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A non-invasive on-site Raman and pXRF study of the pigments and glassy matrix of 17th-18th century enamelled French watches



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Background and Scope of the Study

The first half of the 17th century witnessed the emergence of enamel portrait miniatures which were introduced to France by goldsmiths (e.g. Jean and Henri Toutin). All productions of painted enamels on various metal substrates displaying pictorial decorations generated an artistic manner which is similar to oil painting on wood or canvas.

The emergence of watches with painted enamel miniatures occurred circa 1630 in France. Their decorations represent the highest level of enamelling technology achieved at that time, allowing the reproduction of the works of famous painters.

The present study reports the on-site analytical characterization of 12 rare enamelled watches from Musée du Louvre, mostly produced in France during the 17th and 18th centuries [1]. The material characterization and production technology of the painted enamels are discussed, regarding the colouring/opacifying agents and glass compositions of the painted enamels [2]. It is significant that the spectroscopical analysis by Raman and pXRF allows to get a first representative view of the evolution of the painted enamelling technique on gold.

[1] C. Cardinal, La collection des montres et horloges de Table du musée du Louvre, Tome 1 (1984); Tome 2 (2000), RMN, Paris.

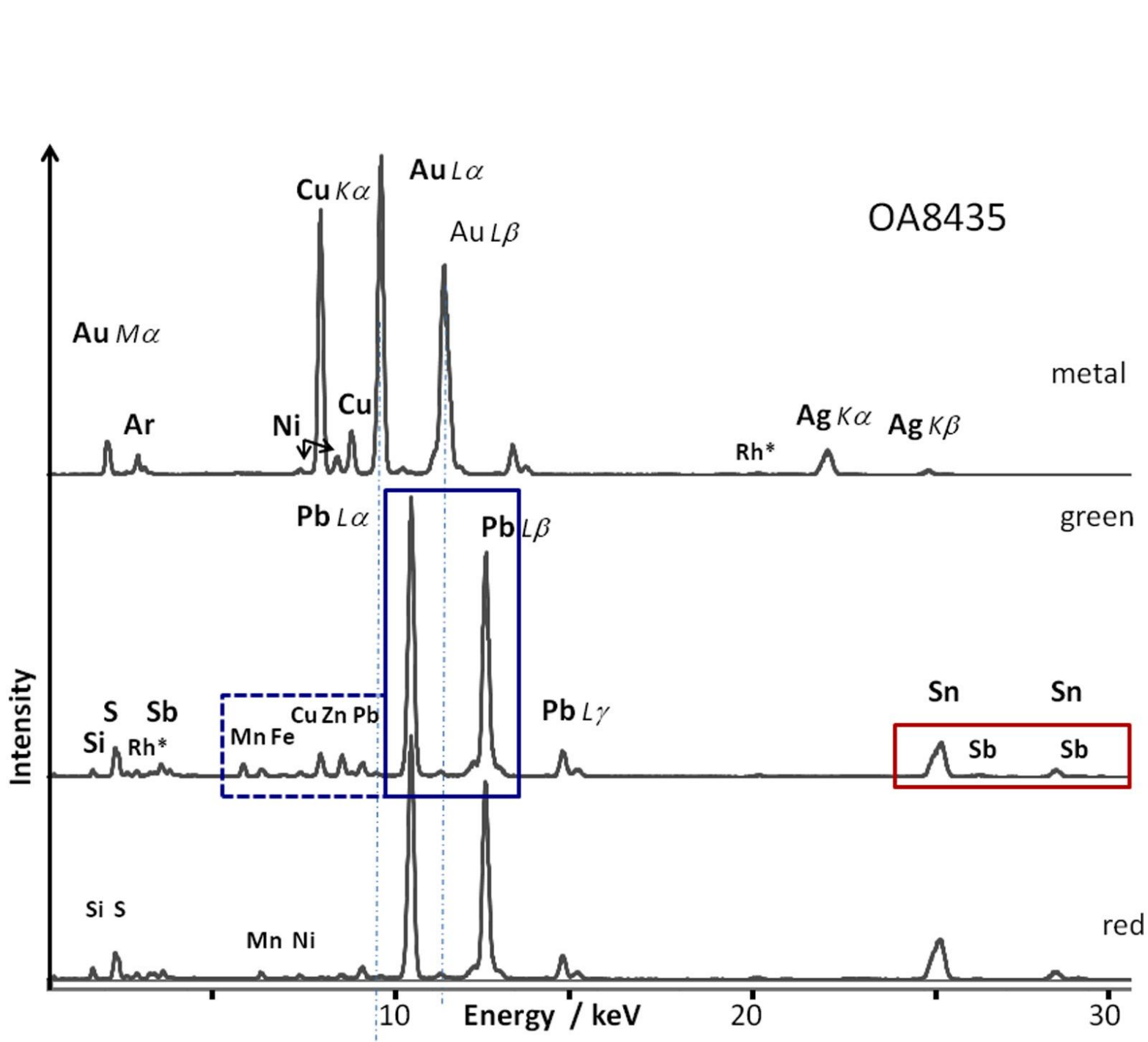
[2] P. Colomban, B. Kirmizi, C. Gougeon, M. Gironda, C. Cardinal, Pigments and glassy matrix of the 17th-18th century enamelled French watches: A non-invasive on-site Raman and pXRF study, *Journal of Cultural Heritage*, 44, pp.1-14, 2020.

