ANALYSIS OF PIGMENTS USED IN A JAPANESE PAINTING

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ABSTRACT

Materials used in a Japanese painting were analyzed directly and nondestructively by X-ray fluorescence spectrometry and X-ray radiography. A pair of six-panel folding screens entitled The Irises Screens by Ogata Korin, a National Treasure of Japan, was examined. A scientific approach had never been incorporated into its investigation, and its materials and techniques had remained unknown. It had been previously believed that this folding screen used only two types of coloring materials, blue-colored azurite and green-colored malachite, but this investigation revealed that three types of materials were used for each color.

INTRODUCTION

Recent years have seen an increasing number of cases where a variety of analysis methods have been introduced to investigate the materials and coloring techniques of works of art, such as paintings and sculptures. In some cases, chemical analysis is performed on object fragments and paints peeling. In Japan, however, “nondestructive, no-contact analysis” is almost always the chosen technique for the protection of invaluable works. This “nondestructive, no-contact” restriction narrows down the number of investigative options available, leaving researchers to resort to methods which utilize radioactive and infrared rays. Among the X-ray-based analysis methods most widely used in the investigation of artwork are X-ray fluorescence spectrometry (XRF) and X-ray radiography [1–3]. Compact portable devices featuring each of these two techniques have been developed since the 1990s, making it possible to carry out on-site investigation within a museum, without actually having to move the objects themselves [4–7].

This report describes the findings of an investigation into the materials used in the Irises screens (National Treasure of Japan) by Ogata Korin (1658–1716), which is among the most well-known paintings in Japan. A scientific approach had never been incorporated into its investigation, and its materials and techniques had remained unknown. For the purposes of this investigation, a high-definition digital camera was used to take photographs of the painting’s surface for close observation, and an attempt was made to identify its materials by utilizing such techniques as XRF and X-ray radiography.

THE IRISES SCREENS

A property of the Nezu Institute of Fine Art, Tokyo, Japan, the Irises screens (Figure 1) is a pair of six-panel folding screens measuring 150.9 × 338.8 cm each created by Ogata Korin, and is one of the artist’s most important works. With its superb composition and décor being highly appreciated—portraying a cluster of irises with blue petals and green leaves against a gold background—this is also one of the representative paintings of Japanese art.
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During its restoration between 2003 and 2004, the materials used for the *Iris* screens were examined. It had been previously believed that this folding screen used only two types of coloring materials, namely, azurite [blue pigment, $2\text{CuCO}_3\cdot\text{Cu(OH)}_2$] and malachite [green pigment, $\text{CuCO}_3\cdot\text{Cu(OH)}_2$], but this investigation revealed that three types of materials were used for each color.

![Image of the *Iris* screens by Ogata Korin, a National Treasure of Japan.](image1.png)

**Figure 1.** The *Iris* screens by Ogata Korin, a National Treasure of Japan.

**METHODOLOGY**

*X-ray fluorescence spectrometry*

A portable XRF spectrometer (SEA200, Seiko Instruments Inc.) was brought into the museum for the investigation (Figure 2). Weighing 5 kg, the X-ray spectrometer and power supply unit are connected by a 10 m long high-voltage power supply cable. X-rays are generated through an X-ray tube (Rh target), and the spectrometer’s tube voltage and tube current can be set at up to 50 kV and 100 $\mu$A, respectively. For detection, a Si-PIN X-ray detector was used. A CCD camera installed at the tip of the spectrometer records visual images of the points where X-rays are radiated. Using X-ray beams whose diameter had been narrowed down to 2 mm, the measurements were taken at 46 points throughout the two screens (100 seconds per point).

![Analysis inside the museum with a portable XRF spectrometer.](image2.png)

**Figure 2.** Analysis inside the museum with a portable XRF spectrometer.

*X-ray radiography*

An X-ray generator and apparatus was brought into the museum. Under irradiation conditions of 30 kV $\times$ 3 mA, films or imaging plates were employed for image recording. A total of 96 films were used to take X-ray radiography of the screen in its entirety, and imaging plates, which achieve much higher resolution than film-based X-ray radiography, were used to examine each part. Exposure time was 6 min for the films and 4 min for the imaging plates.
RESULTS AND DISCUSSION

Blue portions of petals

Observation with the naked eye reveals that the blue petals can be divided into three sections: blue coarse-grained sections (deep blue, B1), blue fine-grained sections (light blue, B2), and deep blue contour lines (B3). X-ray radiographs also confirmed the existence of the three types of blue. Figure 3 shows a color and imaging-plate-based radiograph of the upper section of the first panel on the right screen. Table I shows the XRF findings for these three types of blue portions.

Blue course-grained portions: the blue coarse pigments (B1) were used to depict the exterior of the petals, looking white (slightly radiopaque) on the radiograph in Figure 3. The only element detected by XRF in this portion was Cu. Its detection intensity was as high as between 940 and 1190 cps, and was fairly constant with little dispersion from one section to another. Since azurite is a blue pigment whose main component is Cu, this finding supports the conventional presumption of the use of azurite.

Blue fine-grained portions: the blue fine pigments (B2) were used to depict the reverse side of the petals, looking dark (slightly radiotransparent) on the radiograph in Figure 3. XRF detected Cu and a small quantity of Ca. Although it did not vary from one section to another, Cu’s detection intensity ranged between 490 and 740 cps—about two-thirds of that for the blue coarse-grained portions described above. It is believed that the detected Cu was derived from the main component of azurite, but it is highly likely that a material whose grain size differs from that of azurite used to depict the blue coarse-grained portions was used. It is also highly possible that Ca existed as a component of a white pigment, such as powdered calcium carbonate (CaCO3).
Table I. XRF results for blue petals and green leaves.

