Micro X-ray diffraction of cultural properties

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1. Introduction

There are two basic objectives in scientific analysis of tangible cultural properties: appraisal of authenticity, and investigation of materials for purposes of preservation or restoration. Targets of these analyses are buildings, sculptures, paintings, craft objects, old documents and so on.

Many art and craft items have become the objects of speculation by collectors throughout the world. As a result, the field has an aspect that drives incidents of theft and forgery of and damage to works by improper restoration. In the case of paintings, it is not unusual even with famous works for the artist himself to make changes in the underlying sketch or picture composition prior to completion, or for a third party to work on the picture after the artist has died. One such example is the "Madonna del Granduca"(1505) by Raphael. This image of the Madonna and Child, which was publicly exhibited in Japan for the first time in March 2013, is known for having a jet-black background—a feature not seen in other works by Raphael. During the exhibition of this masterpiece of the Madonna and Child painting genre, the results of scientific analysis of the jet-black area were also presented. An X-ray image taken in 1984 showed that Raphael had originally painted a different scene in the background, but that scene had been covered with jet-black paint by someone in a later generation.

To determine authenticity by analyzing the painting process and the time and place where the materials were produced, it is essential not only to carry out verification by humanities or social sciences, but also to analyze based on the knowledge of natural science using the results available from X-ray equipment.

It was in 1960 that Rigaku X-ray instruments were used for the first time to investigate a cultural property. There was a question of forgery regarding a Koseto (old Seto pot from the Kamakura period (1185−1333) that was designated as an important cultural property in 1959. This controversy became known to the public as the "Einin Pot Incident." When the pot was measured with Rigaku's X-ray fluorescence (XRF) spectrometer, it was determined that it was a forgery because some elements in the glaze and substrate had a composition that did not exist in the Kamakura period. At that time, Yoshimichi Emoto of the National Research Institute for Cultural Properties, who entrusted this analysis to Rigaku, contributed an article to the *Rigaku-Denki Journal* No. 11, published in November 1961, entitled "The Einin Controversy" and giving an overview of this incident[1].

X-ray analysis is a non-destructive method and, since the "Einin Pot Incident," X-ray techniques such as X-ray diffraction (XRD), X-ray fluorescence (XRF), X-ray transmission (XRT) and X-ray CT (computed tomography) have come to play an extremely important role, particularly in preservation and restoration science. These techniques are used for scientific analysis of important cultural properties, including national treasures such as the Shosoin Temple treasures (756 C.E.) and the wall paintings of the Takamatsuzuka Tomb (694 C.E.).

This paper presents examples of measuring cultural properties using the latest Rigaku micro-XRD instruments, including measurements relating to investigation of the Takamatsuzuka Tomb, where methods of preservation and restoration have been studied since 1972 and research is still ongoing.

2. Cultural properties and trace/micro-XRD measurement

In order to appraise the authenticity of cultural works and ensure proper preservation and restoration, it is crucial to first accurately carry out scientific analysis of the materials of the cultural property, and then develop a comprehensive understanding of factors such as changes in materials due to the passage of time. On the other hand, a major precondition for the measurement of cultural properties is ensuring that the materials are not destroyed. Measurement can be done by setting a large item into an analyzer as is, or by conducting point analysis of a tremendous number of points using a portable system. In measurements using large instruments, there are strong constraints on the equipment itself, and if a portable device is used, analysis precision is unlikely to be adequate. However, the latest XRD equipment enables measurements at an ordinary laboratory even with extremely minute trace samples, such as pigments that have peeled from a painting due to the passage of time, plaster fallen from the wall of a ruin due to weathering, or a fragment of pottery unearthed in an excavation.

3. Requirement of XRD equipment for cultural properties measurement

First, we would like to discuss the requirements for carrying out XRD measurements of cultural property samples. Generally speaking, samples of cultural properties can only be removed in extremely small amounts, typically a few μg. In addition, grinding

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is impossible in some cases, and evaluation must be performed on a specific micro region. Therefore, micro-XRD is essential because it only requires a sample in the range of tens of μm for evaluation. To carry out this kind of measurement, the equipment must satisfy the following requirements.

