The musée municipal de l’Evêché in Limoges: Actor and crossroads in Limoges painted enamels research

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The museum of Limoges was created in 1845 by the Société archéologique et historique du Limousin. Since then, it has been in the heart of the research on Limoges enamels in general, and on Renaissance painted enamels in particular.

Its resources make it a reference study place:

**By its collections**, recognized a long-time ago as one of the ten firsts in the world. They are regularly increased by a steady acquisition policy.

**By its specialized library**, rich in ancient and modern works on enamels, in exhibition and sale catalogs, in periodicals and other research tools (Illustrated Bartsch, Bulletin de la Société archéologique et historique du Limousin).

**By its picture library**, containing sets of clichés acquired by purchase or exchange with diverse museums collections. Some are still not published (as for the imagegs of the Écouen and Victoria and Albert Museum enamels collections); clichés made by the C2RMF at the concusion of the research launched by the museum of Limoges; all the amateur clichés made by Madeleine Marcheix, a big specialist in Renaissance enamels and curator of the museum from 1963 until 1988; negative glass plates made by Émile Lachenaud (1835-1923), amateur and engravings collector and author with Louis Bourdery (1852-1901) of a vast investigation on Renaissance enamels.

**By its archives**: Émile Lachenaud’s notes and documents, Louis Bourdery’s descriptive files, as well as Madeleine Marcheix’s documents and working notes.

Contributions of the museum to the research on enamel on metal: some examples

**On the history of enamels:**
- Thanks to the Bourdery’s files and to Lachenaud’s clichés, a set of plates by Pierre Reymond illustrated with Works of the Months (today scattered), was exactly dated in the year of 1565.
- A group of 14 plates from a set of Pierre Reymond dedicated to Jason and the conquest of the Golden fleece, was first published by Marquet de Vasselot in 1913. He was able to identify the group by tracking down the models and the financier. Lachenaud, by studing the inventory of Jabach after his death in 1696, identified a 15th plate. Further research led to the acquisition of 4 additional plates of the set by the museum between 1993 and 2007. This brings to 22 the number of plates known today of the 26 originally made for the set.

**About engraved models:**
- Identification of two plates recently attributed to Jean III Pénicaud: scenes of the Exodus, according to Bernard Salomon’s engravings.

**About the enamellers:**
- In 1990 Madeleine Marcheix identified a mysterious enameler, active in the middle of the 16th century, who signed his works with the monogram MDI or MDPP: Martial Ydeux.

- The study of Jean Guibert's style and a first corpus of enamels which are attributed to him was published in 2007, following the acquisition by the museum in 2005 of a medallion with the monogram IG. The artist was active at the beginning of the 17th century and the city library of Limoges possesses a work which belonged to him, in which he wrote his name in 1609 and added pen-and-ink drawings.

**Museum’s collaborations in:**

**Multidisciplinary programs**
- Collaboration with Isabelle Biron at the C2RMF (within the framework of the group émail). The museum loaned enamels from its collections for physical and chemical analysis in order to establish a database on 19th century enamels and gildings;
- Collaboration with Béatrice Beillard (within the framework of the group émail) for conservation treatments. The museum loaned enamels from its collections for structural analysis and for a general study on the assemblage systems of the pièces de forme;
- Organization by the museum of an international conference in Limoges in September 2004: *Les émaux peints limousins : au cœur des arts décoratifs de la Renaissance* (22 communications during 3 days).

**Collective programs**
- Collaboration with the *Petit Palais - musée des Beaux-Arts de la Ville de Paris* (Françoise Barbe): exhibition in Limoges and a catalog by 4 authors (*La Rencontre des Héros*, 2002);
- Collaboration with the national museum of the Hermitage in Saint-Petersburg (Tamara Rappé and Larissa Bulkina): exhibition in Limoges and research assistance for the study of the objects for their publication: history, identification, objects comparison (*Émaux limousins du musée national de l’Ermitage à Saint-Pétersbourg*, 2004).

**Other short and middle term projects:**
- Renovation of the museum with a new display of the collections and a more accessible library (in progress).
- Creation of a web site (in progress).
- Publication of the general catalog of the enamels collection.
- Creation of a database on Renaissance painted enamels.
About Limoges painted enamels. Chronological evolution of the glass composition

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Introduction
The stylistic approach is often not sufficient to answer the important question, whether or not a painted enamel is a genuine work from the Renaissance or rather dates to the 19\textsuperscript{th} century. The aim of this scientific study was to characterise the Limoges School painted enamel production from its beginning at the end of the 15\textsuperscript{th} century until its revival in the 19\textsuperscript{th} century with regard to glass composition and fabrication techniques. Because glass supplied to the enamellers was continually improved in composition over time (also type and origin of raw materials changed), the glass chemical compositions of the Limoges painted enamels were expected to change over these four centuries. This study has been carried out by two laboratories: the Technische Universität Berlin and the French Museum Research and Restoration Centre (Laboratoire du Centre de Recherche et de Restauration des Musées de France - C2RMF) in Paris focusing mainly on German and French collections and utilizing two different non-destructive analytical methods.

Analyses of Limoges enamels by the portable micro X-ray fluorescence (µ-XRF) spectrometer of the Technische Universität Berlin were realised by Stege (née Bronk) and Röhrs during a research project between 2000 and 2003 (Bronk and Röhrs 2002, Röhrs 2003, Röhrs and Stege 2004, Röhrs and Stege 2004b). Here the focus was on German collections but objects from other collections were also investigated. Objects from French collections and the Wallace Collection, UK were analysed at the C2RMF by Isabelle Biron (Biron 1999, 2002, 2004) using Particle Induced X-and gamma-ray emission (PIXE, PIGME).

A joint database was established which will help to find criteria on which to authenticate and even to “date” doubted objects.

Database entries
The results of these two methods were used to build up a joint database of all compositional results. In total 165 objects were analyzed by portable µ-XRF and 67 objects by ion beam analytical techniques at AGLAE in the C2RMF. On these 232 objects 1250 measurements were completed and collected in the database.

To use the database for authentications of undated or unascribed enamels it was necessary to link the results of secure “reference objects” with a given production date.

In order to ascertain the compositions of genuine Limoges painted enamels. All the dates recorded in the database were provided by art historians from the respective collections specialising in this field. Some enamels are precisely dated since they are inscribed with a year, in other cases the attribution to a production period is more
vague, e.g. the attribution to the 2nd half of the 16th century. This uncertainty is obviously individual for each object. Beside the dating and composition further information on the object and the individual analysed spot were registered concerning the collection, inventory number and the name of the artist as well as the enamel type, colour, and transparency level. Since the production output of Limoges painted enamels had its fluctuations over the time, the number of database entries varies from period to period depending on the availability of objects. The number of database entries shows a maximum around the middle of the 16th century. In contrast, almost no objects and therefore very little data were available for the 18th century and for the first half of the 19th century. For detailed comparison of the chemical compositions the data set was subdivided into three main enamel types due to their substantial difference in composition: transparent enamels, opaque enamels and counter-enamels.

**Conclusions on compositional changes**

In general, changes in the type and accessibility of raw materials for the preparation of enamel glasses show strong parallels to glass-making technology. For enamels, which require lower melting temperatures and stronger colouring than glass, the quantity of ingredients had to be varied. There is only scarce archival information on enamel recipes related to Limoges and about the supply of the workshops with raw enamels and copper (Speel and Bronk 2001). This circumstance makes the scientific approach all the more necessary. As expected, the Limoges School enamel recipes were found to change over time and Limoges enamellers used different sorts of glass compositions between the 15th and 19th century.

This chronological evolution of the glass compositions enables us to authenticate and even to propose a “period of manufacture” for doubted objects. Most elements show changes in concentration which allowed grouping into three main periods by their variation in the glass composition: 1480 – 1530, 1530 – 1700/50 and 1850 – 1900. The compositional differences between these periods are mainly characterised by the levels of the lead oxide, the change of cobalt sources and by the lead and tin oxide contents for opaque white enamels as well as the introduction of modern colorants and opacifiers. Furthermore, between 1600 – 1700 the arsenic content revealed significant variations and, most valuable as dating markers, the introduction of several new colorants occurred in the beginning of the 19th century. Still unresolved are the enamel compositions of the 18th and early 19th century since few objects are attributed to this production period and were available for analysis.

