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Non-invasive on-site Raman and XRF study of the 17th-18th century painted enamelled Chinese metal wares and porcelains: Comparison with French enamelling technology

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Background and Scope of the Study

Both Chinese and European historical records report that French Ambassador of Louis XIV and the French Jesuit missionaries were hosted at the Kangxi Court during the 17th century, and they presented outstanding enamelled artefacts as gifts to the Chinese emperor. Among these presents were enamelled metal objects which offer a complex realistic painted decor of enamels. It is also known that according to the demand of Kangxi Emperor, this advanced enamelling technology was taught to Chinese craftsmen at the workshops inside the Beijing Forbidden Palace. Royal archives mention that pigments and ingredients required to make such enamels were imported from Europe and this trade was regularly followed [1-2].

In this study, we present the non-invasive on-site study of 10 enamelled metal wares dating to the 17th–18th centuries (Qing Dynasty) from the collections of Musée du Louvre and Château de Fontainebleau (Musée Chinois) by non-invasive mobile Raman microspectroscopy and portable X-ray fluorescence spectroscopy. These metal wares were produced by cloisonné and/or painted enamel techniques. The objective of the study is to compare the enamelling technology used in these artefacts, regarding the different types of enamels with the identification of pigments/opacifiers and glass compositions used [3].

The study is expected to provide arguments to identify the use of imported enamels and/or enamel recipes from Europe to China at the end of the 17th century under the guidance of Jesuits as reported in the historical records.

[1] B. Zhao, G.Y. Wang, I. Biron, P. Colomban, L. Hilaire-Pérez, La circulation des techniques de l'émail entre la France et la Chine du XVIIIème au XIXème siècle. *Le CNRS en Chine Bulletin*, 21, 20–25, 2016

[2] C.F. Shih, 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. Q.* 24, 45–94, 2007

[3] P. Colomban, B. Kirmizi, B. Zhao, J-B. Clais, Y. Yang, V. Droguet, Non-invasive on-site raman study of pigments and glassy matrix of 17th-18th century painted enamelled Chinese metalwares: Comparison with French enamelling technology, *Coatings*, 10(5), 2020

Analytical Techniques

➤ Mobile Raman set-up (HORIBA Jobin-Yvon, Longjumeau France)

- 532 nm Ventus 300 mW laser (Laser Quantum) and x50 (NIKON) and x200 (Mitutoyo Corp.) long working distance objectives.

The mobile Raman analysis @ Musée chinois

➤ Portable Elio XRF instrument (XGLab Bruker, Italy)

