Microchemical Journal 137 (2018) 37–44

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

In situ study of Limoges painted enamels by portable X-ray fluorescence supported by laser ablation inductively coupled plasma mass spectrometry analysis of micro-samples

Olga Syta [a], Luiza Kępa [a], Anna Mistewicz [b], Catia Wesołowska [c], Barbara Wagner [a,*]

[a] Faculty of Chemistry, Biological and Chemical Research Centre, University of Warsaw, Żwirki i Wigury 101, 02-089 Warsaw, Poland
[b] National Museum in Warsaw, Aleje Jerozolimskie 3, 00-495 Warszawa, Poland
[c] Department of Conservation, National Museum in Gdańsk, Toruńska 1, 80-822 Gdańsk, Poland

ARTICLE INFO

Article history:
Received 27 July 2017
Received in revised form 13 September 2017
Accepted 13 September 2017
Available online 15 September 2017

Keywords:
Limoges
Enamel
Platinum
La-ICP-MS
XRF

ABSTRACT

Portable XRF (X-ray fluorescence spectrometry) was used during non-invasive measurements of Limoges enamels from the collection of the National Museum in Warsaw (Poland). Four tiny micro-samples with dimensions below 1 mm^2 were collected from 3 objects and subjected to multi-elemental LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry) investigations, including oxides quantification and data imaging approach. Comparison of the obtained LA-ICP-MS data and literature glass compositional information allowed for possible dating of the investigated plaques to 16th or the first half of 17th century. The XRF spectra revealed the unexpected presence of Pt in one of the analyzed objects within areas of evident intervention/restoration recognized by a conservator. These results were confirmed by LA-ICP-MS imaging of a tiny silvery foil fragment sampled from the restoration inserts. Probably the first or one of the first examples of identification of Pt foil in a repair on a Limoges enamel restoration is reported in this work.

1. Introduction

1.1. Historical background

The first enameled metal objects were found in Cyprus and were dated back to at least 1500 BCE (Mycenaean period) [1]. Earlier glassy fragments or gemstones, *e.g.* in Egypt, were mechanically fixed by clasps, rather than fused onto the metal support. Cypriot craftsmen introduced the enamel technique called *cloisonné* that consisted on padding colorful glaze inside the metal wire separated cells [2]. The technique of painting with enamels, perfected in Limoges, places for the first time the enamel layer as the principal material and the metal purely as a support. This technique, widely known as Limoges painted enamels, began in the 15th century for the making of devotional items and later widening its scope to include secular pieces.

Limoges enamel painting may have started as early as the 1450s. Although this timing overlaps with Netherlandish enamels and Italian painted enamels of the 15th century, Limoges work was stylistically and technically of a different nature [3]. The production of Limoges painted enamels was very sophisticated not only from the craftsman workshop point of view, but also from a physical-chemical perspective. The main difficulty consisted on their multi-layered structure based on various materials characterized by different hardness, transparency, melting temperature and chemical reactivity. Cu was used as a support due to its high melting point (Tm = 1083 °C), suitable thermal expansion coefficient and good bonding properties. The probable source of the Cu were Spanish mines. Due to the proximity of the city to the pilgrimage routes to Santiago de Compostela, there was a great deal of commercial traffic in both directions [3,4].

To prevent Cu oxidation, the support was covered on both sides with Pb-rich enamel layer. The underside layer was named as counter enamel. This layer played an important role as it minimized contraction and expansion of the plate during firings and subsequent cracking of the enamel layer. In the next step, either opaque Pb and Sn white enamel or Ag foil in the case of cold colors such as green, blue and violet or Au foil in the case of warm colors such as red and amber was applied. Ag or Au foils or so called *paillons*, were placed underneath colored transparent enamel to obtain high brilliance. Ag *paillons* were used more frequently due to its lower price. Sometimes gilding of particular details as a final accent was applied over the last enamel layers, with a low melting point flux to fire them quickly [5]. Generally, each subsequent firing process was performed at lower temperature not to damage or change the previous layer.

Popularity of painted enamels declined in early 17th century, but later returned in the 19th century together with first professional studies, publications, copies and forgeries. This time Limoges was not the only artistic center of Limoges-style enamel but new workshops arose in Paris, Vienna, Geneva and Cologne. According to recent publications,

* Corresponding author.
E-mail address: barbog@chem.uw.edu.pl (B. Wagner).