**Acknowledgement**

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**References**


Translucent enamels on silver: examination of the metal substrate on a group of European 14\textsuperscript{th} and 15\textsuperscript{th} century objects

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A group of objects made of silver with translucent enamel dating from 14\textsuperscript{th} to 15\textsuperscript{th} centuries were the focus of a research study carried out at the Victoria and Albert Museum, London. The objects were diptychs, triptychs, plaques and box, acquired by the Museum shortly after its foundation in 1852.

The aims of the study were to identify the materials and methods of manufacture and relate these to the present state of preservation of the objects, and focused principally on the metal substrate. Results are also intended to reflect on the medieval goldsmiths’ skills and knowledge of materials.

Scientific analysis was applied for the understanding of materials but to a limited extent, and the results were taken foremost from visual and comparative analysis. Precise results are not necessary for the purpose of this study to obtain the final picture, particularly as 14\textsuperscript{th} and 15\textsuperscript{th} century goldsmiths did not accurately measure their compositions. Enamelling was already in use for centuries before this period, and goldsmiths no doubt continued the traditions of generations. But \textit{basse-taille} (low relief), a new technique in enamelling which developed in the 13\textsuperscript{th} century probably in Italy, required different material compositions and fabrication methods. The metal substrate preparation, as well as changes in the composition of the enamel used in \textit{basse-taille} enamelling (which are noted in this study) strongly suggest an understanding of materials by the goldsmith.

Unfortunately it is not possible to determine the provenance based on the composition, and is mostly based on stylistic evidence. Studies on availability and sources of raw materials, particularly for the enamels, have been published (Richter, Wypyski, 1997; Freestone, 1997), and are used as reference.

Identification of materials
Non-destructive qualitative X-ray fluorescence was applied to analyse the metal substrate. All objects were found to contain above 94\% silver, with copper as secondary or trace element, and both zinc and lead as trace elements (except for 218:1+2-1874, which was found to contain a lower content of silver, and zinc, lead and iron as secondary and trace elements). A high content of silver, or in some cases possibly even fine silver (99.9\% Ag), was used to achieve the best results for the translucent enamels.

Translucent enamels from this period have been the focus of previous publications (Richter, Wypyski 1997; Freestone 1997), and because it is not in the remit of this study to fully analyse the enamel composition, the available results have been considered as standards.

Condition and previous interventions
The main causes of deterioration of the enamels appear to be mainly mechanical rather than chemical. Firstly from physical impact, this has caused cracking of the enamel and in some cases lifting. Secondly from fluctuations in temperature causing
any air bubbles trapped in the enamel, metal or enamel/metal interface to expand and subsequently cause the enamel to break off. This initial deterioration has progressed to cause the metal substrate to oxidize. Considering the overall environmental conditions the objects in this study have been exposed to, the chemical composition of the enamels was found to be fairly stable. The metal substrate, exposed to the environment, formed a layer of silver sulphide. It is suggested in this study that the volume occupied by the sulphides being larger, has caused further lifting around the broken edges of the enamel. The sulphide surface also created a very poor adherence for the enamel. It is further believed the oxidation will only travel through the interface where the enamel is not completely fused to the metal substrate or in the presence of air bubbles. Through visual examination it can be seen that the objects in this study have had in most cases previous repairs/restorations, which may have been carried out before or after being acquired by the Museum. Old repairs to enamels have included the use of waxes and resins among others. All the repairs in this study have, without exception, failed in at least one of their purposes; types of deterioration include discolouration, crazing, further loss and damage to metal substrate. Historical repairs have been studied and published and will not be the focus of this study.

**Conservation and current trends**
Currently, the conservation of these objects is carried out in most cases by both ceramics and metals conservators, each dealing with their own discipline. One of the main problems encountered by metals conservators is the removal and stabilisation of the silver sulphides, particularly on the interface of the metal and enamel. Firstly, to what extent should the sulphides be removed on the exposed silver; secondly how to stabilise the sulphides which are inaccessible, along the cracks beneath the enamel. Current conservation procedures include the partial removal of silver sulphides. Protective coatings are not used for silver with enamels due to the possible damage to the enamels. The removal of previous coatings has been a point of debate, since in some cases these are securing fragments of enamel. Likewise the deterioration of the coating has caused further damage to the enamel and metal surfaces. The issue of the remaining silver oxidation needs to be addressed as in future the further deterioration of the metallic surface may cause lifting and possible loss of enamel. Currently the stabilising factor is the environment where the enamels are to be stored/displayed, and these require further monitoring. The current environmental specifications are described.

**Conclusions**
The materials and methods of manufacture were identified and strongly suggest a great knowledge by the medieval goldsmith. The preparation and composition of the metal substrate appears to be paramount to the final physical stability and durability of the enamel. From this study it also appears that although the depth of engraving adds a key to the enamel, it is not the main securing factor.

From other published research, it is agreed that a different composition of enamel was in use with the introduction of the *basse-taille* technique (Wypyski, Richter 1997; Freestone 1997). This was a high alkali composition, often totalling in excess of 20% by weight, with potash in excess of soda, but both soda and potash being high,
whereas lime is low at about 5%. We can conclude that there were certain advantages as well as disadvantages in the use of this composition:

- **Advantages of a high alkali composition:**
  - Compatibility with silver (high expansion coefficients and low melting temperatures)
- **Disadvantages**
  - Unstable composition; requires a conditioned and controlled environment

Future analysis of the glass composition would enable the comparison with published examples, and results would allow for further in depth study.

This study has shown that the main causes of the deterioration to the enamels are threefold:

1. **Mechanical damage**, causing cracking and loss of the surface. The poor environmental conditions subsequent to this initial damage have caused the silver to oxidise but not the chemical deterioration of the enamels;
2. Inherent **air bubbles**, which under large fluctuations of temperature have cracked and caused loss of enamel.
3. **Previous interventions**, enamel ‘infills’ have deteriorated and are often difficult to remove; previous ‘protective’ coatings have degraded, yellowed causing the surface to appear matt and discoloured.

It can be further concluded that the fluctuations in temperature may not always cause chemical deterioration to the enamels, (although there appear to be problems with particular coloured enamels such as the blue), but there is strong evidence to suggest physical damage may occur from expansion of air bubbles.

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Renaissance enameled gold and 19th c. imitation

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A recurring problem in museum collections, perhaps particularly in American collections, is that of distinguishing authentic works of art from later imitations. Of particular interest in recent years has been the question of 16th to 17th enameled gold jewelry.

Jewelry in the Renaissance was valued not only as a visible display of wealth, worldliness and social status, but was also highly valued and appreciated in itself as fine art. This jewelry, usually combining precious stones, pearls and gold was also commonly decorated with both translucent and opaque enamels. The modern fashion of collecting Renaissance jewelry for its artistic and historical interest apparently began as early as the 18th century, although it was during the 19th century that large jewelry collections were assembled, notably that of J. P. Morgan, much of which today is in the Metropolitan Museum of Art in New York. The limited availability of authentic Renaissance pieces coupled with a growing demand by collectors in the nineteenth century, not surprisingly, encouraged the sale of imitation works. Recent stylistic re-evaluations as well as documentary evidence, however, have raised questions as to the authenticity of some of these pieces, as well as many in other collections.

This study presents the analyses of enamel compositions from a group of European enameled gold jewelry dating from the sixteenth and seventeenth centuries, as well as from a group of enameled gold objects from the late nineteenth century, from the collections of The Metropolitan Museum of Art in New York and the Walters Art Museum, Baltimore. Quantitative analyses of the enamel compositions were done using X-ray microanalysis in the scanning electron microscope (SEM-EDS/WDS) to characterize the overall compositions as well as to identify the opacifiers, colorants and associated elements.

The 16th and 17th century translucent enamels can generally be described as having soda-lime-silicate glass compositions, with relatively large amounts of potassium, but only relatively small amounts of magnesium and aluminum and calcium. Little if any lead is typically found, although small amounts of lead were found in many of the reds. Unlike the translucent enamels, the opaque enamels all contain significant amounts of lead oxide, typically about 15 to 20 percent, but up to 50 percent in opaque yellow.

