been reconstructed with four non-original glass elements. Although they fit into the chapel window opening, technical details visible on these four elements reveal that this was not their original placement. For example, the silver stain on these pieces is much stronger than on the original glass, and the texture differs slightly. Similarly, the top part of Window 2 is supplemented with an ornamental lattice; without doubt, this later interpretation is an addition to the window.

The use of simple diamond lead-lights for Windows 3 and 4 demonstrates that the glazing in the chapel was incomplete at some point, with only two of the windows including figurative stained glass. To a modern eye, the aesthetic of the lead-light glazing is at odds with the original intent to create a cohesive aesthetic inside the chapel.

**Conservation and Restoration Approach**
The art of stained glass is inextricably linked with architecture; however, it occupies a somewhat ambiguous position within conservation theory and practices. Its nature as a material that combines light and colour to create a picture presents significant challenges for conservators.
The eclectic mix of conservation approaches taken at Dzierżoniów, detailed below, could be perceived today as controversial, or too much embedded in the traditions of the 19th century. However, the expectations of the congregation, the chapel’s function, and the desire to create an aesthetically pleasing and unified interior were of paramount importance in determining the appropriate course of action. The Superior of the Congregation, Sister Bożena Cichańska, and the Congregation’s economist, Sister Barbara Matyjak made the decision to renovate the entire chapel, and the restoration of the stained-glass windows assumed a role of central importance in this plan.

In the case of the Dzierżoniów windows, it was not possible to transfer stained-glass windows to new frames without repairing the damage to the glass and lead profiles. However, the Dzierżoniów community did not have the necessary funds to commission a qualified professional conservator to complete the project. Therefore, it was decided to organize a work placement for students of the Ceramics and Glass Conservation and Restoration Department at The Eugeniusz Geppert Academy of Arts and Design in Wrocław. During this work placement, students carried out the conservation and restoration of this historical stained glass under supervision and in accordance with best conservation practices.

For Windows 1 and 2, only minimal interventions were necessary, as the damages to the windows were relatively minor. The surface of the stained glass panels was slightly dirty, paint had been lost in some areas, and some glass pieces were broken. When the windows were taken out, it was revealed that the lead came at the circumference of the panels were also damaged. Some panels were warped, with crumbling putty. Also, as noted above, the banner inscription on Window 1 had been coated with oil paint. The decision was made not to conserve the existing diamond net pattern lead-lights. Restoring these panels would have been a difficult job, as they required re-leading. Also, the student work placements were time-limited. Finally, these panels did not fit within the aesthetic context of the original design of the chapel. Thus, the decision was made to create replacement panels for Windows 3 and 4 instead.

Conservation Treatment
The condition of each panel in Window 1 and Window 2 was documented before treatment. The procedures used were based on CVMA “Guidelines for Conservation and Restoration of Stained Glass” (CVMA 2004). The panels were cleaned primarily with dry brushes, then using a 1:1 solution of distilled water and ethanol. The external lead frames were removed as the existing ones were badly damaged. The broken glass elements were bonded with Araldite 2020.

Designing and Producing Replacement Windows
All of the double-framed windows in the chapel (external and internal) were replaced during the restoration process. The two glazed lead-lights panels in Windows 3 and 4 were removed and replaced with new stained glass.

The new panels were developed and designed in consultation with art historians and the proprietors of the chapel. The aim was to create an ‘enclave for prayer’ in an aesthetic context. The style of the historic stained-glass windows (Windows 1 and 2), especially their ornamentation, was studied. As the historic windows reflect the mainstream German ‘Neo-Baroque’ style, the replacements for Windows 3 and 4 were designed in line with 19th-century stylistic principles. A fusion of these elements was created in order to inter-relate the two different historic stained-glass windows. The designs were made using monumental stained-glass ornamental patterns, and included figurative designs, one of which depicts Saint Maria Domenica Mazzarello, the patron of the order.

During the design process, the restorers first considered placing the figure of the order’s founder, John de Bosco, in Window 4. De Bosco believed his calling was to help...
poor, orphaned, and neglected youth. His strength and persistence in the everyday struggle to help and defend the young resulted in the formation of international congregations of male and female Salesians, as well as secular movements called the ‘Salesian Family.’ However, it was finally decided that the figure of Saint Maria Dominica Mazzarello, the founder and patroness of the Order should be depicted in Window 4 instead.

It was decided that Window 3, which is the only bisected one in the chapel, would be decorated solely with ornamentation referencing the windows designed by Ostermann & Hartwein. The dimensions of the ornament were matched with the size of the panels; the architectural elements in the fanlight element were transposed so they appeared consistent with the original design scheme (figure 6). Also modeled after the design of Window 1 by Ostermann & Hartwein, the figure of Saint Maria Mazzarello was placed in the central panel in the bottom row of Window 4 (as in the scene with Jesus) (figure 7). Architectural ornaments that framed the figure of the enthroned Madonna in Window 2 were transferred—or more precisely copied—to frame the figure of Saint Maria Mazzarello. The old and the newly designed window panels did not differ significantly in technique, which allowed the retention of similar proportions in both the new and the original elements.
The surrounding panels were filled with an ornament based to a great extent on the pictorial motifs and formal divisions in the ornamental part of Window 1, but the design was adjusted to fit the different dimensions of the window. There is the bust of the Angel, situated above the main scene in the Window 1 highlighting a banner with a quotation from the Bible. This was redesigned because of the size of the Window 4. However, a section of the banner was depicted and an inscription with the name of the saint and dates of her birth and death was added to it.

The figure of Saint Maria Mazzarello features colours associated with her life and activity. In particular, fragments of the background point to the blue Italian sky and fields with crops where one can enjoy strolls with children in a natural landscape, all in accordance with the teachings of Saint Francis. A lily appears in the window as an attribute of Saint Maria Mazzarello, while the habit indicates her vocation. The division of the window mirrors the division of the form in the window with Madonna; yet, Art-Nouveau-style sections in the lily component were deliberately used to mark the historic inconsistency of the window, visible to the knowledgeable observer. The realistic painting style in Saint Maria Mazzarello’s face, which appears more contemporary and refers to post-war art, serves the same function. Most of the glass used in the window was selected for the project from antique glass manufactured by Lambers Glass Works, in Waldsassen, Bavaria, Germany. The structure, thickness, luminosity, and colour depth of stained-glass sheets correspond with the glass used by German studios in the preserved historic windows. The stained-glass paints were selected to match the painting in the historic windows. In order to match a relevant colour, samples were made with eight types of silver stain applied in different ways. Matte contour paint, along with black grisaille, was also used to match the appearance of the historic stained-glass windows when exposed to partially reflected light.

Additional Restoration Work

Additional work focused on an issue related to the panel representing Mary, Saint John, and Saint Joseph that filled the fanlight of the historic Window 2. Already the first inspection of the ensemble revealed that three carpet-patterned panels originated from a much later period than the figurative panels. However, during treatment, it became clear that the workmanship and technology used in these panels ranked far below that of the historic stained-glass windows. In consultation with art historians, including Dr. Magda Ławicka, custodian of the 19th and 20th-century collection at the Museum of Architecture in Wrocław, a course of action was implemented. The restoration of the panels involved entirely re-leading the pieces. It was decided that they would be exhibited in a different location.

In respect of the fanlight, it was designed and rendered identically to its counterpart with the figure of Saint Maria Mazzarello (figure 8). Following the example of 19th-century restoration, which was central to the approach to this project, an inscription was added on the banner surround-
ing the Angel’s face, to indicate all changes that were introduced to the appearance of the windows. The content of the inscription was determined in consultation with the Polish ministry expert in stained-glass window restoration, and a member of ICOM, Dr. Paweł Karaszkiwicz. The inscription reads: “A.M.D.G. Renovatio A.D. MMXV,” which is a traditional Latin abbreviation standing for “Ad Maiorem Dei Gloriam Renovatio Anno Domini 2015” and means “For greater glory of God, restoration in Anno Domini [Lord’s Year] 2015.” Following the example of 19th-century art conservators and restorers, the author inserted a secret message to record her participation in the works, hiding herself in the facial features of the Angel who presents the above-mentioned inscription (figure 9).

Conclusion
As a result of conservation, restoration, and arrangement procedures, the chapel gained an aesthetically and artistically coherent appearance. The quality of the space for prayer was elevated, allowing for the greater possibility for sacred contact. The replacement of the window armature, the conservation of the stained glass, and conservation of the arrangement of stained glass in the remaining two windows coincided with the replacement of the chapel interior (figure 10). A new altar, a rood screen, a tabernacle, and Stations of the Cross were designed and constructed. The educational function of the chapel played a significant role in the decisions taken with regard to the details of the conservation arrangement.

The Venice Charter calls for “the full richness of authenticity,” which can be interpreted as the plenitude of material and the spiritual components that make up a monument, thus its substance, form, contents, tradition and function (Tomaszewski 2012, pp. 54-55).

Combining some motifs from two of the existing windows into the replacement stained glass made the chapel look more coherent, underlining the internal sacrum by creating a solemn atmosphere. An educational target has been
achieved by those means, as children absorb the aesthetic standards subconsciously. Most importantly, the old panels exposed in new surroundings gained a new context, emphasizing their historical and artistic values, allowing them to continuously act in their primary function in the chapel. This type of stained-glass window restoration and design has the advantage of being fully reversible. Reversibility is important when, in the face of changing aesthetics, the glazing loses its reason for existence and consistency with the originals and it is then possible to adopt another conservation concept, related to more contemporary aesthetics. The subsequent approach might not be better than the previous one, but it will be more consistent with contemporary style. It is conceivable that after another few decades the ongoing development of conservation and restoration of historic artifacts as a discipline will dictate a new approach to this issue that differs from what has been chosen for today.

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The Application of Non-invasive Analytical Techniques in the Investigation and Documentation of Medieval Stained-Glass Windows from the Grodziec Collection

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Key words
Stained glass; non-invasive investigation; XRF; OCT; glass composition

Abstract
This paper presents the results of an investigation of 14 medieval stained-glass panels from the Grodziec Collection. The main objective was to investigate the origin, dating, history and previous conservation treatments of the panels. The investigation of glass composition and corrosion products was carried out by means of scanning macro X-ray fluorescence and portable XRF spectrometers. The study revealed that some glasses have a composition characteristic of medieval potash-lime-silicate glass while other pieces could be classified as sodium glass. Surprisingly, the original paint layer of Grodziec panels contained two different types of contour paint. Additionally, corrosion products, such as gypsum, or dark areas caused by manganese browning, were observed. The results were completed by optical coherence tomography (OCT) examination, which permitted the authors to observe multi-layered glasses and their corrosion phenomena with spatial resolution.

1. Introduction
Historic stained-glass panels are complex objects, comprised of parts with differing provenances. Some parts are original while others are introduced during restoration work over centuries. There are several analytical techniques available for investigating stained-glass windows (Janssens 2013). Many of the techniques, such as scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDX), inductively coupled plasma mass spectrometry (ICP-MS), and atomic force microscopy (AFM) require the dismantling of the panel and/or the collection of samples. Others, such as laser-induced breakdown spectroscopy (LIBS), cause microscopic damage of the glass (Schreiner 1988; Müller and Stege 2003; Szelagowska et al. 2008; García-Heras et al. 2005). X-ray fluorescence (XRF) has been commonly utilized as a non-destructive method for examining stained-glass windows (for example: Rodrigues et al. 2013). Portable XRF (pXRF) spectrometers enable in situ measurements, which are particularly useful when investigating a panel that either cannot be removed from the window or is placed at a high altitude (as is often the case with church glazing). Dungworth provides very interesting discussions on the limitations of pXRF, pointing out that the detection of light elements by this technique could be limited by both the presence of outer corrosion layers and the thickness of historic glass (Dungworth 2012).
Pixel-by-pixel XRF, which is used for the non-destructive investigation of large artefacts, was introduced by M. Schreiner and M. Mantler (Schreiner and Mantler 1992; Mantler and Schreiner 2000). Spatially resolved macro-XRF scanning (MA-XRF) was recently used in the investigation of stained-glass windows (Kamińska et al. 2015; Van der Snickt et al. 2016). Caen used a MA-XRF to investigate two stained-glass panels: one originated from 15th century England and the other from 17th century Leuven (Caen et al. 2015). The XRF macro-scanner has been commercially available since 2013 (Alfeld et al. 2013) and has aroused much interest among art conservators. Due to the large dimensions of the investigated objects, macro-XRF scanning is usually conducted in air; this allows the detection of elements between potassium and niobium based on their K-lines, as well as heavier elements based on their L-lines.

In the present study, a collection of 14 medieval panels from Grodziec Castle in Poland were investigated. The macro-XRF examination was complemented with the results obtained by pXRF in He flow, which permits the sensing of light elements such as sodium, magnesium and silicon—all important constituents of glass. Optical coherence tomography (OCT) was also used to examine the sub-surface morphology of the glass panels to determine the locations of the coloured layers and the range of atmospheric corrosion. OCT is a non-invasive technique for optical sectioning of transparent and semi-transparent objects (Drexler and Fujimoto 2015; Kunicki-Goldfinger et al. 2009; Targowski et al. 2010; Hughes 2010; Targowski and Iwanicka 2012).

2. Experimental
2.1 Objects of Investigation
The Grodziec Collection consists of 14 stained-glass panels that depict several figures on architectural backgrounds (figure 1). Eight of them are exhibited at the Jagiellonian University Museum, Krakow, Poland, while the other six belong to the National Museum in Wroclaw, Poland. All the panels have undergone multiple conservation/restoration campaigns at different times, performed by different workshops. The six Wroclaw panels differ from the other eight in that they have surrounding glazings, which were most likely added at the beginning of the 20th century (not shown in figure 1). Minimal information about the history of the collection is known, and what is known, concerns the time after WWII. The earlier history of the collection remains unclear. There is, however, a possibility that the panels date back to 1425–1430 and originate from the area between Carinthia and Styria, Austria. This dating is unconfirmed due to the lack of archival evidence, but similar medieval stained-glass panels can be found in the churches in Austria, namely Maria am Waasen in Leoben, Maria Höf in Metnitztal, and some churches in Tamsweg and Gaisberg, (Gajewska-Prorok 2015).

2.2 Macro-XRF
To obtain information about the composition of the glass and paint layers, X-ray fluorescence analysis was conducted using a macro-scanner (M6 Jetstream, Bruker). This device enabled the scanning of large surface areas of up to 80 × 60 cm². A rhodium X-ray tube, polycapillary optics, and a 30-mm² SDD detector were used for the process. In the measurements presented throughout this paper, the X-ray tube was used without a filter and the voltage and current were 50 kV and 0.6 mA, respectively. X-ray spots of 600 and 800 µm were used. The distance between the object and the measurement head ranged between 0.8 and 1.5 cm. Dwell times of 20 and 50 ms per pixel were employed.

2.3 Handheld XRF
The light elements were detected by X-ray fluorescence measurements using a Bruker TRACER III-SD portable analyser equipped with an X-ray rhodium tube and a Peltier-cooled 10 mm² XFlash SDD detector. The spectra were recorded for 60 s without the use of additional filters. The measurements were taken in two modes, at 40 kV and 30 µA for the detection of metals, and at 15 kV and 27 µA in a helium flow of 0.4 L/min for the detection of light elements.

2.4 Optical Coherence Tomography
The technique and instrument used in this study are described elsewhere (Targowski et al. 2015). However, the key aspects necessary to interpret the images provided in this work are presented in this paper for the convenience of the reader. The OCT virtual cross sections are shown here with a false colour scale; the tomograms
Fig. 1. 14 Medieval panels from the Grodzicz Collection. Photographs were taken in transmitted light. From the right: St. Peter, St. Lawrence, St. Erazm, St. Wolfgang, Madonna, Man of Sorrows, Archangel Gabriel, Mary, St. Barbara, St. Margaret, St. Jacob, St. Andrew, St. Nicolas, St. Leonard; approximate size of panels: 40 x 80 cm (photo credit: Daniel Podsock, Corpus of Medieval Stained-Glass Windows in Poland).
encode the scattering properties of the examined structures. Non-scattering media, such as air and clear glass, are shown in black. The low-scattering structures are shown in cool colours; the high-scattering ones in warm colours, namely, yellow and red-to-white. For all images, the probing light approached the surface from above and through air, and the uppermost line corresponds to the glass surface. The strongly scattered structures on the surface cast shadows that obscured the details below. However, indications of vanishing signals (tales) can be observed below the structures, evidencing multiple scattering by the structures. The scale bars indicate distance within the object and the vertical scale bars are based on the optical distances, with the refractive index estimated to be 1.5. The images are vertically stretched to enhance the readability.

3. Results and Discussion
The results revealed an important difference between the qualitative elemental compositions of the original and replacement glasses. Figure 2 shows the elemental distribution maps for the panel depicting St. Wolfgang (external and internal side of the window). Figure 3 compares the XRF spectra for different types of glass in the panel depicting St. Barbara (external side), as obtained by pXRF. OCT tomogram of medieval red flashed glass is shown in figure 4. In figure 5 the potassium distribution on the external side of St. Wolfgang panel (face area) is compared with the presence of manganese, while figure 6 presents OCT tomograms of corroded medieval glass.

3.1 Composition and Structure of Glass
The most important information required for the dating of stained glass can be obtained from the flux components, which decrease the melting temperature of the silica. Glass pieces for which both XRF techniques employed recorded intensive signals from the potassium K\textsubscript{a} line were considered medieval (figures 2 a, d and 3). The presence of potassium oxide, which was introduced by using wood ashes in glass production, is typical of the medieval period (for
example: Müller 1992; Dungworth 2011 and 2012). In the maps of the interior side of the panel the $K_{\alpha}$ potassium photons at 3.3 keV were absorbed by the paint layer (figure 2 d). The potassium signal is also relatively low in the deteriorated areas of the glass, which could be particularly observed in the maps of the exterior side of the panel (figure 2 a). This is because $K^+$ ions are leached out during the deterioration process and replaced by hydrogen ions from water through the hydrolysis reaction that occurs on the glass surface. Thus, there is a depletion of alkali ions on the surface of the glass, although it remains silica-rich, resulting in the formation of the gel layer (Müller 1992). The presence of sodium and a small amount of potassium was detected by pXRF in the greenish glazing and in the yellow border surrounding the figures in the Wroclaw Museum panels (figure 3 a and b, respectively). These glasses were classified as 20th-century soda-lime glass. The main glass network former observed in the investigated medieval panels was silicon oxide: figure 3 shows the Si $K_{\alpha}$ line at 1.74 keV. A phosphorus $K_{\alpha}$ line was also
detected, likely indicating phosphorus oxide, with calcium (from calcium oxide) and magnesium (from magnesium oxide) acting as stabilizers. Aluminium (Al K$_\alpha$ line at 1.49 keV), iron, barium, and titanium were also detected, which are explained by impurities in the raw materials used to produce the glass. The following metals were likewise detected (some results are represented in figures 2 and 3): manganese (in medieval violet and colourless glass, and 20th-century yellow border), copper (in flashed red glass), iron (in green glass), cobalt (in medieval blue glass), and chromium (in greenish 20th-century glazing).

The structure of the flashed red glass was examined by OCT. In figure 4, a layered structure of flashed red medieval glass is visible and a transparent layer of 42 $\mu$m thickness can be observed immediately below the surface. A weakly scattering coloured layer with a total of 162–165 $\mu$m thickness can also be observed further below. Furthermore, an air bubble can be detected under this layer.

### 3.2 Paint Composition

The distinctions between the deposition (dirt), deterioration products and the thin original vitreous shading paint layer (grisaille à modeler) on the internal and external sides of the panels were not obvious. The analysis of the composition of the surface layers is important for an elaborate conservation treatment proposal, especially for the cleaning stage. The shading paint can be identified by the presence of lead and iron. In the case of the trace line paint (grisaille à contourner), the results presented in figures 2 e and f reveal the use of two types of paints in the Grodziec medieval stained glasses. One of the paints contains copper oxide and a small amount of iron oxides, and the other is based on iron compounds. The copper-based paint was used for the outlines of the compositions, while the iron-based trace lines were found in the decorative and repeatable motifs such as leaves and other ornaments, mainly in the background of the composition. To the best of the authors’ present knowledge, this would be the first time that such difference in composition of paint is reported. This observation provides some insight into the organization of the workshop where the panels were produced, and considering that it is characteristic of all the investigated panels, it confirms the integrity of the collection.

The macro-XRF results for the panels depicting St. Wolfgang (figure 2) and St. Barbara (figure 3) indicated that the original medieval composition of the panel had been modified to fit the panel to a bigger window. It was observed that small medieval glass panes had been connected to new ones in the top part of the panel (not shown in the figures), and the outer glazing had also been added (figure 3).

### 3.3 Deterioration Phenomena

The macro-XRF results enabled the characterization of the different corrosion products and other deposits. Predictably, the external surfaces of the glasses were more deteriorated than the internal surfaces. Several symptoms of the deterioration process, ranging from small isolated pits to craters and dark stains, could be detected visually. The pits appeared to be distributed rather evenly over the surfaces of all the glass pieces. Potassium leaching was typical of the black areas (indicating no signal) in the spatial distribution of the element on original medieval glass pieces (figure 2 a).
Strong manganese signals were observed in the elongated areas on the inside of some of the original panels (for example St. Wolfgang, presented in figure 5). Stains had a dark opaque appearance in transmitted light, while in reflected light they were seen as light — almost white to dark brown dots of annular structure resembling grains. Those stains seemed to occur in the subsurface of the glass. Their shapes were either round of a size from below 1 mm in diameter to a few millimetres or resembling damp patches even a few centimetres long. This may indicate a process known as manganese browning (Cagno et al. 2013). According to Müller manganese can accumulate in the gel layer (Müller 1992). Panels most affected by that phenomenon were windows depicting St. Peter and St. Wolfgang. There, the process of browning was much more advanced than in the case of the remaining windows, and was therefore the subject of a closer investigation. The stains were mainly present within the figural depiction. As in the case of the remaining panels, the dark stains on the borders were arranged vertically. Obviously, the shape was not accidental. A closer look onto the external surface was sufficient to understand the reason of that appearance. Affected panels were back painted with a very thin layer of shading paint adjusted to the composition on the internal side. Therefore, the layer of shading was removed with appropriate tools in places destined as the brightest. In the case of the face, the back painting was applied complementary to the depiction on the internal side, following the features. In the clothes,
the shading paint was worked out with a brush according to the folds. The same method was used for the attributes held by the figures. Undoubtedly, the arrangement of dark brown stains was somehow related to the external paint layer, but it is not entirely clear whether they had developed in the uncovered areas or under the thickest layers of paint. The latter option seemed most probable, since the stains could be seen within the places that should be the most shadowed.

The elemental distribution maps of the external side of the medieval part of the St. Wolfgang panel (figure 2 c) revealed higher contents of calcium compounds along the lead came, due to the presence of putty. A weaker, but clear signal could also be detected over the entire external surfaces of the glass panes. This may be attributed to the glass composition and/or a thin layer of gypsum deposits.

The morphology of the corroded surface was observed by OCT. Figure 6 shows small corrosion pits, some of which contain flakes that are almost detached from the glass surface, while some can only be observed, in OCT tomograms, as scattering areas within the bulk glass below the surface.

4. Conclusions
The investigation of medieval stained glass is a multidisciplinary challenge. The present study found a combination of XRF and OCT to be very effective for the examination and documentation of stained-glass windows. Non-destructive methods enable researchers to distinguish original medieval glass pieces within panels from new replacements. In the particular case of the Grodzic collection, macro-XRF facilitated the distinction between the original medieval potash-lime glass and the soda-lime glass that was added at a later time. Detailed inspection of the spatial elemental distribution maps revealed evidence of the presence of two types of trace line paints (grisaille à contourner) in the different compositions, and confirmed the presence of corrosion products. Complementary data on the presence of light elements were obtained by pXRF measurements in a helium flow, while OCT was used to obtain information about the glass structures and the corrosion features. Interpretation of results always relies on the collaboration of art historians, conservators, and conservation scientists and will continue in the team established for this project.

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The Application of Non-invasive Analytical Techniques in the Investigation and Documentation of Medieval Stained-Glass Windows…

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Cold Paint on Stained Glass from Nuremberg: Technical Insights into the Art of Stained Glass around 1500

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Keywords
Cold paint; painting technology; stained glass; Nuremberg

Abstract
The conservation campaign on stained-glass windows of St. Lorenz church and the church of St. Sebald in Nuremberg provided an opportunity to examine the painting technique of stained-glass production around 1500 in detail. In addition to the extensive and skilled use of silver stain, etching techniques, and iron red on monumental stained glass, there are various layers of paint that are difficult to categorize. New findings support the hypothesis that some of these layers represent residues of cold paint, applied on top of the classic three-layer structure of fired paint. The systematic, extensive, and highly variable use of cold paint in the late 15th and early 16th centuries is illustrated with examples of windows executed at the workshops of Wolgemut and Hirsvogel and the Strasbourg Workshop-Cooperative. Individual findings are described to support the interpretation of these painted surfaces. The visual concepts and the resulting technological limitations and requirements are discussed.

“It is not seldom that the disappearance of the internal detail was because today's rightfully praised 'Schwarzlot' was not a Schwarzlot, not a fired paint. Even the esteemed senior glassworker was familiar with a 'botched job'...” (Oidtmann 1898, p. 109)

Introduction
There was an increased interest in stained glass in Nuremberg in the last quarter of the 15th and the early 16th century. The completion of the choir hall of St. Lorenz church, the choir glazing renewal in the church of St. Sebald, and the artistic upheaval during the age of Dürer spawned a large number of monumental creations and small window panels. Recent conservation campaigns and regular maintenance over several years provided the opportunity to examine these glass paintings. It was possible to study the artistic techniques used to create these stained-glass windows in detail.

Stained-glass production remained nearly unchanged over the centuries. Glass paint, which consists of glass powder mixed with a binder and stained with iron or copper hammerscale (the so-called Schwarzlot or Braunlot — black or brown trace paint), is applied to the glass surface and adhered by firing in the kiln at about 600°C. Classic painting on glass is usually described as a three-layer structure: wash, trace lines, and shading. The use of unfired paint—so-called ‘cold paint’—on stained-glass windows is mentioned in different historical sources and has been described in various case studies (Clerkin Higgins, Pilosi, and Wypyski 1996; Fontaine, Van Bos, and Wouters 1996; Trümpler, Dold, and Wolgemuth 2002, pp. 55, 56). Unfired paint is mentioned in the old guild regulations, guild rules (Oidtmann 1898, p. 110; Caen 2009, p. 284), and instructions provided to the workshops by clients (Merrifield 1999, p. 446).
In these sources, it is mentioned as an auxiliary technique that serves to compensate for errors on the spot, and does not meet the standards of a proper glass paint. To date, it has often been assumed that these organically bound, non-fired paint layers could hardly have survived over the centuries. The careful examinations of monumental stained-glass windows in Nuremberg, however, have revealed an unexpected range of well-preserved paint, here assumed to be cold paint. This paper describes observations made during the close examination and analysis of four examples:

1. Bamberger window (St. Sebald, Nuremberg, workshop of Hirsvogel, 1501)
2. Holzschuher window (St. Sebald, Nuremberg, workshop of Michael Wolgemut, 1480)
3. Markgrafen window (St. Sebald, Nuremberg, workshop of Hirsvogel, 1515)
4. Volckamer window (St. Lorenz, Nuremberg, Peter Hemmel / Strasbourg Workshop-Cooperative, 1481)

Non-fired Glass Paint: Historical Sources
A comprehensive analysis of the historical sources for cold paint on glass was not within the scope of this investigation. However, two historical sources are of major interest and shall be discussed here: Antonio da Pisa (Lautier and Sandron 2008) and the Marciana manuscript (Merrifield 1999). Each of these sources describes the application of non-fired paint in some detail.

The Marciana manuscript mentions the use of three layers of oil (linseed oil or walnut oil). The application of glue and egg is described, always in combination with a coating of oil or as an oil emulsion to be resistant to moisture. Antonio da Pisa mentions boiled linseed oil as well as "liquid varnish" or "resin varnish" (Lautier and Sandron 2008, pp 114, 115).

Copper compounds, such as copper resinate or verdigris, are mentioned as pigments. In oily binders, these pigments form nearly transparent coatings and simultaneously act as a siccative. There are also references to the production of yellow colorants, and the use of red iron pigments, as well as carbon black, azurite, burnt lapis lazuli pigments, and others (Vaassen 2013).

The presence of cold paint on stained glass raises the question as to whether such an addition was part of the original window design or if it represents later retouching. There are a few arguments for why it is likely that the cold paint on the examined stained-glass windows was applied during original manufacture:

— Given the large-scale and very sophisticated use of these cold paint layers, it would have been impossible to apply all of the cold paint after the panels had been mounted.
— The use and appearance of these paint layers is very similar across a large number of panels from different workshops and periods.
— The cold paint is not found within losses of the fired paint, but only on top of fired paint.
— The cold paint retouching found on losses to the fired paint is clearly distinguishable from the presumably original cold paint.

Appearance and Identification of Cold Paint
The identification of layers of cold paint on an actual stained-glass window is not straightforward, and requires a very precise visual inspection with appropriate magnification.

On the four windows examined, these unfired paint layers were identified by visual examination. Aesthetic criteria and the creative function of the cold paint layers within the pictorial context of the stained-glass windows have been described to understand the purpose of this artistic technique.

Three samples of cold paint were taken each from the Volckamer, and the Markgrafen window and four of the Bamberger window. The samples were analyzed using Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM-EDS), polarized light microscopy and Infrared (IR)-spectroscopy. In addition, the melting temperature of each sample was measured (Drewello and Weißman 2015).

This analysis was undertaken to support the visual examination of these objects and aid in characterizing these artistic techniques. All pigments and binders discussed in this paper were commonly used in the 15th and 16th centuries (Schramm and Hering 1995).

Well-preserved cold paint is often hard to distinguish from a fired paint layer (figures 1 and 3), whereas a strongly deteriorated cold paint is often no longer recognizable and can be easily misinterpreted as an accumulation of dust or encrustation (figure 6). The unfired paint layers are best
identified if they are in different states of preservation on a single piece of glass (figure 1).

The interpretation of these surfaces is aided by a close examination of interrupted paint layers, specifically in places where a fired paint is exposed beneath a cold paint. This can be seen in areas cleaned during previous restoration campaigns (figures 2 and 4). In some cases, a clear answer is found by completing stratigraphic analysis of a small area, comparable to a paint layer analysis on wall or panel paintings (figure 3).
The present appearance of the cold paint crucially depends on its state of preservation. Manufacture of the paint, the binders and pigments used, and the environmental conditions are parameters that can all play a role, as does the nature and intensity of the paint layer. The appearance of cold paint in reflective light is often dull and gray, sometimes crossed by ridges and lines (figure 2). In transmitted light, it appears either umber-colored, reddish-brown, sometimes gray to black, semi-transparent or nearly opaque. Depending on its condition, the cold paint can sometimes only be identified as such by its design function within the image context. Purposefully placed traces of painting techniques, such as brushstrokes, scrapings or other toolmarks can be found in highlights (figures 7 and 8). In contrast, in thinly-applied and well-preserved areas these layers appear homogeneous, semi-transparent, and glossy. In this instance, cold paint can sometimes only be distinguished from a fired paint layer by the presence of embedded brush hairs (figure 1).

On all of the panels examined, the fired paint layer is exclusively restricted to washes, hatching and tracing on the front, as well as shading on the back. All other layers were applied as cold paint; in particular, half-tones and shades that are situated on top of scrapings or highlights (figure 7). Weathering or aging of the cold paint layers often results in increased tonal contrast or “blackening” of the passages used to create shading (figures 2 and 5).

Fig. 3. Bamberger window in reflective and transmitted light: the matte grey layer represents a thinly distributed cold paint. An area of 2 mm x 2 mm of the cold paint has been removed to reveal the fired paint underneath (red arrow).

Fig. 4. Bamberger window: residues of multi-layered cold paint (red square). Otherwise only the fired underpainting—trace-lines, hatchings and a light wash—is still well-preserved.
Fig. 5. Volckamer window: extensive use of cold paint as shading on entire facial areas.
Fig. 6. Volckamer window: the cold paint has aged and flaked off; dark gypsum crusts remain including embedded pigments.
Identification of the cold paint can be complicated by losses and alterations to these layers, caused by exposure to high humidity and condensation, or by previous cleaning efforts. An aggressive cleaning might leave only the fired paint layer, which results in a significantly reduced visual impression (a "skeleton") of the original appearance of the glass painting (figure 4). Often fired areas of hatches were exposed, which actually fulfilled the function of an undercoat and were shaded by flat cold paint (figures 4 and 5). The juxtaposition of relatively well-preserved areas of cold paint with over-cleaned fired undercoatings illustrates the importance of cold paints in creating the image (figures 4-7). The uneven cleaning of the Bamberger window exemplifies the difficulties previous conservators had in defining these layers precisely; they were often referred to as "encrustations," dirt or deposits (figures 2 and 4).

**Typical Applications of Cold Paint**

The following section outlines the typical applications of cold paint on the four windows examined in this study, as well as characteristic condition issues observed.

**Coloration / Tone Modeling**

The use of cold paint makes it possible to add small color accentuations without having to introduce disturbing lead lines (comparable to the subsequent application of enamels).

For example, it was applied to depict precious stones (as seen in the Bamberger, Volckamer, and Holzschuher windows) or to color leaves and rose petals. Today, these colorations mostly appear completely opaque and black, and exhibit a characteristic crack pattern in transmitted light. The application of tinted varnishes also supports softly painted transitions and color-shading within a single piece of glass. Apart from the already known green (possibly blue) copper pigments, black pigments and yellow, red, and brown iron pigments were detected during analysis. There are indications from the historic literature (Lautier and Sandron 2008, Merrifield 1999) as well as from the analysis (Drewello and Weißmann 2015), that mostly oil-based binders combined with proteins or resins were used. However, further analysis is necessary to identify the organic compounds precisely.

**Flesh Tones**

The examination of the flesh tones reveals a very extensive use of cold paint for the representation of different skin
tones. This is best exemplified on the Volckamer window (figures 5 and 6), where the cold paint layer was applied after the firing of wash, tracing, and shading. For lighter skin tones, the reddish-brown, opaque or semi-transparent cold paint layer was partially used as a shadow. For darker skin sections—for example, faces of older men—the cold paint was applied on the entire surface and highlights were created by removing the cold paint in selected areas (figure 5). In transmitted light, these cold paint layers appear reddish-brown to umber in color. The use of cold paints as flesh tones can be explained in a similar way for all examined windows. Sometimes the aging of the cold paint results in a strong light/dark contrast (figures 2, 5, 6). In such cases, the weathered cold painted areas have been frequently removed or thinned during previous restoration campaigns.

Modeling / Fine Graduation of Brightness Values / Shading
Cold paint is also used to deepen the shading and for modeling shapes, particularly for areas of shadow in tendrils or hair (figure 7), draperies (figure 8), or architectural elements. The analysis of samples taken from the four windows indicates that, similar to panel painting, the shadows were tinted with colored pigments. For example, red paint was used for shadows on red glass, and yellow or brown shadows were made on yellow or clear glass. Today, the chromaticity of these areas is barely recognizable in transmitted light. The cold paints are sometimes situated with the light contours over the fired paint, but in other cases, are also scraped from the fired paint (figures 7, 8).

Gold and Silver Imitation / Brocade
The cold paint was applied relatively thickly and in a versatile way to imitate shiny surfaces such as harnesses, crowning superstructures, and gilded or silvered altarpieces (figures 2, 3, 4, 7, 9). In these cases, cold paint was frequently applied in multiple layers to enhance trace-lines and modeling. It was also used to imitate the shiny golden or silver surfaces of the drapes in the brocades (figure 9). For the shadings in the brocades yellow and red iron pigments were detected during analysis. The shadings of the grey-blue harnesses in the Markgrafen window were tinted with green copper compounds and red-brown iron pigments.

Post Contouring / Hatching
The high firing temperatures of glass in 1500 and the limited thickness of the applied fired paint layer to avoid “cooking” sometimes resulted in incompletely covered trace-lines after the firing. Especially when these are exposed to direct sunlight, the intentionally black or intransparent areas still appear semi-transparent. The cold paint used for this post-contouring of the trace-line areas is also used for subsequent trace-line reinforcements.

Technological Needs
The use of unfired paint layers can be justified as a means to overcome the technological limitations of glass painting: some red and yellow glasses darken in the kiln, covering trace-lines “cook” at a certain thickness, and the brightness values of the fired decoration may vary. Therefore a concluding harmonization of the overall presentation after the firing, particularly across the increasingly volumetric designs of stained-glass windows around 1500, was inevitably necessary.
Application Technique / Tool Marks
Cold paint primarily served as a tinted varnish; it was therefore often applied over the entire surface and then altered using negative techniques that were also available within classic glass painting. However, in contrast to fired paint, unique tool marks are rarely noticeable. This indicates that the reworking of the cold paint layer occurred mainly in its wet state. The slow drying properties of the oil-based paint layer may have been an advantage in comparison to the quickly drying glass paint. It allowed for a very long period of reworking and the correction of mistakes.

Development of Technology
All presented examples of the three different workshops (Wolgemut, Hemmel, and Hitsvogel) show similar applications of cold paint. Apart from the option of a more restrained coloration, cold paint technology allows for the continuation and completion of stained-glass designs, as well as the addition of color-tinted paint layers, without an extra firing.

Interpretation / Evaluation of Results
The visual examination of the featured glass panels revealed a surprising range of large areas with well-preserved cold paint. These results suggest that in many cases the cold painting technique on stained glass was an independent, purposeful process of creation, comparable to the final ‘a la secco’ reworking used in fresco painting or the final oil glazes found in panel painting. Based on these results, it
can be assumed that since the 15th century at the latest, stained glass in Nuremberg was largely created using mixed painting technologies (cold paint and fired paint).

Conclusion
The close examination of four stained-glass windows in Nuremberg, dating from the last quarter of the 15th century to the early 16th century, revealed a wide range of differently colored cold paint. This paper raises the question of whether the extensive use of cold paint on these windows was specific to production in Nuremberg and Strasbourg, where there were no guilds or guild rules restricting the operation of glass painters until well into the 16th century. This paper also suggests another possibility: that the extensive application of unfired paint layers can be explained by the fact that Wolgemut produced panel paintings as well as stained glass and that Hirs vogel worked in cooperation with local panel painters like Albrecht Dürer, Hans von Kulmbach or Hans Baldung Grien. Finally we want to go back to the beginning of this publication where Heinrich Oidtmann refers to the use of cold paint as a “botched job” (Oidtmann 1892). This view regarding the application of unfired paint on stained glass—as an unrecognized artistic technique—must be reversed. The findings described in this publication offer a new perspective on the painting technique of stained glass around 1500. These cold paint layers are an integral part of the artistic design. For the examined stained-glass windows, the use of the “cold technology” has been planned from the outset in the creative process. The technique of cold paint on glass was tried and tested; an increased use of “cold technology” to expand the artistic possibilities in this way may have been influenced by the development of oil painting techniques and the ever-changing creative ideas of the 15th century.

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“The Throne of Grace” – the History and Conservation Strategy for a Medieval Stained-Glass Panel from the Dominican Monastery in Kraków, Poland

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Keywords
Reconstruction; past interventions; archives; ethics

Abstract
“The Throne of Grace” is a 15th century stained-glass panel from the Dominican Monastery in Kraków. At the beginning of the twentieth century, it was subjected to a few conservation treatments involving considerable alterations, such as the change in the positioning of the Medieval panes of glass and the enlargement of the panel. These modifications were based on an 1895 design by an important Polish artist, Stanisław Wyspiański. Basic conservation treatment was initially planned based on information from visual and instrumental analysis, but during the treatment it became apparent that more invasive action might be required. This paper describes the approach that was taken to solve an ethically complicated conservation issue.

Introduction
This paper discusses issues that were faced during the conservation of a Medieval stained-glass panel from the Dominican Monastery in Kraków, which was partially rearranged and enlarged in the first years of the twentieth century. An archival drawing yielding information on the original appearance of the panel was available for reference, as well as a design on the basis of which the panel was enlarged. The main goal of the work presented in this paper was to outline an appropriate conservation proposal based on archival, visual and instrumental analysis. The issues addressed include the cleaning of the exterior of the glass, the stabilization of the whole panel, and most importantly the degree of reconstruction of the missing parts. This paper also considers the pertinent issue surrounding the extent of a conservator’s intervention.

History of the Panel
“The Throne of Grace” is a round panel with a diameter of about 100 cm (figure 1). The Medieval composition has a diameter of about 63 cm and constitutes approximately 30% of the panel. The remainder of the panel such as the decorative border, was added in modern times (figure 2). The panel belongs to the collection of twenty-one stained-glass windows from the Dominican Monastery in Kraków, dated to between the 13th and 15th centuries. It was created in the first half of the 15th century, probably in a local workshop (Pieńkowska 1949). It has been speculated that the panel was originally located in the tracery window situated in the western part of the cloister (Markiewicz, Szyma, and Wålczak 2014, p. 44). During the great fire of Kraków in 1850, the Dominican Monastery was severely damaged, although all the panels survived. In 1895, they were removed from the windows and Stanisław Wyspiański, an important artist representing the Polish Art
Nouveau movement, was commissioned to draw transfers, to document the state of preservation, and to design the reconstruction of the missing parts. The panels were restored according to Wyspiański’s designs, in the first years of the twentieth century at the workshop of Teodor Zajdżikowski in Kraków, before being reinstalled in the windows of the cloister. At the beginning of World War I, the collection was removed again, and stored in wooden boxes in the monastery (Czapczyńska-Kleszczynska and Szybisty 2014, p. 152). After World War II, “The Throne of Grace” and ten other panels were given to the stained-glass studio of S. G. Zaleński in Kraków in 1949 for conservation treatment. Around 1990, three panels, including “The Throne of Grace”, were returned to the Dominican Monastery and have remained in storage until now.

Past Interventions
The archival photographs and drawings allowed for the study of the past interventions within the panel. The history of the aesthetic modifications of “The Throne of Grace” appeared to be quite interesting, and will be described in detail below. According to a watercolour paint-
ing by Ludwik Łepkowski in 1863-64 (figure 3), the panel originally had a smaller diameter probably of around 75 cm that includes a decorative border dated to the Medieval period. The vertical bar of the crucifix was shorter, as well as the robe of God the Father. The painting also showed the presence of infills and mending leads. On Wyspiński’s design created a few decades later (figure 4), there were three ringed borders instead of one, and the lower part of the central composition was modified: the crucifix was lengthened, and the throne as well as the robe of God the Father were enlarged in such a way that they overlapped and interrupted this border.

The panel was modified by Zajdzikowski according to Wyspiański’s design probably after 1902 (Czapczyńska-Kleszczyńska and Szybisty 2014, p. 152). Since it required adjustments in the proportions of the crucifix, the Medieval panes (or broken glass fragments) forming the legs of Christ were relocated and combined with new panes in order to lengthen the vertical bar. As a result, the shorter Medieval shins were replaced by longer ones and re-fitted at the bottom part of the crucifix. The left arm of Christ was modified as well by introducing a new pane instead of the original fragment, which was also

Fig. 2. Dating of glass panels (Diagram: M. Kamińska).

Fig. 3. Watercolour painting by Józef Łepkowski (Photo provided by Fototeka Instytutu Historii Sztuki Uniwersytetu Jagiellońskiego).

Fig. 4. Design by Stanisław Wyspiański, 1895, 110 x 79 cm, ink, watercolour, tracing paper (glued on canvas), Inventory no. MNK III-2227 (Photo provided by the National Museum in Kraków).
transferred into the vertical bar of the crucifix (figure 5). Subsequently, the Medieval panes were separated with modern ones, lacking a logical arrangement. The purpose of this relocation was unclear. Perhaps it was considered preferable to paint new shins on a single pane instead of introducing additional lead cames disturbing the composition. It could also have been the result of a mistake by a craftsman who incorrectly interpreted the fragments of the composition. Regardless of the reason, the original arrangement of the Medieval glass fragments has changed.

Copies of the current versions of “The Throne of Grace”, as well as the remaining panels belonging to the collection, were recently made by a stained-glass workshop in Kraków and placed in the windows of the cloister in the monastery.

