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Gerhard Eggert (Ed.)

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Preface ↘ Gerhard Eggert

No one expected that, the least myself: When looking for the ICOM-CC WGs Glass & Ceramics and Metals into fields of common interest, we got the chance to organise a COST supported meeting in Chateâu de Germolles (F) in 2006. And thanks to the energy and charisma of Agnès Gall-Ortlik, who convinced the Académie de France à Rome to host another meeting at the Villa Medici in 2008, and lead the ENAMEL network since then, we're now up to the 7th (!) biennial meeting (for more details, see Agnès article on the history).

This wonderful tradition now meets in Stuttgart 2018 with another one: Since 2005, I organised annual objects' conservation colloquia with varying themes. 2005 was devoted to metals in general, 2007 and 2012 to bronze, 2010 to archaeological iron. For the G&C conservators we had ceramics in 2006, glass in 2008, and glass deterioration in 2015. With enamel on metals in 2018, we hope to attract people from both communities.

You cannot convene such meetings without the continuous, reliable support of many people and institutions. Once again, the Academy dipped into its purse, our Institute of Book and Media Design cared for the layout and also helped financially, as did the Institute for Conservation Sciences. Our friends' association (yes, you can get a member: http://www.foerdervereinobjekt-restaurierung.de/) added its mite. On their free Saturday, our colleagues at Landesmuseum Württemberg will not hesitate to show us some highlights of the exhibition and the conservation department. The session on 'Scientific Investigations of Enamel' will be supported by Fonds der Chemischen Industrie (FCI). Cátia Viegas Wesolowska was a great help in editing this publication of the extended abstracts of the contributions to ENAMEL 2018. And Agnès added an extra: her updated bibliography of the enamel literature is added as second part. Thank you all!

Last, not least: It's my students who always do all they can to make the conferences an enjoyable experience for everyone. That's why I am looking forward quite relaxed to welcoming all participants to the 2018 colloquium. Accepting my age, this will be the last conference I will ever organise. It was fun!

↘ **2006** Chateâu de Germolles

History of the ENAMEL network

↘ Agnès Gall-Ortlik

The ENAMEL network is the result of a joint initiative launched in 2006 by Gerhard Eggert on behalf of Christian Degrigny and Lisa Pilosi, at the time co-ordinators of the Metal and the Glass & Ceramics working groups (WG) of ICOM-CC. In early 2006, Gerhard sent out a questionnaire to members of both working groups, as well as to the participants of the ICOM-CC triennial conference in The Hague in September 2005, asking them what were their interests in relation to composite objects (with a close link between metal and glass or metal and ceramics), such as stained glass, scientific instruments or metallurgical crucibles. Out of thirty-five responses obtained, thirty indicated enamel on metal as subject of interest (stained glass came as second, with sixteen votes).

Therefore, conservation of enamels on metal was the subject chosen for a first discussion meeting. Thanks to the financial assistance of the European programme COST (European Cooperation in Science and Technology), the meeting was quickly organised and took place in France on July 1–2, 2006. The circa twenty participants were warmly welcomed by Christian Degrigny in the Castle of Germolles, Burgundy. Nineteen presentations related to the conservation of enamels on metal were shared and confirmed the need for research and communication on the subject. At the end of these two days the participants decided to create the “Enamel on Metals Conservation Network” (EMCN), having as main goal the improvement of communication and exchanges on the conservation of enamels on metal. In the spring of 2007, Hannelore Römich, at that time COST officer, disseminated the CDs of the presentations and Gerhard Eggert published the first newsletter of the network, with already thirty-three members listed in it.

I had the chance to attend the first meeting with great interest. After writing my final dissertation at the *Institut national du patrimoine* (Inp) in Paris on the conservation of two Limoges enamels, I noticed the obvious lack of bibliographical references on the conservation of this type of composite objects and the difficulty in finding reliable information to support treatments. Since the late 1980s, there is a working group in the *Service des musées de France* responsible for identifying and documenting the conservation condition of painted enamels in public collections, a group coordinated by the *Musée municipal de l’Evêché* in Limoges. But its activities had not been made public. The meeting

in Germolles was therefore an intense and stimulating moment, the first in a long series, gradually transforming the network of 33 people into an international and interdisciplinary group of currently more than 110 professionals, bringing together not only conservators and curators, but also scientists and enamellers from 19 different countries.
Having published a first bibliography on the conservation of enamels in 2001 and an article in 2002 on the history of treatments carried out on these objects, together with Béatrice Beillard, reference conservator for enamels in France, Gerhard proposed me to assist him in the coordination of the network. In 2008, the year of the second meeting, I had the opportunity to invite its members to Rome, at the *Académie de France*, where I was resident to undertake the study and condition report of the enamel collection of the *Musei Vaticani*. With eighty participants from more than ten countries who had the chance to be welcomed at Villa Medici on March 10–11, 2008, this meeting was one of our most successful. In contrast to Germolles, short summaries of the presentations were printed and distributed to participants in the form of a booklet. A special visit was organised to the Vatican Museums for the authors, who benefited from the guide of Guido Cornini, curator of the Department of Decorative Arts and responsible for the collection of enamels and that of Flavia Callori, metal conservator, head of the conservation laboratory of archaeological objects. It was during this meeting that Gerhard Eggert proposed to the members of the network to appoint me as new coordinator of the group in his place, with Cátia Viegas Wesolowska as assistant. The majority of participants approved this 'perfect couple', consisting of a glass conservator (myself) and a metals conservator (Cátia), both members of one of the network's founding ICOM-CC working groups.
The successful formula of the symposiums of the ENAMEL network also took shape in Rome: a day and a half of lectures, followed by a half-day of a special visit reserved for authors, and the publication of oral presentations in the form of abstracts. Short summaries turned into extended abstracts, but the choice of not publishing full papers was voluntary, so that authors could publish their research in other journals or organisations. This lightened formula is also more relevant to the purpose of the network, to communicate in a leaner way between all its members. A newsletter is published every year, and from 2008 the group changed its name from EMCN, the name chosen in Germolles, to ENAMEL.
In 2010 we were fortunate enough to be invited to the United States by Julia Day, object conservator working at the Frick Collection (New York), who was starting research on the renovation of the showcase of painted enamels from the Renaissance period. Our symposium that year took place in between the

ICOM-CC Glass and Ceramics WG interim meeting in Corning, NY, and the Metal WG interim meeting in Charleston (SC). This allowed some of our colleagues specialised in one of the two materials to meet in New York around enamels at the Frick Collection. It was also the first time that we welcomed posters and the presentations were published as bound extended abstracts. Some of the presentations were also filmed and are viewable on the internet, such as those of Angelo Agostino, Birgit Schwahn, Fredric Schneider, and my own presentation on the bibliography (https://www.frick.org/tags/enamel). Since this conference, Julia Day has teamed up with Cátia and myself to take care of the network.
In 2012 I managed to invite members of the network again, this time to Barcelona, Catalonia, thanks to a grant from the Spanish Ministry of Culture obtained through my own heritage conservation company COREBARNA SL, based in Barcelona. The symposium was held at *The Museu d'història de Catalunya* (MHC), a museum without an enamels collection but a welcoming spirit! The presentations were published in the form of a bound booklet.
The special visit took place at the *Museum nacional d'Art de Catalunya* (MNAC), during which the authors were able to observe some less fortunate treatments to Limoges medieval enamels by non-specialised restorers. The novelty of this meeting was the organisation of a workshop of enamel techniques three days preceding the conference. Thanks to the presence of the artistic enamelling training department of the Llotja School of Applied Arts and the passion of its two professors, Andreu Vilasís and Núria Lopez Ribalta, eleven participants were able to practice painted enamel, with application of paillons, opaque and transparent enamels, miniature enamel with vitrifiable colours and had a glimpse at the work of grisaille and at the making of *cloisonné* enamels. The majority of the participants were conservators but we also had three art historians among us. Suzanne Higgott of the Wallace Collection was lucky enough to do a "hot repair" on her enamel during the masterclass!
In 2014 David Thickett welcomed us to London to the Ranger's House (Greenwich), where, among his main position as senior conservator scientist, he is responsible for the preservation of the painted enamels at the Wernher collection on display in the 17th century manor house. David explained how the system used to maintain a stable climate in the showcases of the Wernher collection works, and Suzanne Higgott and David Edge offered speakers a visit to the enamel collections of the Wallace Collection and, finally, Catherine Nightingale gave the authors a special tour of the enamelled jewellery of the Cheapside Hoard at the Museum of London. This was a hands on tour, where participants were able to handle the artifacts and examine them closely.
In 2016, Cátia Viegas Wesolowska, based in Poland, was the local organiser of

↘ **2010** New York City

↘ **2008** Rome

↘ **2012** Barcelona

↘ **2014** London

↘ **2016** Warsaw

the colloquium, together with her colleague Anna Mistewicz, metal conservator working at the National Museum in Warsaw. Since its ten years of existence the network visited for the first time Central Europe, to a country whose language does not facilitate international exchanges and access to publication sources. The presence of two professionals from Taiwan among the audience was also a first for our network. In front of an audience of fifty professionals from twenty different countries, fourteen presentations and four posters were presented. Faithful to the tradition, special visits were also organised, like that of the enamel collection of the National Museum in Warsaw, which keeps an exceptional group (over 300 objects) of Chinese and Japanese enamels of the 18th and 19th century, and a guided tour of the city of Warsaw. A special visit for speakers was also held at the Wilanow Palace to introduce us to its collection of Limoges enamels and Asian painted enamels.

Invited by Gerhard Eggert, ENAMEL 2018 is convened in Germany at the *Staatliche Akademie der Bildenden Künste Stuttgart* in cooperation with *Landesmuseum Württemberg*. The network continues to exist, communicating mainly at the time of its meetings, more “sleepy” during the interim years. But its existence is still justified by a constant need for information on enamels on metal, their methods of manufacture, their ways of alteration and their means of preservation. Discrete but fascinating objects, with a very wide diffusion in time and geographically, many museums in the world preserve some of them, whether they are painted enamels from Limoges or *cloisonné* enamels or medieval *champlevés*, or jewellery on gold or silver and even cooking utensils enamelled on iron. Since the existence of the ENAMEL network, the number of publications has increased significantly and research groups have been created around the world, remarkably enriching the useful information for all those who need to preserve or treat enamels on metal. Let’s wish a long life to this network of international experts!

Extended Abstracts

Exploiting the power of large statistics: how portable XRF and ancillary techniques can still implement knowledge on Medieval enamels. The Musée de Cluny collection

Angelo Agostino

The *Oeuvre de Limoges* is the largest surviving corpus of metalwork from the Middle Ages (O'Neill 1996) and its artefacts are scattered within European museums and beyond. Several studies addressed the development of this monumental production, both in what concerns stylistical and iconographical features and the technique and materials used to produce the metal support and the enamel decoration (O'Neill 1996; van der Linden et al. 2011; Agostino et al. 2014; Biron 2015). Moreover, as the *Oeuvre de Limoges* extends from about the 12th to the first half of the 14th century, the analysis of the enamels is of particular interest due to the evolution of the glass production model occurring in Europe and the Middle East during the Middle Ages, affecting the primary/secondary production sites relationship and location and the use of fluxes and opacifiers.

The present work refers to a set of 28 artefacts kept in the Musée de Cluny (Paris), the majority being considered to belong to the *Oeuvre de Limoges*. The objects have been analysed in situ by portable X-Ray Fluorescence (p-XRF) and UV-Vis Fibre Optic Reflectance Spectroscopy, in order to characterise both the enamels and metal support. In particular, p-XRF data has been processed to produce quantitative information following a well established analytical approach (Agostino et al. 2014). Particular interest was given to the artefacts of the transition period, characterised by the concomitant presence of different glass matrices and opacifiers within the same object or enamel area, aiming to collect more specific information on the chronology of matrix and opacifier changes according to different colours. The set of analysed objects included some *en style de Limoges* artefacts, belonging to a class of enamels produced as copies or forgeries during the Gothic Revival of the 19–20th centuries (Röhrs & Stege 2004), a Botkin Byzantine plaque and finally, some enamels compatible with the Medieval period but not fitting within the Limoges production.

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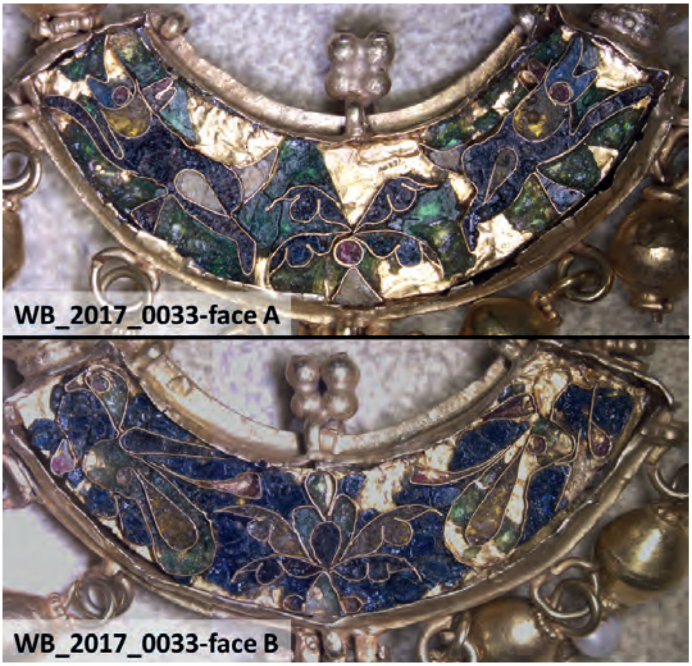
The Preslav treasure – Insight into the Byzantine enamelling techniques ↘

Marlène Aubin
Matthias Heinzel
Antje Bosselmann-Ruickbie
Susanne Greif

The Preslav treasure illustrates the importance of the ancient Bulgarian capital, Veliki Preslav. Made up of gold and silver artefacts, it is one of the most significant archaeological discoveries connected to the Byzantine period in Bulgaria. Probably concealed during the Byzantine invasion in 971, it remained in the soil for ten centuries. The treasure consists of goldsmiths' masterpieces such as a diadem, a two-faced enamelled necklace, enamelled earrings, and gold appliques. There is currently a deficit in information and research on Byzantine techniques for enamels and goldsmith's artefacts, as only a few examples have survived, in particular from a known context. Our project is an interdisciplinary teamwork, studying these objects from an art historian's, archaeologist's, goldsmith's and scientist's point of view and joining the Archaeological Museum Veliki Preslav, the Römisch Germanisches Zentralmuseum Mainz (RGZM), and the Johannes Gutenberg University. In this work, we will focus on two artefacts from the Preslav treasure: a pair of enamelled gold earrings.

Enamelled earrings Among the artefacts already studied so far was a pair of richly decorated gold earrings. Damaged and incomplete, it is the combination of the remaining parts that enables to picture the whole earring. They are composed of a central curved enamelled cell preserved on the first earring ↘ Fig. 1.1, on top of which would have been present another enamelled cell only remaining on the second earring ↘ Fig. 1.2. These earrings show different decorations on both sides. On the central panels are represented two multicoloured dogs on both sides of a plant (face A) whereas, on the other side, two peacocks replace the dogs (face B). The cloisonnés on the second earring present also two different faces with floral decoration.

All enamels of both earrings, which show a variety of colours, were analysed: green, brown, yellow, white, blue, and red are dedicated to a specific part of the animals, vegetal forms, and backgrounds. Each glass colour is contained in a separate cloisonné cell, sometimes really tiny, as for the dogs' red eyes. The aim of this article is to enlighten the composition of those enamels. As no sampling was allowed, the analytical process performed on such



↘ **Fig. 1.1**

↘ **Fig. 1.2**

↘ **Fig. 1.1** Photographs of enamelled earring WB_2017_0033 from the Preslav treasure. Face A presents two dogs on both sides of a plant as decoration whereas Face B depicts two peacocks around a central plant. © RGZM.

↘ **Fig. 1.2** Photographs of enamelled earring WB_2017_0034 from the Preslav treasure. Both faces present a floral decoration. © RGZM.

national treasure artefacts must be adequate and efficient to ensure the integrity of the precious artefacts.

Analysis of the enamels Our analytical strategy is to combine non-invasive and non-destructive techniques such as micro-X-ray Fluorescence (in this case on non-prepared surfaces), which provides elemental semi-quantification, X-ray radiography and Raman spectroscopy, which provides structural information. Combining the results of these three techniques helps to determine glass composition, colouring agents, and opacifiers, thus enlarging our knowledge on Byzantine enamel techniques and their influences. The fragility and value of the artefacts prevented us to perform analyses under vacuum, limiting the information we could collect. Light elements as sodium, aluminium or magnesium could not be quantified. All data presented here are values without these major elements and marked by an asterisk: the elemental quantification of this work is calculated to 100% from the elements we could actually detect. The results are not comparable to quantification results from other studies. The glass type was therefore determined comparing our Raman results with the classification of Colomban et al. (2006) who used Raman spectroscopy as a new methodology to distinguish different types of glasses.

Green enamels Raman analysis revealed that the emerald green translucent enamels belong to the third group of glasses according to Colomban's classification which corresponds to a soda-glass. The high amount of potassium ($K_2O^* \approx 4$–7%) can result from the use of plant ashes as sodium source which was common for emerald green glasses of the Roman period (Jackson 2015). The green colour could be obtained from a copper rich bronze (Cu>90%) as the glass contains tin and lead with traces of zinc (Biron 2015). All green enamels present a similar composition with slight differences probably due to the heterogeneity.

Brown enamels The shade varies from a brownish red to a dark purple translucent glass depending on light and the glass' thickness. This colour is otained by the addition of a high quantity of manganese ($MnO_2^* \approx 4$–5%) combined with iron ($Fe_2O_3^* \approx 3$–4%). The type of glass matrix is the same as the one used for green enamels: an ash glass with less potassium ($K_2O^* > 1.5\%$) as revealed by Raman spectra of these areas.

Yellow enamels There are two kinds of yellow enamels on the earrings. The first one is a bright translucent yellow glass and the second one is a light yellow opaque glass. The translucent yellow glasses are soda glasses characterized by low potassium contents (so-called natron glass), typical from the Roman period. The extremely low contents of lead, antimony, and tin reveals a yellow pigment not based on lead compounds. The high amounts of iron (Fe_2O_3* ≈ 9–17%) and manganese (MnO_2* ≈ 3–5%) suggest iron has been oxidised from Fe^{2+} (blue colour) to Fe^{3+} (yellow colour) by manganese ions Mn^{3+}. However, iron must be also partially trapped in another complex structure so the yellow hue is not too dark (Donald et al. 2006).

The opaque yellow glasses are typical lead glasses known as early as the Egyptian glass production. The Raman spectra of those enamels reveal the presence of quartz (SiO_2) as well as bindheimite ($Pb_2Sb_2O_7$), the last one suggesting the use of Naples yellow type pigment. It is well known from literature that lead antimonate pigments were used in the Roman period to produce yellow opaque glass. Normally the substrate containing the yellow pigment was prepared beforehand and added to a natron glass (Paynter and Kearns 2002). Quartz crystals combined to a high ratio of lead to antimony may enhance the formation of a lead-rich glass in which lead antimonate can precipitate and be stabilised.

White enamels The white dots on face A have homogeneous quantification results with a high content of calcium and antimony. This is correlated with the Raman results were we have found both calcium antimonates $CaSb_2O_6$ and $Ca_2Sb_2O_7$. These white compounds were used separately as a white pigment or combined to another pigment to modify the hue and translucency. The same observation and results are obtained on face B but the quantification is more heterogeneous. It is interesting to notice that no use of tin oxide SnO_2 has been detected even if this pigment was already widely used in western enamels (Biron 2015).

Blue enamels Based on the compositional variations, we have distinguished three types of blue enamels on the two earrings. The first one is an opaque blue glass lighter than the rest of blue glasses. It is a soda glass from Colomban´s Raman group 3 corresponding to natron-glass. The colour is provided by the presence of cobalt. To obtain this light opaque blue, the glassmaker used calcium antimonate as an opacifier.

The second type of blue enamel is a translucent dark blue. The dark shade is due to a high amount of cobalt (over 1% CoO*) distributed in a natron glass. The high amount of cobalt was possibly intended to convey the strong blue shade. If the translucent blue glass were too light, the combination of the gold substrate and the blue shade would probably make this glass appear greener.

The last type of blue enamel is a dark blue natron glass but with less cobalt content (around 0.3 – 0.4 %*). From the quantification results we distinguished what should be two different batches of this blue. The elemental compositions of these two batches are slightly different but with probably the same initial recipe, giving evidence that these blue enamels were made using two different sources or batches of blue glass powder.

Red enamels There are also three types of red enamels on the earrings. Red enamels are used for the small cells. The first type of enamels is the most encountered: it is a red lead glass with colour resulting from the presence of copper, most probably cuprite and elemental copper particles (Tichane 1998). The high amount of lead (over 30% PbO_2*) can serve two purposes: first, it helps to produce cuprite (Welter et al. 2007) and gives a shiny light red and secondly it decreases the glass' melting point, making it technically easier to fill in small cells.

The second type of red enamel is also a lead glass (17 – 18 %*) with a significant tin content. The red shade, a little bit darker than the previous one, is probably due to copper particles even though they were not formally identified.

The last type of red is a totally different formula. The lead content is distinctly lower (5%*) and the iron content higher (10%*). We propose that the colour is due to the presence of copper particles ($CuO \approx 5\%$*). The random appearance of this red suggests it might have been made to complete irregular enamels.

These Byzantine enamels are typical glasses inherited from the Roman glass technology with the use of soda glass for green, brown, and blue, lead glass for yellow and red, and calcium antimonate as white pigment. Some questions remain regarding the manufacturing process of the translucent yellow glass containing a high amount of iron. Plans to reproduce this type of enamel will allow for a better understanding of the chemistry occurring inside the glass matrix.

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A project to improve an existing showcase for conservation and presentation of the Limoges Early Painted Enamels at the Louvre Museum ↘

Françoise Barbe
Joëlle Le Roux

Introduction At the 3rd Experts' meeting in the Frick Collection in 2010, Françoise Barbe explained the conception and making of an adapted climatic box to exhibit two very important Limoges painted enamel plaques circa 1500. From the studies made by Isabelle Biron in the C2RMF, it appears that the Early Limoges Painted Enamels have an unstable chemical composition which explains their elevated sensitivity to climate fluctuations. To be displayed in good condition, the ideal climate for these unstable enamels would be relatively dry, i.e. with a relative humidity of circa 40–42 % and a temperature of circa 19 °C.
A few months after their installation in the Louvre exhibition room, it appeared that the climatic box for display was not hermetically sealed and the enamels passed through the same climatic variation as the others in the room. The authors decided to change the climatic conditions of the whole display case and began investigations which lasted several years.