The translucent red enamels differ from most of the other colors, generally containing less sodium and more potassium than the other enamels, and may often be described as mixed-alkali compositions, rather than soda-based, many with more potassium than sodium. The reds also contain much more calcium and magnesium than generally found in the other translucent enamels, as well as somewhat more aluminum.
In contrast to enamels from the Renaissance period, enamels from the 19th century have been observed to have lead-potash-silicate or lead-alkali-silicate compositions, generally with much less sodium than in the earlier enamels. Lead oxide values in these enamels generally range between about 20 to 30 percent, although some, particularly the opaque whites, contain as much as about 50 percent. These enamels also typically contain extremely very low levels of other common glass-forming elements such as magnesium, aluminum and calcium. Arsenic is also present, at least in small amounts, in nearly all of these enamels, while in the earlier enamels arsenic is usually only found associated with cobalt containing colors.

Renaissance period enamels were colored by the addition of relatively large amounts of colorants such as iron, manganese, copper and cobalt, with the cobalt usually associated with nickel, arsenic and bismuth. Opaque enamels contain either white crystalline tin oxide or yellow crystals consisting of lead antimonate, sometimes mixed with lead-tin yellow. In the 19th century enamels, however, the main opacifier was a lead arsenate compound, although examples have been found which contain a mixture of crystalline tin oxide and lead arsenate. Other differences between the earlier enamels and those from the 19th century include the use of chromium oxide in the greens, antimony oxide in the reds, and the use of a purified form of cobalt.

_Cristallo_ glass, noted for its clarity compared to the more common type of glass, was developed in 15th century Venice, and appears to have been produced with the purified plant ash, which reduced the amounts of magnesia and lime, while increasing the levels of soda and potash. The similar composition of many Renaissance enamels also suggests the use of purified plant ash, although apparently with an even higher proportion of purified plant ash than that generally used in _cristallo_, and possibly the addition of a high potash source such as ash from ferns or from _tartaro_, a deposit that can form from red wine.

The finding presented here reveal definite chemical differences between enamels from the Renaissance and those typical of the nineteenth century, and can provide objective evidence to help distinguish between authentic Renaissance period pieces and later pieces done in Renaissance style, confirming or sometimes refuting evaluations based on visual evidence alone. However, evidence has also been found that some enamlers may have continued to use traditional enamel types well into the nineteenth century, and these compositions appear to be indistinguishable chemically from Renaissance period enamels. Thus certain compositions discussed here can with a great deal of assurance be described as modern and incompatible with Renaissance production, but the finding of Renaissance-type compositions, while favorable evidence of authenticity, is not absolute proof of a Renaissance date.

To complicate matters even further, technical examination of some questioned Renaissance jewelry has revealed a number of objects which apparently have had later additions or embellishments, or were remounted to form a pastiche of old and new material, with both Renaissance and 19th century type enamels on different parts of the same objects.
‘Émail en résille: Fact or Fiction?’

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The main aim of the present research is to understand the little-known and delicate enamelling technique of émail en résille sur verre (French for ‘enamel in a net on glass’). The second aim is to find and list as many objects as possible made with this technique, taking into account that some of the objects are in private collections and difficult to track down. The third aim is to compile a literature database on the subject.

The first impression when looking at émail en résille is its close resemblance to cloisonné enamel where fine metal lines separate the enamel colours. However, as the name of the technique suggests, the main substrate is glass and not metal. The objects are small and the glass varies in thickness from approximately 3 to 7 mm. In the glass there are shallow cavities lined with gold foil and these are filled with opaque and translucent enamels. The metal ‘lines’ seen on the surface are the edges of the gold foil lining the cavities. It is the gold foil and enamels that make up the design. The metal used for émail en résille is always gold. In the most delicate examples the ‘net’ made by the gold foil filled with brightly coloured enamels appears to float on the glass.

The émail en résille objects range from single unframed plaques to sets with several components. Some plaques provide a backing for a framed miniature or mirror, some plaques are placed on the front and back of watch cases including curved plaques around the sides. Some objects consist of several sections, such as girdle belts comprising around 20 framed plaques with links, whereas in other objects the enamelled components are inset into a larger whole, such as metal pomanders with enamelled segments. It seems there are two groups of émail en résille, grouped by technical and stylistic characteristics, as well as comparison with related objects made at the time. The first group may have been made in France at the end of the 16th century and would include watch cases and locket cases, pendants and mounts. The second group could have been made around 1620 in Central Europe, somewhere in South Germany, or in Prague. To this group may belong the girdles and a variety of plaques with images that appear to be based on engravings by Valentin Sezenius, a German engraver and artist (working 1619-24). Sezenius himself could have been the maker as well. Some objects could make up a third group formed by a revival of the technique in the 19th century involving the Parisian jeweller Froment-Meurice, or some of these pieces may have been made by forgers like Reinhold Vasters and Alfred André who may have been selling them as belonging to the 17th century. In the absence of evidence, the ‘grey areas’ continue to grow making any definite statements quite difficult.

The most recent attempt to use the technique seems to have been by the American jeweller Margret Craver who became interested in the technique from the late 1950s until the 1980s. She is said to have reinvented the technique through
experimentation. She was inspired by the appearance of the enamel floating on the glass and was able to develop a technique that suited her aesthetic requirements.

To date 21 objects have been closely examined; references to a further 18 objects have been found in books and catalogues, not including Craver’s contemporary work. There is little to be found in the literature and the descriptions of the technique differ. Some sources state that the difficult technique accounts for the rarity of the pieces. There is the added complication of the three possible periods, forgeries and that the technique may have subtly changed. The most quoted version of the technique states that cavities are ground into the glass, then lined with thin gold foil and finally enamelled. To date no evidence has been found for this technique. A more possible theory involves the use of steel or hardened pear-wood moulds to shape and hold the gold foil which was then backed with glass. After removing the glass and gold from the mould, the gold-lined cavities were filled with enamel and fired. Finally the surface was ground down and polished. It seems likely that some sort of mould could have been used since some designs are repeated in the so-called ‘second group’ of objects, namely the girdle sections. However, the question arises as to why these pieces are so rare if moulds were used.

The glass seen thus far was either blue or colourless, sometimes with a lilac tinge, one piece was a very light red and another light brown. There are references to dark brown, green and dark purple glass and a pomander with opaque white glass. The blue glass is often backed with metal foil, possibly silver. Sometimes the glass appears red, however under magnification or with transmitted light it can be seen that the glass is in fact colourless, and that the red colour comes from a red lacquer applied to a backing plate or from a resin used to attach the plaques themselves to the metal plate of a frame. The red colour of the lacquer is sometimes patchy or completely faded. The Reverse de mirroir (E.Cl. 20 867) in the Musée de la Renaissance at Écouen is made with transparent glass that appears red because of a coating of translucent red lacquer on the metal backing plate. This frame can be removed and the glass taken out to appreciate the maker’s intentions. When the transparent glass containing gold and brightly coloured enamels is placed over a red background, the design gains contrast and definition; on the other hand, details in dark colours tend to get lost in the busy design.

Condition of the objects:
- **Glass**: breaks with associated chips, the breaks sometimes affect the gold foil; some plaques are loose within their frame. Glass surfaces vary from slightly pitted, matt, scratched, to very shiny. Two similar watch cases have émail en résille plaques on the front and back and one also has four curved plaques on the sides. The glass appears to be chemically unstable, all four plaques have breaks and the glass appears to be crizzled; the glass in one watch case appears to be more degraded than the other with large amounts of green corrosion products to the metal around the edge of the glass.
- **Metal foil**, possibly silver, generally in good condition, although a few degraded spots were seen.
- **Gold foil**: solidly attached to both glass and enamel; gold disrupted locally at glass breaks and missing small pieces of foil. Slight tarnishing seen in areas of damage to girdle sections.
- Enamel: generally the enamels appear in a fair condition and although there are small losses the enamel is well attached to the gold. In one piece the white enamel was cracked and degraded with small losses, in one object the red enamel appeared slightly degraded. Ground and polished surfaces have open air bubbles with ingrained dirt.

- Red lacquer: has often lost its red colour (dye?), is often crackled, flaking and generally aged and degraded.