**The Condition**

Amongst the three panels that were found in the monastery, “The Throne of Grace” was in the worst condition.

Its structure was weakened due to the incomplete and damaged lead matrix. Glass losses were detected mainly within the upper and bottom parts of the border. The external ring of the border was also missing. Many panes of glass from the twentieth century were cracked. Moreover, the paint used for the trace lines from that time was of bad technical quality. The outlines were cracked, badly fired and therefore incomplete, especially on the red panes of glass.

Fragments of Medieval glass were missing as well, and the Medieval painted composition was not entirely legible. The painted trace lines were partially lost, as illustrated by figure 6. The Medieval glass was deteriorated on both sides. The internal surface of the unpainted glass was rather smooth but covered with dark dots which, in transmitted light, appeared as opaque areas mainly observed on the purple glass. The condition of the external surface was worse. It was rough, matte and covered with weathering products (figure 7), which in some places was quite difficult to distinguish from the severely deteriorated glass.

The advanced degree of deterioration was evident when comparing the protected borders of the glass panes under the lead cames to their exposed surfaces (figure 8). Above all, the difference between the thickness of the protected and unprotected glass was tactile. Furthermore, the remains of the trace lines found on the backside of the pane depicting God the Father’s head evidenced that a considerable part of the paint layer had been lost (figure 9).
The Inpainted Infills Introduced in the First Quarter of the Twentieth Century

The differences in the aesthetic quality of the inpainted infills introduced in the twentieth century denoted that at least two glass painters were involved in the work on the panel. The areas depicting the light parts of the robe of God the Father seemed to have been executed by an inexperienced painter. The layer of thin grisaille was applied unevenly, and the disturbing effect was highlighted by the rough outlines. The folds of the robe painted on the red flashed glass were probably done by the same painter. The outlines within the body of Christ on the light purple glass seemed to be of better aesthetic quality. This was also seen within the decorative border. The border was painted exactly on the same kind of glass as the light elements of the robe, so there was no doubt that all the glass panes were created in the same workshop. In that case, it was surprising that infills reflecting such different skill levels were introduced within the panel. Finally, all of the external surfaces of the new panes were covered with a thin layer of grisaille to match the deteriorated Medieval glass.

Fig. 7. External side of the panel seen in reflected light, before cleaning (Photo: P. Gąsior).
Glass and Paint Analysis -
Materials and Methods

We decided to carry out instrumental analysis in order to obtain specific information on the composition of the Medieval and twentieth-century glass and paints. The aim was to broaden our knowledge of the panel, and possibly, to find a relationship between the condition of the twentieth-century paint and its composition. X-ray fluorescence (XRF) spectroscopy was chosen for a preliminary, non-invasive investigation. Prior to the conservation treatment, we also decided to identify the layers present on the external surface of the Medieval glass by means of X-ray powder diffraction analysis (XRPD).

XRF analysis was conducted with a Bruker M6 Jetstream macro-scanner equipped with a rhodium X-ray tube, polycapillary optics, and a 30 mm² SDD detector. For the measurements, the X-ray tube was used without a filter and the voltage and current were set at 50 kV and 0.6 mA respectively. The spot size used was 800 µm. The distance between the object and the measurement head ranged between 0.8 and 1.5 cm. Dwell time of 50 ms per pixel was used.

XRPD analysis was carried out using a PANalytical–Empyrean diffractometer, equipped with Cu Kα (λ = 1.5406 Å) radiation source, within the 2θ range from 5° to 908° and with a step size of 0.028°/min.

Glass and Paint Analysis:
Results and Discussion

The elemental maps obtained with macro-XRF showed significant differences between Medieval and twentieth-century glass and paints. A strong signal from potassium was detected in the unpainted Medieval glass, and a weaker one from the areas overlaid with a thin layer of grisaille. However, the presence of potassium was also noticed in the twentieth-century yellow and red flashed glass (both the clear and red layers). The results showed that all of the modern glass panes were distinguished by the presence of chromium. The Medieval paint was iron-based, while the paint used for the border and the infills within the halo contained mainly copper, cobalt, and manganese. The paint used for the modern composition, which was earlier referred to as being of worse aesthetic quality, was rich in zinc (figure 10). According to the results, the twentieth-century paint was also characterized by a higher lead content.

The results provided a general overview of the composition of glass and paints. The obtained results were in agreement with published data on glass analysis and paint (Caen et al. 2015). Macro-XRF images provided interesting information on elemental distribution, specifically concerning the vitreous paints, but in order to draw reliable conclusions, more data is needed.

The analysis of the layers on the external surface of the Medieval glass revealed the presence of gypsum CaSO₄·2H₂O, syngenite K₂Ca(SO₄)₂·H₂O and arcanite K₂SO₄. This corresponded to what was to be expected according to published data on medieval glass and its corrosion products (Melcher and Schreiner 2013, pp. 626-633).
Conservation and Restoration Proposal

Since the lead matrix was a modern reconstruction and partly damaged, most of the panel was dismantled, in order to allow for a precise bonding of the broken panes and to compensate losses in the missing areas. The internal surfaces of the Medieval and modern glass panes were cleaned with a solution of ethanol and distilled water to remove loose dirt. The cleaning of the external surface, however, required special care. The distinction between the gel layer on the Medieval glass and the weathering crust was difficult. As known from various studies (Müller et al. 2000), the crust contains hygroscopic salts and thus represents a potential danger to the glass. However, the depleted gel-layer acts as a barrier preventing the core glass from further deterioration. Any risk of over-cleaning should therefore be avoided. For this reason, only the brittle and loose crust was reduced by mechanical means using a scalpel, over the few areas where it disturbed the legibility of the panel.

Two types of adhesives were considered for the bonding of the broken glass panes. Epoxy resin (Araldite© 2020) was used for the modern glass. The Medieval glass was to be bonded with an adhesive with a higher viscosity, such as Paraloid B72, to prevent excessive penetration into the deteriorated substrate.

The main challenge was related to the treatment of the inpainted infills introduced in the first years of the twentieth century. Specifically, it had to be decided whether the panel should be kept in its current state or returned to its original Medieval state documented by Łepkowski. According to the current condition of the panel and based on an archival picture, there was no doubt that the border was originally larger and corresponded to Wyspiański’s design. Consequently, the border contained one more ring, and the throne was equipped with a decorative step at the bottom.

Owing to the copy by Łepkowski, we were able to define the original form of the depiction. Despite the fact that the painting was not precise, it was obvious that the proportions of the crucifix, as well as the composition and colour of God the Father’s robe were different. We had strong archival evidence showing the modifications that were made at the beginning of the twentieth century.

A few solutions were discussed. The first option was to bring the panel back to one of its past states according to the copy made by Łepkowski. The second option was a reconstruction based on Wyspiański’s design. The first solution was immediately considered as being too invasive. Indeed, the panel could be brought back to its original size, but approximately 50% of the actual panel would have to be removed, and that was out of the question. The second option involving the reconstruction of the border and the throne according to Wyspiański’s design seemed more appropriate and in accordance with the Corpus Vitrearum Guidelines (CVMA 2004). The losses could be reconstructed based on the existing design, so there was no risk of introducing incongruous elements. Nevertheless, such intervention seemed quite intrusive. A safer and more ethically appropriate option was to not modify its composition, but to perform only necessary conservation treatments and to compensate missing parts without any reconstruction of the painted composition. However, some of the missing twentieth century fragments of the throne were found in the conservation workshop of the monastery during the course of treatment. These fragments obviously

Fig. 10. MA-XRF image showing the zinc distribution (Image: M. Płotek).
needed to be reintroduced into the panel. As they extended beyond the actual composition, the addition of a surrounding border for structural reasons was necessary. Therefore, it seemed appropriate to reconstruct the panel according to Wyspiański’s design.

In addition, the reconstruction of the body of Christ had to be considered. As shown in figure 5, the fragments of the legs and the arm could easily be returned to their former state by attaching the broken and displaced pieces of glass. These pieces were amongst the most valuable parts of the panel, so it seemed reasonable to put them back in the correct configuration. This would also improve the panel’s legibility, though it would introduce significant modifications within the crucifix. The bonding and relocation of the Medieval glass panes would require the removal of the modern infills, although this also allowed for their replacement with new infills that were better matched aesthetically.

After many discussions involving conservators, art historians and the owners, and weighing the pros and cons of each option, we decided to bring back the original arrangement of the Medieval panes, according to the copy made by Łepkowski, and to replace the twentieth-century fragments within the crucifix with new reconstructions. An additional surrounding border had to be introduced for structural reasons, as mentioned above. With regards to the reconstruction of the painted decoration, we decided that the infills and new panes of glass within the crucifix and background would be integrated in such a way that they fit in terms of colour and transparency (toned with vitreous paints), without reconstruction of the painted depiction. In this way, the conservation intervention would be distinguishable but will remain aesthetically acceptable.

Conclusion

The preliminary scientific analysis provided us with additional information on the condition and the materials used in the panel. Undoubtedly, more advanced analyses have to be carried out to obtain more quantitative data about the composition of the glass. The dark areas on the purple glass also bear further examination. Perhaps a relationship between the deteriorated modern paints and their composition will also be found.

Regarding the difficult decision of selecting the visual composition to which the panel has been restored, the archival drawings proved to be most helpful. Łepkowski’s watercolour painting provided insight into the original composition of the panel, without which the determination of the original location of the Medieval panes of glass would not be evident. Wyspiański’s design confirmed the presence of one additional surrounding border, and on its basis a reconstruction could be made. Conservators commonly encounter the issues presented in this paper, where difficult decisions on the reconstruction and treatment of later additions have to be made (Cortés Pizano 2001; Pinto 2001). This paper shows that compromises are necessary and priorities have to be set in order of importance where no perfect option is available.

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Notes

1. In 1963–4, Ludwik Łepkowski painted watercolour copies of all known medieval stained-glass panels in Małopolska (Małkiewiczówna 2000, p. 9).
2. The original diameter was calculated based on the present diameter of the Medieval part.
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Protection of Stained-Glass Windows – Case Studies in Poland

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Keywords
Stained glass; protective glazing; glass dosimeters; outdoor pollutants; weathering

Abstract
Several restoration projects of stained-glass windows have been performed in Lower Silesia (Poland) since 2010. The aim of the projects was to protect stained-glass windows against environmental impact of industrial pollutants and acid rain by installing a protective glazing. The usefulness of protective glazing has been proved by climate measurements and determination of environmental impact before and after its installation. The concentration of acid pollutants such as SO₂ and NOₓ inside the church has decreased considerably after installation of the glazing. The relative humidity near the historic windows was about 70-90% instead of more than 90% without any protective glazing. Condensation will not occur on the original stained glass with paint layers anymore. The results of a glass dosimeter study prove that the environmental conditions are much better after installation of a protective glazing.

Introduction
The German-Polish Foundation for Cultural Care and Monument Conservation has the task of promoting the protection of cultural assets in Poland through restoration and conservation measures. This task includes measures to sustainably protect endangered objects. As a result of these projects, model solutions are being developed which can then be generally adopted for similar problems elsewhere. In this context, particular attention is attributed to important artefacts that are already showing visible signs of damage and where it is almost certain that further dramatic transformations and material losses can be expected in the near future if no effective protective measures are taken.

The project presented here has included three such cases. Protective glazing has been installed on stained-glass windows in the Catholic parish church in Ścinawka Dolna, the Catholic parish church of the Guardian Angels in Wałbrzych, and the Church of Peace in Jawor to provide examples and to sustainably protect them from environmental impacts. The design and installation of the protective glazing for the restoration of the stained-glass windows was carried out by the Creo Beata Oleszczuk restoration workshop in Wrocław in close cooperation with the experts and the monument authorities involved in the project. Efficacy of the measures performed was confirmed by means of scientific studies such as climate measurements, pollutant measurements, and the assessment of the damage potential of the environmental conditions using glass dosimeters.

Why Must Stained-Glass Windows be Protected?
Basic conclusions on the causes and mechanisms of glass weathering can be drawn from the study of historical stained-glass windows (Müller et al. 1997; Torge et al. 1998). In medieval stained-glass windows the sensitive glass substance itself is affected, while in the more stable
19th century glasses it is the paint layers that lose their adhesion to the glass surface. Both corrosion mechanisms constitute distinctly different decay processes. From the fact that comparatively little changes occurred even in medieval windows before the start of the industrial era (damage by vandalism and contamination excluded), and dramatic deterioration of the condition has only been seen since the last decades of the 19th century, it could be concluded, and later scientifically proven, that the interaction between high humidity and pollutants emitted by the industry and the traffic is responsible for the damage. Acidic gaseous pollutants such as SO$_2$ and NO$_x$ are considered as having been major parameters causing degradation (Fuchs et al. 1991; Brinkmann, Bornschein, and Fitz 2000; Davison 2003; Sterzing 2010).

**Protective Glazing**

Historic stained-glass windows damaged by the environment have been restored responsibly for decades, in accordance with the principles of sustainable conservation. To provide protection against further environmental influences, protective glazing can be installed. Modern flat glass replaces the original glazing, which in turn is offset by only a few centimetres inwards and fixed to the exterior protective glazing by suitable mounting systems. Between the original and external protective glazing there is a gap through which air from the interior of the church flows. This ventilated and so-called isothermal protection system has predominated across the European continent (Oidtmann 1994). Systematic studies on the effectiveness of protective glazing have been carried out in many places in Europe (Bernadi et al. 2013; Godi, Kontozova and Van Grieken 2006; Kontozova-Deutsch et al. 2008; Kontozova-Deutsch et al. 2011; Hör 2012) and have provided satisfactory information about the basic technical and design requirements (internal ventilation, gap width, air-tightness). The claim of a "quasi-museum" protective effect stipulated for stained-glass windows has not yet been achieved. Extensive climate measurements that were carried out in the vicinity of the stained-glass windows, especially in the space between the protective glazing and original windows, showed very strong influences arising from the buildings, physical condition, thermal characteristic, orientation of the windows, and outdoor climate (Oidtmann 1994; Oidtmann et al. 2000). Therefore it is practically impossible to make a general prediction about the protective effect for a concrete object and it is advisable to check the specific type of glazing for every object. Several monitoring campaigns on protective glazing are published in the literature, for instance in the Marienkirche in Frankfurt/Oder (Hahn 2008) and in the Divi Blasii church in Mühlhausen (Garrecht et al. 2011). The effectiveness of restoration measures combined with the installation of protective glazing was verified in projects in the cathedrals of Havelberg, Halberstadt, Stendal, and Erfurt, and in the churches in Panschwitz-Kuckau and Quedlinburg (Torge, Bücke, and Feldmann 2011; Hahn 2011).

**Ścinawka Dolna Parish Church**

The Ścinawka Dolna (Niedersteine) Catholic parish church was built in 1900-1903. The collection includes 26 windows with stained glass rich in colourful designs with figurative and ornamental representations. Franz Xaver Zettler Royal Bavarian Court Stained-glass Workshop (Königliche Bayerische Hofglasmalerei Franz Xaver Zettler) produced the uniformly designed cycle. The windows were only protected by wire mesh until 2012. Within this project, protective glazing was installed on each of the three transept windows on the northern and southern side. Laminated safety glass (LSG) was chosen as the protective glazing material because of the low height of the windows and the potential of mechanical damage. Right-angled lead lining was used as the protective glazing in the windows’ ornamental areas and the main lines of the compositions were highlighted using contour lead lining in the figurative areas (figure 1, 2).

**Walbrzych Parish Church**

The Catholic parish church of the Guardian Angels in Walbrzych (Waldenburg) was built by the architect Alexis Langner from 1900-1904. Franz Mayer Royal Stained-glass Manufactory of Munich (Königliche Glasmalereianstalt Franz Mayer, München) made the stained glass in an ornamental design in 1910. Twenty-three of a total of 31 windows have been restored and re-installed with protective glazing during the past two decades. On the northern side of the nave, two large 11.50 m high, 2-lancet, un-restored
Fig. 1. 2. Ścinawka Dolna parish church: Windows nIV, nV, and nVI after restoration and installation of protective glazing. (Photo: Federal Institute of Materials Research and Testing, Berlin, Germany).
windows interrupted the otherwise harmonious appearance of the church interior (figure 3, 4). These two windows were removed in 2013, restored, and re-installed with a state-of-the-art protective glazing. The remaining protective glazing with external ventilation, which was not very efficient at reducing contaminants, moisture, or dust, has been replaced by a modern system with internal ventilation. Small-sized rectangular laminated safety glass was used for this protective glazing.
Church of Peace in Jawor

The Protestant Church of Peace in Jawor (Jauer), a three-aisle basilica with galleries integrated in the side aisles, has been on the UNESCO World Heritage List since 2001 and is an example of the sophisticated Silesian timber and wood technology. The Wrocław fortress engineer and architect Albrecht von Säbisch designed it from 1654-1655. Three stained-glass windows in the choir area represent a special feature. They originate from the late 19th century and already show significant damage of the paint layers (Gajewska-Prorok and Oleszcuk 2001). The windows consist of hexagonal bull’s-eye panes with painted edging and pictorial representations in the upper areas. A protective glazing was considered necessary to protect the windows against environmental impact and mechanical damage.

While protective glazings for stained glass in stone window openings have been state of the art for many years, such...
structures have not yet been used for wooden churches. Heavy construction and complex systems needed to be avoided. A contracted structural engineer calculated that the protective glazing would increase the load on the wooden studs only by about 2%, if laminated safety glass is used. All major stakeholders decided on the installation of this preferred protective glazing, and its design details (figure 5, 6). Different variations of protective systems were discussed based on sample panels and a design that appeared practicable and appropriate was adopted for all three windows.

Environmental Monitoring on the Windows with Protective Glazing
The efficacy of protective glazing was checked with climate and pollution measurements and glass dosimeters on selected windows over a 12-month period. Temperature and relative humidity (RH) on the inside and outside of the original glazing (Position 1, Pos. 2) and on the inside and outside of the protective glazing were measured (Pos. 3, Pos. 4) during the project. Air velocity was determined in the gap between the original and protective glazing.

Emission measurements were carried out with passive samplers both at Pos. 1 and 4 and in the gap over a period of 4 weeks. Glass dosimeters can help record complex corrosive impacts site-specifically on monuments or parts of objects.

The operating principle of glass dosimeters is based on the fact that changes in sensitive glass surfaces can be detected qualitatively and quantitatively by infrared (IR) spectroscopy based on their exposure (VDI 1993). Measurements before and after exposure can determine the extinction difference ($\Delta E$ value) in the $3350 \text{ cm}^{-1}$ band range, which is a measure for the expected damage potential of complex environmental conditions. The larger the $\Delta E$ value, the greater the damage potential. The glass dosimeters were exposed at Pos. 1, 2, and 4. They were prepared and evaluated by the Fraunhofer Institute for Silicate Research Würzburg (ISC), Bronnbach Branch (Maas-Diegeler 2013). Specific features of the glazings and the measurement periods are given in Table 1.

<table>
<thead>
<tr>
<th>Monument / window</th>
<th>Time period for climate measurement</th>
<th>Specific size and features of the protective glazing</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ścinawka Dolna</td>
<td>12th Dec. 2012 – 09th Dec. 2013</td>
<td>5.32 m x 1.57 m</td>
<td>glass dosimeter</td>
</tr>
<tr>
<td></td>
<td></td>
<td>air inlet (bottom) 1-2 cm</td>
<td>passive sampler</td>
</tr>
<tr>
<td></td>
<td></td>
<td>air outlet (top) 1 cm</td>
<td>11th Dec. 2012 — 11th Jan. 2013</td>
</tr>
<tr>
<td>Ścinawka Dolna</td>
<td>17th Sep. 2012 – 26th Feb. 2013</td>
<td>11.50 m x 2.10 m</td>
<td>glass dosimeter</td>
</tr>
<tr>
<td>nXII</td>
<td></td>
<td>air inlet (bottom) 3-4 cm</td>
<td>passive sampler</td>
</tr>
<tr>
<td></td>
<td></td>
<td>air outlet (top) 1-2 cm</td>
<td>11th Dec. 2012 — 11th Jan. 2013</td>
</tr>
<tr>
<td>Jawor</td>
<td>10th Dec. 2013 — 19th Aug. 2014</td>
<td>3.50 m x 1.26 m</td>
<td>passive sampler</td>
</tr>
<tr>
<td>sII</td>
<td></td>
<td>5-6 cm gap</td>
<td>11th Dec. 2012 — 11th Jan. 2013</td>
</tr>
<tr>
<td></td>
<td></td>
<td>air inlet (bottom) 2-3 cm</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>air outlet (top) 1-2 cm</td>
<td></td>
</tr>
</tbody>
</table>

All measurement results are shown in detail in the final report of this study (Torge et al. 2015).

Table 1: Time period for measurement and specific size and features of protective glazing.

Effect of Protective Glazing on Climate and Airborne Pollutants
Temperature and relative humidity are key factors that influence the degradation of historic stained-glass windows. An increase of 10 K in temperature doubles the rate of many chemical reactions. In addition, rapid temperature changes may cause tension in composite materials with different coefficients of expansion, leading to material loss.

The average temperatures measured were between 0 and 20°C, both on the northern and southern side in Ścinawka Dolna and at the northern window in Walbrzych. Windows on the south side reached peaks above 30°C.
and the temperature increased with increasing height of the window. Therefore, stained-glass panels at greater heights are more vulnerable to high temperatures and temperature changes than those at the bottom. A protective glass also leads to a temperature increase in the gap, which likewise affects the temperature of the outer side of the original glazing. On south facing windows, temperatures up to 8 K higher were measured at the outside of the original glazing (Pos. 2) than at the outside of the protective glazing (Pos. 4). However, rapid temperature changes impacting the original glass are diminished, as the outer protective glazing prevents any direct shock from sudden weather changes (such as sudden rain); therefore, temperature changes are slower on the original glazing than those seen directly on the protective glazing.

In winter the protective glazing produces a temperature gradient from the outside inwards. It is always colder outside than on the original glazing. Thus in Walbrzych values of up to -4.5°C were measured on the inside of the original glazing (Pos. 1) at ambient external temperatures of about -10°C.

The interaction of temperature and relative humidity can cause damage from ice or condensation on painted glass surfaces. Relative humidity has an influence on the formation of moisture films on material surfaces and the associated diffusion that produces an ion exchange in near-surface areas, which starts corrosion processes in glass. Therefore, relative humidity near the original glass should not exceed 80%. However, the windows examined failed to permanently adhere to this ideal value. The values most commonly measured on the original glazing over the year were between 70 and 80% RH, but also between 80 and 90% RH up to one third of the time. Maximum values were just over 90% (RH\textsubscript{max} 90.3%), so condensation can be excluded. On the other hand, maximum values of up to 100% RH were recorded at Pos. 3 and 4 on the protective glazing. Running water was observed, in particular, on the inside of the protective glazing of the windows facing south in Ścinawka Dolna. Without protective glazing, the high humidity of the external environment would also produce precipitates directly on the outside of the original glazing.

The benefit of protective glazing in terms of improving relative humidity values can be determined by comparing the RH on the outside of the protective glazing (Pos. 4) with RH on corresponding positions on the outside of the original (Pos. 2) during the course of a year. The efficacy of the protective glazing clearly lies in the fact that ranges of high relative humidity (90-100%) are no longer found at Pos. 2, or they are significantly shorter than without protective glazing, which prevents condensation on the originals. This effect was clearly demonstrated with results from climate measurements (figures 7, 8).

Emission measurements using passive samplers show that a well-functioning protective glazing is able to significantly reduce the concentration of airborne pollutants (SO\textsubscript{2}, NO\textsubscript{x}) on the stained-glass windows. High pollutant concentrations measured outdoors are no longer detected inside (figure 9). In combination with a lower humidity relative to the outside, the damage potential of the environment can be regarded as significantly lower with protective glazing.

Fig. 7. Ścinawka Dolna parish church: Frequency ranges of relative humidity on panel IV1, Pos. 2, Pos. 4 in % of the measurement time. (Photo: Federal Institute of Materials Research and Testing, Berlin, Germany).

Fig. 8. Walbrzych parish church: Frequency ranges of relative humidity on panel nXII1b, Pos. 2, Pos. 4 in % of the measurement time. (Photo: Federal Institute of Materials Research and Testing, Berlin, Germany).
Fig. 9. Concentration of pollutants measured with passive samplers in Wałbrzych, window nXII, and Ścinawka Dolna, window nV and nV (P1, P2, P4). (Photo: Federal Institute of Materials Research and Testing, Berlin, Germany).

Fig. 10. ΔE-values of glass dosimeter studies on external protective glazings in Wałbrzych and Ścinawka Dolna (Maas-Diegeler 2013). (Photo: Federal Institute of Materials Research and Testing, Berlin, Germany).
Glass dosimeters have been established in monument conservation for decades and can be used for comparative assessment of complex environmental stresses (Römich 2004). The investigations show that the glass dosimeters (type MI) react very sensitive to environmental influences and provide significant data for the evaluation of damage potential. The professional installation of protective glazing resulted in better environmental conditions for the stained glass windows in all cases studied (figure 10). High ΔE-values were found at Pos. 4 (outside) in Wałbrzych and Ścinawka Dolna. The ΔE-values correlate with SO₂ and NOₓ-concentrations. The outside concentration of SO₂ and NOₓ is higher in Wałbrzych than in Ścinawka Dolna, and so are the ΔE-values. In the gap between the original and the protective glazing (Pos. 2) and inside the church (Pos. 1) the NOₓ and particularly the SO₂ concentration are very low. The ΔE-values of the glass dosimeter at Pos. 1 and 2 are also very low and indicate a low risk of damage on stained-glass windows. Microscopic investigation of the glass dosimeter surface showed significant glass corrosion only at Pos. 4 (Maas-Diegeler 2013).

Summary
The project demonstrates a great example of Polish-German cooperation in the field of restoration, conservation, and protection of our common cultural heritage. The specific arrangement of the protective glazing, its design, and its financial aspects was decided by all major stakeholders for every object. These specific solutions are models for continuation of the work, as has been done already in the Catholic parish church of Wałbrzych in the last few years. The efficacy of protective glazing clearly lies in the fact that high relative humidity (90-100%) virtually no longer occurs on the outside and inside of the original glazing, and formation of condensation on the original glazing is prevented. In 19th century glasses it is the paint layers that lose their adhesion to the glass surface by chemical corrosion processes. This was detected in all three churches in the beginning of the restoration project. Damage is expected if high humidity and high concentrations of acidic airborne pollutants occur simultaneously. Pollutant measurements show that a well-functioning protective glazing can keep airborne environmental pollution (NOₓ, SO₂) away from the stained glass. High concentrations of pollutants found outside are much lower inside the church.

Complex corrosive effects were quantitatively determined site-specifically for the Catholic parish church in Ścinawka Dolna, the Catholic parish church of the Guardian Angels in Wałbrzych, and the Protestant Church of Peace in Jawor in this project. Results obtained at the three monuments investigated in Poland confirm results obtained at other sites in Europe. The glass dosimeters indicated only very low corrosion rates on the inner sides of the originals both by IR spectroscopy and microscopy; the outside however, showed significant glass corrosion.

Protective glazing is a well-established preventive measure for avoiding the loss of valuable cultural assets and sustainably preserving them for the future. Proper scientific studies and examples of practical implementation of this type of program provide an incentive to continue the installation of protective glazing in Europe.

Acknowledgements
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Glacier Transparencies Research and Conservation Challenges

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Keywords
Glacier; stained-glass imitation; tracing paper; copal varnishes; transparencies

Abstract
This paper presents research focused on transparencies: lithography prints on paper adhered to a glass pane to imitate stained glass. This popular nineteenth-century technique was significantly improved by McCaw, Stevenson and Orr Ltd and patented as the Glacier. The complex nature of the transparencies pose interesting and challenging conservation issues, requiring a multi-disciplinary approach. Often overlooked in terms of conservation treatment, these disappearing curiosities have suffered extensive damage and loss. Supported by art historical research and chemical analysis, each stratum of these multi-layered structures is identified. An exploration of their function, installation and exposure to environmental factors, will lead to a better understanding of the deterioration processes.

Introduction
Innovation, a theme central to this conference, can be interpreted as a new creation or solution. The nineteenth century was a period of great innovation, and the development of Glacier stained-glass imitations typifies this in several ways, supplying the market with a new technology. This innovative product combined materials not traditionally merged, and thus poses a new challenge for today’s conservators. The deterioration of these complex multi-layered objects challenges the conventional separation of conservation disciplines. It requires a collaborative approach and new treatments. This paper is based on preliminary research aimed at the identification of key issues through an investigation of the manufacturing process, material characteristics and aging issues inherent to the technique, in order to inform the conservation of this vulnerable medium.

What is the Glacier
The nineteenth-century Gothic Revival hailed a renewed fascination with stained glass, and as a result inspired the creation of alternative techniques in imitation of this traditional craft. Stained-glass imitations, commonly called transparencies, form a varied group which usually is comprised of a mass produced translucent lithographic print on textile or paper, always adhered to clear glass and coated with varnish. Glass is not the primary aesthetic element, instead it forms an integral structural part of the object, upon which the decoration is mounted. The Glacier is a patent trade name of a particular form of transparencies manufactured by McCaw, Stevenson and Orr Ltd (McSO), a Belfast company. While the transparency is a generic name of any type of stained-glass imitation, the Glacier refers only to the lithography paper prints mounted on glass and manufactured by McSO. The Glacier closely resembled stained glass, sharing similar designs, functions, installation methods and destinations, and aspired to compete with the stained-glass market. A wide variety of designs were available, as evidenced by surviving catalogues (figure 1). Designs often imitated stained glass by copying existing windows, complete with lead lines (figures 2, 3).

The Glacier was patented by McSO in 1880-2. Whilst they cannot be credited with the invention of stained-glass imitations (Blondel 1993, p. 333; Allen 2013, p. 149), they significantly improved upon pre-existing techniques,
modernising the technology and marketing strategies. They simplified the craft making it possible to apply a factory-premade product at home by non-professional customers. The Glacier was cost and labour-effective and marketed to new audiences, mainly women, who were not traditionally associated with the professional art world. Unsurprisingly, transparencies raised considerable criticism from the nineteenth-century professional stained-glass world, and were consistently excluded from academic writings of the time—a practice that has largely continued to today.

Fig. 1. Glacier lithography design of the Ascension displayed in the catalogue of McCaw, Stevenson and Orr Ltd. (image source: McSO n.d., p. 31).

Fig. 2. Ascension (SGM, ca. 1890, size 445 x 2045 mm). Transmitted light image showing the creative application of various Glacier designs onto one panel (photo: M. Adamczak).
The Glacier was the most popular type of transparency sold in the UK until the First World War, when the fashion for imitations significantly dropped (McCabe 1990, p. 99) due to changing tastes and visible deterioration with aging. Glacier panels must have been readily discarded as only a handful of examples have been found in the UK. Among those identified, only two schemes remain within their original context: two panels (St Paul and St Peter) from St Peter Church in Prickwillow (figure 4), and three panels (the Parables of the Sower and the Lost Sheep, ...
and the Ascension) from St. Hilda’s church in Cowcliffe, Huddersfield, UK (figures 2, 3). However, the panels from Prickwillow were de-installed in the summer of 2013. Two of these were acquired by the Stained Glass Museum in Ely (SGM). The Parable of the Lost Sheep, was later rejected by the Museum due its very poor condition, and given to the University of York in April 2014, where it became the focus of research (Adamczak 2014).

Materials Used
The manufacturing processes for Glacier were highly secretive, thus identification of the materials used and production processes was a challenge, and made possible only through the study of written archival sources, technical analysis and direct observation. Two samples from the Parable of the Lost Sheep panel were sent for compositional analysis to the laboratory of Dr. Erhard and Professor Elisabeth Jägers, Labor Jägers in Bornheim, Germany (Jägers 2014). An evaluation of the test results, alongside archival research and direct observation enabled the successful identification of the types of paper, adhesive, and coating materials applied on the glass. The letters of Stephenson, the inventor and owner of the Glacier patent, are an essential archival resource, particularly his letter to the solicitors, describing vaguely the stratification and materials used (McCabe 1990, pp. 16-7).

Paper
Stephenson’s letter mentioned only that a new kind of paper was used, specially processed in order to achieve better transparency. Indeed, in the 1870s, new wood pulp paper processing was developed that increased transparency through excessive beating of the pulp (van der Reyden 1993; Page 1997; Laroque 2000, p. 22). Translucent effects were also achieved by impregnating papers with oils, gums, and resins (Bachmann 1983; Homburger and Korbel 1999). The sample analysis confirmed that wood pulp was used (Jägers 2014).

Paper Sizing
According to the laboratory results, it is uncertain whether or not the paper was sized (Jägers 2014). A water extraction of the sample confirmed the presence of a carbohydrate (probably starch), and of proteins that could have been part of the paper sizing. Both were traditionally used as sizing, and the latter could be gelatine obtained from animal sources (Schellmann 2007, p. 55). The Glacier catalogues mention a gelatine layer, and the company is known to have had a separate “gelatine” department (McSO, n.d. b). Alternatively, starch or animal glue could have been used as an adhesive.

Furthermore, a lead-based pigment, “Kremnitz white,” was mentioned in the letter (McCabe 1990, pp. 16-17). It supposedly reflected light better and more strongly, giving vividness to the colours in daylight. It is possible that this lead white was added to the sizing.

Printing Inks
According to the tests carried out, the printing inks contained drying oils as binders (Jägers 2014).

Varnish – Applied by the Manufacturer
Laboratory tests identified a layer of copal resin mixed with oil applied on both sides of the paper (Jägers, 2014). It must have been the varnish mentioned by Stephenson, which was applied on all Glacier prints during manufacture. It was described as a gum solution, insoluble in water, and more flexible than a spirit varnish due to its long drying time. During the nineteenth century, copal resin was commonly called gum (Treatise 1773, p. 5; Scientific American 1872, p. 383). Neither Stephenson’s letter nor the test results reveal the solvents or additives used in the varnish. Nevertheless, the nature of copal varnish preparation was presented in recipes published in the eighteenth and nineteenth century, which advised thermal processing and the use of numerous solvents: turpentine, vegetable oil and colophony; turpentine and ethereal oils; sulphuric ether and rosemary oil; or alcohol with added camphor as solvents (Treatise 1773, pp. 4, 30; Geitner 1813, pp. 125-6; Scientific American 1872, p. 383). Copal resin was very popular, but mostly used on wood, leather, metal and paintings. The use of the resin on paper is evidence of an innovative application of a pre-existing material in a new context (Treatise 1773; Geitner 1813; Fearon 2009).
Adhesive
The laboratory report was inconclusive regarding the presence of an adhesive. The presence of starch and proteins could suggest the use of glue, though more likely was an element of sizing, implying the varnish itself as a potential adhesive. This hypothesis can be supported with archival findings.

According to Stephenson, the oil-copal varnish also acted as a binder: "[w]e used a different and more flexible varnish…we passed the label entirely through a solution of gum making them adhesive all over front and back faces" (McCabe 1990, pp. 16-17). Apparently, this varnish, when soaked in room temperature water for 20 minutes, became sticky enough to adhere it to the glass (McSO n.d. b, p. 4a). Nevertheless, it is a very confusing note, since even the “soft” copal resins would not be activated in water (Fearon 2009, p. 105).

It is worth mentioning that the catalogues recommended a layer of binder as an adhesive, produced and sold by McSO. Preparation instructions suggest using an animal glue (McSO n.d. b, pp. 6-7). These catalogues also provided recipes for homemade adhesives based on gelatine or “fine glue” soaked in vinegar (McSO n.d. a, p.7).

In the test results, the layers from either side of the paper were described as a varnish and a binding medium (Jägers 2014). The presence of two separate layers could suggest that one was the original applied during manufacture, the other could have been applied at home as a coat of glue that would stick the print to the glass. Alternatively, the paper might have been varnished twice during manufacture. Aforementioned types of adhesives may have been applied at home by customers, thus in addition to a basic range of adhesive ingredients used by the manufacturer, further variation may be found when compared against other case studies.

Varnish – Home Applied
The tests identified a final layer of drying oil with some resin, containing dirt, soot and dust, suggesting that one side had been exposed to the environment. Indeed, the catalogues recommended that all assembled pieces should be unified with an oil of fine quality. They recommended “copal” or “carriage” varnishes as the most suitable, which was evidenced by the laboratory results (McSO n.d. a, pp. 6-7; Jägers 2014).

Deterioration Issues
Although Glacier decorations were advertised as durable and everlasting (Graphic 1890, p. 517), the catalogues also provided instructions on their removal. The panels from Cowlcliffe and Prickwillow were examined in situ, and are all in a very poor state. An examination and comparison of their exposure to various conditions can increase understanding of their aging characteristics and further define the environmental parameters that may have been harmful to them.

Location of the Panels and Deterioration Issues
The Prickwillow panels remain installed in the redundant church in their original locations. However, the Cowlcliffe panels were removed from the church in 2013, and replaced by a new window. Thus installation details were gathered from photographic evidence, archival findings and detailed descriptions given by David Morris (personal communication, March-July 2014), the Glass Design stained-glass workshop, who removed the Glacier panels. All of the lithography prints had been adhered to sheets of glass. Those panels were then installed in a church window, the glass side facing the viewer, and screened by the exterior quarry glazing (figures 4, 5). As such, the fragile paper layers were trapped in a sealed environment, creating a microclimate due to the lack of ventilation, which is likely to have affected the condition of the transparencies. Noteworthy, quarry panels were the church’s primary original windows, whilst the Glacier was a later addition and formed a secondary, purely decorative internal glazing. The Prickwillow panels appear to have been adjusted recently, and are tilted within their frames to enable the run off of moisture from the decorated surface, presumably in response to issues of humidity.

The air flow was measured during a site visit to Prickwillow, which confirmed the lack of air movement. The quarry glazing behind both windows was in a poor state with numerous lacunae. Consequently, rainwater could easily leak through the glazing and become trapped in the interspace. High humidity was evidently an issue within the church, confirmed by relative humidity readings that exceeded those recommended for glass or paper objects. Furthermore, condensation marks were visible on the sills beneath the Glacier windows, and algae was observed
exacerbated deterioration. Another key consideration is the light levels, to which the materials used in transparencies are so sensitive. The quarry glazing provides little protection against light damage, only partially filtering ultraviolet light, and not filtering the infrared (Schaeffer 2001, pp. 26-8). Evidence of light damage can be noticed on the panels from Prickwillow, where St Peter, orientated to the north, is in much better condition than St Paul, south oriented. Although both have cracked prints, the loss of decoration is much more severe on the latter.

Panels from Cowcliffe also indicate the adverse impact of light on transparencies. In particular, the Ascension and the Parable of the Sower bear marks clearly affected by light. A shadow of quarry glazing remains visible on the surface of the transparency, where it has screened the light (figure 5).
The Parable of the Lost Sheep shows extensive fabric loss mostly in the middle section—the part most exposed to the light. Moreover, it is apparent from the deterioration of materials in the white and red areas that these colours were the most fragile, leaving only a brown cross-hatching sufficiently attached to the glass (figure 6). Interestingly, some of the white and red areas, protected from direct sunlight by southern stonework, have survived in a better state, evidence of photochemical reactions (Ashley-Smith 1983; Horie 1987; van der Reyden 1992; Schaeffer 2001). Furthermore, the impact of air pollution on the impurities in the wood pulp, and the resulting acidification of the paper, leads to opacity, discolouration, weakening and brittleness. Environmental factors also affect other materials present in the transparencies such as resins, printing inks, drying oils, and starch (Boustead 1976; Hartwell 1999). The laboratory results identified that the outer resin layer of the print contained dust and dirt. Poor air ventilation can lead to a temperature build up, which may have softened the varnish sufficiently to enable the absorption of the accumulated dust. On the Cowcliffe panels, soot and dust trapped within the last layer of drying oil has darkened the prints. Those accretions additionally formed small but numerous dark spots, particularly visible on the Ascension panel (figures 7, 8).

The close examination of the printed red flowers suggests the delamination of varnishes and binders containing pigments, probably due to stress and different coefficients of expansion. These have cracked and occasionally curled along the edges, sometimes flaking away to reveal layers beneath (figure 9). Perhaps this could explain why the dirt does not cover the whole surface equally, but creates black spots. The glue has lost its adhesive properties making the decoration fragile and prone to mechanical damage; careful handling is therefore vital (figure 3). The transparencies in Prickwillow have deteriorated similarly to those from Cowcliffe, with cracks visible throughout all of the printed elements. Interestingly, the colour appears to have influenced the formation of cracks. Darker areas cracked into larger sections, with the cracks themselves forming broader lines, uncovering larger areas of the glass surface (figure 10). Lighter coloured areas fractured into smaller and finer cracks. Furthermore, areas that were strongly affected by long exposure to condensation can be seen on all of the analysed panels in the form of significant loss of decoration and adhesion, as well as staining (figure 3, 5).

In comparison to the fragile surface layers, the glass has survived remarkably well, suffering only from minor scratches and slight iridisation, an indication that it too has been affected by the humid environment. Over the long term, the deterioration of the glass may also encourage degradation of other materials, with a potential risk of saponification of the oil binder in the ink layer. However, the separation of this layer from the glass surface by the layers of paper and varnish, may help to prevent this process. Finally, high humidity can lead to hydrolysis, particularly of acidic papers and glass exposed to high temperatures, providing further catalysts for deterioration.
Conservation Considerations
The poor condition of these artefacts calls for further research towards conservation and treatment options. Preliminary tests applying paper conservation techniques for softening varnishes to flatten and re-adhere the flaking decoration to the glass, were found to be unsatisfactory and ineffective (Adamczak 2014). A key issue is the safe removal of dirt when engrained in the layers of varnish, without the disruption of fragile layers beneath. The re-adhesion of individual decoration flakes to its glass support using Paraloid® B-72 and starch recipes was found to be effective, but due to the extent of application required, combined with the pressure required to flatten the brittle paper, this was problematic. Therefore until a treatment solution can be devised, preventive conservation measures, tailored to suit the circumstances of each case, are essential to slow down deterioration. Environmental monitoring, particularly in terms of light exposure, temperature and humidity, in addition to appropriate handling and display, is fundamental to stabilisation.

Conclusions
The deterioration of Glacier decoration creates a complex conservation challenge. Such a multi-layered combination of materials (glass, paper, varnishes, printing inks, binders) with different properties is likely to cause tensions leading to cracking and decoration loss. Even the slightest reactions to environmental changes in one material, may induce the considerable deterioration of others. An additional challenge is the use of unknown products during home application. A case by case compositional analysis is therefore essential to inform the design of preventive measures. Much of the current research into protective glazing and environmental monitoring for stained glass is directly applicable to transparencies installed as a window decoration. Stained-glass conservation and its understanding of the architectural context and its impact on often fragile surface layers is therefore of great significance, arguably making it a well-equipped discipline to address the complex issues faced by these objects. Treatment of the decorative layers necessitates broader interdisciplinary collaboration, following recommendations for the individual materials used in Glacier and established within relevant conservation disciplines. This paper sought to increase understanding of these objects, whilst raising awareness about their existence and potential value, as they have not yet attracted much attention in art historical or technical research. Surviving transparencies are both a rarity and, largely, a mystery.

Acknowledgements
This article arose from the author’s MA thesis at the University of York, under the guidance of Sarah Brown. In ad-

Fig. 9. Parable of the Last Sheep. 50x microscopic magnification image showing the deterioration of the red painted areas of the decoration (photo: M. Adamczak).

Fig. 10. St Peter (Prickwillow). Transmitted light image showing the difference in the cracking of a single paper print (photo: M. Adamczak).
dition to the dedicated support of tutors at the University of York, gratitude must also be expressed to Jasmine Allen, Curator of the Stained Glass Museum in Ely, The Rakow Research Library in Corning, and Dr. Erhard Jägers and Prof. Elisabeth Jägers for assistance with sample analysis.

Notes
1. The Rakow Research Library in Corning (USA), has an impressive collection of Glacier catalogues.

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van der Reyden 1992

van der Reyden 1993
Conservation of Ceramics
A Study of Approaches to the Visible Restoration of Ceramics

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Keywords
Ceramics; ethics; visible restoration; loss compensation; non-mimetic

Abstract
In the field of ceramics conservation, the various approaches to visually differentiating restorations from the original object have attracted inadequate attention. This paper systematically addresses various options, with information found in relevant publications complemented by personal observations and questions for further study. The paper introduces future research to be completed for a forthcoming PhD thesis, whose main goal is to develop a protocol to inform decision-making regarding the visible restoration of ceramics.

