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On-site Raman and XRF study of complex metal patinas and *cloisonné* enamels from 19th century Christofle masterpieces: technological study of the decoration techniques

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Abstract

A major effort in technological developments was conducted during the 19th century. The polychrome surfaces of the metal parts of a corner cabinet, a torch-vase an 'Elephant' vase and a candelabra pair designed by Emile Reiber between 1874 and 1878 for the Christofle & Cie Company were investigated on site by means of non-invasive Raman, FTIR and X-ray fluorescence spectroscopy after examination under white light at different magnifications and under UV illumination. Despite the low thickness of the patinas (a few tens of μm) different (electro)chemically formed phases were identified in these layers (Cu_2O , Ag_2S , CuS or Cu_2S , sulfates). Residues of organic conservation products are identified by Reflectance FTIR. The results are compared with the information available in the patents filed by the company as well as other written sources from that period. The pigments and opacifiers (Naples yellows, lead arsenates, fluorite, spinels, cassiterite, chromates), and the vitreous matrices of the *cloisonné* enamels of the objects above are identified and testify to the deliberate combination of European and Asian enameling techniques.

Keywords: metal plating; electroforming, 19th century; metal patination; *cloisonné* enamels.

1. Introduction

The Universal Exhibitions ^[1,2,3] marked the beginnings of the globalization of decorative object manufacturing technologies with the promotion of both European and Asian productions. Chinese and Japanese productions were taken as inspirational models ^[3-5] for both shapes and decorations by European designers. The five objects (Fig. 1) studied here were designed by Emile Auguste Reiber (1826-1873) ^[6] and made by Christofle et Cie founded by Charles Christofle in 1830 in Paris. The company produced everyday objects: jewelry, table cutlery, statuary and furniture ^[7]. Having purchased patents in 1842 for silvering and gilding by electrolysis, many of its productions used galvanic techniques according to a series of new patents ^[8]. The five studied objects were produced for the Universal Exhibitions of Paris (1874, 1878 and 1889) and Vienna (1873): a corner cabinet, an 'Elephant' vase and a large torch-vase with girandole, which are part of the collection of the Musée des Arts décoratifs in Paris as well as two candelabras respectively 'au soleil levant' (*sun rise*) and 'au lever de lune' (*moonrise*) from the Bouilhet-Christofle Conservatory. The decorative elements are inspired by shapes (dragons at the top and *taotie* handles of the corner cabinet) and Asian aesthetics (woman in kimono on the cabinet door, elephants on the vase bottom, wave decoration inspired by Japanese woodcut prints, flower design, etc.). Cloisonné enamels, a Byzantine technique, reached China during the Ming Dynasty and took off there, continuing under the Qing Dynasty ^[9,10]. The discovery of these productions by Europeans led to a revival of interest in this type of enamel in relation to the aesthetics movements of Japonism and Arts and Crafts.

While many Raman studies of bronze patinas have been published (see e.g. references ^[11-21]), few of these studies using mobile instruments ^[14,23,24], to our knowledge there is no published work dealing with (electro)chemical coloring on copper alloys on western productions of this period, while some studies of galvanically treated steels and noble metals are available ^[21-31]. This study investigates enamel composition as well as procedures used for the decoration of the metal surfaces, especially the chemical coloring in reference to Asian productions. Other aspects like the specific color of the gold coatings (*mise en couleur* and *ors de couleur*) are not presented in this article.

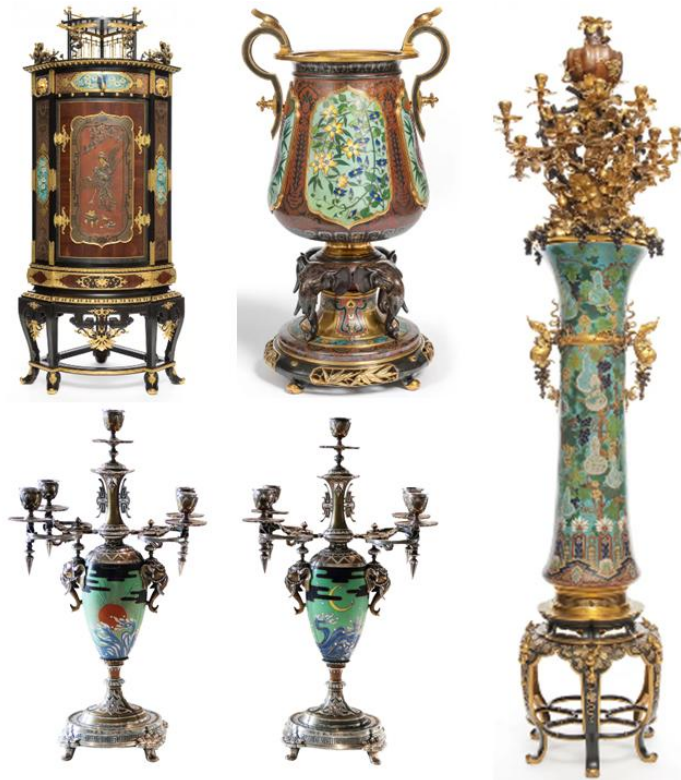


Fig. 1. View of the objects, corner cabinet (left), vase and torch-vase (center) and candelabras, all designed by Emile Reiber for Christofle & Cie (circa 1874-1878).

2. Experimental

2.1. Artifacts

Five artifacts have been analyzed: a corner cabinet, an 'Elephant' vase, a large torch-vase with girandole and two candelabras, respectively 'au soleil levant' (sunrise) and 'au lever de lune' (moonrise) (Fig. 1). Prior to analysis, the surfaces were examined visually and under magnification (x50) with a portable Dinolite AM-413 ZT USB microscope to identify technological traces. The rear sides of some parts could be observed after partial dismantling of the objects. Additionally, surfaces were examined under UV illumination with a portable lamp (main peak emission at 365 nm).

2.1.1. Corner cabinet

The piece of furniture (inv 27662, Musée des Arts décoratifs (mad), Paris) of a pair of corner cabinets (the second piece is currently in a private collection) studied in this work was presented at the Universal Exhibition of 1874 in Paris. These corner cabinets (1.95 m x 0.95 m) are striking for their complex inlaid reliefs, with contrasting gilded, silvered, black, red and brownish ornaments on the central door decorated with a woman and a fantastic animal taken from a Japanese print. The top of the furniture is decorated with a *faux-bambou* superstructure and a pair of dragons on each side. The design is by Emile Reiber (1826-1893) ^[6], the woodwork is by the Grohé Brothers (a family of cabinetmakers known since the Directoire) ^[32], the patinas are attributed to Eugène Guignard and the enamels were created by Jean-Baptiste Tard (1834-1894) ^[33]. The frame and base are made of

rosewood and blackened pear wood. The metal decorations combine several techniques: patinated and gilded bronze parts, inlaid and gilded electroformed copper and cloisonné enamels. The lateral and upper decorative plates on the frontside of the cabinet are very worn. Thus, it's not possible to study the patinas, but it's possible to observe in these areas that the base metal is reddish and not yellow. The original drawings and design for these parts from the collections of the Bouilhet-Christofle Conservatory show that the silver inlays were bright and untarnished, contrasting with blackened copper parts. Visual observation of the backside reveals the presence of electroformed copper plates with reliefs corresponding to the galvanic inlays. On the other hand, a cast brass alloy was used to create all the fittings on the top part of the furniture (decor of bamboo stems and dragons, base fittings). The back of the pieces could be observed behind the base fittings and on the back of the drawer handle as well as on parts removed from the side columns on top of the piece of furniture. Observation of the latter reveals a brass substrate coated with a layer of pure copper before chemical coloring.

2.1.2. 'Elephant' vase

This vase (inv. 28125, mad) was also designed by Eugène Reiber for Christofle & Cie. Made of patinated, gilded and enameled metal it was presented at the Universal Exhibitions in Paris in 1878 and 1889 (dimensions: 0.4 m x 0.175 m). Three elephant heads with bright silver decorations contrasting on a dark patinated background are mounted around the base of the vase. In the worn areas a yellow base metal can be observed. Visual examination of the inner side of the container shows that this part was electroformed with copper. The voids for the decorative silver inlays were conceived during this process. The handles and enameled plates on the vase are attached and mounted in the inner side of the container using a lateral key system. The color of the enameled plate substrate is consistent with copper plate, whereas in some areas of gilding which are worn, a red metal surface is visible.

2.1.3. Torch-vase

The torch-vase (one of a pair, dimensions: 2.2 m x 0.71 m x 0.48 m with pedestal) with gilt bronze girandole dated 1874 (inv. 29920 mad) was presented at the exhibition of the Union Centrale des Arts Décoratifs (UCAD) in Paris in 1874 and at the Universal Exhibitions of 1878 (Paris), 1883 (Amsterdam), 1889 (Paris), 1893 (Chicago) and 1900 (Paris). For an unknown reason a medallion on the object from the mad collections mentions the date 1884 (this could be due to a later version), whereas its pendant shows the inscription 1874. The shape of the vase is made of several assembled parts: i) the neck made of enameled copper (with a brazed copper ring on the internal part?), ii) a gilded brass ring (mounted between the two enameled parts), and iii) the main barrel made of enameled copper. The lateral decoration with gourds and bunches of grapes is mounted on the barrel using a bolting system. Unlike the enameled plates removed from the corner cabinet, no counter-enamel is present here and the surface

shows localized oxidation which could come from heat treatment during the shaping of the copper sheet. The girandole as well as the sub-base and the gourd and grapes ornaments visually appear to be made of cast brass using the usual decorative bronze techniques (and assembled by bolting on the internal face as well as brazed rings onto the internal face) [33].