Technical observations:
- The gold foil is approximately the thickness of a pencil line. This is a visual approximation as no foil has been measured.
- The thinnest glass measured to date is a blue rectangular plaque of 2.5 mm, and the thickest is one area of a blue oval medallion of approximately 7 mm.
  Smallest glass seen: H: 1.8 cm, W: 2.3 cm, D: 0.2 cm.
  Largest glass seen: H: 8.4 cm, W: 6.2 cm, D: c.0.3 cm.
- The air bubbles in the glass vary in shape (round and elongated), number (hardly any, very small, to quite noticeable in size and/or number), and location (near the edges, all over, small ones on the glass against the gold surface, amorphous and relatively large where trapped between the glass and the gold). Air bubbles can be seen on the enamels and are more obvious having been ground down during polishing when on the surface.
- The cavities for the enamel are generally shallow, perhaps 0.5 mm to 1 mm in depth.
- The most common translucent enamels seen: emerald green, bright red, royal blue, pale to burnt amber (yellow) and turquoise; rarely seen: brown, mulberry, grey.
- The most common opaque enamels seen: white, yellow, cerulean blue, chartreuse green, pink, mauve; rarely seen: turquoise and brick red.

The work carried out so far is the first stage of the research. It includes becoming familiar with the objects and gathering information. It is hoped that through study of the objects from a technical point of view, more information and evidence can be gained that will help to date and group these objects.
Investigating conservation approaches to guilloché enamels with silver substrates

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Guilloché enamels are identified by machine-engraved metal over which monochromatic, translucent vitreous enamel is fused. They were predominantly manufactured from the second half of 18th century into the 20th century. As a student in Metal Conservation-Restoration at West Dean College, an MA in Conservation Studies was undertaken in 2007 during which the history, technology, deterioration and conservation of guilloché enamels on silver substrates were researched. The emphasis of the investigation was on the metal substrate.

Damage was observed in a range of examples, but little information specifically concerning guilloché enamels could be found. Guilloché and other enamels share an extent of generic deterioration. Impact damage was identified in surveyed examples, and it was hypothesized that following damage, the low-relief surface engraving may provide channels for sulphide and introduced material travel under semi-adhered or cracking enamel. The resultant sulphide growth can lead to loss of enamel over time, or loss of the original metal surface through repeated or inappropriate cleaning. Conservation approaches to these areas were considered and carried out on model guilloché enamels on sterling silver bases that were made under the guidance of a traditional engine-turner.

Rose Engines and Straight Line Engines are man-operated, lathe-like machines developed in 1756 and produced into the late 1950s to engrave geometric patterning onto flat or formed metal sheet in the process of engine-turning. Visual effects result from the metal surface reflecting light through the overlying enamel. Guilloché enamels were produced in Paris, Geneva, Birmingham, London, Scandinavia and the United States by skilled craftsmen incorporating this early mechanized technique in their work. The makers not only achieved new levels of perfection but also innovation relatively late in the history of enamelling. The advantages of inherited knowledge are observed in their technical mastery and decisions to solve some of the difficulties related to other enamel types. Machine engraving of a uniform depth provides a key for enamel adhesion and a relatively thin, slightly domed enamel layer, set within a slightly recessed area are technical considerations that support the enamel’s endurance against expansion and contraction forces.

Guilloché enamels occupy a unique preservation status. The objects are relatively modern in the history of enamelwork and the machines and accompanying skills that produced the crucial surface engraving are continually less tangible. With the exception of working replicas and few remaining machines in use, it is relatively rare to recreate this work using traditional methods. The objects made were predominantly portable and utilitarian, increasing the potential for unintended damage. Inherent material characteristics elevate the potential and extent of the damage (Carpenter 1984). Many objects, especially later silver and copper alloy
examples, are in circulation or are privately owned, where storage and display conditions are less likely to be controlled to suit the object.

Enamel damage visually diminishes the original state of flawlessness achieved in these objects. As underlying silver becomes exposed, sulphide forms in ambient conditions. If untreated, the sulphide expands along the interface where enamel is no longer adhered, resulting in discoloration that cannot be reached by standard cleaning methods. Cleaning materials and optional surface coating materials may cause discoloration and become irremovable if they travel under semi-adhered enamel during treatment or later, when removed with liquid solvents. Some solvents, such as acetone, will cause damage to fragile enamel and silver foils. Overly abrasive metal cleaning methods will diminish the sharpness of the machine-engraving while removing original material. Repeated sulphide removal will have this effect in time. Many objects incorporate silver plating and faux engine-turning over a copper alloy base, where fine silver foil is stamped or burnished over an engine-turned pattern. These thin layers of silver could easily be destroyed if unrecognized before cleaning. Where the copper alloy base becomes exposed, a localized galvanic reaction takes place, where accelerated corrosion of the less noble metal occurs.

Alongside literature research and discussions with practicing conservators, a range of guilloché enamels from the Victoria and Albert Museum’s collection were surveyed and two private objects were obtained and studied for the duration of the project. To gain greater understanding of the creation of these objects, a series of samples were fabricated using traditional engine-turning and enamelling methods. These samples were used as the foundation for a series of studies. Current conservation treatment options were explored after physical and chemical damage were replicated on model enamels. Three standard cleaning methods, two dry, minimally abrasive and one liquid chemical treatment were considered, compared and practiced to remove deliberately formed sulphide. A limited amount of SEM/EDX analysis was possible, and was used to better understand the enamel/metal bond immediately surrounding areas of enamel loss in the enamel samples.

This study hopes to share the intriguing technology of guilloché enamels and to highlight manufacturing methods that affect deterioration and subsequent conservation options. Preliminary investigations were made through model enamels. Sterling silver was engine-turned, enamelled, distressed and tarnished in order to convey the efficacy and consequences of introducing standard cleaning materials to these areas. The work has set the scene for future research within this subject.

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A survey of enamel studies after fifteen years of activity at the C2RMF

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The aim of this talk is to give a general survey on the glass activity – mainly devoted to enamel studies - in the Research and Restoration Centre of the French Museums (C2RMF) since 1993.

The C2RMF is divided in two parts, the laboratory, located underground inside the Louvre Museum in Paris (scientific studies of art and archaeological objects) and the restoration workshops, located mainly in Versailles and for some inside the Louvre. The C2RMF belongs to the French Culture ministry and is devoted to all French Museums, with also from time to time works in collaboration with foreign museums.

The C2RMF is divided in departments; administrative, research, documentation, preventive conservation, restoration. The research department is organised around techniques, with our accelerator AGLAE, the development of different experimental tools and some dating methods, and around materials with painting, graphic document, polychrome object, metal, glass, ceramic, stone and organic compound.

The “glass speciality” has been established in the laboratory in 1993 with the arrival of I. Biron (specialist in physical metallurgy with a PhD devoted to radiation effects on glass). The team is limited to one permanent scientist, one student (PhD from 2006 to 2008), regularly some students for a few months and one retired scientist from the French industrial research laboratory Saint Gobain Recherche since middle 2007. For glass studies, we collaborate with French research laboratories (mainly SRMP CEA Saclay, Saint Gobain Recherche Aubervilliers, IMPMC Jussieu Paris, CRPG Nancy), with foreign museums (MET New York, Wallace Collection, V&A and British Museum London, Museu national de Arte Antiqua Lisbonne, Museu national de Soares dos Reis Porto) and with foreign institutions (like the National Institute of Cultural Heritage Oslo, Istituto centrale per il Restauro Rome, Stazione Sperimentale del Vetro Venise, Orsoni mosaic tesserae glass factory Venise).

The glass activity started with the collaboration between the Metropolitan Museum in New York and the Louvre Museum for the great exhibition on Limoges medieval enamels in 1995/96 which held both in Paris and New York. Since 1993, glass studies are devoted to:  
- enamels on metal for 80% of the activity (Limoges and Mosan medieval champlevé enamels on copper, cloisonné enamels on copper and iron, Byzantin and French plique cloisonné enamels on gold, basse taille and ronde bosse enamels on gold and silver, Limoges painted enamels on copper) / periods from IXth to XIXth century,  
- enamels on glass (Islamic glass) / XII-XIIIt century,  
- other glass objects for 20% (vessels, sculptures, figures, jewels, beads, inlays, mosaic tesserae, windows, mirrors) / periods from Egyptian Antiquity XVIIIth dynasty to XIXth century.
The activity of the glass group is mainly based on three fields:
1. the study of the fabrication techniques of the objects,
2. the characterisation of the materials
3. material science studies.
Important databases are established for all kind of enamel productions, both for fabrication techniques and for glass chemical analysis. As well as a better knowledge of ancient glass chemical and physical properties and technologies is acquired.

Different experimental tools from the laboratory are used for glass studies such as, ions beam analysis (PIXE, PIGE, RBS, NRA, ERDA), MEB with EDSX, X ray diffraction, m Raman and m IR spectroscopy, TDA, furnaces, climatic chamber (T, HR, light), X ray radiography and microscope observations... Complementary techniques are also employed in other laboratories like MET, FEG, SIMS, EXAFS – XANES ...