Introduction
The various infilling and inpainting approaches for differentiating restorations from the original object in a way that is recognisable to the naked eye are referred to as visible, or non-mimetic restorations. However, a restoration that was originally conceived to be mimetic can become visible because of the ageing of the materials used. To avoid this ambiguity, the author prefers the term “non-mimetic”¹, which clearly indicates that the restoration is intended to be visible.

Non-mimetic restoration has an ethical purpose: differentiating original and modern materials corresponds to a refusal to hide the actual state of the object. Such a refusal is typical for very incomplete or highly fragmented objects, especially when the damage is considered a significant event in the object’s history.

This explains why non-mimetic approaches are frequently associated with archaeological objects. Indeed, many are fragmented and incomplete, and most of this damage is relevant to the object’s archeological history (accidental or deliberate abandonment).

As a consequence, a distinction is typically made between archaeological and decorative ceramics regarding the visibility of restoration. This is questionable for three reasons. First, archaeological ceramics can have highly decorative qualities. Second, decorative ceramics can show historically significant damage too. Third, objects generally have more than one value: most ceramics are neither solely historical documents nor primarily aesthetic objects.

In reality, the best reason for choosing a non-mimetic approach is that the presence of lacunae sometimes makes conservators consider the ethical principle that restoration “must stop at the point where conjecture begins” (Venice Charter 1964, Article 9).

Another, seemingly trivial but practical consideration can intervene: non-mimetic options are generally less time-consuming than mimetic restorations, and is thus less expensive and sometimes preferred by institutions and clients with limited financial resources.

State of Knowledge and Research Goals
Non-mimetic approaches to ceramics restoration date back to at least the first half of the 19th century, as shown in recent research (Bourgeois 2010, pp. 7-10; Milanese 2010).

Given this long history, it is surprising that few of the publications that examined provide historical information about these approaches.

Moreover, to the author’s best knowledge, none of the publications covers the range of non-mimetic approaches to ceramics restoration comprehensively. Addressing this lack
of knowledge is a major goal of this paper. Indeed, because literature on the topic is so scant, the existence of some non-mimetic options might be unknown to some conservators. It is also likely that approaches to the visible restoration of ceramics are subject to cultural differences. As there is a wide range of approaches, it is crucial to know the advantages and disadvantages of each approach and their applicability for a given conservation treatment. Here again, the literature provides inadequate information.

**Results of Preliminary Research**

Using written, visual and oral sources in preliminary research, literature analysis concerned mainly ceramics conservation publications written in French and in English. In addition, studying practical examples and interviewing ceramics conservators helped make complementary observations. These results are organized and synthesised below. Relevant questions are formulated for each section, highlighting the focus of future research.

**Demarcation of Fills**

Two options for physically demarcating fills from original ceramic material have been observed: recessed fills and fills incised along the edge (incised fills).

The practice of using recessed fills seems relatively old. According to Giovanna Bandini, it started as a common practice on incomplete ceramic objects intended for museum display in the 1960s, and is “still widely used in museum circles” (Bandini 2006, p. 99). A recent online publication shows that it is indeed still in use today (Alami-Viguié 2015). Only one example of such fills has been found in the publications written by native English speakers (see figure 1, published in Elston 1990, pp. 75-76).

Recessed fills are presented as a way to avoid ambiguity between original and restored material (Berducou 1990, p. 115), discontinuity between the unfilled break lines and the fills, and overpainting during retouching (Lefevre 1998). In addition, when a good overall alignment of the pieces of an incomplete ceramic object is impossible, fills made at the level of the original surface can be visually disturbing; recessed fills can be an adequate solution to this specific problem.

The downsides of recessed fills are that they cannot be used on extremely thin ceramics (Alami-Viguié 2015), are “sometimes seen as a difference caused by the loss of enamel alone,” and can “cause inappropriate shadow effects” (Bandini 2006, p. 99).

The use of incised fills seems to have a long history as well—the approach was cited in 1972 as an alternative to recessed fills in “Carta Italiana del Restauro: Istruzioni per la salvaguardia e il restauro delle antichità” (paragraph 10). It is thus quite surprising that there is only one published mention of it in ceramics conservation publications: Stephen Koob explains that “fills were separated from the original pottery by simply incising the edge of the plaster, which made the finishing and inpainting of the fill much easier” (Koob 2007, p 116). Few practical examples of such fills have been found (see legs of the figurine in figure 2).

Although incised fills share two advantages of recessed fills (avoiding overpainting and allowing continuity with the unfilled break lines), it does not have the same disadvantages: it can be used on extremely thin ceramics,
it cannot be mistaken with a loss of “enamel” or of any superficial layer, and the shadow effect is less deep.

Questions: What is the frequency distribution of using recessed fills versus incised fills in ceramics conservation? Are recessed fills considered an outmoded approach by some conservators?

Differentiation of Surface Finish

The surface finish of the loss compensation can be contrasted with that of the original ceramic material by having a smoother or rougher texture, and/or a glossier or more matte reflectance.

Only one explicit reference to the use of a rougher texture in a fill has been found thus far: André Bergeron explains that he incised a pattern of small dots into the surface of structural fills in order to make them distinguishable from the original (Bergeron 2007, p. 56).

With regards to contrasts in reflectance, at least three authors consider a matte finish an appropriate way to render the loss compensation discernible (Lefevre 1996; Elston 1998; Koob 2007, p. 116).

An interesting case study is the fragmentary Kyknos Krater previously exhibited at the Metropolitan Museum of Art and which has since returned to Italy. It was first restored by Zdravko Barov, who decided “to give the effect of the original black glaze” to the loss compensation (Barov 1988, p. 173), was and re-restored ten years later by Maya Elston. According to her, Barov chose an “excessively polished and reflective surface” that stood out visually, which she substituted with a surface finish that was “essentially matte with a slight sheen” (Elston 1998, pp. 106, 113).

Questions: How common is the use of differentiation by texture or reflectance in a fill? Is a glossier finish in a fill considered undesirable by most conservators because it stands out too much visually?

Chromatic Differentiation

The loss compensation can be chromatically differentiated from the surrounding area by having a different hue, saturation, or lightness, by having flatter or more modulated colour(s), and/or by being of a single colour.

(a) The colour of the restoration can be distinguished from that of the original by its hue (yellower, redder, bluer or greener), saturation (more or less vivid), and lightness (lighter or darker).

Most adjectives used by authors to describe a chromatic contrast refer to a greater degree of lightness and/or to a lower degree of saturation: “lighter” (Bandini 2006; Buys and Oakley 2011, p. 140), “paler” (Elston 1990, pp. 74, 77) and “softer” (Sannibale 2007, p. 53).

In 1978, I.A. Khazanova stated that the colour of the restoration could be “slightly lighter or darker” compared to the surrounding ceramic (Khazanova 1978, p. 4). This may indicate an evolution in usage. Indeed, in later texts, authors argue that the restoration should preferably be lighter rather than darker—a darker colour can supposedly result in the retouched areas coming to the forefront (Lefevre 1996) or “appearing as lacunae” (Buys and Oakley 2011, p. 140). None of the examined publications refer to a difference in hue or increased saturation. Although some examples have been observed in practice, it is not known whether they were intentional (due to potential ageing of the restoration materials or potential metamorphism).

(b) With regards to the modulated retouching of fills, two main options have been found:

(b1) Tratteggio: Giovanna Bandini writes that tratteggio was “initially conceived for two-dimensional objects (typical of painted surfaces) so there is some difficulty in applying it to three-dimensional objects” (Bandini 2006, p. 101). To corroborate this statement, the only published use of tratteggio that the author has found is on flat funerary plaques (Massar and Bussienne 2011).
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(b2) Pointillist technique:
The idea of using pointillist retouching on ceramics apparently came from Italy, where it is called puntinato. Maurizio Sannibale writes that it was elaborated by Giovanna Bandini (Sannibale 2007, p. 52), while Yvonne Giboteau and her co-authors are more specific, explaining that it was developed in 1985 by Giovanna Bandini and Anna Grossi (Giboteau, Zumstein, and Vinçotte 1992). In Italy and France, the use of pointillist retouching seems to have introduced a significant change (Bandini 2006; Sannibale 2007; Ugaglia 2011), in part by allowing the re-integration of patterns in a manner more suggestive than affirmative (see figure 3). The author has found only one mention of the pointillist technique in publications dedicated to ceramics conservation written by native English speakers (Rozeik, Dawson and Wrapson 2010).

(c) Four main options for the use of a single colour for fills have been found:
(c1) Predominant colour:
Matching the fill to the colour predominantly present on the surface of the ceramic. It has also been termed “background colour” (Buys and Oakley 2011, pp. 140, 151; de Lapérouse, Stamm, and Parry 2007, p. 117) although, in the specific case of resist patterns, the predominant colour differs from that of the background.

(c2) Clay colour:
Matching the fill to the colour of the clay body. For ceramics with glazed or slipped surfaces, the colour of the clay body generally differs significantly from the predominant colour. Some authors refer to the use of this approach (Berducou 1990, p. 116; Guillemard 1998, p. 44; Bandini 2006, p. 99; Sannibale 2007, p. 51; Ugaglia 2011, pp. 31, 40). Giovanna Bandini, Maurizio Sannibale and Evelyne Ugaglia present it as an approach that became obsolete with pointillist retouching (see above, b2).

(c3) “Medium tone”:
In French publications, references to the use of a “ton moyen” have been found (Berducou 1990, p. 116; Giboteau, Zumstein, and Vinçotte 1992). It refers to a mixture of the different colours appearing on the surface of the ceramic object. Yvonne Giboteau and her co-authors give the example of Neolithic ceramics presenting an orange and black appearance for which the medium tone is a brown colour, whose resulting visual appearance they strongly criticise (Giboteau, Zumstein, and Vinçotte 1992, p. 12).

(c4) Achromatic colour:
Some examples of restorations exist where the colour of the fills is achromatic (having a greyish or whitish tone). According to a 1978 paper, the choice of the “uncolouredness of the plaster” was still common at that time (Khazanova 1978, p. 4).
Options c2, c3 and c4 are either not highlighted in recent publications or considered less preferable by some authors. However, c2 is still in use, amongst others on red-figure vases, for which either c1, the predominant black colour (e.g. Elston 1998), or c2, the reddish colour of the clay (e.g. Theofanopoulou and Tossiou 2007), have been observed.

Questions: How ubiquitous is the idea that the fills should have a lighter rather than darker colouration? Do most conservators advocate against the use of a difference in hue or an increased saturation? Is tratteggio more commonly used on flat ceramic surfaces and/or in Italy where it was invented? Outside of Italy and France, where else is the pointillist technique used? Are options c3 and c4 now considered obsolete? Is the preference for option c2 instead of c1 influenced by the cultural background of the conservator?

**Extent of Pattern Reintegration**

On non-mimetic loss compensations, the painted or sculpted pattern can either not be reintegrated at all or be reintegrated in a selective or extensive manner. In addition, a pattern can be differentiated by simplifying it through intentionally omitting some of its features such as drawing lines or fill colours.

Regarding the feasibility of pattern reintegration, Giovanna Bandini differentiates “repetitive patterns” from “figurative scenes” (Bandini 2006), while Suzan Buys and Victoria Oakley make a distinction between “regular” and “random” patterns (Buys and Oakley 2011, p. 140). According to these three authors, repetitive and regular patterns are predictable and can thus be reintegrated, whereas figurative scenes and random patterns are less suitable for reintegration.

However, the issue is more complex. First, repetitive elements can be considered too irregular to be reintegrated, even when it comes to linear elements (see figure 4, published in Ugaglia 2011, p. 77). Second, some figurative elements can be predicted with enough confidence to reintegrate them in a differentiated manner, for instance, by simplifying them (see faces of figures in figure 5, published in de Lapérouse, Stamm, and Parry 2007, p. 118).

These examples bring us back to the ethical principle mentioned earlier that restoration “must stop at the point where conjecture begins” (Venice Charter 1964, article 9). In figure 4, this principle was very scrupulously followed, and in figure 5 differentiation between original and restored areas allowed for a slightly hypothetical reintegration of figurative missing elements.

Question: Is the extent of pattern reintegration that conservators carry out partially influenced by their cultural backgrounds?
About Combination of Non-mimetic Approaches

In practice, the approaches presented above are often used in combination. For instance, if not combined with another approach, an incised fill may resemble a re-adhered shard and fail to achieve a differentiation between the original object and the restoration material.

According to Giovanna Bandini, a style of “philological” restoration invented during the 1960s, tended to combine multiple approaches: fills were recessed, had a single flat colour lighter than that of the clay body and no pattern reintegration was done (Bandini 2006, p. 99). This coincides fully with the restoration shown here (figure 6), which was performed before 1974 at the KIK-IRPA laboratories (Brussels).

Question: Is a combination of approaches such as that of the “philological” style now considered as superfluous?

Future Research

These preliminary research results are part of the author’s forthcoming PhD thesis, entitled “La restauration non-illusionniste de la céramique: vers un protocole décisionnel” (“Non-mimetic restoration of ceramics: towards a decision-making protocol”). The main objective is to inform the decision-making process when compensating losses in ceramic objects by formulating a critical understanding of current practices in ceramics conservation. To do so, conservators will be asked the questions outlined above.

In order to gather a representative sample of the profession at international level, an online survey will be conducted.

Before launching this survey, models for visual comparison will be developed (see figure 7). This was inspired by images of great interest that compare different approaches to non-mimetic restoration on the same ceramic object, such as the four options presented for a red-figure amphora by conservators of the Benaki Museum (Theofanopoulou and Tossiou 2007), and an interactive feature showing two approaches realised on a red-figure krater by conservators of the J. Paul Getty Museum (Fragment to Vase 2008). The latter example was used as a starting point for the model presented below. Specifically, from the two

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Fig. 6. Apulian Calix Krater, first half of the 4th century BC, 38 x 39 cm, Musée de Louvain-la-Neuve (Belgium), ac. no. AC 140 (Photo: Jean-Pierre Bougnet, 2015 ©UCL-Musée de Louvain-la-Neuve).
appreciates originally proposed on the interactive feature (B and D on figure 7), three more were digitally created:

The objective of this model is to show that there are at least five levels in the reintegration of patterns combining linear, repetitive and non-repetitive elements:

— A: not a single element;
— B: only linear elements (the approach dismissed by the J. Paul Getty Museum);
— C: linear and repetitive elements;
— D: all elements (the approach chosen by the J. Paul Getty Museum);
— D+: same as D, minus repetitive and linear elements.

Such models for visual comparison may serve multiple functions. First, they are useful as survey tools—they will improve the understanding of the practices of conservators, and could be used to study the general public’s preferences too. Second, the models can be used as learning tools for students in conservation as they allow one to apprehend the range of visual possibilities. Finally, they are also valuable working tools for conservators, helping curators, heritage professionals or individual clients to visualise the treatment possibilities.

**Conclusion**

The information presented here is only a small contribution to the subject. Indeed, it only dates back to the 1960s and is predominantly derived from literature written in French and English. There are certainly other options for the non-mimetic restoration of ceramics, and definitely more to understand about the origins and uses of the options introduced here.

The forthcoming survey is essential to formulating a critical understanding of current conservation practices regarding the ethical and aesthetic issues of non-mimetic restoration. The author hopes that this paper will encourage readers to participate in this survey.
This topic should be discussed at an interdisciplinary level and deserves to be more accessible to the various heritage professionals with whom conservators collaborate. This will be fundamental to the thought process while developing a decision-making protocol for the non-mimetic restoration of ceramics. In this protocol, the questions that should be asked prior to the intervention will be specified, in order of importance, and accompany them by visual aids, such as the models for visual comparison introduced above.

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Any remaining errors are our own.

Notes
1. Term used in, among other sources, a ceramics conservation paper (Rozeik, Dawson and Wapson 2010, p. 28) and a painting conservation book (Stoner and Rushfield 2012, pp. 573-581).
2. This collection comprises over 500 examples from Western countries. It was constituted mainly by scanning pictures from publications (related or not to ceramics conservation), by taking pictures in European museums (from small local museums to famous ones), and by downloading pictures from online collection databases.
3. Lionel Lefèvre expresses reservations concerning ceramics that are dark and glossy.
4. Hue, saturation and lightness are the parameters used for describing colour perception in the colour space known as HSL.
5. Two options are limited to major losses with clay-colour ed infilling, one option being lighter than the other; two options are extended to minor losses, one with a pattern reintegration more extensive than the other.
6. The red figures are simplified and their flat colouration is lighter than that of the original.

References
Alami-Vigué 2015

Bandini 2006

Barov 1988

Berducou 1990

Bergeron 2007

Bourgeois 2010

Buys and Oakley 2011

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Maya Elston, “Technical and aesthetic Considerations in the Conservation of ancient Ceramic and Terracotta Objects in the J. Paul...
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The Conservation Practices for Archaeological Ceramics of Sir Flinders Petrie and Others between 1880-1930

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ceramics conservation; conservation history; Petrie; adhesives

Abstract
Publications by nineteenth-century archaeologists such as Sir William Matthew Flinders Petrie provide important insight into the surprisingly vast range of natural products and recipes used in the field and laboratory to preserve excavated ceramics. The materials used by these professionals, who were responsible for developing the field of scientifically-based archaeology, are contrasted with those used in the contemporaneous ‘menders’ trade. A survey of the available literature, dating 1880-1930, demonstrates that a wide selection of adhesives, consolidants, solvents, acids, and tools was recommended for treating ceramics during this period. A summary of recommended materials and methods for the preservation of ceramics—in particular those recovered from archaeological contexts—is presented in illustrated charts. These provide a comprehensive summary of materials that may remain extant on ceramic collections that underwent treatment during the late 19th and early 20th centuries. This paper advocates for greater attentiveness on the part of the conservator today when examining older collections and considering the retreatment of ceramics collected during this period, as they may encounter residues of these materials.

Introduction
Conservators responsible for archaeological collections have long been familiar with historic ceramic repairs. During an archaeological excavation, pottery is typically found as fragments that require reassembly in order to be studied, cataloged, and displayed in their complete or incomplete vessel form. In general, archaeological collections consist of many vessels in the form of jars, bowls, cups, vases, and other containers because these objects are commonly excavated from ancient habitation sites and have survived well as sherds. Ancient ceramics were rarely repurposed or repaired after their original breakage because it was difficult to restore their original function as a useful container. Thus, when they are excavated, they represent evidence of a particular time, place, and culture. Sherds recovered in the layered strata of an excavation trench could be compared in sequence and dated relatively because forms and styles of manufacture change over time. This technique of using ceramics to date archaeological deposits is commonplace today, but was first utilized by Sir William Matthew Flinders Petrie in 1890 (Petrie 1899). The emerging field of conservation and its legacy of intervention by early practitioners of repair are linked, in large part, to the development of archaeology as a scientific discipline, following existing models in geology and botany. Petrie (1853-1942) stands out as a leading figure in archaeology, especially during the last two decades of the 19th century (Sease 2001). Petrie, his colleagues, and his students excavated over 50 sites throughout Egypt, Israel, and Jordan. His techniques of careful digging and full documentation of recovered finds was not ordinary at the time and he influenced many archaeologists working in the Mediterranean region. Petrie’s meticulous record-keeping in the field is reflected in extant recovered materials and his publications. Excavated artifacts are labelled with their exact find spot and notebooks include records
of associated finds, while published volumes include tables, photographs, drawings, and text. Petrie had a lasting impact on students at the University College London (UCL) where he was a professor from 1892 until 1933 (Drower 1995, pp. 199-230). The excavated collections made by Petrie and the young professionals he influenced are now scattered across the Western hemisphere due to his long career and numerous excavations, and because he rewarded his funders with artifacts. Under Petrie’s supervision, archaeologically recovered ceramics were stabilized from a wide range of sites in Egypt, Israel and Jordan. His early career in Egypt (1880-1900) focused on excavations of large architectural complexes, including temples and pyramids, and the ceramics held within them, while his later career there and in Israel and Jordan concentrated on vessels recovered from cemeteries and tombs. The quality and condition of the excavated ceramics were of great importance because he gifted artifacts to patrons, who in turn sold or donated them to other museums. As a result, artifacts recovered under Petrie or his direct supervision can be found in museum collections all over Europe and North America (Stevenson 2014, pp. 95 and Appendix 1).

Perhaps most relevant to the field of conservation is Petrie’s concern for the deterioration he observed on excavated artifacts and his commitment to perfecting the use of various materials and techniques for preservation purposes. Particularly noteworthy is the publication of The Treatment of Small Antiquities in 1888 and the expanded chapters on preservation and packing in Methods and Aims in Archaeology (1904). His numerous publications describe the materials, techniques, and commentary for his approach to the preservation of delicate and fragmented finds. For example, he writes favorably about the use of paraffin wax, tapioca, and shellac (Petrie 1888 and 1904).

Petrie was not alone in recording his observations about deterioration phenomena and developing preservation protocols for use in the field and the laboratory made during his excavations in Egypt beginning in 1880. The dramatic condition changes observed in freshly excavated ceramics and metals (in particular) during archaeological expeditions in Egypt inspired German scientists such as Tischler, Voss, Rathgen and Krause, to investigate these chemical mechanisms and develop new stabilization treatments (Gilberg and Vivian 2001). Efforts to conserve the finds excavated through scientific archaeology “enable[d] objects to be photographed, described, and more particularly packed and transported in safety” (Lucas 1924, pp. 4).

The materials and methods developed for use in scientific archaeology can be compared with those advocated by the longstanding ‘menders’ trade. The traditional group of practitioners known as ‘menders’ specialized in the repair of ceramic products including earthenware, porcelain, and bone china (Thornton 1998; Garachon 2010; Albert 2012). In 1896, Charles Godfrey Leland, an American folklorist, traveller, and journalist, wrote during his years in Europe that “a thorough knowledge of this art of repairing, mending, or restoring various objects is of very great value” (1896, pp. vii).

Leland collected recipes from ‘menders’ and published A Manual of Mending and Repairing in 1896 based on his travels throughout much of Europe. Other publications written specifically for ‘menders,’ dating to the late 19th through early 20th centuries, include those by Ris-Paquot (2010 [1872]); Barthelot (1884); Leland (1896); and Howarth (2013 [1900]). Many of the recipes for artful restorations include natural adhesive products, and materials similar to those used in archaeology. However, as Garachon points out, “the dividing line between repairing and restoring ceramics was often vague, and the two approaches existed alongside each other and sometimes even together… until the 1960s” (2010, pp. 28).

Between 1880 and 1930, ceramics from archaeological sites were analyzed by studying the vessels themselves and noting the size, form, and surface appearance. Archaeologists developed classifications for pottery based on form and size, and the interpreted vessel functions were used to construe how space was used within a site. For archaeologists, ceramics were scientific evidence, and they were not intended to be made functional again. However, for purposes of publication photographs, exhibition and sales, it was often important for vessels to be visually attractive and complete. Thus, a distinction between the process of restoration (loss compensation) and repair (reconstruction) of archaeological ceramics is often hard to discern in field reports and articles published at the turn of the 20th century.

The works of Petrie and his contemporaries can provide important insights for conservators working with older archaeological collections, in particular those excavated and assembled during the late 19th and early 20th centuries. Preservation activities were considered a necessary archaeological endeavor that occurred during and immediately following excavation, as well as part of later analysis and publications phases. As a result, many archaeologists un-
 undertook the work themselves using a range of techniques and materials, including waxes, shellac, bitumen, animal glues, and gum Arabic. Lesser-known options such as tapioca and silicate of soda (waterglass) were recommended for use as adhesives, consolidants and coatings.

Later campaigns of treatment executed and documented in collection and museum conservation reports often illustrate a failure to recognize what material had been used previously, or an understanding of why or how earlier interventions were completed. As a result, most retreated ceramics can be characterized by an uneven and incomplete removal of adhesives and fills, often resulting in further damage, as well as a loss of historic information regarding preservation interventions. By exploring the materials used for ceramic conservation during 1880-1930, a better understanding of some of the present conditions observed on ceramic vessels in museum collections is possible.

Drawing on significant experience and expertise working with pottery from numerous archaeological contexts, we reviewed the writings, teachings, and collections of Sir William Matthew Flinders Petrie in order to identify and assess these repair techniques on collections at the Institute of Archaeology, University College London (IoA-UCL). The Tell el-‘Ajjul, Tell Fara, and Tell Jemmeh assemblages from Palestine were excavated in 1926-1938 when Petrie was 73-85 years of age and represent the combined work of Petrie, his colleagues, and students. Access to the Petrie collections provided the opportunity to study this era of conservation in considerable depth through comparison of published books, site reports, and articles with conservation laboratory documentation associated with several hundred ceramics. A comparison of the current condition of ceramics to the materials and techniques noted in the surveyed literature from this period can deliver insight to the complete intervention history of archaeological ceramic collections.

Surveyed Literature

Petrie’s contribution during this pivotal period in the development of archaeological and ceramic conservation is profound. His 1888 and 1904 works demonstrate a keen eye for recognizing degradation processes and the impact of interventive treatments, while relating both to scientific principles and an understanding of material properties. Petrie’s publications and subsequent training of future generations of archaeologists occurs at the same time that natural and synthetic adhesives (organic and inorganic) begin to be developed commercially (Fay 2005). Along with scientific publications describing mechanisms and patents for adhesive production, a number of technical handbooks describe the physical, chemical, and mechanical properties of adhesives. Sigmund Lehner produced one of the most influential and popular handbooks used by archaeologists and scientists alike, which was published in at least 44 editions between 1877 and 1927 in both German and English (OCLC 2010).

Early publications from this period (Tischler 1883; Petrie 1888; Leland 1896; Rhousopoulos 1905; Petrie 1904; Rathgen 1905; Rhousopoulos 1911; Rathgen 1913a, 1913b; Lucas 1924; Scott 1922, 1926, 1932; Woolley 1930; Delougaz 1933) suggest a number of materials, solvents and techniques were used to stabilize and treat ceramics from archaeological and historic contexts (see figures 1-5). Unsurprisingly, similar materials were used in the preparation of fossil specimens during this period—in particular shellac, gums, gelatin, cellulose acetate and nitrate, as well as a variety of waxes, many of which are referred to in the geological literature as early as the 1830s (Howie 1984, pp. 92-93). These resources would have been available to archaeologists and probably discussed in professional society meetings, suggesting an open discourse. Building on this dialogue, the approach of archaeologists reflects a particular concern for arresting the damaging impacts of saline burial environments, as well as restoration of appearance rather than function.

A survey of the literature identifies a number of materials and methods designed to arrest deterioration due to soluble and insoluble salts. These include the use of paraffin wax as a consolidant during recovery of ceramics or shortly thereafter (Petrie 1904, pp. 88-89, 112; Rathgen 1905, pp. 71, 85; Rathgen 1913b, pp. 163; Droop 1915, pp. 26, 41; Lucas 1924, pp. 19-22, 41, 48, 101; Delougaz 1933, pp. 41-2, 55-7). In addition, authors recommended the use of water for desalination (Petrie 1888, pp. 88; Leland 1896, pp. 28; Rhousopoulos 1905, pp. 254; Petrie 1904, pp. 88; Rathgen 1905, pp. 57-67, 78; Rhousopoulos 1911, pp. 141; Rathgen 1913b, pp. 161; Lucas 1924, pp. 8, 46, 99; Scott 1926, pp. 15; Scott 1932, pp. 490; Delougaz 1933, pp. 52), as well as hydrochloric acid to mitigate against the deleterious effects of salts in ceramic fabrics (Rathgen 1905, pp. 78; Rhousopoulos 1911, pp. 141; Rathgen 1913b, pp. 161; Droop 1915, pp. 41;
Lucas 1924, pp. 42, 99-100; Scott 1926, pp. 20-21). Plaster of Paris is frequently recommended as a material for loss compensation (Leland 1896, pp. 13, 17; Rathgen 1905, pp. 88; Droop 1915, pp. 41; Lucas 1924, pp. 18-19, 41, 43, 48, 101; Scott 1926, pp. 62-63; Delougaz 1933, pp. 42). Finally, most publications comment on the impor-
tance of stabilizing low-fired clay objects through baking (Rathgen 1905, pp. 83-84; 1913, pp. 162; Scott 1922, pp. 337-338; Lucas 1924, pp. 42, 100; Delougaz 1933, pp. 45-53).

A wider range of adhesives and additives are suggested for consolidation and mending. These include a number of water-soluble proteinaceous glues such as casein, egg white, Cologne (an animal glue made from leather straps).
(Doerner 1934), fish and hide glues, as well as seccotine (a refined fish glue patented in 1894 by John Stevenson MA) (Room 1982, pp. 156), and Syndeticon [reported as liquid fish-glue (Rathgen 1905, pp. 87) or mixture of burnt lime, sugar and good glue (Leland 1896, pp. 243)] (figure 1). Sugars (gum Arabic, tragacanth), starches (dextrin, rice, and tapioca), and solvent soluble tree resins (colophony, copal, dammar, mastic, and shellac) are recommended, as are a number of waxes and petroleum derivatives (figure 2). The use of synthetically produced adhesives focuses particularly on cellulose derivatives including acetates (Necol, Plastic Wood, and Zellon) and nitrates (celluloid, collodion, non-inflammable Plastic Wood, and Zapon) (figure 2). A number of fillers are included as additives for adhesives, protective coatings, and loss compensation (figure 3).

Surveyed authors also note the importance of a wide variety of acids, solvents, and tools for use with the previously-mentioned materials and techniques, and make specific recommendations for their use (figures 4 and 5). Authors cite problems associated with the purity of solvents available in remote field locations where language barriers may exist and note the deleterious impact of potential contaminants on long-term preservation (Lucas 1924, pp. 129). Notably, most publications acknowledge the difficulty in sourcing materials for preservation by indicating where materials are easily available in remote locations and discussing in what cases practitioners should ensure the purity of materials and solvents before use in treatment. This attests to an ethic of sustainable preservation. The lists included in figures 4 and 5 might assist current conservation efforts with identifying residues, deposits, or marks left by the use of such acids, solvents, and tools. For example, acids and solvents may have left residues or deposits if they were contaminated or were not thoroughly rinsed after the treatment. Also, tool marks left on the surface of ceramics may suggest the type of adhesive, consolidant, or filler that was once used.

Efforts to identify and understand these early historic interventions can be problematic, particularly if the object has undergone a number of campaigns of repair. However, careful assessment of the object in tandem with primary and secondary sources, including original treatment records and archaeological handbooks, enables the conservator to better interpret the evidence preserved in ceramic objects.
Survey of Petrie Palestinian Ceramic Collections at the Institute of Archaeology, University College London

The Petrie Palestinian collections, held by the IoA-UCL, include artifacts recovered from the Tell el-ʿAjjul, Tell Fara, and Tell Jemmeh excavations carried out by Petrie between 1926 and 1938 (Sparks and Ucko 2007, pp. 13). Approximately 20,000 objects have served as a study and teaching resource since their acquisition from Petrie in 1935, following his 1934 retirement from UCL. The collection has had a convoluted history and received piecemeal preservation attention until the 1990s when flexible storage and archival support materials were upgraded (Sparks and Ucko 2007, pp. 16-17). Stabilization of artifacts by staff and students began as early as the 1930s following their unpacking, cataloguing, and organization by Dame Kathleen Kenyon, a respected archaeologist best known for excavating Jericho (Sparks and Ucko 2007, pp. 15-16). Unpublished records predominantly take two forms: (a) single entries listing artifacts, their description, numbers, and markings; the owner; the student assigned to complete the work; and dates of intervention; and (b) records of treatment that include day-by-day descriptions of interventive activities.

A survey of the Petrie collections at the IoA was undertaken to determine the condition of conservation treatments made between 1880 and 1930, to observe the range of conservation materials used, and to relate the material identification to possible re-treatment conservation reports made since the 1950s. The following case examples illustrate common observations and demonstrate that the conservators undertaking a re-treatment were generally unaware of the materials likely used in the original treatments.

Object Case Examples

Each object is presented with a chronological summary and interpretation of available archaeological and conservation data, as well as our observations made during a series of inspections. Observations are discussed within the context of the object’s complete history, as well as the conservation practices discussed above.

1928-30 Field Record: EVII.28/2, Tell Fara Tomb 625, ceramic strainer jug (figure 6)

2015 First Examination: Vessel is complete with localized surface darkening associated with applied surface paint, sherd repair to rim.

Treatment Documentation: None.

2015 Second Examination: Under ultraviolet (UV) light, the surface absorptions suggest possible use of wax as consolidant.

Discussion: Petrie advocated the use of wax in the field to stabilize delicate/painted surfaces. Examples examined in the Petrie Museum of Egyptian Archaeology collections at UCL have applied surface wax. The use of this material to consolidate paint is consistent with a field treatment from 1928-30 and is probably a repair from that time.

1930-1934 Field Record: EXII.6/6, Tell el-ʿAjjul Tomb 1406, ceramic piriform juglet (figure 7)

2015 First Examination: Vessel appears is nearly whole and reconstructed with complete toned loss compensation fills.

Fig. 6. Ceramic strainer jug, EVII.28/2, Tell Fara Tomb 625 (Photo: authors; courtesy of UCL Institute of Archaeology).
The Conservation Practices for Archaeological Ceramics of Sir Flinders Petrie and Others between 1880-1930

Nancy Odegaard and Caitlin R. O’Grady

1976 Treatment Documentation: Old joins reversed with acetone; washed with warm water and Lissapol; form reconstructed and sherds adhered with HMG cellulose nitrate adhesive; gaps filled with plaster and toned with water-soluble colours.

2015 Second Examination: Under UV light, the surface and joins have no fluorescence.

Discussion: The smoothed edges of the sherds are consistent with many repairs made in the 1880-1930 period and the dark staining suggests a pervious adhesive. The reversal of ‘old joins’ using acetone suggests a solvent soluble adhesive, while the use of warm water indicates a water soluble adhesive was present. Cellulose nitrate was known and used in 1930-1934, but Petrie generally employed natural products for conservation. It seems likely that if cellulose nitrate was used in 1930-1934, some fluorescence would be visible with UV light. The use of both warm water and a detergent for cleaning in 1976 suggests that a water-soluble adhesive such as hide glue had been used in 1930.

1930-1934 Field Record: EXIV.4/5A, Tell el-`Ajjul Tomb 1074, ceramic double handled juglet (figure 8)

2015 First Examination: Vessel is incomplete with sherds adhered, loss compensation, a recessed and toned fill, and a locked-out associated piece is stored with it. There is an extraordinary amount of surface damage suggesting that cleaning techniques were very aggressive.

1979-1980 Treatment Documentation: Old adhesive reversed with acetone; during desalination, a white surface coating swelled with suggestion that soluble nylon may have been used in previous treatment. The film was removed successfully with industrial methylated spirit and cotton wool; reconstructed with HMG cellulose nitrate; gaps filled with AJK dough 2 toned with Cryla colours.

2015 Second Examination: Under UV light, the surface and joins have no fluorescence.

Discussion: The smoothed edges of the sherds are consistent with many repairs made in the 1880-1930 period.
The need to reverse the old adhesive in acetone suggests a solvent soluble adhesive had been present, however the use of warm water suggests a water soluble adhesive was present and more likely, especially since the detached sherd edge did not fluoresce. The appearance of the swelling white surface coating during desalination suggest a wax was present because it was soluble in methylated sprit and would be consistent with a Petrie treatment. It is not clear why there is the suggestion that Soluble Nylon had been used previously. There is an extraordinary amount of surface damage to the vessel suggesting that cleaning was very aggressive.

### Conclusion

The materials and techniques of earlier repairs and restorations can provide conservators with important insights regarding accepted techniques and materials used in conservation practice in the early 20th centuries to a contextual time and place. As the conservation discipline has professionalized, many conservators have argued that previous repairs are part of the objects’ history. We suggest that knowledge of earlier conservation methods and materials is important in documenting object history and agree that documenting the previous restoration history is necessary background for new conservation treatments.

Although the materials used in conservation treatments have changed considerably since the 1930s, a careful study of early publications from the late 19th and early 20th centuries provides evidence that the majority of techniques that were developed for the preservation of archaeological artifacts during this early period remain in use today. These publications illustrate a burgeoning sense of responsibility for the long-term preservation of artifacts, and demonstrate significant initiative and invention on the part of the authors to meet these aims.

Our discussion and tables provide further understanding of the beginnings of the conservation of ceramics in archeology. We advise that the residues of all post-archaeological treatment be interpreted and documented by conservators as part of any re-treatment process. Many early treatments found on archaeological ceramics excavated at the time of Petrie and his contemporaries represent an important legacy in both conservation and archeology.

### Notes

1. HMG is the proprietary name used by H. Marcel Guest, England to produce cellulose nitrate (Selwitz 1988, pp. 57).
2. AJK Dough refers to a fill material comprised of Alvar (polyvinyl acetate), jute flock and kaolin powder mixed with solvents developed in the 1960s by Ione Gedye at the Institute of Archaeology, University College London (Fulcher 2014, pp. 32).

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Preserving the Story of Restored Objects: Combining Technical Data with Historical Sources

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Historical restorations; historical sources; analyses of conservation materials

Abstract
Major refurbishments to the Greek Galleries in the National Museum of Antiquities (Leiden, The Netherlands) provided a unique opportunity to research and restore objects that had been on permanent display for a long time. Financed by the BankGiro Lottery, a large conservation project allowed us to research the objects to a greater degree than before. In addition to analysing old conservation materials, we were also able to study sources related to their conservation histories. We can thus write the biographies of some objects and their 19th century repairs, linking them to specific dates, people and locations. We use this large-scale project as a case study to discuss practical and ethical issues concerning the proper treatment of historical restorations.

Introduction
The National Museum of Antiquities in Leiden (NMA) was founded in 1818 and has about 180,000 objects in its collection today, from Egypt, Classical Antiquity, the Ancient Near East, and the Netherlands. Major refurbishments of the Greek Galleries provided a unique opportunity to research and restore objects that had been on permanent display. A thorough examination of their condition made it clear that many objects from the Greek department were restored in the past, with some of them in poor condition and others mainly unsightly in appearance. A number of objects needed renewed conservation treatment, some of them for the first time since their arrival in the museum. The museum always treats historical repairs and restorations to its collection with great care. Through funding by the BankGiro Lottery, the huge project entitled “Greek Vases in Context” now allowed us to restore and research the objects at a much larger scale than before. More importantly, apart from analysing old conservation materials, we were now able to study historical sources related to their conservation. These include private letters, damage reports, and old photographs from the museum archives. They provide us with invaluable information about the conservation biographies of various objects and the people connected with them. In this paper, we discuss several historical repairs, specifically those that we have been able to link with sources from the museum archives. Combining technical and historical data, we attempt to write the biographies of some objects and their earlier repairs, linking them to specific dates, people and locations. In this way, we gather information about the techniques and materials that were used in the past, in order to more clearly define future conservation strategies.

Several studies have been conducted into the history of conservation (an overview can be found on the ICOM-CC website of the Glass and Ceramics Working Group; History Group). Less work has been done on historical restorations specifically pertaining to Greek ceramics, although an important conference on this subject was organised in Berlin in 2006 (Bentz and Kästner 2007). Important research into 19th century restorers from Italy and conservation practices of the time has been done by Bernard 2008, Bourgeois and Matz 2010, Dooijes 2007, Dooijes and Megens 2010, Tjon Sie Fat 2012.
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Salt Efflorescence
While checking the condition of the objects following deinstallation of the permanent exhibition, we encountered a few Greek vases with salt problems (figure 1). These salts were identified as calcium acetate thecotrichite (see Eggert et al. in this volume). The objects originated from the collection of the Prince of Canino (discussed below) and arrived in the museum in 1839. To find out more about the possible causes that introduced salts into these objects, we investigated the general condition of objects in the museum collection in the early 19th century. We were especially interested in the environment within both the museum and the cabinets in which the early collections were presented. Furthermore, we searched for archival material concerning the use of certain chemicals, materials or conservation techniques that may have caused the salts to form.

Conditions in the Early Museum Building
Prior to 1918, when the National Museum of Antiquities moved to its present location along the Rapenburg canal in the centre of Leiden, the collection was housed at other places in the direct vicinity. Our archives tell the story of these buildings, of which the first was located on the Houtstraat (from 1821 to 1837). When the collection increased in size, a larger venue was needed and the museum was moved in 1837 to a former residential house at Breestraat 18.

Annual reports proved to be especially valuable for research into the second venue of the museum at Breestraat 18. Soon after the move, Conrad Leemans (director from 1835 to 1891) did not cease to complain to the government about the poor conditions in the building (see amongst others, the annual reports between 1874 and 1880). There were many leaks in the roof, the drains had a strong smell, and heating was not available until 1877 (Leemans 1877, p. 41). During wet periods, the papyri that were displayed on the walls became mouldy, while in the warm summer they would crack. Camphor was used to dry mummy coffins (Schneider 2015, p. 123), and naphthalene was used to take measures in response to worms and insects damaging the mummies (Pleyte and Holwerda 1895/96, p. 3). Some items from this collection became so badly deteriorated that Leemans had them buried at the local cemetery Rhijnhof (personal communication, curator Maarten Raven). Ceramic vessels were damaged because of vibrations, and one report specifically mentions that the glue, most probably an animal glue, did not work sufficiently in these circumstances (Leemans 1878, pp. 63-64). Furthermore, stone statues and other monuments were damaged and fell apart because of the moisture (Leemans 1875, p. 17).

Sometimes the yearly reports were used to record damage. We stumbled upon an interesting record indicating the many salt problems that existed at the time in the collection. In a report from 4 May 1859 (Leemans dr 1859), Leemans describes a small Greek hydria (inventory number KvB* 51) and writes: “Most probably the salts that were already present in the object before it arrived in the museum, through the variable dry or moist climate here in our country, caused the surface of the vase to crumble away and to partly decompose into dust, so that with the surface also the decoration was lost; even complete parts of the object broke off without the possibility to repair the damage.” Leemans concludes the damage report with the following statement: “And I, the undersigned, have thus written this...”

Fig. 1. Oinochoe with salts on shoulder (PC 25; height 15.7 cm, diameter 10.1 cm) (Photo: National Museum of Antiquities).
statement as to clarify when and because of what cause the named vase was lost for the collection of the State, so that the director cannot be held accountable for it.” After some years the overall conditions in the building improved slightly through renovations, but the annual reports continue to lament the poor conditions until 1918, when the museum was finally able to move its collections to the far better conditions of the building at Rapenburg 28. Vapours evaporating from wooden showcases are often the cause of salt problems. Archival research of financial records from 1839 to 1954 suggests that in the 19th century most showcases were made of pinewood. In the 20th century, oak was used until cheaper materials such as plywood and medium-density fibreboard (MDF) came into use. Another well-known cause of salt problems is the use of chemicals, especially acids, for cleaning ceramic objects. Historical sources show that the Prince of Canino himself used aqua fortis (nitric acid) to clean pottery (Bernard forthcoming). The only information we found that specifically refers to a harmful conservation technique used in the museum is recorded in a collection of Leemans’s personal notes. Following an account on the fabrication of Greek pottery, Leemans mentions that it is often difficult to distinguish between fake and original vessels (PA Leemans, p. 553). He writes that a new method is mentioned in The New Quarterly Review of 1846 (nr. XVI), which suggests that false pots would lose their colour after the application of nitric acid. There is no information about the technique actually being used but we do hope that Leemans did not decide to use nitric acid on the entire collection. If so, it may well have caused salts to form in the pottery.

The Accident with the Marble Vase
One of the objects included in the current conservation project was an early Cycladic marble vase, dated to

Fig. 2. Early Cycladic marble vase with old repair (RO III 11; height 24.5 cm, diameter without handles 16.3 cm) (Photo: National Museum of Antiquities).
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around 3000 BC (inventory number RO III 11) (figure 2). Although it is a marble object, we include this vase here as it gives important insight into 19th century conservation practices, a time when specialisation did not exist as it does now. The vase is part of the Rottiers Collection, which is one of the earliest collections of the museum. In the early 19th century, Colonel B.E.A. Rottiers (1771-1857) made several trips around the Mediterranean area, during which he assembled a large collection of antiquities. This vase was acquired from him in 1825, not long after the museum was founded. The old restoration was particularly unsightly and dirt and dust had settled on the object.