3.1. Point focus X-ray source

To measure small amounts of sample or micro regions, it is necessary to collimate the X-ray beam, and thus point focus X-rays are useful. If line focus is used, the X-ray beam can be formed into a point using a slit, but in this case only part of the entire X-ray beam is used as output, and thus the X-ray intensity is only 1/10 or less compared with the point focus.

In addition, in recent years, the combination of high-brilliance microfocus X-ray tubes and multilayer mirrors[(2)] has become popular with advances in multilayer coating techniques that enable high reflectivity of the X-rays. Microfocus tubes have been used for a long time to obtain transmission images, such as medical X-rays, but the focus size was set to a few μm to increase spatial resolution. Thus, adequate X-ray output could not be obtained and the method was not sufficient for use in X-ray diffraction. Recently, X-ray tubes with a few tens of μm focus have become commercially available. This allows scientists to obtain usable diffraction patterns from samples in the range 100 μm to a few μm. Figure 1 shows a comparison table of X-ray intensities from a 100 μm sample. In the range of 100 μm or less, the microfocus tube exhibits an even greater difference compared to a fine focus tube.

3.2. 2-dimensional detector

If a point focus X-ray source is used, there is no need to suppress vertical divergence with a slit since there is no smearing, as there is with a line optic system. Therefore, the use of a 2-dimensional detector (2D) with a larger detection area has advantages. Examples of 2D detectors include: IP (Imaging Plate), CCD (Charge Coupled Device), CMOS (Complementary Metal Oxide Semiconductor), PSPC (Position Sensitive Proportional Counter), and HPAD (Hybrid Pixel Array Detector). Each type of detector has its own features and uses depending on the application. In trace/micro area measurement, the detection area and low noise are crucial elements. Table 1 shows the detection area and noise specifications for each detector. In trace measurement, an important issue is how efficiently the weak reflections can be measured. With a large detection area, it is possible to capture more reflections at once, and measurement can be done even with weak reflections by integrating. Also, the detecting area has a relationship to exposure time. A large detecting area enables measurement in a shorter time. Since effects of crystal grains size appear with samples subject to micro area measurement (ranging from a few μm to a few tens of μm), Debye rings from such a small area are usually recorded like diffraction from a single crystal and do not provide powder XRD pattern. These diffraction patterns have certain crystal orientations, thus diffraction is not observed on the equatorial line, which means a part of the Debye ring cannot be captured if the detection area is too small. Figure 2 shows an example of the measurement of a 5 μm iron grain. Measurement was performed with an IP, which has a large detection

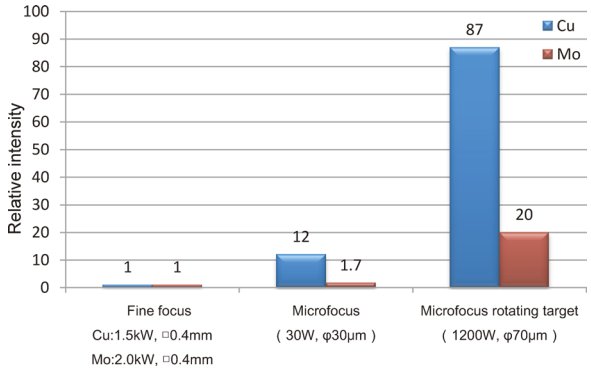

Fig. 1. X-ray intensity ratio (normalized with fine focus).

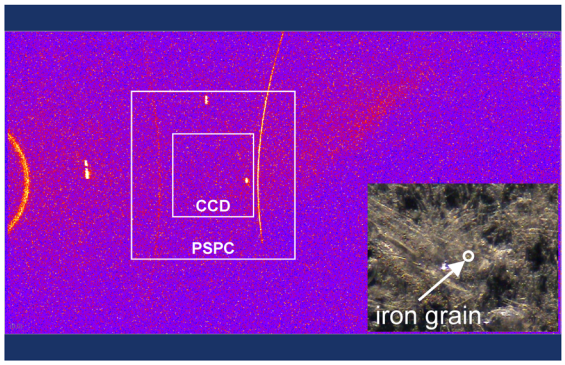

Fig. 2. Diffraction image of 5 μm iron grain.

Table 1. Main specifications of each detector (with camera length of 127 mm).