2.1.4. "Moonrise" and "Sunrise" candelabra pair

The candelabra pair dated 1873 (from the Bouilhet-Christofle Conservatory) was designed by E. Reiber, enameled by Jean-Baptiste Tard on copper substrate and made of patinated, gilded and silvered cast brass (dimensions 0.55 m x 0.29 m). One is decorated with a sunrise and the second with a lunar croissant on one side, and a bird on the reverse side (Fig. 1). The metal base as well as the frames and the partitions are gilded by bath after enameling as evidenced by the traces of gold in the gaps in the counter-enamel on the reverse. The inner side of the enameled parts could not be examined. The enamel is shiny. Against a sky of a delicate green hue, animated in the upper part by dark, almost black clouds, an orange sun and a yellow half-moon stand out graphically above a turbulent blue sea.

2.2. Spectroscopic Analysis

The studied corpus of artifacts shown in Figure 1 was analyzed with mobile Raman HE532, FTIR and/or pXRF spectrometers in the storage rooms.

2.2.1. Elemental Composition

X-ray fluorescence analysis was performed on site using a portable NITON GOLDD instrument (Thermo Fisher Scientific, Waltham, MA USA) equipped with a SDD detector. Measurements were performed in a point mode with an acquisition time of 110 s, using a tube voltage of 50 kV and a current of 40 μ A (Ag anode). No filter was interposed between the X-ray tube and the sample. The analysis depth for enamel measurement is estimated using the Beer–Lambert law (analysis depth, defined as the thickness of the top layer from which comes 90% of the fluorescence can be calculated for each characteristic X-ray peak using the online calculation program provided by Bruker [34]) to be close to 6 μ m at Si K α , 170 μ m at Cu K α , 280 μ m at Pb L α and 2.5 mm at Sn K α . It is obvious that for the patinas (their thickness is estimated to a few tens of microns by measuring the intensity of the Raman signal as a function of the controlled displacement of the focal point) the contribution of the supporting metal sheet will be the majority. The thickness of the cloisonné enamels being significant, in the range of mm, the XRF measurements will then be fairly representative of the enamels' composition. The portable XRF instrument is connected to a camera allowing the area analysed to be selected.

The separation between major phases (>20 %wt), minor (~1 to 20 %wt) and traces (< 1 %wt) is made according to the intensity of the characteristic peaks and the known compositions of reference glasses. Due to the heterogeneity of the enamels (microzones of different colors are visible for an enamel

described by its main color) the separation remains approximate for minor phases and traces. Of course, the light elements (magnesium, sodium, boron, lithium) cannot be detected.

2.2.2. Phase identification

Raman spectra were recorded using an HE532 mobile spectrometer (HORIBA Scientific Jobin-Yvon, Palaiseau, France) excited with a 532 nm YAG laser Ventus (Laser Quantum, Fremont, CA, USA) with power of illumination ranging between 5 and 20 mW, fiber optic coupled with a remote Superhead® equipped with a long working distance (17 mm) 50× (Nikon, Tokyo, Japan) or a LWD 200× (Mitutoyo, Sakado, Japan) magnification microscope objective (Figure 2). Most of the better spectra have been obtained with the x200 objective. The use of an objective combining both a long working distance (~13 mm between the focal point and the front lens) and a very high magnification (200x) makes it possible to obtain 'good spectra' on very thin phases (a few μm) or on small pigment grains while avoiding as much as possible the contribution of the substrate or the vitreous matrix. Focusing is more difficult than with the 50x objective but this prevents only the phase(s) giving a strong Raman signature from being detected, thus masking the variability of the phases or their degree of crystallinity. As we will see later, it is sometimes necessary to record the first spectrum obtained very quickly to avoid local heating and compound degradation under laser irradiation. Indeed, on-site measurement with a mobile device requires higher laser powers than in the laboratory on a sample in the dark.

The 920 g/mm grating used allows the recording of a spectrum with a large spectral range (~100–3300 cm^{-1}) and a ~4 cm^{-1} spectral resolution. Analyzed spots are smaller than $\sim 5 \times 5$ and $1 \times 1 \mu\text{m}^2$, respectively; the in-depth penetration is rather similar for the colorless and poorly colored glazes, but about 5–10 times smaller for darker colored areas. Three to five spectra were recorded for each colored area to ensure representativeness. Focusing is controlled to the nearest micron by 3 dimensional XYZ micrometric movements. The analysis spot is determined visually by observing the optimal focus of the laser at very low power. A black cloth is then placed to cover the object and the Superhead®; the laser power is increased to the desired value and the focus is optimized by observing the spectrum, first by maximizing the signal of the fluorescence background and then by maximizing that of the silicate matrix or pigments/opacifiers.

The contactless infrared spectroscopy analyses were performed in a specular reflectance (SR) mode with a FTIR portable R-Alpha spectrometer (Bruker Optics, Germany). This spectrometer is based on an interferometer with a KBr beam splitter associated to a Globar source (SiC) and a DLaTGS (Deuterated Lanthanum α -alanine doped triglycine sulphate) detector. Within this SR module a built-in video-camera gives a magnified view of the measurement area and allows exact positioning of the spectrometer in front of the sample by displacing the whole instrument (Figure 2). The IR beam is focused and collected by a set of mirrors with a 45° incidence angle, promoting the collection of the specular reflection. The beam diameter focused at the sample is about 5 mm at the working distance of 15 mm. The distance to

the object to be analyzed is achieved by gradually moving the instrument with the hands or with a microscopic stage until the video image is focused. Typically, 128 scans were made per spectrum (650-3600 cm^{-1} range, spectral resolution 4 cm^{-1}). In the SR-FTIR analyses, the reflectance spectra showed a large number of bands with a pole shape profile. Pseudo-absorbance spectra are calculated from SR spectra by applying the Kramers-Kronig Transformation (KKT) algorithm included in the OPUS software (Bruker Optics, Germany).

Examples of the experimental setups are shown in Fig. 2.



Fig. 2. Examples of instrument positioning: a) remote Raman head connected to the laser and spectrometer (black cylinder) by optical fiber; note the black fabric protecting the eyes against scattered laser light and the spectra against pollution of the measurement by lighting; the sheets of paper adjust the height of the spot and eliminate vibrations; b) FTIR spectrometer on its micrometric displacement support; c) in-situ XRF setup.

3. Results

3.1. Choice of analysis areas.

The access to the artefacts being limited, a choice of analyzed areas is made based on several criteria: i) selection of areas with different colors and aspects; ii) accessibility of these areas to instruments without danger and without contact for the object (this implies the positional stability of the instrument (no vibrations) and perpendicularity to the surface to get reliable spectra); iii) minimization of instrument positioning preparation time. We will first consider the decoration of metal parts and then of the *cloisonné* enamels. Let us recall that Raman analysis can be very sensitive for detecting minor phases due to intrinsic resonance effects (carbon for example), to Surface Enhanced Resonance Effect (rough surface or nanoparticle aggregate of noble metals) or the presence of highly covalent bonds but it should

be noted that many phases have low intensity spectra and are therefore 'invisible', even when in significant proportion.

These main selected areas of metal decoration are presented in Fig. 3 for the corner cabinet (the areas relating to other objects and to the *cloisonné* enamels will be specified in the following figures). The moving parts such as the drawers are placed on a table which facilitates measurement.

3.2. Corner cabinet. Metal decoration

The areas of metal having the color of brass which could be analyzed by XRF on the back of the handle of the corner cabinet correspond to an alloy of copper and zinc associated with smaller quantities of tin and lead as well as traces of iron and nickel; the latter elements could be impurities in raw materials or arising from a surface contamination during shaping (wear of tools used for manufacturing). Representative XRF and Raman spectra are shown in Fig. 4. The representativeness of the spectra can be checked by comparing with the spectra given in Supplementary Materials (Fig. S1). This composition is characteristic of that used in the 19th century in the field of furniture bronze^[34] with levels of copper, zinc, tin and lead which allow easy melting of the alloy.

Table 1 compares the information obtained by XRF and Raman scattering on the polychrome patinas shown in Fig. 3. Representative Raman spectra are given in Fig. 4 and XRF spectra in Figure 5. The attributions were made from the critical examination of the signatures of the patinas and corrosion layers made in a previous work^[14] and from additional literature on silver salts^[36].

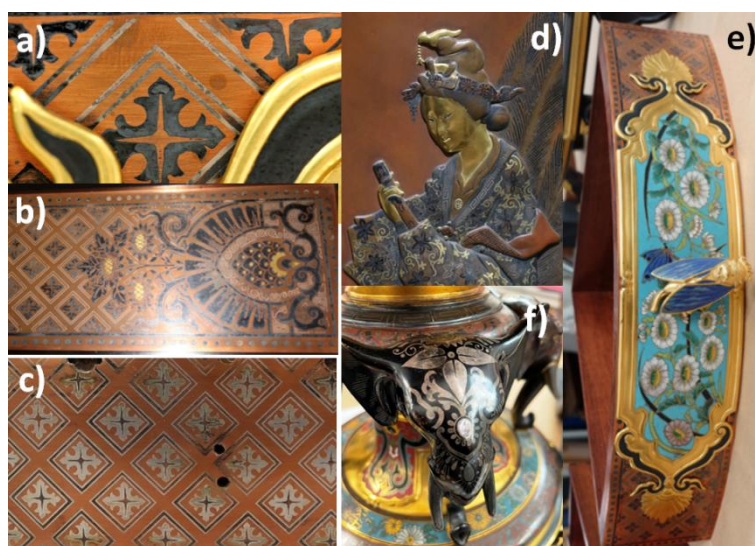


Fig. 3. Detail view of the decorations on metal in red, black, silver and gold colors of the corner cabinet (a-e) and the 'Elephant' vase (f).