Before dismantling the vase we wanted to find out more about its condition over the past two centuries. Was the object already restored when it arrived at the museum, or was this restoration treatment carried out at a later stage? We were fortunate to find a detailed damage report about the object from 1885 (Leemans dr 1885) (figure 3):

“On Thursday, 7 May, while closing the blinds, a marble vase from the Rottiers collection, marked RO III 11, was hit by the iron bar that is used to close the blinds of the room. It fell on the floor and broke in several pieces. The pieces were collected and the fragments were repaired as well as possible.” The director of the museum, Conrad Leemans, signed the report. We were very excited to find this information because it gave us a specific date and place for the old restoration. Moreover, we now know that it was carried out in our museum.

When we examined the vase we found that the repair was not very skilful (figure 2). The sherds were re-adhered with animal glue, of which residue was present on the surface of the vase near the breaks. The gaps were crudely filled with plaster. We do not know for certain whether there was an attempt to match the plaster to the colour of the vase because the paint had darkened over time. To learn more about the materials that were used in the museum in this specific period, the old paint was analysed by the Cultural Heritage Agency of the Netherlands (RCE) in Amsterdam. Using Gas Chromatography-Mass Spectrometry (GC-MS), it was found that the binding medium of the paint was linseed oil mixed with pine resin. As a finishing layer, beeswax was used (Dooijes and Düring forthcoming).

The next step was to try and find out more about the context of this restoration. Was there a specialist conservator working in the museum at the time? Can we find out who restored this vase to the best of his ability? While looking through other damage reports we came across a similar report from 1871, which mentions the breakage of a Greek vase, and its subsequent mending by the “amanuensis” (general assistant) of the museum, named Hooiberg (Leemans dr 1871), also well-known from the lithographic studio of the museum (Schneider 2015, p. 11-12).
His restoration was not documented. Furthermore, the annual reports regularly mention that objects are being repaired (for example, Leemans 1879, pp. 68, 73, 77, 80). We do not yet have a complete picture of the persons that were responsible for the maintenance and conservation of the museum objects. In the early years we come across the above-mentioned function of general assistant and “the person who is responsible for repairing the objects” (Pleyte and Holwerda 1891/92, p. 1). The general assistant was responsible for the building and care of the collection, and had several persons working under him on a daily basis. These are not mentioned by name, but we know that in 1890 they included a carpenter, a lithographer with an assistant, and a person charged with writing and drawing, repairing and marking objects, as well as other services (Leemans 1889/1890, p. 1). The job title of “restorer” was first applied to general assistant Koene (Pleyte and Holwerda 1903, p. 2). An important step towards professionalization was taken after Koene retired in 1919. His successor, Melman, was sent to the Römisch-Germanisches Zentralmuseum in Mainz, Germany, to be educated in the art of restoring and copying objects. The then director of the National Museum of Antiquities, J.H. Holwerda (director from 1919 to 1939), proudly announced in the annual report of 1920 that he considers it a great privilege that the museum now employs a restorer who is fully aware of modern techniques and technology (Holwerda and Holwerda 1920, p. 3) (figure 4).

**The Canino Collection**

The first director, Professor C.J.C. Reuvens (director from 1818-1835), formulated an extensive collecting policy in order to compete with national museums in France, the United Kingdom and Germany. One of the collections he acquired is especially relevant to our conservation project: the ninety-six vases from the collection of the Prince of Canino (figure 5).
This collection consists of Classical Greek black and red figured ceramic vases. They originate from ancient Greece, but were excavated from 1828 (excavations were carried out until the beginning of the 1850s) on the estate of Lucien Bonaparte, the Prince of Canino, near Vulci in Italy (Halbertsma forthcoming). Lucien Bonaparte was the younger brother of Napoleon, but had fallen out with his important brother because of his marriage with Alexandre de Bleschamps (Lawrence 1994, p. 125). Napoleon refused to support him financially and the couple lived in constant shortage of money (Nørskov 2002, pp. 58, 90). Greek vases were in fashion at the time and were sold for high prices. In total about 3000 vases were excavated and eventually auctioned off (Nørskov 2002, pp. 59-61). Other major collections of Canino vases now exist in museums in London, Paris, Munich and St. Petersburg.

Many of the vases in the Canino collection have not been restored since they came to the museum. We therefore have a good sample size with which to research the restorations that were carried out in the early 19th century on the Bonaparte estate in Italy. We have tried to find out more about the conservation practice at the time. What materials were used, and was there a common standard or technique for restorations?

We started by inspecting the condition of all ninety-six vases. Quite a lot of the smaller objects turned out to be in good condition with no previous restorations and no major damage. A second group was re-conserved in the past decades. About one third of the objects still had the original restorations from the beginning of the 19th century. These objects in particular were examined closely and some were selected for conservation treatment.

Unfortunately, little useful information was found about the objects in the archives of the museum. The vases were simply registered and the descriptions focused on their design and iconographic aspects (Dooijes and Düring forthcoming). However, there is some information about the conservation practices on the estate of Canino, mostly about the crude way in which objects were handled and restored (Nørskov 2002, p. 91). Contemporary critics of Lucien Bonaparte claimed that he threw away undecorated parts of pottery, or used these sherds to fill gaps in other, incomplete vases. In correspondence from this time, a new conservation technique is mentioned: using a filling material that consists of ground potsherds (Bernard forthcoming).

**Typical Canino Restorations**

By closely examining the old restorations on the selected objects, we found some common features on the Canino vases. Additional analyses and in-depth discussion of the results will be published in the forthcoming proceedings of the conference *The Canino Connections* (2015) (Dooijes and Düring forthcoming).

GC-MS analyses by the RCE have shown that the restorers on the Canino estate generally used animal glue to mend the sherd (Dooijes and Düring forthcoming). We see that objects were quite skilfully re-adhered. It is remarkable that after more than 150 years the adhesive is often still quite stable. When there was a problem fitting the sherds together, the restorers simply adjusted them by cutting away some material (figure 6). Misalignments between joins were disguised by applying a filling material over the poorly joined sherds. For more stability, a metal pin was sometimes inserted between two sherds, and a hole...
was drilled for this purpose. Remnants of ancient repairs such as rivet holes were concealed (as seen on PC 94, figure 7).

Inside closed forms, a mixture of plaster of Paris (calcium sulphate dihydrate) and animal glue was applied roughly over the break lines. We assume this was done to give extra support to the breaks (Dooijes 2007, p. 106). In one case (PC 5), the mixture had been coloured with ochre pigments too. Larger gaps were filled with plaster of Paris. In some cases the plaster was mixed with other components, like sawdust, pigments, or animal glue (Dooijes and Megens 2010, p. 232). Interestingly, on one vase we found a filling material that appeared to consist of plaster of Paris mixed with ground potsherds. This was later confirmed through analyses with an energy dispersive X-ray spectrometer (EDX) coupled to a Scanning Electron Microscope (SEM) at the RCE (Dooijes and Düring forthcoming). It was very exciting to come across this direct link with the above-mentioned sources (Bernard forthcoming).

On three of the treated objects, we suspect that indeed parts from other vases were used when the loss was too large, or had a specific shape, such as a handle or foot (PC 1, PC 42 and PC 94). In all three cases, the shape and colour of these parts matched very well with the objects. Figure 7 shows how one of these objects, a kylix, (PC 94) has a foot that must originally have been part of another object. The X-ray clearly shows that the foot does not fit well to the body of the kylix (figure 8).

After 150 years, the 19th century restorations have naturally deteriorated and darkened (figure 9). They have also

Fig. 7. Kylix with disguised ancient repairs, before restoration (PC 94; height 8 cm, diameter 23.4 cm) (Photo: National Museum of Antiquities).
become difficult to remove. Samples of paint from these restorations were analysed at the RCE using X-ray fluorescence (XRF) and GC-MS (Dooijes and Düring forthcoming). The retouching medium that was used by the Canino restorers turned out to be oil, and not shellac as we had assumed (Dooijes 2007, p. 108).

Furthermore, it was interesting to find that the binding medium that was used for the black paints differs from the red ones and often varies between objects. On many objects,

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**Fig. 8.** X-ray showing kylix with alien foot PC 94 (Photo: National Museum of Antiquities).

**Fig. 9.** Detail of amphora PC 78, showing deteriorated retouches (Photo: National Museum of Antiquities).

**Fig. 10.** Detail of hydria PC 73 showing overpainting (Photo: National Museum of Antiquities).
the red paint medium proved to be much more difficult to dissolve. Further XRF analysis of the pigments shows that the components of similar colours also differ between objects. This could mean that they were mixed especially for each separate object, to match better with the surrounding surface colour (Dooijes and Düring forthcoming).

We note that there is often some overfilling and overpainting of the original surface (figure 10). The hidden decoration was then repainted on the fill. At the same time, missing decoration is often not completed on fills, even when it was clear what it originally must have looked like—revealing a rather modern ethical decision. Several vases have been restored more than once. Analysis by GC-MS revealed that for the fill on the kylix (PC 94), a pigment called “Red 3” (Toluidine Red) was used. This pigment has only been in use from 1905 onwards (personal communication, Matthijs de Keijzer (RCE)). Although its appearance did not differ from other Canino restorations, this shows us that the kylix must have been restored again during the 20th century.

Discussion and Conclusion
The restoration project for the new Greek Galleries is still ongoing, but having processed the data up to this moment we present some interesting results and considerations. Apart from the valuable information gained through archival research, this large-scale conservation project was very useful as a case study to discuss practical and ethical issues concerning the proper treatment of historical restorations. Practical issues include the short time span that we had available to treat a large number of objects. Was our planning feasible and could we do justice to the individual objects we had to treat? Our main conclusion is one familiar to many restorers: time limitations are always an issue when fully restoring an object, including all the documentation, research, and possible material analyses. We therefore had to make individual choices for each object. In some cases, we removed objects from the list because we did not want to compromise on the degree of treatment that we thought necessary. This resulted in a number of practical decisions that were made, where some objects were fully dismantled and re-restored, while in other cases they were only touched up aesthetically. Treatment decisions for each object were fully documented. For example, the marble vase (RO III 11) was completely dismantled (figure 2), because the old repair had deteriorated badly and was of a low quality in the first place. The kylix (PC 94) from the Canino collection was dismantled because the glue had become unstable. In this case, we also wanted to show the ancient repairs that had been disguised by the 19th century restoration (PC 94; figure 7). We did re-use the historically valuable replacement of the foot that was executed on the estate of Canino. The appearance of the foot fit well with the shape and colour of the body and we wanted to exhibit the complete object.

An advantage of dismantling and retreatment is that one can be certain of the object’s long-term stability. Samples can be taken for analysis and old restoration techniques can be observed and documented. Characteristic examples of old restoration materials are also kept for future research. Many other vases, especially from the large Canino collection, were treated in a less invasive manner. While we did remove old, degraded and unsightly fillings and restorations, we left intact the stable parts of the old repairs. The reason for this was twofold: it saved time so that we were able to restore more objects, and at the same time met the wish to exhibit aesthetically pleasing objects. One often forgets that this wish is an important factor, and reminds us that the conservator is only one voice among several that influences the outcome of conservation practices. As an additional benefit, we were able to retain parts of the interesting 19th century restorations in situ. We must keep in mind that all previous restorations are an important part of the history of an object (Caple 2000, p. 127). It is an irreversible intervention to the object to remove these traces (Dooijes 2007). This perspective has interesting parallels to the practice of cleaning objects as described by Koller, who views the surface of an object, and in this case also the object itself, as an archive of its own history (Koller 2000).

Although we had to remove some interesting old repairs, we fully documented the objects’ histories and have placed the old restorations in their historical context, thus preserving their stories. The new Greek galleries of the National Museum of Antiquities in Leiden reopened in mid-December 2015.
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The Extra Piece of the Puzzle: A Combined Stylistic and Analytical Study for the Reconstruction of Two Fragmented Glass Goblets from the Collection of Ferdinand II of Portugal

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Abstract
In the 19th century, around 200 glass objects of diverse origins, provenance and chronological periods could be found on display in the Glass Room of the Palace of Necessidades, as part of the collection of King Ferdinand II of Portugal. Unfortunately, after several transfers and eventual incorporation into the collection of the Museu Nacional de Arte Antiga (MNAA), some of these fine objects are now in dire need of treatment.

In this collection there is a set of two glass goblets in the Venetian style that are quite peculiar, and deserve an in-depth investigation. Both in terms of typology and iconographic interpretation, and their conservation-restoration treatment, the two goblets present themselves as a challenge to the conservator.

The use of X-ray fluorescence analysis yielded information about the chemical composition of the several glass fragments and has been correlated with technological, iconographic and typological information. Conservation decisions were made based upon all the combined collected data and treatment is underway.

Introduction
King Ferdinand II of Portugal (1816-1885) was a collector and lover of the Arts. He displayed his glass collection in the National Palace of Necessidades (Lisbon), alongside many other objects that he had gathered (Teixeira 1986). This palace was also the residence of his successors, namely King Manuel and King Carlos, the latter of whom acquired part of his grandfather’s glass collections (AHCB n.d.). By 1910, the custody of the Palace had been delivered to the Ministry of Foreign Affairs; the glass displays were dismantled, and many objects were placed in the safe deposit of the Palace (Casa Forte das Necessidades) (Martinho and Vilarigues 2013). It is thought that these objects might have entered the storage rooms of the MNAA (Lisbon) in 1957. The transfer of most of the objects from Casa Forte das Necessidades took place during this period (ANTT 1910). Apart from an exhibition in 1989 called “O vidro em Portugal”, at MNAA (Alarcão 1989), and some Portuguese objects permanently on exhibition, the main part of the Museum’s glass collection was kept in storage. And it was there that the part of the glass collection originally from the Palace of Necessidades has remained for the last 60 years.

In 2013 when studies on the goblets began, they were located in the storage rooms of the MNAA. Unfortunately, these fragile and fragmented goblets were stored in poor conditions, which compounded their already damaged state. Two bowls with stems, a fragmented foot for each goblet, and a very large number of fragments, formed what the curator called a possible set of two glass goblets (MNAA1129vid, Goblet A, and MNAA1130vid, Goblet B; see figures 1A and 1B). The fragmentary goblets were found together with several other damaged glass pieces. Consequently, the association of fragments to each of the goblets was based on proximity (fragments stored close together) and typological
resemblance. But it is necessary to point out that the objects have an unusual iconography and similar decorative elements (flowers, leaves, etc.), and that their physical reconstruction depended on this information. Moreover, the documentation available in 2013, relating to the two objects, was limited to the inventory dating back to 1957, in addition to two black and white pictures from the same year (figures 2A and 2B), and one colour picture from 1995 (only of Goblet A). None of these had a complete description of the objects or presented the objects before damage. Since they have probably been broken for more than 60 years, the missing glass parts that might have been lost during this period make re-assemblage an even more demanding task. The condition of the objects was also a matter of importance, since the stem of Goblet B presented an opaque-white layer, whilst the rest of the fragments belonging to the same goblet (as well as Goblet A) were not covered by this layer. The different states of corrosion of the glass fragments were taken into consideration in every step of the process.

To distinguish and attribute the fragments to each goblet, the conservator working on the goblets had to make use of the history and description of the 19th century display in
the Palace of Necessidades. Unfortunately, the description only exists for one of the objects; a search for the second description is still being undertaken. Furthermore, other tools were used, such as visual examination, iconographic interpretation, comparison with similar typologies, etc. Ultimately, understanding these fragments, and the possible reconstruction of the two goblets as a means of preservation, are the goals of this study.

The Reconstruction of the Two Goblets

The Glass Fragments

Among almost 220 glass fragments, the main structures of two goblets were identified. The majority of the remaining fragments were quite indistinguishable. Their attribution to a specific glass object was difficult, due to the variety of glass colours and the applied decorative details. When found, the first goblet (Goblet A, figure 3A), or its tall stem and bowl (glued together by what is now a yellowed adhesive), are mainly made of colourless glass and are about 32-34 cm in height. The central part of the stem is flanked by two twisted colourless glass arch-shaped decorations. Leaves of blue, opaque-white, yellow and green are still attached to the arches and top of the stem; many visible break edges are evidence of other missing elements.

A small naked human male figure, facing forward, can be seen on the left side, encircled by half of the arch decoration. On the right side, a tiny foot in the base of the arch indicates the presence of a missing second figure. Entwining the central cylindrical-shaped part of the stem—decorated with twisted brown glass threads—one can see a purple serpent, facing right. Green leaves and small apples decorate the central part of this level. The lower level of the stem is made of colourless glass and is baluster-shaped with gadroon decoration. On the right side, a mythical creature, a dragon of colourless and blue glass with colourless wings, can be seen. On the left side, evidence of a second symmetrical figure can be seen near the fracture. Close to this goblet, a fragmented foot was found.

The other fragments, stored close to this object, consisted of two other human figures: a male figure with outstretched arms, half undressed, that can be interpreted as Christ crucified, and what appeared to be the naked female figure of Eve (based on her physical attributes and her logical coupling with Adam – figure on the goblet). Green, blue and yellow leaves—or fragments of this kind of decoration—were found in large numbers, with and without apples. Two twisted, colourless, arch-shaped glass decorations, with yellow wings, as well as a pair of unattached wings were also found. Finally, a fragmented flower centre and stem, a cherubim’s head with only one wing, some flower petals, and a fragmented dragon figure complete this set of fragments.

When found, the second goblet (Goblet B, figure 3B) consisted of a tall stem and bowl, separated by a break, with a broken foot stored close to this set of fragments. These are mainly made of colourless glass and are about 30-32 cm in height. The stem is made up of a series of rings put together around a central cylindrical colourless cane. The conical bowl rests on a conical element, made of colourless glass and decorated with blue and white threads on its surface, belonging to the top of the stem. Immediately below this conical element, is a fragmented colourless glass ring with no decoration. Beneath this, is another colourless ring with three leaves of coloured glass: green, light-green and yellow. The first two rings have the same morphology, and the third is quite dissimilar. The forth decorative element is another colourless ring fragmented in two, a fifth ring is decorated with yellow and green leaves, and below that, a sixth ring is decorated with a dragon figure made of colourless and blue glass. A second broken and separated dragon element was found near the object. The lower end of the stem consists of a seventh ring, followed of a hollow baluster-shaped element. The baluster and the colourless central cane would have been attached to the foot of the goblet.

The other fragments recovered close to this object included: between seven and nine different flowers (each one composed of several fragments), a figure easily identified as Mary, Mother of Christ in a blue robe, purple and green fragments, some colourless fragments, and a fragmented dragon figure, all associated with the goblet, as well as a few additional fragments that did not belong to the goblet (they were labelled with different inventory numbers).

Decorative Elements, Iconography and Old Records

The section above describes the state of the objects in 2013. When compared with the condition of the objects in 1957 it is apparent that they have deteriorated further, although they were already in poor condition in
Fig. 3. Reconstruction/set of fragments. A) Goblet A; B) Goblet B; C) Other. Areas analysed by μ-EDXRF are marked in orange.
1957. It was from these old records and the iconography of the pieces, that the investigation to understand the location of the decorative elements began. It is likely that the decoration of Goblet A, represents “The Fall of Adam and Eve”: the two figures, naked, before a great tree (the central part of the stem) covered with fruit, with a serpent entwined around it, with its head is turned towards Eve (Didron, Millington and Stokes 1981). However, the Cherubim’s head, the figure of Christ, and the existence of two other figures associated with this goblet (one likely Mary and the other a possible representation of St. John in a purple and green robe) suggest a more complex iconography. Some of them can actually be seen in the record of 1957 (figure 2A).

Unfortunately, no record of the object as a whole piece was found; we therefore have no evidence to sustain the association of the additional figures. The combination of Adam and Eve in the Garden of Eden with the Snake, and Christ Crucified is more likely than the application of the figures to the second goblet (see below), and can be related to the following passage of the Holy Bible: “For we are members of his body, his flesh and of his bones | For this cause shall a man leave his father and mother, and shall be joined unto his wife, and they two shall be one flesh | This is a great mystery, but I speak concerning Christ and the church…” (Ephesians 5:29-32).

A portion of the meaning of the passage has been interpreted by many 19th century authors (Formby 1851; Macknight 1810; Scott 1830) as: “Adam, in whom the whole human race began, was a natural image of Christ, in whom the human race was to be restored: and his deep sleep, the opening of his side, and the formation of Eve of a rib taken out of his side, were fit emblems of Christ’s death, of the opening of his side on the cross, and of the regeneration of believers by his death. The love which Adam expressed towards Eve, and his union with her by marriage, were lively emblems of Christ’s love to believers, and of his eternal union with them in one society after the resurrection” (Macknight 1810, p. 342). On the other hand, one can also interpret the two scenes as two separate moments: the Fall and Rise of the Church (figure 3A). The Church had to fall with Original Sin, to be reborn after Christ sacrificed Himself for the sins of the human race.

In Goblet B (figure 3B), a series of colourless rings comprise the stem, onto which some decorative figures have been applied: two mythical figures of dragons very similar to the ones from Goblet A, distinguishable by the shape of their wings and by the fact that most of the fragments could be joined together. Below these figures, a hollow baluster shape with two blue and colourless glass wings terminates the stem and connects it to the foot. The winged baluster shape had a similar appearance of the glass, and similar colours to the two dragons, and could evidently be linked to the upper and lower elements attached to the stem. Knowledge of the existence of a set of five flowers decorating the top part of the stem came later, from a description of the Glass Room in the Palace of Necessidades in 1886, one year after Ferdinand II’s death. In one of the pages of the inventory, one can read the following description of a goblet (AHCB 1886, p. 109): “A white Venetian goblet” with a “bell-mouthed top” and a “baluster stem.” “Five flowers come out from the base [of the bowl] with the colours: blue white yellow pink green and red.” “Two dragon motifs [can be seen] on the sides.” Decorations of “yellow and green leaves above”, and “by the foot, there are ornaments in white and blue glass.” This description fits with what is left of Goblet B (see figure 3B); therefore, one can surmise that this object was whole in 1886, and was on display.

**Previous Repairs**

The evidence of previous repair and restoration is commonly seen on glass objects, which have been in a collection for a number of years (Davison 2003). In this case study, several questions arose from the previous interventions to these objects. As mentioned above, Goblet B was on display, and was therefore likely in one piece in the mid-19th century. No adhesive was detected on this object. Nevertheless, one cannot disregard the hypothesis of it being an all-glass hybrid (by definition “damaged glass vessels repaired by the addition of one or more pieces from one or more other glass objects in order to make up a complete glass vessel” (Navarro and Higgott 2013). This goblet is built (its stem in particular) by placing glass elements side-by-side around a glass cane, without the structure of a whole piece as in a free-blown glass vessel. Perhaps these elements were put together by the antiquary or dealer, as was common practice at the time (Navarro and Higgott 2013).

The presence of an adhesive join between the stem and bowl of Goblet A was detected. The pictures from 1957 and 1995 are also good chronological markers since they...
depict an object more fragmented than it is today. This allows us to work out which repairs were performed before, and which occurred after, these records. In relation to this object, no records exist that can confirm whether it was already broken when it came into the collection. Besides, it is also not possible to establish if back then it was not an all-glass hybrid (since its foot has been ground down to be attached to the stem with some sort of adhesive), or even which fragments are and are not part of the original piece. All of the listed possibilities of composition and previous repairs throughout the objects’ history set up an even more complex situation.

A Challenging Approach
These two (?) glass objects and associated fragments pose a number of challenges to the understanding of the objects’ history, form and consequent interpretation, and to the practical conservation approach. In summary, the challenges the conservator had to face were as follows:
1. incomplete records and information;
2. difficult iconographic interpretation (i.e., both goblets were decorated with some similar elements – e.g. the dragon figures);
3. time past since the damage (The objects have been broken for more than 60 years and missing glass fragments make re-assemblage an even more demanding task);
4. doubts about the objects ever being “one piece” and questions relating to the original appearance of the objects. It is unclear if they were one piece while they belonged to Ferdinand II’s collection;
5. the fact that several fragments showed different stages of corrosion with no apparent relation to the glass object itself but, instead, to their storage environment;
6. mixture of fragments with possibly different origins, which changed the approach to one resembling a more archaeological methodology;
7. and, finally, the need to gather and join the fragments due to the high probability of continued loss in the future.
These challenges created the necessity for scientific research to ensure that the pieces were assembled correctly.

Analytical Studies
The benefits and limitations of the use of micro Energy Dispersive X-ray Fluorescence (µ-EDXRF) analysis are well known (Bronk et al. 2001; Janssens 2013). The fact that this technique is non-invasive and requires minimal or no sample preparation, together with the fact that the elemental composition with qualitative results could be obtained within minutes, were seen as great advantages, and reasons for the use of this technique as a source of complementary information to stylistic interpretations.
The glass composition was analysed by µ-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). 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.
The fragments analysed were chosen based on their aesthetic similarities, and on the fact they were the ones lacking a clear association with one of the goblets:
• the human figures of St. John, Mary Mother of Christ, Christ and the Cherubim, as well as the human figures still attached to the Goblet A;
• all colourless glass of Goblet A, all colourless glass of Goblet B and other colourless fragments (namely, the flowers);
• and the fragmented leaves, which were compared to the leaves attached to both goblets.
Initially, a qualitative comparison was carried out by overlapping the spectra of the fragments assuredly belonging to each goblet with the fragments, which were in doubt. After this visual comparison, the WinAXILBatch software package was used to obtain the areas of the peaks of the elements identified in each type or group of glasses. The ratios of major and minor elements were plotted for groups of glass presenting the same elements and close peak intensities. For an easier interpretation of groups and results, several glass types were plotted on the same ternary plot (see figures 4 to 7).
There was no overlap in the glass compositions of the feet or bowls of the two goblets, but the spectra for the stem structures overlapped. In Goblet A, all of the colourless glass used has no lead; the coloured glass of the decorative groups (also of two different compositions) has lead-based matrices. For Goblet B, the bowl and foot are made from one colourless glass type, whilst the elements of the stem are made of a different colourless glass. The coloured glass
of the decorative elements is the same for Goblet B as for Goblet A.

From what can be seen in figure 4A, it is very clear that the colourless glasses that make up part of the stem of Goblet A are of one type, and that some of the flowers and fragments (those presented on the left in figure 3C) should be part of this goblet. The rosebud and the twisted arch analysed do not match the composition of the decorative elements and other fragments belonging to Goblet A as can be seen by overlapping the spectra, or by the two groups formed in figure 4A. Nevertheless, we believe it is possible that the twisted arch might be part of a structure related to Goblet A, despite its different chemical composition (see figure 3A).

The skin of all figures analysed seems to be the same type of glass (figure 4B). The same lead-based glass might have

Fig. 4. Ternary plot giving the ratios between element-peak areas from the µ-EDXRF spectra of the glasses composing Goblet A, and non-joining fragments; A) colourless glass, B) coloured glasses.
been used for white, flesh, and blue colours, with differences in the colouring agents (e.g. cobalt for blue), since, except for these elements, the spectra of these glass fragments overlap, and the areas of the element peaks group together (figure 4B). Moreover, the decoration of the dragon and the decoration on the base of the figure of Saint John, which form a second group of glass (visibly more transparent), seem to be a perfect match.
These results seem to indicate that all the figures belong to Goblet A, which is in accordance with what is seen in the photograph from 1957. Nevertheless, we cannot establish where the figures of Christ, Saint John and Mary might have been located. Perhaps Goblet A might have had a third level of decorative elements on its stem, or most likely, they might have belonged to a lid. Unfortunately, we have no indication as to its original appearance. Figure 5 shows the ternary plots of the structural and decorative colourless glasses composing Goblet B, as well as some of the fragments that do not present a clear connection with the main body. It is possible to observe two distinct groups: the bowl and foot are of a different type of glass from the rest of the elements of the goblet (note: dragon fragments are slightly different due to lead diffusion from the blue-glass decorations). All the fragments plotted—excluding the foot and bowl—seem to be grouped together in terms of both major and minor element-peak areas ratios, with the exception of the rosebud and the flowers BY, IYW and BWR (which also cannot be correlated with the other goblet). This supports the idea that the grouped fragments of the flowers might belong to Goblet B (green elements of figure 5 can be seen in figure 3C), and that the other two are clearly not a match. Nevertheless, some flowers and fragments are overlapping in both goblets.

Figure 6 shows the ternary plots of all of the leaves that are not clearly correlated with one of the goblets, as well as some clearly belonging to each vessel, in addition to that of the FAA flower, where the yellow colour was analysed. Two groups of yellow glass are evident. The FAA flower evidences the presence of the two types of yellow, and therefore the two types of yellow are correlated and were probably applied as hues. It is unfortunately not possible to relate the leaves that have no joins with one of the goblets, since all analysed leaves seem to have a similar composition including the ones attached to each one of the goblets stems.

A binary plot with the ratios of some minor and trace elements is shown in figure 7. Most of Goblet A measurements have lower Ba/Pb peak-areas ratio, below the tendency line presented, whilst the same ratio for Goblet B is above this line. Some of the flowers (BWYF, sYWF, PBF) seem to group with Goblet A ratios, and others (PWF and sBYF) are not far from the ratios shown in the measurements of Goblet B. The ratios of fragments of the set AIV and ATF are also
mostly distributed above the line, which suggests a relation with Goblet B. This plot shows the ability to distinguish the stems of the two goblets, and that some of the fragments could probably be attributed this way. Thus, although many of the questions of attribution are now answered, the results also add a further problem to an already complex challenge: while some of the flowers can be linked with the goblet by their glass type, as was the hope at the onset of this project, others do not seem to belong to either goblet. Three flowers belonging to Goblet B are yet to be identified, and some of the flowers analysed cannot be attributed to either of the goblets by these methods. However, if either of the goblets is an all-glass hybrid or, if the glassworkers chose to use different glass types for the decoration of the same object, the fragments that cannot be related to either of the goblets may still have been a part of them at some point in their history.

Concerning the limitations of this study, the state of corrosion of some of the fragments was an important factor. As a surface sensitive technique, µ-EDXRF is limited for corroded glasses when interpreting the analysis’ results. Throughout this study, variations in the intensities of elements most affected by corrosion processed (e.g. Si, Ca, K) – especially in the fragments of the stem of Goblet B that showed visual alteration – were taken into consideration. Analyses from several points were acquired until the results were satisfactory. Fortunately, on one hand, the spectra of the structural cane were overlapping the spectra obtained for the stem of Goblet A. On the other hand, the deconvolution of the spectra by WinAXILBatch package takes into account many of the matrix effects and measurement errors; therefore, the areas of the elements’ peaks (i.e. fluorescence lines) are complementary information to the visual examination of the spectra overlapping. This way, it was possible to obtain quite reliable results as can be seen in figure 8.

Conclusions

Through the use of µ-EDXRF, information on the chemical composition of numerous glass fragments complemented the technological, iconographic and typological interpretation of the glass objects. Decisions on the assembly of the fragments can now be made on the basis of this combined data. A deeper understanding will support decisions, since a large number of fragments do not have obvious joins with either of the goblets. This study of the chemical composition allowed the joining of such fragments to the two main structures. Moreover, it was shown that different glass compositions were used in the same object (e.g. different for colourless
parts). Since Goblets A and B are not as a free-blown vessel would be, but a set of separate pieces mounted around a colourless glass cane (not hot-fused), there is the possibility that both the goblets are all-glass hybrids. Although it is not yet known how all the fragments and goblets were connected, the insight gained by the study has made new interpretation possible and increased the conservation options for these two glass objects. μ-EDXRF can be recommended for future studies to provide information on the attribution of glass fragments of unknown origin to two or more broken glass objects with typological resemblance.

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Weeping Glass:
The Identification of Ionic Species on the Surface of Vessel Glass Using Ion Chromatography

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Weeping glass; glass sickness; glass deterioration; ion chromatography

Abstract
Aqueous films on the surface of unstable vessel glass were analysed. Five cation and eight anion species from eleven glass items in the Rijksmuseum, Amsterdam, the Hamburg Museum and the Corning Museum of Glass have been quantified by ion chromatography. Sodium, potassium, magnesium and calcium cations and acetate, formate, chloride, nitrate, carbonate and sulfate anions are deemed most significant. The results indicate that the compositions of moist films on weeping glass are more complex than generally recognised. The findings are discussed in relation to the sources of the ions and the implications of their diversity for the choice of a suitable relative humidity (RH) for display and storage of unstable vessel glass. The compounds which may form have deliquescence RH values which span the range 11-99%, demonstrating the difficulty of making recommendations about storage RH to prevent the onset of weeping.

Introduction
This paper is part of a more extensive investigation primarily designed to pinpoint glasses of unstable composition where visual inspection is inconclusive in assigning surface effects, often described by terms such as ‘haze’ or ‘cloudiness,’ to an unstable glass composition (Lamain et al. 2013). The focus of the research presented herein is, in contrast, an investigation of those glasses incontrovertibly displaying signs of deterioration, specifically the presence of the distinct moist films or droplets on the surface which characterise weeping glass. This investigation is motivated by the need to understand more precisely the identity of ionic species present in these aqueous films for two main purposes; firstly, to gain a better understanding of the origin of ions and, secondly, to be better placed to provide sound, analytically-based recommendations for storage and display environmental conditions for weeping glass.

The nature of the species present depends on the glass composition (and, specifically, the ions leached from the glass by the action of atmospheric moisture), the reaction of these ions with atmospheric carbon dioxide or with gaseous atmospheric pollutants, and, additionally, the surface deposition of ionic compounds from the atmosphere or from handling. These three sources of ions can potentially give rise to a wide range of crystalline products or ionic solutions on the surface of unstable glass objects in museum collections. Whether these species remain in solution or crystallise as efflorescence salts depends on the deliquescence relativity humidity (DRH) of the crystalline compounds and the relative humidity (RH) of the storage or display environment. At any RH above its DRH, a compound will exist as an aqueous solution, whereas at RH levels below the DRH it will be in a crystalline state. This consideration underpinned the choice of a recommended storage RH for unstable vessel glass in museums, first pro-
posed by Organ (1957). He argued that, in order to avoid the effect of weeping, glass should be maintained at a RH below 42% so as to prevent the deliquescence of potassium carbonate, the compound which he considered would have the lowest DRH of all those that might form on glass. This has remained a prime recommended storage or display target RH for unstable glass to the present day (see, for example, Erhardt and Mecklenburg 1994; Koob 2006; Kunicki-Goldfinger 2008).

However, despite almost sixty years of general acceptance of this recommendation, no analytical study has been undertaken specifically to explore its validity. A number of studies have subsequently identified crystalline compounds on the surface of unstable glass items in museums but no comprehensive identification and quantification of the species present in solution on the surface has been reported. Accordingly, the focus of this ongoing analytical study, the preliminary results of which are presented and discussed in this paper, is the elucidation of the composition of the aqueous films on weeping glass.

In this research, ion chromatography (IC) is the main analytical technique used as it provides the possibility to quantify low concentrations of cations and anions in aqueous solutions. A detailed description of the IC technique and the sampling protocol adopted for our research has been reported previously (Lamain et al. 2013). Using the IC setup chosen, quantification is achieved for thirteen cations and anions of which we consider sodium, potassium, magnesium, calcium, acetate, formate, chloride, nitrate, carbonate and sulfate most relevant to the formation of salts on the surface of unstable glasses.

Using IC as the main analytical technique provides three major advantages. Firstly, the analytical procedure is relatively straightforward and allows rapid analyses of samples from many objects. Secondly, the technique offers low detection limits (ideally, parts per million or even parts per billion), with the ability to detect ions on artefact surfaces where no apparent surface alteration has taken place (Tennent et al. 1992). Thirdly, sampling can be very straightforward. By using simple cotton swabs a representative sample from the glass surface can be obtained. The protocol used in this paper is still being refined for use as an early-warning system for detecting unstable glass, and validation for quantitative comparisons between different objects is yet to be achieved. Nonetheless, for understanding the phenomenon of weeping glass and for discussing the choice of optimal display and storage RH values, important progress is already achievable by consideration of the relative quantities of the ions present. This paper therefore reports results of IC analyses of eleven unstable glass items from three museums: the Rijksmuseum, Amsterdam, the Hamburg Museum and the Corning Museum of Glass.

Experimental
Objects and samples
Five vessel glasses from the Rijksmuseum (RM), five items from the Hamburg Museum (HM) and one vessel glass from the Corning Museum of Glass (CMOG) were included in this study. Table 1 lists the objects with their registration numbers and sample codes.

The RM samples were taken from glasses clearly demonstrating signs of deterioration, described by the museum conservators as “droplets,” “greasy” and “wet.” The samples were taken during a condition survey of a part of the glass collection. Of the many samples gathered, a selection of those with pronounced moist surfaces was made for this study.

Samples from the HM were taken from the inside of cover glasses of daguerreotypes and painted miniatures. These glasses exhibited symptoms of glass deterioration in storage which in some cases had led to the formation of corrosion products on the copper frames (Beiner-Büth 2015). The cover glasses had a moist surface film which appeared greasy.

Four samples were taken from the foot of a Venetian glass from the CMOG, one from each quadrant. Samples CMOG_92.3.36_4i to iii are three samples taken consecutively from one quadrant of the foot. This Venetian glass was considered by the museum conservators to be of unstable composition but at the moment of sampling there were no obvious signs of glass deterioration.

Sampling and extraction
Samples were taken using a previously-developed sampling protocol (Lamain et al. 2013) for which the sampling materials have been evaluated (Verhaar, van Bommel, and Tennent 2015). Sampling at the Rijksmuseum was performed by the conservators in collaboration with one of the authors (GV). A sampling kit was sent to the HM along with sampling instructions. A kit was also sent to
the USA but never arrived. Therefore, the samples from the CMOG were obtained (by NHT) with swabs prepared at the museum. All samples were sent back to Amsterdam in closed polypropylene vials. Sampling was performed using cotton swabs moistened with deionised water. An area of circa 2 cm² was sampled. In order to bring the soluble salts into solution for IC analysis, the swabs were placed in a polypropylene centrifuge tube and extracted for an hour in 1.5 mL deionised water. After removal of the swabs from the centrifuge tube the samples were centrifuged for ten minutes at 2000 rpm to remove possible fibres and other larger particles from the sample. Extraction of blank swabs was also carried out for comparison.

**Analysis**

Anion concentrations were determined using a Dionex ICS-2100 IC system equipped with a Dionex DS6 conductivity detector, an Ionpac AS17-C 2x250 mm analytical column and AG17-C 2x50 mm guard column, and a Dionex anion electrolytically regenerated suppressor (AERS 500). The eluent used was potassium hydroxide with a gradient ranging from 1-45 mM at a flow rate of 0.37 mL·min⁻¹ over a runtime of 20 minutes. Eluent concentrations were established using a Dionex EGC-III eluent generator cartridge. A Dionex CR-ATC trap column was used to remove anionic contaminants from the eluent. This setup allows for the analysis of fluoride, acetate, formate, chloride, nitrite, bromide, nitrate, carbonate, sulfate and phosphate ions in concentrations below parts per million levels.

The analysis of cations was performed using a Dionex ICS-1100 IC system equipped with a Dionex DS6 conductivity detector, an Ionpac CS12-A 2x250 mm analytical column and a CG12-A 2x50 mm guard column, and a Dionex cation electrolytically regenerated suppressor (CERS 500). A 20 mM solution of methane sulphonic acid (Fluka chemicals, >99% pure) was used as eluent at a flow rate of 0.25 mL·min⁻¹. This setup allows for the analysis of lithium, sodium, ammonium, potassium, magnesium, and calcium ions in concentrations down to parts per million levels. Samples were stored in polypropylene vials and injected using a Dionex AS-AP autosampler. All standards and samples were prepared using HPLC grade deionised water (Thermo Scientific Barnstead Genpure UV-TOC, Ultrapure 18.2 MΩ·cm water, TOC: 1 – 5 ppb).

**Results and discussion**

**Blanks**

In order to determine the contribution of the blank swabs to the total amount of ions in the extracted solution, dry cotton swabs were extracted and the solutions were analysed using IC and compared to the deionised water blank. For the sampling of the objects from the RM and the HM collections cotton swabs from a drugstore were used. Anal-

<table>
<thead>
<tr>
<th>Collection</th>
<th>Object no.</th>
<th>Description</th>
<th>Sample codes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rijksmuseum</td>
<td>BK-KOG-139</td>
<td>Bottle, c. 1675-1700, Dutch</td>
<td>RM_BK-KOG-139_1</td>
</tr>
<tr>
<td></td>
<td>BK-NM-758</td>
<td>Bottle, Willem Jacobszoon van Heemskerk (engraver), c. 1675-1685, Dutch</td>
<td>RM_BK-NM-758</td>
</tr>
<tr>
<td></td>
<td>BK-NM-776</td>
<td>Glass, Anonymous, c. 1550-1600, Venice</td>
<td>RM_BK-NM-776</td>
</tr>
<tr>
<td></td>
<td>BK-NM-7995</td>
<td>Wine glass, Anonymous, c. 1600-1650, Venice</td>
<td>RM_BK-NM-7995</td>
</tr>
<tr>
<td></td>
<td>BK-NM-9811</td>
<td>Wine glass, Anonymous, c. 1675-1700, Dutch</td>
<td>RM_BK-NM-9811</td>
</tr>
<tr>
<td>Corning Museum of Glass</td>
<td>92.3.36</td>
<td>Goblet, 1600-1699, Venice</td>
<td>CMOG_92.3.36_1</td>
</tr>
<tr>
<td></td>
<td>1912.438</td>
<td>Miniature painting, Portrait of an unknown man, possibly from the Goos Family, c. 1810</td>
<td>HM_1912.438</td>
</tr>
<tr>
<td></td>
<td>1912.452</td>
<td>Miniature drawing, Portrait of Rosalie Cohen with her son Albrecht, 1820</td>
<td>HM_1912.452</td>
</tr>
<tr>
<td>Hamburg Museum</td>
<td>1929.223</td>
<td>Miniature painting, Portrait of Karoline Amalie Herzfeld, c. 1805</td>
<td>HM_1929.223</td>
</tr>
<tr>
<td></td>
<td>1932.174</td>
<td>Daguerreotype, Portrait of Johan Gottfried Unbehagen as teacher, 2nd third 19th C.</td>
<td>HM_1932.174</td>
</tr>
<tr>
<td></td>
<td>1934.295</td>
<td>Daguerreotype, Portrait of Lady Kunhardt, 2nd third 19th C.</td>
<td>HM_1934.295</td>
</tr>
</tbody>
</table>

**Table 1:** List of objects and sample codes included in this study.
ysis of the extracted solutions of blank swabs indicated that the contribution of sodium is most significant and exceeds the concentration of sodium in the deionised water blank (Verhaar, Van Bommel, and Tennent 2015). Furthermore, it was found that the polypropylene centrifuge tubes do not contribute significantly to the concentrations of ions in solution.

For the CMOG samples, swabs were handmade from cotton wool and fine glass rods available in the CMOG conservation studio. Analysis of a single cotton wool blank showed that it contained more calcium and less sodium than the other swabs but no additional samples were available for confirmatory replicate analyses.

The results of the blank extraction are presented adjacent to the concentration of the ions in the sample solutions (figures 1-4). In this way, the contribution of the swab material to the concentration of each ion can be easily appreciated.

**Museum glass samples**

The results provide information on the nature of ionic species on the surface of weeping glass. The measured ion concentrations for the RM and HM are listed in figures 1 and 2. For the RM and HM samples the major cations found were sodium and potassium. Calcium and magnesium were present in small amounts. Large amounts of formate and chloride were found during anion analysis of the RM and HM samples. Sulfate was present in medium to high concentrations and bromide was found in small concentrations. Acetate was only detected in two samples. Fluoride and nitrate were found in RM samples, but not in samples from the HM.

For the CMOG samples (figure 3) the main cation was sodium, with low concentrations of potassium and calcium and trace amounts of magnesium and ammonium. The main anion found was chloride, which was found in all samples, as was sulfate. Acetate, fluoride and bromide were

![Fig. 1. Anion and cation concentrations for the samples from the Rijksmuseum.](image-url)
Fig. 2. Anion and cation concentrations for the samples from the Hamburg Museum.

Fig. 3. Anion and cation concentration for samples CMOG_92.3.36_1-4i.
not detected. Nitrate was identified on two samples in high concentrations. Formate was found in only one sample in very low concentration.