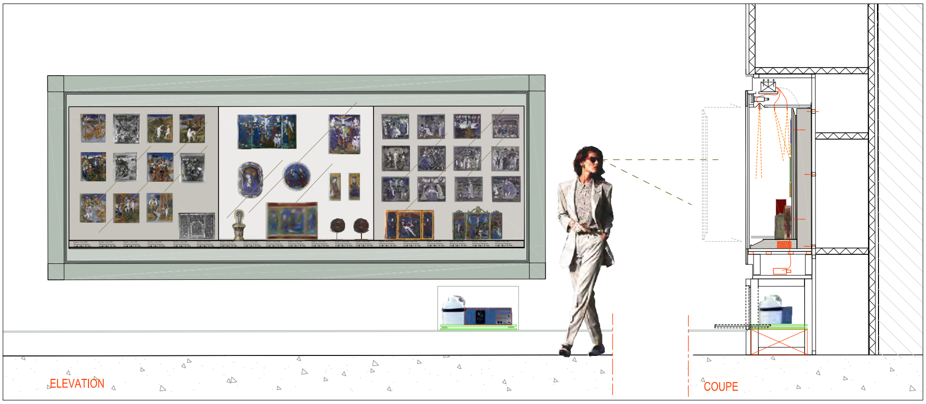
This research made it possible to determine precisely the needs of the collection, to characterise the performance of the showcase in relation to its envi-ronment, and to choose the appropriate improvement paths. The layout of the enamels has also been redesigned as well as the lighting. This project was the occasion for collaborative in-house work, involving the decorative art department, the preventive conservation department, the museology services, and the technical equipment service. The showcase was refurbished in December 2017, so, after a few months of operation, a synthesis of the entire process and its result will be presented at the meeting in Stuttgart in 2018.

Alteration process of early painted enamels Within its rich collection of Limoges enamels, the Louvre keeps a beautiful set of painted enamels from the end of the 15th and the beginning of the 16th centuries. Most of the works are plates of small dimensions which were originally part of altar-

↘ **Fig. 2.1**

↘ **Fig. 2.1** Master of Louis XII triptych, Virgin, Musée du Louvre, Département des Objets d'art OA 11170: detail of the altered blue glass (© Musée du Louvre / Département des Objets d'art / Françoise Barbe)

↘ **Fig. 2.2**



↘ **Fig. 2.3**

↘ **Fig. 2.2** Showcase of the early painted Limoges enamels prior to renovation (© Musée du Louvre / Département des Objets d’art / Françoise Barbe)

↘ **Fig. 2.3** Project of the renovated showcase: elevation and profile with the miniClima® in the lower part and the Prosorb® under the tray (© Musée du Louvre / DMPC / Patricia Cabotse) pieces today dismantled, and small triptychs of private worship, representing most often scenes of the life of Christ.

On these works, some of the coloured translucent glasses are chemically altered ↘ Fig. 2.1. Studies led by Isabelle Biron demonstrated that changes observed on the blue, purple, and the red-violet glasses made between 1480 and 1530 approximately came from the instability of their chemical composition due to the employment of recipes rich in potassium (Biron 2015: 360 -361). Since 1993, the early enamels collection has been exhibited in a wide showcase (Richelieu, 1st floor, room 11), in the area dedicated to the Medieval and Renaissance works of art designed by the architect Michel Wimotte ↘ Fig. 2.2. Since then, the curators in charge of the collection have been trying to improve climatic conditions.

Unsuccessful attempts to control climate The climate of this case was checked over several years. Annual readings showed variations between 44 and 55% for relative humidity (RH) and between 20 and 25 °C for temperature. Over the last 10 years, salts have appeared on the surface of enamels and have had to be cleaned on some enamels repeatedly. The humidity was therefore unsuitable for the preservation of early enamels if one refers to the recommendation of RH 40–42% and a temperature of 19 °C for this type of enamels.

To improve these conditions, we tried to modify the climate with passive moisture absorbers. Nine Prosorb® boxes with RH 40% were added to a compartment in the display case. Unfortunately there was no effect! The hypotheses explaining this failure are the poor sealing of the showcase, as well as the small passage of air between the technical compartment and the volume of the presentation area. Another problem is the wooden facing of the showcase. This material puts itself in equilibrium with its environment and contains moisture which prevents the setting up of a dry climate.

The second attempt was a project of a climatic box for the two enamelled plaques, placed inside the permanent display case. It was decided to create an airtight box containing silica gel conditioned to 40% RH. The main structure was constructed using maple wood with a compartment in the back devoted to store silica gel and the thermo-hygrometer.

The back was sealed with an aluminium rigid board. An aluminium tape sealed the glazing all around the box, to maintain it absolutely air tight. Over the period studied (September 2011 to March 2012), the RH was maintained between 44% and 47.5% with temperatures ranging from 18.8 to 24 °C. The humidity was still too high, as salts appeared again on the surface of enamels in March 2012. In this case, the hypothesis was that insufficiently dry wood acted as a buffer, preventing the area reaching 40% from the silica gel.

Assessment of needs and modification of the showcase The Wilmotte showcase consisted of a metal box and an MDF internal facing (wood fibres and synthetic binder). MDF has an interesting buffer capacity which minimises the humidity variations inside the showcase but does not allow the setting up of a specific dry climate. The MDF is also known to emit formaldehyde and could have had an adverse effect on the enamels.

The sealing of the showcase presented some defects, notably in the connections between the three glass panels of the facade. The showcase is located in an alcove well insulated from outside and has a year controlled climate in temperature and humidity (RH from 45 to 55% and temperature from 19 to 25 °C). It was necessary to achieve a drier and stable RH in the showcase. To achieve this specific climate, we needed to improve the sealing of the showcase in order to decrease air exchange with the room, to replace the MDF with non-hygroscopic facing materials and achieve adapted internal climate control.

We made the choice to use Forex, a non-hygroscopic, water-vapour-impermeable and emission-free material (Oddy-tested). The sealing of the showcase was improved after leak tests with a tracer gas and ultrasonic test.

The means for regulating the humidity may be passive or dynamic. The volume of the showcase determines the means for achieving this. This showcase represents a volume of nearly 2 m^3, so we have chosen to use a dynamic device, in this case a miniClima® (Schönbauer GmbH). This device allows the humidity to be regulated to the desired value by a sealed pulsed air network permanently regulated by a probe. A second recorder thermo-hygrometer is placed in the display case for long-term monitoring. The miniClima® was placed in a new technical compartment made to measure and well ventilated to avoid heating up the showcase and prevent the device from malfunctioning.

A load of 40% Prosorb® has also been planned to improve stability, on a daily basis (less use of the device) or in case of a failure. A place with good air circulation has also been planned for the Prosorb®, in the base of the presentation area. The renovated showcase was refurbished in December 2017.

Conclusion In June 2018, we will have a few months of feedback to check the effectiveness of the case refurbishment. It is expected that the enamels accommodate to their new environment and reach equilibrium before being cleaned of their salts.

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Evaluation of the interactions of materials employed in the restoration of *champlevé* enamels on a silver artefact ↘

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Mari Yanagishita

Introduction During conservation treatment of enamelled silver artefacts, it is not unusual to face the challenge of both consolidation of enamels and protection of silver. In many cases, the dimensions of the areas being treated are so small that the overlapping of materials for consolidation and for protection cannot be avoided.

This was the case on a *Bossolo per votazioni* (ballot box), evidence rare example of civil art in Florence between the Middle Ages and the Renaissance, which is stored in the Museum of Palazzo Vecchio ↘ Fig. 3.1. According to ancient documents, the artefact probably dates back to around 1390 (Bemporad 2013) and was used in the ballot session for decision making of the ruling councils of the town.
The artefact consists of two cups decorated with crests, made in a silver alloy and *champlevé* enamels, with a cylinder connecting the two cups. Eight crests are present on the upper cup: four related to the *Comune* and the city and four related to the *guelph* side of the citizenship. In the lower cup twenty-four crests are present: among them the seven *Arti maggiori* (Major Guilds) and the fourteen *Arti minori* (Minor Guilds) crests.
In 2013 some of the red enamels required temporary consolidation with Japanese paper due to their fragility, and to avoid loss of vitreous fragments during handling ↘ Fig. 3.2. Further degradation effects were observed such as loss of fragments of blue enamels and the presence of tarnishing and green salts on the silver alloy.
The ballot box showed also many structural and surface alterations such as mechanical damages on the metallic edges of the enamelled plaques proving different interventions of dismounting and reassembly, porosity of blue enamels and alteration of red enamels probably due to unsuitable or later firing procedures.
Investigations performed by the Scientific Department of the Opificio delle Pietre Dure confirm later intervention. The cylindrical element, for example,

↘ **Fig. 3.1**

↘ **Fig. 3.2**

↘ **Fig. 3.1** *Bossolo per votazioni* (ballot box), Florentine goldsmith, about 1390, *champlevé* enamel on silver, H. 33,5 cm, L. 21,5 cm. Florence, Museo di Palazzo Vecchio (Inv. n. MCF_PV 2004–10678) after conservation procedures.

↘ **Fig. 3.2** Detail of the *Bossolo per votazioni*, red enamels, before treatment.

seems to have been produced by a different silver alloy compared to the other parts, proving possibly a later replacement. Furthermore, some original blue enamels seem to have been replaced by later ones: the presence of arsenic, bismuth and nickel, elements connected with cobalt, found in some of the blue enamels, can be related to minerals excavated in ores discovered after 1520–1530 (Zucchiatti 2006) assessing a later production comparing to the other enamels, where these elements were absent.
A typical alteration pattern of red enamels was found and can be the origin of their deep fragility: the fragments show an opaque red core of unaltered glass and a transparent colourless external layer. This effect was probably due to oxidation of copper, preventing the precipitation of metallic copper and/or copper oxides responsible for the colour and opacity of the glass. Another alteration pattern, in some areas, is the presence of a yellowish opaque layer in contact with silver: this effect is connected to the reduction of silver oxide, diffused from the surface of the alloy into the glass matrix, to metallic silver (Bowman and Freestone 1997).
The unstable condition of enamels determined the conservation procedure, an enamel consolidation before a silver protection treatment. The closeness of the silver alloy to the enamels makes it impossible to avoid overlapping and contact between the two materials, even when working with a microscope ↘ Fig. 3.3.
Therefore, it is of outmost importance to assess that no negative interaction between the two materials will take place in future storage. An experimental protocol was established during a previous restoration (regarding the silver San Giovanni Altar of the Baptistery in Florence in 2007) and performed until now to assess the possible modifications of the materials used for consolidation and protection.

Experimental procedure Tests were carried out in the Jewellery Conservation Department of the Opificio, applying two well-known conservation materials used respectively for the consolidation of glass (Mowital B60HH, a polyvinyl butyral resin) and protection of silver (Zapon, a nitrocellulose lacquer). Tests were made on an enamelled silver sample plaque. The plaque was prepared by firing grinded glass (Transparent Vitreous Enamel, 60 Mesh, Schauer, Germany) on a silver alloy plaque. To that aim, the glass was manually grinded using an agate mortar to obtain a homogeneous powder that was rinsed with water and slightly acidic water many times until the water was clear, to ensure an efficient purification. The silver alloy plaque was chiselled to ensure an effective anchoring for the glass. The plaque was put in an oven at 800 °C for an appropriate time and then left cooling slowly. The

enamelled surface was polished with pumice stone and glass fibre. The plaque was re-fired to obtain a glossy surface.
Different parts of the enamelled plaque (both glass and metallic surfaces) were treated using different methods and materials: Mowital and Zapon were applied either alone (M and Z areas respectively) or together (M+Z area, where Zapon was laid on top of a Mowital coating simulating a conservation procedure) ↘ Fig. 3.4. At first the plaque was artificially aged in a climatic chamber (HC 4030 Heraeus) via cyclic modifications of humidity and temperature for 465 hours simulating a non conditioned environment. In each cycle a first three hours period at 15 °C and 80% RH, followed by a three hours second period, at 40 °C and 20% RH, were used assuring that the changes of parameters for each step were gradually done in an hour time.
Then the plaque was left in a conditioned environment for 10 years, at a temperature ranging from 19 to 25 °C and a relative humidity from 48 to 60%.
The modifications of the different areas were monitored at different times: just after the protection of the enamelled plaque (T0), after the ageing in the climatic chamber (T1), after three years (T2) and after 10 years in a conditioned environment (T3). A variety of analytical techniques were used:

- optical microscopy using a Leica M205C microscope;
- scanning electron microscopy (SEM) using a EVO® MA 25 Zeiss microscope;
- colourimetric analysis using a Minolta CM 2006d spectrocolorimeter;
- Fourier Transform Infrared (FTIR) analysis in reflectance mode using a THERMO NICOLET NEXUS™ (software OMNIC™) infrared spectrophotometer with a CONTINUUM™ microscope.

Results The macroscopic observation of the plaque shows no detachments of the protective layers or macroscopic modifications of the surface. The observations using a stereomicroscope confirm the results: the protective film surface seems flat and even, neither cracks are visible nor other morphological features that could be related to decay processes induced by the interaction between the two polymers.
Cracks are not visible even observing the coating surface with a scanning electron microscope although the surface appears slightly more rough after ten years of natural ageing. Micro reflectance infrared spectroscopy pointed out no statistically meaningful spectral changes during the ten years monitoring period: small differences of the spectral profile before and after ageing (in terms of appearance and disappearance of peaks and shift in their position) occurred at but these variations are recorded also in spectra acquired before ageing in different areas. So there is no evidence of interactions between the two polymers.

On the four areas, 10 colourimetric measurements at T0, T1, T2 and T3 were performed, each repeated three times. No significant variations of the three parameters and ΔE values (lower respect to the eye detection level) between T0 and T3 were detected on the area treated with Mowital (ΔE=1,56 ±0.28), Zapon (ΔE=1,61 ±0.71), the area treated with Mowital and Zapon (ΔE=1,12 ±1,0), and the untreated area (ΔE=0,92 ±0.83).
Since no changes of morphology, molecular structure or colour were recorded over time, the possible overlapping of the two materials can be considered safe and stable.

Conservation treatment The conservation intervention consisted in consolidating enamels, cleaning of the surfaces to eliminate materials harmful to future preservation and preventing the oxidative process of the silver alloy. The first step was the cleaning of silver surfaces, keeping the enamel protected with Japanese paper for safe handling of the artefact. The enamelled plaques were cleaned applying mixtures of organic solvents and water. Mowital B 60HH in alcohol at different concentration was used to consolidate the enamels, while the silver surfaces were protected using Zapon.

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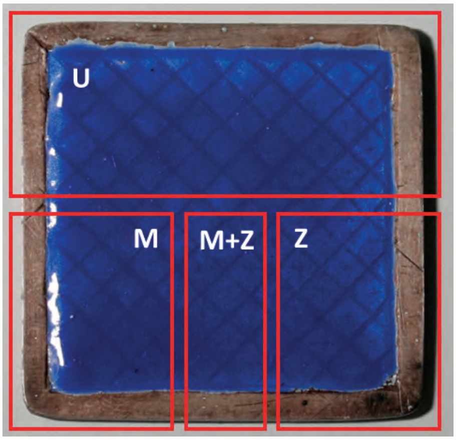
↘ **Fig. 3.3** Detail of the *Bossolo per votazioni* during treatment, showing the strong bond between enamelled areas and the silver alloy surface.

↘ **Fig. 3.4** Silver alloy enamelled plaque used as sample object. M: area treated with Mowital, M+Z: area treated with Mowital and Zapon, Z: area treated with Zapon, and U: area left untreated.

↘ **Fig. 3.3**



↘ **Fig. 3.4**

Non-invasive analysis of medieval *émail champlevé*: empowering the technique to widen the statistics. ↘

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Stefan Röhrs,
Lothar Lambacher
Ina Reiche

Introduction The study of medieval enamels has previously been undertaken with the main focus on the *Oeuvre de Limoges*, the largest remaining corpus, and to productions in the Mosan and Rhenish areas (Biron et al. 1996, Röhrs and H. Stege 2004, van der Linden et al. 2011, Agostino et al. 2014, Biron 2015). However, the quantity of analysed objects still represents a small proportion of the existing artefacts. For example, very few studies have been performed on German collections.

In the present study, a non-invasive approach was applied to a set of *champlevé* enamels belonging to the *Kunstgewerbemuseum Berlin*. Most of the artefacts, listed in ↘ Fig. 4.1, are attributed to the Mosan and Rhenish area while two are from Limoges. All enamels have undergone micro X-ray fluorescence (μ-XRF) and micro Raman Spectroscopy aiming to characterise the composition of the enamels, the colourants and the opacifiers. Furthermore, the Trier artefacts were analysed using an Environmental Scanning Electron Microscopy (ESEM) with Energy Dispersive X-ray (EDX). Particular attention was given to the production of quantitative data, and a tentative quantitative approach to Raman spectroscopy was made applying the model proposed by Robinet et al. (2008).

Results and discussion All the analysed enamels were produced with opaque glasses, the opacifiers' particles being finely dispersed within the glass matrix. The presence of crystalline phases signals can interfere with the extraction of the Raman features necessary to classify the glass matrix, whether according to reference glass families (Colomban et al. 2006) or when applying a more in-depth spectra analysis based on the deconvolution of the spectral components (Robinet et al. 2006). Specific attention was thus given to reduce their contribution to the final spectra.

In general, XRF confirmed the use of the typical chromophores to obtain the colour. Apart from red enamels where no clear identification could be made, Raman spectroscopy allowed the direct characterisation of the crystalline phases dispersed in the matrix, in the majority of cases these being opacifier particles. Feldspars, generally considered as undissolved raw ingredients (Ricciardi et al. 2009), were also identified in all turquoises with a soda-lime matrix bearing calcium antimonate. ↘ Fig. 4.2

The conjoint use of µXRF and µRaman was especially beneficial when different types of glass grains where observed within the same enamel, as in the case of the ornamental hinge element K 4252 with Rhenish provenance. ↘ Fig. 4.2.a. This artefact shows evidence of the coexistence of two opacifiers and flux typologies. Whereas most of its colours indicate a soda-lime composition with a mineral flux and antimonate-based opacifiers, white and turquoise also contain about 0.6–0.8 wt% SnO_2 suggesting the presence of cassiterite (tin oxide). In the turquoise two typologies of grains were observed, the first characterised by a soda-lime matrix and $Ca_2Sb_2O_6$ particles, while the second has lead-silica features and cassiterite particles. The red enamel has about 2 wt% K_2O and Raman could again differentiate two matrices, respectively with higher and lower K_2O. In the yellow enamel, $Pb_2Sb_2O_7$ was recognised as opacifier and colourant. In most of the spectra, the presence of two peaks at about 330 and 450 cm^{-1}, characteristic of the modified form of this compound including a third oxide, along with small SnO_2 contents suggest its presence in the Sn-modified form (Rosi et al. 2011).

The artefact O.1973,186 ↘ Fig. 4.2.b is also of Rhenish provenance. In this case, all shades of colours, apart from the red, indicate a soda-lime composition and the use of antimonate-based opacifiers. $Ca_2Sb_2O_6$ and $Ca_2Sb_2O_7$ show in variable ratios in the white, blue and turquoise enamel, the particles being finely dispersed in the matrix. As a result, this is one of the cases where difficulties in excluding crystalline phases signals may lead to errors in the extraction of the Raman features. Indeed, these indicate a similar clustering of blue and turquoise matrices whereas XRF data suggests a mineral flux source for the white and blue, with K_2O being below 0.8 wt%, and a plant source for the turquoise shades with K_2O between 1–2 wt%. Both techniques agree in indicating a soda-lime matrix and a plant flux for yellow and green enamels, containing the Sn-modified form of $Pb_2Sb_2O_7$ as yellow colourant and opacifier. The red enamel is a high potash lime glass, containing about H2wt% P_2O_5, Rb_2O and BaO traces.

The analysis of the two Limoges artefacts gave particularly interesting results. For instance, the enamels of the incense vessel K4195 ↘ Fig. 4.2.c are not consistent with an original medieval Limoges production. XRF results indicate a mixed alkali matrix with low CaO and the use of pure ingredients. About 20 wt% PbO and 5–8 wt% As_2O_3 in blue and turquoise enamels suggest the use of lead arsenate as the opacifier, confirmed by a strong Raman

Inventory No.	Description	Dating	Location
K 4184	Apostle (Paulus)	end 12th	Lower Saxony
K 4184 – 1967,14	Apostle	19th	(?)
W-1989,32	Nimbus	beginning 13th	Northern France
O-1973,186	Angel	1170	Köln (Rhenish)
K 4252	Ornamental hinge element	1200	Köln (Rhenish)
1996,42 a	Ornamental element	1230	Trier (Mosan)
W-1984,25 (K 4215 h)	Ornamental element (rosette)	1230	Trier (Mosan)
K 4195	Censer	13th	Limoges
F 2870	Cross base	19th / 20th	Limoges

↘ **Fig. 4.1**

↘ **Fig. 4.2**

↘ **Fig. 4.1** List of analysed artefacts

↘ **Fig. 4.2** Artefacts a) K 4252, b) O-1973,186, c) K 4195 and d) F 2870.

Acknowledgements

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signal at 830 cm^{-1} (Caggiani et al. 2014). Its presence is generally considered an indicator of *en style de Limoges* artefacts produced during the 19th-20th centuries [Biron et al. 1996, Biron 2015). However, the metal composition is consistent with a medieval artefact (Biron et al. 1996; England 1986). The object is probably a medieval artefact that underwent an extensive re-enamelling and a new amalgam gilding, a technique consistent with Middle Age products (Anheuser 1997) but used up to mid-19th (Arminjon and Bilimoff 1998).

The cross base F2870 ↘ Fig. 4.2.d, acquired by the museum as an original artefact of the mid 13th, was later assumed to be a modern product. However, according to the recent analyses, all the enamels are consistent with an early Limoges production pre 13th century. The enamels have a soda-lime composition with a mineral flux source and contain antimonate-based opacifiers, whereas the red has a plant soda-lime flux. The source of the cobalt used in the blue shades is associated to nickel and copper traces for both the medium and light blue, whereas in the dark blue it is associated to nickel and arsenic. Moreover, the calcium antimonate phase observed in all enamels is $Ca_2Sb_2O_7$ except for the dark blue, where only $Ca_2Sb_2O_6$ was observed, suggesting that a shorter heat treatment was undergone by the glass used to produce this enamel (Lahlil et al. 2010).

