

Electron Probe Microanalysis of a Jean II Pénicaud grisaille plaque from the Kunstgewerbemuseum Berlin - a first dating attempt of Limoges painted enamels by scientific investigations

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Abstract

A Limoges painted enamel *en grisaille* from the collection of the Kunstgewerbemuseum Berlin which is attributed to Jean II Pénicaud was examined by different analytical methods to prove its dating. Latest art-historical research arose doubts in the 16th century genuity of that plaque. Though there exist no possibilities for a direct age determination of glass and enamels characteristics of the material composition may allow to draw conclusions on the manufacturing time. For this purpose Electron Probe Microanalysis (EPMA) was combined with Laser-Microanalysis and optical examination of fluorescence under a UV lamp. The composition and layer arrangement of the piece in question was compared with those of so far analysed Limoges enamels from the 16th and 19th centuries.

Keywords

painted enamel, Limoges, dating, electron probe microanalysis, laser microanalysis, UV fluorescence

Introduction

Over the past years Scanning Electron Microscopy (SEM) investigations on arts and crafts enamels have proved a valuable tool for the characterisation of deterioration processes as basis for the development of conservation strategies [1, 2]. For that purpose EPMA with energy or wavelength dispersive detection of X-rays is especially suitable since it requires only a minimal sampling of the historical objects, at the same time it offers broad analytical information including separate quantitative analysis of different layers, visualisation of sample morphology, elemental distributions and characterisation of corrosion products. Investigations which focus on the understanding of chemical stability and corrosion processes of Limoges painted enamels were mainly published by the Laboratoire de Recherche des Musées de France [3, 4, 5].

Not only for restoration applications but also for the recognition of forgeries and replicas of the 19th century an exact knowledge of the elemental composition of historical enamels is very helpful in addition to the stylistic research. Richter and Wypiski [6, 7] found specific changes in the composition of enamels of various provenance regarding the centuries from medieval

till modern times - either by introduction of new, formerly unknown raw materials or changes in technology and recipes.

Within the collection of *Limoges* painted enamels at the Kunstgewerbemuseum Berlin there are a few pieces for which a 16th century genuity is strongly doubted after new stylistic research of Netzer (see this volume). To prove the dating of a Jean II Pénicaud plaque with the profile head of Bacchus painted *en grisaille* (see Fig. 1 in the contribution of Netzer) EPMA analysis together with Laser-Microanalysis (Laser-abrasive Optical Emission Spectroscopy) for the qualitative detection of the element boron was done on two enamel fragments. The *grisaille* white and black parts of the piece were additionally tested to fluorescence by optical examination under a UV lamp.

Experimental

Sampling and Sample Preparation

The slightly damaged rim of the plate allowed to take two small samples of about 1 mm² size with a scalpel. The first fragment originates from the black part of the foreside, which appeared as a very dark purple. The second sample was taken from the colourless counter-enamel at the backside of the plate which purpose it is to reduce tensions between metal and glass during cooling.

Quantitative EPMA with high accuracy requires flat and smooth surfaces. Therefore the samples were embedded in resin and cut perpendicular to the original surface in order to study the chemical composition in the different layers of the enamel. After polished using diamond paste they were covered with a thin carbon film for conductivity.

Electron Probe Microanalysis

Measurements were carried out at an ARL- microprobe (SEM-Q). The instrument is equipped with five wavelength dispersive spectrometers and an energy dispersive spectrometer (KEVEX-WINEDS) with a Si(Li) detection system with a thin polymer window for light element detection.

The conditions have to ensure that no migration of Na⁺ and/or K⁺ takes place during the measurement (smallest possible irradiating electron current and defocused or moved beam). Operation and theoretical background have been described in detail in literature [9].

Laser-Microanalysis

Following the EPMA a Laser-Microanalysis with a LMA 10 and UV spectrograph Q24 (Carl Zeiss, Jena) was done at the embedded counter-enamel sample for the qualitative detection of boron. This element was often used in 19th century enamels but not or in only few cases before the late 17th century.

With this method a small quantity of enamel is vaporised by a ruby laser yielding a crater of 40 to 50 µm diameter. The vapour is stimulated to optical emission in a spark between two graphite electrodes. Three laser shots on a standard glass containing 5.6 % B₂O₃ give two clearly visible spectral lines for boron near 250 nm on a photo plate. This comparison is sufficient to decide over an intentional use of borax for producing the enamel material.

Visual examination under a UV lamp

The appearance of the opaque white enamel of the Bacchus head and the black enamel in the rear was examined under a UV lamp (Camag) using 254 nm and 366 nm wavelength. This method was proved to be suitable for the identification of the nature of opacifiers in cases where sampling is not possible [10]. Furthermore 19th century enamels of different colours often show characteristic fluorescence which is caused by the addition of uranium (Na_2UO_4) since the 1830s [7].