The significance of these generalised observations is discussed below. Additionally, attention is focused on the occurrence of carbonate which is considered to be of particular importance in weeping glass studies to date.

Interpreting the analytical results

The low detection limits of IC for quantification of the ions of interest offers the potential to permit extremely detailed interpretation of the formation of ionic species on glass surfaces. To date, several issues in the development of a robust analytical protocol have been tackled (Lamain et al. 2013; Verhaar, Van Bommel, and Tennent 2015). In order to ensure that the analytical results can be confidently interpreted as a true quantification of the total ions present on each glass, a crucial additional step, yet to be completed, is the optimisation and validation of the sampling protocol for glass surfaces. As a result, at present, inter-comparisons between objects are restricted and the analytical results can only be considered in terms of the range of ions and the relative amounts of these ions in any single sample. Thus, for example, no firm conclusion can be drawn from the consistently lower concentrations present in the HM samples compared to those from the RM. For the success of our ultimate goal—an early warning system for detecting glass deterioration—experiments towards an optimal sampling procedure are planned as the next phase of our research programme.

Nonetheless, the results presented in figures 1-4 provide compelling evidence that the range of ions on the glass surface is more complex than generally thought and that, in consequence, Organ’s assessment of weeping glass display and storage requirements (Organ 1957) is an oversimplification that needs to be reconsidered. These issues are discussed in more detail below in terms of the results from the samples from the eleven glasses in this study.

Before addressing the implications of these findings, the results from the single CMOG glass studied are important in an assessment of our current ability to draw conclusions from the ion chromatograph results. The value of these results, with six samples all from a single object, is that,
even without a rigorously-applied sampling protocol, they provide confidence for our methodology and indicate the steps that need to be taken to improve this. Figure 3 shows that for similar samples from a single object the same ions are detected but there is a spread in concentrations of each ion from sample to sample. In order to be able to compare ion concentrations between objects, more quantitative determination of the ions on the glass surface will be necessary. The first steps will be to improve the sampling efficiency (the percentage of ions gathered from the glass surface during sampling), the reproducibility (the ability for similar samples to provide similar quantitative analytical results), and the recovery (the ratio of sampled ions that is extracted and analysed) based on experiments with synthetic glass of unstable composition. It must be borne in mind, however, that for future inter-comparisons between objects, the uniformity of the ions present on different areas of the surface in a single object will be an intrinsic uncertainty.

A second experiment carried out with the CMOG glass investigated the results of repeat samplings from the same area. Three samples were taken consecutively from the same location (CMOG_92.3.36_4i, 4ii, 4iii). The results presented in figure 4 demonstrate that the concentration of ions decreases significantly, especially after the first sampling. Since the sampling procedure for this glass was not rigorous (ten swipes of the swab over the 12 cm$^2$ surface), it was not expected that all ions would be removed in the first sample; ions could have been collected in the later samples from previously untouched areas. Interestingly, the only ion which shows no sequential decrease is carbonate, indicating that further research into the detection of carbonate is necessary.

### Deliquescence of salts

In previous studies, sodium formate has been identified as the main crystalline species on the surface of unstable glass (see, for example: Schmidt 1992; Robinet et al. 2004; Eremin et al. 2005). Despite the fact that the results from our study also suggest that sodium formate is one of the main compounds on the surface of weeping glass, the equally large concentrations of different anionic species also need to be taken into account.

In a key paper (Eremin et al. 2005) it was suggested that, due to the low DRH (16-17%) of potassium formate, this compound may have a dominant role in the maintenance of moist surfaces on weeping glass even at moderately low RH (for example, c. 40%). The likelihood of the formation of this compound on certain glasses is confirmed by our results. For the RM glasses (figure 1), formate was detected as the dominant anionic species in four of the six samples. For each of these samples potassium is also clearly detected, thus supporting the proposition that potassium formate may make an important contribution to the moist surfaces on weeping glasses.

The wide range of ions found on the glasses sampled emphasizes the complex chemistry of the weeping glass phenomenon and the difficulty of making general recommendations about storage or display conditions for unstable glass. Table 2 lists the DRH of sodium, potassium, magnesium and calcium salts that may be present on the glass surface, based on the results of this investigation. An added complication is that mixtures of salts result in an overall DRH different from that of the individual salts (Price and Brimblecombe 1994). A further uncertainty is that such unusual mixtures of ions may lead to the forma-

<table>
<thead>
<tr>
<th>Anion</th>
<th>Sodium salt</th>
<th>Potassium salt</th>
<th>Magnesium salt</th>
<th>Calcium salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetate</td>
<td>43.5-45.2% (8)</td>
<td>23% (5)</td>
<td>n.d.</td>
<td>100% (6)</td>
</tr>
<tr>
<td>Formate</td>
<td>50.2-52.1% (8)</td>
<td>16-17% (3)</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Chloride</td>
<td>75% (5)</td>
<td>85% (5)</td>
<td>33% (5)</td>
<td>32% (2)</td>
</tr>
<tr>
<td>Nitrate</td>
<td>75% (5)</td>
<td>95% (5)</td>
<td>54% (5)</td>
<td>11% (1)</td>
</tr>
<tr>
<td>Carbonate</td>
<td>91% (4)</td>
<td>43% (5)</td>
<td>~100% *</td>
<td>~100% (7) *</td>
</tr>
<tr>
<td>Sulfate</td>
<td>84% (10)</td>
<td>97% (5)</td>
<td>41-56% (9) **</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

Table 2: Room temperature values for the deliquescence relative humidity of salts possibly associated with weeping glass surfaces.

(1) Al-Husney et al. (2005); (2) Davila et al. (2010); (3) Eremin et al. (2005); (4) Erhardt and Mckellenburg (1994); (5) Greenspan (1977); (6) Kremer, Hunsche, and Noga (2009); (7) Onatich, McGrath, and Imre (2000); (8) Peng and Chan (2001); (9) Steiger et al. (2011); (10) Tang and Munkelwitz (1994); * Magnesium and calcium carbonate are poorly soluble in water. Therefore the DRH is estimated to be 100%; ** The DRH of magnesium sulfate depends on the phase of the compound.
tion of complex compounds, possibly unknown to science. This is a topic of related research interest concerning the juxtaposition of weeping glass with metals (Eggert 2010). The HM items in this study also show evidence of weeping glass/metal reaction.

The sources of the ions in the samples investigated

Principal ionic components

It is generally accepted that the sodium and potassium alkali cations on the surface of unstable glass originate from the glass (Kunicki-Goldfinger 2008) and the results from all samples are in accord with this. For sodium, the identification of high levels of chloride in all samples is indicative of the additional ubiquitous presence of sodium chloride, deposited from handling and/or from aerosols in the atmosphere. The contribution of the latter source was also postulated in the glass studies of Robinet et al. (2004) and finds support in specific investigations devoted to the museum environment where an atmospheric source of sodium chloride was identified in Californian museums (Nazaroff et al. 1992). Of particular relevance, these levels were found to be similar to those outdoors for museums with no HVAC systems. The source of calcium and magnesium, also detected in all samples, is assumed to be the glass itself as these alkali earth elements are also present in unstable glasses (Brill 1975).

The anions derive from the environment in which the glass is kept, either as a result of off-gassing from storage or display materials or as a result of their presence in the outdoor atmosphere. The detection of formate and acetate is undoubtedly primarily due to the emission of formic acid, acetic acid and formaldehyde from wood or wood composite materials. As mentioned above, chloride is associated with the presence of sodium chloride. The presence of sulfate and nitrate is likely to be due to infiltration of outdoor pollutants into the museum environment (Nazaroff et al. 1992).

The question remains whether detection of formic and acetic acid on the surface of unstable glass can be a result of ambient atmospheric concentrations of carbonyl compounds. IC analytical evidence has recently been adduced for the hypothesis that formate and acetate found on unstable mosaic glass is the result of parts per billion concentrations of ambient formic and acetic acid (Tennent and Carthy 2016). Nevertheless, the storage and display history of the objects is undoubtedly crucial in understanding the formation of salts on the glass surface and in making recommendations for suitable museum environmental conditions. It is, however, difficult to trace back the entire storage history—or even the recent history—of objects for study. Frequently, poor documentation on the movement from storage cabinets to display cases, on episodes of cleaning and on changes in the storage location or the materials comprising storage case make it especially difficult to identify those glasses with an impeccable ‘biography.’

Carbonate

Since the publication of Organ’s influential paper in 1957, the formation of carbonates of the alkali ions has been regarded as a central process in the degradation of unstable vessel glass. The DRH of potassium carbonate was, and has subsequently remained, the cornerstone of the recommendation he first promulgated for the avoidance of what is generally referred to as weeping (Organ 1957). Organ, however, carried out no analyses and had no experimental evidence for the actual presence of potassium carbonate on the surface of unstable glass. However at that time, Organ was justified in his supposition that no compound was likely to form on the glass surface with a lower DRH than potassium carbonate. It was only after many years that formates and acetates were recognised as widespread reaction products on vulnerable museum objects (FitzHugh and Gettens 1971). Still later came the first report of the formation of sodium formate on glass (Schmidt 1992). In contrast, no clear-cut analytical evidence for the formation of sodium or potassium carbonate on the glass has been published. Furthermore the presence of carbonate salts was sought but not found by Eremin et al. (2005). A possible explanation for the absence of carbonates on unstable glass surfaces is that they may act as intermediates in the formation of other deterioration products, as is thought to occur during the formation of sulfates on medieval stained glass windows (Newton and Davison 1989). The results in figures 1-3 support the likelihood of chemical conversion of carbonate, formed initially on the glass surface by absorption of carbon dioxide in the atmosphere. At the CMOG, formate and acetate are absent and carbonate is present whereas at the RM and HM carbonate appears to have been consumed with the formation of formate/acetate.
However, calibration of the IC system for the quantitative detection of carbonate is problematic. As a result of absorption of carbon dioxide by the concentrated potassium hydroxide eluent solution carbonate is formed, which interferes with the analysis. The difficulty of quantifying the carbonate concentration in solutions is underlined by the high relative standard deviation in the blank swab extractions. Furthermore, the quantitative detection of carbonate salts is restricted by the poor solubility in water of magnesium and especially, calcium carbonate. When carbonate is detected it is likely to originate primarily from potassium or sodium carbonate, due to their higher solubility (Lide 2005). For these reasons, further investigations of the detection of carbonate using IC and further research on the presence of carbonate on the surface of unstable glasses are necessary.

**Bromide and fluoride**

The source of bromide and, to a lesser extent, fluoride in the RM and HM samples is unclear. The presence of these ions in the extracted solutions may be a result of the materials used for sampling or the storage of the samples. As bromide is used in the preparation of daguerreotypes, its presence in the HM samples may originate from the daguerreotypes themselves (Barger and White 2000).

**Conclusions**

The results obtained in this study are of fourfold importance for the care of unstable museum glass. In the first place they demonstrate, though at a preliminary stage, the value of ion chromatography in providing valuable information on the range of species present on glass surfaces. In the second place, they pave the way for establishing relationships between the surface species present and the composition of the glass itself, as well as that of extraneous compounds, notably atmospheric gaseous pollutants. Thirdly, the results are important in the development of an ion chromatography-based analytical approach as an early warning system for pinpointing glasses of unstable composition; they provide a proof of principle of the sampling and analytical protocol. Finally, the findings establish the need to optimise yet further the sampling/sample work-up protocol in order to ensure better efficiency and reproducibility so as to distinguish unambiguously unstable from stable glass at an early stage, prior to a clear visual manifestation of instability.

Of prime significance, the results demonstrate the need for a re-evaluation of Organ’s recommended target RH to avoid the symptoms of weeping glass. The range of species that have been identified points to the need for a more sophisticated argumentation leading to preferred storage conditions for unstable vessel glass. The species on the glasses sampled from three major museum collections indicate that a greater variety of salts than Organ anticipated may crystallise on the surface. In particular, the possibility of potassium formate formation with deliquescence relative humidity of 16-17% means that the prevention of the onset of weeping is more complex than generally accepted. It may be that for certain glasses in certain environments there is no acceptable RH that will prevent weeping. The results also reinforce the concept that the ideal display or storage RH is dependent on both the composition and the environment of an individual glass, a fact not taken into consideration in the specification of a single preferred target RH for all unstable glass.

All the above considerations will be explored further as this research programme develops. The primary target of future research will be the development of a reproducible sampling protocol aimed at drawing conclusions from inter-object comparisons. This research will largely be based on analyses of deterioration products on the surface of artificially aged synthetic glasses with a composition comparable to unstable historic glass. This will, in addition to the results presented in this paper, allow exploration of the relationship between the composition of the surface liquid film and the glass itself, providing more insight into the nature of unstable glass. Finally, recommendations for storage and conservation strategies will be based on the study of synthetic glasses in varying environments as an extension to the study of museum objects.

**Acknowledgements**

The authors would like to thank Robert van Langh (Rijksmuseum) for his ongoing support of the research.
Isabelle Garachon, Margot van Schinkel, Roosmarijn van Beemen, Bodill Lamain (Rijksmuseum) and Mandy Slager (private conservator) are acknowledged for their critical thinking during the development of the sampling protocol and for providing samples for analysis. Thanks are due to Silke Beiner-Büth at the Hamburg Museum for providing samples from weeping glass. The authors are also grateful to Stephen Koob and Robert Brill from the Corning Museum of Glass for their stimulating discussions and access to the collection.

References
Al-Hosney et al. 2005

Barger and White 2000

Beiner-Büth 2015

Brill 1975

Davila et al. 2010

Eggert 2010

Eremin et al. 2005

Erhardt and Mecklenburg 1994

FitzHugh and Gettens 1971

Greenspan 1977

Koob 2006

Kraemer, Hunsche, and Noga 2009

Kunikcki-Goldfinger 2008

Lamain et al. 2013

Lide 2005

Lide retrieved from http://www.hbcpnetbase.com (4-3-2015)

Nazaroff et al. 1992

Newton and Davison 1989

Onasch, McGraw, and Imre 2000
Organ 1957

Peng and Chan 2001

Price and Brimblecombe 1994

Robinet et al. 2004

Schmidt 1992

Steiger et al. 2011

Tang and Munkelwitz 1994

Tennent et al. 1992

Tennent and Carthy 2016

Verhaar, Van Bommel, and Tennent 2015

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Efflorescence X? Case Solved: 
\[ \text{Ca}_3(\text{CH}_3\text{COO})_3\text{Cl(\text{NO}_3})_2 \cdot 6\text{H}_2\text{O}! \]

The Research History, Identification, and Crystal Structure of Thecotrichite

Gerhard Eggert*, Andrea Fischer, Nanna Wahlberg, Robert Dinnebier, Tomče Runčevski, Rebekka Kuiter, Marian Schüch, Svenja Kampe, Eva Sulzer, Astrid Wollmann

* Corresponding author

Keywords
efflorescence X; thecotrichite; ceramics desalination; calcium acetate; powder X-ray diffraction

Abstract
The hairy, needle-like efflorescence on tiles stored over long periods in wooden cupboards was identified as the calcium acetate chloride nitrate compound thecotrichite. Since 1971, a number of studies have been devoted to this efflorescence and are discussed here. Oddy testing of wooden cabinet samples, with metal coupons and limestone platelets, showed them to emit harmful gases. Qualitative tests for the detection of acetate were compared for their practicality in conservation labs. Thecotrichite samples were used to measure ATR-FTIR and Raman spectra and high-resolution powder X-ray diffractograms for reference. The crystal structure could be determined from these powder X-ray data by sophisticated data handling. This resulted in the sum formula being revised to a hexahydrate: \( \text{Ca}_3(\text{CH}_3\text{COO})_3\text{Cl(\text{NO}_3})_2 \cdot 6\text{H}_2\text{O} \). The application of this method to determine crystal structures from powders will likely become more widespread in the future and has great potential for conservation science.

Introduction:
From Efflorescence X to Thecotrichite

Many museum exhibits contain calcium carbonate such as marble, limestone, lime plaster, corals, mother of pearl, shells of mussels, snails, and eggs, or calcareous encrustations on archaeological finds such as ceramics. White efflorescence on molluscs was noticed by Kenyon (1896, assumed reason: “saline particles…in the atmosphere”) and investigated by Byne (1899) giving rise to the name “Byne’s disease.” Byne detected acetate in the efflorescence, but it took decades until it was realized that acetic acid emissions from wood in storage cabinets were the culprit. These efflorescences often appear as hairy, needle-like crystals (figure 1). Van Tassel (1958) characterized one compound as calcium acetate chloride pentahydrate, \( \text{Ca(CH}_3\text{COO})\text{Cl-5H}_2\text{O} \), and named it calcacite. FitzHugh and Gettens (1971) distinguished a similar compound by X-ray diffraction (see table 2) where the same ions could be detected. For convenience, they called it “efflorescence X.”

Tennent et al. (1992) analysed samples using ion chromatography and found that this compound also contained nitrate. They proposed the name thecotrichite (“a hairy mineral from a storage cabinet”). Unfortunately, this is no longer accepted as an official mineral name (in opposite to the name calcacite given earlier) by the International Mineralogical Association because there is some human involvement in its formation. Grzywacz and Tennent (1994) measured carbonyl pollutants in display cases where thecotrichite occurred but did not find a simple concentration-deterioration relation. Gibson et al. (1997)
calculated the composition of thecotrichite (by averaging ion chromatographic results for 12 samples from different objects and using $^1$H-NMR for the degree of hydration) as 

$$\text{Ca}_{2.95\pm0.01}(\text{CH}_3\text{COO})_{2.91\pm0.03}\text{Cl}_{0.97\pm0.04}(\text{NO}_3)_{2.03\pm0.04}\cdot6.55\pm0.03\text{H}_2\text{O}.$$  

They suggested \(\text{Ca}_3(\text{CH}_3\text{COO})_3\text{Cl(NO}_3)_2\cdot7\text{H}_2\text{O}\) as the formula of thecotrichite. Gibson et al. (2005) studied the phase diagram of the system calcium acetate/calcium nitrate/calcium chloride and found that thecotrichite precipitates incongruently, i.e. not from solutions which contain the ions in stoichiometric ratio. Nevertheless, the small stability field for thecotrichite in the phase diagram can be used to produce it as a synthetic compound. Gibson (2010) explained why thecotrichite is so often formed despite the narrow field of formation: If large amounts of both calcium nitrate and chloride solid salts are present in a porous system and then water is taken up by capillary condensation, a solution is automatically formed saturated with both salts. If a small amount of acetic acid diffuses into this solution, it will be just the right composition to form thecotrichite.

**Thetcotrichite on Ceramics**

FitzHugh and Gettens (1971) have reported cases of thecotrichite on both limestone and ceramic finds.

The first ceramic object showing thecotrichite in the Stuttgart Objects Conservation lab (causing awe and wonder) was a kylix from the Goethe Nationalmuseum Weimar (AK Nr. 2593, figure 2). When presented to the participants of the ICOM-CC Glass & Ceramics Interim Meeting 2001 in Budapest, no one present had ever seen anything similar on ceramics. A later call for samples in the Glass & Ceramics Conservation Newsletter No. 11 (summer 2002, p. 9) yielded only two other cases: a glazed terracotta figure of St. John the Baptist as a child (15th cent.) from the V&A and a cuneiform tablet from the Museum für Angewandte Kunst Frankfurt. Although the occurrence on ceramics is apparently rare, under the right environmental conditions, whole collections can be affected as Halsberghe, Gibson, and Erhardt (2005) reported in their study of 160(!) glazed tiles from the Broelmuseum in Kortrijk (Belgium). This inspired a search for efflorescence in the tile collection of the Landesmuseum Württemberg (LMW) in the castle of Ludwigsburg. These tiles from...
Southern Germany (16th/17th cent.) were formerly stored for long periods in wooden cupboards. One tile with hairy needles was presented in the Stuttgart laboratory at the Ceramics Conservation Colloquium 2006, thecotrichite was identified with FTIR and Raman spectra (Schönemann et al. 2006). In 2013/14, more affected tiles were detected in this collection in preparation for a desalination exercise for freshmen in the Stuttgart Objects Conservation course. Samples from tile E3004 (figure 3) were used for the investigations reported here. White efflorescence was found all over the back of the tile (figure 4) showing the typical hairy growth under the stereomicroscope (figure 5) and the fibre structure under the electron microscope (figure 6).

Oddy Tests: Take Limestone?
The (un)suitability of materials for storage and display can routinely be checked with Oddy tests using metal coupons at 60°C and 100% RH for four weeks in a closed tube (Thickett and Lee 2004). Lead is very sensitive to organic acids – the historic production of lead white makes use
of this. All samples from wooden cupboard materials (com-posite panels) used in the storage of the LMW tiles caused severe white and yellow corrosion of the lead coupons as expected.

According to research at the Library of Congress, corrosion of metal coupons "does not necessarily correlate well to the Library's primarily paper-based collections" (Breitung 2014). Tests using paper were therefore developed. This led to the idea to compare the classical Oddy test with tests using calcium carbonate materials. To make changes easily visible highly polished marble and limestone (used for lithography) platelets were used. The human eye is very sensitive to changes in gloss. For instance, this has been used to visualize that sodium tripolyphosphate (STPP) dissolves trace amounts of copper from polished malachite (Stelzner and Eggert 2008).

In general, the more porous limestone was more sensitive than the marble and showed some matting. However, it was not as sensitive as the lead, and no corrosion products were seen under the microscope which could have been analysed with µ-Raman spectroscopy. Therefore, using limestone instead of metals in the Oddy test has no advantages.

Qualitative Analysis of Anions

Conservators routinely check salts in ceramics for the presence of chloride (with silver nitrate) and nitrate (e.g. with diphenylamine). These tests can also be used for thecotrichite. But how do chemical tests for acetate work when executed by non-chemists without laboratory experience? To test this, conservation students tried acetate tests given in laboratory handbooks (e.g. Feigl 1966) using laboratory chemicals and thecotrichite: iron(III) chloride (recommended for thecotrichite by Halsberghe et al. 2005), lanthanum acetate-iodine, and the formation of indigo. All these tests proved to be less sensitive and reliable than expected. This holds also true for a test for the detection of acetate in the sample! In samples taken from ceramics or limestone, the only interference could be a larger amount of formate resulting in the pungent odour of formic acid superimposing the smell of acetic acid, if it is present.

Vibrational Spectroscopy

Gibson et al. (1997) and Schönemann et al. (2006; sample from the same LMW tile complex published and discussed conventional Fourier Transform Infra-Red (FTIR) spectra of KBr-pellets for both calcite and thecotrichite. To avoid the preparation of KBr discs by careful grinding and pressing, spectrometer accessories using the Attenuated Total Reflection (ATR) technique are becoming more and more widespread (e.g. in forensics as a quick test for illegal drugs). Without any preparation, the sample is pressed against a highly refracting crystalline platelet through which the FTIR beam is guided under total reflection at the surfaces. Quick measurement comes at the price of intensity (the interaction between the radiation and the sample is much lower than in transmission). The absorption bands at smaller wavenumbers are relatively more intense, since the depth of penetration into the sample increases with the wavelength (Derrick, Stulik, and Landry 1999). As reference for ATR-FTIR measurements, figure 7 shows spectra and peak maxima of thecotrichite and, for comparison, calcium acetate hydrate and calcium nitrate tetrahydrate.

µ-Raman spectroscopy is now available in more and more conservation labs. It enables the measurement of individual particles in mixtures under the Raman microscope. Spectra of a sample from the tile E3004 are shown in figure 8 with tentative assignments of vibrations (Wälberg et al. 2015). The results are in good agreement with those in Schönemann et al. (2006).

X-ray Diffraction and Crystal Structure

Data reported from Debye-Scherrer films by FitzHugh and Gettens (1971) and from diffractograms by Gibson et al. (1997) allow thecotrichite to be easily identified — if the analyst knows where to find these reference sets. There is no entry in the PDF/ICDD reference files: a crystal structure for the compound proved elusive and without it it is hard to access the quality of a measurement. The needle-like growth prevents the formation of single crystals
Fig. 7. ATR-FTIR spectra: thecotrichite (black), calcium acetate-hydrate (red), calcium nitrate-tetrahydrate (green) (both from Merck, instrument: Perkin Elmer Spectrum One with ATR accessory, ZnSe crystal) (image: J. Schultz, SABKS).

Fig. 8. µ-Raman spectrum of thecotrichite. Tentative assignment of the low Raman shift region (a) and high Raman shift region (b). In (c) the complete recorded spectrum is shown (image: A. Fischer, SABKS).
of suitable size for conventional crystallographic structure determination. Modern high precision powder X-ray diffraction and sophisticated data analysis can now overcome this limitation. Success with powder X-ray diffraction (PXRD) in finding the structure of the sodium copper formate (Dinnebier et al. 2015)—formerly wrongly abbreviated as “socoformacite” (Eggert et al. 2010; Fischer and Eggert 2013)—encouraged us to deal with a sample from the LMW tile as well. The diffractogram of the ground sample confirmed the identification as thecotrichite. It was collected on a rotated sample (for better particle statistics) packed in a glass capillary, for a period of 6 hours covering the range 5−60° in 2θ with a step size of 0.015°. The TOPAS 4.2 programme suite and an iterative least square algorithm was used to index the PXRD pattern and to determine the data for the unit cell followed by a Pawley refinement (table 1). The positions of the atoms were determined by charge flipping, simulated annealing, inspection of Fourier difference maps, Rietveld whole pattern refinement, application of restraints for bond length, and calculation of the hydrogen positions with the Mercury software (for details see Wahlberg et al. 2015). The crystal structure and further crystallographic information is available in the crystallographic information file (CIF), deposit number: CCDC 1043649. Table 2 lists the theoretical powder diffraction file calculated from this structure for reference, which closely matches the measured diffractogram and is in good agreement with the earlier literature.

Gibson’s formula was confirmed with one exception—there are only six, not seven water molecules:

$$Ca_3(CH_3COO)_3Cl(NO_3)_2·6H_2O.$$  

Thecotrichite consists of a network of calcium ions, connected through acetate and nitrate ions, forming a metal-organic framework. Five of the six chemically different water molecules are directly coordinated to the calcium ions. The structure has channels running along the c-axis, which are occupied by chloride ions and the sixth uncoordinated water molecule (figure 9). The interstitial water molecules are bonded to the coordinated water molecules and to the chloride anion via hydrogen bonding. Some of the uncoordinated water is lost during heating, as shown by thermogravimetry (TG) and differential thermal analysis (DTA), however, the structure is stable up to 110°C, as shown by in situ PXRD.

According to the Bravais-Friedel and Donnay-Hacker model, the growth rate in a given crystallographic direction is inversely proportional to the distance between the corresponding lattice planes. As the lattice constant c is much smaller than b and a for thecotrichite, this results in a needle-like crystal, elongated in the direction of the c-axis, where the interaction is highest. The channels might also allow some ion diffusion during growth.

Fig. 9. Crystal structure and unit cell content of thecotrichite, presented along different directions. Polyhedra colours for the differently coordinated cations: Ca1: blue, Ca2: orange, Ca3: green (image: N. Wahlberg).
Apropo, we recently noticed that hairy crystals can also be developed on calcareous encrustations on bronze finds. In a case observed on a Syrian bronze bowl, the compound looked like thecotrichite. It contains calcium, but no chloride (SEM-EDX), so it is neither calcitite, nor thecotrichite. The Raman spectrum points to the presence of acetate. The diffractogram proved it to be a hitherto unknown crystalline compound, it could be indexed with a triclinic elementary cell. It is different from the acetate-formate compounds reported by Tennent and Baird (1985). Clearly, further research on the identity of such calcareous efflorescences is needed.

Conclusion
Using ATR-FTIR and Raman reference spectra and the diffraction data (table 2), thecotrichite can now be easily identified. The presence of acetate can be proven by a qualitative test. If wooden cupboards themselves are not of historic value, e.g. as part of a display ensemble, they should be strictly avoided in the 21st century and the age of preventive conservation.

Structure determination from PXRD measurements will likely become more widespread and develop into an invaluable tool in conservation science. This technique can be applied to any crystalline material, be it corrosion products or pigments. It will greatly improve our understanding about what is happening with heritage materials during production or decay. Last, but not least, this project exemplifies how close cooperation of conservation scientists and educators, museum conservators, and scientists from a research institute can allow BA and MA conservation students to be an integral part of an exciting research project; learning by research, an academic ideal fulfilled!

Crystal structure data

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Table 1: Crystal structure data for thecotrichite

Acknowledgements
The Danish National Research Foundation is thanked for supporting the stay of Nana Wahlberg at the MPI (DNRF93). We would also like to thank Daniel Weber (MPI) for the thermal analysis, Dirk Kirchner (Deutsches Bergbaumuseum Bochum, Germany) for taking the FE-SEM images, and Julia Schultz (SABKS) for the ATR-FTIR spectra.
Table 2: Comparison of the diffraction pattern calculated from the structure (only $d > 1.865 \text{ Å}$ and $I > 1.0\%$ given here) with literature data (FitzHugh and Gettens 1971, USNM 305934; rel. intensities, visually estimated from Debye-Scherrer films to steps of 10\%)

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Efflorescence X? Case Solved: Ca(CH$_3$COO)$_2$Cl(NO$_3$)$_2$·6H$_2$O! The Research History, Identification, and Crystal Structure of Thecotrichite

Gerhard Eggert, Andrea Fischer, Nanna Wahlberg, Robert Dinnebier, Tomče Runčevski, Rebekka Kuitier, Marian Schüich, Svenja Kampe, Eva Sulzer…


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Reflectance Transformation Imaging of Glass Objects

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Keywords
Reflectance Transformation Imaging; Digital Imaging; Interactive; 2.5-D Documentation

Abstract
Reflectance Transformation Imaging (RTI) is an easy and inexpensive method of documentation that aids the analysis of surface detail in an interactive viewing software. The use of RTI on transparent glass has often been considered impractical, as the material lacks an optical (i.e. visible) surface. However, with a simple setup, it is possible to make use of this technology for the documentation of glass objects. RTI helps to visualize and enhance surface phenomena such as scratches and engravings, as well as bubbles and other inclusions in the glass body. The usefulness of this method is illustrated by various examples. Transmitted light RTI is introduced as an addition to other documentation techniques. This approach helps to document structures in colored and semitransparent glass that were previously difficult to document.

Introduction
The invention of glass has provided mankind with countless new possibilities to produce objects for various applications. However, it is the material’s transparency that makes it unique. This fascinating property of the material greatly increases the difficulty of documenting phenomena both on the surface and within the glass matrix. Traces of manufacturing and aging are often easy to see but present serious issues when recording them by means of traditional photography. Therefore, new and easy ways of documenting glass objects are highly appreciated. Reflectance Transformation Imaging (RTI) is a simple technique that often helps to visualize and further investigate phenomena barely visible in conventional photography. The use of RTI on transparent glass has often been considered impractical as the material lacks an optical (i.e. visible) surface. In this work, as part of a Masters thesis in the Objects Conservation Program at the State Academy of Arts and Design in Stuttgart, Germany, the potential use of RTI in the documentation of glass objects has been investigated in depth for the first time.

What is RTI and how does it work?
RTI is a method of computational photography that records and enhances details of an object’s surface. An RTI is compiled from a series of pictures captured from the same position but with different light directions. The result is an interactive file where active relighting is possible. Thus, surface details like scratches, tool marks, flaking paint, etc. can be investigated in the same manner as would be done on the physical object by using a raking light. Furthermore, these phenomena can be enhanced using filters that algorithmically amplify the surface information recorded in the RTI file. RTI was developed by Cultural Heritage Imaging (CHI), a non-profit organization based in San Francisco dedicated to the documentation of heritage objects (CHI 2016). The method is based on a precursor method called Polynomial Texture Mapping (PTM), first introduced in 2000 (Malzbender et al.). The process of recording and generating RTI files is very simple: all that is needed is a digital camera with tripod, a laptop, a lamp to illuminate the object and two spec-
ular spheres. First, using a stable tripod, the camera is placed in an ideal position above or in front of the object. To ensure the quality of the resulting RTI file, it is of vital importance that the camera does not move at all between each picture. Therefore, it is most practical to trigger the camera by remote control. The two black spheres are placed next to the object so that they are visible in the pictures. A series of images are created; in each successive image, the light source is in different position but always at the same distance from the center of the object. In each image the light source is at a different angle to the surface. Eventually, a hemisphere of light positions is generated around the object (figure 1). The light source can be held by hand and the distance from the object can be measured by a string (CHI 2014, p. 9) or with two crossing lasers (Dittus 2014, pp. 47). To simplify the process and to create more reproducible results, the use of a light dome can be considered. (See Artal-Isbrand and Klausmeyer 2013, p. 340 for a good example of such a dome.) A small-scale light dome or light arm with bright LEDs is also an essential tool for the creation of Micro-RTIs. Micro-RTIs are generated like regular RTIs but by making use of microphotographs. A very tiny calibration sphere is needed (e.g. the ball of a ballpoint pen).

As soon as enough images have been recorded, usually between 24 and 60 (CHI 2014, p. 30), they are loaded into the RTIBuilder where they can be compiled into an RTI file. The RTIBuilder is a free software program that can be downloaded from CHI’s website www.culturalheritageimaging.org. After following a few simple steps (see CHI 2011), the software calculates a mathematical model of the object’s surface. A more in-depth description of this process is necessary here as it is important for the understanding of RTIs recorded from glass objects. An object’s surface can be approximated as consisting of many small planes. In the context of RTI, one could say that each of these planes is depicted in one pixel in the initial photography of an object. For each plane, the surface normal (i.e. the direction the object’s surface is facing in this particular pixel) is calculated. This is possible because the software knows the position of light in each photograph from the light source’s reflections on the two shiny spheres in each frame. Depending on the surface angle of a particular pixel in relation to both the camera and the light source it appears brighter or darker. From the variations in brightness in relation to the position of the light source, the direction of the surface normal is calculated and saved together with its true color value in the RTI file (figure 2).

With this information, it is possible to simulate multiple lighting conditions in the viewing software, called the RTIViewer. The RTIViewer is also freely available from CHI’s website.

Every result of the chosen lighting and filters can be saved as a high resolution static image. To distinguish image files generated from RTI files (which never depict a ‘real’ lighting situation) from digital photographs, it is advisable to follow a certain standard. For example, the direction of the digital light is shown by a sphere that can be copied from the RTIViewer. Additionally detailed parameters should be included in the caption and metadata. These suggestions are further explained in Dittus 2015 (p. 25).

Also, it is necessary to mention which of the filtering techniques was used. The various filters (‘rendering modes’) available in the RTIViewer influence the resulting image by making use of the surface information saved in the RTI file. There are three or ten rendering modes available, depending on which algorithm was used for calculating the file. Three of these modes proved most useful for the investigation of glass:

Fig. 1. Virtual dome showing light positions for recording the necessary photographs with the corresponding light reflections in the black sphere and setup for RTIs from glass: (a) glass plate, (b) object, (c) flat, black background, and (d) reflecting sphere. Photo by the author.
the ‘Specular Enhancement Mode’ (SE), which renders an artificial gloss to the surface and makes it possible to completely turn off the surface color.

— the ‘Image Unsharp Masking Mode’ (IUM), which dulls the luminance value of the colors.

— the ‘Normals Visualization’. In this rendering mode the directions of the calculated surface normals of each pixel are displayed in false-colors.2

**RTIs of glass: acquisition of images**

As mentioned above, RTI files are generated from the information that is contained in the light reflected from an object’s surface. Glass objects, however, lack a definite optical surface; due to the material’s transparency it is not possible to see the surface layer that builds up the object’s physical surface. At first glance this would render RTIs of glass objects unrealistic. However, a human viewer is able to recognize a transparent glass because of the reflections on its surfaces; these reflections can also be used by the RTIBuilder. The biggest problem is that they are quite weak and therefore easily superimposed by other reflections from the background. In order for this technique to work, it is of vital importance to eliminate the reflections not related to the glass. The easiest way to do this is to use a black (light-absorbing) and flat (with no distracting surface details) background. The capture process itself is identical to that used for non-transparent materials. The best results so far were achieved with dull black velvet as a background. It is advisable to place the object on a glass or acrylic glass plate with some distance to the black background below when the object needs to be documented from above (figure 1). This prevents the casting of shadows and optical caustics3 from the object on the background plane, which might cause errors in the calculation of the RTI file.

When investigating the results in the RTIViewer, special care has to be taken to identify a phenomenon that only occurs for transparent materials. As glass reflects light on every phase boundary, there are multiple surfaces piled on top of each other in every point of the RTI file. Even on a flat sheet of glass, there is information from two reflecting surfaces combined in every pixel (the surface facing the camera and the surface pointing away from it). When a hollow glass is recorded from the side, there are four surfaces, and so forth. This should be kept in mind when interpreting the data.

The capabilities of RTI in the investigation of transparent glass objects are vast; the following examples aim to give a short overview.

**Irregular surfaces**

Thin glass objects with regular shapes are fairly easy to investigate with RTI, since distracting reflections from various layers are minimal. As an example, the fine lines and ripples in the upper surface of crown glass can render quite well in the RTI file. To interpret the orientation of a surface the “Normals Visualization” mode is very useful. To understand this data it is necessary to learn to read the false colors visualization. Every color represents a certain surface orientation with a lilac tone depicting surfaces facing straight upward (z-direction). This way...
of displaying data helps when it comes to investigating and documenting glass surfaces. The usefulness of this filter can be shown on the example of a broken stained-glass window. Two fragments of glass were orientated slightly differently in the lead came (figure 3). The different blue colors in the normals visualization clearly indicate this detail of alignment. This would have been nearly impossible to show by means of traditional photography. The normals visualization’s big advantage is that the surface can be shown completely independent from any lighting. So even if an object’s surface is very difficult to properly illuminate, the false color rendering gives an overview of the whole surface shape at once. But not only surfaces as a whole can be documented well. Smaller phenomena, like casting seams, show up very well in the RTI with its rendering modes.

Multiple neighboring surfaces can provoke a problem as they can lead to a superposition of different phenomena. However, this is not always the case. The imaging of a 17th century ‘Monolithscheibe’ (small painted glass window) from the Landesmuseum Württemberg, Stuttgart illustrates the success of RTI on an object with multiple neighboring surfaces. During a previous restoration, the window had been sandwiched between two flat glass panels, but the documentation with RTI produced great results. The glass panels were very flat and clear so it was possible to record the surface structure of the object’s glass and its painting through them. Also, the bubbles and cracks within the glass could be shown in a manner that would have never been possible with traditional photography as they were enhanced by the rendering modes and thus became more obvious.

Inclusions

Inclusions in transparent glass can be divided into two categories. On one hand, there are inclusions that were intended by the manufacturer and on the other hand, there are impurities and other errors that resulted during manufacturing. If one glass contains another type of glass as decorative element (Weiβ 1986, p. 25) these inclusions do not show very well in the RTI. This can be explained by the fact that both glasses (both the body glass and the embedded glass) have very similar refractive indices. This results in very little reflection at the surface of the inclusion because most of the light will be transmitted. For non-intentional inclusions, better results were achieved. Impurities such as pieces of fireclay from the kiln render very well in the RTI. Furthermore, the Normals Visualization helps to illustrate their shape.

Bubbles can be found in many historic glass objects. In some cases, they are an intentional method of decoration (Weiβ 1986, p.46) but more often they are a result of poor manufacturing. Because bubbles are inclusion of air in a medium that is a lot denser, their surface has very good reflecting properties. They render so well in the RTI files (figure 4b) that they can be imaged even in hazy or low-transparency glasses. The first surface of bubbles (i.e. the one facing the camera) seems to play the largest role in the generation of the surface normals. Therefore, it is possible to determine the shape of the bubble’s surface from the normals visualization. Another advantage of the normals visualization is that all bubbles in an object can be shown at once. This often is impossible in conventional photography for various reasons. This is valuable because the shape and direction of bubbles often helps in reconstructing the manufacturing process of an object (see e.g. Davison 2003, p. 127; Eska et al. 2014). In conclusion, one could say that the difference in density between
Fig. 4. Cold paint (a), bubbles (b) and tiny cracks (c) show up clearer in an RTI (right) as compared to a regular photograph (left), SE-mode (HSH) X 0.37, Y 0.57 (Object: Franziskanermuseum Villingen, Germany). Photo by the author.

Fig. 5. Photograph (top), SE-Mode (middle) (HSH) X 0.00, Y 0.87 and contrast enhanced normals visualization (bottom) (HSH) of a reverse glass painting. The loosening paint creates brighter areas. (Object: Kunstmuseum Stuttgart, Germany). Photo by the author.
glass and inclusions correlates directly with the visibility in the RTI file.

**Painted glass**

Glass can be painted with various techniques and materials. The non-transparent black color used in stained glass follows the rules for intransparent materials when it comes to documentation with RTI. The same applies to oil colors on top of glass as they also do not transmit the incoming light. They can be found in folk art from the German Black Forest region an example of which can be seen in figure 4a. Reverse glass paintings are a special case found both in Asian and European cultures. Mirdrikvand and Bevan (2011) showed the use of RTI for investigating the paint layer from the back side. But what if the documentation of the color layer is not possible from the back or if the glass itself is in the focus of interest? If the latter is the case, RTI cannot help because any reflections from the glass surface are much weaker than those coming from the paint layer. Therefore, the paint is more ‘interesting’ for the software than any phenomena in the glass. Both SE-mode and normals visualization provided very good information on where the paint layer lost adhesion to the glass. This phenomenon is also visible in the conventional photograph of the object but the data in the RTI were much clearer and easier to read (figure 5).
Engravings
Engraving glass objects was and is still a widely used technique for decorating glass. The abrasion of material roughens the glass surface and changes its reflection properties. Therefore, engravings show up very well in conventional photographs. Nevertheless, RTI holds some advantages for the documentation of these decorations. In SE-mode the surface of the engraved grooves appears much clearer. This can be helpful in determining the angle of the engraving wheel. If texts or motives are scratched into the surface, the Image-Unsharp-Masking-Filter (IUM) can be very helpful in documenting them. The same applies to unintentional scratches. If a micro-RTI is generated using a microscope, it is even possible to visualize the traces of single grains of the abrasive (figure 6).

Fractures and cracks
Fractures in glass objects are often filled with adhesive during conservation. In this case, their visibility depends on the difference between the two refractive indices (RI) of the glass and the adhesive. If this difference is smaller than 0.01, no perceptible reflections will occur (Tennent and Townsend 1984, p. 221). It is nearly impossible for a conservator to perfectly match the refractive index of a glass (Davison 2003, p. 215). The resulting reflection can be detected by the RTIBuilder. But in most cases the match of the RIs is too good for a clear result in the RTI. However, if the fracture or crack is not completely filled with adhesive, the thin layer of air contained provides good reflective properties. In this case, very good surface normals can be calculated: the crack shows up perfectly in both SE-mode and normals visualization. The latter encodes the orientation of the cracks in false colors. From this visualization, it is possible to (approximately) tell the angle of the crack in relation to the surface. The determination of this surface orientation of ‘damaged’ areas can also be helpful for documenting stone points/arrow heads that have been knapped from glass (e.g. the so-called Kimberley points of the Australian Aborigines) or rock crystal (e.g. from the Middle and South European Neolithic).

Corrosion
Glass objects show various phenomena of aging that are sometimes hard to document. One of the most obvious corrosion forms is the iridescent layer that often occurs on archaeological glass. The visibility of this shiny effect depends on the direction of incidental light. In this case, the key advantage of RTI is the possibility to interactively manipulate the angle of light incidence. The iridescence renders better when documented using the HSH-algorithm (as opposed to the PTM-algorithm). If the corrosion layer is thick enough, it becomes opaque and starts to peel off. It is possible to show where the iridescent layer started to peel of (and thus changed its orientation in relation to the object’s surface) with normals visualization. Crizzling is harder to document both in photography and RTI. The SE- and IUM-modes seem to enhance this phenomenon (at least in an advanced stage). The latter filter appeared to be the better choice as the reflections on the object’s surface are also digitally reduced, as shown in figure 7. Accretions, as found on archaeological glass, can be interpreted very well in normals visualization. Also SE-mode and other filters help to enhance such accretions further.

