IDENTIFICATION OF PAINTING MATERIALS USED FOR
MURAL PAINTINGS BY IMAGE ANALYSIS AND XRF

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ABSTRACT

The Takamatsuzuka tumulus in Nara Prefecture in Japan, discovered in 1972, is famed for the beautifully
colored murals on the walls and ceiling in a small stone chamber inside it. In this study, we investigated the
materials used for the mural paintings in this tumulus directly and non-destructively using a combination of
X-ray fluorescence (XRF) analysis for inorganic materials, and image analysis for organic materials. By
combining data obtained from a portable XRF and data obtained from image analysis (including
photoluminescent imaging), we were able to acquire detailed information regarding the painting materials
and techniques used in the Takamatsuzuka murals.

INTRODUCTION

X-ray fluorescence (XRF) analysis has been used extensively in archaeological investigations because it
deliver accurate, speedy, and non-destructive determinations of elemental composition [1, 2]. In recent years,
moreover, portable XRF spectrometers have been developed that can perform elemental analysis on-site
[3-5]. However, XRF is generally only useful for analysis of inorganic materials, and yields no information
about organic materials; these generally have to be investigated by analyzing images obtained with various
types of lighting. Light excitation to detect photoluminescence, for example, can be useful in the detection of
organic dyes. In addition, whereas XRF analysis generally yields results for small areas measurable in
millimeters or centimeters, image analysis can provide information regarding extensive areas.

In the present study, the paints and pigments used for the mural paintings in Takamatsuzuka tumulus were
investigated directly and non-destructively by using a combination of XRF and image analysis.

TAKAMATSUZUKA TUMULUS

The Takamatsuzuka tumulus, thought to have been built between the late seventh and early eighth centuries,
features a small stone chamber 1 m wide, 1.1 m high and 2.6 m deep, whose walls and ceiling feature
richly-colored paintings. The east wall features a group of women, a group of men, a sun and a blue dragon;
the west wall features a group of women, a group of men, a moon and a white tiger; the north wall features a
painting of a snake-tortoise; while the ceiling features constellations. These murals are the earliest
richly-colored paintings in the history of Japanese art, and so the tumulus is extremely important for
understanding the materials and techniques of early Japanese painting. The tumulus was discovered in 1972,
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and photographic documentation of the paintings was carried out immediately after the excavation. Chemical analysis of the pigments using trace samples collected in the stone chamber was also carried out at this time. However, after that, for a period of thirty years, no scientific investigation of the materials used for mural paintings took place. Our investigation in 2002 was thus the first one after the original discovery of the tomb, and we were able to make use of the latest scientific instruments, which have advanced considerably in the thirty years that had elapsed, for a non-destructive and non-contact analysis.

The Takamatsuzuka tumulus posed several difficulties for the investigation. The interior of the stone chamber is very small, too cramped to set ordinary instruments for investigation, while the humidity inside the chamber is close to 100%. The photography apparatus and XRF instruments thus had to be modified for this special environment—namely, protected against moisture, and set up on specially fashioned, small stands.

ANALYTICAL INSTRUMENTS

(1) IMAGE ANALYSIS
Color imaging with polarized light and photoluminescence imaging with light excitation were used for the optical investigation. Multishot high-resolution DigitalBack cameras (SinarBack 54HR, SinarBack 44HR) were used for the color imaging, and a singleshot DigitalBack camera (Kodak ProBackPlus) was used for the photoluminescence imaging. All images were taken in 16-bit. For the color imaging, polarized light creates fine separations of the colors and achieves high-saturation, reflection-free images. For the photoluminescence imaging, fluorescence from organic substances was detected by irradiating visible light for excitation. In this investigation, the excitation was applied with a wavelength of 460nm, and the photoluminescence of 530 to 640nm was detected and recorded. The photoluminescence spectrum from some areas was obtained by a sensitive spectrometer.