<table>
<thead>
<tr>
<th>Points measured</th>
<th>Number of points measured</th>
<th>X-ray intensity (cps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue petals</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(B1) Course grain</td>
<td>4</td>
<td>940 to 1190</td>
</tr>
<tr>
<td>(B2) Fine grain</td>
<td>5</td>
<td>490 to 740, 4 to 12</td>
</tr>
<tr>
<td>(B3) Contour lines</td>
<td>5</td>
<td>590 to 1030, 2 to 7</td>
</tr>
<tr>
<td>Green leaves</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(G1) Course grain</td>
<td>6</td>
<td>510 to 1080, 2 to 3</td>
</tr>
<tr>
<td>(G2) Fine grain</td>
<td>4</td>
<td>780 to 1330</td>
</tr>
<tr>
<td>(G3) Under-layer</td>
<td>3</td>
<td>500 to 840, 2 to 3</td>
</tr>
</tbody>
</table>

Dark blue contour lines: as with the blue fine-grained portions, the dark blue contour lines (B3) which border the petals appear rather dark (slightly radiotransparent) in the radiograph in Figure 3. XRF detected Cu and a small quantity of Ca. Although the same kinds of elements as those detected in the blue fine-grained portions were found, the detection intensity of Cu was characteristically large, ranging between 590 and 1030 cps. The Cu detection intensity was comparable to that of the blue coarse-grained portions, but differed between the left and right screens, favoring the right.

Green portions of leaves

Apparently, three different materials were used for the green portions of the leaves: coarse-grained materials (dark green, G1), fine-grained materials (light green, G2), and light-green materials that are visible at places where those materials peeled off (G3). The difference amongst them manifests itself in the radiograph (Figure 3) as well. Table I shows the XRF findings from these three types of sections.

Green course-grained portions: the green coarse-grained sections (G1) appear white (slightly radiopaque) in the radiograph in Figure 3. This is because a thick layer of coarse grains exists. XRF detected a large quantity of Cu, as well as small quantities of Zn, As, and Ca. The detection intensity of Cu varied considerably between 510 and 1080 cps from place to place, but the detection intensity of As was found to range between approximately 1/10 and 1/20 of Cu, and the Cu/As ratio was almost constant. Among green pigments, malachite [CuCO$_3$·Cu(OH)$_2$] is known to have Cu as its main component, but little is known about green materials that contain Zn and As as well.

In another of the author’s research projects to examine the materials of approximately 200 pigment samples that existed in Japan in the early 19th century [8], all samples were prepared in a fine powder using a mortar for XRF and XRD analysis. XRF found green pigments that contain, along with Cu, a small quantity of Zn and As (Figure 4), which were subsequently identified by X-ray diffraction analysis as Adamite [(Zn,Cu)$_2$(AsO$_4$)(OH)] or Philipsburgite [(Cu,Zn)$_6$(AsO$_4$,PO$_4$)$_2$(OH)$_6$] (Figure 5). Originating in copper and zinc deposits, these minerals are known to be produced near areas where malachite is mined.
Green fine-grained portions: because they are painted thinly with fine grains, the green fine-grained portions (G2) look dark (slightly radiotransparent) in the radiograph in Figure 3. The only element that was detected by XRF was Cu, whose intensity differed between both screens: around 780 cps on the right screen and 1330 cps or over on the left screen. Since malachite is a green pigment whose main component is Cu, this finding supports the conventional presumption of the use of malachite.

Light-green portions: observed where either green coarse grains or fine grains peeled off, light-green portions (G3) let the X-rays pass through, preventing their existence from being clearly confirmed on the radiograph in Figure 3. XRF detected Cu only at some sections, but detected Cu and small quantities of As and Ca at others. No Zn was detected from the light-green portions, however. From this, it may be presumed that Zn is contained only in the green coarse-grain portions and not in the light-green portions which lie underneath.

Gold background

On the gold background there are straight lines that are aligned regularly both lengthwise and crosswise. Also at other locations are many irregularly-curved lines. Most of these irregularly-curved lines are aligned in a longitudinal direction at almost regular intervals. These lines are believed to be created by the overlapping of neighboring gold leaves. On a radiograph, both the straight lines regularly aligned in a matrix and the irregularly-curved lines in a longitudinal direction were barely visible. XRF detected a small quantity of Au, along with Ca and Cu (Figure 6). Au’s detection intensity was quite low. In fact, the intensity at many points was lower than the Au intensity of a 0.1 μm-thick gold leaf, the thinnest leaf that can be obtained currently. Au’s intensity showed little difference between the gold background and the matrix-like straight lines.
The small amount of Cu that was detected from the gold background could be presumed to be an impurity contained in a gold leaf; however, detailed observations of enlarged images of each section taken with a high-definition digital camera subsequently confirmed that tiny green grains are scattered among the gold background, and that these green grains were responsible for the detection of Cu. It is assumed that a small fraction of any of the aforementioned green pigments might have lost its adhesive force when the panels were folded, sticking at various places onto the gold background. It was, however, difficult to determine if Zn and Ca were also contained, since Cu’s detection intensity was far too small. It goes without saying that the possibility of blue grains having been dispersed should not be denied, but most of the grains confirmed on color images were green.

CONCLUSION

The materials used for Ogata Korin’s *Iris* screens were examined by X-ray fluorescence spectrometry and X-ray radiography. In X-ray-based investigations, it is difficult to obtain detailed data on coloring materials, which are mainly composed of light elements and organic substances, and thus not all of the coloring materials may be identified with the data produced by this research alone. This being said, that data on pigments and other inorganic compounds have been collected in and of itself marks major progress in research on the coloring materials and techniques used in these screens, and as such should contribute to further advancement of the study of Japan’s art history.

REFERENCES