Rigaku

Application Note XRD 5005

Qualitative analysis of a trace amount of pigments used in Japanese painting

Application

Cultural properties

Instrument

Curved Imaging Plate (IP) X-ray diffraction system combined with Confocal Max-Flux (CMF) optics
D/MAX RAPID II-CMF

Keywords

Pigment
Micro-sample
Qualitative analysis
Coarse particle

Introduction

Japanese paintings consist of pigments and dyes laid down on substrates such as Japanese paper and silk. Deterioration of substrates and the fading and discoloration of pigments occur over time. For renovation and preservation of cultural properties, it is important to understand the deterioration of paintings scientifically.

In this report, qualitative analyses of five small pieces (named “Uchi-gi”, “Matsu”, “Nami”, “Kimono”, and “Hakama” in Figure 1) of deteriorated Japanese paintings were performed to identify the pigments remaining on the substrate.

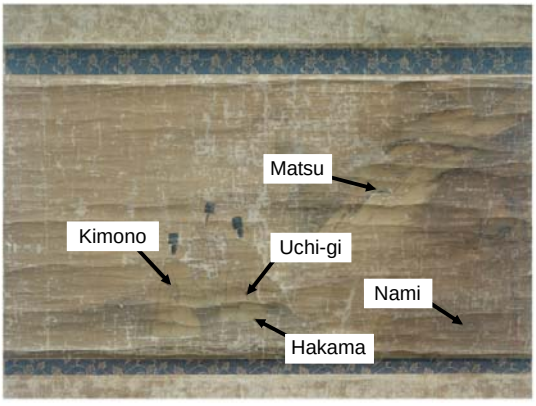


Figure 1. Overall view of Japanese painting used for measurement

Materials

One of five small pieces of Japanese painting in Figure 1, “Uchi-gi”, was used for qualitative analysis (upper figure of Figure 2). There were two different colored parts, red and white, on the “Uchi-gi” sample. Direct observation with CCD camera showed a latticed pattern of the bare silk support of which pigments were peeled off from the surface. Then it revealed that extremely small amount of pigments was remained on the substrate (lower figure of Figure 2).

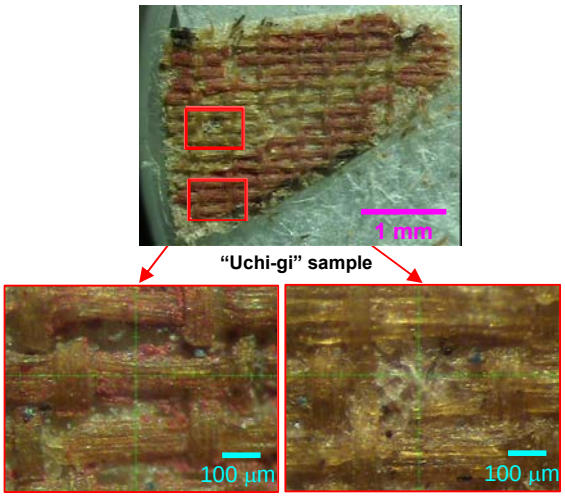


Figure 2. “Uchi-gi” sample of Japanese painting (Upper) and enlarged view of measurement area (Lower)

Instrument

The D/MAX RAPID II-CMF is an X-ray diffractometer with a large curved imaging plate detector. As shown in Figure 3, this system is equipped with a microfocus rotating anode X-ray generator (MicroMax-007) which provides high intensity for micro-area analyses, and side-by-side laterally graded multilayer optics (confocal mirrors: CMF) to focus the beam. Featuring a high-intensity incident X-ray source and large-area two-dimensional detector, the D/MAX RAPID II-CMF can significantly reduce exposure time for micro-area X-ray diffractometry of regions as small as several tens of micrometers and of small amount of samples as well. By integrating the intensity over a wide area along the Debye ring, this system can provide the X-ray intensity needed to identify substances, even with low diffracted X-ray intensity or coarse crystal grains. Therefore, the D/MAX RAPID II-CMF is the best instrument for measurement of a sample which contains a trace amount of target compound having coarsened crystal grain, such as the pigment remaining on the Japanese painting presented in this report.