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Enamel-induced copper corrosion: A review of research in Stuttgart ↘

Andrea Fischer
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Introduction Due to their composition, a great number of historic glass (including enamel) objects are unstable. Alkaline liquid films on the glass surface may serve as an electrolyte, resulting in the corrosion of adjacent metals. The effect of formaldehyde, formic or acetic acid from indoor air leads to the formation of specific corrosion products.
This phenomenon, known as glass-induced metal corrosion, has been investigated at the State Academy of Art and Design since 2006. Initial studies describe damage to thirteen combined glass/metal objects, including three enamels (Eggert 2010). Alterations and characteristic corrosion products were detected on a 17th century game box with enamels and two early Limoges painted enamels. In 2012, the GIMME-Project (glass-induced metal-corrosion on museum exhibits) was set up to investigate in detail the occurrence and causes of this kind of corrosion. Up until 2015 more than 250 combined glass/metal objects were examined, including 52 enamelled copper and silver objects. Damage could be observed on numerous painted enamels from Limoges made in the fifteenth and sixteenth century, as well as on portrait miniatures made in the 17th and 18th century. Also affected were various champlevé enamels and early 20th century Japanese cloisonné vases (Fischer 2016). Since 2015, another 11 examples of damaged enamels have been added to our research project which show the high damage potential for enamels and the need for a preventive action.

Corrosion products Bright blue to green corrosion products are formed at the interface of enamel and copper alloys. Frequently the enamel surface shows clear signs of deterioration such as crizzling, small aqueous droplets, flaking, efflorescence, or pitting. The occurrence of various rare copper formates characterises the corrosion phenomenon. A sodium copper formate, $Cu_4Na_4O(HCOO)_8(OH)_2{\cdot}4H_2O$, could be identified on 43, a dicopper trihydroxide formate, $Cu_2(OH)_3HCOO$, on 33 of 66 sampled enamels. The sodium-containing copper formate was first detected by Trentelman et al. (2002) on archaeological bronzes and was characterised as sodium copper formate acetate. At the time it was not possible to determine the crystal structure. Sodium copper formate forms thin tabular micro-crystals with an edge length of only 1–2 µm, which excludes a structure determination from single crystals. Recently, X-ray powder diffractometry examinations (XRPD) were carried out in the context of our research at the Max Planck Institute for Solid State Research in Stuttgart. This allowed a structural determination of the compound (Fischer et al. 2017). In the last decade the potential of XRPD has increased substantially, due to a new generation of powder diffractometers and sophisticated data analysis. In the laboratory, the compound can be synthesized by storing chalconatronite, $Na_2 [Cu (CO_3)_2H] 3H_2O$, or copper coupons wetted with soda solution in a formaldehyde-rich atmosphere. Since no acetate group is present in the crystal lattice, the abbreviation “socoformacite” (sodium-copper-formate-acetate), introduced in 2008, is no longer used.

The occurrence of dicopper trihydroxide formate on joint glass/metal objects is described by Eggert et al. (2011), their crystal structure and formula were determined on synthesised single crystals. $Cu_2 (OH)_3HCOO$ is formed at pH values > 8, which can be produced by hydrolysis on historic glass surfaces. Regularly, both copper formate compounds occur side by side, which suggests that the formation conditions are similar.

In addition, the sodium copper carbonate chalconatronite was identified on three enamels and sodium copper acetate carbonate on two other.

Limoges painted enamels Evidence of active deterioration on Limoges enamel plaques causes great concern in many collections. The objects suffer severe damage due to developed crizzling, a moist surface, flaking, and efflorescence. Various studies have investigated the phenomenon in detail and have shown that transparent blue and purple areas of enamels made in the late 15th and early 16th century are at particular risk. Biron (1999) analysed the composition of these enamels and emphasised an increased content of alkali, consisting of a Na_2O content of more than 10 per cent in addition to a similar high K_2O level.

The exchange with colleagues of the ICOM-CC Enamel Network enabled us to investigate corrosion products from 25 Limoges enamels. The majority, samples of eight exhibits, were provided by the Frick Collection. The collection includes 46 Limoges enamels; 24 showed symptoms of unstable glass, as a survey in 2001 revealed (Day 2012). Further samples were made available by the Herzog Anton Ulrich-Museum Braunschweig, the Victoria and Albert Museum, the British Museum, the Rijksmuseum Amsterdam, the National Museum in Warsaw, the Focke Museum in Bremen, the Bavarian National Museum Munich, and the Museum of Applied Arts Berlin.

Corrosion on the enamel plaques had formed particularly in exposed areas of the copper substrate and along cracks in the enamel, where copper formates crystallise at the enamel surface. It was also observed in pits or areas of loss on the back of the plaques or in contact with gilt-brass mounts. Copper formates were found without exception on all Limoges enamels, the sodium-containing copper formate on 23 of 25 items. Areas of blue and purple enamels are indeed affected most frequently. However, metal corrosion also occurred adjacent to other colours such as brown-yellow or white. The majority of the plaques dated from the period from about 1480 to 1530, specified by Biron (1999) as endangered, unstable enamels. Glass-induced metal corrosion implies a high risk potential to painted enamels. Vivid examples are two enamels from the Herzog Anton Ulrich-Museum and another from the National Museum in Warsaw including paillons, silver foils which were frequently used and act as reflectors under transparent enamels. Sodium copper formate had formed between the enamel layer and the paillon. The crystal growth had caused the spalling of transparent enamel and the underlying bright silver surface became visible.

Italian Renaissance enamels Glass-induced metal corrosion was observed on an enamelled copper plate in the collection of the Austrian Museum of Applied Arts Vienna. The plate belongs to a group of so-called Venetian Renaissance enamelled copper objects, but according to latest research results it was most likely made in Florence in the first half of the 16th century (Verità et al. 2018). A sample of copper corrosion was obtained from the blue enamelled reverse side of the plate and identified as chalconatronite and a so far unknown copper-carboxylate. A similar Italian Renaissance plate at risk was investigated in the Bavarian National Museum Munich ↘ Fig. 14.1. The damage to this plate is huge. The corrosion covers large parts of the surface, blue enamel flakes of several millimetres have spalled in many places. Sodium copper formate, chalonatronite, and sodium copper acetate carbonate were identified.

Enamel miniature paintings Enamel portraits have been common since the 17th century. They were made as medallions, but also other small items such as vessels, snuffboxes, or watches were painted with colouring metal oxides on white enamel ground. Twelve objects from the Swiss National Museum, the Landesmuseum Württemberg, and the Schlossmuseum Ellwangen were examined. The enamel surface of some objects showed clear signs of glass degradation, others appeared only slightly dull. Frequently corrosion was observed where spalling of the enamel occurred, or on exposed edges of the copper plate. Some items were set within gilt-brass frames.

↘ Fig. 14.1

↘ **Fig. 14.1** Renaissance enamelled copper plate (R 116.1–2) showing glass-induced metal corrosion with the loss of enamel flakes (see arrows). Diameter 41.5 cm. ©Hans-Jörg Ranz, Bavarian National Museum Munich.

Copper formates were identified on all objects. The cause of the corrosion on snuff boxes with opaque white enamel could not be explained with certainty. According to a number of studies on the degradation of painted enamels, opaque white enamels are described as stable. The reason for this is a high lead oxide content, which we also identified in two opaque white enamels. The formation of sodium-containing corrosion products can also be caused by residues of cleaning agents used in previous treatments.

Japanese *Cloisonné* In preparation for the exhibition "Japanese *Cloisonné*, The Seven Treasures" at the Victoria and Albert Museum, the conservator in charge observed corrosion on various objects. She collected corrosion products from areas around wires and provided samples from fourteen items for analysis. Another sample was obtained from the National Museum in Warsaw. The enamels were made in the early 20th century, the golden age of Japanese *cloisonné*. Dicopper trihydroxide formate was detected on all cloisonné pieces. The absence of sodium copper formate can be explained by the use of potassium-containing fluxes.

Conclusion Our research revealed several kinds of enamels that are most frequently affected, although the risk potential due to glass-induced metal corrosion varies from case to case. The crystal growth of copper corrosion products can cause the spalling of enamel layers. Early Limoges painted enamels, which are noted for their unstable glass composition, are particularly at risk. By comparison, the risk to other combined glass/metal objects like glass vessels with metal mountings, reliquaries with glass gems or daguerreotypes with cover glasses, seems less substantial, because the damage is not obviously associated with loss of material.
The compounds that occur most often on enamels are copper formates. In cooperation with the Max-Planck-Institute for Solid State Research in Stuttgart it was possible to determine the crystal structure of a sodium-containing copper formate, which was detected on two-thirds of the enamels under investigation. In addition to formates, carbonates were occasionally found.
A significant impact on the damage due to glass-induced metal corrosion is related to the storage of enamels in show cases, cabinets, or shelving systems made of wood or wood composites, as they are exposed to pollutants over long periods of time. Copper joined to unstable enamel behaves like a dosimeter, which indicates air pollutants shown by the formation of corrosion products. In order to identify a potential risk at an early stage, it would be possible to exhibit enamelled copper test specimens in showcases,

using highly unstable enamel. This approach could contribute to the establishment of binding quality standards regarding preventive preservation.

Acknowledgements

This research would not have been possible without the support of a large number of colleagues and the cooperation of numerous museums who allowed access to collections and made samples available for analyses. The GIMME-Project was funded by the Friede Springer Stiftung and is published in full in the PhD thesis of Fischer (2016). The German Federal Environmental Foundation promotes our ongoing research.

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A rare 12th century enamelled *phylacterion* from Mainz: a short note on its manufacture ↘

Matthias Heinzel
Marlène Aubin,
Stephan Patscher
Dorothee Kemper

Context of the find The pendant was excavated in the old town of Mainz during a campaign from June 2008 to April 2009 in the courtyard of the “Jüngerer Dalberger Hof” (1718). Prior to that building the manorhouse of the family “Brendel von Homburg” existed on this site. On the 9th of October, 2008, the pendant was found in an ancient dump.

Restoration The restoration and conservation was performed in the laboratory of the Generaldirektion Kulturelles Erbe (GDKE), Direktion Landesarchäologie Mainz.
It was entirely covered with a thick layer of corrosion products. Nevertheless the quatrefoil shape of the object was already recognisable before restoration. ↘ Fig. 5.1.1
A radiograph of the pendant was performed in the RGZM. The X-rays revealed the exact shape of the quatrefoil and some figural representations.
↘ Fig. 5.1.2. The burial in a corrosive environment lead to very thick and strong corrosion layers.
The copper corrosion products were removed mechanically with diamond tip grinding tools and fine mechanical tools. During the process the original surface with enamel and gilded copper appeared. A very careful preparation was essential. During the conservation, small parts had to be stabilised with epoxy resin Araldit 20/20 due to the very fragile condition of all materials.
After restoration, the pendant measures 57 mm in length and width, 11–12 mm in height, with a total mass of 70.5 g. In total, the conservation work on the pendant took 500 hours.

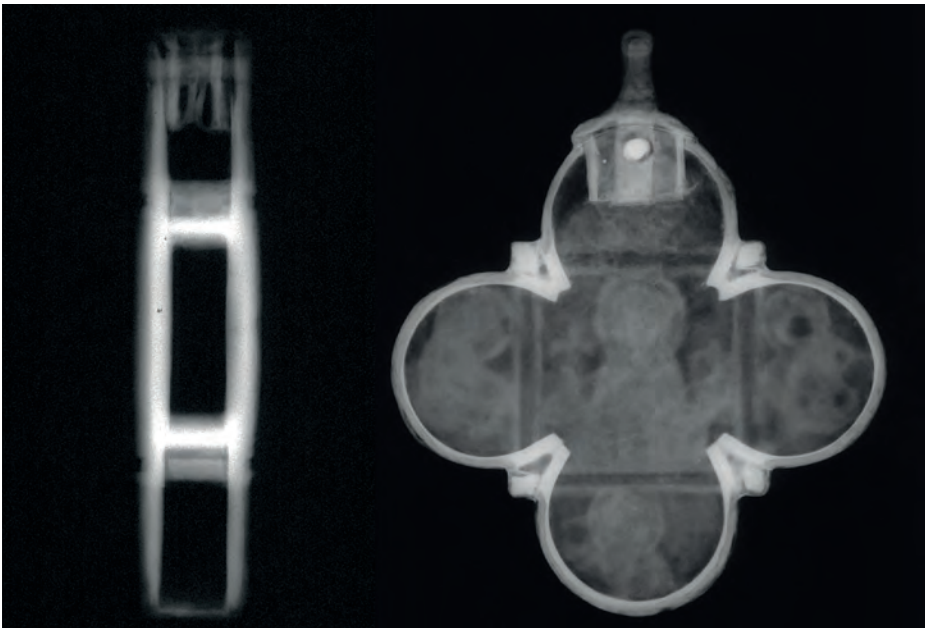
Description The *phylacterion* (reliquary) is made of gilded copper. Front and verso are enamelled using the technique of *émail champlevé*. All figures carry a nimbus and are partially gilded. The background, the inner area of the nimbus and the frame of the central characters are enamelled. ↘ Fig. 5.2

Iconography and Form On the front, the central squared enamel represents Christ holding a cross in his right hand. In his left hand he is holding an object,

↘ **Fig. 5.1.1**

↘ **Fig. 5.1.1** Pendant before restoration with thick layers of corrosion products. ©RGZM.

↘ **Fig. 5.1.2** Radiograph, side and front view. ©RGZM.



↘ **Fig. 5.1.2**

which in analogy to other representations, could be identified as a book, despite the damaged surface. Four semicircle fields frame the central square. They show the symbols of the four evangelists in their typical zoomorphic shapes.

On the verso, the central square shows a female person holding a book in her left hand. In analogy to other *phylacteria* of this type, the figure can be identified as Mary. In each of the four surrounding semicircle fields is a female bust, possibly representing virtues or saints ↘ Fig. 5.2

Analysis Chemical analyses were performed on this artefact to reveal the materials used. The elemental analysis was done using µ-X-ray Fluorescence with the following results (in weight %): Substrate metal: Copper Cu 99.2 % / Pb 0.4 % / Ag 0.2 % / Sn 0.2 %

Gilding: mercury gilding approximately Au 83 % / Hg 17 %

On this artefact, there are three enamel colours, all opaque, white, blue and green. They are used for the background of the saints, their nimbus and the square frame. The enamels were analysed by Raman spectroscopy to identify glass type and pigments and µ-XRF.

White enamel The white enamel is made from a soda glass containing a high concentration of antimony. Raman spectroscopy revealed the white pigment is composed of calcium antimonate (mainly $Ca_2Sb_2O_7$ with traces of $CaSb_2O_6$).

Blue enamel The blue enamel is also made out of soda glass. The colour of the transparent blue glass is mainly due to the presence of cobalt. It contains calcium antimonate ($Ca_2Sb_2O_7$ and $CaSb_2O_6$) as a white opacifier.

Green enamel The green enamel is made out of a blue transparent glass coloured by copper ions. It contains lead antimonate, so-called Naples yellow ($Pb_2Sb_2O_7$/$PbSb_2O_6$). This yellow pigment is also responsible for the opaque appearance of the green enamel. As with the other enamels, a soda glass was used as glass matrix.

Manufacturing technique The pendant consists of a base and an upper copper sheet. The frame is composed of four nearly circular segments. ↘ Fig. 5.1.2

At the intersections of each petal, a rhombic peg creates the corners of the central square frame. All parts are soldered together forming the quatrefoil shape. The upper nearly circular segment is cut open in order to insert the

closing part, which is also gilded. This separate part is composed of a folded metal strip, a lid to close the aperture and one strong loop at the top. Finally, a rivet attaches it to the main part. Even the decoration takes this into account: the upper figures are tilted to one side to give place to the closing system ↘ Fig. 5.1.2.
Base and top sheets are enamelled using the technique of *émail champlevé* and the figural decoration and outlines are gilded. The side section with cross-hatched decoration is also gilded. The high concentration of mercury revealed by μ-XRF indicates that mercury gilding was used.

Conclusion This artefact was produced with the aim to contain small relics, even if there is no opening left after mounting. Considering the religious decoration, it probably held a sacred relic, which could be confirmed by the cut open part of the upper nearly circular segment. The presence of this closing mechanism clearly indicates, that the object was constructed with the intention to contain valuable relics. No object could be seen in the interior on radiographs but neutron imaging could be performed and reveal new information on this artefact.
This quatrefoil pendant is dated to the last third of the 12th century and was very probably made in Hildesheim. This results from the general form and characteristics, which occur quite similarly in other objects of this type, today in Halberstadt, Boston and Rome.
This object is one of only four phylacteria known of this type from the Hildesheim workshop today. Once belonging to a cleric for private use, it is proof of the expansion of products coming from Lower Saxony, this can be assumed as it has been found in its historic context. It is a rare example of such an object from controlled excavations.

Analytical details μ-XRF: Eagle III spectrometer (Röntgenanalytik, Taunusstein), rhodium source, maximal power at 40 kV and 1 mA, beam diameter 0.3 mm, Vacuum, the surface was analysed in a cleaned condition, but without further surface preparation.
Raman spectroscopy: LabRam HR800 (Horiba Jobin Yvon company), laser 532 nm, 1800 lines/mm grating, 50× long focal lens objective.

↘ **Fig. 5.2**

↘ **Fig. 5.2** Left: Front of the pendant with Christ and the four evangelists, after conservation.
Centre: Side of the pendant with gilded cross-hatched decoration.
Right: Verso of the pendant with Mary and four virtues or saints.
© RGZM.

Rentrer bredouille – manufacturing technique of 30 enamelled gaming pieces ↘ Lena Hönig

Introduction In 2017, an extraordinary total set of 30 backgammon gaming pieces ↘ Fig. 6.1 were subject to a conservation and research project, which is still in progress. Each gaming piece is composed of three parts: two decorated copper plates and a frame with a height of about 14 mm. The front and the back consist of round copper plates decorated with a surface relief mainly made of light blue and white molten glass, additionally in green, yellow, black, and gold. Medals, made by different medallists over the course of several centuries, were taken as templates. Fifteen of enamelled copper plates are framed with ivory and the other fifteen with ebony.

Object history The game set in the collection of the Germanisches Nationalmuseum in Nuremberg dates back to 1709 or later. The set it attributed to Christian Wermuth, the court medallist of Saxe-Gotha. The gaming pieces are not only elaborately created, but also absolutely unique.

Manufacturing technique Every gaming piece is constructed in a multilayered way ↘ Fig. 6.2. The copper plates are coated double-sided with a rough impure enamel layer. Additionally, the front is covered by a thin light blue enamel layer. On top of this layer lies the cameo-like white glass depicting scenes from the medals. This can surely be seen as a non-conventional enamel technique. The junction of the white and blue molten glass ↘ Fig. 6.2. indicates that fine frit was filled into a negative form and molten afterwards in the furnace similar to the nowadays *pate-de-verre*.
The X-ray images of seven different gaming pieces show even circular dark areas, which are similarly arranged on every plate ↘ Fig. 6.3. After dismantling some of the gaming pieces it became clear that these dark areas are rear indentations in the enamel on the reverse ↘ Fig. 6.4. Up to now it was presumed that they are the effect of a support system used during the firing process in the kiln (a support possibly made out of seven tubes).
Both enamelled copper plates of the first and the second gaming piece show a curious phenomenon: along the represented motif another partially flat “overprinted” medal pattern is visible ↘ Fig. 6.5. This might originate from the molded medal or from the embossed stamp or from the negative form in which the glass frit was filled (re-used material).

The golden area is of special interest. It is made out of a thicker gold foil or a thin gold sheet. The gold foil was punched or embossed in the shape of the template, put into the negative form and covered with the glass frit ↘ Fig. 6.6. During the firing process it was embedded into the glass, with the result that the borders of the gold foil were partially covered with molten glass from the front side.

The investigation of the gaming pieces leave many questions unanswered:

- How many firing processes were necessary to make the different enamel layers?
- What temperatures were necessary for the individual firing processes?
- What caused the circular recesses?
- How was the negative form made?
- How did the "overprints" come about?
- How was the gold foil embedded?
- Why did they use this gilding technique instead of a subsequent leaf gilding?
- Do similar objects exist?

The author aims to deal with these questions as part of her scheduled master thesis.

Acknowledgements

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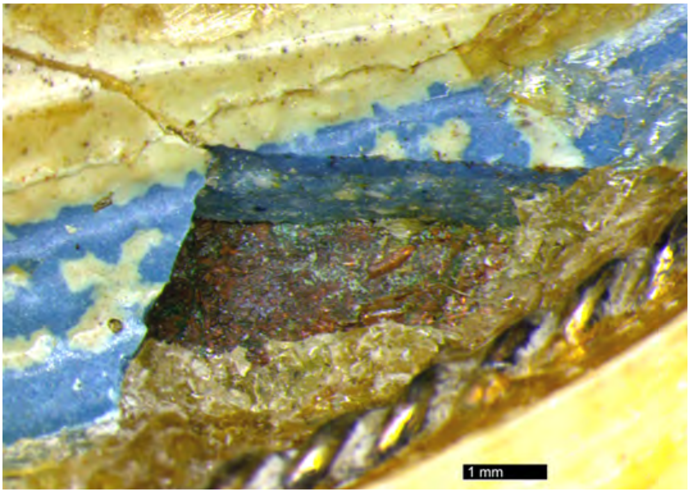
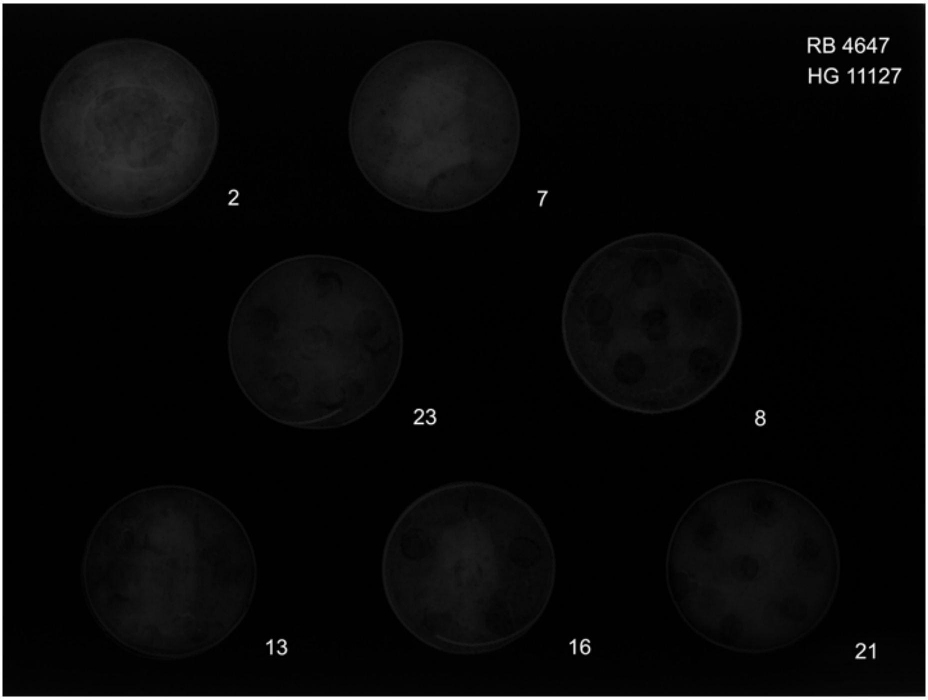
↘ **Fig. 6.1**



↘ **Fig. 6.2**



↘ **Fig. 6.3**

↘ **Fig. 6.1** The set of 30 gaming pieces (HG 11128) in the collection of the Germanisches Nationalmuseum, front sides. © Lena Hönig, GNM [IKK].