Color	Characteristic Raman peak (cm ⁻¹)	Remarks	XRF Major, (minor) [traces]	Assignment
black (chignon)	1360/1584 220/430/510/620b,w	Fast measurement	Not measured	C Cu ₂ O

Black line (in between gilded stripe)	215/420/523/632/ <u>462</u>	-	Cu (Zn,Sn) [Ag,Fe,Ni,S,Cl,K,Ca,Pb,Si]Au	Cu ₂ O <u>Quartz</u> (SiO ₂)
Red (door, close to women head)	145/215/420/523/632	-	Cu (Cl,Si,S)	Cu ₂ O
Silver decoration, naturally tarnished	250-260 1078/1155 1580 2930/2970	SERS effect enhancing organic residues	Not measured	Ag ₂ S Sulfates (traces) C C _n H _m

Table 1. Phases identified in the decoration of the corner cabinet (objective x200).

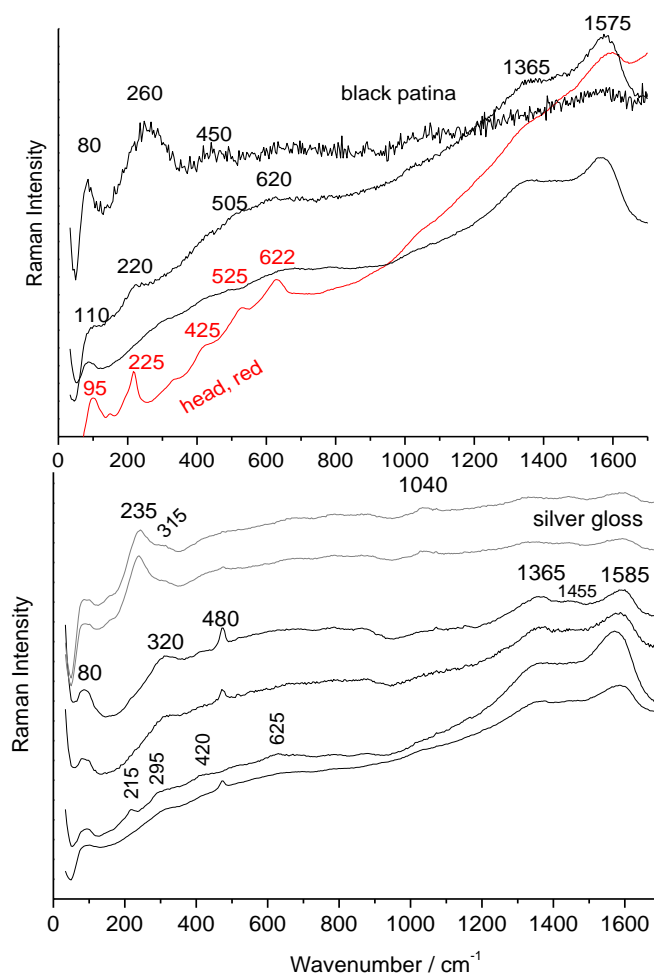


Fig. 4. Representative Raman spectra recorded with a LWR (200x) objective on the black and red areas of the female figure (top, see Fig. 3d) and on the geometric decoration (center, see Figs 3a, 3b and 3c) of the corner cabinet (the 480 cm⁻¹ peak corresponds to a light bulb emission line due to the weakness of the signal, the very small part of the neon light passes through the black fabric poorly covering the object due to its shape and large size). See in Supplementary Materials the whole spectral range showing the strong fluorescence background at higher energies for silver areas. The lack of fluorescence for most of black area is a proof of the resonance effect.

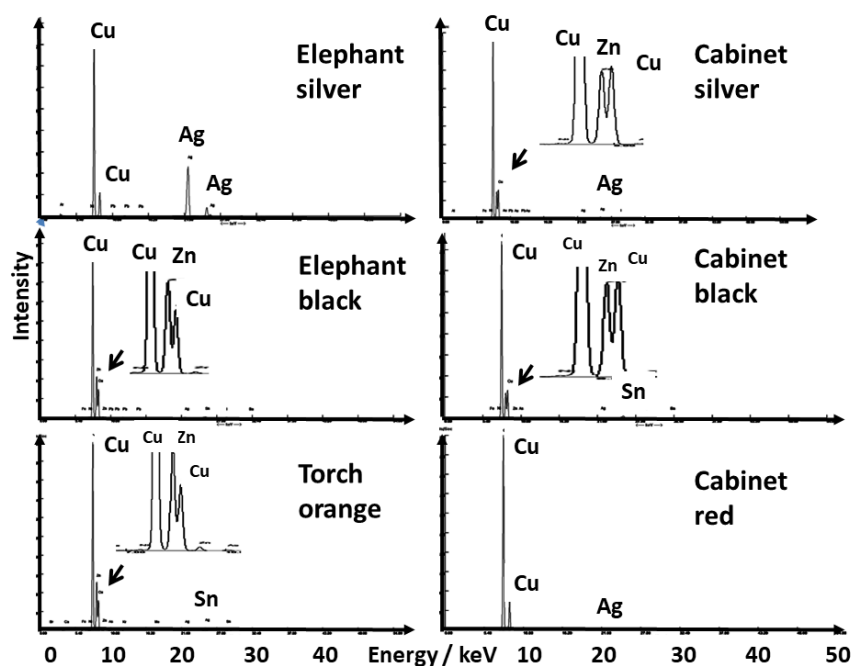


Figure 5. Representative XRF spectra recorded on the silver inlay (‘Elephant’ vase and corner cabinet), black (‘Elephant’ vase and corner cabinet), red (corner cabinet door) and light-brown patination (gourd on top of the *girandole*) are shown. Copper and zinc signals are dominant (inserts show zoom of the main peaks) with much smaller peaks of silver and tin. Traces of iron, nickel, etc. (see Tables 1 and 2) are detected after magnification of the spectra.

Three types of Raman signatures are observed: i) those presenting a peak around 240 to 260 cm^{-1} , ii) those presenting the series around 220 , 500 and 620 cm^{-1} , iii) those presenting the series around 225 , 295 , 425 and 625 cm^{-1} . In addition, the characteristic doublet of amorphous carbon around 1365 and 1585 cm^{-1} is observed. The spectra obtained are of a lower quality than what had been obtained with the same instrumentation for the thicker bronze patinas^[14], which is consistent with the low thickness of the electroplated copper coating. The first type of signature obtained mainly on the black deposits corresponds to the spectrum of Ag_2S ^[36], testifying to the presence of naturally tarnished silver; the second spectrum was obtained most clearly on the red background with Cu_2O . Note that for silver sulfide the spectrum degrades very quickly during the measurement and the best spectrum is obtained after a few seconds (hence the significant noise, Fig. 4). Some signatures of quartz (main peak at $\sim 462\text{ cm}^{-1}$) are sometimes observed, ascribed to a likely grain relic of the sand used for some polishing at certain steps and afterwards incrustated into the metal surface.

3.3. Organic residues

Figure 6 shows a FTIR spectrum obtained on a residual deposit on the back of a gilded drawer handle of the corner cabinet. This isolating material was applied prior to the gilding bath and was later removed on purpose. However, residues remained trapped in porosities of the metal and could be localized due to their yellowish fluorescence under UV illumination. - Raman analysis detects during the optimization of the signal setting the presence of organic residues by a spectrum with a high level

of fluorescence transforming in a few seconds or less into a carbon spectrum, which generally then disappears. Indeed, in on-site measurements, the power at the sample level is high, being several mW. Examination of these regions in FTIR Reflectance allows one to obtain after KKT conversion the spectrum presented in Fig. 6.

Vibrational bands indicate that the coating composition might not be a pure component, but is probably rather a complex mixture (a resin-oil mixture?). Bands at respectively 3402, 2917, 2850, 1730, 1714, 1583, 1554, 1435, 1415, 1378, 1160 and 720 cm^{-1} are characteristic of the presence of cured linseed oil. The yellowish hue of the coating's UV fluorescence is consistent with the possible presence of an oily or wax-based medium. However, the presence of bands at 1316, 1239, 1113, 1030, 914, 471, 458 and 419 cm^{-1} could be related to the presence of another material (natural resin possibly but shellac could be excluded) and partially overlap in this range with bands of linseed oil which are not clearly visible on the spectrum. Also, the isolating material is expected to be colored in order to facilitate its application with a brush. XRF did not detect traces of a specific material which might be attributed to a mineral pigment such as chrome.