https://doi.org/10.1016/j.microc.2017.09.017
0026-265X/

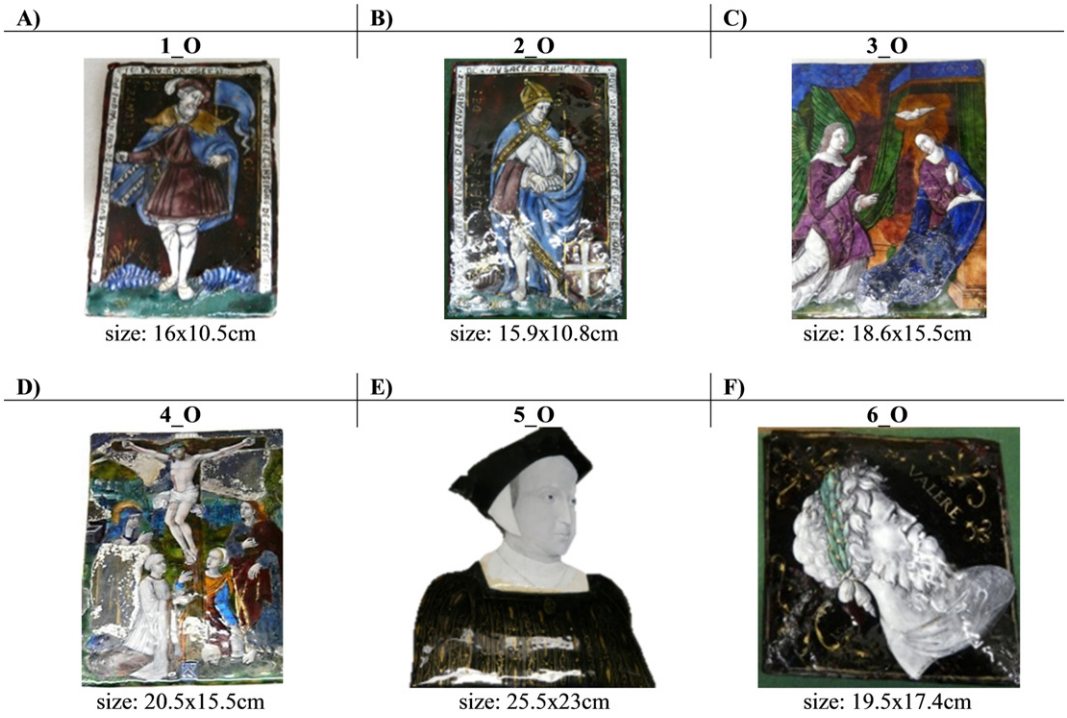

Fig. 1. Pictures of Limoges painted enamel plaques analyzed by means of portable XRF: A) **1_O;** B) **2_O**; C) **3_O**; D) **4_O**; E) **5_O** and F) **6_O**.

quantitative information about enamel elemental composition might help to distinguished between Limoges plaques from different periods [6,7]. Roehrs et al. [6] observed that the earlier the enamel, the lower its PbO content, while Van der Linden et al. [7] showed clear discrimination between variable enamels based also on their Na_2O, K_2O, CaO, P_2O_5 and As_2O_3 content. Apart from elemental analysis, Raman spectroscopy was used to identify the chemical composition of Limoges enamels [1] and confirmed the earlier observations of Roehrs [6].

The need for restoration of precious items arouse together with 19th century interest in Limoges painted enamels which was followed by investigations of technological aspects of these artifacts. Drayman-Weisser [5] focused on past repairs conducted on Limoges enamels belonging to the Walters Art Museum, while Schwahn [4] studied the materials and technique used during 19th century renovation of plaques from the Getty Institute collection. She noticed that the majority of repairs were performed not on the enamel edges, but in the central areas of them. Destruction occurred due to bonding failures between the enamel and the silver foil support, corrosion of the original enamel layer or metal foil, less adhesion of enamel to Ag than to Cu substrate, non-matching properties of enamel and stresses caused by *paillons.*

1.2. Aim of the work

Opening of a new decorative arts gallery, Gallery of Old Masters, at the National Museum in Warsaw was an impulse to conduct conservation treatment of Limoges enamels from the museum's collection. Before conservation began, elemental analysis of selected objects (Fig. 1) was performed. Majority of the analyzed Limoges painted enamel plaques belong to the Gołuchów collection, created in the second half of the 19th century by Princess Elżbieta (Izabela) Gołuchowska née Czartoryska [8]. One rhomboidal plaque comes from the collection of Józef Choynowski, who was a Polish amateur-archaeologist and collector from the second part of the 19th century. This was the object of unknown attribution, possibly with the depiction of Valerius Maximus. All artworks represent examples of translucent and opaque enamels with the use of silver, eventually gold *paillons* and gold painted details over enamel layers.

The plaques are attributed to different workshops of enamellers active in Limoges in the 16th century. Recently art historians have raised concerns about their authenticity suggesting the plaques might be 19th century fakes. **1_O**/SZM 1006 MN/ and **2_O**/SZM 1240 MN/plaques with Peers de France - Count of Champagne and Bishop – Count of Beauvais are attributed to Colin Nouailher. **3_O**/SZM 1243/MN depicting the Annunciation was considered to be made in Jean I Pénicaud atelier. **4_O**/

Table 1
Operating parameters of XRF measurements.

Lamp voltage, kV	45
Current, μA	9.6
Acquisition time, s	60
Pressure, Tr	1–3

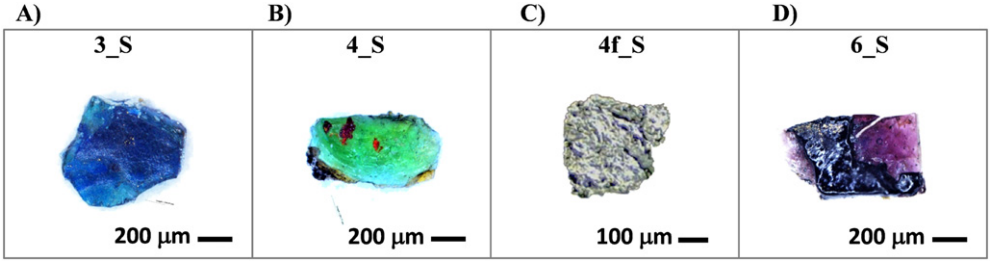

Fig. 2. Fragments of Limoges painted enamels and silvery foil analyzed by means of LA-ICP-MS: A) **3_S**; B) **4_S**; C) **4f_S**, D) **6_S**.