↘ **Fig. 6.2** Enamel layers visible on a outburst on HG 11127.18 (front side): On the copper plate, the counter enamel, the thin light blue enamel layer and the cameo-like white glass are applied. © Lena Hönig, GNM [IKK].

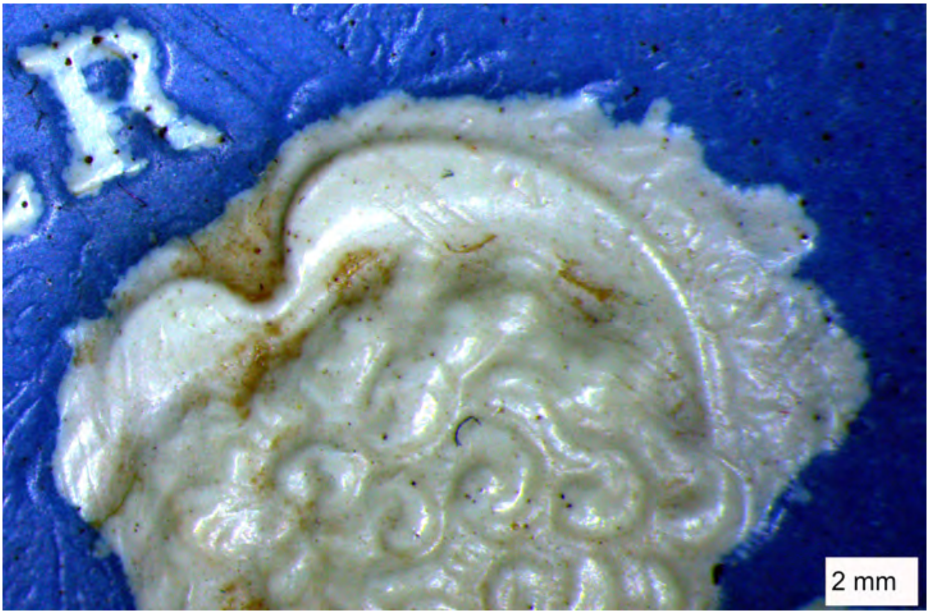
↘ **Fig. 6.3** The X-ray image shows the seven circular recesses on seven different gaming pieces. © Lena Hönig, GNM [IKK].

↘ Fig. 6.4

↘ **Fig. 6.4** Reverse of the enamelled copper plate of HG 11127.15 shows the seven circular recesses as an imprint in the counter enamel. © Lena Hönig, GNM [IKK].

↘ **Fig. 6.5** Flat second medal depiction "overprinted" above HG 11127.02, front side. © Lena Hönig, GNM [IKK].

↘ **Fig. 6.6** Leaf gilded crown of Queen Anna (HG 11127.04), front side. © Lena Hönig, GNM [IKK].



↘ **Fig. 6.5**

↘ **Fig. 6.6**

Conservation of enamelled ware from the collections of Auschwitz-Birkenau State Museum in Oswiecim

↘ Andrzej Jastrzębiowski

The Auschwitz Memorial consists of more than extensive grounds and original camp blocks, barracks, and guard towers. It also contains tens of thousands of objects of a very particular nature, meaning, and symbolism. These are mainly personal belongings of the people who were sent to the camp, found after the liberation of the camp. They make up a unique collection of items connected with the suffering of the people deported to Auschwitz for immediate execution, and with those forced into slave labour by the Germans.

In this collection there are around two hundred thousand items of common everyday use, among which are several thousand mainly enamelled pots, dishes, cups, pans, and other utensils.

The current shape and condition show their story. Traces of the history of these objects can be found in every scratch and dent, and which are evidence of the tragic history of humankind where the objects are the only proof of existence. These objects are interesting also from another point of view. Bearing in mind the scale of the deportation of Jews in the 3rd Reich occupied Europe, the enamelled ware are a significant collection of objects of everyday use from the European household.

During routine inspection of the permanent exhibition as well as part of an upgrade of the exhibition room in 2015, the condition of the objects was reassessed. Furthermore, light cleaning from dust and dirt was also carried out. The poor conditions of some of the objects meant that these had to be removed from exhibition.

Enamelled ware as a part of collections of Auschwitz-Birkenau State Museum were preserved in the 1970's. Surfaces were coated with a protective coating (PVAL). Due to the coating enamelled ware appears well preserved, but the coverings after 40 years of light and humidity exposure changed its colour, cracked, and started to peel off because of its degradation. It currently requires a new coating. Over twelve thousand objects require a renewal of the coating.

Besides the vast amount of objects, their condition is also an issue. Most of them are deformed which have caused the enamel layer to fracture and in some cases to loosen from the metal substrate, causing subsequent losses.

↘ **Fig. 7.1**

↘ **Fig. 7.1** Enamelware from the collection of Auschwitz-Birkenau State Museum. © Hanna Kubik.

↘ **Fig. 7.2**

↘ **Fig. 7.3**

↘ **Fig. 7.2** Condition of an enamel pot, removed from exhibition. © Andrzej Jastrzębiowski.

↘ **Fig. 7.3** Detail of an enamel pot. © Andrzej Jastrzębiowski.

Quite often, the only binding material which glues enamel to the surface of the ware is a layer of the protective coating from the 70's. Another common type of damage to the museum objects are mechanical, which have caused the enamel to splinter.
The main task for conservators working in Auschwitz-Birkenau State Museum is to preserve their objects in a state closest to the state they were at the moment of Camp Liberation. These objects are as important as written documents because both bear witness of the history. This is why it is crucial to keep every trace of history on an individual object even if it is only dirt and rust. It is a huge challenge to minimise ongoing degradation of an object and at the same time minimise conservation interference.
The complexity of conservation of such objects will be exemplified based on the maintenance of a few enamelled ware samples.

Reinventing Tradition – June Schwarcz's Early Explorations of *Basse-taille* ↘

Bernard N. Jazzar
Harold B. Nelson

June Schwarcz (1918 – 2015) was among the most innovative artists working in the late 20th-century enamels field. Celebrated early in her career for her inventive approach to *basse-taille*, Schwarcz later pioneered the use of electroplating to create sculptural forms in metal that she embellished with rich enamel colour. Throughout a career spanning sixty years, Schwarcz produced a multifaceted body of work which, while referring to time-honoured vessel-making traditions, defied convention because, as she wryly noted, "they simply don't hold water."

Trained in three-dimensional design at the Pratt Institute in Brooklyn, she was introduced to enamelling in 1954 through friends in Denver. In her groundbreaking work of the 1950s, Schwarcz introduced a modernist aesthetic to enamelling. Her unorthodox approach to *basse-taille,* in particular, as well as her use of an abstract visual vocabulary formulated a radical break from tradition and established her reputation as an emerging leader in the field.

In much of her earliest work, especially those pieces made between 1954 and 1962, Schwarcz focused her efforts on *basse-taille.* With unbridled enthusiasm for this technique, she cut, gouged, scraped, and etched the surface of her copper plates, plaques, and bowls to create complex, compositions in metal visible through layers of transparent glass.

Much of the work Schwarcz produced during this period foreshadows her lifelong interest in landscape and nature. Inspired by the landscape surrounding her homes in Connecticut, La Jolla, and Sausalito, she produced compositions in enamel which were, at times, closely observed and detailed and, at times, abstract, expansive and all-encompassing.

Among the earliest of these compositions, *The Barn* (#327) ↘ Fig. 8.1 was produced when Schwarcz was living in Connecticut in the mid 1950s. Somewhat unusual in Schwarcz's overall body of work because of its detailed depiction of a particular place, it was inspired by an old wooden shed on her property. Though this work depicts the façade of a specific building, its vivid non-descrip-tive color and underlying rectilinear structure underscore Schwarcz's early commitment to a formalist aesthetic.

↘ **Fig. 8.1**

↘ **Fig. 8.2**

↘ **Fig. 8.1** *Barn* (#327), 1956 Etched copper and enamel, 22 x 30 cm. © M. Lee Fatherree

↘ **Fig. 8.2** *Wood Grain* (#302), 1957, Etched copper and enamel, 31 x 18 cm. © M. Lee Fatherree

↘ **Fig. 8.3** *Bowl* (#316), 1957, Etched copper and enamel, 2.5 x 13 x 31 cm. © M. Lee Fatherree

↘ **Fig. 8.3**

↘ **Fig. 8.4** *Paracas Bowl* (#323), 1958, Etched copper and enamel, 7 x 24 cm. © M. Lee Fatherree

↘ **Fig. 8.5** *Nut Bowl II (#332), 1959, Etched copper and enamel, 6 x 30 x 24 cm. © M. Lee Fatherree*

↘ **Fig. 8.4**

↘ **Fig. 8.5**

Another early work that reflect Schwarcz's interest in nature is *Wood Grain* (#302) of 1957 ↘ Fig. 8.2 in which the subject of the composition is, as its title suggests, the complex, linear patterns she saw in a simple piece of wood. In this work, Schwarcz observes the natural world from a more intimate perspective, recording the wood's rich figure and markings. This piece is among the first in which she placed a *basse-taille* panel in a mount made from a contrasting material – in this case Plexiglas.

Three works Schwarcz produced in the late 1950s exemplify her increasingly inventive approach to basse-taille and her growing commitment to abstraction. Two of the pieces also demonstrate her use of ethnographic materials as inspiration. *Bowl* (#316) of 1957 ↘ Fig. 8.3 is vividly coloured in hues of gold, copper, pale blue, and black. It's shield-like shape and its roughly symmetrical, geometric decoration bring to mind examples of the tribal art that so fascinated Schwarcz throughout her life.

Paracas Bowl (#323) made in 1958 ↘ Fig. 8.4 similarly reflects Schwarcz's interest in the art of indigenous people, in this case the Paracas culture that flourished in the Andes between 800 and 100 BCE. A great admirer of Peruvian textiles, Schwarcz etched the exterior of this hand-raised and chased bowl using motifs inspired by a pattern from a pre-Incaic design. She then applied green enamel, resulting in a rich, deep, and iridescent surface that provides a sharp contrast to the bowl's warm interior.

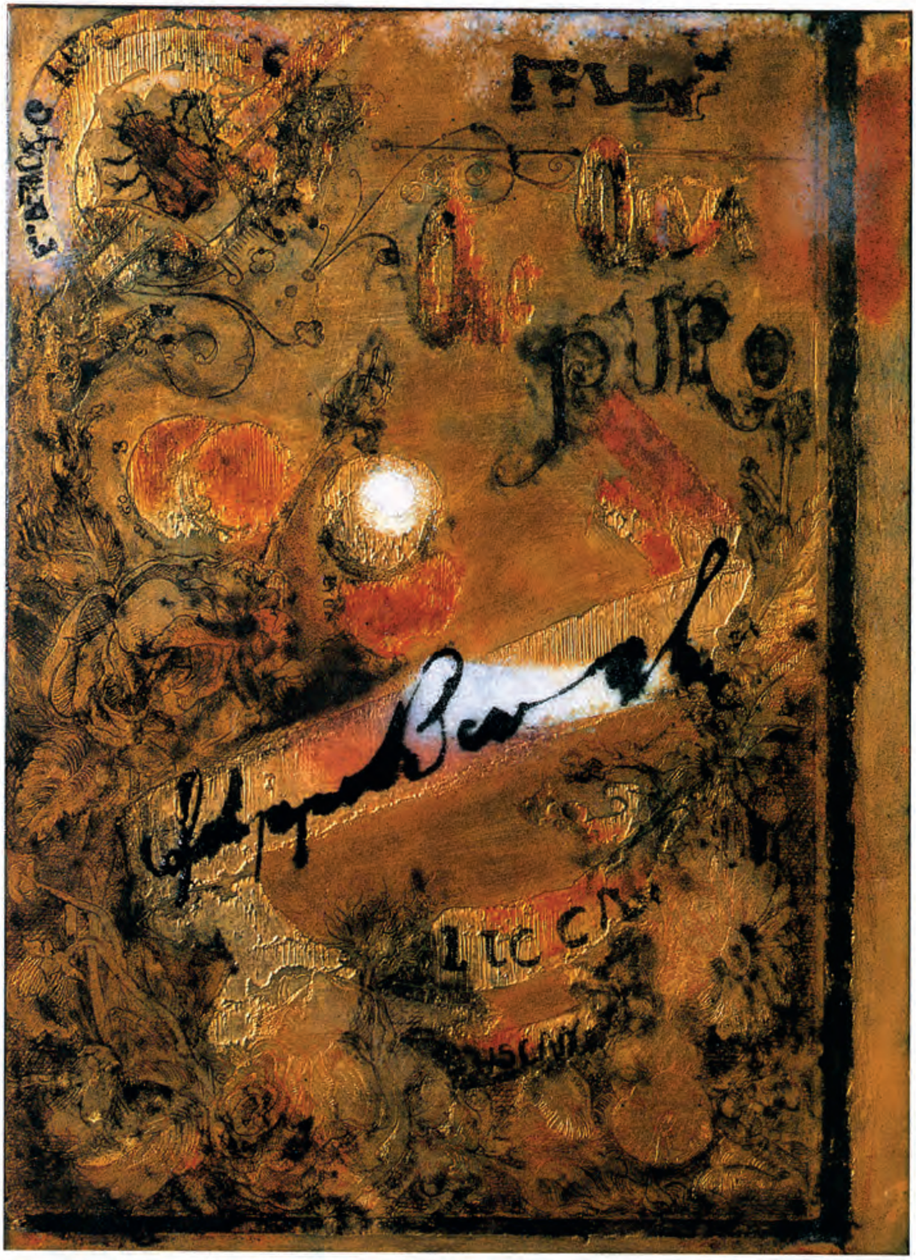
Her more abstract *basse-taille* composition *Nut Bowl II* (#332) ↘ Fig. 8.5 was commissioned by the Museum of Contemporary Crafts (now known at the Museum of Arts and Design) in connection with their 1959 exhibition Enamels. Schwarcz was one of nine artists invited to create a unique piece using one of the traditional enamelling techniques. While inspired by the inner shell of a walnut, this composition is loose and gestural, and it represents the artist's increasing commitment to a non-referential vocabulary.

Ever since childhood Schwarcz had been fascinated with words – their expressive potential as well as their ability to communicate ideas. She was equally intrigued with how verbal signs and symbols appear on the page. As a reflection of these interests, in the late 1950s Schwarcz began to incorporate words and calligraphic markings in her *basse-taille* compositions.

In *Paracas Bowl* (#323) Schwarcz created signs and symbols in the body of her vessel using an acid etching process. However, in subsequent works she used both etching and the application of opaque enamel to create a layered mix of words and visual imagery. *Tribute to Filippo Berio* (#338) of 1959 ↘ Fig. 8.6 was among the first of Schwarcz's *basse-taille* compositions to combine techniques in this way. Inspired by a metal container for a popular brand of olive oil that appealed to her because of its "ornateness," Schwarcz extracted various marks and images from her source, etching some in the metal plate and inscribing others in opaque black enamel. She subsequently placed this very special composition on a white marble mount.

While Schwarcz used *basse-taille* primarily for vessels, she also produced luminous compositions on two-dimensional panels that she then framed and mounted on the wall. *Mountain Landscape* (#704), made in 1977 ↘ Fig. 8.7 is representative of this type. With its upward-soaring vertical masses brought to life through light shimmering across an intricately etched surface – further enriched through the addition of lines produced through an electroplating process – Mountain Landscape is reminiscent of Chinese landscape paintings of the Sung Dynasty of which Schwarcz, with her abiding passion for all aspects of Asian art, was undoubtedly aware.

As with everything she produced, June Schwarcz's early work in *basse-taille* was improvisatory and highly experimental. In a field known for visual opulence, preciousness, and adherence to traditional craft practices, Schwarcz was a rule breaker, a renegade. Learning enamelling on her own, she adopted an idiosyncratic approach to process, devising both new ways of creating unique forms in metal and new strategies for their embellishment. In her tireless commitment to experimentation, she was a model to young and emerging artists, helping to formulate a new direction for the late 20th-century enamels field.



↘ **Fig. 8.6**

↘ **Fig. 8.6** *Tribute to Filippo Berio* (#338), 1959,Etched copper and enamel, mounted on marble, 29 x 22 cm. © M. Lee Fatherree

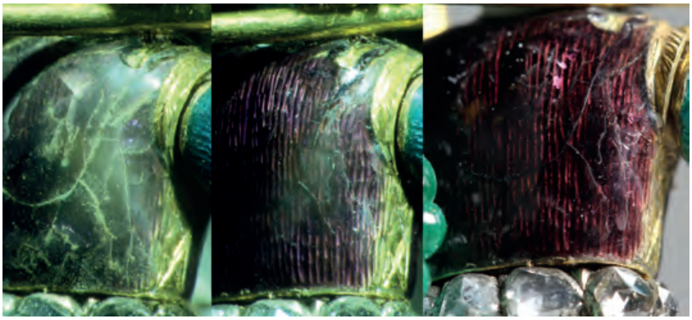
↘ **Fig. 8.7**

↘ **Fig. 8.7** *Mountain Landscape* (#704), 1977
Etched copper, fused electroplated copper, and enamel, 26 x 19 cm.
© M. Lee Fatherree

Research project on new consolidants for enamels based on Ormocers: evaluation of case studies from the Green Vault ↘ Katharina Klein

In conservation practice, the consolidation of structurally severely damaged materials is often required for the preservation of the original substance. Interventive measures of this kind have to be classified as practically irreversible. Therefore, the long-term stability of the treatment has to be ensured by means of a non-ageing, extremely long lasting consolidant. These and other requirements turn the choice of a suitable consolidation agent into a challenging task. At present, current stabilisers, such as acrylic or epoxy resins, are not ideal means for the preservation of glass or enamel materials due to a number of disadvantages. In this context, the ORganically MOdified CERamics (= Ormocer), developed by Fraunhofer ISC in the early 1990s, moved into the focal interest of the field of glass and enamel conservation due to its promising stability and glass-like structure .

In two consecutive interdisciplinary research projects, the Federal Institute for Materials Research and Testing in Berlin (BAM), the Fraunhofer Institute for Silicate Research in Würzburg (ISC) and the Green Vault of Dresden's State Art Collections (SKD) developed a model preservation concept for the severely damaged enamels of the Dresdner Schatzkammer. This project was substantially funded by the German Federal Foundation for the Environment (DBU). An important result of this work was the development of a specific enamel consolidant from a combination of the two already existing hybrid polymers, the Glass- and Bronze-Ormocer (= Enamel-Ormocer = OR-G50 + OR-B30). In addition to interventive treatments, the prevention of environmentally induced deterioration of the enamels came increasingly into the focus of attention. Corrosion phenomena and flaking of enamels had been considerably aggravated by the fluctuation of the humidity level and the presence of indoor pollutants. The long-term success of consolidation measures is entirely dependent on a proper preventive conservation strategy. This research objective was achieved by the model development of a climate- and pollution-controlled showcase, as an important basis for the preventive conservation measures for the consolidated enamel.
The reopening of the New Green Vault in 2004 provided the opportunity to



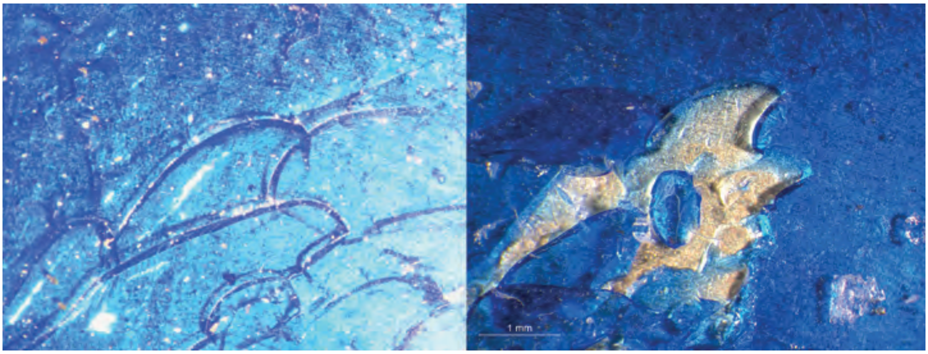
↘ **Fig. 15.1**

↘ **Fig. 15.2**

↘ **Fig. 15.1** Joshua and Caleb with the grape. Back of the figure before the consolidation 2001, after the consolidation 2001 and the condition 2017 (left to right)

↘ **Fig. 15.2** White elephant. Court of the Grand-Mogul. Condition after cleaning 2017

↘ **Fig. 15.3** Model enamel. Not consolidated. Condition (x25) 1999 and 2017



↘ **Fig. 15.3**

redesign the exhibition wand storerooms in accordance with conservation requirements.

My Master's thesis, written between April and August 2017 evaluates in an exemplary manner the practical implementation of the model conservation concept which was largely completed in 2004. This can be used to gain extraordinarily valuable first long-term experience on the measures taken some 13 to 18 years ago. For this purpose, the current state of preservation was recorded macro- and microscopically by means of a representative selection of the model enamels created and consolidated for test purposes in 1999, as well as of treated enamel objects from the collection. These observations were compared as far as possible with written and pictorial documentations filed in previous years. In general, it can be said that the improved environmental situation in the Green Vault has proved to be crucial and very beneficial. The original enamels are mostly in a stable condition.

New losses on the examined objects could not be detected. This applies in particular to showcases with purely inorganic objects on display, in which a slightly lower relative humidity (45%) prevails. A somewhat different picture was offered by the enamel samples (model enamels), which were stored in closed containers in the conservation studio of the Green Vault over the years. This microclimate as well as the slightly higher relative humidity (50%) showed the enormous influence of the storage conditions for the preservation of the objects.

A further focus was the current research project of the Green Vault with the Fraunhofer ISC: the lack of a strict quality-control for the synthesis process of the Ormocer mixture and, above all, the observed deficiencies in the performance of the consolidation agent led to a provisional delivery stop in 2012. Since the middle of 2015, the new research project has been working on a quality tested and reproducible method for the synthesis of the Ormocer-consolidant. This also includes optimising the choice of the used solvents. Based on previous research projects, the properties of the new Ormocer were examined from the user's point of view. Preliminary applications were carried out on model enamels so that a first laboratory evaluation by conservators was carried out within the framework of the master's thesis.