These three fields help us to develop the following research themes:

- **Authentication**
  (with a good knowledge of the fabrication techniques and the glass elaboration recipes)
- **Dating**
  (with the chronological evolution of the glass chemical analysis)
- **Chemical degradation of glass living in air and in archaeological context**
  - Characterisation
  - Mechanisms
  - Reproduction of glass degradation in laboratory (ageing)
- **Mechanical degradation**
- **Glass technology**:
  *The rediscovering of ancient antimony opacified glass technologies throughout history (PhD Sophia Lahlil)*
  - Characterisation of crystals and vitreous matrix
  - Syntheses of opaque glass in laboratory
- **Glass decoration techniques**:
  *Gilding on enamels (techniques and dating) (I. Biron/ S. Röhrs)*
  - Characterisation
  - Experimental gildings with enamellers
  - Syntheses of gildings in laboratory
- **Glass restoration products**
  - Ageing of organic consolidation products on a degraded glass surface
  - Study of the physical and chemical interaction between glass surface/consolidation product before and after ageing
- **Advice for the conservation and restoration of glass objects**

Some examples will be presented for the different themes of the glass/enamels studies.
Chalconatronite and socoformacite: joint copper glass corrosion

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Wood, especially when used for closed display cases, is a known source for pollutants like formic or acetic acid. While calcium acetate efflorescences on shells stored in oak cupboards ('Byne’s disease') have been known for over a century, in the last decades acetates and formates have been found on copper and lead alloys, glass, and calcareous materials like mother-of-pearl, coral, limestone, ceramics, etc.

A green corrosion product was detected during conservation on a 17th century limewood box of board games from the Hessisches Landesmuseum Kassel. Richly decorated with jasper, gilded silver, enamel, and inlay work it was made in the 1670s for Countess Hedwig-Sophie of Hesse-Kassel. It has fields for chess and Nine Men’s Morris on the outside, and backgammon in the interior. The box exhibits many traces of old repair and restoration. Some of the turquoise enamel (made from saline plant ash, ca 13-16 per cent Na₂O, WDX microprobe) used for the decoration of the silver alloy (ca 5.5 per cent Cu, AAS) backgammon fields flaked off. In some of the now open silver grooves, where there was formerly enamel (and only there), a light green crystalline corrosion product was found. It could not be matched with anything in the Powder Diffraction File (PDF) database, apparently an unknown copper corrosion product.

Astonishingly, the same compound was later identified on an object from a totally different cultural background – a ca 100 year old Chinese theatre hat (Ethnological Museum of Heidelberg, inv. no. 30406) which has long been stored in a wooden cupboard made from oak. The hat consists mainly of silk stabilized with cardboard. Silvered copper wire and glass beads were used as decorative elements. One metal spiral was covered with a light green blue corrosion product where it was in direct contact with an apparently weathered glass bead, showing iridescence and crizzling.

The compound was at last found to be identical to one described by Trentelman et al. in 2002 (Studies in Conservation 47(4), 217-227). According to their XPS and Raman data it is a mixed sodium copper (1:1) formate acetate (here abbreviated as 'socoformacite'), with the formate/acetate ratio estimated between 1:2 and 2:1. The ratio need not necessarily be whole-numbered so that the general formula might be given as NaCu(HCOO)₁₋ₓ(CH₃COO)ₓ·₂·₉, with 0 ≤ X ≤ 1. It has been observed on a number of archaeological copper alloy artifacts at several institutions (Only one object was non-archaeological). Egyptian or other arid soils can be quite rich in soda, so that sometimes even chalconatronite (Na₂Cu(CO₃)₂·₃H₂O) is found as a corrosion product. But this compound may also be found as consequence of prolonged immersion in sodium sesquicarbonate solutions (Pollard et al. 1990), a traditional conservation treatment for bronze disease. When copper and sodium ions are present in a hydrogencarbonate/carbonate buffer solution (e.g. a humidity film on a corroding object) chalconatronite may form on drying. Caustic soda solutions as have been used in now outdated electrolytic or electrochemical treatments might remain in
pores of the corrosion crust. They will then also form sodium carbonate by uptake of carbon dioxide from the open air. But for the objects described here, both soil logging and immersion in sodium carbonate solutions can be absolutely ruled out as sodium source. From the particular circumstances (copper containing alloy in direct contact to glass with wood present in a closed space), it is clear that the sodium must originate from the glass, while the acetate and formate come from the wood. This is the first time socoformacite formation has been observed with the sodium coming from glass corrosion.

To further test the frequency of this phenomenon, green corrosion products from enamel objects were sampled in another collection which was known for storage problems from wood (as indicated by the occurrence of thecotrichite, a calcium acetate chloride nitrate on ceramics). All 7 samples (from 2 different objects) consisted of the same corrosion product.

The detailed mechanism of the formation of socoformacite remained to be studied. One possible route is the intermediate formation of solid carbonates like the normal metal or glass corrosion products malachite (basic copper carbonate) and sodium carbonate in the presence of carbon dioxide from the air. The mixed sodium copper carbonate chalconatronite has already been found by others as corrosion product on a 15th century Italian enamel covered cup (tazza) under flaking enamel on a copper alloy substrate and on a copper wire inside a 18th cent. Venetian (?) glass figure. Chalconatronite may later transform into the formate-acetate when exposed to carbonyl pollutants (i.e. organic acids or aldehydes as their precursors). Interestingly, the sample from the game box contained a little carbonate. Nevertheless, this hypothesis could not be verified so far in a number of experiments exposing synthetic chalconatronite to various acid vapour concentrations in desiccators.

An alternative route to socoformacite would be the direct formation from solutions (such as humid films on objects during high relative humidity phases) containing all four ions of the compound simultaneously. The occurrence of socoformacite on a number of bronzes from various collections led to the hypothesis that its formation might occur over a wide range of concentrations and other parameters like rH and T. Therefore, in an attempt to synthesize socoformacite and grow single crystals (our crystals and those observed by Trentelman et al. (2002) were too small to allow a crystal structure determination), 4 x 4 = 16 solutions of varying contents from 20, 40, 60, and 80 per cent for the anion formate (the rest being acetate) and for the cation charge of sodium (the rest of the positive charge being divalent Cu$^{2+}$) were mixed. A number of phases were observed but no mixture precipitated socoformacite on drying. Apparently, the conditions for the formation of socoformacite seem to be more special than expected. Further attempts at synthesis should also take the pH into account and perhaps vary it additionally. As long as there is no good synthetic or natural single crystal for analysis, the crystal structure of this compound will remain unknown.
Conservation contributions in the study of enameled services

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This talk continues another one given at the Limoges conference in 2004 (Les émaux peints limousins : au cœur des arts décoratifs de la Renaissance). This former communication was centered in the analysis of enameled dishes techniques, and the joining techniques for cups was described showing two types of assemblies: before and after enameling. After a brief reminder of these two techniques, I will describe several other joining types observed during conservation treatment.

During the 16th century, the enameled objects couldn’t be soldered because there was no alloy resisting the temperature needed for the firing of enamels: the copper/silver brazings melt at lower or equal firing temperatures. The enameling would then cause the breaking of the assembled parts. The assemblies were thus made mechanically.

The derestoration of several enameled dishes allowed us to have an access to the copper support. According to the shape of the foot, the assembly can be sewn (salière R 306 at the Louvre museum), riveted (cup 364 of Pierre Reymond, at the musée de l’Evêché), with pulled-down rivets (Pierre Reymond’s pair of salières "Tritons, Nereids and Centaurs " at the Hermitage museum in St-Petersbourg) or with rings (cup Genesis of Pierre Courteys). Very often different types of assembling techniques appear on the same object, notably at the end of 16th c. as in the the cups of Jean de Court on baluster stem (example of the salière of the Maître I.C, R 263, Louvre).

During the 17th century, the techniques are simplified and the objects are essentially assembled before enameling. The two-handled vases in black enamel with gilded decoration of the musée de Chièvres in Poitiers (inv. N 3898 and 3899) are a good example of joining before enameling with multiple fixations (Figure 1). It is also the case of small polyfoiled dishes at the beginning of the 17th century (as in the small dishes of the musée des Beaux-Arts in Dijon).