	IP	CCD	CMOS	PSPC	HPAD
Detection area (mm)*	465×256	70×70	100×100	140×140	83×106
Detector shape	Curved	Flat	Flat	Flat	Flat
Measurement range (vertical)	−45°+163°	±15°	±21°	±30°	±22°
Measurement range (horizontal)	208°	30°	42°	60°	36°
2θ scan	Unnecessary	Necessary	Necessary	Necessary	Necessary
Dark current	No	Yes	Yes	No	No

* Except for IP and HPAD, average values are given for the detection area. HPAD indicates values for PILATUS3 R 300 K.

area. The white squares in the image show the detection areas for a CCD and a PSPC, which have relatively small detection areas. As can be seen, since the diffraction appears in random positions, these cannot be captured by a small area detector, and it is necessary to use a detector with a large detection area such as an IP. Lastly, there are noise issues. The diffraction is very weak so it is necessary to have low noise and a long exposure time. Typical exposure times are a few tens of minutes to a few hours, and some cases may require day-long exposures. In this case, measurement by CCD or CMOS is very difficult since these detectors have a dark current that increases noise depending on the exposure time, as shown Table 1.

3.3. 2-axis goniometer with very accurate sphere of confusion

In micro area measurement, the diffraction pattern is observed at random positions, as described in 3.2. The detection area is limited, and thus even with a large detector it is impossible to capture the diffraction patterns completely in some cases. However, this problem can be solved by rotation of the sample. In order to measure half of reciprocal space, the goniometer must have at least two axes. An example is shown in Fig. 3. The ϕ-axis is set at an inclination of 45° relative to the ω-axis. This is the same principle as the Gandolfi camera, which is frequently used to measure micro particles[3]. Since the sample is small, the goniometer must have a very small sphere of confusion. If the sphere of confusion is too large, diffraction from the skirt area will appear because the X-rays diffuse into the surrounding area, making it impossible to obtain only diffraction from the desired micro area. Typically, a good sphere of confusion is 1/4−1/5 of the size of the sample to be evaluated. For example, with a 20 μm sample, the required sphere of confusion is 4−5 μm.

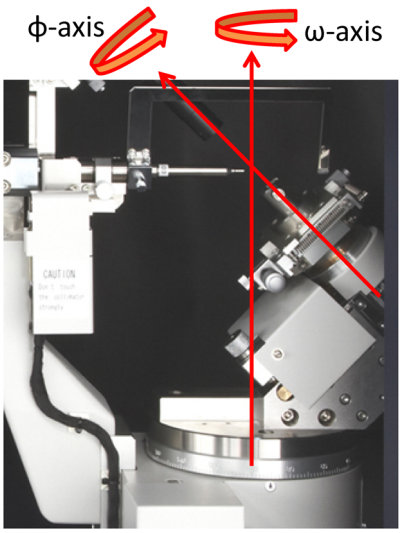

Fig. 3. Example of the 2-axes goniometer.

3.4. Automatic XY stage

In some cases, especially for minerals, measurement must be performed at several positions within the same sample. In trace and micro area measurement, exposure times can be very long; therefore, it is best to have an automatic XY stage so that several measurements can be carried out at designated random positions.

4. Example of state-of-the-art analysis using micro-XRD instruments

The following presents several measurement examples. Rigaku's D/MAX RAPID II MM007 micro-XRD instrument was used for the measurement (Fig. 4). This system is equipped with a microfocus rotating anode X-ray generator and a curved IP detector. This produces 10 times more X-ray intensity than the microfocus sealed tube system described below. The measurement time is short, and the evaluation of a 10 μm sample is also possible with reasonable exposure times.

4.1. Structural analysis of joint plaster surface from stone chamber of the Takamatsuzuka Tomb[4]

The Takamatsuzuka Tomb located in Asuka village, Takaichi district, Nara prefecture, Japan has been designated as a special historical site. Both composition and structural analysis are being carried out in order to optimize the preservation environment and investigate restoration technologies. Reports indicate that valuable information can be obtained, using multiple scientific analysis techniques, regarding the fine structure of the wall surface and joint plaster pigments inside the stone chamber, and the ocher-colored layer of discoloration

Fig. 4. D/MAX RAPID II MM007.

Fig. 5. Fragment of surface of joint plaster from stone chamber of Takamatsuzuka Tomb.