The new test series with the Enamel-Ormocer have highlighted the enormous influence of the solvents. The quality fluctuations observed over the years resulted, partly from previously unknown problems with the use of methyl ethyl ketone as a solvent. The stepwise approach to meet the requirements with the given possible variations was very time consuming and characterised by a close cooperation with the Fraunhofer ISC. The experimentally determined properties of the Enamel-Ormocer so far satisfy the expectations towards a consolidation agent but will be further checked in the ongoing research project. The requirement of infiltration capability, even with very fine crack structures, is fulfilled.

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Shades of grey: Issues in dating *grisaille* Limoges painted enamels in the collection of the Harvard Art Museums ↘

Elizabeth La Duc
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Eva Helfenstein

Introduction Among its encyclopaedic collection, the Harvard Art Museums hold a small but choice group of 16 Limoges-style painted enamels thought to date from the 16th century. The enamels were the recent subject of compositional analysis and technical examination which led to a re-assessment of the dating for several objects when compared to studies by Biron (2015), Röhrs and Stege (2004), and Wypyski (2004).

Background Perhaps owing to its small size, the painted enamels collection has received relatively little attention either from within the museum or from the outside community of enamel specialists. Thus, a plate depicting the labours of the month, from a well-known set bearing the "De Forti Dulcedo" motto, could be found "hiding in plain sight", missed by recent publications (Notin 2002, Descheemaeker 2012) but present in the museum's collection since 1943. Although the entire corpus of enamels was studied in this project, this paper will focus on the grisaille enamels within the collection, and the polychrome enamels will be presented separately at a later time.

Analytical methods: XRF and X-radiography The objects were analysed by X-ray fluorescence (XRF) spectroscopy and X-radiography. X-ray fluorescence spectra were collected using a Bruker Artax energy dispersive X-ray spectrometer. The excitation source was a Molybdenum (Mo) target X-ray tube with a 0.2 mm thick beryllium (Be) window, operated at 50 kV and 600 µA current. The X-ray beam was directed at the artefact through a masked aperture of 0.70 mm in diameter. Helium purging was used to enhance sensitivity to light elements. Spectral interpretation was performed using the Artax Control software.

X-radiographs were taken using a Comet MXR-320/26 X-ray tube, with a 3.0 mm focal spot size and a 3.0 mm copper filter, and an Industrex HR computed radiography flexible plate, which was scanned with a Carestream

HPX-1 system. The objects were exposed at 260 – 320kV and 4.65 – 5 mA, for 30 – 60 seconds. Lead screens were placed in front of and behind the plate to prevent back scatter. Industrex EDGE filter "display 6" was applied to the X-radiographs.

Case studies *Plate depicting the Harvest* from a set of the months (1943.1305) A calendar plate, initialed "P·R", was attributed to the prolific enameller Pierre Reymond. The plate, painted in grisaille with flesh tones and gilding, bears a crest and the motto "De Forti Dulcedo". New art historical research connected it to a set of calendar plates with the same emblem (Notin 2002). Nine of the set were sold from the collection of the Duke of Marlborough in 1883; Harvard's plate would appear to be the missing August plate, showing the harvest and the sign of Scorpio. There seems to be no question about the attribution of the set to Pierre Reymond, who counted calendar plates among his specialties (Notin 2002). Two of the plates from the set bear the date 1565 (Notin 2002, Descheemaeker 2012).
Compositional analysis corroborates a mid-16th century date: the transparent black enamel background is a low lead enamel coloured with manganese and iron, and the white enamel is opacified with tin oxide.

Plaques of *Apollo Slaying Coronis* and *Chiron and Ocyrhoe* (1950.87.A-B)
These two small plaques were dated to 1530 – 1570 and attributed to an unidentified artist ↘ Fig. 16.1. The scenes, painted in grisaille with gilding, are taken from woodcuts by Bernard Salomon used to illustrate Ovid's *Metamorphoses* (Lyon 1557).
While woodcuts by Salomon are known to have been used as sources by enamellers in Limoges (Baratte 2000), these plaques have technical and stylistic issues which raise questions about their dating. There is no pink or red toning of flesh areas, as is commonly seen on grisaille enamels (Speel 2008). The gilding is not applied as typical, discrete lines of highlighting, but rather as a thin wash, creating golden clouds in the background. Furthermore, in some places the gilding is topped by additional white enamel. In typical 16th century Limoges practice, gilding was the last step applied before a final firing at a lower temperature (Röhrs, Biron, and Stege 2009). Finally, the signature on one of the plaques (1950.87.B), "LB" in the lower right corner, is also unusual: it was made in the *sgrafitto* technique, with the white enamel scraped away to form the letters, instead of the more common method of being painted in black enamel or gilding.
Compositional analysis also indicates a 19th century date: the enamel has low

↘ **Fig. 16.1**

↘ **Fig. 16.3**

↘ **Fig. 16.1** Plaque of *Chiron and Ocyrhoe* (Harvard Art Museums © President and Fellows of Harvard College).

↘ **Fig. 16.2** Vase with scenes of galloping horsemen (Straus Center for Conservation © President and Fellows of Harvard College).

↘ **Fig. 16.3** X-radiograph of vase with scenes of galloping horsemen (Straus Center for Conservation © President and Fellows of Harvard College).

↘ **Fig. 16.2**

calcium and high lead, and the white enamel is opacified with lead arsenate, used only from the 18th century onwards (Röhrs and Stege 2004).

Cup and saucer (1931.110.A-B) The cup and saucer, painted in *grisaille* with flesh toning and gilding, were ascribed to an unidentified artist from the 17th century. The cup originally had a handle on one side, as indicated by holes in the enamel. Again, the shape is atypical for the 16th or 17th century. In fact, the closest parallel is a pair of demitasse cup and saucers, made circa 1865 by Jean-Baptiste-César Philipp, who worked at Sèvres (illustrated in Speel 2008).

Compositional analysis strongly suggests a 19th century date: the transparent black background enamel is high in lead, with manganese, iron, and copper present as colourants. However, unlike the plaques, the traditional tin oxide is used as the opacifier for the white enamel rather than the later lead arsenate.

Pair of vases with scenes of galloping horsemen (1957.215.A-B) These pair of small vases, painted in *grisaille* with flesh toning and gilding, were dated to the 16th century and attributed to Jean Courteys ↘ Fig. 16.2. However, study of these vases suggests the dating may not be clear cut.

The shape of the vases is unusual, with the closest parallel being a much larger vase in the collection of the Victoria and Albert Museum (c.2443–1910). In addition, the interiors of the vases are coated in translucent colorless enamel, not the usual opaque white.

The pair originates from the collection of Frédéric Spitzer, as shown by a paper label from the 1893 sale of his collection adhered to the bottom of one of the vases. Spitzer was a prominent dealer of Renaissance art who is now known to have worked with talented artisans to create forgeries of Renaissance enamelled jewelry and Limoges painted enamels (Speel 2008). Thus the provenance of the vases adds to doubts to their origins.

Compositional analysis was inconclusive, with work ongoing. The transparent black enamel background has a moderate lead content, neither clearly 16th century nor 19th century. Similarly, the calcium content is higher than expected for 19th century enamels. Manganese and iron were used as colourants for the background, and tin oxide was used as the opacifier for the white enamel.

X-radiography of the vases was useful but did not firmly establish a production date ↘ Fig. 16.3. The bodies of the vases are each comprised of two pieces attached by holes threaded with thin wire, with some later solder also present. The neck and feet are separate pieces, with the latter mechanically joined to the body. The mechanical joins present are similar to those seen in 16th century enamels by La Niece et al. (2009). In contrast, the unusual silver gilt handles are attached with modern screws and may be a later addition.

Discussion Grisaille enamels pose a special challenge for dating because of their limited palette. They lack the bright colours which often contain elements indicative of the 19th century such as chromium or uranium. Although the presence of lead arsenate as an opacifier for white enamel is indicative of the 18th century or later, some use of more traditional tin oxide also occurs (Röhrs and Stege 2004). However, in some instances a combination of technical examination & compositional analysis of the black and white enamels and study of the manufacturing techniques, together with art historical research, enables some conclusions regarding dating.

Conclusion

Collaborative art historical research and scientific analysis have resulted in revised dating of several Limoges-style painted enamels in the collection of the Harvard Art Museums. The date of a calendar plate attributed to Pierre Reymond was established as 1565, while the dating of two plaques and a cup and saucer was revised to the 19th century. However, the production date for two vases, while strongly suggestive of 19th century, is yet to be determined conclusively. Research continues on the two vases and the polychrome painted enamels in the collection.
The differences between enamel composition of objects thought to be from the 19th century suggests that, in combination with art historical and provenance research, connections between objects and workshops could be made in the future.

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Conservation of a Chinese *cloisonné* enamel from the Museum des Arts décoratifs of Paris ↘

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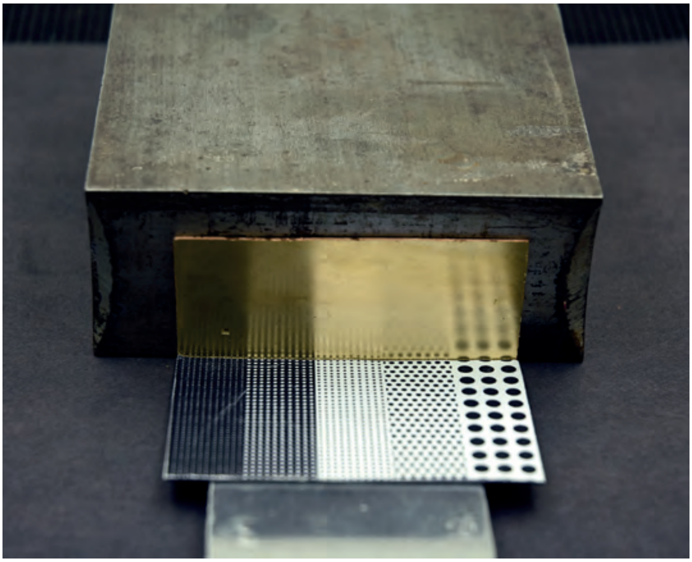
Anne Genachte-Le Bail
Marie-Anne Loeper-Attia
Béatrice Quette
Mandana Saheb-Djahromi

Introduction Chinese *cloisonné* is a famous technique, nevertheless the lack of publications and research on this type of objects is one of the major obstacles to their understanding, both historically and technologically. In the final year of conservation studies at the *Institut national du patrimoine (Inp),* one of the authors had the opportunity to treat a Chinese *cloisonné* enamel, in the shape of a *Qilin*, from the *Museum des Arts décoratifs,* in Paris (Lafitte 2017). The *cloisonné* enamel, bequeathed by David David-Weill in 1923 to the museum, was made of an assembly (with nails) of different hammered copper elements, enamelled and gilded with gold-mercury amalgam (Quette 2011). Some questions remained unanswered, in particular the symbolism of the animal, akin to a dragon or a *qilin;* it seems that it was only a decorative object ↘ Fig. 17.1.

Previous treatments Analyses were made to understand how the object was manufactured and to determine what was originally there. First, we used an endoscope for internal observation. It revealed that the head, the mane, the goatees, the tail, and the paws were made separately. Under the head, the top of the body had a dome irregularly cut in its centre which does not seem original ↘ Fig. 17.2. We suppose that it was made probably to repair or reassemble the elements together. This hypothesis cannot be confirmed, but the presence of different nails proves that the *Qilin* was disassembled on one or more occasions. Some nails, added in previous treatments, are thinner than the original holes and cause instability.
Observation with UV light has highlighted an invisible varnish coating, only applied on the front side of the animal. This heterogeneous layer seems to have been applied as a cleaning treatment. In fact, some residues of a white product have been identified below this protecting layer. Further analysis using X-Ray micro-Fluorescence showed the presence of calcium, which suggests that a calcium carbonate-based treatment was carried out on the object, subsequently protected by a layer of unidentified varnish (Navarro 2010).

↘ **Fig. 17.1**



↘ **Fig. 17.3**

↘ **Fig. 17.1** *Qilin*, Chinese cloisonné from the Museum des Arts décoratifs, Paris.

↘ **Fig. 17.3** Mercury-gold sample with a reflectance scale for shooting.

↘ **Fig. 17.2**

↘ **Fig. 17.2** *Qilin* without the head: a dome with an irregular cut is visible.

Additional Infra-Red spectral analysis (by Maroussia Duranton at the Inp laboratory) was performed on the brown layer, present under the object and in some hollows of the decoration. Polysaccharide lacquer was identified. It appears to be a voluntary patina applied during manufacture of the *Qilin*.
The conservation treatment shall preserve this layer assumed as original.

Research on rubber for the cleaning process To clean the metal wire *(cloisons)* an investigation has been carried-out to avoid the use of liquids or viscous products which could penetrate between the *cloisons* or in the assemblies and cause a reactivation of the corrosion processes.
Therefore, we decided to test the use of sponges and rubbers as mechanical cleaning. Homemade and commercial rubbers as well as sponges have been studied in order to identify the efficiency in cleaning of the metal, as well as potential scratching, change of surface gloss on the gold and possible residues of pollutants. The products selected for this study were selected according to previous studies performed on the cleaning of metallic artefacts: Staedtler® Mars Plastic (commonly used for metalwork cleaning), Staedtler® PVC-Free, Factis® Magic Black 18, Gomme crêpe® (used in paper conservation), Muji® synthetic sponge and a tool made with nacre (routinely used by the Victoria & Albert Museum for metal corrosion).
The tools (rubbers, sponges, and nacre) were tested on mercury gilded copper samples and *cloisonné* enamel samples similar to the studied object.
Each tool was applied with a lateral movement of 200 strokes at a rate of 160 beats per minute. The strength was controlled thanks to a foam of 4 cm thickness beneath the sample limiting the pression with the wrist and producing the same movement on all the samples.
To analyse the scratches and the surface finish of the samples, we developed a method based on the use of analytical tools accessible to conservators.
First, we designed a rectangle of different black and white circles printed on hard paper (Florescu 2015) used as a reference scale. This scale was placed at 10° relative to the ground, while the sample was placed vertically ↘ Fig. 17.3. to compare the reflectance before and after treatment.
Secondly, a photograph of the samples was made with a binocular magnifier, before and after the rubber treatment, and the photograph of the scratches were analysed with Photoshop® CS6 software using contrast enhancement. The images were converted into black and white to highlight the scratches in white. The software is able to select and to quantify every white pixel of the picture, to calculate a percentage of scratches on the surface of the samples (1.71% for both Staedtler® rubbers, 0.15% for the Muji® synthetic sponge and 4.74% for the nacre tool).

The rubbers seem to be the best tool to clean the corrosion on the *cloisons* without scratching the metal too much. However, inorganic pollutant residues were identified on the metal by X-Ray micro-Fluorescence after treatment with the tools ↘ Fig. 17.4. Regarding all these results, the Staedtler® PVC-Free rubber appears to be the best choice for the conservation treatment of the *Qilin* in terms of efficiency and safety. In addition, artificial aging of the products using the mercury-gilded samples confirmed that no corrosion has been developed in contact with the tools.
To further study the action of this rubber on the materials and ensure the safety of the cleaning method, artificially corroded mercury-gilded samples were cleaned with the rubber. The soft non-adherent corrosion products were removed but the rubber could not go deeper in the details of the decoration to remove hard encrusted corrosion products.
Tests have been carried out on enamel and confirmed that both the nacre tool and the rubber did not scratch the surface. A last test attested that the residues of the rubber were easy to remove with a micro-vacuum and a soft brush.

Conservation treatment Firstly, the object was dusted with a micro-vacuum avoiding the loss of fragments of the weakened enamel. The prior disassembly of the different elements of the *Qilin* precluded any degradation. A jeweller clip was protected with TESA® tape to avoid scratches, and the three nails maintaining the mane were removed. The head of the animal was pulled out and every nail was referenced.
The varnish coating was removed with ethanol on the surface of the enamel. To limit the use of solvent, a thick paper (Bolloré® 20 mg) was used like a blotting paper to apply the solvent on the enamel, without penetration. This treatment allowed to homogenise the surface and limit the preferential development of corrosion.
The corrosion on the *cloisons*, the dirt and the calcium residues did not permit a good visibility of the decoration. According to the study of the cleaning process, it was decided to combine two cleaning tools:

- The nacre, applied parallel to the enamel, to smooth down the hard and adherent corrosion,
- The Staedtler® PVC-Free rubber, to clean the surface without scratching the enamel and the mercury gilding. The rubber was cut for more precision during the cleaning of the metal and the enamel. The cleaning was stopped once the gilding was revealed.

Moreover, to recover the colour of the enamel overlaid by a dark adherent coat of dirt and grease, a wooden tool was designed to insert a razor blade,

Tools	S	Cl	Ca	Ti	Zn	K
Staedler® Mars Plastic	•	•	•	•		
Staedler® PVS free			•	•		
Factis® magic Black 18	•	•	•	•	•	
Gomme crêpe®						
Muji	•		•	•	•	•

↘ **Fig. 17.4**

↘ **Fig. 17.5**

↘ **Fig. 17.4** Elements detected in the tools

↘ **Fig. 17.5** Cleaning of the enamel with a tool with a razor blade, under magnifying glasses.

softer than a scalpel blade. The blade was applied parallel to the enamel to prevent scratches and to pull out the dirt ↘ Fig. 17.5. In the same way, every pebble eye (Brinker and Lutz 1989; little hole in the enamel caused by air bubble during the fabrication) and its original filling with tinted beeswax were cleaned with a toothpick, cotton and ethanol. The removal of dirt and varnish made visible the filling of beeswax under ultraviolet light (Liu 1978).

On the large golden areas it was decided to use a peelable gel, a technique developed by the C2RMF based on nerve glue (beef) and Japanese paper (Paulin and Leblanc 2013). The nerve glue was mixed with citric acid, water and TEA (triethanolamine) to obtain a neutral pH around 7 at 10% of triammonium citrate. The mixture was then warmed in a bain-marie to obtain a viscous gel applicable on the metal surface. A Bolloré® paper, cheaper than Japanese paper, was applied on the gel and covered by another gel coating. After 10 minutes, the gel was peeled off by pulling the paper. This cleaning enabled the elimination of most of the corrosion products, though local application of EDTA gel (tetrasodium salt at 1% in distilled water in methyl cellulose) was necessary in the hollows.

As previous treatments and disassembly have weakened the structure of the *Qilin,* one of the main challenges was to stabilise the head, goatees, and the tail using glass fibre stems coated with Paraloid® B72. Some holes of the mane which enabled the access to the nails were consolidated with epoxy resin (Araldite® 2020) and fibre glass. Some nails used to put the elements together were consolidated to maintain the structure. After this stabilisation, the head and the mane were reassembled and a new head of one nail (cut in a previous treatment or disassembly) was made in epoxy resin and fibre glass to stabilize the movement of the *Qilin's* head.

At last, some fillings and retouchings were made to homogenise the overall aesthetic aspect of this fine artwork. For the enamel filling we choose to use Modostuc® (aqueous PVAC dispersion) with two coats of Paraloid® B72 at 15% in ethanol to prevent the migration of some components into the cracked enamel. The Modostuc® was applied at a lower surface level relative to the enamel to make it discernible without being unsightly. It was impossible to fill the holes in the metal by the interior because there was no access. Thick films of Paraloid® B72 in ethyl acetate/diacetone alcohol (70/30) (Koob 2006) were made. The films were cut at the filling form and glued with Paraloid® B72 in 20% in ethanol. The retouch of all the fillings was made with acrylic painting for the satin-like appearance similar to the enamel. As copper chlorides are only present at a low concentration, no protection was applied to the object which will be deposited in the controlled environment of the museum's storage area (Mourey 1996). Finally, a head cushion and a tray were designed for the transport of the object, damping the mechanical shocks. It is recommended not to manipulate the object by the head and the tail which remain fragile elements.

Conclusion The conservation process has stabilised the *Qilin* in order to avoid potential degradation during future transportation. It has also allowed to unify the overall aesthetic aspect. The Chinese cloisonné is now able to return to the Museum to be displayed once more.

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Two painted enamel artefacts in Portuguese collections

Ana Paula Machado

In 1881–82, at the *Great Exhibition of Portuguese and Spanish Ornamental Art* held in London at the South Kensigton Museum and later in Lisbon, about 80 painted enamel artefacts from the 16th and 17th centuries were gathered for the first time in Portuguese collections. Most of them belonged to King D. Fernando II and the Dukes of Palmela collections (both now dispersed to several European and American museums), others came from other private collections, religious institutions and museums.
From the artefacts presented then and still in Portugal today, two stand out: a triptych of the Passion of Christ belonging to the Manuel do Cenáculo Museum in Évora (FMCM) and a series of twenty-six plaques depicting the Passion of Christ housed at the National Museum of Soares dos Reis, in Porto (NMSR).

The triptych of the Passion of Christ at FMCM This Triptych belonged to the collection of D. Frei Manuel do Cenáculo Vilas-Boas (1724–1814) who was Archbishop of Évora, a politician close to King D. João V, but also a bibliophile, an erudite and a collector. He founded one of the most important collections of art and archaeology in Portugal.
The triptych he bought for his collection consists of a central panel with the Crucifixion, perhaps inspired by a printing of Thielman Kerver's Book of Hours, published in 1505 (or possibly a German engraving from an earlier date), and two wings that closely follow four of the engravings of the Little Passion of Christ by Albrecht Dürer, published between 1509 and 1511. Its enamel plaques have been alternately attributed to Nardon and to Jean I Penicaud.
There is a wooden box, associated to the triptych and of unknown date. A presumed eighteenth century piece of writing in Latin, printed on paper, is glued to the lid, and the writing describes a fantastic story about the object.
In 1921, Marquet de Vasselot described the Évora triptych as a "culminating point" in Jean I Penicaud's production (c.1480 – after 1541) and more than that, of Limousin enamelling in general.
The framing structure of this triptych is for other reasons worthy of attention. It is formed by three wooden panels, partially covered in the interior side with eight mercury-gilded copper-alloy sheets and a narrow embossed frame in the same material. The outside and edges are covered with red satin.

