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Philippe Colomban, Burcu Kirmizi, Bing Zhao, Jean-Baptiste Clais, Michele Girona, et al.. 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. 5th International Conference on Innovation in Art Research and Technology (inArt 2022), Jun 2022, Paris, France. hal-03964497

**HAL Id: hal-03964497**

**<https://hal.science/hal-03964497v1>**

Submitted on 1 Feb 2023

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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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inART  
2022

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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  $\mu$ A current, 40 s acquisition time

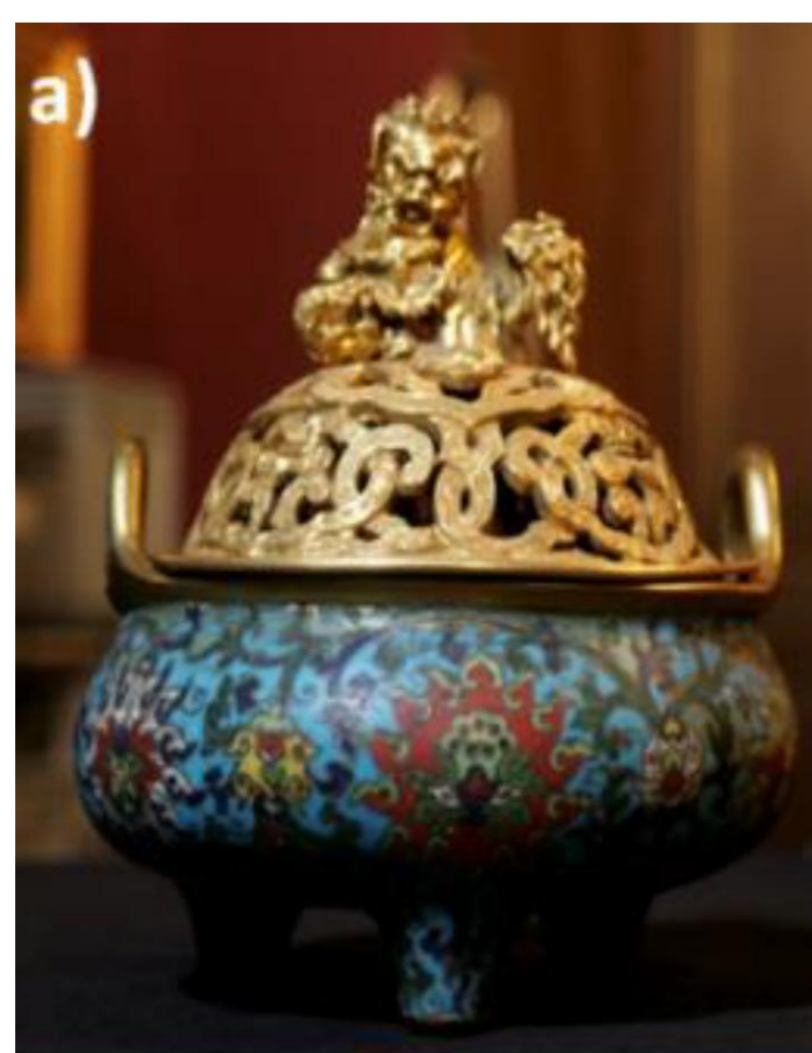
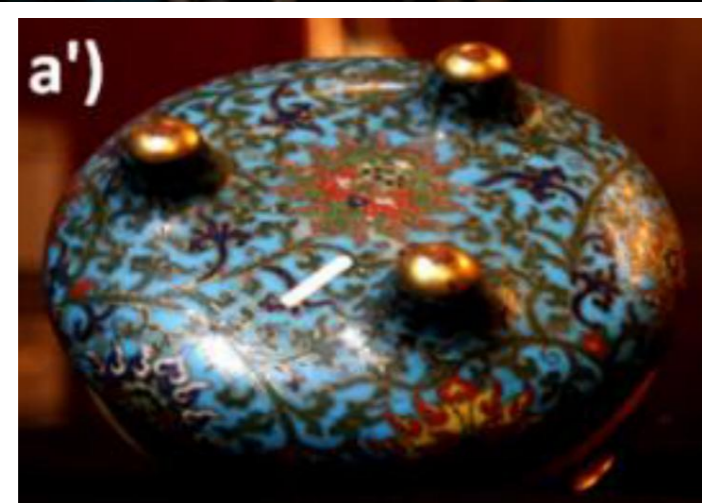