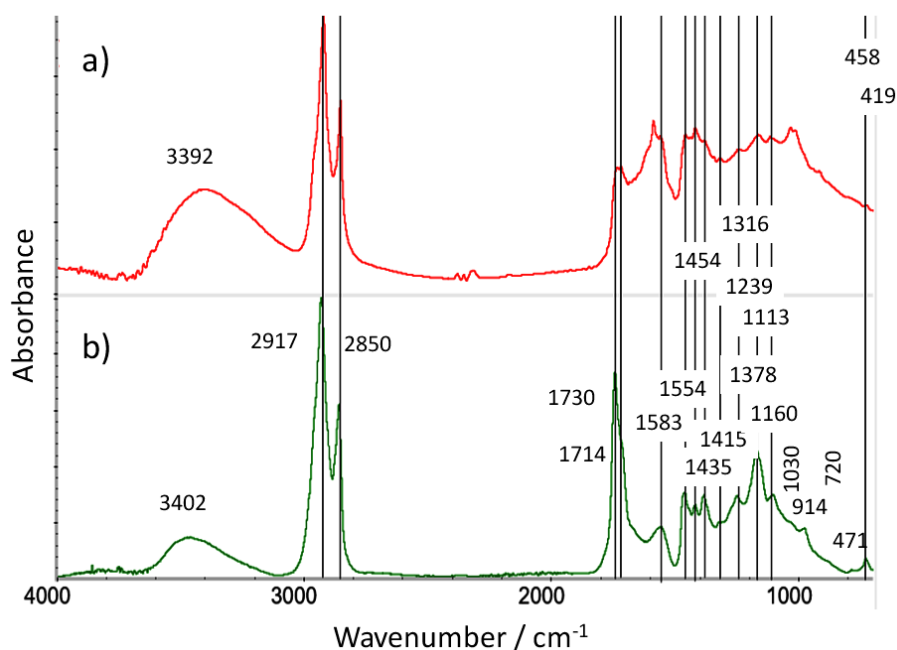


Figure 6. FTIR spectra recorded a) on the back of the drawer handle of the corner cabinet (residues of the isolating varnish), b) Reference spectrum for heated linseed oil.

3.4. 'Elephant' vase. Metal decoration.

The XRF spectra of the gilt handles as well as the direct analysis of the yellow base alloy underneath the stand show a copper-rich alloy with minor additions of zinc, tin and lead (Fig. 5). The protective plate on the underside of the elephant vase contains only copper, zinc and tin but no lead. It can be concluded that this is not a cast alloy, but rather a rolled plate.

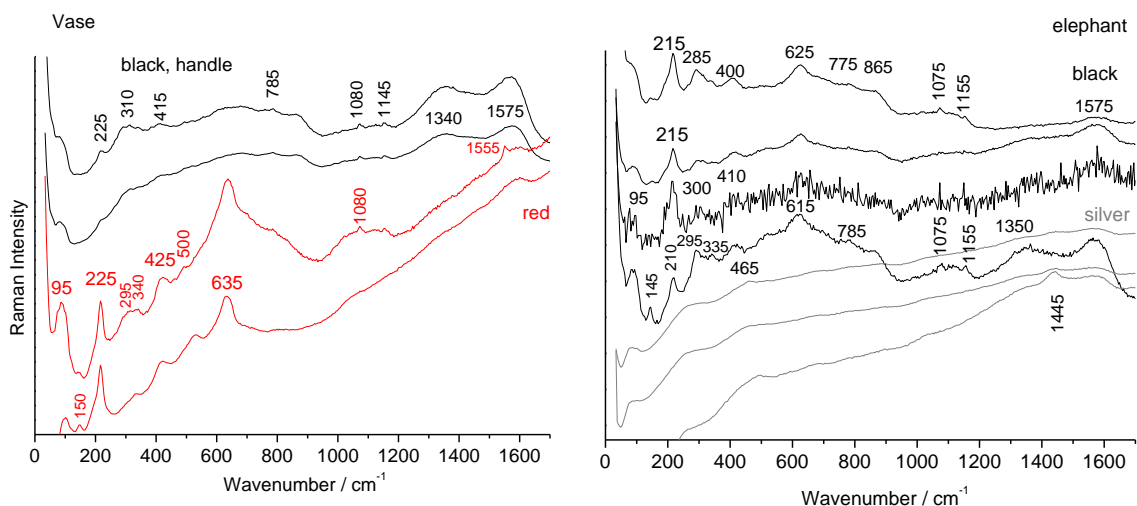


Figure 7. Representative Raman spectra recorded on the black and red background of the 'Elephant' vase (see Fig. 1) and of the black and silver areas of the elephant head (right, see Fig. 2f).

Three different types of Raman signatures are also observed (Fig. 7); the representativeness of the spectra can be checked by comparing with the spectra given in Supplementary Materials (Fig. S2): i) those presenting the series of rather narrow peaks around 225, 295, 425 and 625 cm^{-1} characteristic of Cu_2O ; ii) those with a component at 300 to 310 cm^{-1} and small narrow peaks at ~ 1080 and 1145 cm^{-1} ; iii) those with a broad background with components at 280 and 400 cm^{-1} . The characteristic doublet of amorphous carbon around 1365 and 1585 cm^{-1} is always present. In addition, we observe weak narrow peaks at ~ 1075 and 1155 cm^{-1} . The first type of signature obtained mainly on the red background with Cu_2O . The spectra are of better quality than for the corner cabinet that indicates a thicker and more crystalline coating. The black decoration exhibiting narrow peaks at 1075-1080 and 1145-1155 cm^{-1} is probably prepared using sulfate as made for the black Japanese patination^[14]. The small wavenumber shift can be due to different phases and/or thermal induced shifts due to the high laser powers used.

Color	Characteristic Raman peak (cm^{-1})	Remarks	XRF Major, (minor) [traces]	Assignments
Black (handle)	217/ $\sim 300/304/400/\sim 480/635$ 1070/1155 1350/1585	Expected at ~ 280 , 350 and 470 cm^{-1}	Cu (Zn) [Ag,Sn,Sb,Ca,Fe,Ni,Pb,Cl,S]Au	$\text{Cu}_2\text{O}/\text{CuS}/\text{Cu}_2\text{S}?$ Sulfates (traces) carbon
Black (vase)	145/214/291/ $\sim 300/$ 403/ $\sim 480/ 627/$ 1078/1155/ 1358/1573		Cu (Zn) [Ag,Sn,Sb,Ca,Fe,Ni,Pb,Cl,S]	Cu_2O $\text{CuS}/\text{Cu}_2\text{S}?$ Sulfates (traces) carbon
Red (vase)	150/214/420/532/631	Narrow peaks	Cu (Au) [Fe,Cl,Ca]	Cu_2O
Silver inlay (elephant)	276/492 1343/1436/1574		Cu (Ag) [Fe,Ni,Pb,S,Cl,Ca]	Ag_2S C traces
Gilding	No spectrum		Cu	Au coating

			(Zn,Au,Sn) [Ag,Pb,Fe,Ni,Cl,K,Na]	
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Table 2. Phases identified by Raman microspectroscopy in the decoration of the ‘Elephant’ vase (200x objective) and XRF detection of metal elements (Au is generally due to adjacent or worn off gilding).

3.5. Torch-vase. Metal decoration

The XRF spectra of the top gourd of the torch-vase girandole (Fig. 5) correspond to a copper alloy of composition similar to that of the corner cabinet: it is still a brass (copper with ~10 % wt Zn) with a small amount of tin and lead, and impurities of nickel and iron. Traces of arsenic are also present. Given that the arsenic is highlighted on a worn area (and not on the patinated area), almost free of patina, it seems unlikely that the arsenic comes from a surface finish but was incorporated into the alloy voluntarily or because of the raw materials used.

3.5. Corner cabinet. Cloisonnés enamels

Fig. 8 shows areas of the *cloisonné* enamel decoration studied by both methods. They belong to the squared and curved drawer (See Fig. 1).

Raman analysis identifies 'standard' coloring agents for the European enamel technique:

The blue colors are obtained by dissolution of Co^{2+} ions in the silicate network of a mixed lead-alkaline glass (Fig. 9), without precipitation by cobalt saturation, because the Raman spectrum is exclusively that of the amorphous silicate matrix, as usually observed for many blue glasses [37,38].

Visual examination of the enamels shows the great mastery of enameling. The zones, for example blue (Fig. 8d), red (Fig. 8d), purple (Fig. 8c), green (Fig. 8c) and turquoise (Fig. 8e) are perfectly homogeneous on a sub-millimeter scale. It is the same for the white and yellow zones (Fig. 8a, 8b and 8d) where this shows deliberately heterogeneous zones.

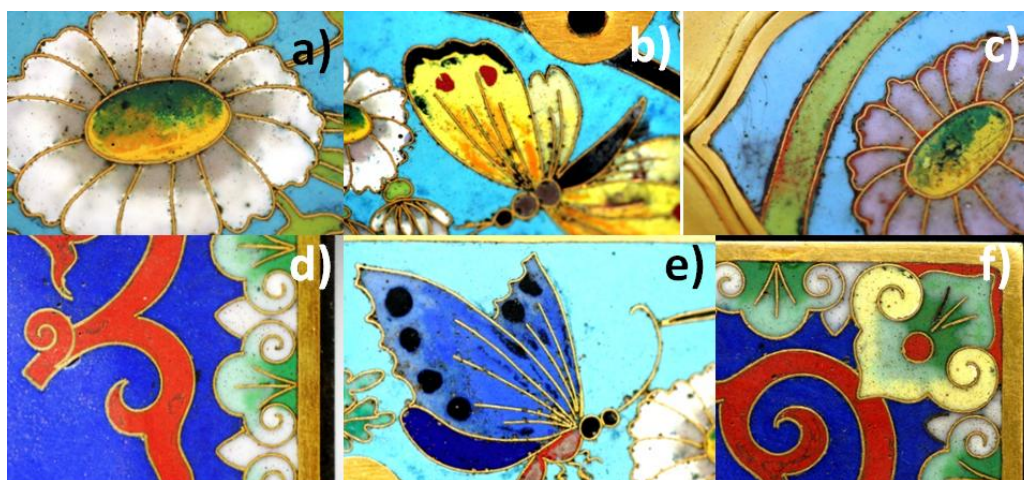


Figure 8 . Detailed view of the studied enameled areas of the colored areas analyzed of corner cabinet drawer.