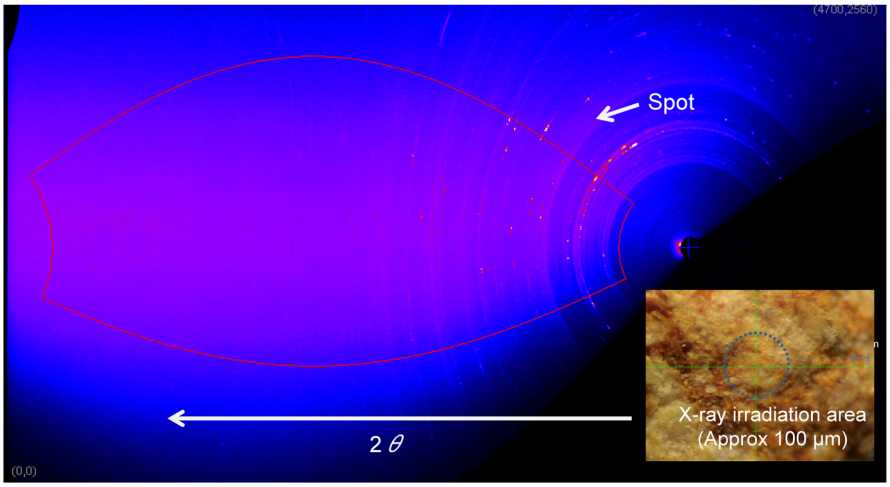

Fig. 6. XRD image for thick ocher-colored layer.

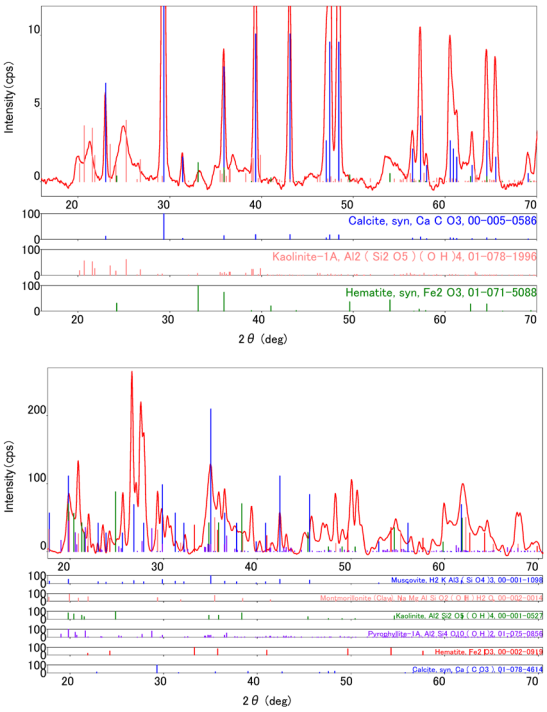

Fig. 7. Result of Qualitative analysis thin and thick ocher-colored layers.

seen on the surface. Here, we would like to present an example from these reports of structural analysis of the ocher-colored layer of the joint plaster in the stone chamber of the Takamatsuzuka Tomb performed using X-ray diffraction (sample provided by: Masahiro Kitada, Professor Emeritus, Tokyo University of the Arts, and a member of the Nara National Research Institute for Cultural Properties; the Agency for Cultural Affairs).

Figure 5 shows a macro image of the sample measured using XRD. The evaluation region was set to 100 μm, and comparison between the part with the thin ocher-colored layer and the part with the thick ocher-colored layer was done. Figure 6 shows an XRD image of the region with the thin ocher-colored layer. Looking at the image, it is obvious that Debye rings are not observed and a lot of spotty reflections are recorded. This shows that the sample contains coarse grains. Figure 7 shows the results of qualitative analysis after converting the 2D images of the thin and thick ocher-colored layers to a 1D profile. There is a difference between these two results. The thin ocher-colored layer part contains the calcite $CaCO_3$, which forms the white colored plaster, kaolinite $Al_2Si_2O_5(OH)_4$ and hematite Fe_2O_3, but in the thick ocher-colored layer part, additional substances were identified: muscovite $KAl_2(AlSi_3O_{10})(OH)_2$, montmorillonite $NMgAlSi_2(OH)_2$ and pyrophyllite $Al_2Si_4(OH)_2$. This analysis proved that the thick part is comprised of multiple materials.