Analytical Techniques

- Mobile Horiba Scientific Jobin-Yvon (France) Raman set-up
 - 532 nm Ventus Quantum 300 mW laser; x50 Nikon (~17 mm long working distance) objective
- Portable Elio XRF instrument (XGLab Bruker, Italy)
 - The point mode, 40 kV tube voltage, 100 μ A current, 40 s acquisition time



The mobile Raman spectrometer and the on-site pXRF analysis



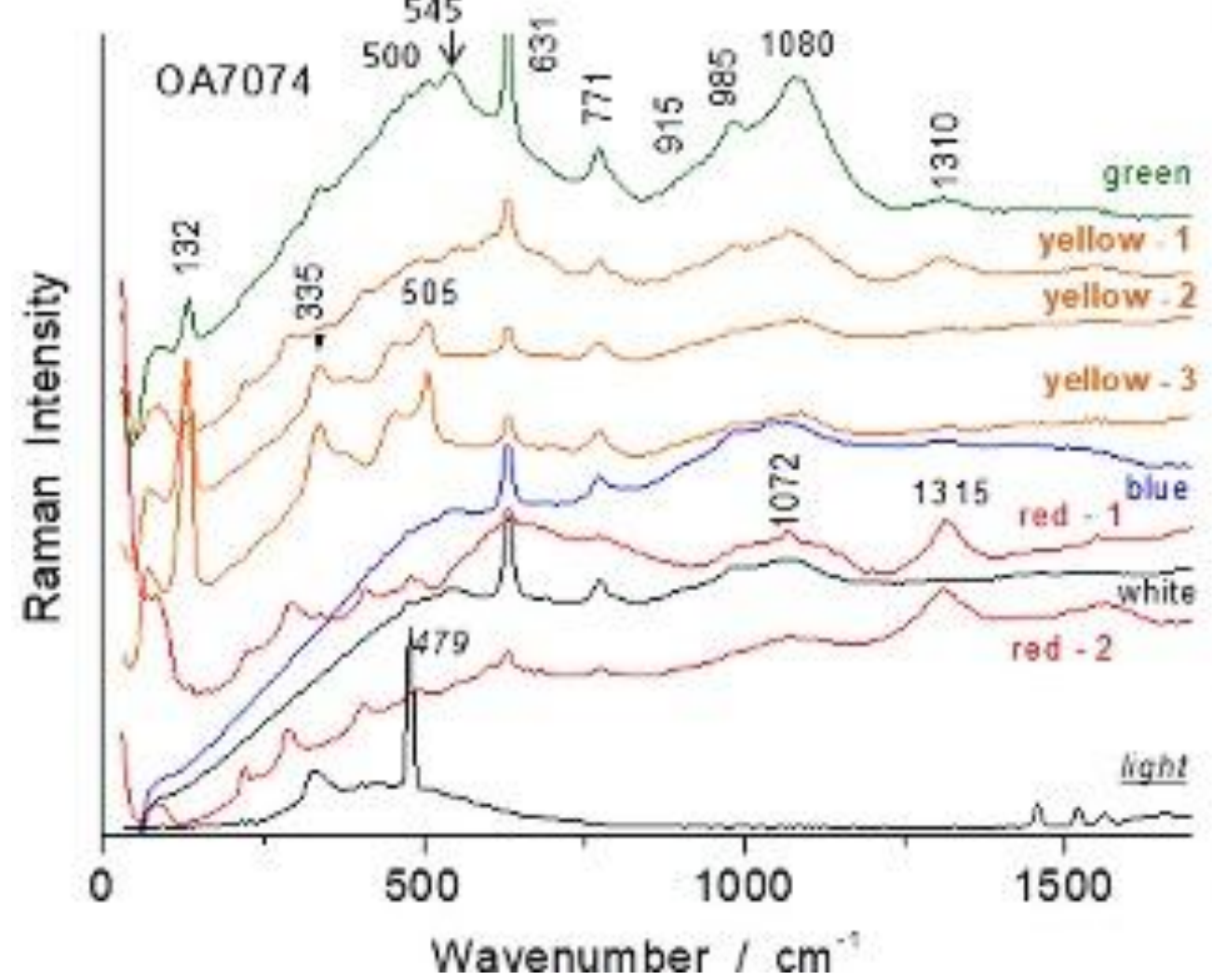
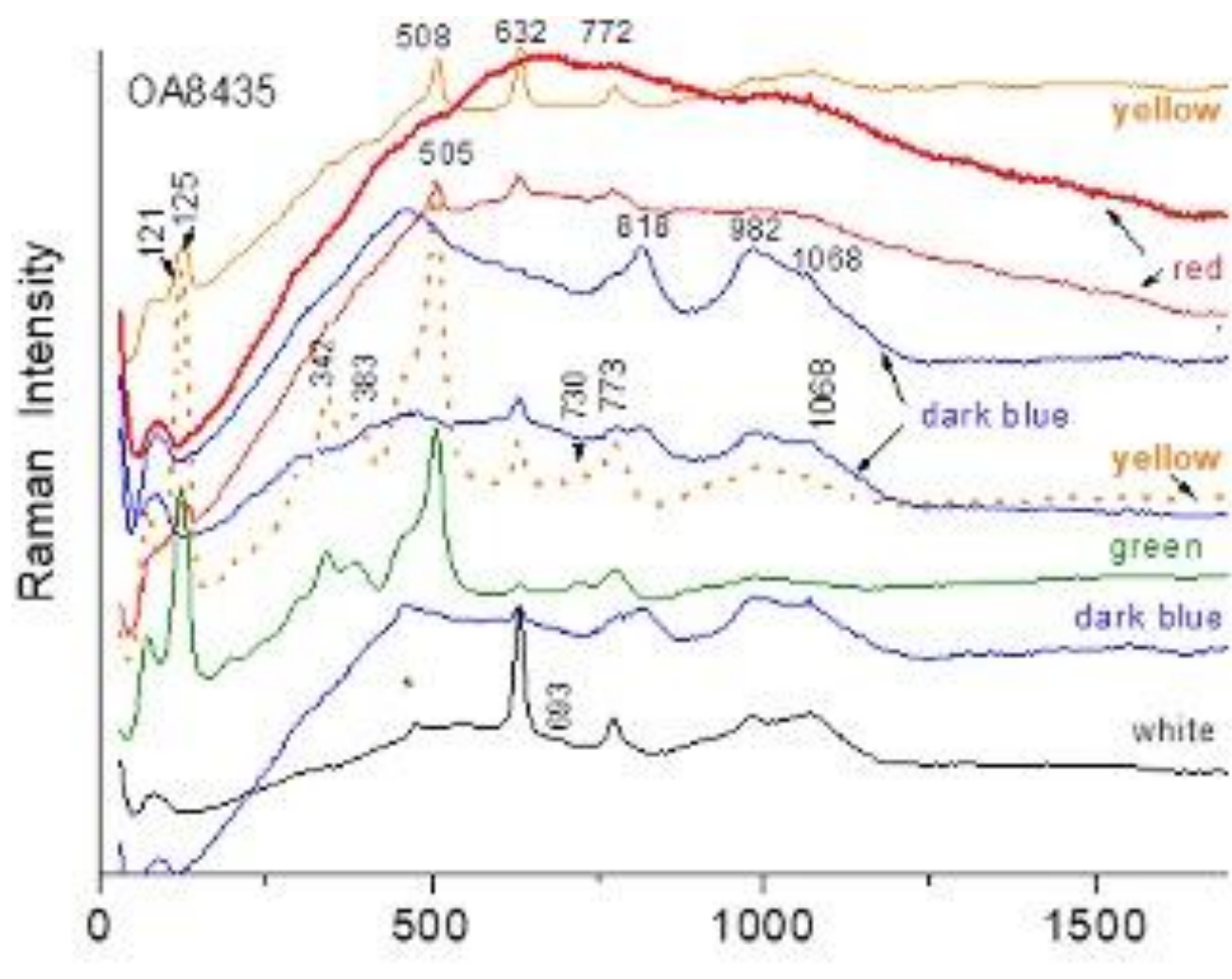
Representative pXRF spectra recorded on the metal substrate, green and red enamels of the OA8435 watch.