The on-site pXRF analysis @ Musée chinois



Kangxi Emperor

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

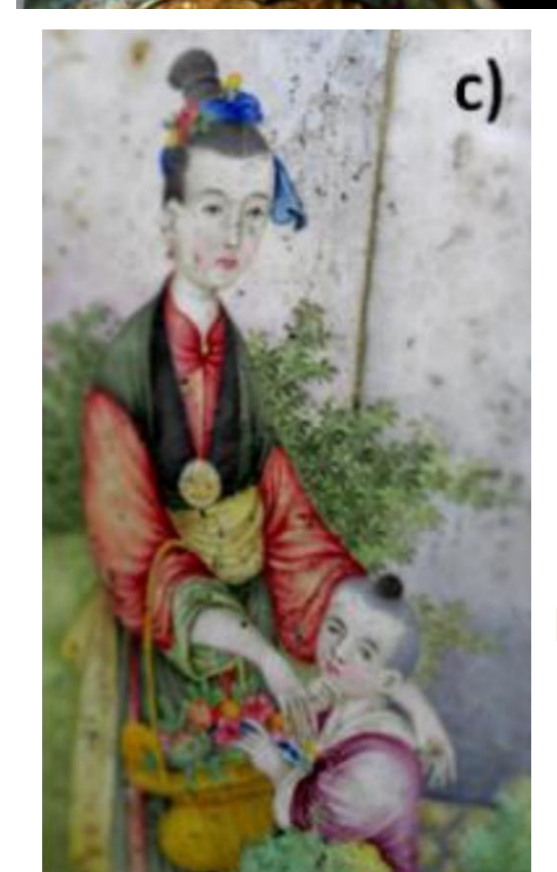


F1448C @ Chateau de Fontainebleau, Musée Chinois  
H:27 cm / D:26 cm



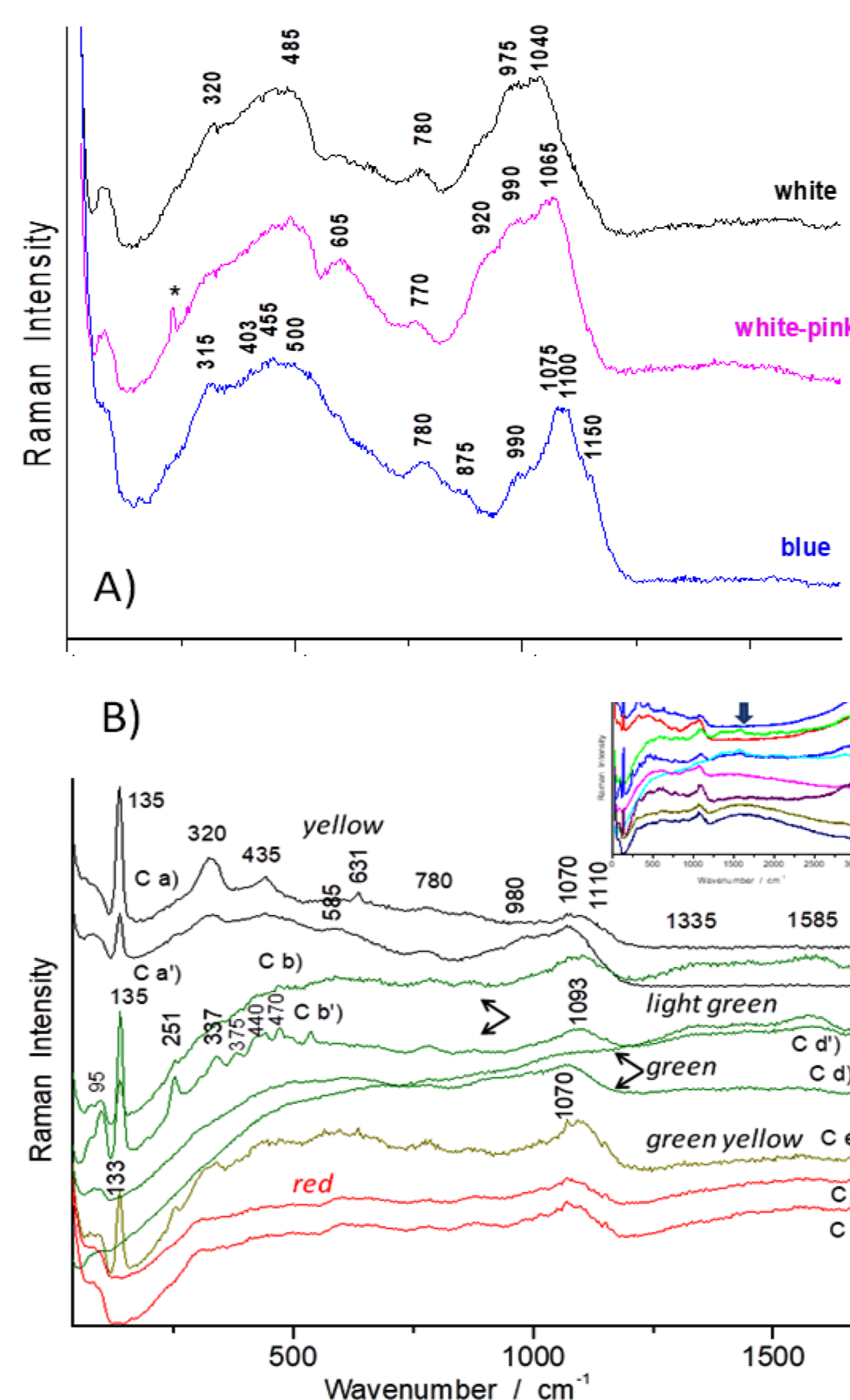
Qianlong Emperor

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

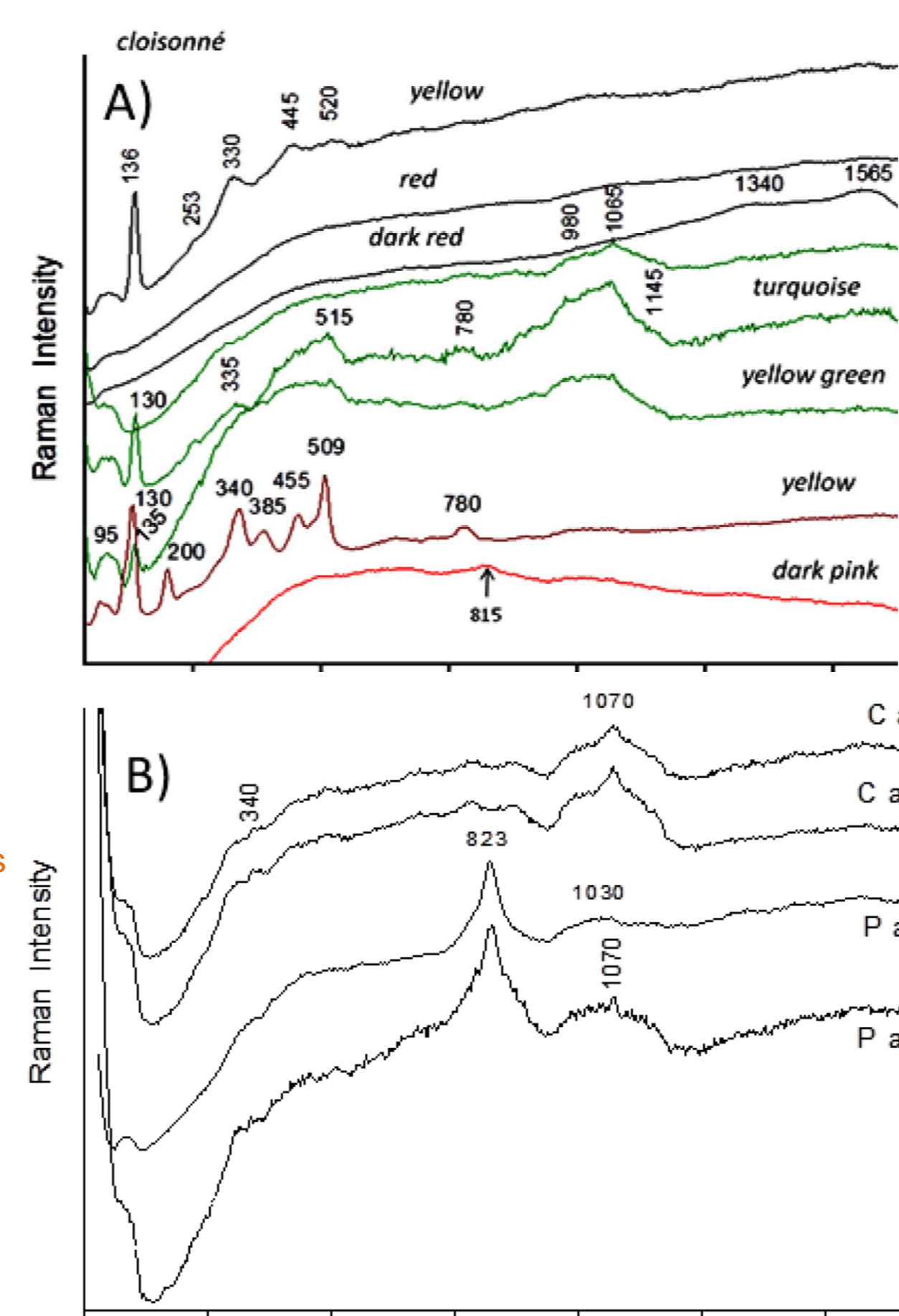


F1467 @ Chateau de Fontainebleau, Musée Chinois  
H:40 cm / D:20 cm

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  $\sim 1030$  to  $1050$   $\text{cm}^{-1}$ , b) rather similar intensity of  $\sim 975$  and  $1045$   $\text{cm}^{-1}$  components, c) the strongest component at  $\sim 1065$ – $1070$   $\text{cm}^{-1}$ , d) the strongest component at  $\sim 1080$ – $1100$   $\text{cm}^{-1}$