Fig. 7. A crizzled glass in a photograph (top), IUM mode (middle) X 0.09, Y - 0.12 and SE mode (below) (HSH) X -0,08 Y 0,63. (Object: Landesmuseum Württemberg, Stuttgart, Germany). Photo by the author.
Transmitted light RTI

RTI is a reflection-based technique, and thus seems to be quite unsuitable for transmitted light investigation. When both the lamp and the camera are not on the same side of a transparent object, it is impossible to detect the reflections caused by the lamp. Nevertheless, the brightness of each pixel varies depending on the position of the lamp behind the object. Thus, it is possible to create RTI files from the recorded data even if they are based on transmitted light, not reflected light. In order to capture RTI source images with transmitted light, a camera and light dome are positioned in front of a stained-glass window. Another camera is placed behind the window (figure 8). For each light position, an image was taken from the front and the back of the object. Through post-capture photographic editing, the reflective sphere was copied from the front pictures, mirrored, and pasted into the corresponding backside picture. As a result, the RTIBuilder was able to calculate the ‘correct’ light positions. The resulting data differ from traditional RTIs. However, for colored glass or glass with low transparency, this method proved to be extremely useful. Bubbles in the glass showed up while they were barely visible in a regular RTI or conventional photography (figure 9). When examining these results, it is important to bear in mind that these data do not originate from reflected but from transmitted light.

Conclusion

Being an easy and ready-to-use technology, RTI bears great potential for various fields of conservation. Until now, it has been essentially overlooked for the documentation of transparent glass. As shown above, with a simple setup, very good and helpful results that would be impossible to achieve with other methods, can be generated. The key to applying RTI to glass and getting good, usable results to document the object, images have to be recorded in front of (or above) a flat, black (i.e. light-absorbing) background. The optical properties of glass as a transparent material have to be taken into account when investigating the results. It is not one surface that is depicted in the finished RTI file, as in non-transparent materials, but every surface of the glass object that can be found in the camera’s axis. RTI data provides the user with interactive manipulation of the incoming light and a number of filters to further enhance surface phenomena. Especially ‘Specular Enhance-
Fig. 9. Transmitted light photograph (top left), reflected light RTI (top right), transmitted light RTI with (bottom left) and without (bottom right) semitransparent screen behind the object (Object: Franziskanermuseum Villingen, Germany). Photo by the author.
ment’, ‘Image Unsharp Masking’ and ‘Normals Visualization’ proved to be very useful for investigating glass objects. In some cases, the technique of transmitted light RTI might be useful. For other research interests micro-RTI appears promising. In conclusion, it can be said that RTI can be a very helpful tool for the documentation of a range of glass objects. It may be worth considering this method when it comes to recording phenomena of interest in glass.

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Notes
1. The RTIBuilder provides the chance to chose between two different algorithms: PTM or HSH. The latter one proved to be more accurate in most cases for documenting glass objects.
2. This is known from the field of computer graphics, where images showing the 3D-model’s normals in false colors are called normal maps.
3. Light phenomena caused on a projection screen by light rays reflected or refracted from transparent materials.
4. To date there has been no investigation of the early stages of crizzling with RTI.

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Testing Bulked Adhesives for the Restoration of Stained-Glass Windows

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bulked epoxy adhesives; micro-fillers; nano-fillers.

Abstract
In this study, bulked adhesives were examined regarding changes in properties for their use in the restoration of stained-glass windows. Two epoxy adhesives commonly used in the restoration of flat glass, Araldite® 2020 and Hxtal NYL-1™, were investigated. The adhesives were mixed with various silica-based micro- and nano-particles as fillers. Different tests were carried out on the adhesives with and without fillers in order to characterize their chemical and mechanical properties. The tests included colorimetry, dynamic-mechanical methods of analysis and tests on bending strength. No property changes could be ascertained in the bulked adhesives that would be negative for the restoration of delicate flat glass.

Introduction
The industrial use of bulked adhesive systems has been common and proven effective for many years. Low-cost fillers are added to influence properties such as hardness or viscosity and reduce costs. Bulked adhesives display an increased viscosity and are also regularly used for filling gaps in the restoration of wooden and stone artefacts (Young, New and Marchant 2002; Williams 2009). They serve as replacements for losses or are applied for joining complex fractures that have voids or gaps. For some time, bulked adhesives have also been applied in ceramic and porcelain restoration with good results (Buys and Oakley 2002), but apart from field tests or empirical reports (Elston 1990), there are only a few scientific investigations available (Byrne 1984; van Giffen, Koob and O’Hern 2013). This is why their use is associated with many questions and uncertainties regarding aspects such as elasticity or a change of adhesion. Even in glass conservation, common difficulties are gaps that are too wide to fill using conventional adhesives (Davison 1998), but bulked adhesives are rarely used. In the restoration of stained-glass windows, gaps occur when repair leads are removed. One possible application for bulked adhesives is to bridge these gaps.

This was the reason for starting the investigation presented here. Questions and research parameters were worked out together with the Peters Glass Painting and Restoration Studio in Paderborn, Germany and the Glass Conservation Studio at Cologne Cathedral. The main question was how the addition of fillers affects the physical and chemical properties of the adhesives, and how these might negatively affect their use in restoration. Ideally, bulked adhesives should display similar properties to non-bulked adhesives, sufficiently increase viscosity in gap filling and not lead to great changes in transparency and brittleness. Transparency must be evaluated depending on the condition of the object, as stained-glass windows frequently display corroded surfaces. Elasticity is relevant in balancing occurring tension during the bridging of larger gaps, in order to prevent tears to the adhesive joint or secondary fractures in the glass. Beside this, strength should be commensurate with the glass but not so strong as to cause failure within the original glass.
Conservation studies concerning thermal stability are often primarily concerned with non-bulked adhesives and investigate factors such as temperature or light stability (Coutinho et al. 2009; Tennent and Koob 2010). Increasing strength by adding nano-particles is known in industrial applications (Wetzel et al. 2006) and restoration works (Byrne 1984). In comparison, investigations into micro-fillers such as glass beads indicate a reduction in strength (Wetzel 2006). This shows that the strength of bulked adhesives, depending on the type and amount of filler being used, can be both increased or reduced (Skeist 1990). Furthermore, it is known that nano-fillers, which include Aerosil®, for example, can affect material properties. These include effects on flowability (when gluing), on the hardness or an improvement in thermal stability (Gysau 2014). In restoration work, the increase in viscosity when bridging gaps and imperfections is beneficial. Nano-fillers, for example, influence the flowing behaviour and thixotropy by making a gel out of the adhesive. Such filled adhesive systems improve handling characteristics and the bulked system can be applied without dripping and remain in the joint.

In order to clarify some questions regarding property changes, tests were carried out on chemical and mechanical stability of two commonly used adhesives bulked with various micro- and nano-fillers. Colour measurements were used to assess transparency, and changes in elasticity and thermal resistance were recorded using mechanical-thermal analysis (DMTA). Investigations using the scanning electron microscope (SEM) provide information on the distribution and arrangement of fillers in the adhesive. At the same time, a test was carried out on whether the fillers could lead to a change in the matrix through absorption of the adhesive binder, and thus, under certain circumstances, to associated micro-cracks or to separation of the adhesives (Tan, White and Hunston 2010). Investigations using the 4-point bending test compared mechanical properties. In order to compare the results of the bulked adhesives with non-bulked adhesives, non-bulked adhesives were tested as reference material.

**Experiments**

**Production of Samples**

Two adhesives were selected and combined with fillers: Araldite® 2020 and Hxtal NYL-1™; both are frequently used epoxy resins in the restoration of flat glass. Micro-filler Glassflake® 003 (thickness 3 µm, particle size < 50 µm) as well as 0 - 50 µm glass beads and transparent glass powder 63 - 80 µm were tested as fillers. Furthermore, nano-particles (particle size 1 - 100 nm), Aerosil® 200, 380 and R 812S, as well as Acematt® HK125, were investigated in combination with Araldite® 2020.

To produce the most transparent adhesives possible, a corresponding refractive index of materials used is important. The refractive index of the Glassflake® 003 is 1.52 (MSDS) and for the Aerosils® used is between 1.45 and 1.5 (Evonik 2015). The refractive index for adhesives is 1.55 for Araldite® 2020 and 1.54 for Hxtal NYL-1™ (both entries from the MSDS) and is relatively close to that of the filler material.

Cube-shaped (19 x 10 x 7 mm) and cylindrical (ø 30 mm, h 3 mm) samples were produced with a filler content of 5 wt.% micro-particles and 2 wt.% nano-particles. For the bending test, adhesive joints were produced using float glass and the gap width of the adhesive joint was 4 mm. The curing time of all samples produced before testing was at least four weeks.

**Colorimetry**

Colorimetry was carried out using the "spectro-guide sphere gloss" colour spectrometer from BYK®-Gardener. Measurements were taken in the spectral range of 400 - 700 nm in reflectance mode. The measurement conditions were: reference white absolute, illuminant D65 and the standard observation angle of 10°. The L*a*b* values were collected using an average of three measurements in different test areas. Measurement conditions such as white standard or averaging are integrated in the equipment and no standard deviation was noticed. The measurements are supposed to indicate a change in transparency of the bulked adhesives in comparison to adhesives without fillers.

**DMTA**

Using dynamic-mechanical-thermal analysis (DMTA), visco-elastic material properties can be determined depending on temperature, frequency and mechanical stress. This method is primarily used for the mechanical characterisation of elastomers and polymers, and is therefore outstanding when determining the ageing behaviour of polymers.
(Stuart 2007). The measurement conditions of DMTA included measurements with eight different frequencies and a temperature range of -20°C to 90°C on samples measuring 20 x 10 x 7 mm. The Gabo Eplexor 500N device was used, which can apply a dynamic load of up to 500 N. The measurements were used to detect any possible changes in elasticity and temperature resistance caused by the addition of fillers.

**SEM/EDX**

SEM/EDX investigations were carried out using an ESEM Philips XL30 to obtain more detailed information on the distribution, grain size and shape of the filler. To this end, the compounds were investigated, especially with regards to delamination between fillers and the adhesive matrix.

**Bending Test**

Four-point bending tests were carried out on the Instron 8572 bending machine. The test speed was 2 mm/min without pre-load; the bearing surface was 25/50 mm. The tests were carried out to identify any changes in the adhesion with the glass caused by the filler. Furthermore, observation of the fracture surfaces was important. In the case of adhesion failure, the interface between the substrate and the adhesive fails; in the case of cohesion failure, the adhesive layer breaks; whilst in the case of a break in the substrate, a so-called secondary fracture is present (Rasche 2012). It is imperative that the latter be avoided, particularly in the case of conservation applications.

**Results**

**Mixing Process**

For the initial investigations into the mixing process, Araldite® 2020 epoxy resin was selected in combination with Glassflake®, glass beads, glass powder, Aerosil® 200, 380 and R 812S, and Acematt® HK125. Aspects used in assessing the fillers were homogeneous distribution in the adhesive, transparency and air inclusions in the mixture. All the fillers could be mixed with Araldite® without any problems. In the case of nano-fillers Aerosil® 200, 380 and R 812S, as well as Acematt® HK125, a very good distribution could be identified in the adhesive, low quantities (from 1 wt.%) visibly increased the viscosity. The low transparency and the high number of air inclusions were problematic. By varying the mixing process, an attempt was made to reduce air inclusions and therefore improve transparency as well. Magnetic stirrers, a platform shaker and a vacuum chamber were used. The sequence when mixing in the components (filler, resin and hardener) was varied, and different stirring techniques and speeds were tested as well as the subsequent connection to a vacuum. Placing the bulked adhesive in a vacuum chamber after the mixing process visibly reduced air inclusion, but consequent stirring led to new air inclusion. In the case of the Aerosils®, additives such as chemical ventilators and de-foamers were tested; here, the wetting and dispersing additive BYK® W985 yielded the best results. In addition to the tests to optimise the mixing process, various quantities of nano-fillers (1 - 5 wt.%) and sample thicknesses (2 - 4 mm) were tested to improve transparency. The combination of magnetic stirrers for mixing in the filler, shakers for removing larger air inclusions and the application of a vacuum of approximately 10 mbar yielded the best results. With a sample thickness of 3 mm and Aerosils® and Acematt® filler quantities of a maximum of 2 wt.%, an acceptable transparency was achieved (figure 1).

Additional mixtures were produced using the micro-fillers of Glassflake® 003, glass beads 0 - 50 µm and glass powder 63 - 80 µm in combination with Araldite® and Hxtal NYL-1™. These fillers could also be easily mixed into the adhesives. To increase the viscosity, the micro-filler amounts had to be increased (at least 3 wt.%) and depending on this, they sedimented very differently.

![Fig. 1. Comparison of transparency with vacuum treatment, samples with Araldite® 2020 and 5% glass beads (left) and 2% Aerosil® 380 (right).](image-url)
This was noticeable predominantly with larger sample thicknesses (7 mm). In the case of Araldite® 2020 after curing, a larger bubble formation was noticed than with Hxtal NYL-1™. This is presumably related to the quicker curing time for Araldite®, which leaves less time for air to escape, while the slower curing of Hxtal™ allows more time for the air bubbles to escape (curing time: Araldite®: 16 hours; Hxtal NYL-1™: starts to cure in 48 hours, full setting in 14 days) (Koob 2015).

Combinations with 5 wt.% micro-fillers also display sufficient transparency without a vacuum. If the amount of micro-fillers is increased to 10 wt.%, transparency is clearly improved by vacuum treatment. In comparison, nano-fillers with 2 or 3 wt.% showed strong opacity without a vacuum. A comparison of samples created without a vacuum can be found in figure 2.

Further tests such as colorimetry, REM, DMTA and the bending test were carried out with the epoxy resins Araldite® 2020 and Hxtal NYL-1™ without a filler (control samples) and in combination with Glassflake®, glass beads, glass powder, each at 5 wt.%, and the Aerosil® 380 and R 812S and Acematt® HK125 (each at 2 wt.%). The Aerosils® and the Acematt® were evenly distributed in the adhesive, and no accumulations could be identified in the lower areas of SEM images. The agglomerates of different sizes were clearly visible in the form of light-coloured spots. The agglomerate size of the Aerosils® was between 1 µm and 80 µm. In the case of Acematt®, the agglomerates were clearly smaller and more compact with sizes ranging between 2 - 20 µm. It was clear that all nano particles, even those with dispersing additives, formed agglomerates, as shown in figure 4 a, b. In the case of Glassflake®, glass beads and glass powder on the other hand, there was no homogeneous distribution; a clear settling could be observed in the adhesive (figure 4 c, d). Here, the upper sections of the samples

**ESEM**

ESEM investigations were carried out on filler samples of Araldite® 2020 bulked with micro-fillers Glassflake®, glass beads, glass powder, each at 5 wt.%, and the Aerosil® 380 and R 812S and Acematt® HK125 (each at 2 wt.%). The Aerosils® and the Acematt® were evenly distributed in the adhesive, and no accumulations could be identified in the lower areas of SEM images. The agglomerates of different sizes were clearly visible in the form of light-coloured spots. The agglomerate size of the Aerosils® was between 1 µm and 80 µm. In the case of Acematt®, the agglomerates were clearly smaller and more compact with sizes ranging between 2 - 20 µm. It was clear that all nano particles, even those with dispersing additives, formed agglomerates, as shown in figure 4 a, b. In the case of Glassflake®, glass beads and glass powder on the other hand, there was no homogeneous distribution; a clear settling could be observed in the adhesive (figure 4 c, d). Here, the upper sections of the samples
Fig. 3. Reflection curves for combinations with Araldite® 2020, and micro- and nano-fillers, without and with vacuum treatment (V).

Fig. 4. ESEM images, distribution of micro- and nano-particles in the adhesive Araldite® 2020, a) Aerosil® R 812S, b) Acematt® HK125, c) Glassflake®, d) glass beads.
were almost free of fillers. Glassflake® was distributed better in the adhesive than the glass beads or glass powder. No micro-cracks or changes in the adhesive matrix caused by the fillers could be identified in the filler contents used with 2 or 5 wt.%.

**DMTA**

With the illustration of loss factor tan δ, statements can be made about the internal damping of the material; the measurement of energy dissipated by the material. A higher loss factor therefore means a lower elasticity. At the same time, the glass transition temperature (T<sub>g</sub>) above the peak of the loss factor can be determined. Here, one must note that T<sub>g</sub> is not a material constant; instead, it varies depending on the measurement method, sample size and frequency. The width of the peak enables statements to be made about the molecular weight distribution; a wide peak indicates a wider molecular weight distribution and shorter chain lengths. Combinations of Araldite® 2020 with micro- and nano-fillers showed a different influence on elasticity and glass transition temperature (figure 5). Glass beads and glass powder only had a slight influence on the values; elasticity improved somewhat, and the T<sub>g</sub> was between 59 °C and 61 °C, remaining almost the same. When combined with Glassflake®, the T<sub>g</sub> also hardly changed (60 °C), but Glassflake® clearly improved the elasticity, which was reflected in the low loss factor tan δ. This was reduced from a maximum value of 1.3 in the reference adhesive to 0.85 in the Glassflake® combination. The addition of nano-fillers improved both the elasticity and the glass transition temperature. In the combination with Acematt® HK 125, at the peak of the loss factor tan δ, the readable glass transition temperature increased by up to 10 kelvins, from 59 °C in the case of Araldite® 2020 with no filler to 69 °C. The addition of Aerosil® R 812S also increased both the elasticity and T<sub>g</sub> to 66 °C, albeit not as strongly as with Acematt® HK125. The fillers in the case of Araldite® 2020 therefore displayed a clear influence on the adhesive. In contrast, in the case of Hxtal NYL-1™, only a very minor influence of the filler could be shown (figure 6). The relatively low T<sub>g</sub> of 54 °C was hardly changed by the filler; it increased to a maximum of 56 °C. The combi-
nation of fillers also had little influence on the loss factor and therefore the elasticity, as shown in comparison with Araldite® 2020 in figure 6. In the case of Hxtal NYL-1™, this only shows a minimal influence on elasticity and Tg caused by the combination with micro-fillers.

After reaching the glass transition temperature with the peak of the loss factor tan δ and progressive softening of the material, the samples as the curve descends behaved almost consistently with the complete softening at around 90°C. The peak width of the loss factor was relatively similar to the reference adhesives and the combinations, therefore showing a constant molecular weight distribution. Only in the case of Araldite® 2020 in combination with Glassflake® could a change be seen.

**Bending Strength**

To examine the bending strength of the bonds, adhesive joints were produced with a 4 mm clearance. For the tests, adhesives Araldite® 2020 and Hxtal NYL-1™, each with 5 wt.% micro-fillers Glassflake®, glass beads and glass powder were mixed, and reference adhesives without fillers were tested for comparison purposes. Eleven samples were made from each combination, in order to enable a statistically safe reading. Adhesive joints with Araldite® 2020 were also combined with Aerosils® and Acematt® HK125, and different weight amounts were tested as individual samples in order to gain an impression of the changes in strength caused by nano-fillers.

In the case of Araldite® 2020, the samples with micro-fillers showed a somewhat higher bending strength (16 - 19 N/mm², standard deviation σ 3 - 5 N/mm²) than samples without filler (14 N/mm², σ 5 N/mm²), whereas the bending strength values for fillers were very close together (figure 7). The characteristic bending strength of new float glass is around 45 N/mm², and aged glass with surface defects has a significantly lower bending strength (Baunetzwissen 2015).

In the case of the samples produced using Hxtal NYL-1™, the bending strength of the pure adhesive samples at
22 N/mm² (σ 4 N/mm²) was somewhat higher than that of samples modified with micro-fillers (18 - 20 N/mm², σ 3 - 5 N/mm²). The bending strength was also generally above that of the samples with Araldite® 2020 (figure 7). The crack bonds (Aerosil® 200, 380, R 812S and Acematt® HK125) with nano-filler proportions of 1 wt.% and 5 wt.% did not enable any statistically safe readings that could be used to assess the influence of the fillers. The values of a total of 16 samples were between 12 and 38 N/mm² and showed no clear relationship either to the filler materials used or the filler quantities. However, it can be established that the bending strength of adhesives with nano-fillers is only slightly above that of micro-fillers. No separation or particularly high adhesion could be identified. In all samples examined, the fracture pattern showed an adhesion fracture, i.e. the connection in the border area between the glass substrate and the adhesive failed. Thus, in the bonds and/or the combinations used, there is no risk of a secondary fracture in the glass.

Conclusions
Important questions are be settled in this investigation. In experiments varying the mixing procedure to improve the transparency, the addition of micro-fillers shows a tendency towards sedimentation, but sufficient transparency could be achieved with amounts of 5 wt.%. As fillers, the nano-materials investigated showed themselves to have a good distribution in the adhesive, but only with the use of vacuum treatment the transparency increased sufficiently, with the result that they could be used for glass adhesives. Depending on the adhesive used, the results of the DMTA showed a different influence on elasticity and glass transition temperature by the fillers. While the elasticity and glass transition temperature of Araldite® 2020 was improved by the combination of micro- and especially with nano-fillers, micro-fillers had only a minimal effect on the values of the samples with Hxtal NYL-1™. The bending strength was also influenced by the fillers in samples with Araldite® 2020, and this increased slightly, whereas with Hxtal NYL-1™ in the combination of fillers it decreased somewhat, but the bending strength was generally higher than that of Araldite® 2020.

Essentially, on the basis of this investigation, the tested micro- and nano-fillers can be recommended to increase the viscosity of adhesives. It is apparent that by adding fillers to Araldite® 2020, thermal resistance improved and in the case of Hxtal NYL-1™, the combination of fillers had no negative impact on the mechanical properties.

Materials and Suppliers
Araldite® 2020: Bodo Möller Chemie GmbH, Senefelder-strasse 176, D-63069 Offenbach am Main, Germany
Hxtal NYL-1™: Kremer Pigmente GmbH & Co. KG, Hauptstr. 41 – 47, DE 88317 Aichstetten, Germany
Glassflake®, micronized, grade GF003: Glassflake Ltd., Forster Street, Leeds, West Yorkshire LS10 IPW, United Kingdom
Glass beads 0 - 50 µm, article number 59822
Glass powder 63 - 80 µm, article number 39004 and Acematt® HK125, all: Kremer Pigmente GmbH & Co. KG, Hauptstr. 41 – 47, DE 88317 Aichstetten, Germany
Aerosil® R 812S, Aerosil® 380: Evonik Industries AG, Rellinghauser Straße 1-11, 45128 Essen, Germany
BYK® W985 dispersing additive: BYK-gardener GmbH, Lausitzer Str. 8, 82538 Geretsried, Germany

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Chemical and Mechanical Stability of two UV Curing Adhesives for the Conservation of Glass – Preliminary Results

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Keywords
glass; UV curing adhesives; tensile strength tests; colorimetry; infrared spectroscopy

Abstract
The efficacy, properties and stability of two acrylic UV-curing adhesives—Verifix® MV 760 (Bohle) and Vitralit® 7561 (Panacol)—were assessed by comparing them with two traditionally-used adhesives, Hxtal® NYL-1 and Paraloid® B-72. Accelerated ageing experiments were performed in a SolarBox, and by exposing the samples to high humidity conditions. Colour and chemical changes of the four adhesives were assessed by colorimetry and infrared spectroscopy. Finally, in order to study the adhesion strength of each polymer, tensile strength mechanical tests were performed. Verifix® MV 760 was shown to be the more stable of the two UV curing adhesives. It displayed fewer alterations at the molecular level, did not exhibit colour changes and had a higher value of mechanical resistance after ageing experiments.

Introduction
In the conservation and restoration of glass and stained glass, as in other fields of conservation, the conservator’s work is quite often subject to time constraints. In these situations, the use of adhesives which allow for a fast and effective bonding of broken glass fragments would be advantageous. Additionally, it is sometimes problematic to keep fragments in position in a simple way, during the setting of the adhesive (with strips of adhesive tape or rubber bands for instance), and more complex and creative support systems are needed. In these situations, it would be useful to have a very fast-setting adhesive at hand that would allow the conservator to hold the fragments in place manually during the setting time.
The epoxy resin Hxtal® NYL-1, one of the most widely-used adhesives in the conservation of glass, has good optical and mechanical properties allied to good photo-chemical stability, but has a long curing time (48-69 hours mostly cured; 14 days fully cured) (Koob 2006); the acrylic adhesive Paraloid® B-72 has a relatively fast setting time (ca. 24 hours) and very good chemical stability, but has a tendency to develop air bubbles within the joint line because of solvent loss. Thus, the present research study arose from the need to find alternative adhesives that are equally effective in the bonding of glass, but that take less time to cure than the traditionally-used adhesives.
The well-known ultraviolet (UV) curing adhesives, which, as the name implies, are adhesives that polymerise through the action of radiation, can be an alternative. They cure rapidly, providing secure bonding of the glass fragments, normally in a few minutes. An additional advantage, when compared to epoxy resins, is that UV curing adhesives are ready-to-use products and thus do not require previous preparation. These adhesives have already been studied (Haddon 1991; Goss 2002; Moon 2005; Hernández 2011) and their general properties are described by manufacturers. However, in the conservation and restoration of glass, although they have already been used (Davison 1998; Hernández 2011 and included references), there has been
no detailed study on the mechanical and chemical behaviour of these adhesives. Therefore, this study aims to carry out a detailed investigation of two selected UV curing adhesives, as a means of understanding and evaluating the advantages and disadvantages of their use in the conservation and restoration of glass and stained glass. Commercially, an enormous range of adhesives is available for diverse applications and with a great variety of chemical and mechanical properties and behaviour, in both the short and long term. When selecting an appropriate adhesive for the conservation of glass, several requirements have to be considered (Koob 2006). In particular, we highlight the following:

i) the adhesive should allow for an effective bonding to the glass without damage during application, curing or aging;

ii) the adhesive should be easy to apply and remain stable after curing and long term use;

iii) the removal of the adhesive should be possible if necessary, without causing any stress or damage to the glass object.

With these requirements in mind, the most important features taken into account in the selection of the UV curing adhesives to be evaluated in this work were:

i) adhesion strength;

ii) long term behaviour, not only in terms of the yellowing of the adhesive but also its resistance to fluctuations with humidity, as the adhesive should be appropriate for the conservation of stained glass which is often exposed to uncontrolled environmental conditions;

iii) viscosity, as it should be suitable for application either by capillarity or direct bonding, as well as some filling capacity;

iv) chemical composition, which should be known, since it is essential to further understand the adhesives’ mechanisms of degradation;

v) the refractive index (n) similar to the refractive index of soda lime glasses (n≈1.5)

Thus, two commercially available UV curing acrylic adhesives were chosen, Verifix® MV760 and Vitralit® 7561, the properties of which are presented in Table 1.

The effectiveness, properties and stability of the two UV-curing adhesives, Verifix® MV 760 (Bohle) and Vitralit® 7561 (Panacol), were determined and assessed, by comparing them with those of the traditionally used adhesives Hxtal® NYL-1 and Paraloid® B-72. The ageing of these adhesives was studied by exposing the samples to intensive UV-visible radiation, using a solar box, and to a very high RH. The adhesives were tested on colourless glass and also on blue and green glass, as coloured glasses are widely encountered in stained-glass windows and their UV-Visible absorption characteristics may affect the behaviour of the adhesives.

Before and after ageing, samples were characterised by Fourier-Transform Infrared Spectroscopy (FT-IR) to study possible alterations in the molecular structure, by colorimetry and UV-visible absorption spectroscopy to evaluate optical changes, and by mechanical tensile tests to determine the adhesion strength of each adhesive to the glass substrate.

**Experimental**

**Sample Preparation**

Rectangular pieces of colourless, blue and green glass of ca. 4 cm x 1 cm in size and 3 mm thickness were fractured in the centre, by hand force after scoring with a diamond tip, and then bonded back together. Float glass (St. Gobain) was used as colourless glass. For cobalt blue and copper green blown soda-lime silicate glasses (Lamberts Restaurations-Glas) were used.

For all glass colours and adhesives, five identical samples were prepared for each ageing test (UV-visible irradiation and high RH), totalling 180 bonded samples. Both aged and reference samples were submitted to mechanical tensile tests.

<table>
<thead>
<tr>
<th>Commercial name</th>
<th>Refractive index</th>
<th>Chemical nature</th>
<th>Viscosity</th>
<th>Resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Verifix® MV760</td>
<td>1.502</td>
<td>modified urethane acrylate</td>
<td>medium: 1800 mPa·s</td>
<td>very resistant to yellowing and high humidity</td>
</tr>
<tr>
<td>Vitralit® 7561</td>
<td>1.49</td>
<td>acrylate</td>
<td>low: 500-850 mPa·s</td>
<td>resistant to high humidity</td>
</tr>
</tbody>
</table>

Table 1: Properties of the selected UV curing adhesives, Verifix® MV760 and Vitralit® 7561, according to the product technical data sheet.
Films of the adhesives were prepared by applying a drop of the adhesive solutions on colourless glass slides, aiming to obtain approximately the same thickness in all samples. The samples were submitted to the same ageing tests (two replicates, 24 samples). These films were characterised in three different areas before and after ageing by colorimetry, UV-Visible and infrared spectroscopies. Samples of Verifix® MV 760 and Vitralit® 7561 were cured by exposing them to a UV radiation source with a wavelength of 362 nm for maximum 5 minutes. For Hxtal® NYL-1 and Paraloid® B-72 at 30% (w/v) in acetone, 7 days at room temperature were allowed for the curing of the polymer and evaporation of the solvent, respectively.

Artificial Ageing
– Irradiation and High Relative Humidity
The irradiation tests were carried out in a COFOMEGRA accelerated ageing apparatus (SolarBox 3000e) equipped with a Xenon-arc light source (the radiation λ < 300 nm is cut by a filter) with a constant irradiation of 800 W/m² and a blackbody standard temperature of 50 °C.

The films on glass slides were irradiated for a maximum period of 2000 h (total irradiance 5535 MJ/m²).

To study the effect of high RH on the properties of the polymers under investigation, both films and bonded samples were kept in the dark in a desiccator for 2000 h with controlled and constant RH of 75%-80%, by means of conditioned with wet silica gel.

Samples were characterised after 0, 500, 1000, 1500 and 2000 hours of ageing, in order to follow the progress of the degradation. Only the initial and final results are discussed in this paper.

Mechanical Tests
The tensile strength of samples was determined using a Hounsfield tensile equipment H5K-W. The tests were run at a constant speed of 1.54 mm/min at room temperature (≈25°C). It was necessary to stick smaller coarse sanding strips on the ends of each sample, in order to create friction between the sample and the grips. In an attempt to ensure the reliability of tests, five replicates were tested for each adhesive and standard deviations were calculated. The values of Young’s modulus (E) were calculated being the slope of the linear regression of the plot stress (σ) versus elongation (ε) (E = dσ/dε) and the stress at break was obtained directly from the plot.

FT-IR Spectroscopy
Infrared spectra were acquired with a Nicolet Nexus spectrophotometer equipped with a Continuum microscope (15 x) and a MCT-A detector cooled by liquid nitrogen. Infrared spectra were collected in transmission mode from 4000 to 650 cm⁻¹ on micro samples compressed with a Thermo diamond anvil cell, 128 co-added scans and 4 cm⁻¹ spectral resolution. Spectral analysis was performed using Omnic E.S.P. 5.2 software and all spectra were baseline-corrected (at 4000, 3750, 2500, 1880 and 650 cm⁻¹ absorption frequencies), normalized to CH₂ bending absorption at ≈ 1450 cm⁻¹ (identified as the most stable absorption during ageing) and the CO₂ absorption at ca. 2300-2400 cm⁻¹ was removed.

Colorimetry
Colour values were recorded by using a Datacolour International colorimeter (Microflash). The optical system of the measuring head uses diffuse illumination from a pulsed Xenon-arc lamp, with 10° viewing angle geometry; the reference source was D65. Before taking colour measurements, calibration was performed using bright white and black standard plates. The equipment measuring head was positioned with the aid of a positioning mask on the same area of glass slide film samples before and after irradiation; for L*a*b* values the mean value and the standard deviation of three measurements were calculated. ΔE* was further calculated according to the equation

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

ΔE* values above 2.3 were considered to correspond to just noticeable differences (JND) (Mahy and Eycken 1994).

UV-Visible Spectroscopy
Absorption measurements were carried out using a Cary 100 bio UV-Visible spectrophotometer. The measurements were taken between 200-800 nm with particular focus on the 300-400 nm region most responsible for polymer degradation.
Results and Discussion

Absorption Spectra of Glasses

A comparison between the glasses with different colours was performed, in order to evaluate the effect of the presence of the transition metal ions, which change the absorption spectra of the glass (figure 1) and thus, the UV light absorption of the adhesives. UV-Visible optical absorption spectra of colourless glass exhibit a cut-off in the UV region, at 300 nm. Similar cut-offs can be seen in all other spectra although displaced to 320 nm for Co and 360 nm for Cu containing glasses. Copper green glass absorbs UV at the same wavelength emitted by the UV lamp used to cure the adhesives in this study (362 nm). This might affect the amount of radiation that reaches the polymer decreasing it and thus, have an influence in the curing process as discussed below.

Molecular Changes Observed by Infrared Analysis

Photodegradation

The most evident spectral changes caused by photo ageing ($\lambda > 300$ nm) are shown in figure 2. From this figure, Paraloid® B-72 may be suggested as the most stable adhesive to UV-Visible irradiation (figure 2a). In contrast, both Hxtal® NYL-1 and Vitralit® 7561 show the most clearly visible spectral changes (figure 2b and 2d). The spectrum of the aged Hxtal® NYL-1 shows the formation of new bands at 1725 cm$^{-1}$ and 1655 cm$^{-1}$ (assigned to C=O groups) and the relative intensity increase of the O-H band, between 3500-3100 cm$^{-1}$ (Coutinho 2008). Vitralit® 7561 shows an increase and broadening of the C=O stretching band at 1730 cm$^{-1}$, the appearance of a new band between 3620-3160 cm$^{-1}$ (formation of OH groups) and the decrease of C-O-C relative intensity at 1109 cm$^{-1}$. On samples of Verifix® MV 760 (figure 2c), the relative intensity decrease of both C-O-C stretching band at 1109 cm$^{-1}$ and C-H stretching bands between 2700–3000 cm$^{-1}$ was observed (Coates 2000). These changes may be associated to chain scission mechanisms of acrylic polymers promoted by UV radiation (Melo 1999).

Effect of High Relative Humidity (RH 80%) 

Based on infrared spectroscopy, no clear changes were detected in the molecular structure of the adhesives exposed.
Colour Variation

Colour measurements show that only slightly higher colour variations may have occurred in samples aged by photo-oxidation in the SolarBox as compared to samples kept in the dark and those aged at high RH (figure 4). All colour variations are below Delta E of 2, meaning they are not distinguishable by eye (Darwish 2013; Twitchett 2007).

Mechanical Behaviour

In order to interpret the mechanical behaviour of the adhesive after accelerated ageing and prolonged exposure to high humidity, results obtained under these conditions were compared with those for the reference samples that were kept in the dark.

The results obtained for the Young’s modulus were represented in the form of bar charts (figure 5). These values, obtained through calculation and not direct measurement, have standard deviations (error bars) higher than the corresponding values of stress at break obtained directly from the tensile test plot (figure 6). As expected, the variation of the majority of the latter results follows the trend of the corresponding Young’s modulus (E), being higher for higher E values, which correspond to superior stiffness and energy to break; the exception was observed for the green glass bonded with adhesive Verifix® MV 760 and the blue with Hxtal® NYL-1.

The subsequent analysis of the tested adhesives’ physical behaviour will be based on the mean values of Young’s modulus. The values obtained are only indicative of the general trends, since the experimental variation of the results was very high.

The three adhesives Hxtal® NYL-1, Verifix® MV 760 and Vitralit® 7561 have in common the crosslinking between their polymeric chains, which influences their mechanical behaviour, and they were thus expected to be more resistant to tensile strain. The analysis of the behaviour of UV curable resins shows that Verifix® MV 760 is the adhesive that exhibits the higher value of Young’s modulus in all tested situations (figure 5).

The adhesive Paraloid® B-72, by comparison, is the one with the lowest Young’s modulus and stress at break for all conditions tested (figure 5). This acrylic polymer is a thermoplastic, formed by linear chains having no crosslinking between them, which gives rise to a much lower strength at break than the other adhesives under study, which are thermosets, and whose network structure makes them much more rigid and mechanically resistant.

Fig. 3. Infrared spectra of (a) Paraloid® B-72, (b) Hxtal® NYL-1, (c) Verifix® MV 760 and (d) Vitralit® 7561 before (black) and after (blue) exposure to 80% RH.

Fig. 4. Bar chart relating the colour variations experienced by each adhesive after the accelerated photo-ageing and high RH compared with the reference samples.
Chemical and Mechanical Stability of two UV Curing Adhesives for the Conservation of Glass – Preliminary Results

Ana Ablum, Ana M. Ramos, Susana F. de Sá, Augusta Lima, Márcia Vilarigues

ulus only for the films bonding colourless glass, whereas the films bonding coloured glass show no measurable variations. This response of the material to the mechanical tests might be explained by the possibility of an increased crosslinking of the polymer chains during the accelerated ageing, triggered by interaction with light, which promoted the continuation of the crosslinking reaction occurring during the normal cure, due to the existence of unreacted functional groups as described in the literature (Rabek 1995; Coutinho 2008). This fact makes the adhesive more rigid and resistant and therefore less elastic, leading to breakage occurring with a greater force. However, this behaviour is not observed for green and blue glasses, as the Young’s modulus is very similar to the value of the reference sample. One possible justification for this hypothesis can be the UV absorption of the coloured glasses shown in figure 1, as they absorb in this region of the spectrum.

Contrary to what was observed with Hxtal® NYL-1 under the conditions of irradiation, the UV curing adhesives Verifix® MV 760 and Vitralit® 7561 have generally decreased average Young’s modulus after 2000 h. Furthermore, while Hxtal® NYL-1 shows no change in tensile strength after aging, both Verifix® MV 760 and Vitralit® 7561 present significant changes in stress at break, possibly due to a decrease in the rigidity of the polymer, which leads to breakdown under lower stress values (figure 6). After photodegradation of Paraloid® B-72 the bonding of the colourless and green glasses resulted in a significant decrease in the average Young’s modulus, which suggests that the polymer has undergone degradation by chain scission, becoming more flexible. This situation is in accord with that described in the literature (Rabek 1995; Melo 1999; Bracci and Melo 2003).

Effect of High Relative Humidity (RH 80%)
In what concerns the effect of moisture on the adhesion capacity of Hxtal® NYL-1, no significant changes were observed, since the value of Young’s modulus remains constant compared to the reference sample (figure 5). Taking again into consideration the mean results obtained for UV curing adhesives’ mechanical behaviour is then analysed. In high humidity, in the case of Verifix® MV 760, a very small decrease in the Young’s modulus of the bonded colourless glass was recorded, which can suggest that the adhesive may have undergone some hydrolysis re-
ular level which may have had a reduced influence on its mechanical behaviour. Moreover, in the case of green glass bonding, the opposite occurs but also not very significantly whereas in the blue glass, Young’s modulus remains practically unchanged. In the case of Vitralit® 7561 for blue glass the value for the Young’s modulus doesn’t change, whilst in green glass this parameter increases significantly compared to the reference sample and in colourless glass presents only a small increase.

After exposure to high humidity, the Young’s modulus for Hxtal green bonded glass and Paraloid colorless and green glasses show the same tendency to decrease. However in the case of green glasses the decrease is higher than that observed clear glass.

It can be concluded that the Verifix® MV 760 adhesive, an acrylic polymer modified with urethane bonds and UV curing, is the adhesive that bonds the best with colourless glass. However, it should be noted that the Young’s modulus for intact colourless glass is 0.55 ± 0.12 MPa and, with the latter adhesive, the value determined for the reference glass was 3.15 ± 1.57 MPa. This difference in the stiffness values of the materials may cause internal stresses that may lead to subsequent fracture of glass in adjacent areas.

Conclusions
This work has looked at two adhesives commonly used in the conservation of glass and stained glass, and two UV curing adhesives, in order to evaluate and compare their properties and stability through accelerated artificial ageing in a Solarbox and exposure to high values of relative humidity.

While the exposure to UV-Visible irradiation (λ > 300 nm) led to changes in the adhesives molecular structure and mechanical behaviour, the hydrolytic experiment led to insignificant chemical and physical changes.

In detail, the stability of Paraloid® B-72 was confirmed; Hxtal® NYL -1 underwent degradation during UV-visible light exposure, leading to changes in the FT-IR spectra; Vitralit® 7561 showed the highest instability to UV irradiation as confirmed by spectral changes. Finally, Verifix® MV 760 proved to be the more stable UV curing adhesive; it showed no yellowing, minor spectral changes and the highest mechanical resistance.

UV curing resins appear to be a promising alternative to traditional adhesives in conservation for bonding of glass,

Fig. 6. Stress at break obtained by tensile tests for (a) colourless glass, (b) green glass, (c) blue glass.
nevertheless, the results presented in this paper are preliminary and further investigation is needed to evaluate if these adhesives are to be recommended. In this preliminary study the adhesives’ physical behaviour was evaluated with only five specimens of each sample. Additional data is needed with a more representative sampling, at least ten to fifteen mock-ups in order to obtain more reliable and accurate data testing. Additional parameters such as reversibility and in situ durability also need to be evaluated.

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Coutinho 2008

Darwish 2013

Davison 1998

Goss 2002

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Case Studies
The Glass Beaker of St. Hedwig from the Museum in Nysa/Neisse, Poland:
Preliminary Investigation in Preparation of Future Conservation

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Keywords
Hedwig Beaker; medieval glass; Saint Hedwig; Silesia, Nysa/Neisse

Abstract
The Hedwig Beaker of the Nysa Museum belongs to a specific group of thick-walled glasses from the late twelfth to early thirteenth centuries. Hedwig beakers are characterized by the use of colourless and highly decorated glass with deep relief-cut designs. The origin and production of these unusual vessels remains a subject of debate. Through close visual examination of the beaker in the Nysa Museum commonly associated with Saint Hedwig, the Duchess of Silesia (1174-1243), this paper provides an advanced interpretation of its iconography and potential possibilities for future study. The beaker’s state of preservation and its techniques of manufacture, along with a treatment proposal, are outlined in preparation for future conservation.

Introduction
The Hedwig beakers are truly special examples of glass from the Middle Ages (Baumgartner and Krueger 1988, p. 86-105). They are a small yet unique group of objects found in central Europe. While they are distinct from each other in terms of decoration, they are all made from low-magnesium soda ash, and are clear glasses with shades varying from smoky topaz to yellow-brown. They are thick-walled, conical or “bucket” forms that are decorated in deep relief with a specific group of motifs. Despite speculations from over a hundred years of research, many issues related to the beakers, such as the origin of their manufacture or their intended function, still remain hypothetical. Based on the chemical composition of the glass, which is similar to Levantine glasses (Wedepohl et al. 2007, pp. 267-268, table 1), researchers have proposed a connection with Islamic glass production in the Levant. Other scholars have suggested a Sicilian origin for the motifs on these glasses, based on their pictorial similarities with rock crystal objects (Pinder-Wilson 2004, p.126; Wedepohl 2005, pp. 5-7; Whitehouse 2010, pp. 50-52).

Beyond the allure of Medieval history and mystery, the authors are drawn in particular to the example described here, which is preserved as a reliquary (figure 1) due to its connection with the legend of St. Hedwig, Princess of Silesia (1174-1243). In total, three such glass beakers have been traditionally connected with St. Hedwig1. The first is stored in the cathedral treasury at Wawel Castle in Krakow (Baumgartner and Krueger 1988, no. cat. 37), while the second was located in the German Museums in Breslau (Czihak 1891, pp. 193-195, fig. 48, pl. VI: 5613; Schmidt 1912, pp. 56-57, fig. 1, pl. II) but was lost during the second World War. The third remains in the collection of the local Museum of Nysa in Silesia (Schmidt 1912, p. 60), and is the focus of this paper.
What was the route that led one of these beakers to the collection of the local Nysa Museum? While there is no documentation of the fate of St. Hedwig’s personal belongings after her death, it can be assumed that Ludwig I, Duke of Legnica and Brzeg (1313-1398) had an influence on the preservation of at least part of the heritage of the early Piast Dynasty of Silesia. Ludwig I is remembered in history as a wise and righteous ruler, who saved the integrity of the duchy in difficult times. Religious values and the traditions of the Silesian Piast Dynasty were important to him, and during his reign the Code of Lubin—an illustrated legend of St. Hedwig, whose cult had been propagated by the duke throughout his life—was created. As part of his legacy, the glass beaker of St. Hedwig was kept among the belongings of the duchy of Brzeg and Olawa. A letter written in 1614 by the Wroclaw (formerly Breslau) bishop Charles I of Habsburg to the Archduke mentions that the bishop was to see and keep the glass, which had once belonged to St. Hedwig. The bishop of Wroclaw was then to gift the precious souvenir to the Jesuit College in Nysa, which he founded in 1622. Following the secularization of the church by the King of Prussia in 1810, the object became the property of the Catholic High School (German: katholisches Gymnasium) in Nysa and was stored there until the Second World War. In May 1945, amidst post-war chaos, the Junior High School caretaker Jan Raczek handed the glass to the nuns from the Congregation of St. Elizabeth’s Sisters in Nysa, who eventually donated the object to the Nysa Museum (Czihak 1891, p. 188; Allen 2003; Pawlik 2009).