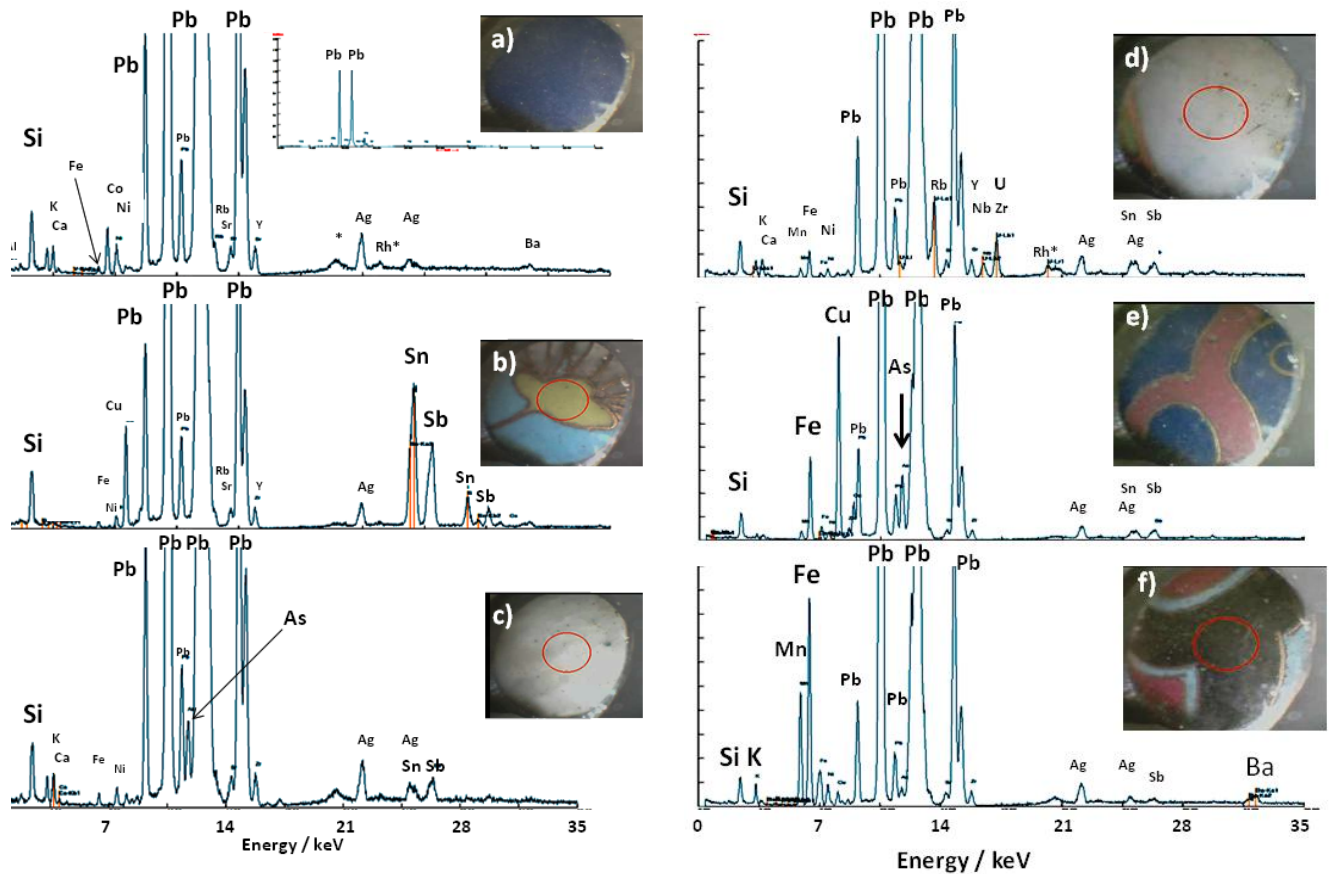
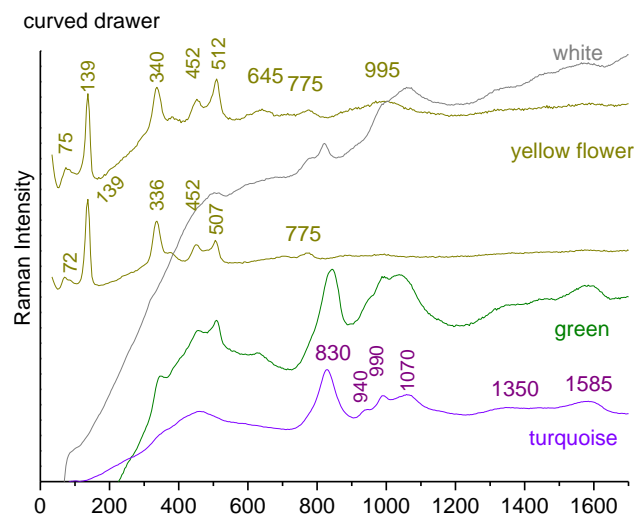


Figure 9. Representative XRF spectra recorded on a) blue (corner cabinet), b) yellow (torch-vase), c) white (torch-vase), d) cream (torch-vase), e) red ('Elephant' vase) and f) black ('Elephant' vase)



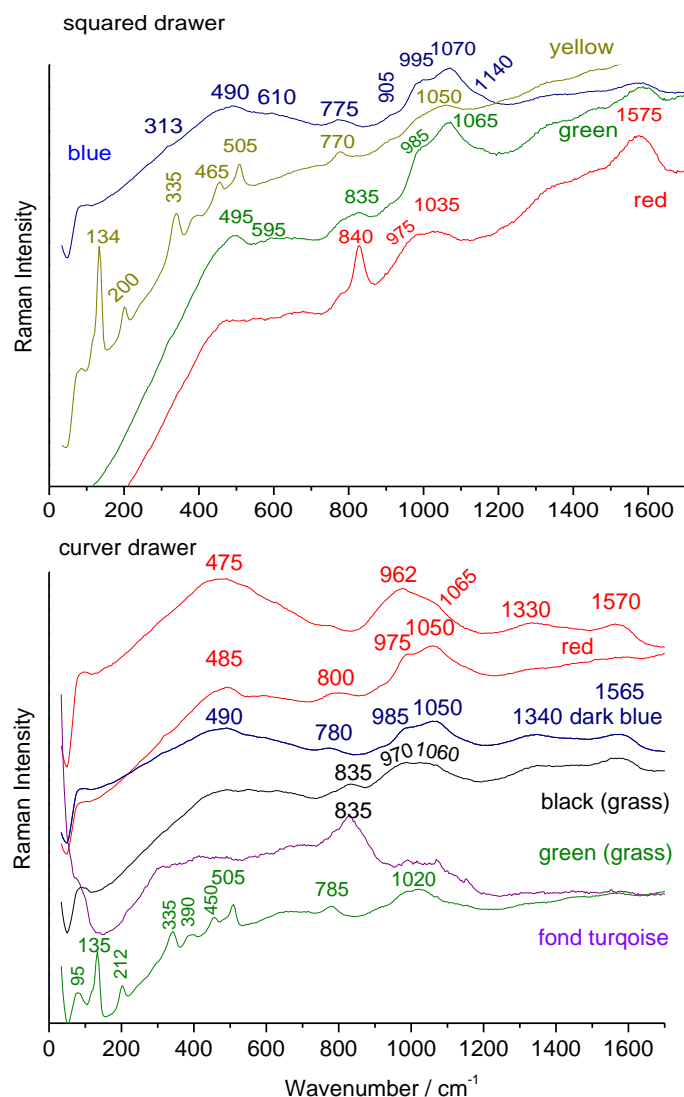


Figure 10. Representative Raman spectra recorded on the different colored *cloisonné* enamels of the corner cabinet drawers.

Additional spectra are presented in Supplementary Materials (Figs S3 and S4). Indeed, the spectra present only the signature of the vitreous matrix, a broad band (bending modes of the vibrational unit of the silicate network of the SiO₄ tetrahedron around 500 cm⁻¹ and stretching modes around 1000 cm⁻¹ [39,40], Fig. 10), indicates that the color is obtained by the dissolution of a coloring ion. This is the case for the blue (Co²⁺) and green (Cu²⁺) enamels in agreement with the XRF measurements (Table 3). We can note the presence of two types of Naples yellow (A and B), recognizable by the presence or absence of the band at ~200 cm⁻¹ [40,41,42]. The high quality of the spectra and the lack of backgrounds (see Supplementary Materials) is consistent with a focus on a single grain. Consequently, the grain size is larger than the laser spot (~1 μm³ with 200x objective). Opacification is obtained by lead arsenates of two types, one giving the typical signature of a lead-calcium-sodium arsenate with an apatite structure (fine band around 820-830 cm⁻¹) with a shoulder around 780-790 cm⁻¹) [43,44,45] and another shape giving a broader band [44].

Examination of the band around 1000 cm⁻¹ allows, from its average position in wave number and the different components, to identify the type of vitreous matrix. According previous studies [39,40,46], four types are identified: i) a type with a principal component around 980 cm⁻¹, i.e. a highly depolymerized glass and meltable at a relatively low temperature, observed for the black and yellow colors, rich in lead; ii) a second type used for the red color, containing a little less lead with a mean band wavenumber of 1005 cm⁻¹; iii) mixed lead-alkaline compositions with an average position around 1015 cm⁻¹ (yellow-green and black color); and iv) compositions less rich in lead (therefore fired at a higher temperature) presenting several stretching bands with two components of equal intensity around 995 and 1070 cm⁻¹ (blue and green).

When it is not possible to make a semiquantitative use of XRF spectra, Raman analysis appears more effective for categorizing glassy matrices.