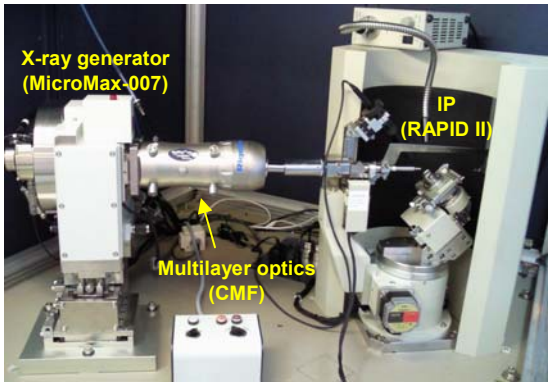
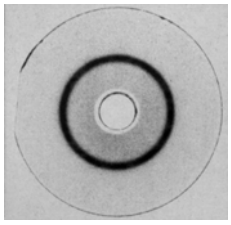


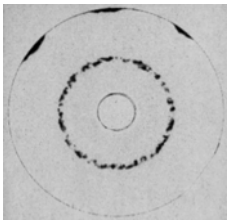
Figure 3. D/MAX RAPID II-CMF dedicated micro-area X-ray diffractometer with curved imaging plate detector.

Methods (Measurement)

For precise evaluation of the diffraction angle and X-ray intensity in the powder X-ray diffraction method, it is necessary to use a powder sample containing an unlimited number of crystallites whose crystal grain size is sufficiently small and the crystal orientations are random. A sample having small grain size shows ring-shaped patterns called Debye rings (Figure 4 (a)), because the number of crystals contributing to the X-ray diffraction in any direction is increased [2]. On the other hand, the Debye ring from a coarse-grained sample is seen to be spotty, which means a few crystals contributed to diffraction (Figure 4 (b)). Therefore, diffraction patterns are not observed when samples having coarse crystal grains are used, depending on their orientation to the X-ray beam. Using D/MAX RAPIDII-CMF, the number of crystals contributing to diffraction is increased by oscillating the sample in an in-plane direction and a wide area is measured simultaneously due to the two-dimensional IP detector having such a large active area.



(a) Fine powder sample with grain size less than 10 μm.



(b) Coarse powder sample with grain size less than 200 μm.

Figure 4. Two-dimensional images of powder sample with different grain sizes [2]

Results

Figure 5 shows the two-dimensional diffraction images of red and white parts of the “Uchi-gi” sample, which was obtained with exposures of 1 minute. These spotty diffraction images indicated that the sample contains coarse crystal grains. Pigment grain growth that was dotted on the surface can also be visually confirmed from the optical microscope photographs shown in Figure 2.

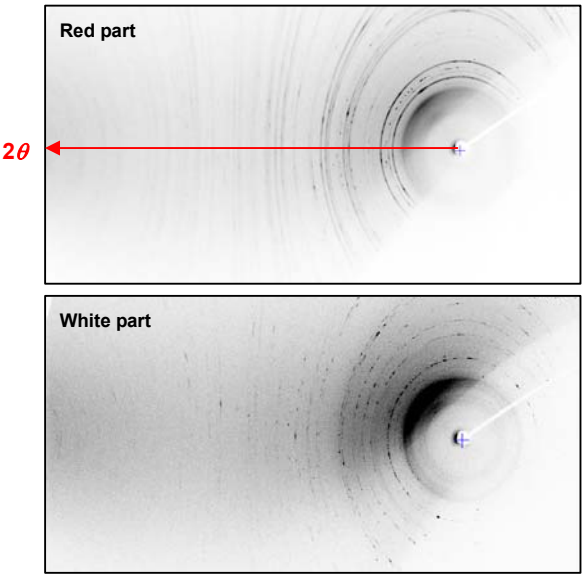


Figure 5. Two-dimensional diffraction image of “Uchi-gi” sample

Methods (Analysis)

Crystal phases can be identified by comparing the diffraction angle and absolute intensity of the obtained diffraction pattern with the large number of patterns included in the databases (qualitative analysis). With X-ray diffraction method, it is also possible to distinguish compounds which have the same chemical formula but different crystal packing (polymorphism) thanks to different diffraction patterns.

