Results of Pigment Survey by X-Ray Fluorescence Analysis

HAYAKAWA Yasuhiro
National Research Institute for Cultural Properties, Tokyo

X-ray fluorescence analysis was conducted on 2 mm diameter area of this painting of Jūichimen Kannon centered on the points of the arrows seen on Plate 107. This analysis consisted of 100 second measurement per point at 50 kV x 0.1mA. While, this analytical method measures the kinds and contents of elements within the analyzed area, the chemical composition of the materials (pigments) cannot be determined solely by this method. Further, because the analysis covers a region that is several hundred μm or more in depth, the information on all pigments in the region are compounded when layered pigments or back-applied pigments are present. Thus these factors must be taken into consideration in pigment analysis by this method.

This report presents data on all 121 points investigated by X-ray fluorescence analysis. The aim of this investigation was to gather and publish the objective data obtained by this scientific method, and to share the information with as many researchers as possible. The scientific analysis of cultural properties is not carried out to determine the value of an object or the merits of its materials or techniques. Rather, scientific analysis allows everyone to work from publicly shared information and elicit the most information on the characteristics of that art work. However, extracting the characteristics of an art work is extremely difficult, and it must be added that eliciting such characteristics comes from the comparison of one work's data with that of a contrasting work.

The following is an overview of the findings of the pigment analysis conducted on this work by X-ray fluorescence analysis.

White Colors

Lead (Pb) was detected as the primary component of the many white areas found on the figure's body and body adornments. There are many lead-based white pigments known today, with the most commonly known lead white having a chemical formula of ($2PbCO_3 \cdot Pb(OH)_2$). This pigment has been long used in Japan and is found in Japanese paintings today. In terms of lead-based white pigments other than lead white, $PbCl_2$ and PbClOH have been discerned in Shôsôin objects, but reports of other examples of their use are rare.

Small amounts of mercury (Hg) were also discerned in several areas of white on this painting. It is possible that a pigment including mercury was also used in these areas. The most commonly used pigment with mercury as a primary component is red-colored mercury sulfide (HgS). The use of X-ray fluorescence analysis alone cannot determine whether this material was mixed into a white pigment or was painted on in layers.

Non-lead-based white pigments used from antiquity include such calcium-based whites as *gofun* (shell white, $CaCO_3$) and clay-based white (principle components $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$). There were several areas on this work that revealed large amounts of calcium, and it must be considered that *gofun* is present in those areas.

Red Colors

The majority of red areas investigated on the painting revealed large amounts of mercury (Hg). Of the mercury-based red pigments, mercury sulfide is the most commonly known, and numerous reports detail examples of it in paintings. The amount of mercury discerned in this painting increased with the darkness of the red area, and there are many instances of lead found in the lighter red areas. Thus it must be considered that mercury-based red pigments and lead-based white pigments were used together.

Other types of red pigments include iron-based *bengara* (red-ochre, Fe_2O_3), and lead-based *entan* (red lead, Pb_3O_4), but since their coloration and feel can be seen, visual observation can be used to identify their usage in a painting. In this image, there were no instances of large amounts of iron discerned in the red-colored areas, and thus it can be determined that *bengara* was not used on this painting.

Green Colors

There are many instances of copper (Cu) discerned in large amounts in the green areas seen in the *kun* garment, and crown. The most commonly known green pigment with a primary component of copper is *rokusho* ($CuCO_3 \cdot Cu(OH)_2$) made from malachite. The tonal range of green is achieved by changing the size of the mal-

achite granules, so the pigment can visually range from a light green to a dark green. Heated malachite that produces a burnt, almost black, green is also used as a pigment.

Because it is hard to detect light elements with X-ray fluorescence analysis, copper is the only element detected when *rokusho* is present. However, investigations by X-ray fluorescence analysis in recent years has found instances of either arsenic (As) or zinc (Zn), or cases of both additional elements, along with the copper discerned in green areas. This means that green-colored ores were produced near where the malachite was produced, and thus there must be a reconsideration of the existing judgment basis that green colored pigment is *rokusho*.

In the case of this image, zinc was found along with copper in several of the green areas measured. There were also many instances where green areas did not reveal zinc, and thus it is possible that two different types of green pigment were used on this image.

Blue Colors

As in the case of green areas, there were many instances where large amounts of copper were detected in blue areas. The best-known blue pigment with copper as its principle is *gunjô* ($2CuCO_3 \cdot Cu(OH)_2$), made from azurite.