The profile that accompanies and fixes the enamel plaques is narrow and concave, decorated with stylised floral sprigs that seem to evoke tendrils (grapevines) and their bunches of grapes. In short, an extremely common typology among objects of the genre.
Marquet de Vasselot considers that almost all the frames that we know today for this type of objects were made in the second half of the 19th century by a relatively restricted and identified number of restorers, especially Alfred Corplet and Alfred André. This belief remains today among researchers. Moreover, these frames have been looked at with little attention. The most systematic study I know of the frames and materials associated with painted enamels is that by Suzanne Higgott in the *raisonné* catalogue of the Wallace Collection enamels, which concluded that the materials involved (velvets, silks, walnut wood) were sometimes contemporaneous with the enamels, but not associated with them from the origin, resulting from reutilisations and adaptations of old materials, perhaps from other objects.
The following aspects should however be considered in the approach to the Évora triptych:

- The earliest known reference to the triptych is the Latin document of uncer tain date, but long before 1814, glued to the box and where the story of the object is told. In this text the triptych is called by the generic term of "sacred image", therefore giving no clue about its configuration at the time.
- In 1814, the triptych is registered among the goods of Cenáculo Vilas-Boas, in the inventory made after his death, as follows: "A two-and-a-half-hand-span oratory with doors, which, open, represents the Calvary, painted in enam el and gold (...) ". The description makes no reference to the brass or textile coating, but it is clear that the piece already had the tripartite structure it presents today.
- In 1865 Alfred Demersay publishes a description of the brass frame exactly as we see it today.
- No record is known so far of the triptych being object of intervention, either inside or outside the museum, ever after (or before) 1814.
- The troubled history of the Cenáculo Museum collections leads to consider as very improbable any initiative to manufacture a frame for the triptych between 1814 and 1865.

Considering these aspects, in 2015 I proposed to the FMCM and José de Figueiredo Laboratory (LJF), Lisboa, to analyse the frame, the wood of the structure, the covering fabric of the exterior and the watermark present on the printed sheet of paper. The aim was to obtain data on the characteristics and form of application of these materials and, with any luck, on their dating. These analyses were however conditioned by the difficulties of sampling and access to the various parts of the object without compromising its stability and conservation. Another difficulty was the scarcity of published studies that allow to conclusively date the coating fabric. The same problem occurred with regard to the composition of the brass and gilding alloy in the period that has been pointed out as the manufacturing of the frame (the call launched in 2015 in the Conservation Distribution List for comparison parameters proved to be fruitless).

In summary the technical information from LJF concluded: The FMCM triptych is built with three oak wood panels of *Quercus sp* species. The coating fabric is a cross-weaving technique that has been used for several centuries, which does not facilitate comparisons with other textiles. Two dyes were identified, red being one of animal origin – cochineal – and another of vegetal origin – Brazil-wood. While the first arrived in Europe in the sixteenth century the second was already common in European medieval markets coming from India and Ceylon. Both were replaced in the twentieth century by synthetic dyes.
As for the selvedge it was possible to carry out the analysis of the weaving technique, however the information collected for the time being provides no clue as to its manufacture.
The fabric was applied without removal of the selvedge and always with the same orientation in each of the three panels and respective edges, except for one.
As for the metal frame the analysis carried out shows that it was not gilded by electrolysis and registered traces of mercury in the gilding. It was not possible to analyse the sheet of paper glued to the lid.
The data are not conclusive mainly due to the lack of parameters of comparison, but the history of the object leads us to think that it should be a frame previous to the nineteenth century, surely produced in a very different context from the one referred to by Marquet de Vasselot.
The existence of the printed text associated with the triptych suggests a change in its path at that time, reflecting an initiative that must have had commercial purposes. Could this also be the date of manufacture of the frame? Is the frame of this triptych an isolated case, or are there other similar frames that may be previous to the nineteenth century?

The series of twenty six plaques depicting the Passion of Christ in the NMSR This series of twenty-six enamel plaques is directly inspired by

↘ **Fig. 9.1**

↘ **Fig. 9.1** *Triptych* of the Passion of Christ at FMCM, 40,7 x 52,2 cm (© José Pessoa (DGPC/DDF))

↘ **Fig. 9.2**

↘ **Fig. 9.2** Noli me Tangere (1 of 26 plaques) at NMSR. 10,2 x 7,9 cm (© Luis Piorro (DGPC/LJF)) twenty-four engravings from the series called the Little Passion, published by Albrecht Dürer in 1511.

The series comes from the Monastery of Santa Cruz de Coimbra and entered the State collections in 1834, following the extinction of religious orders in Portugal.

The series has been subject of different classifications over the last hundred years.

In 2009, a study carried out by Monique Blanc and Isabelle Biron (presented at the 3rd Experts Meeting in the Frick Collection) placed it within the production of a workshop under the convention name of "Master of the Little Passion of Christ" working in the sphere of Pierre Reymond, between the middle of the 16th century and the beginning of the 17th century. Under the production of this workshop are grouped, according to Blanc and Biron, the series of 24 plaques of the Little Passion of the Wallace Collection and several other pieces in different institutions: National Museum of Ancient Art, Lisbon; Musée des Arts Decoratifs de Paris; Musée de Beaux-Arts de Lyon; Musée du Louvre.

The NMSR series has an unusually stable history over the past 250 years. Nothing however is known as to the date and manner in which it entered the Monastery of Santa Cruz.

The first documentary register of its history dates back to 1752. It is an excerpt from a manuscript written by a brother of Santa Cruz, D. José de San Bernardino, in which he describes the so-called throne of relics, ornamented with "lemoge" or with the plaques of the Passion: *"… all placed on the Banquet of the Altar, adorned with lemoges / jars and candlesticks, all of fine beaten silver and the Holy relics placed in beautiful / perspective form, bearing the crown of gold with the Holy Thorn (…)".*

This "throne" was erected in the House of the Relics in the Sanctuary of Santa Cruz. The building, called Sanctuary, was a baroque structure, presumably from c. 1731, added to the architectural complex of the Santa Cruz Monastery (founded in 1133 and, for seven centuries the most important monastic house in the kingdom). The sanctuary was a reserved space, built purposefully to expose in a scenic way the relics of many saints that the monastery had collected during its long existence. It was filled by the most precious objects among the magnificent patrimony of this monastery, some made specifically for this purpose at the time of its construction. Placing the series in this space is therefore the reuse of painted enamel plaques from the 16th century, in a place of election in the context of the Monastery, associated with relics yet in a context of active worship, integrated in the throne surmounted by the Holy Thorn in full Baroque period. The form and characteristics of the structure on which the series was applied then is unknown. In 1834, they were registered as 26 paintings, which suggests that they were now without support and that, in the House of the Relics of Santa Cruz, the plaques, although exposed, would not be framed in a portable format.

In 1914 the series was photographed, already in the NMSR, with a wooden frame in poor condition and in which the scenes are grouped out of the order of the biblical narrative of the Passion.

The history of these two items reveals different aspects of the "life" of altarpieces and oratories in painted enamel, as objects of collection and as devotional objects in the second half of the eighteenth century, which seems relevant to the knowledge of the dynamics of collecting of this type of objects as well as of practices of reassembly and grouping of enamel plaques prior to the nineteenth century.

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The Melfort Ewer

Dana E. Norris
Andrew Shortland

The Melfort Ewer is an 18th century Chinese painted enamel armorial object in the collection of the Ashmolean Museum of Art and Archaeology, Oxford. The ewer was bequeathed to the museum in 1957, and is associated with John Drummond who became Duke of Melfort in 1686. The ewer has a complex construction including several mechanically assembled sections, as well as seams in the copper substrate which have been enamelled over. The object is enamelled in white with polychrome painted enamels and gilding used to decorate the surface. The enamel colours and gilding are high quality, with bold consistent hues, and little evidence of over firing or chemical instability. The motifs are painted in the famille rose palette, and include a combination of registers decorated with traditional lotus flower scrollwork and a stylised ruyi pattern at the foot. Fruit and flora decorate the ground on the lid, body and foot unconstrained by structured registers or reserve panels. The coat of arms demonstrates sophisticated control in the application of gilding, which has been used to paint the body of the lions, rather than simply to highlight details within the patterns. Stylistically the object dates to the later part of the 18th or the turn of the 19th century. The rose pink enamel used throughout the object indicates that it was manufactured at some point after 1720 (Kerr 2000). The construction of the object all but excludes the Kangxi and Yongzhen periods, because objects with this type of construction are uncommon until the late Qianlong period (1735–1796; Jingfei 2012). The decoration is in contrast to tighter designs seen in earlier objects, such as EAX.1236 Dish depicting the visit of the Magi circa 1730, in the Ashmolean's collection (Moss 1976). The painting style is relaxed leaving large areas of undecorated white ground associated with European tastes (Keverne 2017). These stylistic features are consistent with the later 18th century, a time during which it was illegal to export copper from China because it was used to produce domestic coinage (Jörg 2015). The ewer was likely commissioned by a descendant of the first Duke, who died in 1714 (Pine 1972), the most probable candidate being Charles Edouard Drummond, 5th Duke of Melfort (1752–1840). The ewer has been a part of the permanent display in the West Meets East gallery from 2009, as part of the museum wide crossing cultures narrative. In 2013 the object underwent conservation treatment to remove degraded restorations, stabilise the enamel surface and prepare it for redisplay. Treatment coincided with a condition survey of the Chinese painted enamel

↘ **Fig. 18.3**

↘ **Fig. 18.3** The Melfort Ewer © Ashmolean Museum of Art and Archaeology.

Object	Colour	Na_2O	Mg O	Al $2O_3$	Si O_2	P $2O_5$	Cl 2O
EA 1937.56 Ewer	White Base Enamel	0,44	0,00	0,50	37,91	0,00	1,57
EA 1937.56 Ewer	Brown Underdrawing	1,80	0,00	4,77	26,57	1,30	1,15
EA 1937.56 Ewer	Black Painted Enamel	0,53	0,00	2,77	38,49	0,00	9,84
EA 1937.56 Ewer	Yellow Painted Enamel	0,28	0,00	0,76	37,61	0,71	1,47
	DLH1 Target	**1,00**	**1,00**	**4,00**	**26,00**	**NA**	**NA**
	Average of 3 Spots	1,85	0,25	5,04	28,66	NA	NA
	% Error	(+) 0.58	(–) 0.75	(+) 1.04	(+) 2.66		

K 2O	Ca O	Mn O	Fe $2O_3$	Co O	Cu O	Zn O	As $2O_3$	Sn O_2	Pb O_2	Total
6,75	0,69	0,00	0,79	0,00	0,00	0,00	7,65	0,00	43,71	100
4,63	2,97	4,27	17,36	1,13	0,74	1,34	4,62	0,00	27,35	100
1,88	3,62	8,05	0,44	0,44	0,91	0,78	3,08	0,00	29,60	100
6,19	0,90	0,00	0,81	0,00	0,00	0,86	6,20	1,60	42,61	99,99
1,00	**1,00**	**NA**	**1,00**	**NA**	**NA**	**NA**	**NA**	**NA**	**65,00**	**100**
1,01	1,25	NA	1,25	NA	NA	NA	NA	NA	60,37	100
(+) 0.01	(+) 0.25		0.25						(-) 4.63	

↘ **Fig. 18.1**

↘ **Fig. 18.1** ESEM-EDX analysis of enamel fragment from EA1957.36, Ewer

↘ **Fig. 18.2** BT-XRF analysis of fill materials found on EA1957.36, Ewer (spot size 0.5mm, 50 kV at single depth)

Location	Appearance
Vessel Rim	Matt Grey
Handle Attachment	Glossy Ocher
Exterior Lid	Transparent Ocher
Interior Lid	Matt White

S Kα	K Kα	Ca Kα	Ti Kα	Mn Kα	Fe Kα	Cu Kα	Zn Kα	Sr Kα	Pb Kα
•	•	High		•	•		•	•	•
•	•	High		•	•		•	•	•
•	•	•	High		•	•	High		High
High	•	High			•		•	•	

↘ **Fig. 18.2**

collection, which has been used to evaluate the degradation seen in this type of enamel (Norris 2015). Multiple restorations were present on the object as a result of various treatments over time. Resinous fills on the lid had yellowed and distorted lifting adjacent fragments. Whereas, plaster like materials along the vessel rim were associated with accelerated corrosion of the copper body and surface loss. The treatment of the ewer effectively illustrates the condition issues seen across the collection, and provided an opportunity to study the mechanisms behind the deterioration.

Elemental Analysis As a part of a wider project researching the composition of Chinese painted enamels, a fragment from the ewer was analysed with an environmental electron scanning microscope coupled with energy-dispersive X-ray analysis (ESEM-EDX). The enamel fragment was analysed at 20 kV with a variable pressure of 50 hPa at 50–100x magnification for 100 seconds. Glass standard DLH1 was prepared, using the same method as the samples, to monitor analytical drift. Analysis of multiple lead glass standards indicates that there is 5–7% error in the quantification of lead, therefore results must be interpreted as semi-quantitative within this context, and it can be assumed that the lead content is slightly higher than reported. The results of the ESEM analysis of the ewer reflect the compositions of other 18th century painted enamels included in the wider study ↘ Fig. 18.1.

Fills removed from the ewer were analysed using a bench top X-ray fluorescence machine (XRF). The XRF machine is regularly calibrated using manufacturer standards; DLH1 was used to identify and exclude instrument artefacts. It should be noted that most resins are comprised of low Z elements which cannot be detected with XRF. From visual examination the fills on the handle were consolidated with a resin which has yellowed, and the fills on the interior of the lid appeared to have been mixed with a binder. The fill from the exterior of the lid is transparent and resinous, it is assumed that the elements detected are related to impurities and bulking agents within the resin. From XRF analysis it appears that the three opaque fill materials are plaster based, and the fourth is a resin pigmented or bulked with lead, titanium and zinc oxides ↘ Fig. 18.2.

The XRF results confirm that the fills from the vessel rim are a type of plaster, indicating that the hygroscopic nature of the material is responsible for the deeper corrosion layer seen in these areas of loss. Corrosion associated with plaster fills often extends under the adjacent enamel causing lamination and eventual instability in the surface. The areas of loss at the handle and interior of the lid did not have the same extent of corrosion, which may be a result of the fills being consolidated.

Treatment Once the previous restorations were removed from the object, the areas of loss were cleaned with acetone. They were sealed with a 10–20% solution of Paraloid B72 in acetone to inhibit corrosion and to create a barrier layer. Loose fragments of the enamel surface were bonded with the same adhesive; a 5–10% solution was used to consolidate unstable areas of enamel. Treatment goals were discussed with the curator to determine how any restoration work should be resolved. It was decided that the losses on the interior of the object would be left unfilled because it is useful to be able to access the substrate for future study. The exterior was to be filled in white, but the pattern would not be replicated. The fill material was chosen based on a wide range of parameters unique to this object and its use within the museum's collection. The fills must be hydrophobic, and made of a removable high conservation grade material so that they are chemically stable and do not yellow within a short period of time. The fill material must have minimal shrinking during curing and as it ages, because distortion can put tension on the already weakened enamel surfaces adjacent to the fills. In the case of the ewer, the strength of the fill material was also a concern because the weight of the object places stress on a large loss in the rim of the foot.

The losses were filled using a modified version of the traditional colour gap filling technique, which has been developed to reduce stress on the original surfaces by minimizing polishing. Colour filling is a method where a resin is bulked with filler, and then tinted with pigments to match the appearance of an object. Today the technique is used mainly for objects made from vitreous materials such as porcelain and glass; it involves bulking a low viscosity conservation grade epoxy resin with fumed silica to make a paste, and then tinting it with pigments to match the opacity and colour of the object. Colour filling has its origins in the 1980's when several new epoxy resins were introduced to conservation. Byrne (1984) and Koob (1986) both explored the application of fumed silica to conservation adhesives in the mid 1980's, studying the increased strength it gave to adhesives. Over the next decade the technique was refined, and became established in UK museums (Buys and Oakley 1996, Jordan 1999) and conservation training programs (Watt 2017).

Fynebond was used to treat the ewer; it was selected for its high refractive index, non-yellowing properties and physical behaviour during application. In this case the resin was bulked with 0.05% w/w fumed silica, pigmented with titanium dioxide pigment and allowed to cure for several hours. The resulting fill material is a high viscosity gel, which when partially cured can be agitated before application and returned to a near liquid state. If the resin is applied at the correct time, depending on room temperature, it will spread evenly across the area of loss creating a smooth even fill which requires limited mechanical refinement. If applied at this critical point, polishing is unnecessary and any risk of abrading or damaging degraded surfaces adjacent to the loss is mitigated. After filling, the appearance of the object was revisited with the curator. Where the breaks in the patterns were particularly distracting, the banding in the registers was carried across the fills to add continuity to the design using acrylic paints. The registers along the rims were retouched to the yellow ground colour, but the lotus scrollwork was not replicated so that it is obvious which areas are restorations.

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Conservation of a Persian enamelled hookah ↘ Edit Pelles

Introduction The hookah, made in the 19th century in the current Iranian territory, was conserved in the academic year of 2016/17 as a diploma work at the Hungarian University of Fine Arts, at the Branch of Applied Arts Object Conservation. The artefact is the property of the Déri Museum in Debrecen. The purpose of the conservation was to stabilise the object and to improve its visual interpretation and aesthetic appearance. For the aesthetic restoration, the damaged parts were completed with enamel, the original material.

Description of the object and its condition The hookah was originally made from four parts fitting each other, but now it has only two remaining elements; the base (height: 19 cm) and the tobacco bowl (height: 15.4 cm). The stem and the hose are missing. The copper based hookah is decorated with enamel covering most of surface, its main colours being blue, green, white, red and black. Some of the embedded enamels are of one colour, but most of them are finished with painted enamel depicting floral motifs and portraits typical of the Qajar period. The pieces of the base and the bowl are both joined with patterned brass rods. The pure copper surfaces are gilded ↘ Tab. 1.1. The composition of the metals and the enamels was analysed with portable X-ray fluorescence spectroscopy (pXRF). The cells of the recessed enamels are chased and chiselled to create rough surface, to facilitate a strong bond between the metal and the enamel. Microscopic investigation of the cross-sections of the enamel helped to study how it was originally made and its current condition. After disassembling the artefact, it turned out that no counter enamel was used except for the rim at the upper part of the tobacco bowl.

The hookah was deformed, weak in construction, the gilded parts were worn and several brass rods were missing. Black spots were visible on the surface, as well as discolourations near the soldering, at the edges of the enamels. These were investigated with scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDS) which showed that they contain tin and tin-oxide likely from soldering material. Owing to multiple firings, the copper discoloured noticeably in some places. Approximately 15 percent of the enamels are missing from their cells, partially or completely, as a result of the deformation of the hookah.

	Completion with enamelled plate	Completion with enamel fired in negative form
Properties	solid, can be repeatedly removed and repositioned	fragile
	can be burnt many times	in negative form, it can be burnt up to 5–6 times once removed from the negative form, it cannot be burnt again
	easy to retouch with further enamelling	before removed from the negative form, it cannot be integrated into its place so it is harder to retouch with further enamelling
	does not fit to fractured surfaces	almost perfectly fits to fractured surfaces
Device and material requirements	soldering torch	furnace, silicone, plasticine, jewellers plaster
Area of use	completing bigger surfaces	completing smaller surfaces

↘ **Tab. 1.1**

Comparison of the completion with enamelled plate and with enamel fired in negative form

↘ **Fig. 10.1**

↘ **Fig. 10.2**

↘ **Fig. 10.3**

↘ **Fig. 10.1** The hookah before conservation

↘ **Fig. 10.2** Retouching the enamel fired in negative form

↘ **Fig. 10.3** The top of the bowl before and after conservation

Conservation process The first step was to disassemble the object, in order to work on structural stability. During the cleaning process, 1 g/l surfactant (Dialkyl sulfosuccinate, neutral pH) diluted in distilled water was used. Previously, enamel used to be completed by applying wax in the gaps. This technique was employed in the past in the case of the hookah; however, since the goal of restoration was to improve the appearance of the object, the wax had to be removed. It could only be removed with turpentine and mineral spirits as dissolving tests showed. The connecting element at the top of the base, which was partially broken, was strengthened with a copper support and tin soldering. The techniques used for the fabrication of the rods were studied in detail with SEM. After extensive experimentation, the brass replacements were finally prepared with what was presumed to be the original technique.
Physical distortion was removed by hand and with hand tools under the microscope. In order to avoid any more damage to the enamel during this treatment, Japanese paper was adhered to the surface of the enamels with Paraloid B-72.

After removing distortions and the Japanese paper from the enamel surface, the broken and weak parts were supported from the reverse coloured with Japanese paper soaked in a 20 per cent solution of Paraloid B-72. The flaking enamel pieces were consolidated with Paraloid B-72.

The completion of enamel The replacement of missing parts can be solved in two ways, either by applying enamel or an imitation material. In this case, in order to decide on correct method, model experiments were performed in the course of which different types of waxes, acrylic and epoxy resins, polyester and enamel were tested. After these experiments and the observation of earlier restorations, it was decided to apply enamel.
The advantages of completing with enamel are the following; the material is the same as the original, it has similar physical and chemical features. Furthermore, the restorations are adhered with an adhesive, therefore they can be removed easily. Two different techniques were used: the enamelling of sheet copper fashioned into the shapes of missing pieces and the enamelling in negatives taken from fragmented parts. As described in ↘ Tab. 1 where the two techniques are compared, it is easier to produce enamelled copper sheet but it can be used only for bigger missing areas.
The missing form was cut out of a 0.1 mm thin sheet. When the cut out sheet was pasted into the cell, it fitted the cell completely, with all the irregulari-

ties of the surface. First, white primer enamel was fired on both sides, then the top surface was fired with several thin layers of coloured enamel, and the pattern was made with porcelain paint and fired. Finally the section was glued with Paraloid B-72.

This mode of replacement could not have been used with those cells where the remaining enamel was cracked and fragmented. Veronika Szilágyi (2016) described a method for these cases in her diploma work (see also this volume). It is possible to replace the missing pieces with enamel as it strictly joins to the fractured surface. First, a negative of the missing part needs to be taken with silicone putty, then with the help of a special jewellery plaster, a negative is taken from the silicone, and after filling it with enamel, the replacement can be fired. In order to achieve the proper thickness and the same primer colour without shades, it was necessary to fill the plaster negative and fire it several times. Then, the final retouching was prepared and fired again. The lifespan of plaster is approximately 3–5 firings depending on its thickness.

Since the missing parts were irregular in shape and varied in thickness, the replacements frequently broke as they were taken out of the negative. In some cases copper mesh or thin copper wire pieces were put into the negative form and then fired. As a result, the enamel became less brittle, and if it broke, the copper wire held it together. It was hard to paint the perfect shade and continuation of the pattern of those pieces which were made in plaster negative because the replacement could not be inlaid and matched to the original while it was still in the negative form. However, once the replacement was taken out of the negative, it was not possible to refire it because without the plaster form, the edges of the enamel parts started to curl. If the porcelain section is not fired, it needs a protective layer such as Paraloid B-72. The aim was to test a method other than using synthetic materials on the surface of the additions. Therefore after the completions were taken out of the negative and retouched in their future place, they were fixed upside down, cast again in plaster, and refired ↘ Fig. 10.1.