While this beaker remains preserved in Silesia, time has not been kind to the other beakers. Over the centuries, these vessels gradually fell into oblivion. Most recently, the glass beaker from Nysa came into the spotlight again in 1970, when serious damage to the object required nearly two years of conservation work at the State Enterprise for Conservation of Objects in Wroclaw and Warsaw, in collaboration with Jerzy Chodurski from the Wroclaw Academy of Art and Design in 1970-71. The only existing detailed documentation of the object was created during this period (Mitraszewska 1971).

The goal of this paper is to present new findings associated with the glass beaker in the Nysa Museum through the use of scientific analysis and technological studies, in order to situate the vessel in context with similar objects in European glass collections.

**Description and Interpretation of the Beaker’s Symbolism**

The glass beaker from the Museum in Nysa (accession number MNa / R / 1684, formerly PA 3947) is a thick-walled glass with a relatively simple conical/bucket form, decorated by cutting and grinding the exterior (figure 2a). It is difficult to precisely determine the original dimensions of the beaker as it was severely damaged and now comprises fifty-six fragments that are bonded together. It is estimated to be 10.6 cm tall, with a foot diameter of 6.8 cm and a rim diameter of 9.2 cm. The thickness of the wall
at different parts on the rim ranges from between 0.42 to 0.50 cm. As they are of similar dimensions, the vessel of Nysa as well as the vessels from Wrocław and Krakow, almost certainly belong to the larger group of so-called Hedwig vessels (Table 1 and figure 1 in Wedepohl 2005). The glass can be described as naturally colorless and transparent. It has a distinct yellow-brown shade slightly dimmed by greyness due to the thickness of its walls and impurities in the glass. The German term “rauchtopas”, best describes this color. When viewed under magnification, many small gas bubbles were detected. However, no defects such as inclusions and streaks were noticed. Also, preliminary analysis with portable, non-destructive X-ray Fluorescence (pXRF) shows an even distribution of selected elements (Si, K, Ca, Mg, Mn, Fe) across different areas of the vessel, demonstrating a high degree of glass homogeneity (Wachowiak 2015).

The beaker’s ornamentation is composed of repeating motifs. The outer surface of the vessel’s body was deeply carved into a series of facets, leaving motifs in the composition sculpted in high relief. There are twelve vertical facets around the rim of the vessel and eight wider, deeply cut facets in the main decorative area below them. Two of these lower facets correspond in width and alignment to three facets along the rim. This vertical arrangement is accentuated by stylized columns located between every pair of larger facets, which connect the upper and lower portions of the vessel (figure 2b).

Against the background of the facets in the beaker’s body, four main decorative motifs are sculpted and repeated four times on the vessel (figure 3). Below the faceted upper area of the beaker is a horizontal band of incised cross-hatching that is interrupted on four sides with an eye-shaped motif. In the lower area, the main decorative motif presents a recurring symmetrical arrangement of “C”-shaped kidney-like designs, consisting of pairs of facing elements.
The tops of each facing “C” motif are stylized with radiating, mostly vertical carved grooves, alluding to a shell or palmette design. The bottom of the beaker is differentiated by the addition of a stepped foot. Additionally, there are four wide transverse incisions at the base in each location that corresponds to the eye-shaped motifs in the upper part of the beaker.\(^5\)

From the above description, the artistry and originality of the decoration, characteristic of the whole group of vessels referred to as the Beakers of St. Hedwig, emerges. In terms of ornamentation, the vessels have been divided into two main groups. The first group contains figurative motifs such as the lion, the griffin or the eagle. The second group exhibits compositions of abstract elements such as palmette, volute and floral themes, crescents or geometric motifs. At the present, only the symbolism represented by the animal motifs (specifically the lions, griffins and eagles) has been clearly explored in studies, which discuss neither their heraldic or religious significance (Whitehouse 2002; Lierke 2005, pp. 57-65; Wedepohl 2005, pp. 11-16).

We are of the opinion that the beakers decorated with zoomorphic motifs are not the only ones carrying Christian or otherwise religious content in their decoration. Allen (2003) suggests that the beakers were intended for nobility, but it is also pertinent to point out that there are differences between the two groups of beakers. These differences do not relate to religious or heraldic motifs, but rather refer to the male (knighthood, heraldic) or female (palace-related rather than abstract) symbolism in the decoration.

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Comments on the State of Preservation
Preliminary examination of the Nysa Beaker was carried out at the museum using reflected and transmitted light under magnification, and through the analysis of high-resolution digital images. In general, the present state of the object’s preservation has been influenced primarily by multiple campaigns of mechanical damage. The object consists of about fifty-six bonded glass fragments, and it is not complete (figure 3). There are three fills made of colorless lead glass. An epoxy resin, Araldite 2020, was also identified\(^6\) as the adhesive used to bond the fragments of original glass and lead glass fill pieces together (figure 4a-b) (Mitraszewska 1971, p. 4). These restorations in areas of repetitive decoration stand out in color from the original, and are a little too high and fit to the shape of the losses with insufficient precision (figure 4d). We suspect that more recent campaigns of conservation and restoration have erased any traces of other historical repairs and materials on the object. This is due to the varied degree of matching of the original glass fragments, location of the losses at the edge and central parts of the walls, and a complex network of cracks.

In some areas of the vessel, the fragments fit well together, suggesting that bonding occurred soon after breakage, while in other areas, the edges of the fragments are not precisely joined—they are not as clean and sharp as a fresh break due to the loss of small fragments and natural deterioration. Poor fit can also be caused by the loss of very small fragments of the original glass after breakage, which, being unsuitable for merging, have been irretrievably dispersed. As a result, there are lines of wide gaps extending through the body and bottom, accompanied by locally longitudinal and transverse closed cracks and conchoidal fractures.

Next, we noted that there are visible indications of use, occurring mostly on the bottom edge and in the areas of high relief on the walls (figure 4 c). In these areas, we observe matting, scratches, and minor chipping of the glass. Some of these marks may have occurred in the process of manufacture, and may in fact be tool marks ( Richter and Neelmeijer 2012, p. 236).

Additionally, there are a few signs of glass deterioration, such as slight matting of the surface caused by the presence of scratching and pitting (figure 4 a). Moreover, the epoxy resin (Araldite 2020) that was used in a previous conservation treatment has deteriorated. Adhesive joins and minor fills made using the epoxy resin have become visibly distinct, due to physical changes in the material such as yellowing, increased friability, and the local loss of adhesion (figure 4 a-c).
Comments on Techniques of Manufacture

The question of how the Hedwig Beakers were made has drawn interest ever since this group of vessels has become more widely known in the glass community at large. When the scientific achievements of the last few decades were summarized (Baumgartner and Krüger 1988, p. 86-88), the investigation of the glasses’ production techniques were postponed, giving way to more controversial topics. A few years later, the question of the vessels’ manufacturing technique was newly raised by R. Lierke, who advocated for them having been pressed into a rotating mold (Lierke 1999, pp. 140-145; Lierke 2000, p. 201-202; Lierke 2005, pp. 33-46). Scholars have since been divided on the subject. The current opinion of most researchers is that they were perhaps blown in a mold before being wheel-cut (Wedepohl 2005, p. 8; Whitehouse 2010, p. 228).

The Nysa Beaker was examined macroscopically for any signs of the techniques and tools used in the process of manufacture. There are a few fundamental findings related to the underside of the vessel. First, we noted a round pontil mark of a diameter of 1.6 cm (figure 5a). It might be connected to the glassblowing process, and more precisely with the shaping of the upper area of the vessels. This mark could also be a trace from a pontil

Fig. 4. Details of the state of the object’s preservation: (a) glass corrosion, pitting and yellow epoxy resin Araldite 2020; (b) degraded epoxy; (c) mechanical damage, local losses of epoxy adhesion; (d) glass fills and joins in the main area of impact of the vessel edge (Photo: P. Romiński).
rod used for reheating to add a slight fire-polish of pressed glass in the furnace (Lierke 2000, p. 201). Second, there is a groove near the edge of the bottom of the vessel that separates it from the central area of the vessel’s base. The width of the foot on the outside of the groove is variable, suggesting that this separated bottom edge was made from a rolled glass mass that was added. Third, four broad transverse cuts were made at the base of the vessel, closely related in position to the layout of the decorative scheme (figure 2-3). The cuts appear to be made by a grinding wheel in at least two passes, as seen from the change in the angle and width of grinding, which is visible under magnification (figure 5b). Finally, we observe the regular presence and relatively even distribution of gas bubbles in the walls of the vessel. The gas bubbles in the lower part of the beaker, up to the facing palmette or wing designs, are close to spherical in shape. In contrast, the gas bubbles located in the upper part of the vessel are extended horizontally in shape, suggesting gradual deformation in this area. The most deformed bubbles are visible nearest to the rim (figure 5c). We have identified the use of at least five cutting tools responsible for the broad flat cuts, the flat, wedge-shaped cuts of deeper recessed areas, and the oval fluting. This was done by inspection of the outer surface of the vessel, either in the faceted background, or in areas of deep relief.
In the deep, sharply carved areas of the background, there is visible subtle folding that renders the ridgelines between adjacent facets irregular (figure 5 d). There are also other instances of folding and irregularities in the glass surface on the inside of the vessel. This will be the subject of detailed analyses and documentation in future research and conservation work, which will include dismantling the beaker’s bonded fragments. The results of these observations, though valuable, are insufficient for any firm conclusions to be drawn. Finally, there is yet no basis to exclude the manufacture of the Nysa Beaker by a blown technique or the creation of its decoration with the technique of cold grinding.

**Treatment Proposal**

The Nysa Beaker of St. Hedwig is certainly an important work of glass art. Special conservation and preservation care should be taken as it is one of few examples of such beakers in the world preserved almost in its entirety. As a reliquary of a historical figure, the object presents challenges in conservation and restoration. First of all, the program of conservation has to be closely related to the vessel’s current state of preservation, while ensuring that the functional unity of fragments is maintained. The conservation treatment will therefore aim to limit intervention where possible but still consider the dismantling of previously integrated fragments in the glass beaker and reconstruction of the missing fragments. It will be necessary to remove the adhesive as it has yellowed and has weakened bonding strength due to ageing. This will be particularly difficult around closed cracks located along the edges of certain fragments.

This preliminary study, along with photographic documentation at high magnification is useful for research and conservation purposes as it reveals the most important features of the object. Further steps would include determining different phenomena of damage on the beaker based on characteristics of the break edges, elucidating techniques of manufacture from further characterization of the gas bubbles, as well as examining micro-traces of tool marks. A detailed diagnosis of the state of preservation of the glass that includes the continuity and morphology of the surface, the mechanical and chemical damage incurred, and the assessment of closed cracks, will be necessary. Results of chemical analyses will further allow for comparative studies relating to the question of the beaker’s origin and its potential connections, in terms of workshop practices, with the other glass Hedwig beakers. Conservators’ recommendations regarding the object’s safety and display relating to temperature, humidity, lighting and access will be taken into account. It seems reasonable to make a copy of the historic vessel too, first to analyze the process of production and second for the purpose of the exhibiting it at Nysa Museum. The metalwork that was created to hold the Hedwig Beaker, probably first in 1528 and later in the 18th century, is also part of the beaker’s long history, and cannot be neglected. Housing the original glass beaker in metalwork could affect the state of preservation of both the metal and glass components. The future display of the object is a big concern of the authors as total internal reflection of light might mark its impressive appearance (Nowotny 1968, p. 257).

**Conclusion**

The preliminary examination of the relatively unstudied, yet heavily damaged, medieval glass vessel from the Museum in Nysa, demonstrates that it is fully representative of the small and unusual group of St. Hedwig glasses. Investigation of its technique of manufacture, decorative scheme, and state of preservation raise interesting possibilities for scientific study as well as future conservation and exhibition of the object.

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Notes

1. Such beakers are connected to Saint Hedwig due to the local legend that arose around her, described in a manuscript in 1535. “According to the legend, Duke Henry criticized his pious wife for her ascetic habits and in particular for drinking water instead of wine. Determined to make her change her ways, he unexpectedly confronted her while she was dining and snatched the cup from her hand. When he drank from the cup he realized that the water it contained had been transformed into wine” (quoted in Whitehouse 2010, p. 48; Pinder-Wilson 2004, p. 126).

2. Up until 1898 in Museum Schlesischen Altertümere, and later between 1899 and 1940 in Schlesische Museum für Kunstgewerbe und Altertümere.

3. Under low magnification (2.5-5x), possible at the museum in situ, we recognized traces of cutting, but we did not come across any open gas bubbles. One would expect a glass of this quality to contain no gas bubbles - the cutter’s job was to cut them away. A higher magnification will be used after the beaker is dismantled.

4. It must be pointed out here that the technique cannot detect one of the main elements found in glass, namely sodium (Na).

5. This raises the question: was the Nysa Hedwig Beaker, or other beakers from this group, meant to be mounted in metalwork as was often practiced in the Middle Ages or later, or was it designed as a reliquary in the first place (such as in the case of two Namur beakers – probably bishop Jacques de Vitry’s gifts; Baumgartner and Krueger 1988, no. cat. 41-42)? According to known and dated forms of Nysa metalwork, the former cannot be the case for our Hedwig beaker. The metalwork dated to 1528 appears to be designed to fit the glass and not the other way around.

6. Some researchers suggest that the foot—especially the wide cut areas—could have served as a connection to the metalwork (Wedepohl 2005, p. 7), but others do not agree with this suggestion (Baumgartner and Krueger 1988, p.86 and 88 note 2). We require further proof if the latter is true.

7. In the same stylistic convention, there is a “tree of life” motif in the Minden Beaker that is situated near the edge between two facets, (Lierke 2005, fig. 8, p. 28).

8. The resin used was mentioned in the conservation record (Miraszeswka 1971, p. 4).

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The Temple of Love (**Liebestempel**): A Baroque Table Centerpiece by J. J. Kaendler

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**Keywords**
Temple of honor; Meissen; porcelain; table centerpiece

**Abstract**
The Temple of Love, a Baroque centerpiece in the form of a temple, is dated to the 1750s and attributed to the master modeller Johann Joachim Kaendler, who worked for the Meissen porcelain manufactory from 1731-1755. The only centerpiece of its size (height: 116 cm; width: 60 cm; length: 86 cm) extant in the original, it was treated during preparations for the new permanent exhibition of the Museum Angewandte Kunst, Frankfurt am Main, Germany. Earlier unstable and unaesthetic restorations were removed and conservation carried out. In a few cases, minor, reversible restoration measures were chosen to facilitate the object’s readability; small additions were made and coloured as necessary. The overall aim of treatment was to return the Temple of Love to a condition suitable for exhibition, as well as to preserve its historical form as an object of display.

**Introduction**
The Temple of Love (inventory no. 4920) belongs to the category of the so-called temples of honor used in the Baroque era as table centerpieces for display banquets at royal events such as weddings and baptisms.

The temple (figure 1) consists of painted porcelain with a quatrefoil base. On each of the twelve column bases are 24 vine-entwined columns ending at the top in imitation volute capitals. Resting on the capitals is an arcade with twelve shallow arches decorated with tendrils and summer blossoms. Above that a decorative dome consisting of volutes rises up to be crowned by a vase-like tip likewise entwined with tendrils and blossoms. Twelve putti representing the four seasons and eight shield-bearers as well as twelve urn-shaped vases and eight shields further animate the architecture. At the center of the temple is a figural group of Cupid and Psyche before the altar of Juno (Trenkwald 1909, p. 279; Schmidt 1925, p. 247). It was this two-part figural group that gave the centerpiece the name ’**Liebestempel**’ (Schmidt 1925, p. 248).

The Temple of Love is ascribed to the modeller Johann Joachim Kaendler (1706 in Fischbach – 1775 in Meissen, Germany), who worked at the Meissen factory from 1731 to 1775. The attribution is based on the fact that he is verifiably the author of the temple’s figures (Trenkwald 1909, pp. 279–280; Schmidt 1925, p. 247). The temple’s Rococo forms date it to the 1750s. It can be assumed that the design was inspired by French Baroque architecture and the engravings of Jacques-François Blondel (Ferguson 2010, p. 13), although Stefan Bursche proposes the Dresden Kronentor (Crown Gate) as a possible inspiration (Bursche 2010, p. 136). In the Meissen records, several temples of honor in various forms are mentioned. Most of them are single-copy works. With its height of 116 cm and pedestal of 60 by 86 cm, the Temple of Love is one of the larger examples of Baroque temples of honor. The number of individual elements varies considerably, depending on how they are counted. In the literature, the temple is often said to consist of 114 parts (Trenkwald 1909, p. 279; Schmidt 1925, p. 247). A formal count arrives at 88 porcelain elements, some of them bearing metal mounts, and 111 elements made of different types of metal.

The centerpiece was purchased in 1909 from the art dealers J. & S. Goldschmidt and allegedly came from the estate of Albert Townsend. Somewhat smaller comparanda for this centerpiece are today found in the Staatsliche Kunstsammlungen Dresden and in the collection of the Marquess of Bath in England (Honey 1934, p. 110; Ferguson 2010, p. 13).
In conjunction with the expansion of the new permanent exhibition entitled “Elementary Parts: From the Collection,” the object was to be prepared for display once again. Initial assessments revealed that a number of supporting elements were broken and old retouches had yellowed considerably. Moreover, large sections of the vine decorations were missing.

In terms of treatment, it was determined that conservation alone would not have sufficed to ensure the object’s readability, nor would it have resulted in an appearance that reflected the object’s historical role. Thus in addition to conservation treatment, a minimal of restoration¹ was deemed desirable.
Historical background

Table decorations with figures and architectural elements were common at festive occasions such as weddings, baptisms or similar occurrences from the sixteenth century onward. Table decorations were conceived by scholars and then realized by confectioners. Originally the figures and landscape elements were made of wax, tragacanth or confection which had been cast in molds (Brüning-Berlin 1904, pp.135–136; Schmidt 1925, p. 244; Eberle 2010, p. 74).

In the Baroque period, banquets of the upper classes usually consisted of three to four courses, the first two to three being savory and the last a dessert course. The table decorations used on these occasions differed depending on the dishes served. In the case of savory dishes, a so-called plattmanage or epergne—a platter with vinegar and oil, various spices, and sometimes a basket of lemons at the center—decorated the table. For the dessert course table decorations with figures made of confection and wax were used (Hantschmann 2010, p. 107; Eberle 2010, p. 74).

The precise reason for the replacement of wax and confection with ceramic, and later porcelain, has not been conclusively determined. It may have been due to the perishability of the former materials, or perhaps because the fruits used for the desserts—and thus the acid they contained—damaged the silver tableware (Schmidt 1925, p. 244; Eberle 2010, p. 74).

It was not until the mid-1750s to early 1760s that porcelain figures became the standard for table decorations at conservative courts. Table services with porcelain centerpieces were already being produced by the Meissen porcelain manufactory from the 1730s onward for use at aristocratic banquets (Eberle 2010, p. 74; Pietsch 2010b, pp. 97–98). In 1745 a porcelain table service from Meissen presented as a gift by Catherine I of Russia was used at her nephew’s wedding, marking the breakthrough of porcelain for ‘official’ courtly table services. In Saxony itself, the royal family used a silver service for official occasions until 1747. Even the dessert table was still decorated with confection, although porcelain figures are already on record in the inventory books of the Hof-Conditorey from 1744 onward (Pietsch 2010b, p. 102; Cassidy-Geiger 2010, p. 122).

Epernges were verifiably manufactured in Meissen from 1723/24 onward and offered for sale from 1731 onward. The reason for the temporal difference between the initial production of porcelain centerpieces and their official use at court is still unclear (Eberle 2010, p. 75; Hantschmann 2010, p. 108). In principle, it can be assumed that many of the porcelain figures and groups known today served as table decorations and could thus be viewed from all sides. Through the employment of porcelain, a more stable material, centerpieces could be made in ever larger sizes (Brüning-Berlin 1904, p. 131, 134; Schmidt 1925, p. 244, 247; Honey 1934, p. 110). Often entire table ensembles with large architectural elements at their centers were designed for special occasions. These ensembles included additional figures, architectural objects and tableware, all in the same style as the centerpiece (Schmidt 1925, p. 248; Ferguson 2010, p. 13; Pietsch 2010a, p. 28). It can be assumed that the Temple of Love was likewise part of a larger ensemble. The archive of the Meissen manufactory no longer has any records of the period between 1750 and 1763, as a result of which neither the exact date of the production, nor the occasion, nor the client, nor even the other associated elements of the ensemble can be determined.
Fig. 2. The putti representing the four seasons. They rest on a solid base with gold painting. The somewhat thickset figures are dated to the High Baroque.

Fig. 3a/b. The five putti, some of which come from the same form. They vary only slightly in the small details embossed later and in the painted decoration.
To judge from the manner of the tip’s execution, it dates from the same period as the architrave. The blossoms molded onto the tip and the architrave parts are nearly identical. Another possibility is that the temple was produced in various versions (Brüning-Berlin 1904, p. 149).

The two temples differ not only with regard to their tips, but also in the decoration of the architecture. Whereas the Dresden model is embellished with putti and a small number of vases and suits of armor, the Frankfurt version features putti and vases, as well as eight shields.

The Meissen porcelain mark is found on only six putti. Numbers engraved into the bottoms of the putti and one arch constitute a special feature. Meissen is known to have assigned model numbers from 1764 onward. A check of the engraved numbers 45, 80 and 82 in the list of models yielded no results. It can therefore be assumed that these numbers were formers’ marks.

As regards the putti, it is interesting to compare the four-season putti, which are High Baroque in style (figure 2), with the eight more delicate shield-bearing putti, which evidently date from a later point in time (Trenkwald 1909, p. 280; Sponsel 1900, p.136). In the case of the more delicate putti, only five molds were used for the eight putti, and those featuring the same shape differ only in the way they were painted (figure 3a/b).

The Temple of Love appears to have been restored and repaired several times in the course of its history, using a variety of techniques. Simple additions of wooden pegs on the putti are among the more minimal interventions. Based on visual examination, four different adhesives were used: a natural resin, a white glue, and two modern adhesives with differing aging properties. One of the arches, moreover, features holes indicating a former rivet repair at the breakage point. Remarkably, a large number of dowels and pegs were used in the gluing process, which in many cases would not have been necessary.

The restorations made to the fragile blossoms and tendrils are conspicuous. In the arches, primarily porcelain blossoms, leaves and foliage sections fired at a later date were used; in a few places they were enhanced with brass or plastic. The columns and the temple’s tip, on the other hand, received additions made of painted lead wire or lead sheet, which was then coloured. By backing the missing parts with lead it was possible to make replacements in fragile areas such as the petals in a way that would not have been possible with the usual supplement materials (plaster or chalk) alone.

**Conservation and restoration**

Overall, the temple was in fair condition. There were small flaws and fills in the flowers and foliage (figure 4a). The vine leaves on the columns in particular had numerous losses (figure 4b). In a number of cases the grapes were missing and had been elaborately replaced with little beads and then painted (figure 4c). Minor voids in the glaze had likewise been filled in and generously painted over, as had sections that had broken off from the architrave elements, column bases and capitals. The replacement of the upper section of the broken tip was executed extremely well. The largest damages to the temple were in the arches of the dome (figure 4d). Nine of the twelve arches were broken, five of them multiple times, and the stability of the dome and tip could accordingly no longer be guaranteed.

The decorative elements of the temple, the figures, vases and shields, exhibited the usual small losses and breaks. On the putti, fingers and toes as well as small pieces of the decorative blossoms had broken off. Often the wings had broken and been glued back on or, in some cases, replaced by newly fired porcelain wings (figure 4e). The four-season putti and the two central figures exhibited somewhat more damage. Here entire extremities had broken off and been re-mounted. Parts of the Cupid figure’s hands and feet and the lower part of the left wing had likewise been replaced with newly fired porcelain parts.

The Juno figure consists of two parts: a base that had been repaired by gluing, and the actual figure. The two parts are firmly connected with one another; between them is a thin piece of leather serving as a cushion. During former treatment of the temple, the seam between the two parts was cemented and coloured (figure 4f). A number of the porcelain elements exhibit deformations, cracks and voids in the glaze that came about during their production and firing.

Copper alloy sheet supports were soldered onto the backs of the eight shields with the aid of rivet pins. Four of the eight shields were broken, and two of these broken shields were plugged with copper sheet (figure 4g).

The additional stabilization with pegs appeared unnecessary. The handling of the porcelain necessary for fitting the pieces of sheet metal merely led to predetermined breaking points and, in the long run, to the shield’s destabilization. The lower section of one of the larger shields was missing and had been replaced with painted wood (figure 4h). The gilding was repainted in many places where it had been lost.

In some cases, the ram-headed vases displayed damage at the muzzles of the rams and at the necks of vases. A num-
number of the gilded metal mounts on the bases and rims of the vases had loosened and had damages to the gilding. All the temple’s gilded metal elements (frame, cover plate, screws and nuts, plinth rings, capital plates, and angel at the tip), which were based on a copper alloy, exhibited little evidence of corrosion on the whole. In some cases these elements also showed damaged gilding. The gilding had evidently been created by the fire-gilding technique (Anheuser 1999, pp. 8–9). More severe corrosion had occurred in the iron framework and the undersurface of the copper alloy framework, to the interior of which an iron rod is soldered (figure 4i). As is well known, iron reacts far more sensitively to water than copper and its alloys. To judge from the manner in which the corrosion spread, it can be assumed that water had run over parts of the temple at least once, causing the corrosion.

In view of the condition of the temple, preventive measures alone would not have sufficed to return it to a stable state. It was determined that the stabilization of the historic material could be achieved only through additional conservation (Cf. E.C.C.O. PROFESSIONAL GUIDELINES (II): CODE OF ETHICS, § II, Article 8.). Within this treatment, the majority of the earlier restorations and repairs were to be removed, as they were unstable due to the aging of the material. There were also unaesthetic and often covered large areas of the original surface. Conservation treatment alone, however, would have robbed the object of its original aesthetic quality to a certain extent, and thus of its historical significance as a demonstration of power, pomp and opulence. Pure conservation would ultimately have yielded no more than a ‘ruin’ of the temple.
In order to preserve the object’s readability and the context from which it originated, minor restoration measures were also necessary. The guiding principle was: do as much as necessary and as little as possible (Cf. E.C.C.O. PROFESSIONAL GUIDELINES (II): CODE OF ETHICS, § II, Article 5.). To begin with, all of the elements of the Temple of Love had to be cleaned, and any old, unstable and disfiguring adhesives, retouches, additions and filling materials removed. Breaks in supporting elements had to be adhered with an epoxy resin because of the increased stability it offers, while all aesthetic, non-supporting fragments were joined with a reversible adhesive. Small missing details, such as tendrils, blossoms, fingers and toes, were not to be restored in cases where the overall impression of the object was not negatively affected by the loss. In order to lend the overall structure more stability, a new base, complete with supporting construction (rods) was to be made.

In order to undertake the temple’s treatment, it was dismantled. After the individual elements had been documented, treatment could begin. The porcelain elements were cleaned with a steam cleaner and demineralized water and dried with cellulose paper towels. Then the old retouches and adhesives were removed mechanically with a scalpel and chemically with ethanol and acetone, and the breakage points cleaned (figure 5b/f). It was not possible to remove all of the adhesives. Where the adhesive was still stable, or where there was danger of damaging the original object through further attempts to loosen the glued parts, the adhesive was left as it was and merely cleaned. On the other hand, as a rule the old dowels, usually made of wood or copper, were removed.
The temple’s partially gilded copper alloy elements were cleaned with white spirit 100–140. Where necessary, diamantine, a polishing agent made of aluminum oxide was applied. In this case, the respective elements were subsequently cleaned with white spirit to prevent a further reaction of the cleaning agent with the surface. The iron framework was mechanically freed of loose corrosion particles and cleaned with ethanol. Subsequently, two coats of 5% Cosmoloid H80, a microcrystalline wax, in white spirit (w/w), were applied and buffed with a goat hair brush. The wax film should protect the iron framework from further corrosion, particularly where there is direct contact with other metals that have a lower electrochemical potential, to prevent contact corrosion. Additionally, a lost threaded rod was replaced to give the ‘winter’ figure a stable hold on the architrave (figure 5i). The breaks in the supporting elements were adhered with the epoxy resin Araldite 2020 (figure 5d), since a number of the breaks had previously been plugged with metal that could not be removed. This epoxy resin was chosen for the infiltration adhering because, unlike Hxtal NYL-1, an epoxy resin made especially for bonding glass and ceramic,
Araldite 2020 does not react sensitively in contact with metal.\textsuperscript{6}

Smaller loose parts without any supporting function, for example blossom, tendrils and rocaille tips, were reversibly remounted using 20\% Paraloid B72 (w/w), an ethyl methacrylate co-polymer (EMA), in ethyl acetate, partially thickened with glass bubbles. The porcelain flowers and tendrils produced later as replacements were also re-used in order to improve object’s readability (figure 5a/g). Larger voids, especially on the arches, were filled with alabaster plaster and consolidated with 5\% Paraloid B72 in acetone (w/w). In the places where voids would have had a negative effect on the overall aesthetic, smaller lacunae in the vine foliage and the figures were filled with 40\% Paraloid B72 in ethyl acetate (w/w) thickened with glass bubbles (figure 5e). For a few of the columns in the worst condition, vine leaves were cast in moulds and applied to conceal massive losses (figure 5b).

Where necessary, the filled areas were coloured with Lascaux acrylic paints and Golden Acrylic Medium Gloss to imitate the luster of the glaze as closely as possible (figure 5c). In a few cases, areas of the gilding were re-coloured with rich gold, a brass powder bound in the same acrylic resin dispersion. Concurrently with this treatment, a new wooden base was built to support the individual elements of the object to make it possible to lift the object with the base.

Summary

The treatment of the Temple of Love (figure 6) brought to light interesting information concerning the object’s history. The centerpiece proved to have undergone at least three major restoration campaigns, all of which clearly aimed to make the temple look complete. Both the former treatments and the missing parts testify to the fact that the object had already had an eventful history by the time it entered the Kunstmuseum, today the Museum Angewandte Kunst, in Frankfurt am Main, Germany, in 1909.

The aim of the renewed treatment of the Temple of Love was to return the object to a stable state suitable for exhibition. On the one hand, the object’s history was taken into account, while on the other its readability and intended function as a festive display object were also considered. To achieve this balance, the treatment primarily involved conservation with some restoration. As part of this treatment, the temple also received a new wooden base.

The Temple of Love is once again on view in the permanent exhibition of the Museum Angewandte Kunst since November 2015.

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Materials and suppliers

- Araldite® 2020, Kremer-Pigmente.com
- Acetone, Kremer-Pigmente.com
- Cosmoloid H 80, Kremer-Pigmente.com
- Diamantine, www.goldschmiedebedarf.de
- Paraloid™ B-72, Kremer-Pigmente.com
- Silicone Silco MS-Abformmasse, www.Deffner-Johann.de
- All images provided by the author and the Museum Angewandte Kunst Frankfurt am Main.

Notes

1 The terms conservation and restoration are used in accordance with the German definitions: conservation refers to all treatments necessary to stabilize an object; restoration refers to all treatments leading to an aesthetic valorisation.

2 E-mail correspondence of April 1, 2015 with Sylvia Braun, research assistant, Historische Sammlungen, Staatliche Porzellanmanufaktur Meissen GmbH.
3. See previous note.

4. Among the mythological and allegorical groups of 1741, Jean L. Sponsel also describes four putti representing the seasons and, with regard to their attributes, very similar to those of the temple but not identical. It is no longer possible to determine whether Hermann von Trenkwald’s identification was based on this description or whether he used another source.

5. Stainless steel threaded rod M4, shortened to length and adhered in place with 20% Paraloid B72 in ethyl acetate (w/w).

6. Cf. the material information, which describes that contact between Hxtal and metal has a negative effect on the aging properties, see: http://www.kremer-pigmente.com, Hxtal-NYL-1 detail information (PDF), August 3, 2015, and http://www.kremer-pigmente.com/media/files_public/97920.pdf, Araldite 2020 detail information (German), January 5, 2016.

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3D Printing and Fills on Glass Vessels: A Case Study from the Fraunces Tavern Museum

Sarah Barack

Keywords
White light scanning; 3D printing (additive manufacturing); fills on glass

Abstract
This paper explores the use of new 3D scanning and printing technologies for loss compensation on a narrow-necked 18th century American glass vessel. The glass decanter is part of an 18th century campaign liquor set originally owned by General Baron von Steuben, a significant Revolutionary War figure, and is now in the collection of the Fraunces Tavern Museum, New York City. A full restoration of the vessel was desired, but filling a closed loss in the body was challenging using standard casting and epoxy filling methods. A project was launched to investigate the applicability of 3D printing to the conservation of glass. The glass was scanned with a white light scanner and multiple prints were made of both the extant glass and the area of loss. A fill was ultimately cast using the printed copy of the bottle, and secured in place on the original bottle with epoxy. This paper addresses the process, with a consideration of its substantial challenges and applicability to the field of conservation.

Introduction
Fraunces Tavern Museum and the Liquor Chest
“His emotions were too strong to be concealed which seemed to be reciprocated by every officer present. After partaking of a slight refreshment in almost breathless silence the General filled his glass with wine and turning to the officers said, ‘With a heart full of love and gratitude I now take leave of you. I most devoutly wish that your latter days may be as prosperous and happy as your former ones have been glorious and honorable’” (Johnston 1904, p. 96).

And so General George Washington took leave of his troops on December 4, 1783, following the evacuation of the British army, with this emotional farewell at the Fraunces Tavern in lower Manhattan. This continuously operated tavern still offers repose to those in need of refreshment today, and its history is on view for all in the adjacent galleries. Indeed, the Fraunces Tavern Museum operates with the express purpose to preserve and present American history, from the colonial period to the early Republic.

Among the most prized possessions of the Museum is an 18th century campaign liquor chest, previously owned by General Baron Friedrich von Steuben, General Washington’s Inspector General. The chest includes a decorative paper-lined wooden box, which contains 30 cut and gilded glass pieces, including several decanters, stoppers and goblets. This paper focuses on the treatment of one large decanter that exhibited a challenging area to fill. The ultimate approach to the work incorporated a 3D printed model, created in collaboration with New York University (NYU)’s Advanced Media lab. The work involved in this treatment, including expected—and unexpected—difficulties, will be examined and contrasted with a more traditional approach taken on an associated glass goblet.

Before delving into this discussion, it is helpful to understand the significance held by this small collection and why the Museum Director felt a full restoration was appropriate.

General Baron von Steuben and the Campaign
Given that the Tavern witnessed Washington’s final toast, the chest and its association with the Revolutionary War resonate with particular significance for the Museum and its patrons. Though not present at this famous farewell,
Friedrich Wilhelm August Heinrich Ferdinand Steuben, known as Baron von Steuben, was an integral part of Washington’s inner cadre. After a somewhat storied military career in Prussia, Steuben ventured to the colonies (Lockhart 2008).

Realizing that his ragtag army sorely lacked professional training, Washington took Steuben on as his Inspector General. With duties that included proper training and drilling of the soldiers, Steuben’s leadership provided the first systematic approach to this necessary instruction. He was additionally known for his solicitous nature and he no doubt served as a host to many jubilant evenings with peer and junior officers.

As the chest serves to signify both Steuben’s contribution to the success of the American army and his sociability with the officers, its exhibition was considered a high priority for the Museum. Thus, the decision was made to fully restore these pieces in order to provide an appearance that might better integrate with the undamaged bottles. As such, when displayed together in a museum setting, the social aspect of war making, however incongruous that seems, might be examined.

The Glass Objects

Description and Condition

Though the wooden chest holding the bottles is basic and functional without extensive ornament, Steuben’s glassware, which fits perfectly within the container, features hand-cut facets and gilded floral designs. The vessels were blown from colorless glass with seed bubbles and inclusions visible throughout. As expected, the cut facets are not regularly spaced, but instead present variations in width. Analysis of the glass composition was conducted by Mark T. Wypyski, Research Scientist at the Metropolitan Museum of Art. Elemental analysis was performed on a small sample of the glass by energy dispersive X-ray spectrometry in the scanning electron microscope (SEM-EDS), using an Oxford Instruments AZtec Energy Microanalysis system operated with a Zeiss Sigma HD variable pressure SEM. Final oxide weight percentage results were calculated using appropriate glass standards and well characterized reference glasses.

Results confirmed that the glass has a potash-lime-silica composition, with small amounts of sodium, magnesium and aluminum, along with a small amount of arsenic, probably added as a decolorant. Similar glasses were produced by John Frederick Amelung at the New Bremen glass factory near Frederick, Maryland in the late 18th century; however a comparable example is found in published 18th century Bohemian glass compositions as well (Brill 1999). Given the Baron’s European origins as well as his American appointment, it is unclear at this time where the glass was manufactured.

An initial condition survey revealed that most of the bottles were in excellent condition, presenting only surface dirt and some grime. However two of the glass pieces, a decanter and a small goblet, had been previously restored and were in need of further attention. The decanter had at one point broken into multiple fragments, with one large area of loss about four inches across. The piece had been reassembled and the loss filled; this material was extremely yellowed. Surface abrasion and scratches were also visible in the area immediately surrounding the fill and conchoidal fractures were visible along the interior edges of the loss. The joins however were still tight and seemed
stable, and the adhesive presented no discernible discoloration. The goblet had a previous break and loss at the base of the stem, just above the foot. Here, the join was out of alignment and the adhesive was discolored (figure 2).

Treatment
In consultation with the Museum’s Executive Director Jessica B. Phillips, it was agreed that the discolored fills and joins would be removed and new fills created, so that the pieces might be exhibited once more. The aged fill on the decanter was easily removed by softening in an acetone chamber, followed by light mechanical pressure. As the existing joins appeared stable without noticeable yellowing, it was decided to leave these intact in order to reduce the amount of physical manipulation of the object. This decision also reduced the risk that the gilding would be adversely affected during treatment. The location of the loss on the decanter along the side of the object, in conjunction with the narrow neck and colorless body, made for a complex loss compensation challenge. The goblet, a more straightforward treatment project, was tackled first. After disassembling the join at the base of the goblet’s stem, a larger loss than previously realized was revealed. In order to cast an in-situ fill, the glass pieces were temporarily joined with polyethylene hot-melt glue. Soft beeswax was used to create a temporary fill and silicone rubber (SORTA-clear® 18 by Smooth-on) was applied on top of the wax in order to capture the newly built profile shape, and create a mold. After detaching the cured rubber, plaster was cast into it in order to create a positive of the fill. Finally, PVC film was molded around the plaster using a vacuum forming machine, and the film was cut to fit the outline of the loss on the goblet, thus creating an in-situ mold. This technique has been previously published and was first presented by Gorazd Lemajić at the 2007 ICOM-CC Glass and Ceramics conference (Lemajić 2006;
Stamm et al. 2013). Finally, the fill was cast in situ with Hxtal NYL-1™. Although fractures in the glass were still visible, the appearance was much improved and a more accurate shape achieved (figures 2 and 3).

Following the success of this treatment, attention turned back to the decanter. Although the entire piece might have been disassembled at this point, it was preferable for the above-mentioned reasons to approach the work as loss compensation on a closed form. Several means of treating such objects exist, and these have largely been discussed in the literature (Davison 1998). Although attempts were made to cast a fill off the vessel, none were successful without requiring extensive finishing. It was at this time that the idea of creating a 3D printed fill began to take shape.

3D Printing and Conservation
Process and Applications
Adapting 3D printing techniques for restoration is not an entirely novel approach. Laser and/or white (structured) light scanning has seen a good deal of attention within the conservation community, as it offers, to name a few applications, an exciting means for condition recording and monitoring, the study of surface features, and impactful public outreach. Scanning may be followed by the creation of a physical print, and published case studies have illustrated the multiple ways in which these prints are used. This paper will concern itself with additive manufacturing, or fabrication, meaning the creation of a three-dimensional object through the addition of layer-upon-layer of a curable medium. The project itself relied on photopolymer technology, whereby a liquid resin is hardened through exposure to light in the printer. Other techniques of printing include stereolithography and thermoplastic extrusion.

The term “3D printing” will be used throughout the text when referring to this process (for a general discussion, see Wachowiak and Karas 2009.) Although projects are continually being published, we might categorize the most common applications related to conservation as follows:

New artworks: 3D printing to create original artworks. While conservators may not be involved during production, they will certainly engage with printed works as they age, and this area is ripe for consideration as the technology develops. Questions regarding future treatment are complex, including those already parsed by time-based media conservators; these extend from the digital file to actual products.

Replicas: the creation of object replicas, where the original is too fragile to be handled, etc. Promising examples include the scanning and printing of cuneiform tablets, a project under way through the Cornell Creative Machines Lab. This collaboration aims to offer digital files for printing across institutions, such that the pieces might be used for pedagogical purposes (Knapp 2008). Similar efforts have been undertaken at Johns Hopkins University as well. Theoretically, this category might further extend to the printing of parts of an object that are fragile; replicas might be substituted for the original where needed, for instance, a complex object with detachable pieces, some of which are stable and others not.

Secondary support: printing a mount for secondary support. If the actual 3D print is to be used, questions about the long-term stability of the printer resin arise. Of course, casts in a more stable media can be produced from the print.

Loss compensation: scanning and printing fills or missing elements of an object. Previous work in the area has been published (for example: Beentjes 2010). Other, informal projects are currently underway by colleagues with access to this technology. As with the categories identified above, the conservator is tasked with the decision of using the printed piece or viewing it as a model for a secondary casting process.

Fraunces Tavern Museum Decanter
Scanning was executed on New York University’s Media Lab’s Artec3D Spider® white light scanner, with Taylor Absher as the media specialist. The first challenge encountered was to successfully scan transparent glass. As the scanners work by registering information gleaned from the surface of the object under question, the object must be opaque. In order to opacify the transparent glass, opaque gouache was applied to the surfaces surrounding the loss; this paint was selected because it is easily removed with moistened swabs or light mechanical action. Colleagues subsequently related that a thin spray of cyclododecane performs the same task. It should be noted that the glass surface was deemed stable and in good condition and
the gilded details were avoided as best as possible. Only the exterior and break edges were coated—a decision that indeed had ramifications down the road (figures 4 and 5). Other challenges came to light as Absher began preparing to print. As the 3D printer would be creating the area of loss rather than the extant surfaces scanned, a digital file needed to be created of the negative space. At first it seemed that this work might be straightforward, as the hand cut facets on the original glass created successive flat planes of space. Part of the challenge arose from the gouache application, which had been applied by brush and therefore was not completely smooth. This unintentional texture replicated itself in the negative space as Absher worked. Further, small areas of the break edges that had not been completely coated with gouache needed to be digitally filled, potentially complicating the final fit. Ultimately an acceptable shape was created, and fills were printed on a Stratasys Connex® 500 printer, using Fullcure® 720, a transparent/translucent proprietary photopolymer with a slight yellow tint. However, as this resin does not age well (nor do any of the transparent photopolymer resins of which the author is aware) the actual print would only be the intermediary model for a mold, which could be used to create a more stable cast (figure 6).