Color	ν_s SiO ₄ component (cm ⁻¹)	Coloring agent (characteristic peaks / cm ⁻¹)	Opacifier (cm ⁻¹)	Remarks	XRF Major (minor) [traces]
Blue	993-1070 mixed	<u>Co</u> ²⁺	Not detected	C, traces	Pb,Si (K,Ca,Al,Fe) [Co,Ni,Ba,Sr]
Dark blue					
Black blue (butterfly)	977 (Pb rich)	Co ²⁺	Not detected		Pb,Si (K,Ca,Al,Fe, <u>Co</u> ,Mn) [Ni,Cu,As,Sr]
Green	995-1070 mixed	Cu ²⁺	Not detected		Pb,Si (<u>Cu</u> ,K,Ca,Fe) [Sr,Mn,Cr,Zn,As]
Yellow-green	1017	Cu ²⁺ Pb-Sn(Sb,Zn) ^A pyrochlore (133/201/331/455/509)	(pigment)	(782)?	Pb,Si (<u>Sb</u> , <u>Sn</u> , <u>Cu</u> ,K,Ca,Fe) [Sr,Ni,Ba]
Yellow	985 (Pb-rich)	Pb-Sn ^B pyrochlore (136/336/453/506)	(pigment)		Pb,Si (K,Ca, <u>Sb</u> , <u>Cu</u> , <u>Sn</u> , <u>Zn</u>) [Sr,Ni,Fe,As,Cr]
Red	1005	<u>Cu</u> ^o (fluorescence band)	Lead (earth)alkaline arsenate (784/828)	C, traces	Pb,Si (Fe, <u>Cu</u> , <u>As</u> , <u>K</u> , <u>Ca</u>) [Sr,Mn,Cr,Zn]
Black	1015	(555/637/832) Ferrite-chromite	(pigment)	C, traces	Notmeasured (lines too small vs analyzed area)
Turquoise	990-1060 mixed	Cu ²⁺	Lead (earth)alkaline arsenate (828)	C, traces	Pb,Si (<u>Cu</u> , <u>As</u> , <u>K</u> , <u>Ca</u>) [Sr,Ni,Ba,Fe]
White	990-1060 mixed	-	Lead (earth)alkaline arsenate apatite (781/821)		Pb,Si (<u>As</u> , <u>K</u> , <u>Ca</u>) [Sr,Ni,Fe,Cr]

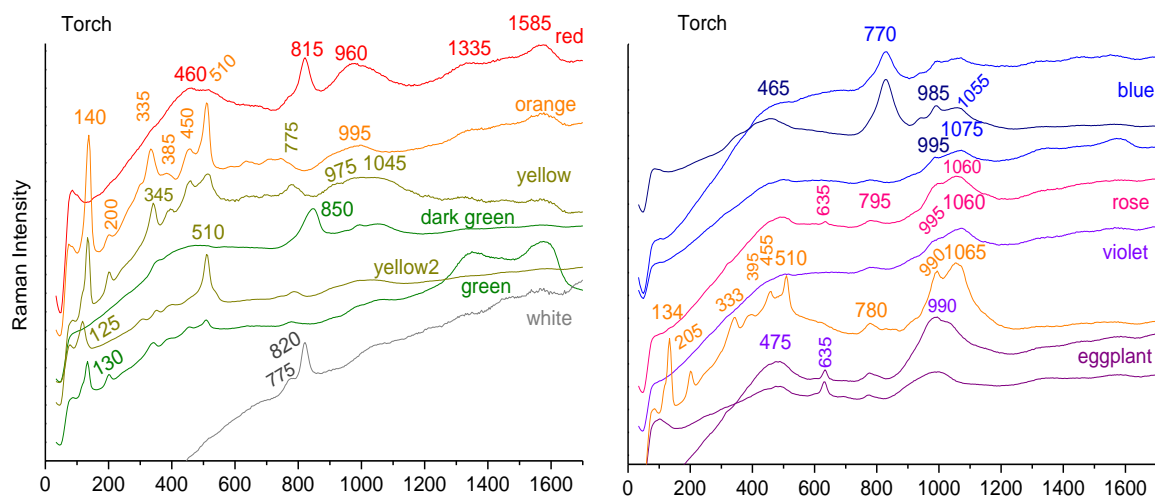
Table 3. Phases identified in the *cloisonné* enamels of the corner cabinet drawer. Elements of coloring/opacifying elements are underlined. **Majors (in bold)**, minors (in bracket) and trace [in squared bracket] elements are given.

3.8. Torch-Vase *cloisonné* enamels



Figure 11. Detailed view of the studied enameled areas of the colored areas analyzed for the torch-vase.

Compared to the corner cabinet enamels, these enamels are much more heterogeneous (Fig. 11). This is certainly manifest to be on purpose for certain areas (the colocynths and the pears have a dominant cream color with many different hues) but probably the heterogeneity of the turquoise background and of certain colors (grapes) is due to the difficulty of creating a very large object. Figure 12 shows the representative spectra of the main-colored areas and the assignments are summarized in Table 2.



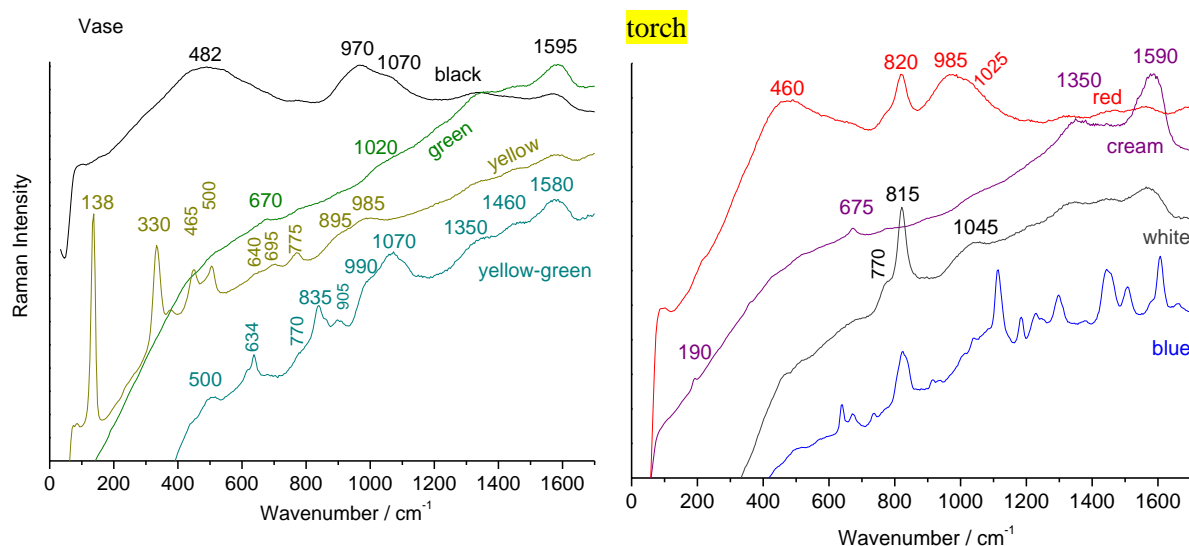


Figure 12. Representative Raman spectra recorded on the enameled areas of the torch-vase (top) and 'Elephant' vase (bottom). Colors of enamels are given.

Additional spectra are shown in Supplementary Materials (Fig. S5). Overall, the coloring agents and pigments/opacifiers are identical (Table 4) with those of the previous object (Table 3). The two types of Naples Yellow (see orange and yellow areas in torch, Fig. 12), the two types of sodium calcium lead-arsenates (see red and white areas in vase, Fig. 12), glasses colored by dissolution of Co^{2+} ions (blue areas, torch). We observe in a new way the use of chromate for the green color (band at 850 cm^{-1} , dark green torch, Fig. 12)^[46], and the use of cassiterite as an opacifier (peak at 635 cm^{-1} , e.g. eggplant ornament area, torch, Fig. 12^[47]). The same categories of glassy matrices are identified from the Raman signature. The red coloring of a glass is only obtained by the dispersion of the hematite pigment, gold or copper nanoparticles or CdSe ^[48,49]. The absence of hematite or a CdSe signature and the high level of the continuous background (fluorescence background due to the plasmons, vase, Fig. 12) should indicate that the color is produced by metallic nanoparticles, which is confirmed by the detection of copper by XRF.