Results

Two-dimensional diffraction patterns obtained from red and white parts of the "Uchi-gi" sample as shown in Figure 5 were converted into one-dimensional 2-theta versus intensity data. Figure 6 shows the results of qualitative analysis for both samples. Cinnabar (HgS), being a red pigment, and calcite ($CaCO_3$), used as a substrate, were identified from the diffraction pattern of the red part (green line in Figure 6). A broadened peak appearing around 2θ at 22.5° seems to be derived from the silk used as a support. Calcite ($CaCO_3$) was identified as a major compound from the diffraction pattern of white part (black line in Figure 6), but the peak corresponding to cinnabar observed in red part was not. Thus, accurate small-area measurement in the region as small as several tens to several hundreds of micrometers easily can be done with the D/MAX RAPID II-CMF. Table 1 shows the results including the compounds identified from all other.

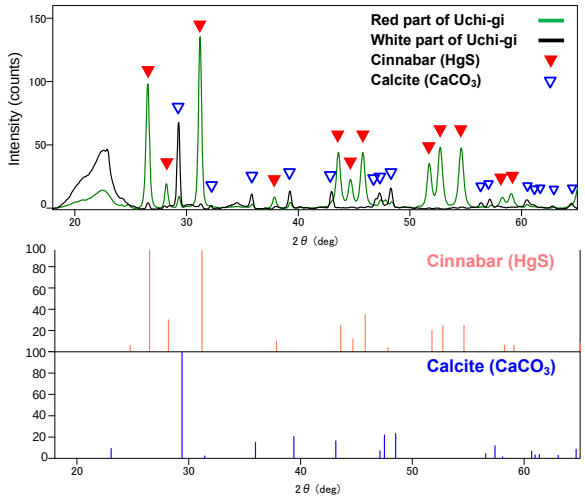


Figure 6. Diffraction patterns of red and white parts of "Uchi-gi" (2θ = 18 ~ 90°: Upper), and peak positions of identified compounds, cinnabar (Middle) and calcite (Lower)

All materials used in this report were provided through the courtesy of Prof. Fumiyoshi Kirino (Graduate school of Conservation, Tokyo University of the Arts). This Japanese painting describes "Ise Monogatari" (The Tales of Ise) and was supposedly painted by Suenobu Kano who was a Japanese painter in the middle of the Edo period.

Table 1. Summary of qualitative phase identification

Analysis area	Phases detected via X-ray diffraction *
Uchi-gi (red part)	Cinnabar (HgS) [Red], Calcite ($CaCO_3$) [White], etc.
Uchi-gi (white part)	Calcite ($CaCO_3$) [White], etc.
Matsu	Malachite ($Cu_2CO_3(OH)_2$) [Green], Calcite ($CaCO_3$) [White], Quartz (SiO_2), etc.
Nami	Goethite (FeO(OH)) [Yellow], Calcite ($CaCO_3$) [White], etc.
Kimono	Malachite ($Cu_2CO_3(OH)_2$) [Green], Calcite ($CaCO_3$) [White], etc.
Hakama	Calcite ($CaCO_3$) [White], Quartz (SiO_2), etc.

*** The list above represents the name of major minerals or compounds followed by its chemical formula shown in parentheses and color of pigment shown in square brackets.**

Prof. Kirino reported interesting conclusions on these results. Although the water is typically colored with blue pigment, goethite (FeO(OH)) which is a material of a yellow pigment was identified by the analysis of the "Nami" sample as shown in Table 1.

Based on the layout of painting, it is thought that the blue pigment used in the original painting may have been changed to yellow goethite due to deterioration over time. There are attempts to reproduce the original painting by using X-ray diffraction combined with the other techniques including X-ray fluorescence and infrared spectroscopy. This application note illustrates how the X-ray diffraction method is successfully utilized for renovation and preservation of cultural properties.

References

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(2) A Practical Guide to X-Ray Powder Analysis: Introduction to the Rietveld Method, edited by I. Nakai and F. Izumi, Asakura Publishing Co., Ltd., Tokyo (2002). (ISBN 4-254-14059-2 C3043)

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