It is worth noting that there is a large amount of research directed towards development of more stable 3D printing media, and indeed, current research focuses on the development of transparent resins. Other companies are working towards the printing of hot glass, and the Massachusetts Institute of Technology recently reported their work with a 3D printer capable of printing transparent glass objects (Klein et al. 2015). Unfortunately, the print created in our study was unusable. The resin had somehow deformed after printing, which prevented it from fitting seamlessly into place. Additional problems were created by both the profile of the print, which did not match the flat facets of the original, and

Fig. 4. Decanter during scanning; note the gouache coating, Fraunces Tavern Museum 1920.4.1.N (Photo: SBE Conservation LLC).

Fig. 5. Decanter with gouache coating, Fraunces Tavern Museum 1920.4.1.N (Photo: SBE Conservation LLC).
the pattern created by the process of laying down the resin, which was deemed unacceptable for a glossy surface. Rather than re-printing the area of loss or re-working the print, the area originally scanned was printed instead, resulting in a replica of one side of the bottle with both front and back accessible. The fill could then be cast in-situ on this print with Hxtral NYL-1™, using the PVC mold technique described above, then detached and fit to the bottle. Three copies of the scanned area were printed in VeroClear®TM, a proprietary transparent photopolymer, to allow for mistakes and multiple attempts at casting (figure 7).

Results and Conclusion
Casting the final fill directly onto the print with Hxtral NYL-1™ ultimately proved the most successful approach. Vaseline® served effectively as a release agent for the fill, and it popped out quite easily when cured, with minimal pressure. Once removed, the cast element was matched
with the loss on the object; the fit was acceptable, however the edges required some mechanical shaving of the epoxy. Though this misalignment was likely due to gaps in the scanned file, such working might have been necessary anyway to prevent "locking out" during final assembly.

As the printing process proceeded over an extended period of time, and the success of the final outcome was unclear, loss compensation initially began by casting a Hxtal NYL-1™ fill directly on the bottle, using the PVC film technique as described above. This in-situ cast comprised about one fifth the length of the loss. Thus, the cast taken from the print was similarly reduced in length before attaching to the bottle with Hxtal NYL-1™. Some mechanical surface reduction with a scalpel was required along the surfaces of the fill, with painter’s tape applied to the adjacent glass surfaces as a physical barrier. A final surface wipe of Hxtal NYL-1™, allowed to cure under Saran Wrap™, helped to re-introduce gloss to the fill and integrate the in-situ cast area (figure 8).

Possibilities and Challenges
While the process was not as smooth as one might have hoped, the possibilities of 3D printing for the field of conservation are intriguing. That a perfect fill might be created in a brief amount of time, with minimal direct work on an art object (particularly a fragile one), is an exciting thought. Still, challenges exist. One major concern is the lack of preservation-grade 3D printing resins. This impediment requires any printed positive to be re-cast in a more desirable conservation material. Of course, if an opaque fill is required, metal and/or glass powder printing media may be an adequate option. In such cases, the powder may be held together with a temporary binder that is then driven off with heat, or, for instance in the case with metals, lasers are used to directly sinter, and fuse, the powder. Companies that provide these services are quite accessible. Alternatively, collaborating with industrial companies in order to develop more stable printing resins might hold promise.

Comfort with design software is also a consideration for those eager to work with these technologies. Conservators who are well versed in model building software have a huge advantage in this arena. Access to the technology itself and the costs associated with purchasing appropriate scanners/printers, etc., is a challenge not to be understated, though the machines become increasingly affordable each year. Further, smart phone applications such as Autodesk’s 123D Catch® allow users to create 3D scans from their phones, and these files can be enhanced and seamlessly printed via partnering companies. While the files created may not be high quality, they may well allow for conservation projects such as the one described in this paper. It is worth an additional investigation into these more accessible options.

Now that work has concluded, the conserved and restored decanter and cup have rejoined the remaining glass objects at the Fraunces Tavern Museum, where they are celebrated once more as enduring testaments to the courage—sometimes in liquid form—and conviction that drove the nation’s revolutionaries.
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Cleaning and Repairing Blaschka Glass Models: Challenges in the Preservation of Exquisite Reproductions of Nature

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Keywords
Blaschka; glass; models; cleaning; re-treatment

Abstract
In preparation for an upcoming exhibition, the authors carried out careful examination, documentation, and treatment on numerous invertebrate glass models made by Leopold and Rudolf Blaschka, two expert European glassmakers who reproduced natural specimens as glass models. The conservation and cleaning of these models is challenging, owing to the complex combinations of glass, metal armatures, organic adhesives and coatings, gelatin, and other materials. The models have suffered from light and atmospheric degradation. Moisture is, without question, the harshest antagonist, which restricts the use of water in any treatments. Minimally invasive cleaning, stabilization, and reconstruction treatments were developed. Techniques included dry-brush cleaning and rheostat-controlled vacuuming; solvent cleaning using ligroine; consolidation using dilute wax or dilute Paraloid B-72; and reconstruction using Paraloid B-72 adhesive and Paraloid B-72 cast films.

Introduction
Leopold (1822-1896) and Rudolf Blaschka (1857-1939) are probably best known as the glass artists who made the "Harvard Glass Flowers," literally thousands of lifelike glass models of flowers and plants. Although Leopold's career first started with making glass jewelry and models of plants, he spent most of his career on the fabrication of marine invertebrate models. He made his earliest models of invertebrates by copying the illustrations in the most up-to-date textbooks of zoology, and later studied and maintained living specimens in seawater aquariums. His son, Rudolf, joined him in this work, and, over a period of 35 years, they made thousands of models. The models served as teaching and study specimens for museums and university zoology departments, solving the problem that natural specimens could only be preserved in bottles of alcohol. Glass was an ideal material for depicting these sea creatures as it could be made transparent, translucent, or opaque as needed, depending on surface modifications (coatings, pigments, or paints). The Corning Museum of Glass owns a few invertebrate models and also stores a large number of Blaschka models that are on a long-term loan from Cornell University in Ithaca, NY. An exhibition of the Blaschka invertebrates will be displayed at the Corning Museum of Glass in 2016. Previous publications on the Blaschkas focus mostly on their history, their working methods, the materials they used, and how those materials affect the stability of the objects (Smith McNally and Buschini 1993; Pantano, Rossi-Wilcox, and Lange 1998; Rossi-Wilcox and Whitehouse 2007; Van Giffen et al. 2010; Van Giffen, Eremin, and Drier 2015). This paper will touch on those subjects but will focus on actual treatments of some of the models, which only a few previous publications include (Brierley 2009).
Construction and manufacture of the models

Although the Blaschka models are primarily made of glass, many other materials were also used, including metal and wooden armatures, a variety of adhesives and coatings, natural and synthetic resins, gums, waxes, enamels, and pigments. Shells (figure 1), paper, cotton batting, and string are just a few of the more surprising materials that were incorporated in some models. The Blaschkas used whatever materials they needed in order to achieve the effects they wanted.

The huge variety of models and the fact that their production spans 35 years means that the techniques used by the Blaschkas were adapted and changed over time. Even models of the same species are not always made the same way. There are, however, some general things that can be said about the production of the models based on careful examination of the models themselves as well as information from the Blaschka archives, especially correspondence in which the Blaschkas, or someone observing them, describe their working methods. Additionally, The Corning Museum of Glass owns some of the material found in the Blaschkas’ studio, which gives some insight into their methods.

The studio material includes 42 match boxes with various glass parts (figure 2) and about 80 larger loose glass parts (such as jellyfish domes and anemone bodies) that were used for the invertebrate models. These materials, along
with descriptions of the Blaschkas’ working methods found in their archives, indicate that they worked in an assembly-line fashion, making batches of specific parts at different times and then using those parts to create their models. For the invertebrate models, the Blaschkas primarily used a commercially available colorless soda-lime glass. Some colored glasses were used as well, especially in the earliest models. They were incredibly skilled glassworkers and made highly detailed, complicated parts for their models, such as the bubbles within bubbles on the hydra model described in Case Study 1. In general, the larger parts of the models, such as the domes of jellyfish, the heads and tentacles of octopi, and the bodies of anemones and slugs, were made of blown glass. Smaller elements, both hollow and solid, like those found in the match boxes, were glued onto the larger parts. Sometimes these parts were fused to a short metal wire. Metal wires coated with glass were also used, especially as jellyfish tentacles. The models were colored on either the outer or inner surfaces (or both) of hollow elements with enamels, paints, and pigments mixed with waxes, gelatin, gums, or resins (Smith McNally and Buschini 1993; Pantano, Rossi-Wilcox, and Lange 1998; Van Giffen et al. 2010). Most of the glass has some kind of coating to make it less shiny, but there do appear to be a few instances where the glass was left bare and uncoated.

After assembly, the models were each attached to a base. Many of the earliest models of anemones were attached to painted plaster bases in the shape of a rocky sea bottom. Other models were mounted on a flat piece of composite material, stiff paper card, or painted wood. The models were either glued onto their base or attached with thin metal wires in a few locations. Each model also has a label with the model number, the name of the species represented, and a reference to the publication that contains the publication plates’ on which the model is based.

Original packing and transport
The Blaschkas shipped their finished models from their home studio in Dresden by horse and cart, train, and, for transatlantic delivery, by boat. In early letters they commented that the packing was not adequate and many models were damaged in transit. They revised their packing methods and materials and were then able to successfully transport and deliver models across Europe and to America, Australia, and Asia.

The Corning Museum of Glass obtained three wooden boxes (figure 3a), which are likely some of the original packing boxes used for the models. The boxes also contain folded tissue that may have been used to secure the models to prevent moving around on the cards, as well as secure the cards within the boxes. Some of the models in the Cornell collection are still secured with pieces of similar tissue (figure 3b). It is uncertain whether multiple models were packed together in one box, but it is likely true for the smaller models.
Conservation challenges
The Blaschka models are clearly very delicate and fragile objects that pose conservation challenges. The use of so many different materials, which aren’t always compatible, has led to a number of different damage and deterioration problems specific to these objects, as previously presented (van Giffen et al. 2010; van Giffen, Eremin, and Dryer 2015). Some of the models treated for this exhibition suffered the types of damage previously described, but new conservation challenges that had not been published yet were also found.

Unknown materials
One of the main challenges came from not knowing what materials were used on specific models. Approximately 75 models, ranging from sea slugs to anemones to octopi, were needed for the exhibition. The variation of the models makes it likely that there were many different materials and techniques used in their production. While previous research gives an indication of what materials were used by the Blaschkas (see above), the limited time and resources available for the current treatment meant that not all of the materials (coatings, adhesives, etc.) used to create each model could be identified. Because of these unknown materials, the protocols developed for cleaning and treatment needed to be less invasive and use as few solvents as possible.

Problems with extremely sensitive and fragile materials
Most of the octopus and squid models have paper and/or a proteinaceous layer connecting the head to the tentacles. In several of the models treated, this area was cracking and lifting. Luckily, none of the cracking or lifting appeared to be active and, because the materials are very rigid, these areas were relatively stable. It was decided that in these cases it was best to not treat this particular damage. Similarly, the corrosion of metal wires and the glass losses from the glass-coated metal wires were largely left untreated.

Previous interventions and restorations
Many of the models had evidence of previous interventions and restorations. Some of the damage likely occurred during their original transport and was repaired around the same time. Other repairs are probably more recent. Relatively recent interventions on the Cornell collection
can be seen in examples of over-cleaning (figure 4) and the re-joining of models with synthetic adhesives, including noticeable amounts of excess adhesive. Unfortunately no treatment or photographic records appear to exist.

**Paper card bases**

One of the most difficult ethical challenges was deciding whether or not to remove the glass models from their supports, which were stiff paper cards (examples of the paper card bases can be seen in figures 4, 5, 6, and 8a). The original cards are part of the objects as a whole, but they are often not treated that way. Several of the models had been removed from their bases in the past which left them more vulnerable during handling and transport. In some cases the cards, and therefore their identifying information, had been lost. In addition, many of the cards are in very poor condition with tears, losses, and staining, sometimes to the point of being unsuitable for display. Some cards appear to have been cut down, as evidenced by ragged edges and oddly placed labels and models. Some curators also preferred to display the models without their cards in order to highlight the beauty of the models. It was necessary to remove some of the broken models from their cards in order to carry out treatment. Re-mounting on new cards is a potential option for the future. The disadvantage of removing any model from its original card is the increased potential for both the original card and its label information to be lost. However, as noted above, many of the cards are extremely brittle, or already damaged, severely stained, or discolored. If the card were to be replaced, with a similar type of card and a digital reproduction of the original label and other information, then the model would again be associated with all the original information. The cards are also an effective means of support, as well as a means of safely handling and packing each model.

**Treatment**

The Conservation Department initially surveyed the condition of all the objects. Most of the models were covered with dust and dirt and some of the models had detached or missing elements. Consequently, detached pieces needed to be re-adhered in order to stabilize the model, reduce the risk of losing the fragments, and make the model complete again.

**Cleaning**

The initial cleaning was done dry. Very soft brushes (sable-synthetic blend, 1/4 and 3/8 inch), in combination with the use of a Nilfisk vacuum cleaner outfitted with variable speed control, were very effective in gently removing dust and dirt. A modified attachment was used to accurately focus the suction, and a small piece of polyester netting was fitted over the vacuum hose. In the event that any small pieces became detached and suctioned up, they could then be easily and safely retrieved. For models with very small parts that were glued on and in some cases unstable, the end of the hose attachment was also covered with a piece of silk. Very fine tweezers were used to safely remove cotton lint or fibers and other debris (e.g. insect casings, spider webs). This was done with the aid of a binocular microscope. Dry cleaning was followed, in most cases, by a light solvent cleaning using ligroine (petroleum distillate) on a soft brush. The brushes for dry cleaning and solvent cleaning were kept separate.

In general, the cleaning was such a dramatic improvement that “during treatment” photographs were taken after half of a model (and card) were cleaned (figure 5).
Deteriorated glasses

Early signs of glass deterioration in the form of droplets, crystals, or both were found on the inside of many closed or partially closed glass elements (figure 7). Signs of deterioration had been noted previously (Brierley 2009; van Giffen et al. 2010) and are likely the result of a slightly unstable glass composition and the shapes of the glass structures which allow moisture to get trapped inside. Where possible, these glass parts were very carefully rinsed with de-ionized water to remove the surface alkalis.

Adhesives and coatings

The most common problems were flaking paints and failing adhesives. These were treated on a case-by-case basis. Flaking paints and coatings were consolidated with small amounts of either Paraloid B-72 in acetone or Renaissance Wax diluted with petroleum ether. The reattachment of loose parts is described below.

Reassembly of detached or broken pieces

After cleaning, any broken or detached fragments were placed back in their original positions with the aid of a binocular microscope. The fragments were reattached using Paraloid B-72 adhesive. A small amount of adhesive was first applied to a watch glass and then a toothpick was used to pick up a minimal amount of adhesive and apply it to the break edges. Excess adhesive could be easily and safely removed by using acetone and a small brush. Careful application of solvent to the adhesive alone did not pose a risk to any of the previous (Blaschka) adhesives, pigments, or coatings.

More complex damages and breaks were dealt with on a case-by-case basis, and several are described in the following Case Studies.

Case Studies

Case Study 1: Model Nr. 173 Podocoryne carnea

Description and condition before treatment

This model (figure 6) represents Podocoryne carnea, more commonly known as a hydra. The cardboard base contains two models: a tiny (roughly 1.5 cm x 2 cm x 2 cm) ‘natural size’ representation and an enlargement (roughly 9 cm x 5 cm x 9 cm), both made in the typical fashion of glass elements assembled with adhesive. The enlargement has an almost flat, roughly oval-shaped glass base that supports five stems, five small hollow conical elements, and one larger inverted conical shape that appears to be missing a center section. The stems and the inverted conical shape are each glued to the base with an internal metal wire support that is roughly 2 cm long and bent at a 90 degree angle in the middle. The hollow conical elements are glued directly onto the glass base. The entire surface of the base and the lower parts of the conical elements are covered in tiny (less than 0.5 mm in diameter) glass spheres. The upper third of the two smaller stems have short glass spikes to which glass bubbles are attached in some cases. The glass bubbles each have another glass bubble with pink glass stripes on the inside. The other three stems are thicker and end in a flower-like top with a crown of glass feelers. On the thickest of these stems the feelers have not yet unfurled. All of the stems were colored with a dusting of pigment on the inside surface. The base is painted on the underside.

The glass base was broken into four pieces. The two larger fragments each hold two stems and two of the hollow conical shapes. There is one fragment that holds the inverted conical shape and one conical element. Finally, the smallest fragment, which holds the remaining stem, is severely cracked and broken, but is held together by the up-
per adhesive layer. There is a small loss near the center of the base. In addition to these breaks and losses, the glass microspheres that were glued onto the base are loose in some places, especially along the breaks. A smear of yellowed adhesive on the card beneath the model indicates that an attempt was made to repair the broken base previously. The stem on the smallest fragment of the base was taped to the cardboard base with masking tape that was very aged and left adhesive residue on the glass and card. The model and its cardboard base were covered in a layer of dust and grime. The card also had a broken corner and a few stains. The larger model was attached to the card with two metal wires, but had to be removed from the card for treatment. The smaller life-sized model was glued onto the card, but came loose during handling.

Cleaning
Cleaning was carried out as described above, first dry and then using a brush dampened with ligroine. However, it was complicated due to the glass microspheres on the base. The adhesive used to attach these microspheres is starting to fail and while handling the model some of the microspheres came loose. Prior to fully cleaning the base, the spheres were consolidated in the most vulnerable areas, especially along the breaks, with drops of 10% Paraloid B-72 in acetone. The spheres that came loose were collected with the hope of replacing them later in the treatment. Cleaning off the thick layer of dust and grime also revealed that the glass bubbles on the two smaller stems were hydrated (figure 7). Hydrated glass, or glass that shows droplets of liquid alkali that has leached out of the glass as a result of high humidity and possibly an unstable composition, was also found on other models in places where moisture could be trapped.

Re-assembly with fills
Reassembly was done using B-72 adhesive as described above. Unfortunately the smallest fragment no longer retained its original shape, so the fragments could not be perfectly aligned. Because of this, the base was further strengthened with two strips of Japanese tissue soaked
in 15% B-72 in acetone which were positioned across the breaks. The missing area in the base was filled with cast B-72 film, shaped and colored to match the surrounding areas. The glass microspheres that had fallen off during treatment were collected and reapplied with 15% B-72 in acetone where they had been lost on the base, primarily along the break edges. New glass microspheres were applied to the fill by wetting the surface with acetone. The underside of the fill was colored with a thin acrylic emulsion paint.

**Observations**
The glass on most Blaschka models is coated either to provide color or to change the surface appearance; however, it appears that the stems and bubbles on this model still have large areas of bare, uncoated, and unpainted glass. While it is possible that these were over-cleaned at some point, especially given the evidence of previous intervention, it does not seem likely since there are still brush strokes visible near the bottom and top where adhesive was used to attach separate elements.

**Case study 2: Model Nr. 260 Ophiothrix serrata**

*Description and Condition before treatment*

This model (figure 8) represents *Ophiothrix serrata*, more commonly known as a banded brittle sea star or starfish. It has a central carapace and five arms with hundreds of small sensory feelers along the two sides of each arm. The alternate gray and black feelers give it a “banded” appearance. The model was badly broken into fourteen larger pieces and some smaller detached feelers. Two of the arms and the central carapace were still attached to the original card but the remaining parts were loose. Several previous repairs were noted, evidenced by applications of thick brown adhesive and thick white putty/adhesive. These appear to have been done while the model was still attached to the card.

**Cleaning**

Cleaning was carried out as described above, first dry and then using a brush dampened with ligroine. Numerous fibers had been caught in the many feelers, as the ends of the feelers are slightly turned inward and easily catch and retain debris.

**Re-assembly**

Reassembly started with the very small feelers, which had become detached but were (presumably) associated with the nearest fragment. They were positioned and reattached using B-72 adhesive with the help of a binocular microscope.
In order to properly address the rejoining of the broken arms, the two attached arms were removed from the card along with the central carapace. The previous adhesive and putty interventions needed to be removed to rejoin the broken glass properly; they were easily softened by a light wetting with ethanol and water and then removed with a pair of fine tweezers. Samples were saved of both adhesive and putty materials for later analysis. The arms were then assembled piece-by-piece using B-72 adhesive. The largest difficulty was positioning the joined fragments until the adhesive had set. This required considerable experimentation using different soft supports. No loss compensation or other touch-up was necessary. After complete reassembly, the model was structurally stable and could be lifted by the central carapace.

**Observations**

The arms of the model were made separately from the central carapace, and were made of solid glass with a flattened, but rounded underside, so that the model would rest almost completely flat, with some undulations in the arms for more of a three-dimensional appearance. The hundreds of small feelers were hot-fused together in small groups and then glued onto the arms. The arms were made with a protruding tenon (figure 9) that was inserted and glued into a hole on the side of the carapace.

**Risk Management**

In preparation for the conservation and the exhibition, all projected risks to the models were considered, assessed, and discussed, in order to keep any potential damage to a minimum. It was necessary to transport many of the models from the off-site warehouse to the museum’s conservation lab for cleaning and treatment, and an initial careful assessment was critical before packing and transit. Cushioning was done using small foam supports and wedges so that all movement was kept to a minimum, which kept the models free of damage from vibrations. No packing materials were placed on top of the models.

**Fig. 8. Before (a) and after (b) treatment of Blaschka model Nr. 260 *Ophiothrix serrata*. Note: the after treatment image shows the model without its card. Image by the Corning Museum of Glass**

**Fig. 9. Detail of model Nr. 260 *Ophiothrix serrata* showing tenon used to attach arm to carapace.**
Since the models should be handled as little as possible, and only by a conservator or art handler who is very familiar with each individual model, all handling was initially restricted to the conservators. Later, after detailed training, the restriction was extended to include the museum’s photographer and mount-maker. The models should be handled with dry, bare hands, not gloves. If possible one should handle the models from their original mounts or support cards.

Environmental control and lighting are also critical to the long-term preservation of the models; 40-55% relative humidity is recommended, with moderate temperatures (19-24 degrees C), and light levels should be low (8-10 foot candles). Light air movement in the display cases is also recommended and can be achieved using a small fan (Koob 2006, p. 130).

Conclusions
The Blaschka glass models of invertebrates are some of the most complicated and fragile objects in museum (or university) collections today. Over 75 models were cleaned and treated for an upcoming exhibition at The Corning Museum of Glass. The nature of the materials used in the models’ construction limited conservation treatments to minimal intervention and individual treatments specific to each model’s condition and needs.

Dry cleaning, solvent cleaning, and the careful use of B-72 adhesive and cast B-72 films resulted in successful treatment and revitalization of these important models. The assessments, approaches, and treatments all provided fascinating challenges to the authors.

Image credit: Corning Museum of Glass

Notes
1. Examination of the models in the Cornell collection as well as those in several other collections.
2. The Blaschka archives include many plates removed from their publications.
3. (n-heptane), boiling range 90-110 degrees C.
4. 50 g of B-72 dissolved in 70 g of acetone with 0.1 g of hydrophobic fumed silica; the mixture is then poured into and applied from a tube.

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The Glass Mosaics of Holy Souls Chapel, Westminster Cathedral: Deterioration and Conservation

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Keywords
glass mosaics; metal-leaf; cartelline; unstable glass; efflorescence

Abstract
This report describes the technical examination and conservation of the Holy Souls Chapel mosaics, undertaken in 1993, and a current evaluation. A large proportion of the metal-leaf glass tesserae required treatment because of disintegration of the unstable glass smalti, the formation of salt efflorescence and the loss of the metal leaf and clear glass cartelline. Diagnostic analysis was undertaken by means of scanning electron microscopy, energy dispersive x-ray microanalysis, x-ray diffraction, infrared spectroscopy and ion chromatography. The conservation approach adopted involved initial cleaning, removal of salt efflorescence, consolidation of the unstable glass smalti and, finally, a novel method of replacing the missing cartelline and the thin metal inter-layer. Metal leaf applied to Melinex® sheeting was cut to the size of each of the coloured glass smalti and affixed, gilded side innermost, with poly(vinylacetate). This technique simulated the original appearance very effectively and is displaying good durability after 22 years.

Introduction
This paper describes the conservation and associated technical analysis of the glass mosaics which are part of the decorative scheme of Holy Souls Chapel at the northwest end of Westminster Cathedral, London. The conservation campaign, executed in 1993, was necessitated by the build-up of almost a century of dirt (primarily from cathedral candles) and the unstable composition of much of the glass comprising the mosaic tesserae. Glass degradation had led to the formation of salt efflorescence and the concomitant loss of the thin clear glass outer protective layers (cartelline), along with the metal inter-layers, of the metal-leaf tesserae.

Description of Westminster Cathedral and Holy Souls Chapel (Rogers 2010)
Westminster Cathedral, situated in the heart of the City of London, was designed and built under supervision of the architect John Francis Bentley. The cathedral, built from 1895 to 1903 in the style of an early Byzantine basilica, was constructed and faced with brick decorated internally with marble and mosaics. The marble decoration is now effectively complete but as yet only a small part of the cathedral has received its mosaics. These areas include nine of the twelve chapels of which Holy Souls was the first to be decorated; the installation of the Holy Souls mosaics took 18 months, from June 1902 to November 1903. Bentley’s concept, “severe and very Greek” in character, can be best seen in Holy Souls Chapel for which, together with William Christian Symons, he helped design the biblical scenes depicted, though he died before the installation of the mosaics was completed.
The chapel is sited on the side of the nave at the northwest end of the cathedral. Two bays of the windows are set into the north wall. The south side of the chapel is open to the body of the cathedral. The roof is barrel vaulted with a tympanum at each end. A reredos stands above the altar at the east end (figure 1). The ceiling, tympanums and window bays are all decorated with glass tesserae. The reredos and inscription panels at either side of the altar are decorated in metal-leaf glass opus sectile. The columns on the north and south sides of the chapel are in decorative marbles. The wall below the marble stringcourse also comprises various decorative marble panels.

The mosaics consist of glass tesserae, c. 1x1 to 1x2 cm in size with a depth of c. 0.5 cm, which were inserted individually into salmon-coloured mastic using the direct method. The work was executed by mosaic artist George Bridge using a team of 26 young female assistants, each of whom worked on the scaffolding with a coloured cartoon, applying the mastic by hand, pricking out the design, selecting the appropriate glass colour from slabs about the size of a breakfast plate from which the tesserae were chipped out and inserted. Since much of Holy Souls Chapel consists of metal-leaf tesserae in shades of gold and silver, the direct method enabled the desired glittering effect of the metal-leaf tesserae, inserted individually and thus at different angles to the light, compared to the then popular direct method in which the tesserae were inserted face down on paper and the assemblage reversed when being applied to the wall. The recreation of the original varied angles for reflection of light from the deteriorated metal-leaf tesserae was an important conservation objective in the work described in this paper. The metal-leaf tesserae are described as being of Italian origin, but some tesserae may be from glass produced in London. Additional information can be found in two authoritative texts (l’Hôpital 1919; Rogers 2010).

Overview of mosaic technology and terminology

For a background to technical issues in the historical development of the glass technology for mosaics, the book chapter by Verità (1996a), in Italian and English, is a masterly overview of the subject. An excellent more general text (Farneti 1993), also in both Italian and English, covers the historical development of mosaic art and a technical description of the methods and materials. Throughout this paper the term mosaic tessera will generally be used and the term smalto reserved for the coloured glass paste underlying the metal-leaf mosaic tessera which are so widely used in Holy Souls Chapel. The term cartellina will be used when referring to the overlying thin covering of protective glass in metal-leaf tesserae. These terms are defined in the Glossary below using the description of Verità (Verità 1996b). Similar, less elaborate descriptions of mosaic glass terms are also available (Verità 2009).

Of particular relevance to Holy Souls Chapel, Verità’s chapter includes technical information on metal-leaf tesserae from antiquity to the present day. Metal-leaf tesserae comprise a sandwich of the base coloured cast glass support covered by a very thin layer of metal leaf (nowadays less than c. 0.15 micron in the case of gold and some ten times thicker, because of its poorer malleability, in the case of silver). To protect the metal layer, a thin sheet (a few tenths of a millimetre thick) of blown glass, the cartellina, forms the top layer of the metal-leaf tessera, the whole process requiring great skills and experience to ensure that the three layers are well adhered and that the cartellina do not detach when the tesserae are cut from the parent circular slabs. Nonetheless, in Holy Souls Chapel, it was reported in 1918 that some of the cartelline had flaked off (Rogers 2010), quite apart from the extensive loss of cartelline which, more than 80 years later, formed a major part of the conservation research and treatment described below.

Four features of glass mosaics (Verità 1996a), three of which are specific to metal-leaf tesserae, have particular relevance to the Holy Souls Chapel conservation project. Firstly, the metal leaf, especially that of gold, is so thin that the colour of the glass support influences the overall chromatic effect of the tesserae. Secondly, it is recognised that silver-leaf tesserae are more vulnerable to the loss of the protective cartelline and the metal compared to gold. The greater thickness of the silver and its higher coefficient of expansion renders these tesserae more vulnerable to stress-induced loss of both the cartelline and the metal foil. Thirdly, modern mosaic technology has replaced silver with ‘white gold’ (an alloy of gold and small amounts of other metals, notably silver, palladium, nickel or zinc). Finally, for glass mosaics in general, the effect of moisture is likely to be more extreme in circumstances where evaporation/condensation cycles occur. In poorly-ventilated buildings visited by large numbers of people during
Fig. 1. Holy Souls Chapel east end, after conservation, involving cleaning of marble and mosaic surfaces and restoration of the glass tesserae.
the day, there is the likelihood of condensation on mosaic surfaces at night.

**Condition of the Holy Souls mosaics prior to conservation**

All wall and ceiling surfaces were covered with black deposit from candles and general dirt. On the mosaic ceiling and tympanum this was particularly thick, almost completely obscuring the design, making it impossible to assess properly the condition of the ceiling from the ground. It was only when the scaffolding was erected for cleaning that the full extent of the deterioration became obvious. In the initial stages of cleaning, the condition of the silver and gold smalti was revealed. The metal leaf and cartelline had become detached from many of the smalti, showing that the underlying glass was disintegrating and salts were forming on the surface. In other cases the detachment appeared to derive from an inherently poor adhesion of the cartelline to structurally sound glass smalti. In areas with metal-leaf glass opus sectile, the glass decay, formation of efflorescence and disruption of the metallic effect were particularly severe (figure 2). There was no evidence of damp penetrating the mosaic, which was laid on the ceiling cement render with a mastic mortar to secure the mosaic.

The project involved three phases; technical examination of the mosaic components, the development of a conservation-restoration methodology and the execution of the conservation-restoration programme of work. In this paper attention is focused on the study of the problems associated with the glass tesserae and their deterioration and the development of a novel method of restoration to deal with this.

**Technical Examination**

In order to build a firm foundation for the development of an appropriate conservation approach, technical examination was carried out on the deteriorating metal-leaf tesserae. The visual disintegration of the glass smalti was supported by scanning electron microscopy (SEM) studies on two turquoise blue samples from an area adjacent to a ceiling crack. Of importance is the observation that the deterioration at the base of the tesserae (where they are bedded into the mastic) was less pronounced, but still

![Fig. 2. East end, showing a section of the reredos (2a), including an area (circled) adjacent to Christ's proper left arm with disintegrating ‘silvered’ turquoise blue glass opus sectile, illustrated in detail in (2b).](image)
significant, than at the upper surface. A sample of blue glass with residues of ‘silver’ metallic foil was examined. The analytical results indicated that the metal was pure platinum. The results of energy dispersive x-ray microanalysis of the composition of the deteriorated glass surface of this sample are given in Table 1.

In order to add confirmatory evidence to the relationship between glass composition and the decay of the glass tesserae, an accelerated weathering experiment was carried out. In this experiment, the effect of water on a synthetic glass, prepared by Pilkingtons for the European Science Foundation (Anon 1977; Tennent 1984) to resemble the composition of an unstable historic glass, was examined. Samples of this glass (76-C-158) were immersed in water for 24 hours. The resultant surface appearance of the glass and its composition were investigated by SEM with energy dispersive x-ray microanalysis. The appearance was very similar to that of the disintegrated mosaic smalto examined above and the concentration of SiO$_2$ (84.3%) matched the surface enrichment in the blue smalto (Table 1) indicative, therefore, of prolonged (90 years), gradual moisture-induced leaching of mobile ions from an unstable glass.

The leaching of sodium ions from the tesserae is associated with the formation of efflorescence, identified by x-ray diffraction and infrared spectroscopy as sodium sulphate (thenardite). A more detailed analysis of a sample of the efflorescence was performed by ion chromatography. These results (Table 2) are consistent with the identification of sodium sulfate as the main component efflorescence but, because of the sensitivity of ion chromatography, additional minor components were found. Most likely, calcium, potassium and magnesium originate from the glass. The sensitivity of the technique is demonstrated by the presence of acetate, formate, nitrate and chloride whose origin is probably, as with sulfate, atmospheric pollution. The good cation/anion balance (Table 2) indicates that all important species in the efflorescence were detected. These results provide attractive evidence of the value of ion chromatography as a probe for atmospheric pollutants ‘fixed’ by unstable glass, a topic also being explored in the study of unstable museum glass (Verhaar, van Bommel, and Tennent 2016). Atmospheric acetic acid and formic acid concentrations in rural and urban environments occur in low parts per billion concentrations (Puxbaum et al. 1988; Nolte et al. 1997) and so the presence of acetate and formate in the mosaic efflorescence is an unexpected observation, the first report of these ions on glass not associated with indoor-generated gaseous pollutant sources such as wooden cabinets.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Composition (%)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>SiO$_2$</td>
</tr>
<tr>
<td>1.</td>
<td>84.5</td>
</tr>
<tr>
<td>2.</td>
<td>85.7</td>
</tr>
</tbody>
</table>

Table 1. Analyses of weathered glass from a blue ‘silvered’ tessera.

<table>
<thead>
<tr>
<th>Anion equivalents</th>
<th>Cation equivalents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetate</td>
<td>0.20 ± 0.01</td>
</tr>
<tr>
<td>Formate</td>
<td>0.10 ± 0.002</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.18 ± 0.07</td>
</tr>
<tr>
<td>Nitrate</td>
<td>0.15 ± 0.01</td>
</tr>
<tr>
<td>Sulphate</td>
<td>13.46 ± 0.38</td>
</tr>
<tr>
<td>Total anions</td>
<td>14.09 ± 0.39*</td>
</tr>
</tbody>
</table>

* Standard deviations of total ions were taken as the square root of the sum of the squares of the individual standard deviations.

Table 2. Anion and cation molar equivalents ($\times 10^3$) for efflorescence from pale green-blue tesserae.
These technical analyses give a clearer understanding of the process of deterioration of the metal-leaf tesserae. Furthermore, the use of platinum (not mentioned by Verità in his comprehensive survey of metal-leaf tesserae) has been established as substitute for silver to avoid potential tarnishing. The loss of cartelline and platinum leaf occurred extensively in Holy Souls Chapel, with approximately equal frequency to the losses observed with gold tesserae. It is interesting to speculate on how platinum’s malleability (less malleable than gold and silver), melting point (much higher than gold and silver) and coefficient of expansion (lower than gold and silver and more similar to plate glass) affect the relative tendency for the loss of cartelline and metal from these metal-leaf mosaic tesserae. On the present evidence, there is no significant benefit of platinum to durability in this respect but the exacerbating influence of the unstable Holy Souls glass smalti complicates the issue.

### Treatment

A team of four experienced conservators under the direction of Deborah Carthy worked on the project from 5 July 1993 to 22 October 1993. The cleaning of all the mosaic and marble surfaces (some of which were found to be, geologically, limestones) was carried out, using 50/50 v/v white spirit/deionised water containing 5% of Synperonic® N non-ionic detergent. (Because of its effect on the aquatic environment, Synperonic® N was subsequently withdrawn and replaced by Synperonic® A7.) Final thorough rinsing with deionised water ensured the removal of any residues. This phase of the project also ensured that the extensive salt efflorescence (figure 3) was removed (figure 4) prior to reinstatement of the missing metal leaf and cartelline.

The design and the impact of the chapel walls and ceiling largely depend on the reflection of light from the many metal-leaf tesserae. Replacement of the decayed smalti (in some areas, as seen in figure 5, more than 60%) was not favoured; the disruption to the well-being of the entire mosaic and the costs, combined with the desire to focus on stabilisation and preservation led to the adoption of the methodology described below.

Several methods of replacement of the lost metallic layers were considered. It was impossible to gild directly on to the glass—the surface was too badly decayed.

![Fig. 3. Tesserae from north side of ceiling, showing salt efflorescence and associated deterioration of the mastic.](image1)

![Fig. 4. Tesserae from similar area to Figure 3, after cleaning, showing the deteriorated surface of turquoise blue and pale green glass with loss of the metal leaf and the protective glass cartelline.](image2)

Practically, it would have been well-nigh impossible to build up the smalti to an even surface using resin. In principle, it was possible to gild on thin glass which could be cut to size and applied to the smalti with adhesive but in practice this proved impossible; glass which was suitably thin (microscope cover glass) fragmented during even the most careful handling and was impossible to cut in size and shape of the smalti.

As a result, an innovative technique was developed and implemented. It was found that Melinex® polyester sheeting (125 micron thick) could be gilded using gilding size to give a durable laminate. This was easily cut to size of the smalti with scissors; the individual leaves were adhered to the smalti with Resin W® poly(vinyl acetate) (PVAc) adhesive with the shiny Melinex® side outermost. It was found that three types of metal leaf were...
Fig. 5. Typical extensive (greater than 60%) area of deteriorated tesserae with salt efflorescence, spalling of glass cartelline and loss of gilding.

Fig. 6. Glass tesserae adjacent to the north side window bays, showing extensive loss of the metal leaf and cartelline, revealing the decayed aquamarine blue glass. The area has been sectioned off with string to facilitate control of the treatment process.

Fig. 7. Detail of the east end mosaic before (7a) and after (7b) replacement of gilding on a single dark green smalto by means of gilded Melinex®.
appropriate; Palladium French leaf, 16ct Green (West German) and 18ct Lemon (German), all supplied by E. Ploton Ltd. (This London-based art and crafts materials supplier is no longer in business but equivalent metal leaf is readily available from other suppliers.)

Areas for treatment were sectioned off using string, as illustrated in figure 6. A useful advantage of the use of gilded Melinex® was that it could initially be cut slightly larger than the tesserae. By applying general pressure where it came into contact with the edges of the tesserae an imprint was left on the metal leaf, allowing the Melinex® to be cut with scissors to the exact profile of the tesserae and thus preserve the subtle character of the precise shape and relationship of the tesserae to each other. Figure 7 illustrates the result for a single dark green smalto.

Consolidation was initially undertaken using Rhodopas® M PVAc dissolved in acetone/xylene. It was found that under the conditions imposed by the scaffolding, the ventilation was insufficient for the safe use of xylene-based products even allowing for the use of facemasks. Not only was there a health consideration to the conservation team but, in a test evaluation, the smell of xylene vapour was noticeable by visitors to the chapel. The consolidation was therefore undertaken with the Resin W® PVAc emulsion which was used to apply the gilded Melinex.

Although not a traditional approach, this technique simulated very effectively the original appearance especially the all-important metallic glint (figures 8 and 9).

The approach is reversible and laboratory tests on samples maintained at high humidity indicated that durability should be good.

The project involved the interaction of a range of disciplines: administrator/conservator/scientist. It is appropriate that the fruits of this co-operation for Holy Souls Chapel were completed for All Souls Day, 1993.

Fig. 8. Section of the reredos, comparable to Figure 2a, as photographed in 2015, showing the good durability after 22 years of the restored ‘silvered’ opus sectile.
Fig. 9. Holy Souls Chapel north side, after conservation, showing the unified metallic reflectance in the area above the window bays as a result of extensive restoration of the decayed metal-leaf tesserae.
2015 re-evaluation of the conservation treatment
The mosaics were inspected with the aid of photographs, taken from the floor of the cathedral, in order to assess their condition, 22 years after completion of the conservation works. Although some minor soiling, as a result of pollution from candles within the cathedral, was visible (especially on the marble surfaces), the general appearance of Holy Souls Chapel was very much unchanged. Of particular interest was the long-term behaviour of the gilded Melinex® repair method. By inspection of photographs of detailed areas, such as those illustrated in figures 2 and 6, it was clear that few losses of the Melinex® replacements of the cartelline had occurred and that the opus sectile repairs adjacent to Christ’s robe were still in perfect condition (figure 8). Particular attention was given to one area in figure 6 where Melinex had been used to restore 175 of 450 (c. 40%) metal-leaf tesserae. No Melinex® losses were visible in a corresponding 2015 photograph of this area. In the adjacent curved area, however, a few tesserae showed only the deteriorated glass of the underlying smalti. Without closer inspection, impossible without construction of scaffolding, it is not possible to draw any further conclusions about the restored tesserae. It is possible that glass decay has continued, despite consolidation with the surface with PVAc, encouraging the loss of adhesion of the Melinex® ‘cartelline’.

Conclusions
The extensive use of metal-leaf tesserae in Holy Souls Chapel is a major factor in the aesthetic impact of the mosaic designs. Technical examination of the disintegrating smalti and the associated crystalline salt efflorescence confirmed the role of unstable glass compositions in the deterioration of the mosaics leading to the disruption of the intended metallic glint in a large proportion of the chapel wall and ceiling mosaics. In order to preserve the multi-angle reflections achieved by the deliberate use of the direct method of installation of the mosaic tesserae, a straightforward method was devised for treatment of the many hundreds of disintegrating tesserae which were distorting the overall harmony of the design scheme. The use of metal foil applied to Melinex sheets is a simple, aesthetically pleasing, reversible process which can be speedily implemented. Furthermore, on the basis of a re-evaluation 22 years after conservation, the method has excellent longevity.

The conservation project and its associated research successfully elucidated several technical features of the Holy Souls Chapel mosaics and their deterioration. The use of platinum as the element used for the ‘silver’ metal-leaf tesserae, the composition of the efflorescence crusts and the unstable nature of many smalti all contributed to a better foundation for the conservation works. Questions remain, worthy of further research, concerning the commercial sources of the glass tesserae and the extent of the use of unstable compositions for the production of coloured glass in metal-leaf tesserae at the turn of the 19th-20th centuries.

Acknowledgements
The authors wish to acknowledge to involvement of Emily Forde and other members of the conservation team, the encouragement of John Phillips, then cathedral architect, and the interest of George Sack, then cathedral administrator, in the execution of the work. English Heritage offered support over the implementation of the innovative conservation methodology and several colleagues, notably Dr Lorraine Gibson, University of Strathclyde (ion chromatography), facilitated the scientific studies.

References
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Puxbaum et al. 1988
Appendix: Glossary

Cartellina (pl. cartelline): a thin layer of blown glass (usually as thin as 0.2 to 1 mm, but occasionally as thick as 10 mm) covering the metal leaf in gold and silver tesserae. The cartellina is applied by firing and protects the metal leaf from oxidation. If the cartellina comes loose, a common phenomenon in ancient mosaics, it leads to the loss of the metal leaf and the tessera is discoloured (Verità 1996b).

Smalto (pl. smalti): in the world of mosaic, smalto stands for particularly brilliant, completely opaque, high-lead coloured glass usually prepared by adding crystalline material (corpo) and coloured material (anima) to the colourless or coloured fused glass. These smalti provide a vast range of shades (several thousands) with obvious advantages over the few dozen hues of glass pastes. The term smalto is also incorrectly used to describe metal-leaf mosaic tesserae. In general glass making, it stands for enamel, that is an intensely coloured low-melting (i.e. it softens before the support material) usually opaque (but also translucent or transparent) glass used in decoration or to clad gold, silver or copper objects as well as blown glass and ceramic (Verità 1996b).

Tessera (pl. tesserae): small, usually square pieces of glass or other material used to make a mosaic. Their size generally ranges from a few millimetres to two centimetres long and five to ten millimetres thick. The term derives from the Greek word meaning ‘four-sided’. They are obtained from a glass slab, initially incised by a diamond–edged tool (or at least a tool made with material harder than glass and thus able to dig into the surface). The glass slab is then placed on a hard-steel sheet and struck with a hard-steel chisel (martellina) to break it up into small pieces.

The same technique may be used by mosaicists to break the tesserae further, as required. The origin of glass mosaic tesserae is uncertain, but they probably date back to the first century AD and may be made of glass paste, smalto or metal leaf (Verità 1996b).

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