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The Discovery and Comparison of the Manufacturing Secrets of Enamelled Masterpieces

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The miniaturization and development of the laser sources, optical systems and computer performance in general use for analytical experiments have profoundly changed scientific instrumentation over the past decade. It is now possible to analyze the objects on-site (exhibition areas or storerooms, open-air exhibition, etc.), which revolutionizes the analytical approach and the non-invasive analysis of objects. Two mobile non-invasive analytical techniques that are particularly suited to the study of coloured glassy materials are now available, namely X-ray fluorescence spectrometry and Raman microspectroscopy. In both cases, the electromagnetic radiation (X-ray or visible to near infrared) interacts with the electronic layers of atoms, comprising deep layers for X-rays while it interacts with the surface layers in the case of visible to NIR radiation, and part of this energy of illumination is re-emitted after interaction with the material under study, giving a physicochemical fingerprint of the area illuminated by the instrument.

Procedure and information obtained

Depending on the instrument and its focusing optics, the area analyzed ranges from $\sim 1 \text{ cm}^2$ to 1 mm^2 for portable X-ray fluorescence (pXRF) and from $\sim 1 \text{ mm}^2$ to $\sim 0.5 \mu\text{m}^2$ ($1 \mu\text{m} = 0.001 \text{ mm}$) for Raman spectroscopy. Mapping is possible to map the distribution of chemical elements or phases present in enamels. The depth analyzed (from a few microns to a few mm) is of the same order of magnitude but depends very strongly on the composition of the area under analysis. Stratigraphic analysis is therefore less effective than that carried out in the laboratory on a broken piece or sample. The small size of the measured area requires perfect control and maintenance of the stability of the instrument and the object.

Figure 1 demonstrates that the operational distance between the object's surface and the Raman or XRF instrument does not require the direct contact between the specimen and the probe head.



Fig. 1. Mobile non-invasive analyses (on the left by Raman microspectroscopy, on the right by pXRF) allow the remote analysis ($> 1 \text{ cm}$ between the probe head and the specimen surface) of different areas to be accomplished. The laser spot give a good visual approximation to the point of analysis which is actually much smaller than the visible halo spot; the example on the left shows an imperial huafalang bowl with the reign mark "Yongzheng yu zhi" (inv. G 4806, National Museum of Asian Arts-Guimet Coll.) and on the right a gold ewer decorated with cloisonné and painted enamel with the Qianlong mark (inv. F1467C, National Museum of

Château de Fontainebleau - Chinese Museum). A camera included in the instrumental arrangement shows the illuminated area at high magnification to facilitate the optimization of the selection of the spot to be analyzed.

Cloisonné and painted enamels

We focus on a few examples selected from among hundreds of enamelled objects that have been studied over several years (see bibliography). This corpus comprises French objects that are representative of European enamelling technologies of the 17th century and the very beginning of the 18th century (enamelled watches, Limoges enamels, enamelled glasses of Bernard Perrot, soft-paste porcelains, etc.) and Chinese enamelled objects (porcelains, *cloisonné* metal wares) from the 17th and 18th centuries (Ming and Qing Dynasties) as well as some Japanese porcelains from the 17th (*Kan'ei* period) and 18th centuries.

A Chinese object in which the unexpected signature of cassiterite (SnO_2) was obtained is presented in **Figure 2**. This incense burner is stylistically characteristic of the Kangxi period and is kept at the National Museum of Château de Fontainebleau (Chinese Museum) in a collection created by the Emperor Napoleon III and the Empress Eugenie. The lower part of the incense tripod (inventory number F1448C, height: 27 cm; diameter: 26 cm) is decorated with *cloisonné* enamels depicting multicolour lotus flowers and foliage scrolls characteristic of the influence of Buddhism on a turquoise background; rim and handles are gilded. The lid consists of golden interlacing on which is a female lion with a baby at the top. The lid is expected to have been made by lost wax technique, subsequent chisel carving and gilding. The three feet of the body are added with rivet visible inside. The handles appear welded. The composition determined by pXRF is about copper (65 per cent), zinc (28 per cent), tin (6 per cent), and iron (1 per cent). The gilding is cold applied using mercury. The *cloisonné* enamelled areas are white, dark blue, red, green, light green and yellow. The centre of the flowers is either yellow, yellow-green or green and these colours are used sparingly, which is consistent with low availability or high cost. Note the use of different greens. Numerous pores and cracks are visible in the enamelled decoration. These defects are frequently encountered in such objects due to the application of *cloisonné* enamelling. The *cloisonné* technique particularly involves the interposition of the glass powder between the metal sheets ('*cloison*' in French) fixed perpendicular to the object by wax or point welded before the filling of the voids in between with enamel powder and then firing. The significant shrinkage on heating / melting the enamels involves repeating the step several times but the duration of the cooking cycles is too limited to eliminate the bubbles. A polishing step is also performed at the end which enhances the open porosity. Macro photographs also show that the yellow colour is obtained with fairly large aggregates/grains of yellow, which makes it possible to collect, by Raman, almost pure spectrum of the pyrochlore phase also called *Naples yellow*). We also see that the yellow glass had smudged during firing (containing a lot of lead, its fusibility implies firing last) and that the polishing did not completely eliminate the drips.