▪ Pigments and Opacifiers

- White:** Fluorite ( $320$   $\text{cm}^{-1}$ )
- Blue:**  $\text{Co}^{2+}$  ions
- Yellow:** Pb-Sn pyrochlore ( $\sim 135, 320, 435$   $\text{cm}^{-1}$ )
- Light green:** Pb-Sb-Sn(Zn) pyrochlore ( $\sim 135, 251, 337, 375, 470$   $\text{cm}^{-1}$ ) + Cassiterite ( $631, 780$   $\text{cm}^{-1}$ ) +  $\text{Co}^{2+}$  ions
- Red:**  $\text{Cu}^{\circ}$  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  $\sim 1070$   $\text{cm}^{-1}$

▪ Pigments and Opacifiers (C)

- Blue:**  $\text{Co}^{2+}$  ions
- Yellow:** Pb-Sn pyrochlore ( $\sim 135, 330, 445, 520$   $\text{cm}^{-1}$ )
- Green:** Pb-Sn pyrochlore ( $\sim 135, 330, 450, 520$   $\text{cm}^{-1}$ ) +  $\text{Co}^{2+}$  ions
- Pink:**  $\text{Au}^{\circ}$  nanoparticles (fluorescence) + arsenate ( $815$   $\text{cm}^{-1}$ )

▪ Glassy Si-O Matrix (P)

- Lead-alkali type of glass with the strongest components at  $\sim 980$   $\text{cm}^{-1}$  and  $1040$   $\text{cm}^{-1}$

▪ Pigments and Opacifiers (P)

- White:** Lead arsenate ( $\sim 820$   $\text{cm}^{-1}$ )
- Blue:**  $\text{Co}^{2+}$  ions + lead arsenate ( $\sim 820$   $\text{cm}^{-1}$ )
- Yellow:** Pb-Sb pyrochlore ( $\sim 130, 340, 455, 506$   $\text{cm}^{-1}$ )
- Green:** Pb-Sn/Pb-Sb-(Zn) pyrochlore ( $\sim 135, 335, 450, 510$   $\text{cm}^{-1}$ ) +  $\text{Co}^{2+}$  ions + Cassiterite ( $632, 775$   $\text{cm}^{-1}$ )
- Orange:** Hematite ( $225, 410, 1318$   $\text{cm}^{-1}$ )

