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Abstract: This application note introduces pigment identification using micro-XRF and Raman microscopy on a Japanese flag “Hinomaru”, which is presumed to be the oldest and designed by an ancient Japanese Emperor Go-Daigo. The two spectroscopic analyses identified that the red pigment used on the flag matched the cinnabar ore (Mercury(II) sulfide) mined from the Mine near the place where the Emperor lived.

Keywords: Archaeology, Textile, pigment identification, micro-XRF, Raman microscopy.

Introduction

Identification of dyes and pigments used in archaeological specimens is significant to estimate their origins and the period when the works were produced^[1,2]. Micro-XRF and Raman microscopy provide us the elemental and chemical composition information of the dyes and pigments non-destructively^[3,4,5]. This application note introduces research on an old Japanese flag which is presumed to be oldest, using the XGT-9000 X-ray analytical microscope and the LabRAM HR Evolution Raman microscope.

Sample information

Figure 1 (a) shows an old national flag of Japan called “Hinomaru” analyzed in this application note. The flag size is 950 mm x 750 mm and a 300 mm diameter red circle is presented at the center of the flag. This flag is considered to be one of the oldest Hinomaru flag, which was expected

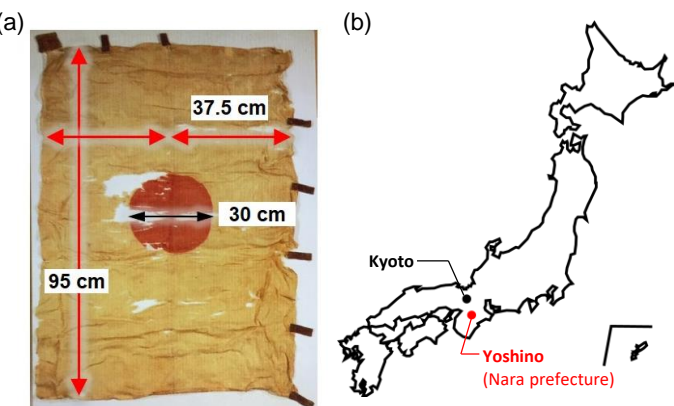


Figure 1. (a) The old national flag of Japan “Hinomaru” analyzed in this application note (b) Location of the Yoshino region.

to be designed by an ancient Japanese Emperor Go-Daigo (A.D.1288-1339). He had been in Kyoto as an emperor, but he moved to the Yoshino region of Nara prefecture due to his colleague’s betrayal, and remained there for the rest of his life (Figure 1(b)). The flag had been passed down for generations in a family in the region, who had served Emperor Go-Daigo^[6]. Now it is preserved in the Anou History and Folklore Museum in Nara prefecture, and was provided by the museum for this research.

Experiment

Two spectroscopic analyses were performed on a red-colored area of the flag to identify the pigment. Elemental analysis was conducted using the XGT-9000 (Figure 2(a)) with a 100 μ m ultra-high intensity probe and a tube voltage of 50kV. The measurement was done under a partial vacuum condition to protect the fragile sample without compromising the sensitivity of light elements such as sulfur. Chemical composition analysis was carried out using the LabRAM HR Evolution (Figure 2(b)) with 100x objective lens. 785 nm laser was selected to avoid fluorescence from the specimen. The laser power was set to 25 mW at the sample to reduce laser damage.

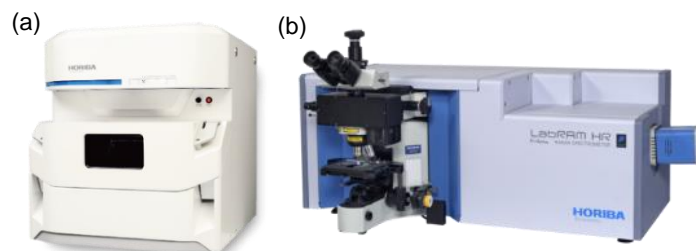


Figure 2. (a) XGT-9000 X-ray analytical microscope (b) LabRAM HR Evolution Raman microscope.

Result

XRF spectrum was acquired using the XGT-9000 to identify the elemental composition of the pigment used on red-colored area of the flag. Figure 3 shows clear peaks of mercury (Hg) and a peak of sulfur (S) on the red-colored area of the flag. It suggests that the red pigment consists of mercury sulfide.