4.2. Analysis of a 15th century Spanish panel painting[5]

Next, we would like to present an example of the analysis of a Spanish panel painting done by McCrone Associates, Inc., an analytical company in Illinois, U.S.A. McCrone Associates, Inc. is a contract analysis company specializing in trace amount or particle analysis. Extremely interesting results have been reported by Joseph R. Swider, who is in charge of its Paints and Coatings division.

The sample in this case was a Spanish panel painting from the 15th century Renaissance. Panel paintings from this era have gaps, and it is known that these have been repaired by repainting as time has passed. However, the problem has been that it was not known when this restoration was done. Swider estimated the time of restoration based on these gaps by determining what pigments were used.

Samples removed from the panel painting were measured with a Scanning Electron Microscope (SEM), and divided into four layers. Using an Energy Dispersive Fluorescence (EDS) method for each layer, it was found that the main components of the blue color in the second layer and the azure color in the fourth layer were, respectively, Cu and Co/Sn. Then XRD measurement was performed with an exposure time of 15 minutes for particles approximately 40 μm in size removed from

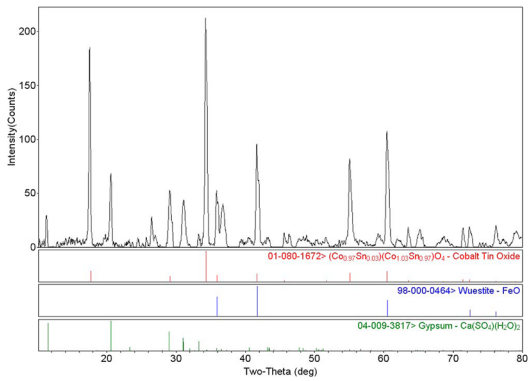

Fig. 8. 1D profile and results of qualitative analysis for 15th century Spanish panel painting.
(From Joseph R. Swider: "Powder micro-XRD of small particles", Powder Diffraction, Vol. 25, Issue 01, (2010). p71 (Figure 7). DOI: 10.1154/1.3308434.)

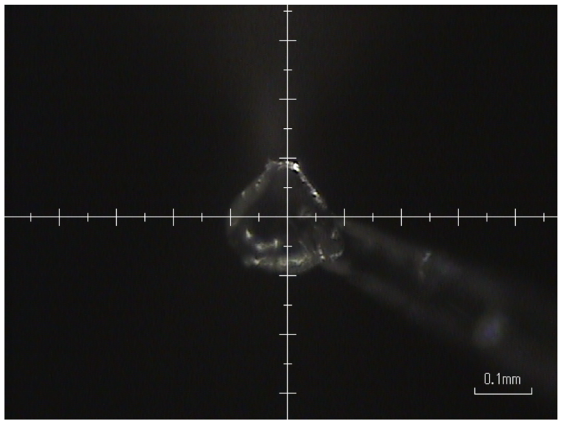

Fig. 9. Image of quartz crystal.

each layer. Figure 8 shows the results after the 2D image was converted to a 1D profile and qualitative analysis was carried out. This qualitative analysis showed that the Co and Sn are oxidized. It is known that pigments comprised of these oxides of Co/Sn were not developed in the 15th century, and only came into use in the 1860s. Thus it was shown that the painting was restored sometime around 1860.

4.3. Gandolfi measurement of minerals

Gandolfi measurement is a technique for obtaining a powder pattern from single crystal-like samples by performing 2-axis rotations. The technique is essential for measuring minerals. Here, an experiment was made to verify its effectiveness by using an approximately 150 μm quartz single crystal. Figure 9 shows an image of the measured quartz crystal. Three types of measurement conditions were used: (1) goniometer fixed, (2) ϕ-axis spin, and (3) a combination of ϕ-axis spin and 130° ω-axis oscillation. The exposure time was set to 200 seconds in case (1), when the goniometer was fixed, and to 800 seconds in cases (2) and (3), when spin and oscillation were applied. Figure 10 shows the 2D images for each case. When the goniometer is fixed, only a few spot-like diffractions from the single crystal are obtained,