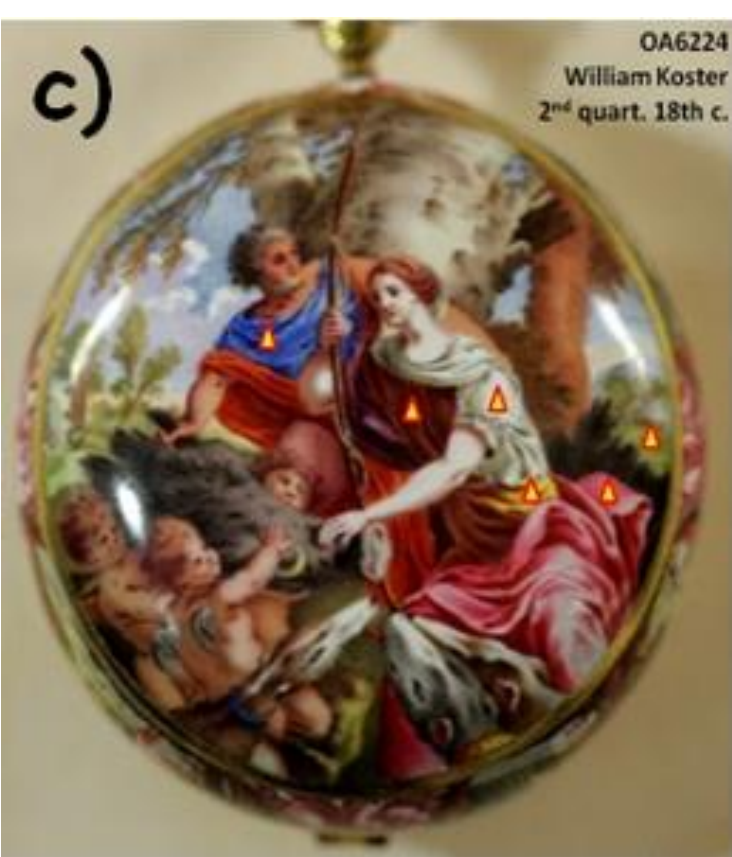
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Vision of St-Hubert Paris