Because X-ray fluorescence analysis can only detect the presence of copper, it is hard to determine whether the color involved is blue *gunjô* or green *rokusho*. Like *rokusho*, the color produced by *gunjô* changes depending on the granule size, and the tones can be further affected by heating the mineral. There are an extremely large number of instances where visual inspection has led researchers to determine that a blue color is *gunjô*. However, recent investigations indicate that there are a number of works where small amounts of zinc were found with copper in blue areas, as were also found in green pigment areas, and thus, careful consideration must be applied to the determination of blue color pigments.

This work reveals two types of blue pigments, one with zinc and one without zinc. Further, there was almost no copper found in the dark blue sections of the jewels and flowers. It must be considered that non-mineral materials, such as organic dyestuffs, were used in these areas.

Gold and Silver Colors

Gold and silver leaf and dust are used to make gold and silver colors. *Kirikane* cut leaf technique is one of the extremely well known uses of metallic leaf, and considerable usage of this technique can be confirmed in the design motifs on this painting's halo and *kun* garment. Changes in the purity of the gold and silver leaf used and layering effects can be used to subtly alter color and mood effects. The thinnest form of gold leaf in general is approximately 0.1 μm, while the thinnest silver is approximately 0.3 μm in thickness.

Gold dust and silver dust are frequently used as painting materials. The color effects of these materials can be modulated by changes in the size of the particles and the amount in the mixture.

Trace amounts of gold (Au) and silver (Ag) can be detected by X-ray fluorescence analysis, but the results do not give a clear indication of whether the element is in leaf or dust format. The thinnest possible thickness of silver and gold leaf can be analyzed by this method. Further, the purity of gold and silver can be determined if there are impure elements present up to 1%.

Black Colors

Sumi, or carbon ink, is the most commonly known black color material. The principle component of *sumi* is carbon (C) and this element is hard to discern in X-ray fluorescence analysis. Other known black materials include iron oxide (Fe_3O_4), but there are few reported usages of this material.

Small amounts of calcium and iron were detected in the black and gray areas on this painting. These materials are thought to originate from either the silk support itself or the ground areas, and thus it is thought that only *sumi* was used as a black color material on this work.

Purple and Brown Colors

Purple is one of the colors in the traditional striped *ungen* coloring technique. The characteristics of the purple color found in these *ungen* areas remain one of the most fraught issues in painting research. There are almost no non-organic pigments that create a purple color, and this means there are many instances where extant colors are explained as either organic dyestuffs or as darkening or changed colors created by organic dyestuffs.

Purple can be identified in the hanging decorations seen in this painting. Lead (Pb), and trace amounts of copper (Cu) and iron (Fe) are the elements detected in these areas by X-ray fluorescence analysis. These areas have lead-based white pigments such as lead white and hence the presence of lead in these areas is attributed to the white pigments. Given the colors generated by the use of copper and iron materials, it is possible that a blue with primary component copper, such as *gunjô*, is present in this area. While the presence of organic dyestuffs must

be thoroughly considered, their presence and the identification of the materals are difficult to prove with X-ray fluorescence analysis.

Areas of light brown to darker brown can be seen on this painting, and it is quite difficult to determine the specific pigments used. In general, these colors are created by *taisha* (red ochre) or *ôdo* (yellow ochre), but there are also many instances in which a pigment with an iron oxide (Fe_2O_3) coloring agent is used. These earthen-based pigments are generally quite small in grain size and hence, their color surfaces do not have the grainy feel found in such pigments as *rokusho* malachite, *gunjô* azurite, and *shinsha* cinnabar.

Medium brown to dark medium brown colors can be discerned in the hair, head nimbus and canopy areas of this painting. X-ray fluorescence analysis detected copper, zinc, calcium and iron in the hair, while copper, calcium and iron can be discerned in the head nimbus and canopy. Judging from the fact that zinc is included in the hair area, blue or green colored pigments can be considered to be used in these areas. Only trace amounts of copper were detected in the head nimbus and canopy, and it cannot be determined whether the source of that copper was a copper-based color such as blue or green, or an earthen-based pigment. If it is a copper based pigment, then originally the color tone would have been a greenish color or a bluish color, rather than the present-day brown color.

(translated by Martha J. McClintock)