Color	ν_s SiO_4 component (cm^{-1})	Coloring agent (characteristic peaks / cm^{-1})	Opacifier (cm^{-1})	Remarks	XRF
Blue	(991-1060)	Co^{2+}	Lead (earth)alkaline arsenates (828)		Pb,Si (Co,Cu,K,Ca) [Ni,Fe]
Violet	(1064)	Mn^{2+}			Pb,Si (Mn,K,Ca,Fe,Al) [Sn,Sb,Ba,Zr]
Eggplant	(990)	Mn^{2+}	(633-775) SnO_2		Not studied
Rose cream	-	(133/200/340/460/512) ^A Pb-Sn/Sb pyrochlore		C, traces (1357/1575)	Pb,Si (U,K,Ca) [Sn,Sb,Mn,Fe]
Rose blue	(1060)	$\text{Co}^{2+}?$	(635) SnO_2		Pb,Si Sn,Sb,U
Yellow (line)	(1015)	(120/511) ^B Pb-Sb pyrochlore			Pb,Si (Sn,Sb,Cu,Zn,K,Ca)

					[Fe,Mn,Ba,Ni]
Red-Orange	(990)	(138/334/511) ^B Pb-Sn pyrochlore Cu ^o NPs			Pb,Si (<u>Cu,Fe,As</u>) [<u>Sb,Sn,Mn,Cr,Zn</u>]
Light green	(1060)	Cu ²⁺ (133/200/340/460/512) ^A Pb-Sn ^B pyrochlore		C, traces (1357/1575)	Pb,Si (<u>Cu,Sn,Sb,K,Ca</u>) [Ba,Fe,Ni,Cr]
Turquoise		Not studied			Pb,Si (<u>Cu,As,K,Ca,Al</u>) [Fe,Ni]
Dark green	(994-1064)	Cu ²⁺	Lead (earth)alkaline arsenates (840)		Pb,Si (<u>Cu,As,K,Ca</u>) [Sb,Sn,Cr,Fe]
White	-	-	Lead (earth)alkaline arsenates apatite (773/819)		Pb,Si (<u>As,K,Ca,Al</u>) [Sn,Sb,Ba,Zr,Fe]
Grey	(1060)	-	-		Not studied
Brown		Not studied			Pb,Si (<u>Cu,Sn,K,Ca,Fe</u>) [As,Sb,Zn,Mn,Ni]

Table 3. Identified phases in the torch-vase *cloisonné* enamels. Characteristic main peak wavenumbers are given. **Majors (in bold)**, minors (in bracket) and trace [in squared bracket] elements are given. Coloring/opacifying elements are underlined. Phases confirmed by XRF are underlined (-: no component detected).

Uranium is usually used in the form of a uranyl salt to obtain a powerful yellow color. In literature, an intense peak around 700 cm⁻¹ is mentioned for uranium-based pigment^[50]. For the cream enamel (figure 12, torch), in which XRF analysis detects uranium (Table 3), the Raman spectrum shows a peak at a slightly lower wave number, 675 cm⁻¹. Better knowledge of the Raman signatures of enamels colored by the incorporation of uranium are necessary to identify the pigment, its composition and its structure.

3.9. 'Elephant' vase. *Cloisonné* enamels.



Figure 13. View of an enameled plate of the ‘Elephant’ vase after removing the handle.

Color	ν_s SiO ₄ component (cm ⁻¹)	Coloring agent (characteristic peaks / cm ⁻¹)	Opacifier (cm ⁻¹)	Remarks	XRF
Dark blue	Poor spectrum	Co ²⁺	-	Restoration (glue)	Pb,Si (Mn,Fe,K,Ca,Al) <u>[Co,Ni,Cu,Ba,As,Zr]</u>
Yellow	(975)	(136/334/450/506) Pb-Sn/Sb pyrochlore	-		Not studied
Red	(970)	Metal nanoparticles (fluorescence) (likely Cu ^o)	Lead (earth)alkaline arsenates apatite (820)		Pb,Si (Cu,As,Fe, <u>K,Ca</u>) <u>[Zn,Mn,Cr,Sn,Sb]</u>
Yellow green	(1063)	(839) (CrO ₄ ?) Cu ²⁺	(635) SnO ₂ cassiterite	C, trace	Pb,Si (Cu,As,K,Ca,Al) <u>[Ag,Sn,Zn,Fe,Ni,Cr]</u>
Dark green	-	Cu ²⁺ ? (+ 672) chromate?	-	C, trace	
White cream	(1050)	(192/672/677) Antimonate?	<u>Lead (earth)alkaline arsenates apatite</u> (780/821)	C, trace	Not studied
White	(1040)		<u>Lead (earth)alkaline arsenates apatite</u> (781/823)		Not studied
Black	(970)	Fe-S? (475) Chromophore amber	-	C, trace	Pb,Si (Mn, <u>Fe</u> ,K,Ca,Al) <u>[Ba,As,Cu,Zr,Fe]</u>

Table 4. Identified phases in the *cloisonné* enamels of the ‘Elephant’ vase. Characteristic main peak wavenumbers are given. **Majors**, minors and trace elements are given, see Table 3. Phases confirmed by XRF are underlined.

With this small object we find a high quality of production of the enamels (Fig. 13) . Only two types of glass compositions are detected more or less rich in lead. Note the creation of the red background with copper nanoparticles as a red dye and the cream color is associated with the detection of uranium by XRF and the presence of peaks at 190 and 675 cm⁻¹. We therefore have the use of innovative techniques in this piece. The suspicion of green coloring by chromate from the peak at 839 cm⁻¹ is in agreement with the detection of chromium by XRF in addition to copper. The band at ca. 480 cm⁻¹

¹(Fig. 12) characteristic of the Fe-S chromophore ^[51] is confirmed by XRF (Table 4). Additional spectra are shown in Supplementary Materials (Fig. S6).

3.10. Candelabras. *Cloisonné* enamels.

If these objects present an innovative aesthetic construction, the coloring agents and pigments are classic (Table 5) with the exception of the use of fluorite (CaF₂, characteristic peak at ca. 320 cm⁻¹, Fig. 14) as opacifier, a Chinese technique ^[9].

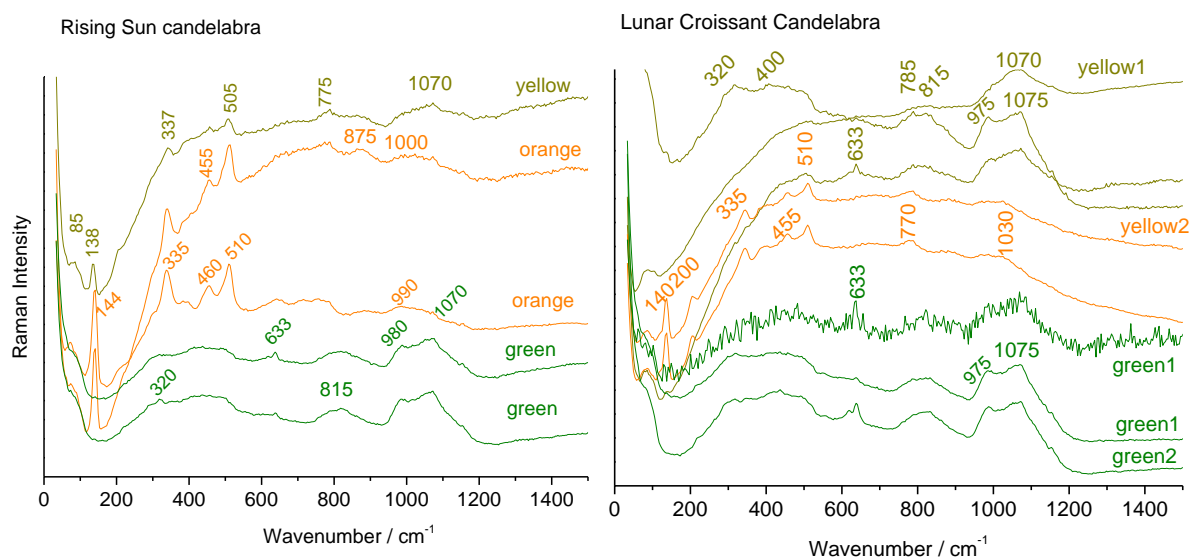


Figure 14. Representative Raman spectra recorded on the enameled areas of the candelabras. Additional spectra are shown in Supplementary Materials (Fig. S7).

Color	Characteristic peaks (cm ⁻¹)	Assignment
Light blue	320 435,489 615-641 785,994,1070	CaF ₂ Glassy silicate (SiO ₄ bending) Pigment Glassy silicate (SiO ₄ stretching)
White	322 440,540 785,985,1070,1160	CaF ₂ Glassy silicate (SiO ₄ bending) Glassy silicate (SiO ₄ stretching)
Black	315 780? 880? 1070	CaF ₂ Glassy silicate (SiO ₄ stretching)SiO ₄) Chromate ? Glassy silicate (SiO ₄ stretching)

Table 5. Identified phases in the *cloisonné* enamels of the candelabras. Characteristic main peak wavenumbers are given.

4. Technical processes behind the polychrome decorations

The information obtained by visual examination -in particular from the observation of the back surfaces of pieces during partial dismantling ^[33] - and analysis of the alloys and the different phases of intentional patinas was compared to written sources: the patent and the patents of addition filed by the Christofle company in 1867 and 1868 ^[52], summarized in Figure 15, give a rather precise description

of the steps involved in the creation of inlays using electroplating and electroforming techniques. These main steps are followed by polishing procedures in order to obtain a completely smooth surface without any relief due to the electrochemical inlays. In a simplified manner, the decoration is produced on the metal substrate by a non-conductive coating which will control the action of dissolutions or electrochemical deposits.

