

Analysis of Lacquerware Using In-air Submilli PIXE Camera

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Introduction

Because lacquerware, pottery, and hardware excavated from historical places provide information related to the culture of that period, many studies have been carried out to investigate their shape and coloration using visual inspection. Recently, scientific studies of the materials of which the archeological objects are composed using various analytical techniques make it necessary to know their provenance, process, and period. Such analyses should be non-destructive, sensitive, and multi-elemental. Particle-induced X-ray emission (PIXE) fulfills these requirements and is suitable for this purpose¹⁾. We developed an in-air submilli-PIXE camera which can measure spatial distribution images of element in the region of several square centimeters with submillimeter resolution. In a usual PIXE analysis, a beam spot size of a few millimeters is used. In this case, elements must be uniformly distributed in quantitative analysis. Therefore, samples are necessarily destroyed and prepared uniformly in quantitative analysis if elements are not distributed uniformly. The submilli-PIXE camera enables quantitative analysis without sample preparation. Furthermore, its high-speed beam scanning and in-air analysis enabled us to measure elemental images without degrading the feasible sample. We applied the submilli-PIXE camera to pigment analyses of lacquerware pieces excavated from the Edo-period stratum at the southern part of Kawauchi campus of Tohoku University. That area is located at the former secondary citadel area of Sendai's Aoba Castle. Elemental images of the decoration of lacquerware will be useful for elucidation of classical lacquer-working techniques.

Sample

The samples are lacquerware pieces excavated from the Edo-period stratum at the southern part Kawauchi campus of Tohoku University¹⁾. The campus is located at the former secondary citadel area of Sendai's Aoba Castle. The castle was constructed by Date Masamune (1567–1636), who governed the Tohoku district in northeastern Japan. The secondary citadel area was a residential area of his chief retainers. A large building was constructed there in the 17th century. The building was demolished and later reconstructed²⁾. The obtained samples were wooden bowls and trays decorated with lacquer resin; they were excavated from two areas with four different strata (early 17th century, late 17th century, late 18th century and early 19th century). Lacquerware pieces analyzed in this study had been colored with black lacquer resin and decorated with red lacquer resin. They were kept in water after excavation.

Analysis

Analysis was carried out using an in-air submilli-PIXE camera. Technical details are described in previous papers^{3,4)}. Submilli-beams are formed using two slits with 1.5 m spacing and are extracted to the air through an exit window of 12.5 μm Kapton foil. A sample was set immediately in front of the exit window. X-rays from a sample are detected using a Si(Li) detector set at 135 deg with respect to the beam axis. The samples were kept in water to prevent their destruction by drying of the wooden part. In a previous study, lacquerware was analyzed without deterioration⁴⁾. Therefore, prevention of drying during analysis is extremely important. Immediately after removing the sample from the water, the sample surface was wiped and analyzed. The Si(Li) detector with 80 cm^2 active area is used in this study to reduce the irradiation time. The samples were fixed directly to a target frame. Irradiation was carried out with 3 MeV proton beams: beam currents of 4–40 nA, total accumulated charges of 6–40 μC , with scanning area of $11 \times 14 \text{ mm}^2$. Polypropylene of 10 μm thickness and Mylar of 100 μm thickness were set in front of the detector to reduce spectrum deformation by recoil protons. Generally, lacquerware is decorated with several lacquer layers, each of which is several tens to several hundreds of micrometers' thickness. Because the range of the 3 MeV protons in the lacquer resin is estimated as 100 μm , proton beams are stopped in the layer. For that reason, the change in the X-ray production cross section and X-ray attenuation in the sample must be considered in quantitative analyses. Quantitative PIXE analyses considering these effects were performed using GeoPIXEII software⁵⁾. In the calculation, the major composition and density of the layer must be set.

The lacquer layer is presumed to be Urushiol ($C_{21}H_{32}O_2$) of 100 μm thickness, with a density of 1.25 g/cm^3 ⁶⁾.