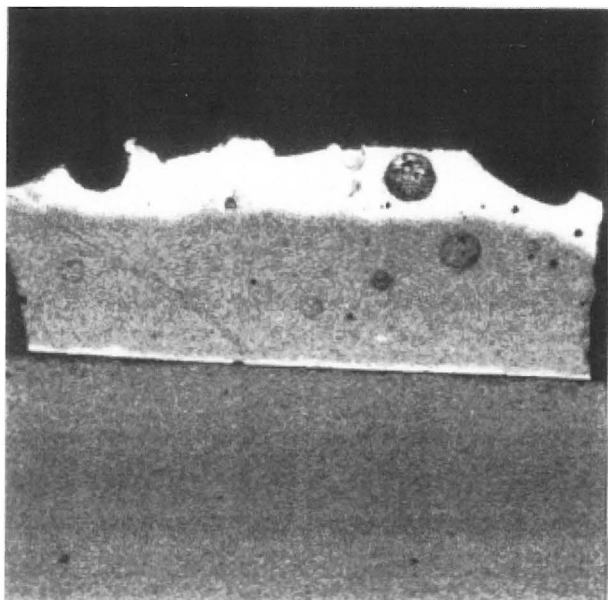


Fig. 1: BSE image of the enamel sample from the foreside showing a 3-layer arrangement (height of sample: 750 μm).

Results and discussion

As already evident under a light-microscope the Backscattering Electron (BSE) Image (Fig. 1) clearly shows three different layers within the first sample from the foreside. Visualising the material contrast the brightness of the two outer layers indicates the presence of elements with higher atomic number (first of all due to lead and/or tin) than in the middle part. This painted enamel consists of a thin opaque white ground on the copper plate (thickness app. 10–20 μm), a broad central (bulk) layer of black enamel (app. 500 μm) and a translucent colourless covering (app. 250 μm).

The chemical composition of the two enamel fragments is given in table 1.

The ground enamel contains lead and tin oxide in a ratio of about 1:1. An exact quantification of the latter by EPMA is problematic because the light-scattering crystals of SnO_2 are distributed inhomogeneously in the opaque enamel. This kind of opacifying agent, in Italy often called *calcina di piombo-stagno*, was used in the 16th century for *Limoges* enamels, too [11]. A gradient of copper concentration was found at the border to the copper plate.

Table 1: Chemical composition of the investigated *Limoges* painted enamel, Jean II Pénicaud, 16th c. ? (n.d. not detected, detection limit app. 0.2 %)

Oxide content in weight-%	Foreside, grinding opaque-white	Foreside, bulk black	Foreside, covering colourless	counter enamel, colourless
SiO ₂	38.1	56.7	45.4	41.6
PbO	16.8	n.d.	23.2	22.9
SnO ₂	~ 25	n.d.	n.d.	n.d..
Na ₂ O	6.1	8.7	7.6	8.9
K ₂ O	8.3	12.3	7.5	5.8
CaO	1.0	9.6	6.3	4.8
MgO	0.6	5.0	3.3	2.5
Al ₂ O ₃	0.7	1.3	1.4	1.0
P ₂ O ₅	0.2	1.8	1.0	0.9
MnO	n.d.	4.0	0.9	n.d.
CuO	< 1.5	n.d.	3.2	n.d.
Cl	n.d.	0.6	n.d..	n.d.
B ₂ O ₃	—	—	—	n.d.

The black-coloured enamel in the middle is of a lead-free mixed-alkali type with slightly higher K₂O than Na₂O content and high amounts of CaO, MgO and P₂O₅. This leads to the conclusion that two different alkali sources of rather low purity - probably sodaash¹ and woodash - were molten together with the silica material. The SEM images present a very homogenous material. Only very small SiO₂ grains could be found but there exist small regions of tin-rich ground enamel in this layer. The black colour, actually a very dark purple, was reached by addition of manganese dioxide in high amounts (the oxidation state in glass is +3 for purple).

The composition of the colourless covering enamel was found to be a lead-rich glass with nearly equal ratio of Na₂O and K₂O and a considerably high content of copper. From the technological point of view this last layer of the so called "flux" might be an indication for a later dating of the investigated piece. The purpose of that covering is to give the surface a uniform brilliant gloss. As Speel [12] pointed out this "crowning" of painted enamels was practised by 19th century Genevan enamel workshops whereas it does not seem to have been usual in the 16th century.

The counter-enamel is quite similar to the covering layer except no MnO and CuO was found. No boron was detected in this sample – so the mass difference of 11.6 % of the microprobe analysis is possibly due to decreased precision because of irregularities of the very small surface which arose difficulties in polishing.