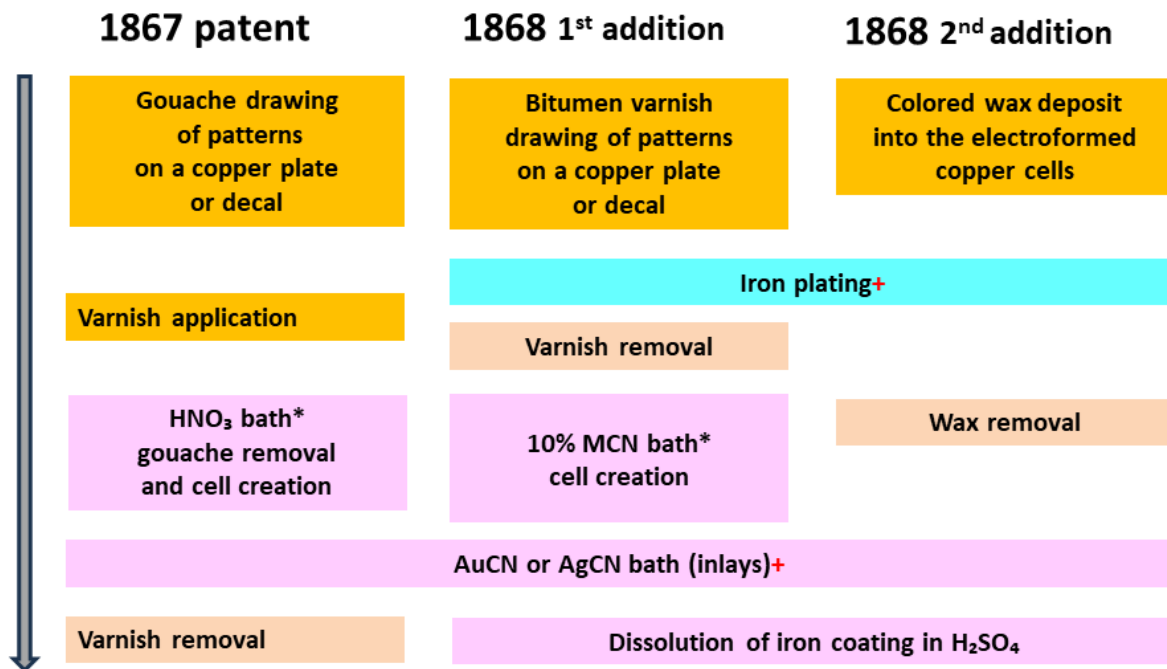


Figure 15. Inlay procedures described in Christofle's patents: main steps [8] (* = anodic bath / + cathodic bath).

4.1. Inlay decorations using electroforming and electroplating procedures

Examination of the back of the central drawer plate dismantled on the corner cabinet and of the internal part of the 'Elephant' vase shows not only the characteristic morphology of electroformed copper, but also the design of the inlay decoration which appears in negative. This observation allows us to conclude that the cells intended to be inlaid were designed directly in the gutta-percha mold. This process made it possible to avoid both bending of the curved plate and to allow engraving before inlaying.

In the case of golden ornaments, complementary techniques seem to have been implemented: on the side plates of the corner cabinet, the contours of the patterns were transferred beforehand by manual engraving. The gilding was applied in a second step. It is clearly in relief compared to the rest of the surface and has sometimes flaked off in places revealing a smooth copper substrate^[33]. Observation of these areas confirms a plating and not an inlay technique. In addition, the application of gilding does not always correspond exactly to the preliminary engraved design (Fig. 16). It seems rather to be a localized electrolytic gilding, or even an alternative technique (possibly cold gilding?).

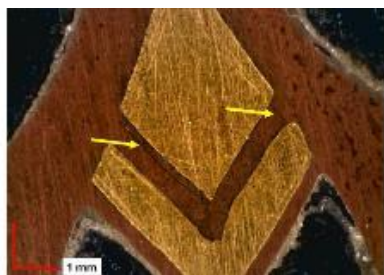


Figure 16. Gilded ornament on the corner cabinet (plate on the right side, top); the yellow arrows show the engraved lines on the copper substrate (50x).

On decorative metal pieces, which are entirely gilded on the front, residues of an isolating varnish could be clearly identified on the back.

The torch does not have any galvanic inlay decoration as it is made of a combination of cast brass and enameled copper sheet. In the case of the elephant heads of the vase, made from solid brass, the silver decoration could have been produced by prior anodic engraving, since the galvanic inlays seem to have been mainly conceived using pure copper by the Christofle company. However, these inlays often have small cracks and porosities.

4.2. Chemical coloring

On the corner cabinet door we can deduce that the patina was carried out in two stages in order to enhance certain parts: a first uniform brownish layer (visible on the cap and the collar in particular), and a second almost black layer which has worn in places. This darker layer makes it possible to highlight the character's hair or even details of the clothing (Figure 3d).

Observation of worn areas on brass castings shows the presence of a reddish layer of metal underlying the gilding or dark patina. It corresponds to a deposit of copper made electrochemically on brass. This deposit was carried out systematically on all the decorative brass pieces which have a gold and brown/black decoration (base and top part with decoration of columns and dragons of the corner cabinet; the base and decoration of the bamboo and clusters on the torch and base of the 'Elephant' vase). On the corner cabinet, dismantling the upper part of a column makes it possible to confirm the brass-copper-dark patina stratigraphy, thanks to the engraved identification marks present. On the galvanic copper parts, the patina could be applied directly onto the metal substrate without intermediate plating.

The elephant heads of the vase appear to be a specific case. Intermediate copper plating on the brass has not been clearly detected, but it could be thinner than on the other elements. The composition of the surface patina is consistent with the analysis carried out on the chemical coloring performed on the galvanic copper container. The gilding on the copper was undoubtedly carried out to obtain a warm tint of the gilding. From a practical technical point of view, intermediate copper plating constitutes an interesting bonding layer for noble metals.

In conclusion, the red patinas are largely composed of copper oxide detected by Raman spectroscopy. Traces of sulfur are detected on these surfaces by XRF; they could be linked to an aging of the patina but as sulfur is not detected on the golden areas or the raw brass and as sulfates are detected by Raman in the dark patinas, more complex chemical procedures might have been used to produce these visual effects. The presence of sulfur could be attributed to brochantite ($\text{Cu}_4(\text{OH})_6\text{SO}_4$) which can produce a dark-green tint. We also note the presence of bands characteristic of copper sulfides that could explain the dark, almost black color. These results are consistent with the metal coloring procedures described by Paul Christofle and Henri Bouilhet themselves in 1874^[53]: preliminary copper plating is recommended for chemical patination in order to produce superficial copper oxides and copper sulfides.

The antimony detected by XRF may be part of the patina. Examples of recipes for brownish/black patinas based on antimony trisulfide can be found in technical literature^[54]. The presence of chromium concentration could have different reasons: a pigment such as chrome yellow (PbCrO_4) might have been used to patinate bronzes^[55]. Another hypothesis is the use of the pigment to color a temporary isolating material. Gilder's manuals dating from this period mention saving varnishes containing oil (notably "fat" varnishes, for example mixtures of a copal resin and drying linseed oil). Other recipes mention a combination of a wax and a natural resin^[56]. These varnishes are mixed with a pigment including chrome yellow to visually control the application^[56].

The technical study therefore shows that the Christofle company combines cast brass parts with electroformed copper parts. The latter are produced using an electrolytic deposit of copper in a gutta-percha mold made conductive to create both shapes and ornamental relief decorations.

A direct link can be established between the observations made on the 'Elephant' vase and the plates of the corner cabinet and the galvanic inlay decoration procedures described in a patent of addition from Christofle [52]. The cells intended to receive noble metal inlays are already designed in the mold. After unmolding the copper parts, the voids are filled with wax to temporarily isolate the rest of the surface with an iron plating. After removing the wax from the cells, the gold or silver is then deposited into the cells using an alkaline galvanic bath. On plates with repetitive decorative patterns, as it is the case on the corner cabinet plates, this technique can be combined with another process: the reversed pattern is reproduced using an isolating colored ink, then the cells to be inlaid are electrochemically engraved before being filled with noble metal. Again, the elephant heads on the vase are a specific case, since they are cast in brass. The decorations could have been produced by prior anodic engraving and a pattern transfer technique using a decal process.

4.3. *Cloisonné enamels*

Visual observations confirm that a traditional technique was used for the *cloisonné* technique. The artisan enameller shapes, assembles and brazes thin strips of copper forming partitions onto the

support. These are filled with a colored vitreous powder, baked in the oven. Before polishing the enameled surface, several firings may be necessary to completely fill the space between partitions and create color gradients (superimposed deposit of powders of different colors). The presence of 4 different compositions for the matrices indicates that the firing temperatures are certainly different. The support – sometimes made of galvanic copper – as well as the frames and the partitions are gilded by bath after enameling as evidenced by the traces of gold in the gaps in the counter-enamel of the reverse side ^[32].

Three types of silicate matrix compositions characterized by 3 different ratios $PbO/([Na_2O/K_2O]+CaO)$ were identified. Enamel opacification is achieved by using the use of cassiterite (SnO_2), lead-calcium/potassium arsenate or fluorite (CaF_2). Cobalt is used for the deep blue, almost black hues, but ferrite-chromite for deep black. Tin-yellow and Naples-yellow (Pb-Sb and Pb, Sn, Sb, Zn/Fe/Si complex compositions) were used as pigments to enhance certain ornaments. XRF proved to be an efficient complementary analysis of Raman spectroscopy. This technique was able to identify the pigments used for the green and turquoise colors (presence of copper). In the case of the red hue, XRF analysis was also able to exclude the use of gold nanoparticles and to indicate the use of copper oxide.

5. Conclusion

Extensive information concerning the phases formed could be acquired despite their small thickness or their inclusion in a matrix of different composition. Furthermore, it was possible to perform analysis in-situ in a completely non-invasive way by joint Raman and XRF at the conservation lab of the museum prior to the exhibition of the objects. Visual observation and comparison of the collected data with ancient written sources provided complementary information in order to reconstitute a possible *chaîne opératoire* for each artefact. Partial dismantling and observation of the backsides of certain parts proved to be crucial/fundamental for consistent technological interpretation. FTIR reflectance and SERS resonant Raman spectroscopy were able to identify organic residues due to electrochemical procedures like saving materials, while Raman and XRF analyses are effective for metallic/inorganic phases. However, due to this non-invasive approach certain morphological aspects of the patinas (stratigraphy) could not be studied. Furthermore, the complex geometry of the objects makes it difficult in some cases to access surfaces and to have an optimal signal.

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Conflicts of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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