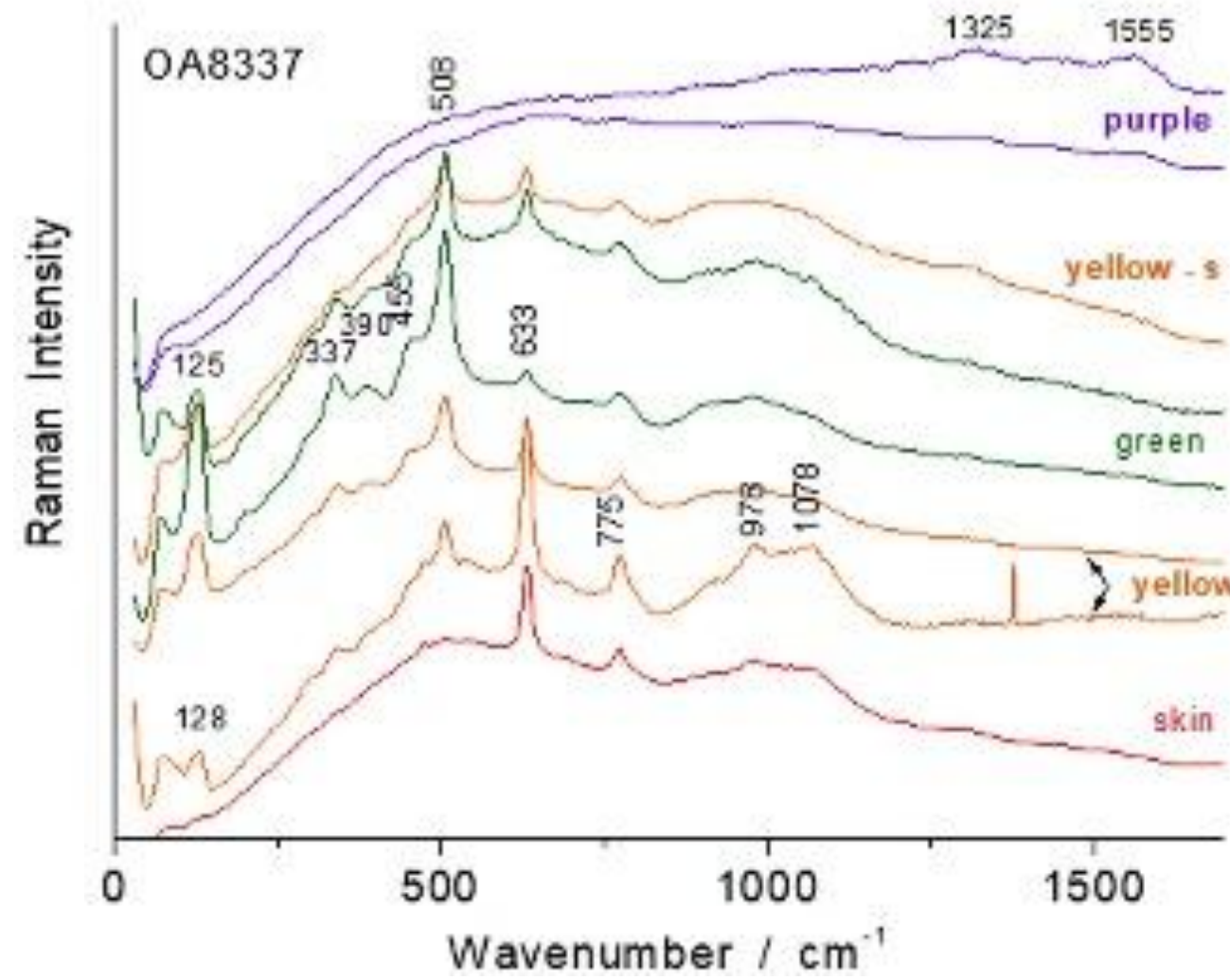
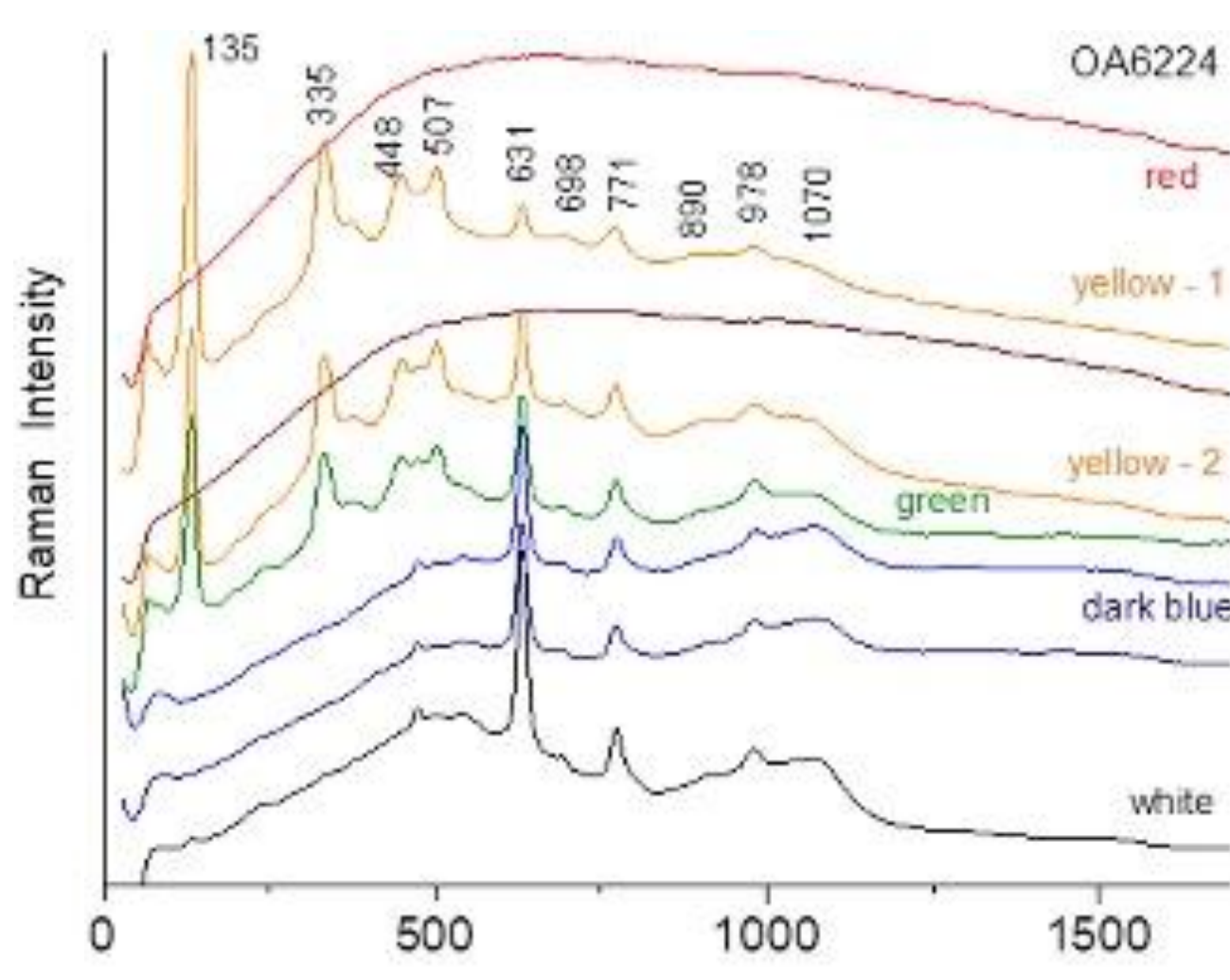
Representative Raman spectra of the watches OA8435 and OA7074



Meleager and Diane, Amsterdam (the Low Countries)