(2) XRF ANALYSIS
A portable XRF XT-35 (Re Target, Si-PIN detector) from EDAX, Inc. was used. This appliance can operate for eight hours with a compact Li ion battery; it weighs approximately two kilograms in total, and consumes a mere 5W of electricity. The X-ray spectrum was obtained by a handheld computer (Cassiopeia E-800 by Casio Computer Co., Ltd.) attached to the spectrometer. Figure 1 shows the scene of the analysis inside the stone chamber. The portable XRF was fixed to the top of a laboratory jack, and X-ray irradiating and counting were accomplished by remote control. The measuring points were fixed using a laser pointer projecting from the end of the spectrometer. The conditions established

Figure 1  Analysis inside the stone chamber with a portable XRF
for the analysis of the murals were as follows:
X-ray tube voltage/current: 35kV-8μA
X-ray radiation radius: approx. 5mm
Measuring time: 100 sec. per point
Distance from tip of spectrometer to mural: approx. 10mm

ANALYTICAL RESULTS

The investigation involved taking color images of all walls and the ceiling, and color and photoluminescent images of selected parts of each painting. Figure 2 shows an example of a color image taken of the west wall. This is the first time that images have been taken of the walls and ceiling in their entirety. XRF analysis was carried out at 173 points, covering all the paintings in the tumulus. Only seven elements, Ca, Fe, Cu, Hg, Pb, Au and Ag, were detected in this analysis. The characteristics of the painting materials used for the murals in the Takamatsuzuka tumulus derived from the results of image analysis and XRF are as follows.

(1) WHITE-COLORED WALLS
Pb was detected at every measurement point by XRF analysis, not only in the painted areas but also in the unpainted areas. The X-ray intensity of Pb detected varied in the painted areas, depending on the materials and thickness of the pigments used. On the other hand, in the unpainted areas, the X-ray intensity of Pb detected differed according to how far they were located from the nearby paintings. These results indicate that color was not applied directly to the underlayer of plaster, but a primer coat was first applied using materials that contained Pb, and the paintings were then painted over this layer.

Figure 3 shows the photoluminescent image of the center of the east wall obtained by excitation with visible light. Intense luminescence was observed on a vertical strip 4 to 5 cm wide stretching from above the figure of the blue dragon. A high Pb content was detected by the XRF in this area, 5 to 10 times higher than that of neighboring areas (Figure 4) was detected. Although no traces of color remain, this suggests the possibility that this part of the painting was done in color with organic matter.

Figure 2 Color image of the west wall of the stone chamber in Takamatsuzuka tumulus
(2) RED-COLORED MATERIALS

Figure 5 and 6 show the color and luminescent images, respectively, of the group of women on the west wall. XRF analysis revealed a distinct presence of Hg in the skirt, belt and lips of the women, all of which have a red tint. The red pigment could have derived from cinnabar (HgS), one of whose major elements is Hg. In contrast, no Hg was detected in the red coat of one of the women, indicating that some kind of organic red-colored dye was used there. The luminescent density falls (that is to say, turns “black”) in those areas of the skirt, belt and lips where Hg is detected, but the luminescence was observed in the red coat, as shown in Figure 6. Further, the men and women in the green coats on both the east and west walls all wear red belts; the belts worn by the women were found to contain a great deal of Hg, whereas those worn by the men contained no Hg whatsoever. This is clear evidence that two kinds of red-colored materials were used for different areas.
(3) BLUE-COLORED MATERIALS
There were likewise two kinds of blue-colored materials. In the group of women on the west wall, as shown in Figure 5, XRF analysis revealed a large amount of Cu in the blue colors of the skirt and the clothes. We can assume that azurite, a blue-colored mineral consisting mainly of Cu, was used. Further, some luminescence was found by exciting visible light with 460nm from these areas. It is common knowledge that minerals do not emit luminescence, but certain ores, such as calcite and fluorite, appear to emit red-colored luminescence when excited with UV-light. The visible fluorescence from these areas was very similar to that obtained from the blue-colored material used in the Dunhuang wall paintings in China, which has been identified as Afghan lapis-lazuli. Figure 7 shows the spectrum obtained from a blue-colored area of the blue dragon on the east wall. The data from the Takamatsuzuka tumulus show close similarities to those of the minerals of Afghan lapis-lazuli.

CONCLUSION
This paper highlights the findings of the investigation of painting materials used in the murals inside the Takamatsuzuka tumulus. A portable XRF enabled us to perform non-destructive on-site examinations. However, nothing has been done to analyze the materials that are composed mainly of organic dyes and light elements. By combining the data obtained XRF analysis with image analysis such as photoluminescent imaging, it was possible to acquire detailed information of the painting materials and techniques used on the murals inside the Takamatsuzuka tumulus.

REFERENCES