The study of the assemblies and the examination of remountings result in a typological study of the forms. Objects reassembled during the 19th century are numerous and the objects that kept their original assembly are precious because they allow to complete the study of forms begun Madeleine Marcheix thirty years ago. During its treatment, the technological examination of the cup N 364 PR of the Limoges museum put in evidence a disparate assembly: the foot by Pierre Reymond does not correspond to the visible tracks of fixation present on the cup.

The derestoration process also brings information on the history of the object and on the history of restoration. The 19th century restorations with tin are common for consolidation or refixing.

The recent treatment of the Laocoon, conserved in Limoges at the musée de l’Evêché revealed the insertion of about a dozen enameled restitutions, inlaid in the original plate and fixed with tin (Figure 2). Such a work testifies of the capacity of the
enameler to copy Pierre Courteys and of the restorer’s ability that inlays these restitutions by means of fine welds. Finally, the decision to modify the original image with a veil of pudeur shows the evolution of the mentalities that touched enamels, as well as it touched paintings, during the 19th century.

Figure 1 - vase du musée de Chièvres à Poitiers
Les huit éléments sont assemblés avant l’émaillage.

Figure 2 - Le Laocoon de Pierre Courteys, musée de l’Evêché à Limoges.
Douze restitutions émaillées sont incrustées sur cet émail en relief. La plus grosse est celle du genou droit du père.
Preserving the enamel on Benvenuto Cellini’s “Saliera”: Analysis of its composition by XRF and SEM/EDX and first consolidation attempts

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Benevenuto Cellini was highly esteemed and richly rewarded as an expert goldsmith and sculptor by the ecclesiastical and secular princes of his age. He made the famous “Saliera” between 1540 and 1543 for the French king Francis I after a wax model designed for the Cardinal of Ferrera, who hesitated to produce the salt cellar because of the high costs connected with this project. Today the “Saliera” is kept in the “Kunstkammer” of the Kunsthistorisches Museum (KHM) and is regarded in history and theory of art as one of the most beautiful and significant works of the goldsmith’s art of the sixteenth century. It is made using a precious gold alloy and major areas are decorated with delicate enamel in different colours.

To enable the “Saliera’s” restoration before re-exhibiting it in the KHM’s permanent exhibitions and for superior historical classification of the enamel used, the compositions of the gold alloy and especially the differently coloured enamels were studied by non-destructive X-ray Fluorescence Analysis (XRF). For these investigations, due to a co-operation of the Conservation Science Department of the KHM, the Atomic Institute of the Austrian Universities (ATI), and the International Atomic Energy Agency (IAEA), Seibersdorf Laboratories, a portable XRF instrument could be applied. This prototype instrument uses a compact vacuum chamber to reduce absorption of the excitation and fluorescence radiation and, therefore, allows performing analysis of chemical elements from sodium (Na) upwards. To (semi)quantify the XRF results, self prepared silver/gold alloy reference materials were investigated by Proton Induced X-ray Emission (PIXE) at the Louvre Laboratories in France for comparison. For the evaluation of the enamel compositions commercially available glass standards as well as reference materials from an enamel project performed some years ago in the “Grünes Gewölbe” in Dresden, Germany, could be used.

Unfortunately the investigations performed on the “Saliera” itself, using the portable XRF instrument, were somewhat restricted by the shape of the object. Nevertheless, it was possible to investigate all the differently coloured enamels distinguishable with the naked eye. For reasons of comparison some minute enamel chips – already detached from the “Saliera” – were analysed by Scanning Electron Microscopy with Energy Dispersive X-ray Detection (SEM/EDX). Partially, probably due to the inability to accurately assign the chips to a certain enamelled part, the differences in the results of the XRF and the SEM/EDX measurements were surprising. Therefore, the elemental distribution of one of these minute enamel chips was verified by
confocal XRF performed at the Seibersdorf Laboratories of the IAEA. A clear insight into the inhomogeneous character of the enamel chips (for an area of about 30 µm in diameter) could be gained.

In parallel to the analysis, the state of preservation of the different enamels present on the “Saliera” was investigated and documented by the restorers of the “Kunstkammer”. The major type of degradation observed is based on tensions within the enamels leading to varying degrees of loss of enamel in the differently coloured parts. For the consolidation of the enamel the ORMOCER® system, developed by the “Fraunhofer-Gesellschaft zur Förderung der angewandten Forschung e.V. München”, will be used.

The presentation mainly discusses the state of preservation of the differently coloured enamels and the problems of performing quantitative analysis of the enamels’ compositions in a non-destructive way.
Conservation and remediation approaches at the Green Vault Dresden. Results of a German research project on enamel artworks

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At the world-famous Green Vault museum in Dresden, Saxonia, Germany, damage had been observed on precious enamel artworks displayed in show cases, like exfoliation or loss of enamel fragments from the gold surface, gel layer formation, salt formation, fissures etc. (see fig. 1).

Early warning dosimeters for monitoring outdoor and indoor room and micro climate have been used by Fraunhofer ISC for the assessment of potential damage risk of artworks, here especially for the validation of atmospheric conditions within showcases of the Green Vault. The environmental impact sensor is conceived for monitoring the overall effect of atmospheric parameters like humidity, temperature effects, pollutant gases, aggressive volatile organic compounds (VOC), and synergetic effects and therefore to avoid subsequent deterioration of original substrates.

In addition, consolidation / fixation measures have successfully been performed by using most promising Ormocer® resin mixtures, developed at Fraunhofer ISC especially for conservation applications.
Environmental impact sensor / Glass sensor method

For the early warning dosimeter, a glass composition susceptible to corrosion and leaching, caused by atmospheric / environmental impacts, is used as sensor substrate. The (glass sensor) method is applicable independently from glass being the original substrate or material of interest. Environmental impacts ("corrosivity" on site) can be validated for all object’s material compositions in any non toxic atmospheric / weathering situation. The method is licensed in Germany as German Technical Guideline VDI 3955/2 (see fig. 2).

It allows the evaluation of long term risks in short term experiments, integrating all environmental influences as well as synergetic interactions. Exposure times of 1-12 months are recommended for environmental monitoring, depending on the environmental situation (indoor, outdoor), sensor material composition, present deterioration state, and background of objects.

The glass sensor response to the environmental total damage impact is carried out finally by infrared (FT-IR) spectroscopy in the transmission mode. The H2O-content of the sensor glass and its IR-absorption correlates with the degree of damage of the corrosion layer, so that the resulting calculated Extinction-value (Delta-E) represents a direct measurement of the damage effect summed up by the dosimeter. Please note: a low Delta-E value corresponds to a low corrosion rate and thus to a low environmental stress situation. In any case, the IR data give reliable results for the evaluation of environmental risks on site by only one distinct parameter (Delta-E value). The Delta-E-values range from 0.01 to about 1.00. For indoor measurements, generally Delta-E values >0,10 represent critical (micro-) environmental conditions.

ATR-FTIR and also Raman spectroscopy (ATR: Attenuated total reflection) offers the possibility to detect the resulting surface species, if present. The identification of these crystal compounds / salts on the surface allows to determine the related impact chemicals or aggressive agents, being responsible for the deterioration effects and therefore for the environmental risk potential.

Figure 3: Enamel artworks at the Green Vault Dresden: Results of environmental impact sensor measurements in the museum (6 months exposure time) 1995 / 1997: Very critical Delta-E values were partly found in showcases (critical: from about 0,15 up to 1,0). Especially 1997: situation after first interventions for the improvement of the micro climatical showcase conditions.
Results of Environmental Measurements / Remediation

The critical micro climatical situation could be clearly detected and verified by the performance of environmental impact sensors measurements (see fig. 3). The dosimeter measurements were completed by individual monitoring of gaseous pollutants. For the precious Dresden enamels, severe and harmful impacts of formaldehyde and acetic acid could be detected, yielding a high risk potential for the artworks. Subsequently, the improvement of the climatical conditions in the showcases after subsequent interventions (e.g., removal of VOC-polluted materials like wooden showcase parts or textiles, mounting of ventilation) had been recorded by glass sensor measurements (see fig. 4).

Conservation measures

Various conservation resins and adhesives have been tested for the treatment (fixation, glueing) of the loose and / or exfoliated enamel fragments. Best behaviour and stability was achieved by the application of an Ormocer mixture, developed at Fraunhofer ISC (ORMOCER®: ORganically MODified CERamics; hybrid inorganic / organic Si-based resins, in this case tailored for conservation applications. Ormocer® is trademark of the Fraunhofer Society (registered association), Munich, Germany). The best performance Ormocer resin consists of a mixture of two Ormocer types, developed for metal (type B) and for glass conservation (type G), and Paraloid B72.