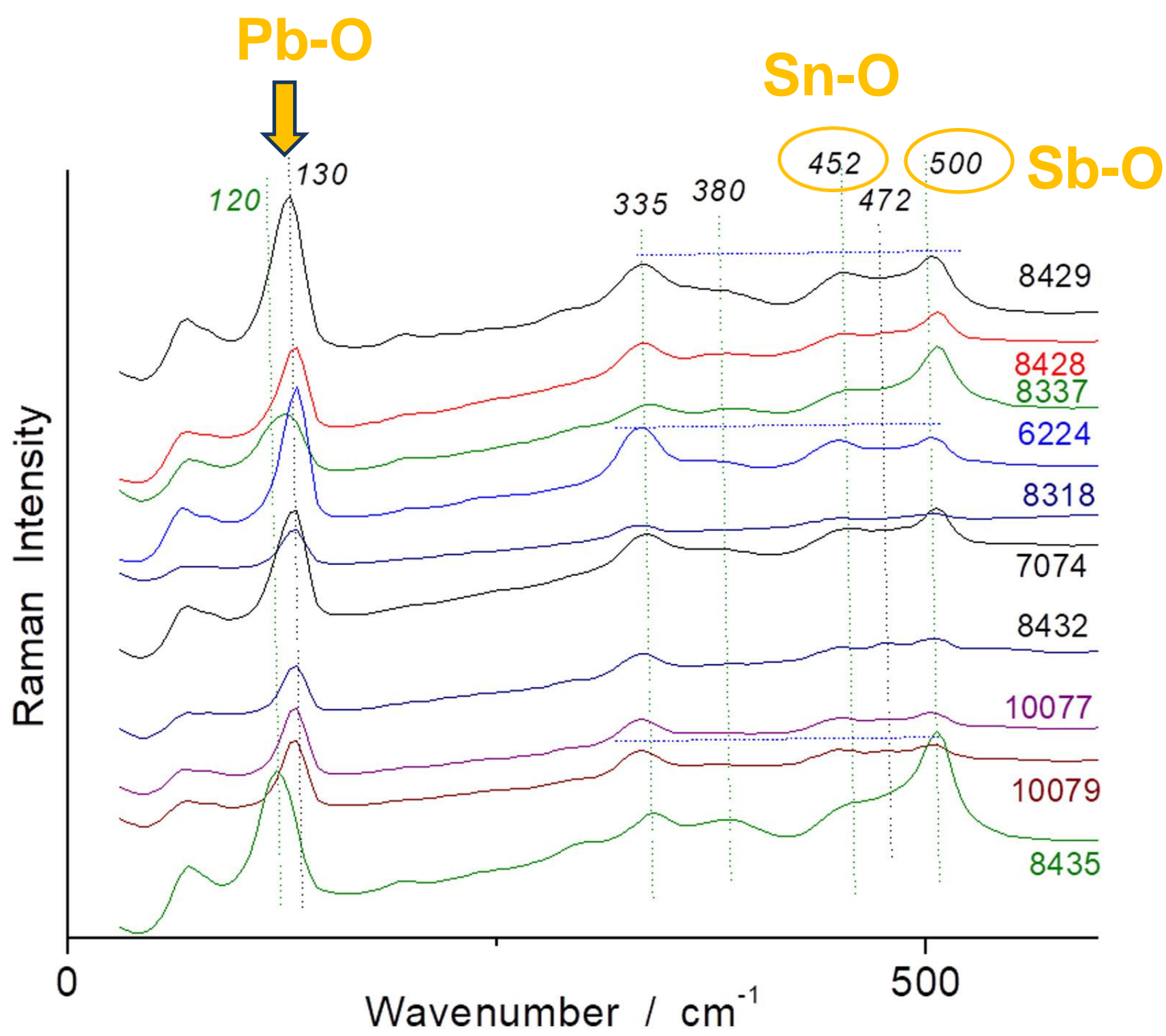
Hercules and Omphale, Paris