- 40 kV tube voltage, 100 μA current, 40 s acquisition time

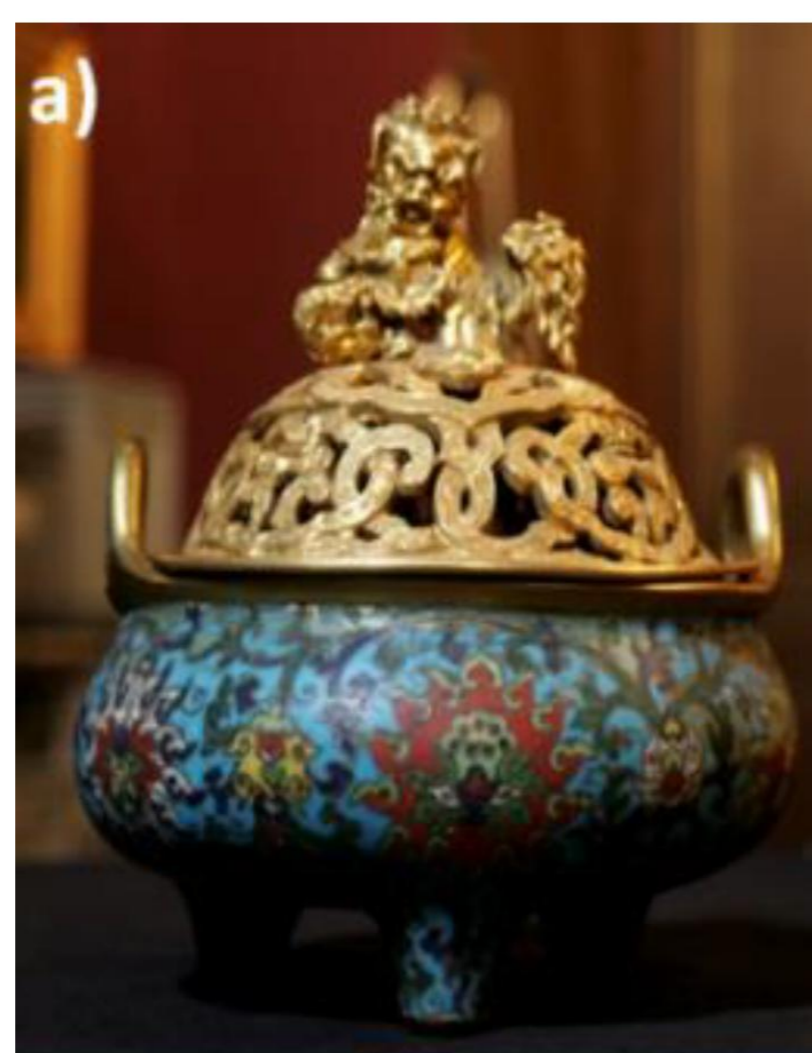


The on-site pXRF analysis @ Musée chinois



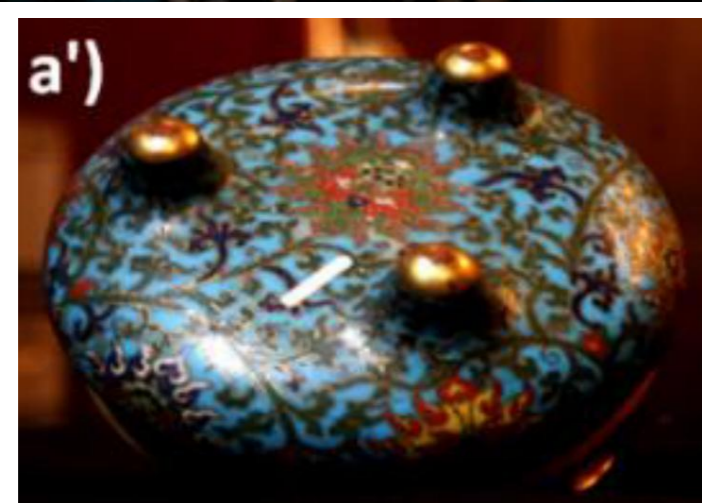
Kangxi Emperor

Incense tripod, cloisonné enamel end of Kangxi reign (1662-1722)