It was possible to form the edges of the final enamel with a rasp where it was necessary. Their gluing was accomplished with a 30 percent solution of Paraloid B-72 after the artefact was assembled.

The assembly of the artefact was achieved with soft soldering since an adhesive would not have given the proper stability. A tin soldering iron and a torch were used. The latter can produce larger warmth with a small jet lance, and soldering can be done faster and in a more localised and accurate way. During soldering, the enamel pieces were protected with aluminium foil.

Although objects comparable to the hookah were investigated, for lack of reliable sources, the missing parts were not reconstructed, only drafts and 3D models were made.

Conclusion The hookah had probably been dropped, therefore it was deformed and, consequently, several enamel pieces were missing. In addition to structural stabilisation, aesthetic restoration was the main goal of the diploma work, for which a durable and reversible process was chosen. The inserts were made of enamel, using two kinds of techniques to restore the appearance of the object ↘ Fig. 10.2.

Acknowledgements

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Comparing the enamel powder preparation of *émail champlevé* by micro X-ray mappings

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Lothar Lambacher
Roald Tagle
Ina Reiche

Introduction The mediaeval *émail champlevé* are commonly opaque and coloured in blue, turquoise, green, red, yellow and white. There are very few available written historical sources on enamel production. The manuscript of Theophilus Presbyter (Brepohl, 1999a, 1999b; Hawthorne and Smith, 1963; Speer, 2014, p. 326f; "The Schedula – Project", 2010) gives an insight about the knowledge of the mediaeval craftsmanship. Despite research performed so far, many questions about the production process of the *émail champlevé* remain open, in particular on the supplies of the glass material for enamelling.

The presence of glass grains in enamel which are coloured and opacified to different degrees have been reported by other authors based on visual examination and electron microscopy (Biron et al. 2010, 30; Biron et al. 1996, 56, 59; Freestone 1993, 39). Aesthetical, technical or economic reasons could have led to the mixing of glass with different colours in the process of the enamel powder preparation. Despite this inhomogeneous character of the enamels the elemental composition is always given as the average of the analysed area (Biron and Beauchoux 2003; Freestone 1993; O'Neill 1996; Röhrs 2010; Stratford 1993).

The aim of this study was to investigate the enameller's workshop practice of mixing glass powders for the enamels preparation by studying the heterogeneity of the material by spatially resolved µ-XRF elemental distribution analysis. A selection of objects from different production centres, all made between the first half of the 12th century and the first half of the 13th century, were analysed by this method:

- Two objects book covers made in Limoges (KGM 1908,38 and KGM W-1974,59)
- One plaque with ornamental decoration, thought to be from Treves (KGM W-1984,25)
- Several plaques from a large reliquary made in Cologne (HLMD Kg 54:239) which were made of 84 enamelled pieces in total.
- A reliquary casket (KGM W 16), which is part of the group of the so called "strongly coloured objects" from Denmark or northern Germany.

Method Elemental distributions were acquired with the Bruker M4 Tornado. This device has a mechanical motorised stage, which moves the object with respect to the fixed measuring head. The measuring head consists of a low-power X-ray tube (max. 30 W) with a polycapillary optics and a silicon drift detector for X-ray detection for energy dispersive element analysis. The polycapillary optic allows to focalise the X-ray beam to a spot size of about 25 μm diameter. The measurements were carried out under atmospheric pressure in air. The rhodium X-ray tube was used without filter and operated at 50 kV and 600 μA. Elemental mappings were plotted by evaluating the counts in the spectral regions of interest corresponding to the chemical elements.

Results & Discussion The inhomogeneous distribution of the elements in the enamels was confirmed by the μ-XRF mappings. Depending on the object and enamel colours, the inhomogeneous distribution of the elements is more or less pronounced. On most objects, the dark blue seems to have the most inhomogeneous composition.

To illustrate the findings of the elemental distribution on the enamel colours, results from a book cover made in Limoges (KGM 1908,38, dating to the 4th quarter of the 12^{th} century, described in Gauthier 1987, 185f, Nr. 17) are discussed here.

Elemental distributions from dark blue enamels are shown in ↘ Fig. 19.1 and ↘ Fig. 19.2.

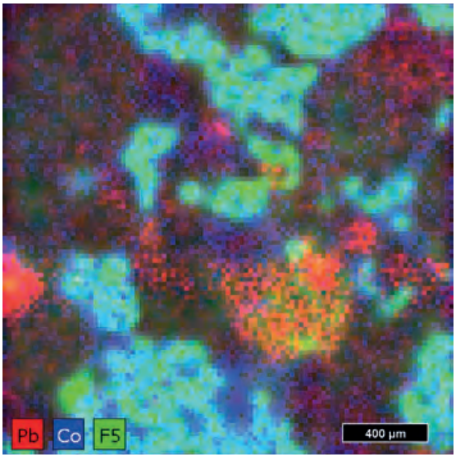
The elements lead (Pb), cobalt (Co), antimony (Sb), labelled as F5, corresponding to a region of interest around the Antimony L-β line chosen to avoid superposition with the calcium (Ca) K-lines, and manganese (Mn) show an inhomogeneous distribution. The distribution patterns give relative sharp borders, which correlate with grain boundaries of the crushed glass used for the enamelling. Some of the grains seem to be larger than 0.5 mm. It is interesting to observe that the elements Co and Sb are correlated, indicating the use of a blue and opaque glass. The lead content is not correlated with any of these elements. Mn is also not correlating in its distribution pattern with the other elements.

In ↘ Fig. 19.3, the elemental distribution of Pb, Co and Sb is shown for light blue coloured enamel. The distribution pattern is much more homogeneous than in the dark blue. Lead shows a certain inhomogeneity in the light blue enamel, but is much more finely dispersed than in the dark blue. Apart from the dispersed lead, no individual grains of glass powder can be observed.

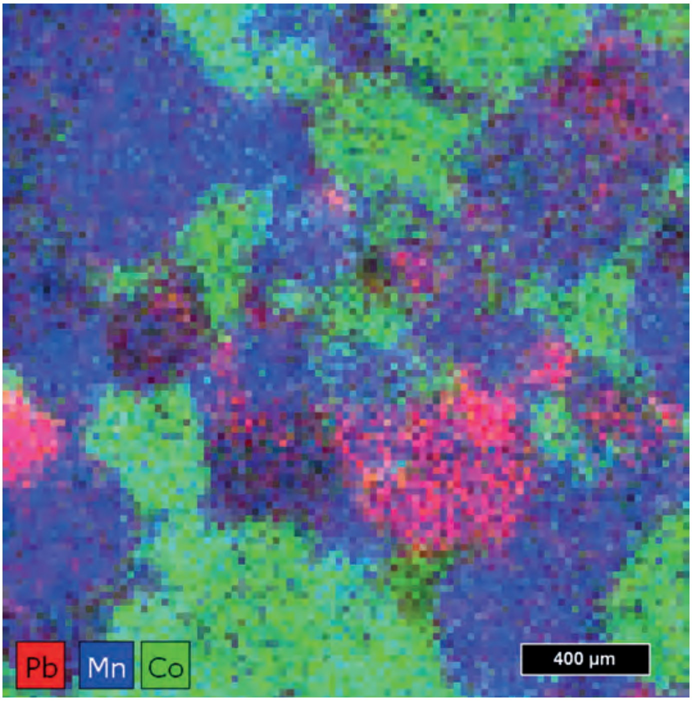
Distribution patterns of Pb, Mn, copper (Cu), Ca and potassium (K) in green enamel are shown in Figures 4 and 5. Here again, the elements distribution seems to correlate to grain boundaries of the crushed glass used for

the enamels. Their distribution is more blurred than in the dark blue enamel. The grains in the green seem to be fused together more strongly.
Mn and Pb distributions are not correlated with each other, neither with the colouring element Cu. An area with stronger signals from K and Ca is shown in the centre of ↘ Fig. 19.4 ↘ Fig. 19.5
Similar finds were made on other studied objects. It was observed that the elements Pb and Mn varied in their concentration, but didn't seem to be connected to the distributions of the colouring and opacifying elements.

Conclusion The characterisation of the different glass compositions used together in one single field of *émail champlevé* provided new insight into the preparation of the enamel powder by the mediaeval enameller. The inhomogeneous distribution of the colouring and opacifying elements had been anticipated because of the inhomogeneous visual appearance of the enamels as observed under the optical microscope. Interestingly, variations of elements which are not related to the colouring or opacifying of the glass, like manganese and lead, had been observed and interpreted as variations in the base glass. It is very likely that the glass preparation was mixed starting from differently coloured powders at the enameller's workshop. Lead and manganese are not correlated to the colouring elements Co or Cu. The observed pattern of lead distribution raises the question of the origin and the possible function of the lead in the enamel. A more comprehensive examination of the individual glass compositions and their full quantitative analysis will allow for a better understanding of the nature and provenance of the glass used in the enamel powder preparation.



↘ **Fig. 19.1**



↘ **Fig. 19.2**

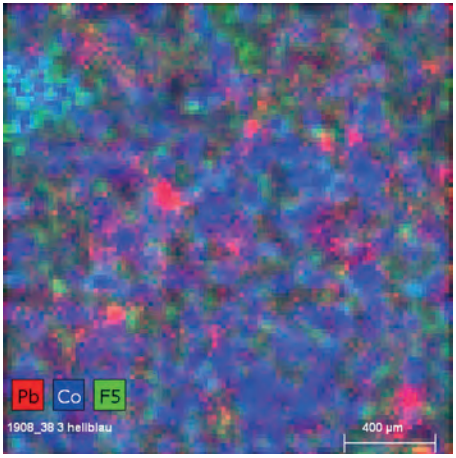
↘ **Fig. 19.1** Elemental mapping of Pb, Co and Sb (labelled F5) on dark blue enamel of book cover 1908,38

↘ **Fig. 19.2** Elemental mapping of Pb, Co and Mn on dark blue enamel of book cover 1908,38 (same area as ↘ Fig 19.1)

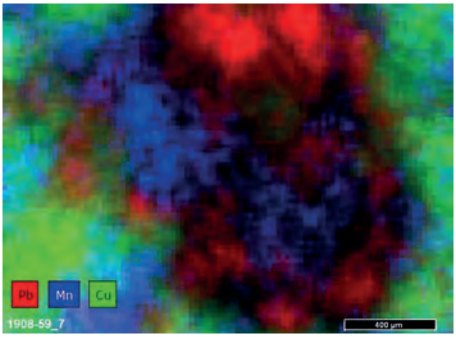
↘ **Fig. 19.3** Elemental mapping of Pb, Co and Sb (labelled F5) on light blue enamel of book cover 1908,38

↘ **Fig. 19.4** Elemental mapping of Pb, Mn and Cu on green enamel of book cover 1908,38

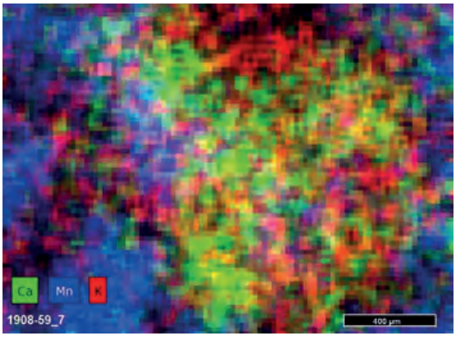
↘ **Fig. 19.5** Elemental mapping of Ca, Mn and K on green enamel of book cover 1908,38 (same area as ↘ Fig. 19.4)



↘ **Fig. 19.3**



↘ **Fig. 19.4**



↘ **Fig. 19.5**

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Considering the suitability of epoxy resin as a fill material for enamels: grounds for cautious optimism

Rachel C. Sabino

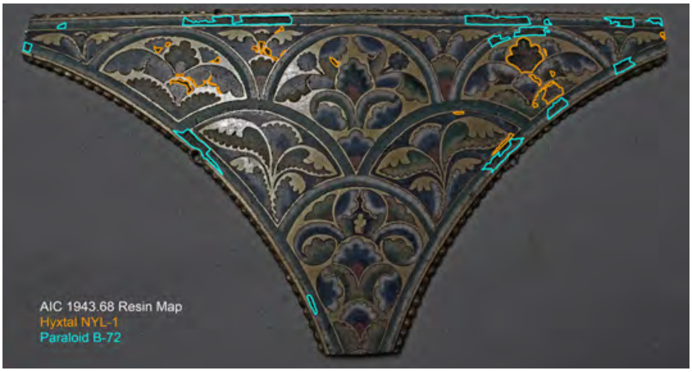
Background In March 2017 the Art Institute of Chicago unveiled the new Deering Family Galleries, presenting nearly 700 objects from the museum's holdings of art from 1200 to 1600. Included was a sizeable group of enamels, several of which required loss compensation to align with the high aesthetic standard throughout the galleries. Such intervention was deemed appropriate chiefly because the objects were stable with no indication of the types of deterioration well documented elsewhere (Smith, Carlson and Newman 1987, Drayman-Weisser 2003). Furthermore, the objects were destined for showcases that would provide the established environmental parameters for their continued stability (Thickett and Studer 2010). The primary criterion for fill specification was precise visual concordance with the original, but obviously this fidelity could not come at the expense of long-term stability.
Numerous substances have been employed for loss compensation in enamels, some with greater success than others (Drayman-Weisser 2003, Beillard 2010, Navarro 2010), and indeed the search for a single, stable material suitable not only for filling but for consolidation, coating, and inpainting is ongoing (Beillard 2010). Among these, epoxy resin appears to have fallen into disfavour, particularly in North America. This disinclination is not formalised in literature but is evidenced anecdotally, interpersonally, and by the current absence of colour filling techniques in the curriculum of ceramics and glass conservation training in the United Kingdom. Arguments against epoxies are: undeniable hardness and resultant potential to stress the delicate enamel ecosystem; localized heating during setting; difficulty of reversal and concomitant damage to surrounding areas; and hazards facing the user during preparation and from the chemicals necessary for reversal. In addition, their finite stability and propensity to yellow has been demonstrated by both experimental methods (Coutinho et. al 2009) and assessments of in-service performance (Tennent and Koob 2010). Given these factors, other materials such as acrylic and ketone resins, even paraffin-based waxes, have been favoured instead. The following three treatments illustrate how individual characteristics of each object suggest varied approaches and materials.

↘ **Fig. 11.1**

↘ **Fig. 11.1** *Plaques from a Reliquary Casket with the Martyrdom of a Saint*, ca. 1200–50, French (Limoges). 4.8 x 15.6 cm (top plaque); 9.7 x 15.6 cm (bottom plaque), AIC 1943.80. Before treatment. ©Art Institute of Chicago.

↘ **Fig. 11.2**

↘ **Fig. 11.3**



↘ **Fig. 11.4**

↘ **Fig. 11.2** *Arch Plaque from a Reliquary Shrine*, ca. 1175–1200. Limoges. 5.4 x 11 cm, AIC 1943.85. Before treatment. ©Art Institute of Chicago.

↘ **Fig. 11.3** *Spandrel from a Reliquary,* ca. 1170–80. German (Cologne). 17.1 x 9.2 cm, AIC 1943.68. After treatment. ©Art Institute of Chicago.

↘ **Fig. 11.4** Annotated diagram serving as supplemental treatment documentation. ©Art Institute of Chicago.

Case studies

Object 1 These two 12th-century Limoges plaques (*champlevé* on gilt copper) feature riveted bosses, lending high-relief to the heads of the personages ↘ Fig. 11.1. Grey-blue enamel predominates with secondary areas of white and green flecked at intervals with russet. Tiny voids and dark inclusions are interspersed throughout. The uniformity of colour made it a good candidate for loss compensation using acrylic resin, but the thinness of the enamel layer presented a challenge that would have been solved more easily using epoxy. In response, a 20 percent solution of Paraloid B-72 in toluene, opacified with titanium and tinted with Orasol dyes was applied drop by drop, overfilling the cells slightly. The slow evolution of solvent permitted the resin to settle in a thin sheet without the distortion and bubbling commonly seen in acetone preparations, conveniently leaving tiny voids mimicking the original. Prior to set but while still responsive to solvent, the fills were made level using cotton swabs dampened with toluene. Gamblin Conservation Colors and Galkyd resin were used to refine the colour and to add dark specks resembling inclusions. The fills lent a welcome visual harmony, and though the resin is anticipated to be extremely stable long term, it is easily reversed by solvent means.

Object 2 This 12th-century Mosan plaque (*champlevé* on gilt copper) is a fragment of an arch ↘ Fig. 11.2. The enamels are similar to those of Subject 1 but with varying shades of blue, a far greater number of inclusions, and increased luminosity and translucence. Loss is limited to the proper right side where the enamel sits without benefit of a protective metal surround and is more likely vulnerable to impact. Losses to green, white, and pale blue areas could be satisfactorily filled with B-72 bulked minutely with fumed silica and tinted with pigments. But the thickness, relative translucence, and overall character of the blue enamel layer, together with its exposed position necessitating the creation of a sharp outside edge, made the use of acrylic resin problematic. Once again, an epoxy-based fill would have easily satisfied all these requirements. Fortunately wax provided a viable substitute. Pigments were dispersed in molten Cosmoloid 80H whose high melting point requires the use of heated implements to build up layers within the cell. The wax cools immediately upon removal of the heat source and the hardened wax can be trimmed and shaped with a scalpel, and a burnished appearance can be selectively introduced with a heated implement. A protective coating of 10% B-72 in acetone was applied, and any refinements were made using Gamblin colors. The wax is stable but reversible by mechanical action, heat, and/or nonpolar solvents.

Object 3 This 12th-century plaque (*champlevé* on gilt copper) in the form of a spandrel is more richly embellished than the previous study subjects, with highly translucent, luminous enamels in specific color combinations and overlapping designs that are cumbersome to render and unsatisfying in outcome when attempted with acrylic resin. Losses were extensive and disfiguring, particularly within the floral elements. Acrylic resin could be put to acceptable use in losses to the turquoise and white within the channels and around the perimeter. The floral components, however, would be best realised using epoxy. Considering the aforementioned concerns, the interior of each cell was coated repeatedly with a 10% solution of B-72 in acetone to build up a thick layer encompassing nearly half the available space inside the cell. The surrounding metal was similarly coated to form a protective barrier. Hxtal NYL-1, most stable of the high-performance epoxies, was tinted with pigments and/or Orasol dyes and laid into the cells atop the thick pad of acrylic resin. When the fills were solid but not fully cured, any excess epoxy was easily swept off with acetone on cotton swabs. The acrylic barrier layer on the surrounding metal was then removed and necessary refinements to the fills executed in Gamblin. The final result was highly satisfying ↘ Fig. 11.3. To aid in future reversal, an annotated map designating the use of different materials by color was added to the object file ↘ Fig. 11.4. To reverse the fills, the surrounding metal can be again coated with Paraloid. Small dots of methylene chloride-based gel are placed at intervals atop the fill and allowed to dwell only briefly before clearing with a swab. This procedure is repeated until the fill takes on a blanched appearance, indicating that it is sufficiently compromised to be broken apart with a scalpel blade or lifted out with a microspatula. This method ensures that swelling of the fill is controlled and that pressure is exerted not on metal or surrounding enamel but against the surrounding cushion of acrylic resin.

Conclusion These treatments illustrate that specification of a fill material can be made on an object-by-object basis, but also a fill-by-fill basis. Sometimes epoxy resin may be the best choice. With correct surface preparation and sufficient documentation, epoxy can coexist peacefully with other materials, not only across the collection but within the same object, keeping its appropriate place in the conservator’s arsenal.

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Japanese enamellers' use of precious metal foils ↘ Fredric T. Schneider

Japanese artists have used reflective foils interposed between substrate and transparent enamels to achieve a wide variety of artistic effects. Here, the history and evolution of these techniques is traced.

Circa 1890, about fifteen years after the introduction into Japan of sophisticated European enamelling technique, Japanese enamellers mastered the use of transparent enamels covering the entire surface of precious and non-precious metal substrates.

Silver substrate was particularly desirable because its high reflectivity made transparent enamel more brilliant. Soon makers enhanced the substrate's visible surface with engraving, the technique known as *basse-taille*. However, both precious metal and engraving were added expense. In the mid 1890s, innovative enamellers in the Nagoya area responded to that cost problem. They achieved a related bright appearance by covering the entire surface of a base metal substrate with heavy silver foil before applying their transparent enamels. The foil was usually impressed with a repetitive pattern to enliven the visual effect. They called this technique *ginbari* ["silver stamped"]. Though money saving, their process was demanding. First, a thin layer of enamel was applied to the substrate, fired, and ground to a smooth surface. Then the foil, flat bottomed but pattern-impressed into its upper surface, was laid over that enamel and the piece was fired again. Before being laid on, the foil was often punctured with minute, essentially invisible, holes, so the gases emitted from the underlying substrate and enamel during subsequent firings could escape more easily to the surface. After the foil was fired to the piece, a layer of clear enamel was placed over it and fired. Finally, using normal cloisonné-enamelling techniques, the transparent surface enamels, usually coloured, and any wirework were added and polished.

Present-day Nagoya enamellers believe *ginbari* was a more creative step than *basse-taille*. *Basse-taille's* substrate engraving did not embody a technical breakthrough, only the additional step of a traditional metal-working skill that enamel workshops usually subcontracted out. *Ginbari,* to the contrary, was an innovation requiring both imagination and those new steps necessary to actualise the use of foils, including fitting a thick foil sheet evenly to a curving three-dimensional surface with a minimum of apparent breaks or overlaps, not a trivial matter. Sometimes, rather than one large foil

↘ **Fig. 12.1**

↘ **Fig. 12.2**

↘ **Fig. 12.1** Maker unknown, vase, copper, individual silver-foil butterflies and chrysanthe-mums under transparent sapphire enamel. 12 cm high. Circa 1900–1910. Collection of the author.

↘ **Fig. 12.2** Maker unknown, vase, copper, silver foil chevrons under transparent blue enamel. 13 cm high. Circa 1900–20. Collection of the author.

↘ **Fig. 12.3**

↘ **Fig. 12.4**

↘ **Fig. 12.3** Hirobyashi Cloisonné Co., Ltd., tray, copper, silver foil under transparent enamels. 25 x 10 cm. Circa 1970–2000. Collection of the author.

↘ **Fig. 12.4** Takeyama Naoki, sculptural object, copper, gold foil circles under clear transparent enamel on black enamel ground. 36 cm high, 30 cm wide at bottom. Circa 2012. Collection of the author.

sheet, multiple individual appliqué cutouts were attached adjacent to each other to produce a similar effect ↘ Fig. 12.1.