Results

Typical elemental images and photographs for NM5W070, NM9W001, NM9W002, NM9W053, and NM9W059 are shown in Figs. 1–5. The numerical value in the color bar shows the maximum weight percentage of a selected element. Sample NM5W070 was excavated from the late-17th century stratum. In NM5W070 (Fig. 1), the mercury distribution corresponds to the decoration painted in red color. In contrast, iron and calcium show a similar distribution and correspond to the black lacquer. It is estimated that the red decoration was painted using pigment of cinnabar (HgS). Samples NM9W001 through NM9W059 were excavated from a different place where NM5W070 was excavated. Both NM9W001 (Fig. 2) and NM9W002 (Fig. 3) were excavated from the early-17th century stratum. In both samples, mercury is distributed in the red decoration, although the iron distribution does not correspond to the decoration. These samples are also decorated with cinnabar pigment. Iron might have adhered to the sample during its burial in the soil. Although calcium shows an inverse distribution to mercury in NM9W001, calcium is distributed uniformly throughout NM9W002. Because the mercury concentration in NM9W001 is almost 10 times higher than that of NM9W002, the red painted layer in NM9W002 is thinner than that of NM9W001, or a clear lacquer resin is painted on the surface. Samples NM9W053 (Fig. 4) to NM9W059 (Fig. 5) were excavated from the late-18th century stratum. Iron and calcium are distributed inversely in the samples. The iron distribution corresponds to the region painted in red. It is apparent that the red pigment contained red iron oxide: Bengala. In NM9W059, the lacquer resin had been partly peeled off. Because the calcium concentration is lower than that of the lacquer resin, calcium is inferred to be contained in the lacquer resin. Elemental analysis using images is effective to discriminate contaminant elements through comparison with the decoration. Elemental concentrations of red lacquer resin obtained from the images are depicted in Figs. 6–8 with those of other samples (NM9W172 and NM9W177), which are not shown in Figs. 1–5. Calcium and iron concentrations are low in the area painted in cinnabar, except in NM9W002. The iron concentration in NM9W002 is almost the same as that painted in Bengala. Because the mercury concentration of NM9W002 is lower than that painted in cinnabar, red pigment is estimated as a mixture of the pigments of cinnabar and Bengala. However, image analysis revealed that iron is merely a contaminant element. The calcium concentration of black

lacquer resin is shown in Fig. 9. Because the NM5W044 sample was decorated only in silver, the elemental concentration is not presented in Figs. 6–8. Elemental concentrations of NM9W001 and NM9W002 are lower than those of the other samples. Two methods were typically used to make black lacquer resin. Classically, black lacquer was made by mixing charcoal into the lacquer. Later, it was made by mixing iron with lacquer during the purification process. The present results might reflect the black lacquer resin production process.

Conclusions

Lacquerware pieces excavated from the Edo-period stratum at the southern part of Kawauchi campus of Tohoku University were analyzed using the submilli-PIXE camera at Tohoku University. Feasible lacquerware pieces were analyzed without sample degradation and without sample preparation. Pigments used in the lacquer resin were determined easily. This analytical method, which uses images, was effective to discriminate contaminant elements through comparison with the decoration. PIXE analysis using the in-air submilli-PIXE camera is an effective tool for use in archeological studies.

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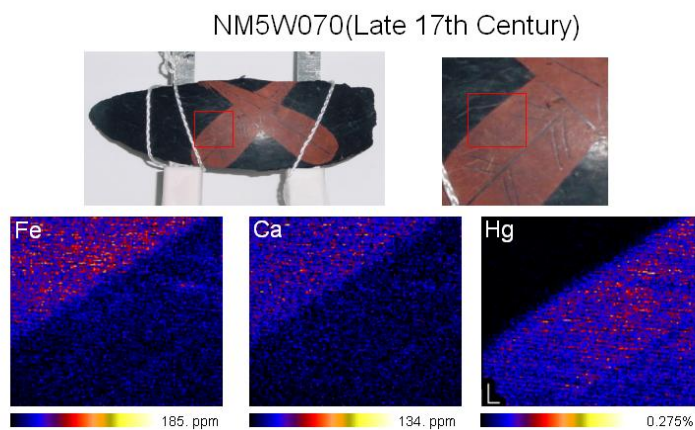


Figure 1. Elemental Images and Photographs for NM5W070 (Late 17th Century).

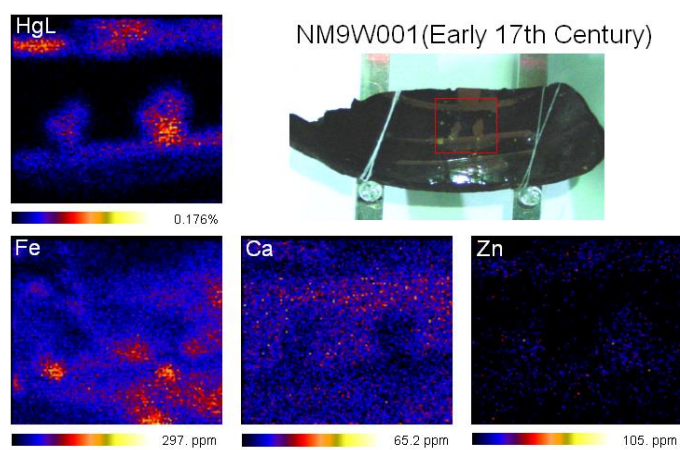


Figure 2. Elemental Images and Photographs for NM9W001 (Early 17th Century).