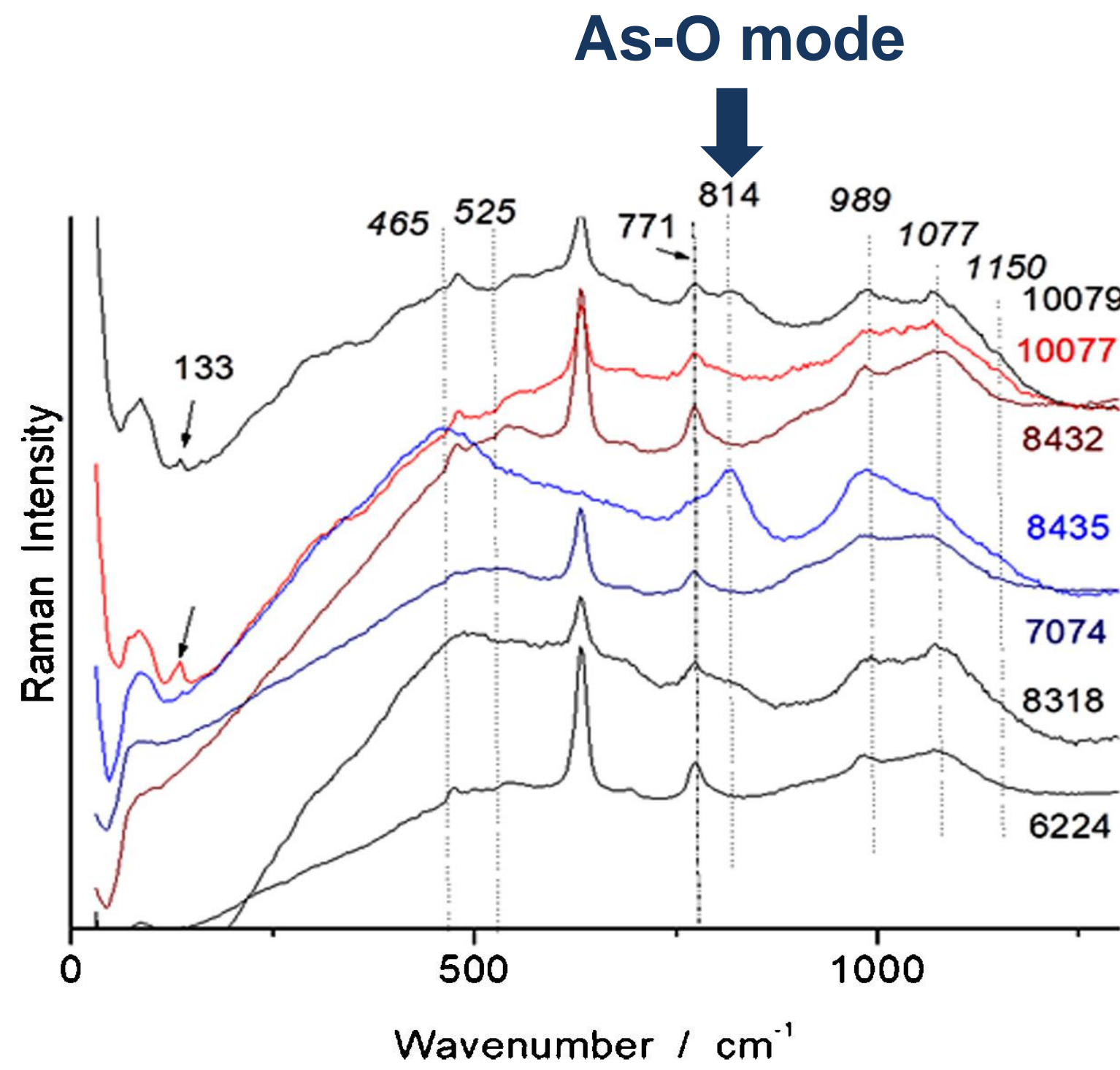
Representative Raman spectra of the watches OA6224 and OA8337