Fig. 2. Detail of the cloisonné enamels of an incense burner tripod (Kangxi reign; National Museum of Château de Fontainebleau (Chinese Museum)). Detail of the coloured areas. The green and yellow areas are opacified with cassiterite associated with Naples yellow type of pigments.

It is known that Ming Dynasty *cloisonné* enamels had been opacified by fluorite and not by cassiterite. This is the case for the white areas in this artefact: note that the Raman spectrum of this phase is very tiny and similar spectra are collected on blue areas. On the contrary the yellow-green and yellow areas are coloured and opacified by mixtures of *Naples yellow* and cassiterite. Cassiterite and *Naples yellow* pyrochlore typically point to European technologies/ingredients. This burner artefact is thus one of the first artefacts made with European recipes, but for some colours only.

On the contrary, the blue painted areas of the gold ewer (Figure 1) give a Raman spectrum with the evidence of a potassium-calcium-lead-arsenate. Indeed, while the cobalt ores used in the Ming (and in most of the Kangxi) period are derived from geologically primary type Asian deposits (these ores contain a mixture of transition metals in comparable quantities: cobalt with also iron, manganese, etc.), the European cobalt ores are of secondary type deposits, resulting from hydrothermal action and are rich in arsenic and generally associated to silver and bismuth. Long times ago mining was only made for the extraction of silver and then of bismuth (added to lead to make cast printing types after Gutenberg innovation) and the cobalt source was only an incidental product recovered by mixing the slag with potassium glass to give the smalt, blue colouring matter. The yellow painted enamel of the ewer has a spectrum identical e.g. to those obtained from the enamelled watches (Figure 3) which date to the mid-17th century to the beginning of the 18th century: the *Naples yellow* pigments are of typically Mediterranean/European origin and have been widely used for the decoration of Byzantine terracotta and then later earthenware/majolica.



Fig. 3. Comparison of enamel decoration techniques: on the left, the transition from the technique of superimposing coloured layers (top, on a watch circa 1640, Paris, inv. OA7074) to the stippling technique (bottom, on a watch, 2nd half of the 18th century, Amsterdam, inv. OA6264) Louvre Museum Coll.; on the right, detail of an ewer decorated with cloisonné and painted enamels (Qianlong mark, 3rd quarter of 18th century, inv. F1467C, National Museum of Château de Fontainebleau (Chinese Museum), Fig. 3); note the use of the stippling technique.

Figure 73 shows that some objects not only use European ingredients and recipes but also the new European painting technique of miniaturists. The observation at high optical magnification of the décor shows dotted touches of colour, this is the technique of the miniaturists of the 17th-18th century contrarily to the ancient technique of brush touches, as used by potters for example on 16th century majolica depicting copy of paintings. The sophisticated decoration of the French enamels first utilises the traditional technique of layering the colours of the potters by superposition (Figure 3, top left). From the end of the 17th century, the stippling technique started to be used, combined with a large palette of hues obtained by mixing pigments before use. Indeed, the analysis of a micron fraction of a green paint dot (Fig. 3, right bottom, dot diameter ~ 1 mm) of the painted décor of a Chinese gold ewer from a pair (see the paper by Bing Zhao in the same issue) is shown in Figure 4: the spot analyzed in Raman is more than ten times smaller than the paint green point visible on the zoom. However, as shown by the bottom spectrum, in this spot at least 4 crystalline phases (cassiterite, Naples yellow pyrochlore, wollastonite, lead-arsenate apatite and carbon) plus the amorphous silicate matrix are identified by their Raman spectrum. This confirms the use of a colour palette obtained by prior mixing of colouring agents to obtain a wide range of hues, as practiced in European easel (oil) painting, in accordance with the archive content which say that with the help of the Jesuits about thirty colours became available for painted enamel decorations. This technique also has the advantage of precision enamelling and minimizing the number of firings required. The example of the decoration of the pair of Qianlong gold ewers from the National Museum of Château de Fontainebleau (Chinese Museum) using simultaneously the techniques of painted and *cloisonné* enamels on metal typically represents one summit of the mixed use of European enamelling techniques. Here the use of *Naples yellows* of different compositions, cassiterite, European cobalt sources that are rich in arsenic as well as the use of gold nanoparticles for the pink colour can all be verified.