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A Conservation Survey and Treatment of Limoges Enamels at the British Museum

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The Department of Conservation, Documentation and Science (CDS) at the British Museum undertakes object condition surveys as part of a continuing programme of regular assessment of the Museum’s holdings. One of these surveys, carried out in 2003, examined a group of enamels comprising both 16th century Limoges and 19th century English pieces. This paper discusses some of the findings of this survey relating to the Limoges enamels. The British Museum’s Limoges collection was established when Hans Sloane founded the museum in 1750. Further bequests from Sir Augustus Wollaston Franks, in 1850, Baron Ferdinand Rothschild (known as the Waddesdon Manor Bequest) in 1898 and Barwell, in 1913, have resulted in this historic and unique collection.

Certain parts of the BM collections can be subject to greater scholarly interest than others, resulting in increased handling. The collection of Limoges enamels, comprising some 230 objects, held in the Department of Prehistory and Europe, is one of these. Curators from that Department were therefore keen to have the collection assessed, with the aim of ensuring that, as part of a study collection, these objects were physically stable and safe for handling. Of equal importance to BM conservators, and therefore a parallel aim of the survey, was to identify those enamels which appeared to show signs of chemical instability, since Limoges enamels are known to be susceptible to this and there had been isolated examples of visible deterioration in some objects on display. The pieces on display were not included in the survey, as they had been assessed on previous occasions. For this project, a group of objects in the reserve collection was selected.

The Limoges enamels surveyed, dating from the 16th century, included plaques, pendants, dishes, plates, ewers and tazzas. The survey was undertaken over a four-week period by two conservators, one of whom (the author) inspected and assessed each object, while the other entered the information and observations onto an Excel database. Since one of the specific aims was to identify enamels showing signs of instability and deterioration, the database spreadsheet was designed to include field headings such as ‘loose or detached flakes’, ‘salts’ and ‘colour’, under which could be recorded observations made of dull or crazed surfaces, or visible salt efflorescence. In the literature it has been well recorded that the blue, purple, wine, ruby red and turquoise colours in Limoges enamels have been observed to exhibit deterioration and so emphasis was given to assessing these colours, as well as amber and brown. Identifying the true colour of enamel can be problematic in practical terms and interpretation and description of the different colours can be, to a certain extent, subjective. For example, the same enamel colour might be described as ‘wine’ in one reference and ‘mulberry’ in another. Extremely deteriorated enamels exhibit loss of original colour which also makes identification more difficult. As previously stated, emphasis was given to the identification of deteriorated enamels, however physical
damage may also have occurred during the life of the object resulting in cracks and lamination and this was also recorded. In other database fields were recorded object identification numbers, location, description, whether any previous repair or restoration was present and the presence and condition of any mount. These objects are often associated with metal mounts which may themselves be deteriorating and causing damage to the enamel.

A classification from A to D was given to each object examined. ‘A’ denoted objects that were stable and clean, requiring no conservation work. Objects given a ‘B’ rating were assessed to be in a stable condition but might require some ‘cosmetic’ work (surface cleaning or improvement of previous stable repairs). ‘C’ indicated a higher conservation priority, where small repairs and stabilization was required, while ‘D’ objects were of the highest conservation priority, requiring immediate attention because of active deterioration evidenced by crizzling, soluble salts on the surface or physical instability. Of the 99 objects examined 54 required no or minimal work (A and B) while 17 required some stabilization (C) and 28 were actively deteriorating or were physically unstable (D).

The first aim of the survey was therefore met, in identifying and programming in the conservation work needed to stabilize those objects that could be made safer for handling and study. Those objects suffering active chemical deterioration had also been identified and could be treated accordingly. However a survey like this, of a specific area of a museum collection, also provides a unique opportunity to examine a number of objects, make comparison between them, gather information and draw inferences that can inform further investigation and research. A conservation survey relies on the knowledge and experience of the conservator to identify instability in objects. When this knowledge is applied in collaborative projects with scientists a fuller understanding of an object’s condition, the factors contributing to it and the options for treatment can be achieved. The aim here was to use the information gathered from this survey to work with the BM’s research scientists towards such a goal.

The deterioration mechanism in enamels is similar to the phenomenon known as ‘weeping glass’, which affects mainly Venetian glass of the 16th century. The deterioration of Limoges enamels dating from 1470 to 1530 is well documented and has been observed on a number of objects within the BM’s collection, but it is often only those objects exhibiting extreme symptoms of deterioration that have been conclusively identified. Careful examination of the surface of an object is necessary to identify those objects which may be in the early stages of deterioration. With the naked eye an enamel object may appear to be stable but its true condition can only be fully assessed when viewed under magnification. Once identified as actively deteriorating, enamels in the BM can be transferred to a storage area in which the relative humidity is controlled to between 38 - 42% ± 3%.

Interventive conservation treatments on enamels vary in the BM. Objects from the reserve collection in, for example the ‘B’ category, receive light cleaning and stabilization, unless during treatment something unusual is observed. Objects for display are on constant view and curators and conservators want them to look good without deceiving the public, so areas of loss may be gap-filled and painted to a close colour match, this type of work is often termed ‘cosmetic’. This often allows a fuller
understanding of the object by the museum visitor, however while having value for aesthetic and educational reasons, this replacement of lost enamel does not necessarily contribute to the long-term preservation of the object.

The restoration and conservation materials that have been routinely used to treat ceramics and glass in the past have also been applied to enamels. Plaster of Paris, Polyfilla, acrylic resins, animal glues, coloured waxes and epoxy resins have all been observed. The use of epoxy resins to repair or ‘consolidate’ enamels is a concern, as the resin will be drawn into all fissures and crevices of the object and will be problematic to remove in the future. Epoxy resin is extremely hard and insoluble when fully cured; the use of abrasive tools and papers to achieve a flat gap fill presents unacceptable risk to the enamel surface.

Many objects have been previously treated to secure unstable areas of enamel which in time become discoloured. Often these materials have been applied quite liberally and cover original enamel surface. With the agreement of the museum curator, areas of such over painting can be removed. However recently there has been an increased awareness of and interest in historical restorations (those applied at an early date by known restorers) leading to an inclination on the part of curators to preserve all previous restorations. This is partly because of a greater understanding of the work of the master craftsman and faker Alfred Andre, who was working in Paris from around 1870 until about 1910. He restored enamelled objects to an extremely high standard, devising a method using enamelled foil patches, which were applied to areas of loss or deterioration. This method would also require the application of cold materials to disguise the repair. The collection of data regarding previous repairs and restorations in this survey was intended to inform work in this area and while none of the repairs identified appear to be the work of his hand, being extremely crude, they will be retained on the objects for the present, pending further study.

**Bibliography**


The Pace of Amalfi. Investigation and restoration of a Venetian enamel of the 15th century

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A small enamelled copper “Pace” of Venetian manufacture dating to the second half of the 15th century, pertaining to the treasure of the Amalfi Cathedral, was restored at the laboratories of Istituto Centrale per il Restauro in Rome, between the late 80’s and early 90’s. The supervisor of the work was Filippo Trevisani, (Paolo Gusso was entrusted with the photographic records).

The “Pace” of the Amalfi Cathedral’s treasure belongs to the tradition of manufacturing enamelled copper artifacts that developed in Venice in the second half of the 15th century, up to the 16th century. Monochrome backgrounds of mainly white, blue and green enamels, either opaque or transparent, were painted on an opaque enamel layer and then decorated with minute gold-leaf patterns, which were sometimes covered with a transparent enamel layer (Germain-Bonne 1996, Smith 1987).

The “Pace” is 20x14x1.6 cm in size, is fitted with a handle on the back to seize it and expose it to the believers’ kiss. A ribbon-like pediment on the top originally tied some small flowers of which only the bottoms of the stems has remained. A painted parchment representing the Annunciation is preserved inside (Lipinsky 1989).