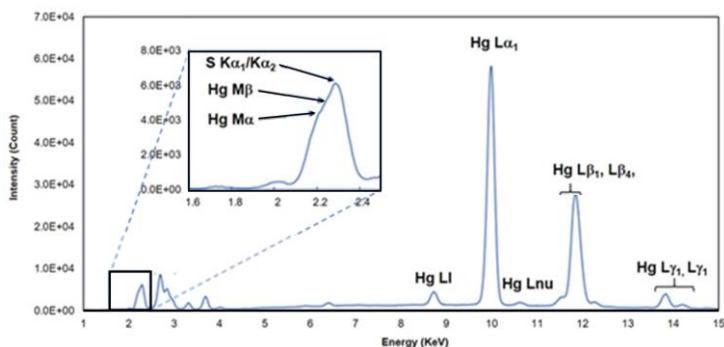


Figure 3. XRF spectrum of the red-colored area of the Hinomaru flag acquired with the XGT-9000.^[6]

Raman spectra were acquired using the LabRAM HR Evolution to identify the chemical structures of the red pigment identified as mercury sulfide by XGT-9000. Figure 4 shows the spectrum comparison between the red-colored pigment and a reference sample of a Japanese cinnabar ore (Mercury(II) sulfide) mined from the Yamato Mercury Mine near Yoshino region where Emperor Go-Daigo lived. This result shows the spectrum of the red pigment matches the cinnabar ore that came the Mine. It is consistent with the presumed origin of this Hinomaru flag.

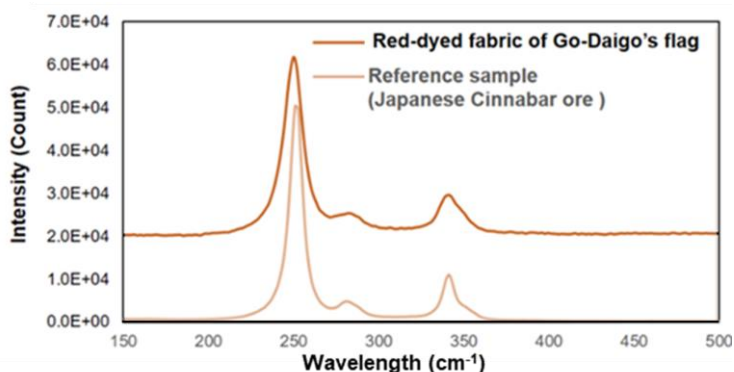


Figure 4. Raman spectra of the red pigment area of the Hinomaru flag and a reference cinnabar ore (Mercury (II) sulfide) acquired with the LabRAM HR Evolution.^[6]

Conclusion

The elemental analysis with the XGT-9000 and the chemical composition analysis with the LabRAM HR Evolution are complementary to each other. The two spectroscopic analyses identified that the red pigment used on the flag expected to be designed by an ancient Japanese Emperor Go-Daigo matched the cinnabar ore mined from the Mine near the place where the Emperor lived. The result could reveal a significant information to prove the presumed origin of the flag.

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Reference

- [1] X. Cheng et al., (2007) Three fabricated pigments (Han purple, indigo and emerald green) in ancient Chinese artifacts studied by Raman microscopy, energy-dispersive X-ray spectrometry and polarized light microscopy. *J. Raman Spectrosc.* 38, pp1274-1279.
- [2] N. M. Hamdan et al., (2012) Integration of μ -XRF, and μ -Raman techniques to study ancient Islamic manuscripts. *IOP Conf. Series: Materials Science and Engineering.* 37.
- [3] C. Boschetti et al., (2008) Raman characterization of painted mortar in Republican Roman mosaics. *J. Raman Spectrosc.* 39, pp1085-1090.
- [4] T. Li et al., (2017) A multi-analytical approach to investigate date-unknown paintings of Chinese Taoist priests. *Archaeol. Anthropol. Sci.* 9, pp395-404.
- [5] Z. Liu et al., (2019) Pigment identification on an undated Chinese painting by non-destructive analysis. *Vib. Spectrosc.* 101, pp28-33.
- [6] Takaya et al., (2019) The Root of "Hinomaru", the Japanese Emperor Go-Daigo's Flag of the Rising Sun. *In Proceedings of the International Council of Museums. 2019.*

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