Qianlong Emperor

F1448C @ Chateau de Fontainebleau, Musée Chinois
H:27 cm / D:26 cm



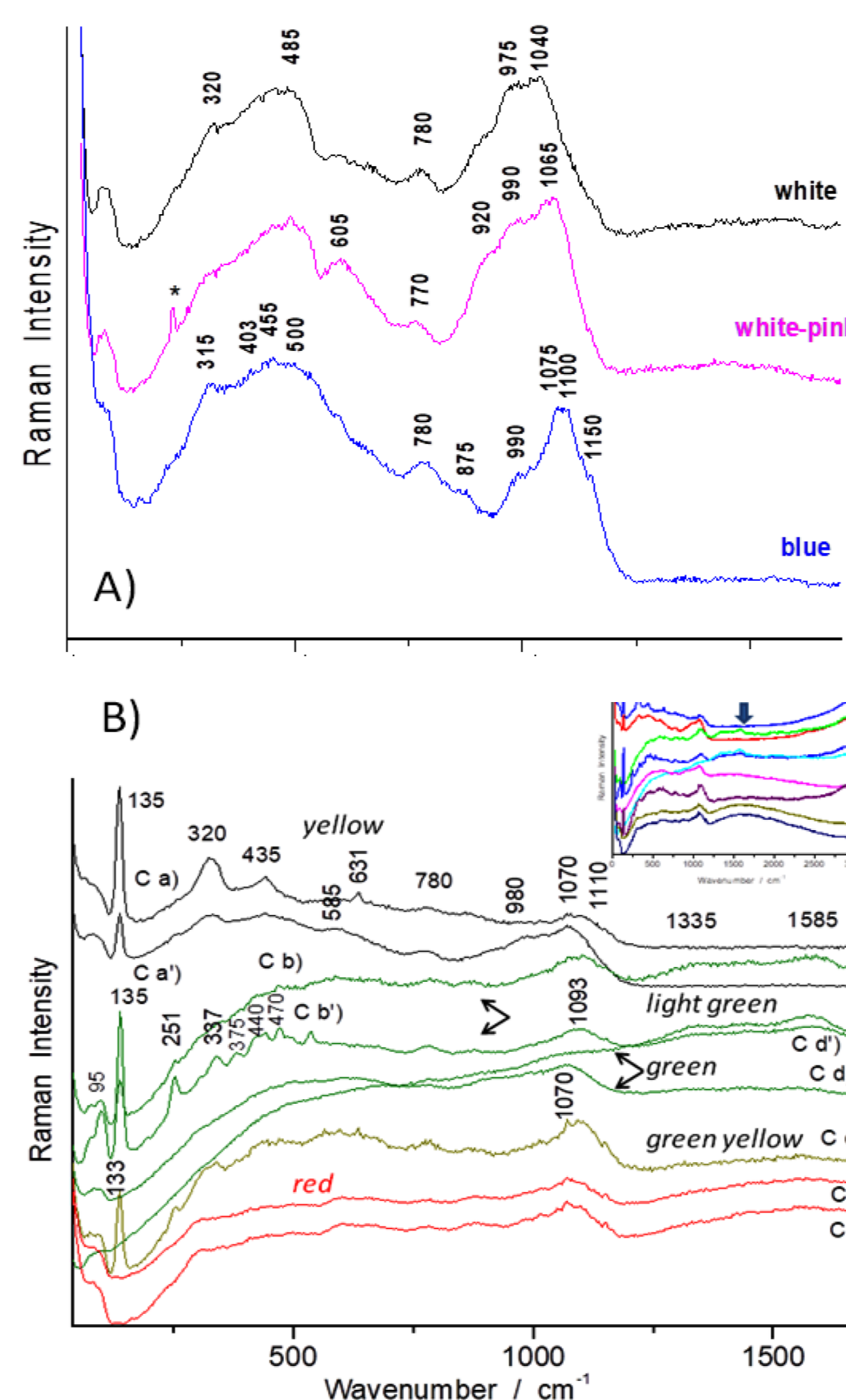
Ewer, painted and cloisonné enamel on gold body
Qianlong reign (1736–1795)