The preliminary investigations carried out in cooperation with Stazione Sperimentale del Vetro in Venice helped to identify both the manufacturing technique (materials and technology) and the state of preservation of the enamels. The copper support was covered with opaque (white and turquoise) and translucent (blue) enamels prepared as a finely ground powder, that were applied on a base layer (in contact with copper) obtained with rough grains of opaque white and transparent colourless enamels. The base layer had two functions: on the one side, it had to form a reflecting base for the superimposed, transparent enamels and, on the other side, to provide a sacrificial layer, because upon heating copper exhibits oxidation phenomena, including the formation of compounds that easily dissolve in the molten enamel, thus producing red-brown or green-blue spots in the enamel at the end of the firing process (Biron 1998, Freestone 1993). A grey-light blue opaque contre-émail is also present. No transparent enamel layer has been observed on the gold leaf.

In Venice, enamels were melt in the glasshouses, and were supplied to goldsmiths and craftsmen in the shape of slabs. A good number of recipes to prepare enamels for gold and silver are reported in the manuscripts of Muranese glassmakers, particularly in the 16th century manuscript called Anonimo edited by Cesare Moretti and Tullio Toninato (Moretti 2001). No prescriptions for enamels for copper have been found.
The manuscript reports interesting indications to purify soda plant ash (used as a flux) and obtain clear and brilliant glass (cristallo), together with clever expedients to improve their low chemical durability. The invention of cristallo, at least for blown glass, is attributed to the Muranese glassmaker Angelo Barovier in the second half of the 15th century (Verità 1985). Other recipes give prescriptions to improve the transparency and brilliance of enamels, and to prepare coloured enamels so that the different colours will melt at the same temperature when applied on the support, without mixing (same viscosity) and with good adhesion to avoid flaking off.

Small detached fragments (less than 3mm in size) were available for analysis. The samples were prepared in polished cross section, observed under the optical microscope and analysed by scanning electron microscopy and X-ray microanalysis. The quantitative chemical composition was determined by WDS X-ray microanalysis ( Cameca SX-50).

The intermediate enamel is made of mixed opaque white and transparent colourless grains. The areas in contact with copper are coloured. The opaque turquoise and white enamels as well as the blue transparent ones were studied. The colourants and the opacifier (SnO₂, cassiterite) were identified. The enamel chemical composition corresponds to soda-lime-silica glass melt from purified soda plant ash and silica (crystal glass). Additions of lead and tin calx were observed in the opaque samples.

The blue enamel was intensely coloured with a cobalt mineral containing also iron, copper, nickel and traces of zinc and arsenic (no bismuth was detected). This seems to be a mineral quarried in the Erzgebirge area in Saxony, Germany (Zucchiatti 2006). The analysis shows that the gold leaf applied onto the surface is made of gold (beyond 99 wt % of the element) with traces of silver (< 1%).

As a whole, the state of preservation of the artifact is rather bad due to the presence of buckling as a result of blows in the metallic support (and the consequent loss of enamel fragments), the chemical deterioration of the enamel, and the presence of several matching cracks (caused by the different expansion coefficients of the enamels and the metal).

The restoration work consisted in a mechanical cleaning performed under the microscope to remove wax deposits, and washing with distilled water. No protective or reinforcing compounds were applied.

References


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The conservation and restoration of the 14 stations of the cross. Enamels made in the 20th century

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The Maria Himmelfahrt Church in Dachau in Bavaria, was built in the 1950s and opened in 1956. 40 years later, the Church was placed under the protection of the Bavarian National Trust.

Stylistically, the Stations of the Cross complement the overall interior design of the Church. The artists Therese and Erhard Hoesle created the 14 Stations of the Cross in 1962. The Stations are made from three different materials that all reacted differently to the changes of relative humidity and temperature. For example, a thin layer of enamel is laid on a thin copper plate fixed to the oak base. Through the climate changes the metal began to move and in some areas even to rise, this caused the pushing away of the enamel. In 1998 it was decided to try to save the Stations of the Cross, with the conservation work beginning on one Station. Actually, the aim was just to conserve the enamel that was left. The treated Station was closely observed over several years and as the treatment showed to be successful then it was decided to save all the other 13 Stations. 2 of the Stations showed significant damage. In this instance, the Church authorities chose endorse a full reconstruction of the 2 images.
The San Giovanni Altar: a comparative study between Fourteenth and Fifteenth century enamels techniques and their conservation

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The San Giovanni Altar from the Santa Maria del Fiore Museum represents a unique masterpiece of highly refined Florentine enamels on metal art created between the years 1367 and 1480 and exemplifies the fervent artistic revolution that was taking place in Florence at that time. Although this is often considered one of the “minor arts”, 14th century Florentine masters and major 15th century artists such as Michelozzo, Pollaiolo and Verrocchio were all exponents of this major artwork, incorporating their own extraordinary and versatile techniques.

The conservation work in progress offers a perfect opportunity to study the different kinds of enamels that adorn the altar like mosaic panels, set within the precious metal that defines its intricate architecture.

The San Giovanni Altarpiece conservation project is sponsored entirely by the Opera di Santa Maria del Fiore. Conservation work began in September 2006 and is expected to conclude by August 2010. Members of the conservation team include Opificio delle Pietre Dure’s scientific coordinator and advisor, Clarice Innocenti, technical advisor, Giorgio Pieri, conservation scientists Andrea Cagnini, Monica Galeotti, and Simone Porcinai, and four conservators trained at the Opificio delle Pietre Dure School for Specialized Conservation, Jennifer Di Fina, Bruna Mariani, Raffaella Zurlo and Mari Yanagishita.

Most of the altar’s enamels (over 1000 plaques) are primarily made using the basse-taille on silver plate technique which uses both flat and concave surfaces. There is a remarkable difference in the state of preservation, as well as in the quality of execution, between the 14th century and 15th century enamels. The earlier 14th century enamels are better conserved: after cleaning treatment, the vitreous compactness of the enamels with their smooth and brilliant surface was intact save for a few small blemishes, and the intense, luminous colors (such as blue, purple, green and yellow) were further enhanced by the decorative engravings underneath. The 15th century enamels, on the other hand, are markedly blemished, suffering from granular disintegration (devitrification), crizzling and spalling due to surface alterations and in some cases because the underlying metal has not been engraved. Furthermore the glass surface on some of the plaques is rough and uneven, probably because they were not polished with pumice stone before the final firing.

The differences in preservation between the 14th century front piece and the two 15th century side panels were quite visible before treatment. In fact, the metal on the two sides shows serious problems of active saline efflorescence. However, the differences in preservation between the 14th and 15th century enamels stem from technical factors such as enamel composition, firing, cooling and, to a lesser extent, from the altar’s history itself (earlier restorations, dismantling and handling, microclimatic changes
due to natural disasters such as floods.) To date, the preliminary lab tests have concentrated on the effects of this deterioration and on those glass compositions that showed major degradation. The Cultural Heritage Nuclear Techniques Laboratory (LABEC-INFN) in Florence undertook more elaborate testing and analysis on several selected samples, to provide both qualitative and quantitative comparisons. Tests were made using Fourier transformed infrared spectroscopy (FTIR) and scanning electron microscopy with an energy dispersive spectroscopy system. (SEM/EDS).

On the 15th century enamels the surface deterioration has produced a whitish powdery appearance, probably composed of alkaline metal sulphates. Traces of organic grease were also found.

Examination of the affected enamels revealed the presence of a grainy, reddish-brown colored substance, underneath the translucent blue enamels, but only on the 15th century plaques. The FTIR and SEM/EDS results confirmed the vitreous nature of this substance and emphasized the enamel’s advanced deterioration.

Another particular issue affects both the 14th and 15th century examples of opaque red enamels that have developed an opaque white coloration in the area in contact with the silver. The polished cross-section, when observed through optical and electronic microscopy, in fact shows two distinct areas: a red surface patch, colored red, probably due to cuprite, and a second area in contact with the silver, colored white and about 35 µm thick, that is more difficult to interpret. The back-scattered electron images and the distribution maps of elements reveal that the only difference between the two areas is the presence of small round formations (less than 1 µm diameter) and a higher concentration of silver in the area next to the metallic plate, which may have caused the chemical change of the adjacent red enamel.

Some of the 15th century plaques with translucent blue enamel appear to have been gilt in gold and silver and at one time to have been decorated with miniatures bearing typical renaissance drawings. Further scientific analyses will help locate and identify the different kinds of decorations used.

And finally, the conservation works rediscovered exquisite drawings of flowers and animals engraved on the metal plaques under the enamels.

Throughout the presentation, slides explaining how the enamels were made will be shown, accompanied by an extensive range of decorations from the different periods.
Comparison between a 14th century enamel and a 15th century enamel.