Under the 254 nm UV light restored parts at the edge of the plate could be recognised by a yellow-greenish fluorescence which is caused by organic compounds like resins used for cold repairs. At 366 nm the white enamel of the Bacchus head appears rather bright but shows the

¹ Sodaash is the sodium-rich combustion product of Mediterranean coast plants like *salicornia* or *salsola kali*.

same appearance as other 16th century *Limoges* painted enamels *en grisaille*. Most of the simultaneously examined 19th century pieces showed no difference in the white parts either, just one of the later enamels was found to give a conspicuously intense appearance of the white parts which might be due to the presence of lead arsenate instead of lead and tin oxide [10]. The black enamelled parts of the plaque with the Bacchus head as well as those of all examined 16th century objects were invisible under both wavelengths. In most but not all 19th century black enamels a green fluorescence (traces of uranium?) was detected which was never found in genuine pieces.

So far there is only one analysis of a *Limoges grisaille* enamel plaque which is suitable for a comparison with this work. Perez y Jorba *et al.* studied the microstructure of a painted enamel plaque of M. D. Pape dated to the 3rd quarter of the 16th century (Musées du Louvre) by

Table 2: Chemical composition of a 16th c. *Limoges* painted enamel *en grisaille* by M. D. Pape [5] and a 19th c. replica of an Medieval enamel in the style of *Limoges* ([15], Cat. No. 7)

Oxide content in weight-%	16 th c. enamel grinding colourless	16 th c. enamel, bulk brown-black	16 th c. enamel grisaille opaque white	19 th c. enamel, opaque white
SiO ₂	42.7	55.7	55.3	53.0
PbO	33.2		23.2	22.0
SnO₂			~ 5.0 (in the clear matrix)	0.06
Na ₂ O	7.9	11.3	5.3 – 9.9	8.40
K ₂ O	5.0	5.3	0.84	6.50
CaO	5.2	9.0	3.0	3.90
MgO	2.7	4.9		0.70
Al ₂ O ₃	1.1	1.5		3.20
P ₂ O ₅		2.2		0.50
MnO	0.9	7.5		0.00
Fe ₂ O ₃	0.4	1.3		0.13
CuO	1.7			0.25
As₂O₃	n.d.	n.d.	n.d.	0.71

wavelength dispersive EPMA [5]. They found a stratigraphy of three layers, too, but the first grinding (thickness 350 µm) was a colourless one with a composition similar to those of the lead-glass covering at the Pénicaud plate from the Kunstgewerbemuseum (see table 2). The 1mm thick bulk layer of very dark brownish black is coloured by manganese and some iron. The elemental composition of a mixed-alkali glass without lead and with high amounts of CaO, MgO and P₂O₅ is nearly identical with the black layer of the here investigated plate with the Bacchus head. In this heterogeneous layer two phases - a clear matrix and dark parts - are described. The covering opaque white layer (*grisaille* white) contains lead and tin oxide as the grinding of the Pénicaud plate does, but significantly lower levels of potassium. The contents of impurities in the vitreous matrix, e.g. MgO, P₂O₅, Al₂O₃ and Fe₂O₃ were under the detection

limit. The content of SnO_2 was separately determined in the vitreous matrix to be 5 %. No colourless covering enamel was found over the *grisaille* white enamel of this Renaissance work.

Analytical data of 19th century painted enamels in the style of *Limoges* are not submitted so far. Thus a comparison with historicism *Limoges* enamels is so far, only possible for opaque white material which was used for the replicas of *Limoges* enamels in the Medieval manner published by Biron, Dandrige and Wypiski [13]. The analysis were done by EPMA and Ion Beam Analysis, one example is given in table 2. As characteristic features the authors often found lower sums of alkali oxides in the later enamels as well as significant levels of As_2O_3 (0.5 – 25 %). This element seems to reveal a dating mark: in 19th century glass recipes the precipitate of lead arsenate is mentioned as white opacifier [14], as a decolorizer As_2O_3 was not used before the second half of the 17th century for glassmaking [15]. Nevertheless the presence of SnO_2 in a questionable enamel can not be regarded as evidence for a pre-19th century date because this traditional opacifier remained in further use.

Conclusion and outlook

In result it is not yet possible to decide with sufficient conclusiveness in which time the enamel plaque with the head of Bacchus was formed.

The **composition** of the *Limoges* painted enamel plaque of the Kunstgewerbemuseum Berlin shows similarities with an investigated plaque from the late 16th century of the Louvre collections although slight differences were found especially in the $\text{Na}_2\text{O}/\text{K}_2\text{O}$ -ratio. No element was found which allowed a definite exclusion of a 16th century genuity of the painted enamel in question.

On the other hand the **arrangement** of the enamel layers was different from that of the 16th century – especially the "crowning" with a colourless flux rather refers to a later production time in the tradition of Genevan workshops in the 19th century.

Further systematic research on genuine and especially on 19th century pieces is required with focus on the creation of a chronology of the *Limoges* painted enamels, especially characteristic changes in composition not only on enamels but also for the copper, *paillons* and gilding.

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