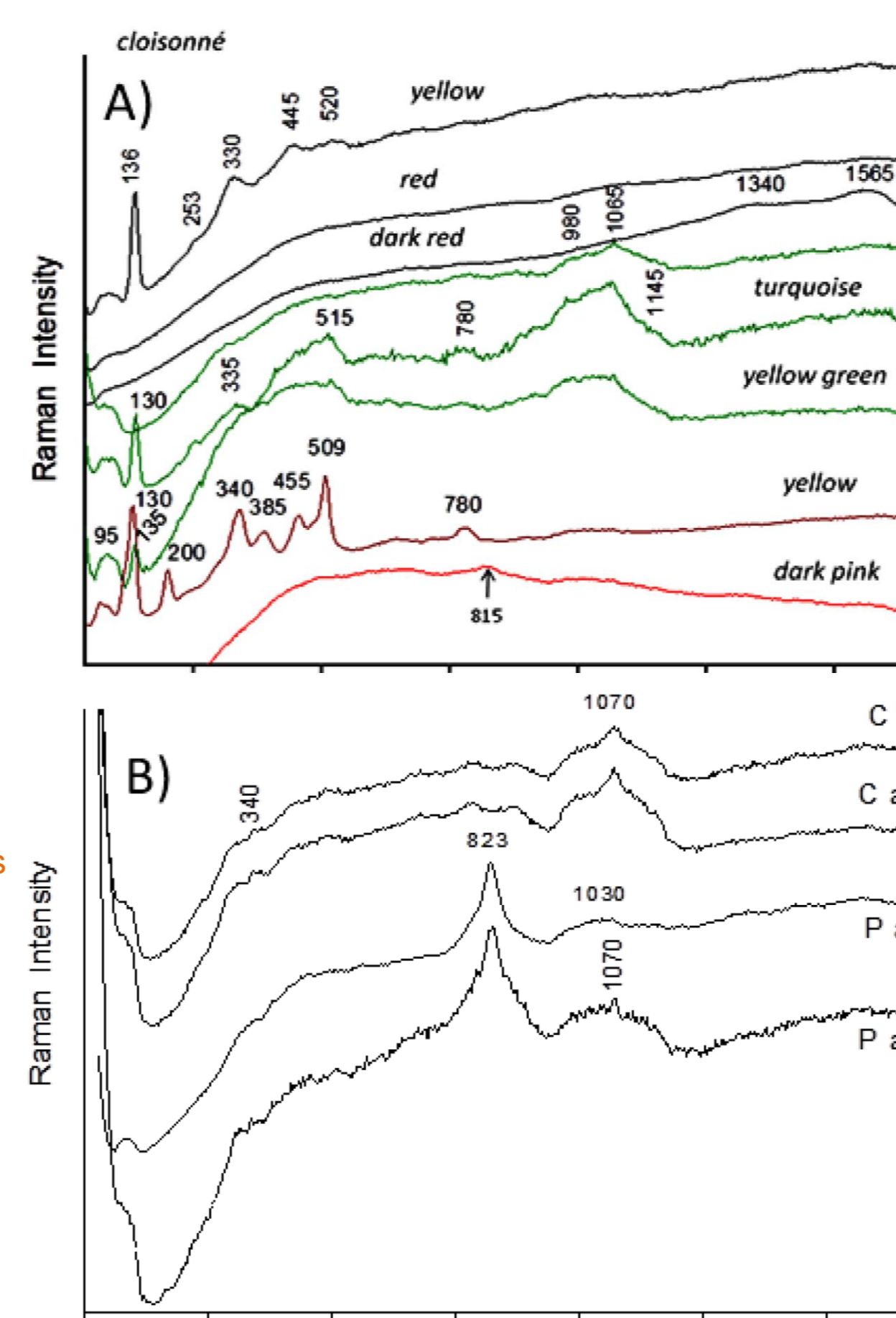
Qianlong mark on the base

Details of the painted enamel medallion

Raman spectra of the F1448C tripod (A-B)



Raman spectra of the F1467 ewer (A-B-C)



Results-Discussion

The Kangxi tripod with cloisonné (C) enamels:

- Glassy Si-O Matrix
 - Variations of lead-alkali type of glass: a) the strongest component at ~1030 to 1050 cm⁻¹, b) rather similar intensity of ~975 and 1045 cm⁻¹ components, c) the strongest component at ~1065–1070 cm⁻¹, d) the strongest component at ~1080–1100 cm⁻¹
 - Pigments and Opacifiers
 - White:** Fluorite (320 cm⁻¹)
 - Blue:** Co²⁺ ions
 - Yellow:** Pb-Sn pyrochlore (~135,320,435 cm⁻¹)
 - Light green:** Pb-Sb-Sn(Zn) pyrochlore (~135,251,337,375,470 cm⁻¹) + Cassiterite (631,780 cm⁻¹) + Co²⁺ ions
 - Red:** Cu⁰ nanoparticles (fluorescence)
- ❖ The Kangxi tripod mostly displays the characteristics of Chinese technology with fluorite opacification and copper red. Only the yellow and green enamels are made with European ingredients/techniques.

The Qianlong ewer with cloisonné (C) / painted (P) enamels:

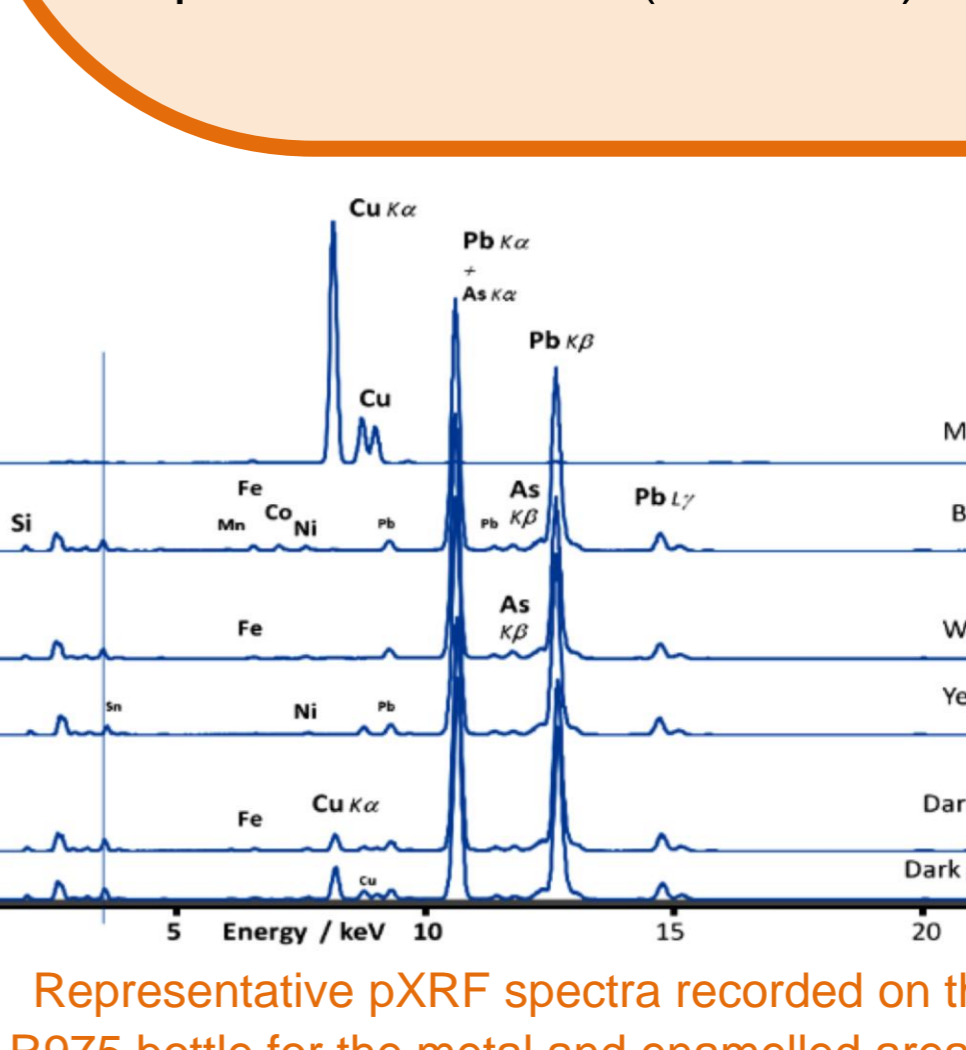
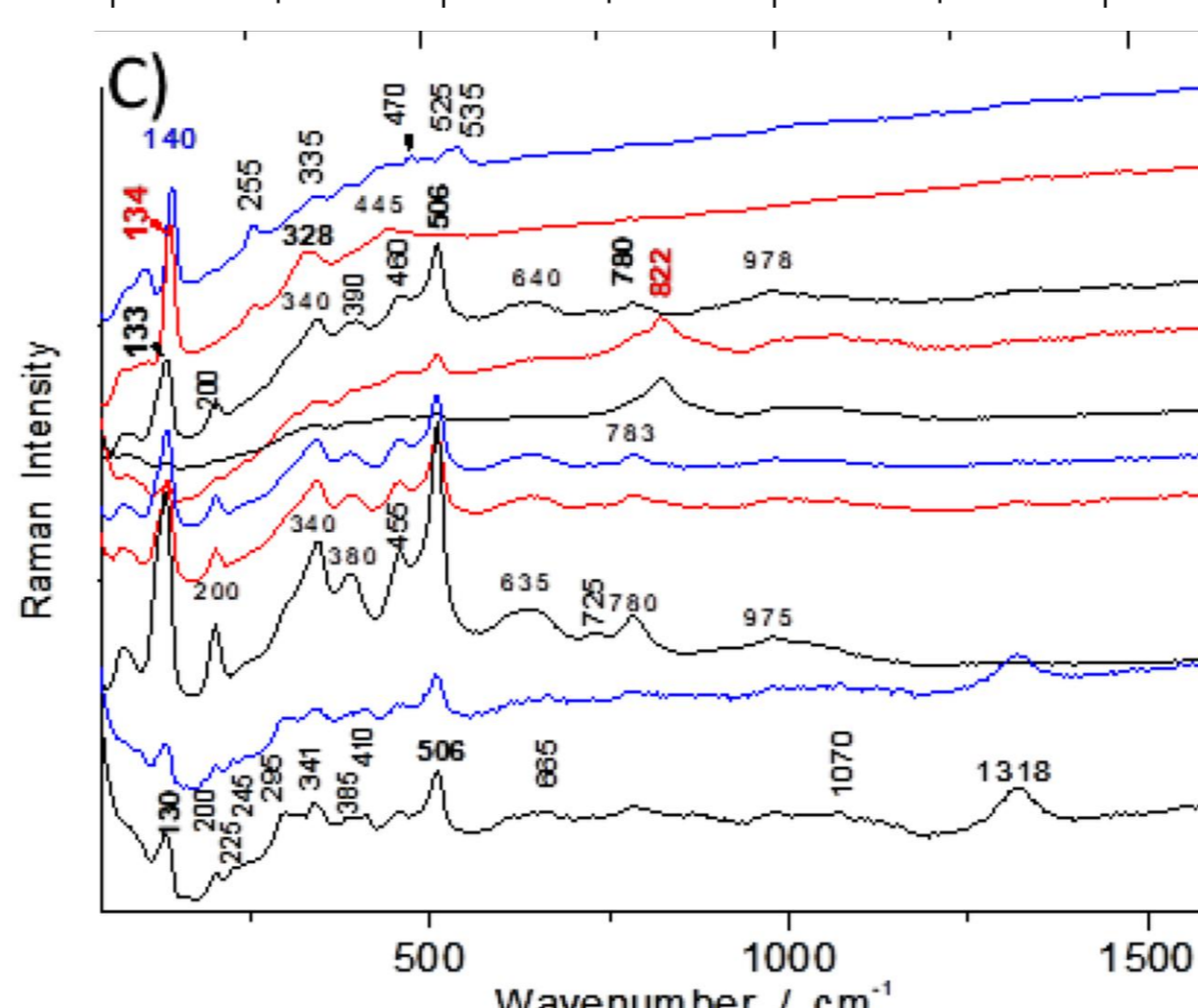
- Glassy Si-O Matrix (C)
 - Lead-alkali type of glass with the strongest component at ~1070 cm⁻¹
 - Pigments and Opacifiers (C)
 - Blue:** Co²⁺ ions
 - Yellow:** Pb-Sn pyrochlore (~135,330,445,520 cm⁻¹)
 - Green:** Pb-Sn pyrochlore (~135,330,450,520 cm⁻¹) + Co²⁺ ions
 - Pink:** Au⁰ nanoparticles (fluorescence) + arsenate (815 cm⁻¹)
 - Glassy Si-O Matrix (P)
 - Lead-alkali type of glass with the strongest components at ~980 cm⁻¹ and 1040 cm⁻¹
 - Pigments and Opacifiers (P)
 - White:** Lead arsenate (~820 cm⁻¹)
 - Blue:** Co²⁺ ions + lead arsenate (~820 cm⁻¹)
 - Yellow:** Pb-Sb pyrochlore (~130,340,455,506 cm⁻¹)
 - Green:** Pb-Sn/Pb-Sb-(Zn) pyrochlore (~135,335,450,510 cm⁻¹) + Co²⁺ ions + Cassiterite (632,775 cm⁻¹)
 - Orange:** Hematite (225, 410,1318 cm⁻¹)
- ❖ The Qianlong ewer represents the use of European ingredients/techniques with the lead pyrochlore pigment, gold nanoparticles and European cobalt ores (rich in As).

Conclusion

This analytical study confirms the capability of on-site Raman analysis with mobile set-up for characterization of the sophisticated enamelled wares from China. The 17th-18th century turn marks the period of close contact between Europe and China through the Jesuits hosted at the Chinese Court. The results particularly contribute to identification of the artefacts where ingredients or recipes from Europe had been used for enamelling.

It is significant that cassiterite was probably used as an opacifier in some of the metal wares. Lead arsenate detected in some of the 17th–18th century blue enamels is related to the use of arsenic-rich European cobalt ores.

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R975 @ Musée du Louvre
Qianlong period
H:26.5 cm / D:14 cm