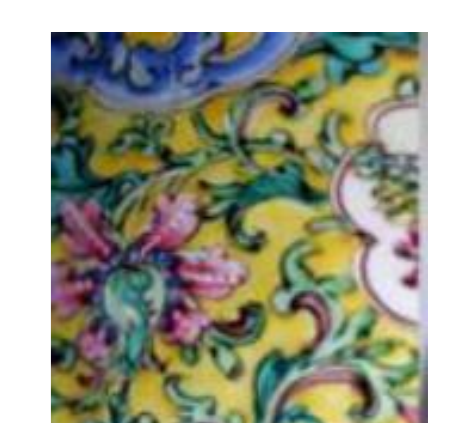
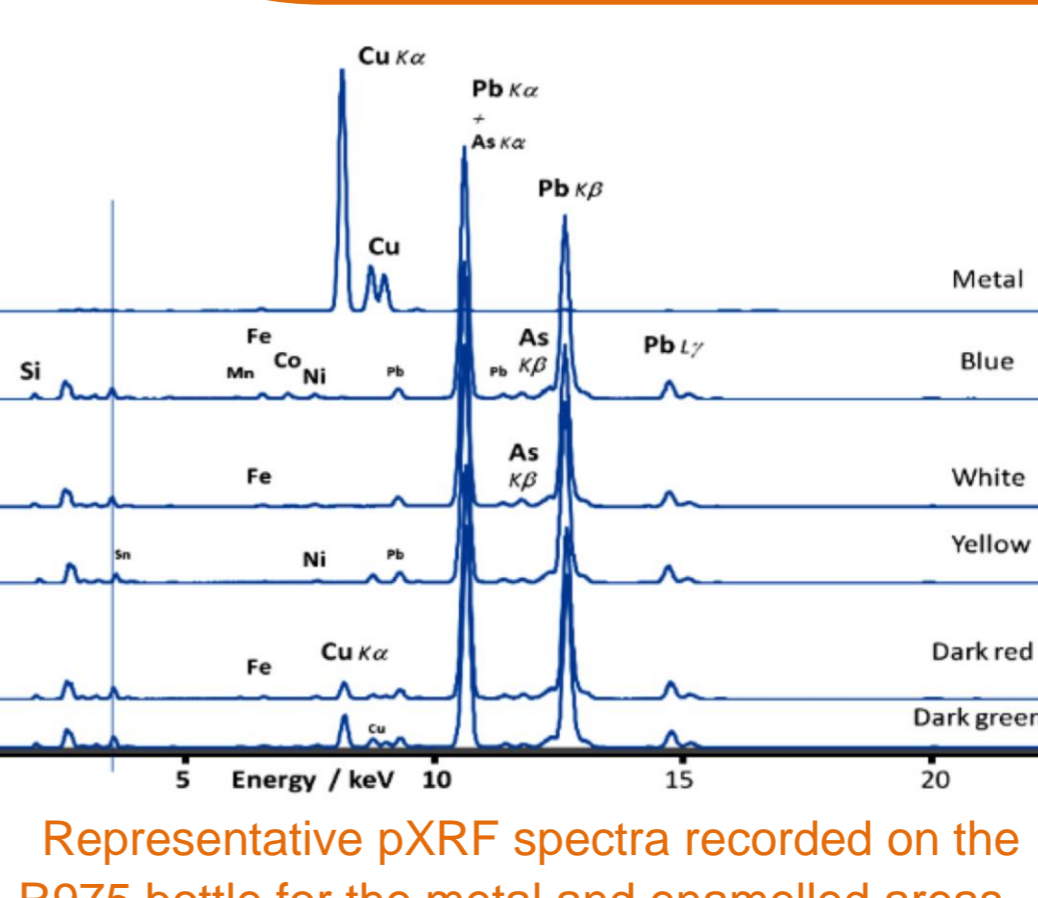
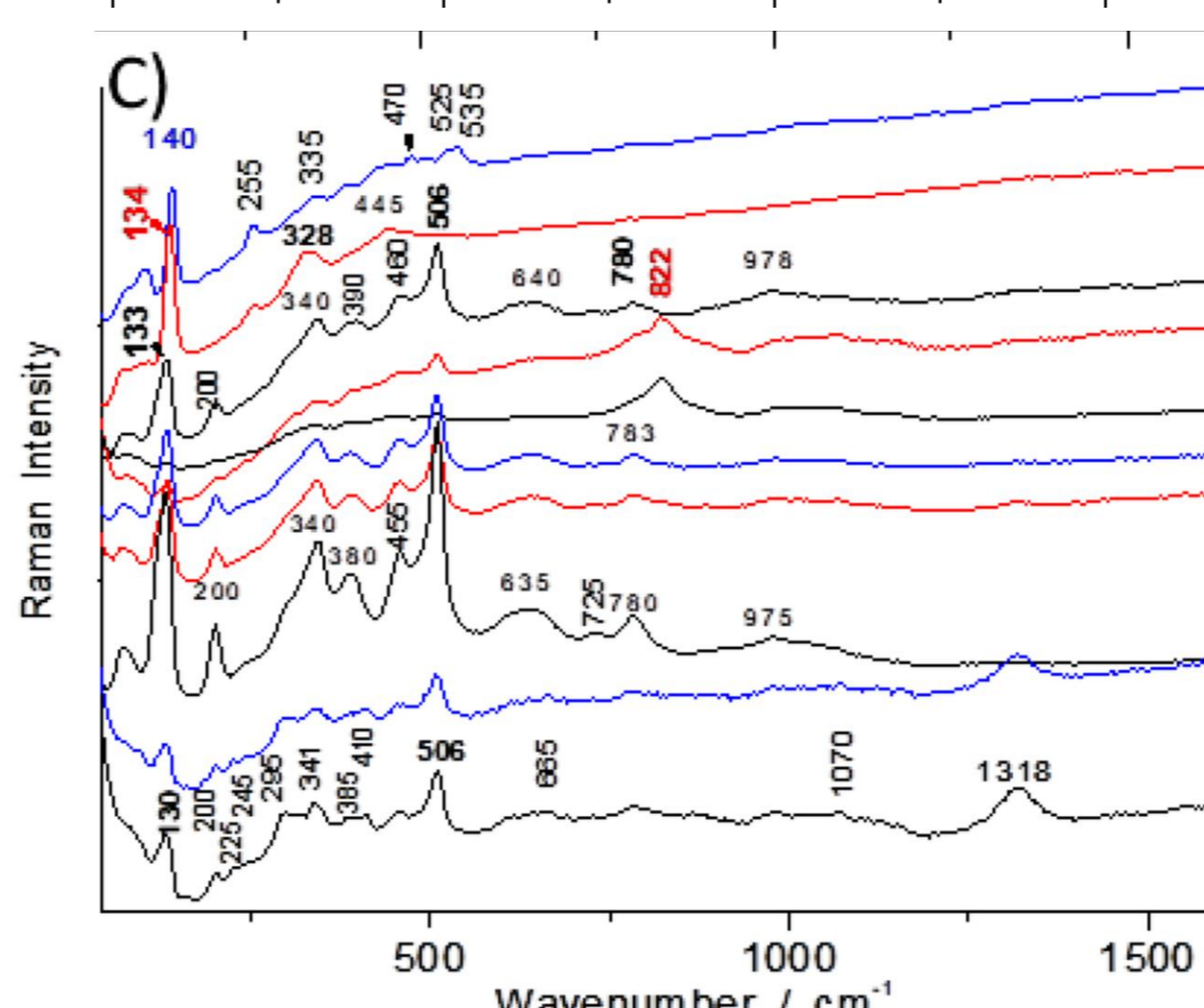
❖ The Qianlong ewer represents the use of European ingredients/techniques with the lead pyrochlore pigment, gold nanoparticles and European cobalt ores (rich in As).

## 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.

❖ This work has been carried out in the framework of the LIA CNRS-Palace Museum and Campus France PHC Cai Yuanpei programs in preparation of ANR EnamelFC. Vincent Cochet, former Head of the Château de Fontainebleau, and Site, Sarah Paronetto, keeper at Chateau de Fontainebleau and Catherine Gougeon from Musée du Louvre are acknowledged for their contribution.



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