Results

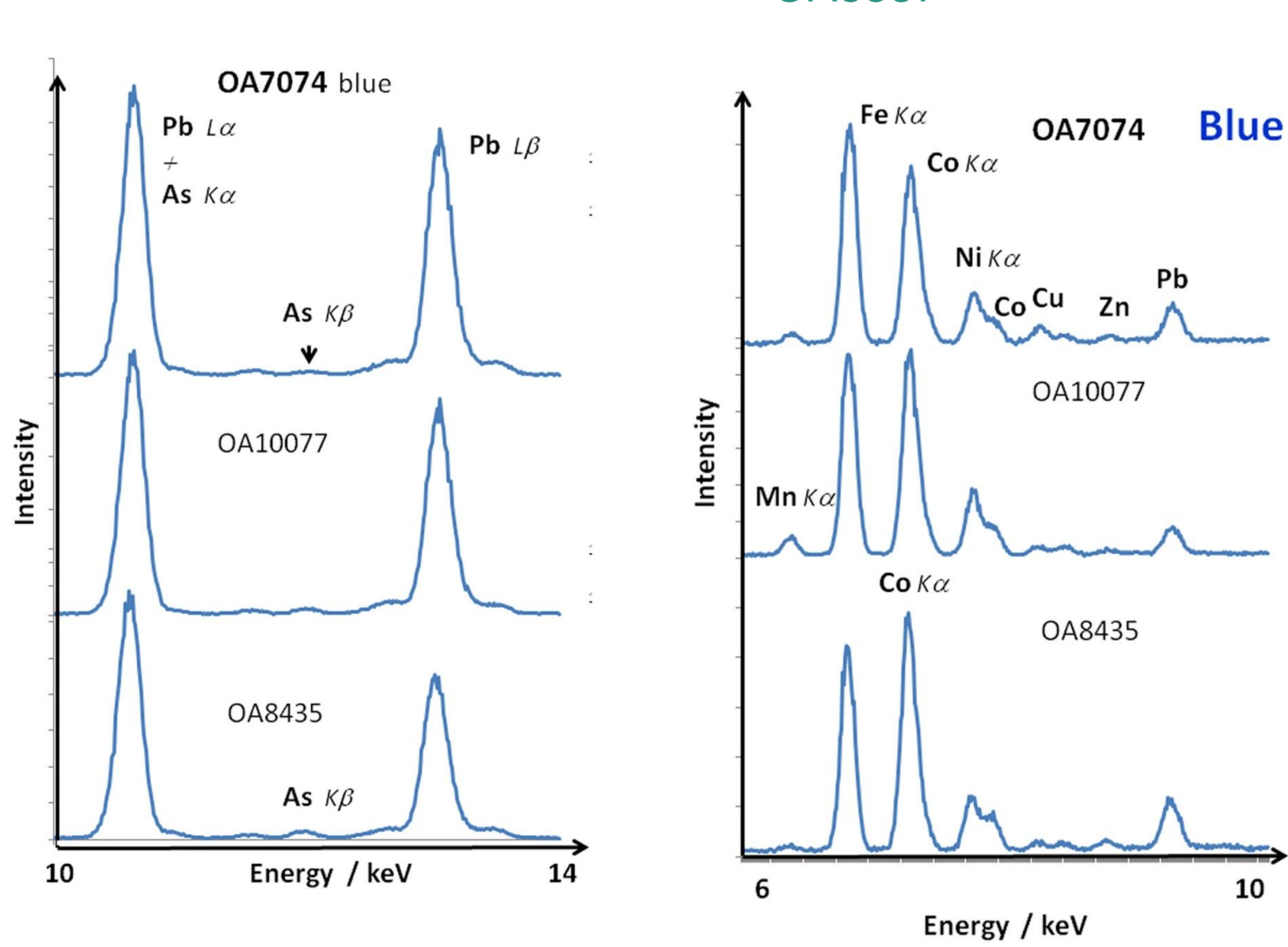
- The Metal Substrate
 - The body of the watches is made of a gold alloy with silver and copper.
- Glassy Si-O Matrix
 - Rather similar glassy matrices with Pb-rich silicate compositions were identified in the glassy matrix of the enamels: the Si-O stretching band between ~900-1200 cm^{-1} with ~980 and ~1080 cm^{-1} components.
- Pigments and Opacifiers
 - **Red:** Hematite (~218, 287, 1310 cm^{-1})
 - **Black:** Carbon (1335, 1555 cm^{-1}), Manganese oxide (580 cm^{-1})
 - **Yellow / Green:** Naples Yellow pyrochlore (~130, 335, 380, 450, 480 and 505 cm^{-1} components)
 - **White:** Cassiterite (631 & 775 cm^{-1})
 - **Red / Purple:** Gold nanoparticles (fluorescence at max ~600 cm^{-1})
 - **Complex colour (skin tone):** Lapis lazuli (~542, 1086 cm^{-1}), restored?



Comparison of Raman spectra recorded on the yellow-green areas of the different watches, showing the different pyrochlore pigment compositions (Pb-Sn, Pb-Sb and Pb-Sn-Sb-Zn)



Comparison of Raman spectra recorded on the blue areas of the different watches, showing the lead arsenate phase at 770-810 cm^{-1}



Representative pXRF spectra obtained on the blue areas of different watches, indicating the use of Co with the companion elements As, Fe, Mn, Ni, Zn.

Conclusion

This preliminary study about the 17th-18th century enamelled watches confirms the efficiency of the combination of Raman and XRF mobile set-ups to obtain technical information on enamelled objects such as the glass compositions, pigments, chromophores and opacifiers used.

The characteristic Raman signature of lead arsenate in the blue decors is related to the use of As-rich European cobalt ores. Different hues of the enamels were obtained by mixing various colouring agents, like in oil and tempera paintings rather than using pure pigments as in the case of Limoges enamels. The difference in the enamelling technology is evident with the classic technique of potters by superimposing touches of different colored enamels in the 17th century or the miniaturist' technique making small colored enamel dots mixing many pigments at the micron scale in the 18th century.

❖ Mrs. Véronique Schloupt from France Scientifique and Dr. Céline Paris are kindly acknowledged for their contribution to the study.

Painting the enamel by multilayering (17th century)



Painting the enamel by dots (18th century)