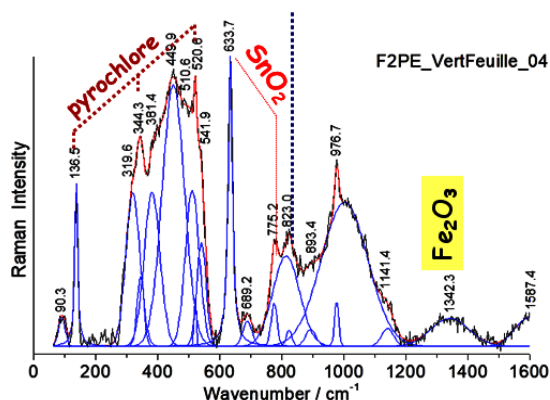


Fig. 4. Characteristic Raman spectra obtained from the green small spot of the painted enamel décor of the gold ewer (Fig. 3). The main characteristic peaks of the silicate matrix of the enamel (broad components) and pigments / opacifiers (Naples yellow pyrochlore (Sb-rich, 136.5-520.6 cm^{-1} doublet), cassiterite (SnO_2 , 633.7-775.2 cm^{-1} doublet), lead arsenate (As-O, 823 cm^{-1} band) and hematite (Fe_2O_3 , 1340 cm^{-1} band) are labelled.

This type of analysis without sampling or contact, carried out on site in order to document from the information remaining in the material of the objects, the transfers of techniques carried out in China by the Jesuits can be used for many other issues and in particular to detection of fakes.

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Bibliography

1. Shih, C.F. Evidence of East-West Exchange in the Eighteenth Century: The Establishment of Painted Enamel Art at the Qing Court in the Reign of Emperor Kangxi. *Natl. Palace Mus. Res. Quarterly* **2007**, *24*(3), 45–94.
2. Kirmızı, B.; Colomban, P.; Quette, B. On-site analysis of Chinese *Cloisonné* enamels from fifteenth to nineteenth centuries. *J. Raman Spectrosc.* **2010**, *41*(7), 780–790.
3. Van Pevenage, J.; Lauwers, D.; Herremans, D.; Verhaeven, E.; Vekemans, B.; De Clercq, W.; Vincze, L.; Moens, L.; Vandenaebelle, P. A combined spectroscopic study on Chinese porcelain containing *ruan-cai* colours. *Anal. Methods* **2014**, *6*, 387–394.
4. Giannini, R.; Freestone, I.C.; Shortland, A.J. European cobalt sources identified in the production of Chinese *famille rose* porcelain. *J. Archaeol. Sci.* **2017**, *80*, 27–36.
5. Colomban, P.; Arberet, L.; Kirmızı, B. On-site Raman Analysis of 17th and 18th Century Limoges Enamels: Implications on the European Cobalt Sources and the Technological Relationship Between Limoges and Chinese Enamels. *Ceram. Int.* **2017**, *43*(13), 10158–10165.
6. Colomban, P.; Zhang, Y.; Zhao, B. Non-invasive Raman analyses of Chinese *huafalang* and related porcelain wares. Searching for evidence for innovative pigment technologies. *Ceram. Int.* **2017**, *43*(15), 12079–12088.
7. Colomban, P.; Ambrosi, F.; Ngo, A.-T.; Lu, T.-A.; Feng, X.-L.; Chen, S.; Choi, C.-L. Comparative analysis of *wucai* Chinese porcelains using mobile and fixed Raman microspectrometers. *Ceram. Int.* **2017**, *43*(16), 14244–14256.
8. Colomban, P.; Kirmızı, B.; Gougeon, C.; Gironda, M.; Cardinal, C. Pigments and glassy matrix of the 17th-18th century enamelled French watches: A non-invasive on-site Raman and pXRF study. *J. Cult. Herit.* **2020**, *44*, 1-14.
9. Colomban, P.; Kirmızı, B.; Zhao, B.; Clais, J.-B.; Yang, Y.; Droguet, V. Non-invasive on-site Raman study of pigments and glassy matrix of 17th–18th century painted enamelled Chinese metal wares: *Comparison* with French enamelling technology. *Coatings* **2020**, *10*, 471, <https://doi.org/10.3390/coatings10050471>.

10. Montanari, R.; Murakami, N.; Colomban, P.; Alberghina, M.F.; Pelosi, C.; Schiavone, S. European ceramic technology in the Far East: Enamels and pigments in Japanese art from the 16th to the 20th century and their reverse influence on China. *Herit. Sci.* **2020**, *8*, 48. <https://heritagesciencejournal.springeropen.com/articles/10.1186/s40494-020-00391-2>
11. Colomban, P.; Kırmızı, B.; Zhao, B.; Clais, J.-B.; Yang, Y.; Droguet, V. Investigation of the Pigments and Glassy Matrix of Painted Enamelled Qing Dynasty Chinese Porcelains by Noninvasive On-Site Raman Microspectrometry. *Heritage* **2020**, *3*(3), 915–940; <https://doi.org/10.3390/heritage3030050>.
12. Colomban, P.; Kırmızı, B.; Simsek Franci, G. Cobalt and Associated Impurities in Blue (and Green) Glass, Glaze and Enamel: Relationships Between Raw Materials, Processing, Composition, Phases and International Trade. *Minerals* **2021**, *11*(6), 633; <https://doi.org/10.3390/min11060633>.