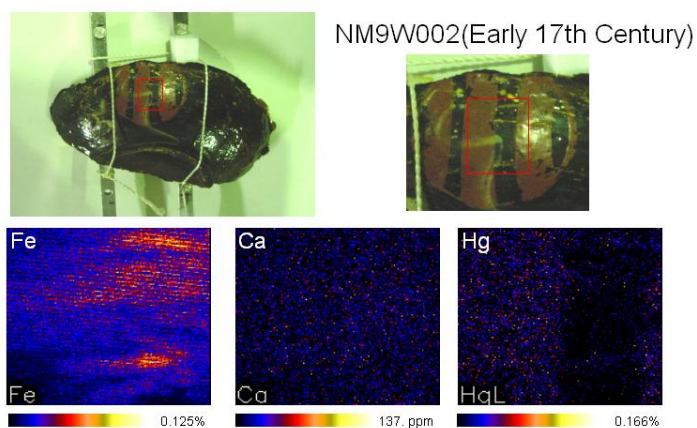


Figure 3. Elemental Images and Photographs for NM9W002 (Early 17th Century).

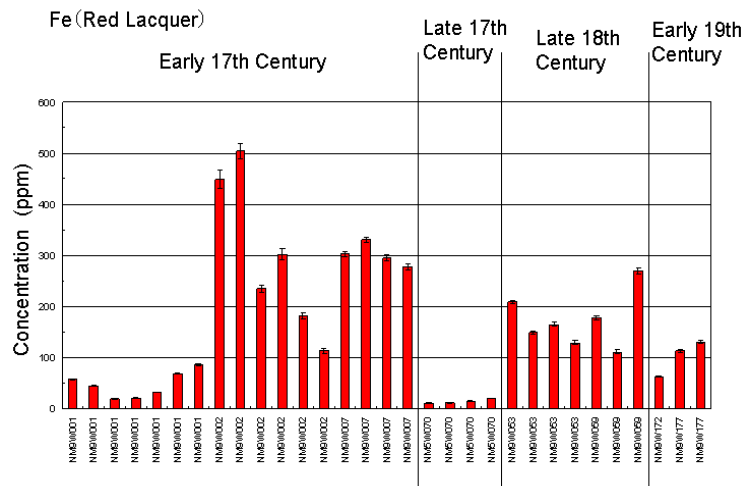


Figure 7. Elemental Concentrations of Red Lacquer Resin (Fe).

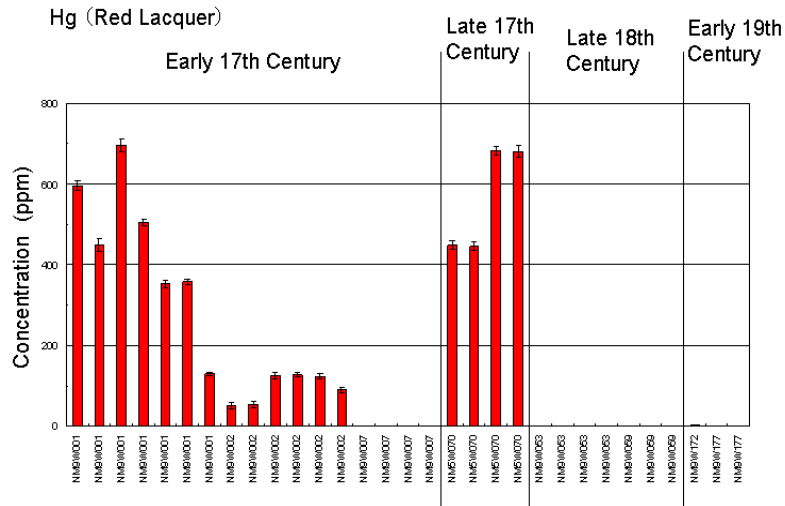


Figure 8. Elemental Concentrations of Red Lacquer Resin (Hg).

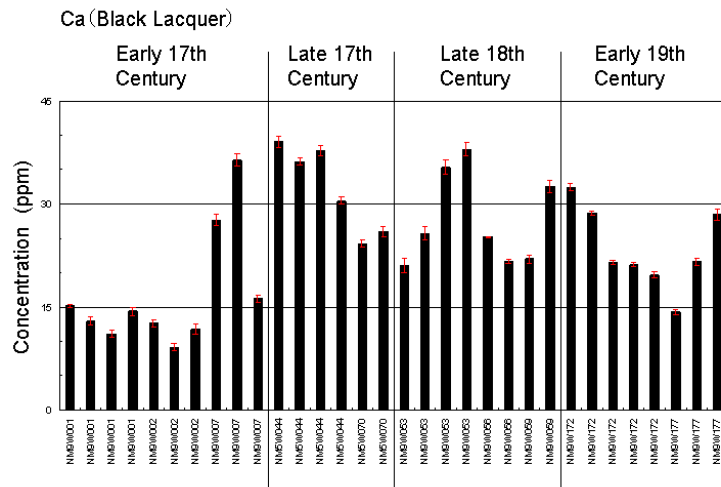


Figure 9. Elemental Concentrations of Black Lacquer Resin (Ca).