The foils were usually produced by subcontractor metalworkers, but subsequent fitting and under- and over-laying with enamel undoubtedly were done by the enamellers themselves.

Once having mastered the use of foils, the *ginbari* maker was free to use the same variations as on engraved *basse-taille* pieces, so there are *ginbari* pieces both with and without wires, including monochromes. Many Japanese masters created both *basse-taille* and *ginbari* pieces.

Soon, their facility with transparent enamels and foils induced Japanese masters to develop creative applications using foils only in limited areas rather than over the entire surface. For example, some began inserting small pieces of foil and transparent enamel cordoned off by wires among predominating opaque enamel to produce effects like the appearance of sunlight passing through the petals of a flower or the gossamer quality of insect wings. Others created design elements by placing patterns of reflective strips that stood out against a darker surface, producing alternating ground effects (chevrons, squares, etc.) readily visible beneath the overlying transparent enamel, but not requiring laborious wiring to achieve a similar effect ↘ Fig. 12.2.

Similar uses could be made of foil under translucent rather than transparent enamels. Another maker employed an even more difficult variation by sandwiching crisscrossed strips of thin silver between the layers of translucent enamel in a *plique-à-jour* vase, thus creating a shimmering net bird-enclosure.

In recent decades, contemporary Japanese enamellers continue to use foils with innovations in both technique and design. Circa 1970, the Hirobyashi Cloisonné Co., Ltd., developed a new less costly system than traditional *ginbari* ↘ Fig. 12.3. However, it, too, requires a complex, many-step process. Here, the substrate, most often a flat plaque or tray with upturned edges, is first counter-enamelled on the reverse twice and fired both times. Then, on the outer surface, industrial enamels of the type employed on bathroom and kitchen wares (rather than decorative-art enamels) are used because they lie flatter on the metal substrate, providing a smoother surface on which to subsequently place and fire the foils; these industrial enamels are then fired to the substrate, again twice. The foil has been produced in a complex manner. First, a flat, paper-thin foil cut to the size of the intended substrate is squeezed – using a manual roller-press – against a bed of thousands of miniscule cut-metal bits, thus creating a textured surface. The textured foil is minutely punctured and then impressed more deeply over a pattern of raised outlines that depict the desired image. These outlines replace *cloisons* as the means to delineate the image. This textured, punctured, and pattern-impressed foil is glued over the industrial enamels and gently smoothed with a sponge to fit any curves of the substrate without flattening the raised pattern and texture. It is then fired at a temperature below silver's melting point. The industrial enamels melt and fill in under the raised pattern lines of the foil sheet so the outlines remain elevated and are bolstered by the hardened enamel. Then, a series of stencils are used, one for each colour. With each stencil, a thin layer of glue is sprayed through the holes to hold the coloured, transparent powders in place on the underlying foil when they are sprinkled over the glue. The piece is fired again. Usually, gluing, sprinkling and firing are repeated for each different colour so they do not run together. Finally, after firing all the colours, clear enamel is laid on and fired to produce the ultimate surface. Thus, in all, ten to sixteen firings are required. Hirobyashi also developed a partial foil technique, using thicker silver that is first reticulated and tinted with transparent enamels before being glued and fired to a dark-enamel piece, after which clear enamel covers the entire surface.

Rather than develop an assembly-line collaborative technique, Takeyama Naoki (b. 1974), in Toyota City near Nagoya, has adapted foils to dramatic artistic purposes. Working entirely alone, he creates arresting contemporary designs using precious-metal-foil lines, circles, ovals, rings and other patterns, achieving international acclaim for his enamel sculptures ↘ Fig. 12.4. Takeyama first produced superb *cloisonné* work, but quickly stopped using wires and instead adopted foil decoration on monochromatic grounds. Initially, he produced functional objects like bowls and vases with a traditional base-plate. Soon, he eliminated the base-plate so his pieces were no longer functional, and thus became sculptural objects.

A Takeyama's enamel sculpture requires time-consuming and difficult steps that can take a month to complete. He begins with a flat copper sheet and, entirely by hand, creates deep folds, bends, and creases using only his table edge and a metal bar to produce a corrugated surface. Then the vertical ends are brought together and soldered to create a continuous form. Takeyama next applies moist powdered enamels covering the entire copper using a small sieve and bamboo paddle to place the powders uniformly among the curves. The piece is fired at about 800 °C in a small kiln. After firing, Takeyama adjusts the piece to remove any fire-induced warps and smoothes the enamels using polishing charcoal. This sequence of enamelling, firing, adjusting, and smoothing is repeated ten or more times until the desired color and luster is achieved. He then decorates his pieces with silver or gold foils that he has cut or punched into the desired shapes. He attaches (using a seaweed- or rice-based glue) at least dozens, usually hundreds, of these foils over the undulating surface of the enamel to produce an all-over pattern with exceptional precision despite the complex form. The piece is then fired, sometimes as many as five or ten times, to properly fuse all the individual foils to the surface. Finally, Takeyama fires a coat of clear enamel over both foil and coloured enamel to produce a uniformly shiny surface.

Takeyama's contemporary use of foils, both straight strips and punched shapes, is resonant of earlier Japanese masters' imaginative use of shaped foils that enhanced their acclaim 100 years ago.

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Study of Limoges painted enamels by X-ray fluorescence spectrometry (XRF) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) ↘

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Six painted Limoges enamels from the collection of the National Museum in Warsaw were the subject of this study. The majority of the analysed enamel plaques, except from one belonging to Józef Choynowski – a Polish amateur-archaeologist, come from the Gołuchów collection owned by Princess Elżbieta (Izabela) Gołuchowska née Czartoryska (Viegas Wesołowska and Mistewicz 2016). Both collections were created in the second half of the 19th century.

The artefacts are painted in translucent and opaque coloured enamels with the use of silver and gold paillons beneath translucent enamel layers finished with gold painted details. The plaques are attributed to different workshops of enamellers active in Limoges in the 16th century:

- SZM 1006 MN and SZM 1240 MN enamels representing Peers de France - Count of Champagne and Bishop – Count of Beauvais are considered to be made in Colin Nouailher's atelier;
- SZM 1243 with The Annunciation scene is attributed to Jean I Pénicaud;
- SZM 1244 MN with the depiction of The Crucifixion is attributed to enameller Jean II Pénicaud;
- SZM 1261 MN representing a portrait of Francis II is attributed to Léonard Limousin (Anon. 1973);
- 31883 MN possibly depicting Valerius Maximus is of unknown attribution.

Art historians have recently raised concerns about the authenticity of the plaques suggesting they might be 19th century fakes. The opening of a new gallery at the National Museum in Warsaw, the Gallery of Old Masters, was an impulse for conservation of the enamels collection as well as an opportunity to attempt to answer art historian questions regarding the authenticity of the enamels. Elemental analysis of selected artefacts

was also possible within the conservation research programme.
The aim of the research was to obtain information about:
1 type of materials,
2 state of preservation,
3 materials used during past conservations.

Two instrumental methods were used to study elemental composition of the enamels: X-ray fluorescence spectrometry (XRF) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The uniqueness of the enamel plaques determined the choice of methods as well as their sequence. The use of the portable XRF spectrometer Tracer III-SD (Bruker) allowed for non-invasive in situ measurements at the museum's Ceramics, Glass and Metal Conservation Section. The XRF spectrometer was equipped with a vacuum system to increase sensitivity for lighter elements (e.g. Mg, Al, Si). In total 56 spectra were collected from the surfaces of the objects to evaluate the elemental composition of glass representing different colours. Each XRF spectrum was acquired from an area of ca. 0.5 cm^2.
Pb and Sn were detected in all colours of enamel. However, the highest signal intensities of these elements were observed for white opaque areas of the analysed plaques. In translucent violet enamel, additionally Mn and Fe were determined. High Fe and Cu signals were present in green areas; Cu, Co and Fe in blue ones. Fe peaks also dominated spectra registered for yellow, orange, red and brown enamel.
The XRF results of qualitative analysis were coherent with LA-ICP-MS quantitative data obtained from the measurements performed on tiny fragments of translucent enamels, which were collected in the form of 3 micro-samples with dimensions of ca. 1 mm^2. These samples were available as loose fragments found in the case where the artefacts had been stored. The samples were adhered with epoxy resin to a paper support and immobilised for the entire time of LA-ICP-MS quantitative analysis. A loose silvery foil sample used as a repair material for the plaque SZM 1244 MN was also analysed using the Inductively Coupled Plasma Mass Spectrometer NexION 300D (Perkin Elmer) equipped with the laser ablation system LSX-213 (CETAC). For all investigations, the samples were placed inside the ablation cell with SRM NIST 610 and Corning B glasses used to calculate the accuracy of the measurements. Standard reference material NIST 610 (trace elements in glass) was used as an external standard. The results for all samples were recalculated to the content of the respective elemental oxides with SiO_2 as the internal standard and normalisation to 100%.

The condition of micro-samples was evaluated under a microscope - no corrosion layers were observed and enamels were rather homogeneous, therefore ablation points (n=3) or lines (n=3) were selected randomly on the micro-samples surface.

LA-ICP-MS quantitative results were compared with literature data (Roehrs and Stege 2004, van der Linden et al. 2010). An initial conclusion based on this comparison found similarities between the elemental composition of the investigated objects and elemental composition of enamels from the 16th and first half of the 17th century.

The composition of the investigated enamel plaques revealed a relatively high content of Na_2O (c > 11.0 wt%) and CaO (c > 3.0 wt%) with the content of K_2O c < 3.5 wt%. Previously suggested dating of these enamels to the 19th century should be rather accompanied with Na_2O content < 5.0 wt% and CaO c < 2.0wt% and a remarkably higher content of K_2O (c > 8.0 wt%). The LA-ICP-MS information about PbO content also fit the new dating.

The lowest content of PbO determined in the enamels produced after 1500 would be still significantly higher than the highest PbO content quantified in the plaques from National Museum in Warsaw (<0.6 wt%).

Among the analysed objects, one was exceptional in respect of the overall elemental composition determined by XRF. The spectra registered from different areas of plaque SZM 1244 MN indicated the unexpected presence of Pt. These areas were visually identified as past repairs, and with increased interest the authors proposed further analysis of the foil micro sample with LA-ICP-MS elemental imaging (11 lines). The presence of a remarkable (even up to 40 wt% in some areas) Pt content in the foil fragment was confirmed. Ag, which was previously supposed to be the main component of the foil, was found predominantly on the edges of the micro-sample. Such distribution of Ag might indicate the junction between original silver foil and the later Pt repair. Pt was co-distributed with Ir, Rh and Pd, which usually accompany Pt ores, therefore their co-presence was assumed to confirm the natural source of Pt used to fill damaged areas of the investigated artefact.

The identification of Pt as a repair material enabled to estimate the dating of the conservation treatment and strengthened the new dating of the artefact. Until 19th century Pt did not have a good reputation. It was cheaper than Au and Ag, so the use of this metal for repairs was economically reasonable. Platinum foil was known from the 19th century, still being described as a rather difficult metal to handle. The platinum foil was mentioned for the first time in 1819 during the Industrial Exhibition in Paris, when lab apparatus, medals and platinum leaf were presented (McDonald and Hunt 1982). The metal quickly started to impress jewellers and goldsmiths, but the real value of it was recognised in the 20th century with the appreciation of its catalytic properties.

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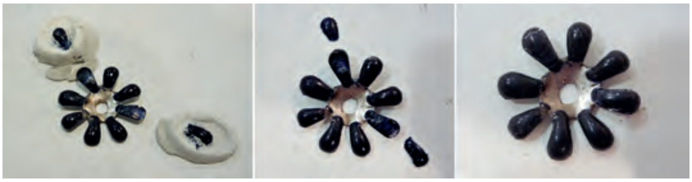
Rebirth of the Gundel Centrepiece – Methodological experiments in the restoration of enamelled metalwork ↘ Veronika Szilágyi

The centrepiece was produced in the Bachruch silverware factory in Budapest in 1907. A special feature of the 80 cm diameter chased ornamental plate decorated with gemstones and enamel is that some smaller ornaments were made by electrotyping ↘ Fig. 13.1. This fact was verified by metallographic investigations (see below). Due to the impressive size of the centrepiece and its spectacular and elaborate decorations, its damaged condition was not immediately apparent. The majority of the damage – besides the surface contamination and corrosion – consisted of deformations and missing parts causing instability. Numerous silver elements, gemstones and pearls had been lost, many together with their settings, while the enamelling had partly flaked away or was completely absent in places or previously replaced with plastic which was ageing.

The main objective of the conservation was to structurally stabilise the object, with an additional aim being to improve the integrity of its appearance. While the enamelled silver pieces were cleaned gently with cotton swabs dipped in acetone the tarnished silver parts were cleaned with acidified thiourea. A mixture of Paraloid B-72 and poly(1-acetyloxiethylene) (polyvinyl acetate) was used as a protective coating.

The infills of most of the damaged enamels were made of kiln-fired enamel. Negatives were made from the missing elements using silicone putty. From these silicone forms positives were made of the type of plaster used by jewellers. Enamel powder was applied to the plaster forms and fired in kiln ↘ Fig. 13.2. This method makes feasible the manufacture of infills that fit precisely in the missing spaces, and which are similar in material and appearance to the original parts. These were adhered into their place with a 30 percent solution of Paraloid B-72. Some of the enamel supplements on the centrepiece needed retouching with water-based porcelain paint (made by Interkerám Co. Kecskemét, Hungary) to imitate the original patterning ↘ Fig. 13.3. Some other infills were made of powdered enamel mixed with a 30 percent solution of Paraloid B-72. The infills of the silver ornaments were

↘ **Fig. 13.1**



↘ **Fig. 13.2**

↘ **Fig. 13.3**

↘ **Fig. 13.1** The Gundel Centrepiece before restoration (© Gábor Nyíri, HNM).

↘ **Fig. 13.2** Replacing and affixing missing enamel with fired enamel elements (© by the author).

↘ **Fig. 13.3** Affixing the missing enamel sections after retouching (© by the author).

↘ **Fig. 13.4**
Replacement parts (© Iván Jaksity, MAA).

↘ **Fig. 13.5** The Gundel Centrepiece after conservation (© Gábor Nyíri, HNM).

↘ **Fig. 13.4**

↘ **Fig. 13.5**

produced out of a 935‰ silver alloy using various goldsmithing techniques like rolling, sawing, soldering, gem fitting, enamel and filigree ↘ Fig. 13.4. The missing gems and pearls were replaced with pieces similar to the original ones ↘ Fig. 13.5.

Appendix: Scientific Investigations

X-ray radiography (by using a portable digital device belonging to the Artwork Examination Laboratory of the HUFA) facilitated a more precise understanding of the hidden structural components. *Ultraviolet photography* (made in the Photograph Laboratory of the HUFA) revealed previous enamel repairs and infills, different layers of coatings, and traces of adhesive. For elemental analysis *X-ray fluorescence measurements (pXRF)* was carried out (by Dr. Zoltán May, Institute of Materials and Environmental Chemistry at the Hungarian Academy of Sciences). *Electron beam microanalysis (SEM-EDS), X-ray diffraction examination of texture and residual stress* (by Árpád Kovács and Dr. Márton Benke in the Complex Laboratory of Image and Structure Analysis (LISA) at the Institute of Physical Metallurgy, Metalforming and Nanotechnology, University of Miskolc (UM)) were performed. Metallographic analysis, which required samples to be taken (by Dr. Péter Barkóczy, UM), verified the use of electrotyping.

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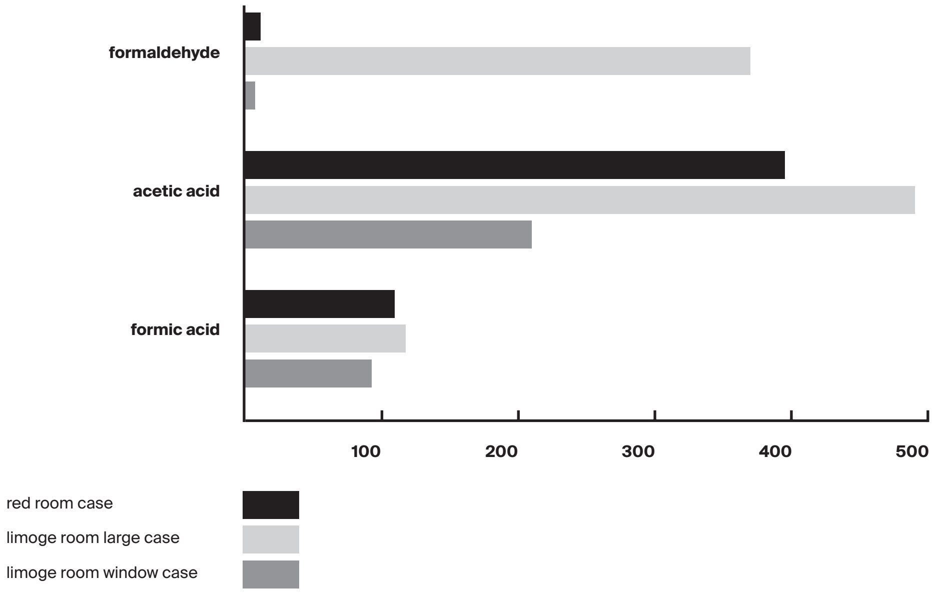
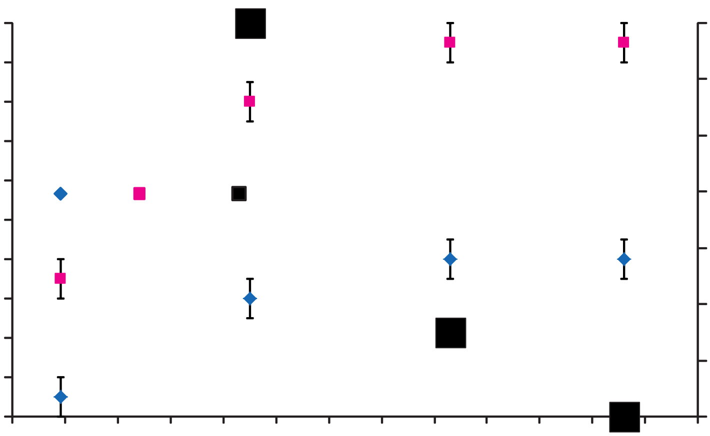
Preventive conservation of Limoges enamels

David Thickett

English Heritage displays the Wernher collection on a 100 year loan at Ranger's House, London. As well as significant ivories, bronzes, ceramics, and early paintings, it includes an important group of Limoges enamels. In 2002 the display was opened with new or refitted original showcases.
Two issues became apparent when the environment was monitored and assessed. The showcases had 2 kg per cubic metre of artsorb to control the relative humidity. This value was based on information published on the manufacturer's website, indicating 1 kg per cubic metre was sufficient and doubled to provide a safe margin. Monitoring (Rotronic hygroclip T/RH probe on Meaco radiotelemetry system) rapidly showed the showcases could not maintain the 35–40% RH target set. The three cases spent 14.2, 9.5 and 7.8% of the time in a year above 40%. Unfortunately the showcase design, evoking Wernher's own display of his collection, did not permit adding additional Artsorb™. The second issue was the use of Dacrylate coated MDF inside the showcases. Research had shown this coating, whilst effective against formaldehyde, does not block acetic and, more importantly formic acid released from the MDF, which can accelerate glass deterioration (Thickett 1998, Robinet et al. 2007). Measurements of the pollution concentrations were undertaken with diffusion tubes for formic and acetic acid and badges for formaldehyde. The measurements took place in late summer when concentrations were expected to be at their maximum values. ↘ Fig. 20.1
The results showed moderate concentrations of acetic and formic acid. The formic acid concentrations are certainly high enough to accelerate degradation of certain glass compositions. Formaldehyde was generally low, except for the large case in the Limoges room. Examination of the internal fittings highlighted a plinth with a screw splitting the coated MDF. This totally negated the benefit of the coating in blocking formaldehyde, which is thought to be beneficial for certain copper-containing glasses (Schmidt 1998).
A number of interventions were made to improve the case environments. Initially, the Artsorb™ was replaced with Rhapid Gel™; a silica gel with a larger capacity in the RH range and slightly better sorption properties for the gases detected. This still proved ineffective and a mechanical system was installed into each case. Hahn RK2 units were selected because, as well



↘ **Fig. 20.1**



↘ **Fig. 20.2**

↘ **Fig. 20.1** Elemental mapping of Pb, Co and Sb (labelled F5) on light blue enamel of book cover 1908,38

↘ **Fig. 20.2** Results for a blue and purple enamel as having the capacity to closely control the case RH and remove pollution, the air is fed into the case through a narrow, 5 mm tube. This could easily be concealed under the carpet edge for cases without a power supply underneath. Extensions were procured to connect the control probe in the case back to the unit.

The degree of deterioration of the enamel glasses was assessed with Fourier transform infra-red spectroscopy, using a Nicolet Inspect fixed focus FTIR microscope running off a Nicolet Avatar 360 bench. This method passes the radiation through the glass, where it is reflected back by the copper. The instrument has a fixed focus and analyses a 100 μm diameter circle. Melinex masks were made with pinholes to reposition the analysis in future. The degree of degradation can be readily measured with splitting of the absorption peak around 1000 cm^{-1}(Earl 1996) This phenomenon has been found to be reproduceable on the curved and rough glass surfaces and relatively unaffected by the phase change effects that often interfere with reflectance FTIR. Measurements were taken on each glass colour until 15 good spectra were obtained ↘ Fig. 20.2.

After 3.5 years the splitting increased dramatically. This was unexpected and further confirmed the environment needed remediation. Replacing the artsorb with Rhapid Gel decreased the amount of time for each case above 40%, the results for the window case are shown in ↘ Fig. 20.2. However, after a further 1.5 years the splitting for the blue enamel appeared to be increasing, but was not statistically significant. The splitting for the purple enamel was statistically significant. This prompted the installation of the Hahn RK2 unit. After 4.5 years with units running, the splitting has not increased. The pollution levels were re-measured and found to be below detection limits (28 μg/m³ for acetic acid, 38 μg/m³ for formic acid and 2 μg/m³ for formaldehyde). The RH has been reliably kept between 36 and 39%. Longer monitoring would be required to assess the new deterioration rate. This will unfortunately be difficult as the instrument has failed and is unlikely to be repaired. It is very unlikely the deterioration rate is zero, but it has been very significantly reduced. Tests have indicated the Bruker Alpha with reflectance accessory, generates similar data and it will be used for further work.

Application of a newly developed high resolution optical coherence tomography unit allowed quantification of the gel layer depths on the enamel surfaces and enamel/metal interfaces. These results agreed very closely with the FTIR derived data from the last measurement set.

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