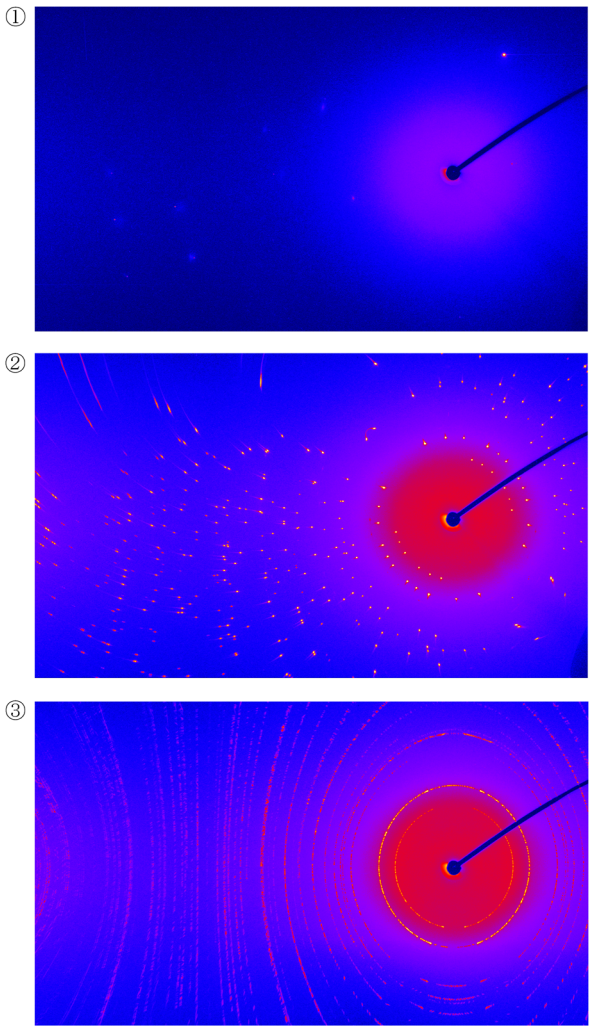

Fig. 10. Diffraction image of quartz.
① Goniometer fixed ② ϕ spin
③ ϕ spinning and ω oscillation

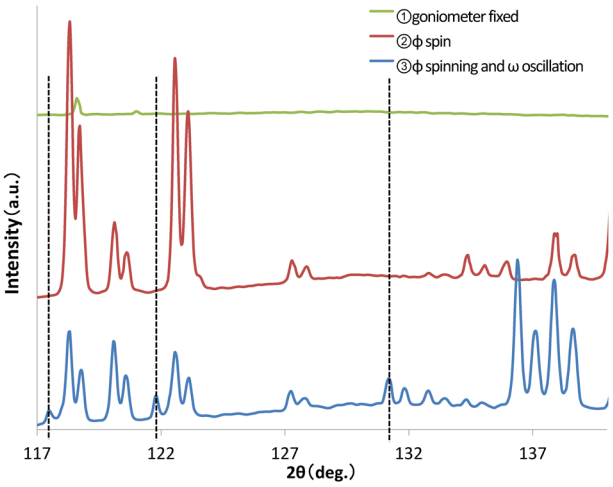

Fig. 11. 1D profile of quartz (enlarged).
The dotted lines are reflections which appear in (3) but not in (2). (To make them easier to see, an offset is applied to the vertical axis.)

but when the ϕ-axis is spun, the diffraction spots increase in number. Furthermore, when ω-axis oscillation is

Table 2. Results of phase identification, 20–7 μm mineral samples.

Sample size (μm)	Phases detected
20	Rutile, quartz and ilmenite
14	Zircon and thorite
10	Corundum and baddeleyite
8	Perovskite
7	Zirkelite

added to ϕ-axis spin, an image like a powder pattern is obtained. In Fig. 11, each case is converted to a 1D profile, and the high angle side is enlarged. When the goniometer is fixed, it is obvious that diffraction patterns do not appear compared to the other two cases. However, as shown by the dotted lines in the graph, there are diffractions that appear in the ϕ-axis spin/ω-axis oscillation case but not in the ϕ-axis spin case. This shows that ω-axis oscillation is also important.

Dr. Swider, who carried out the aforementioned analysis of the Spanish panel painting, has also carried out measurements of unknown minerals, and reported that it was possible to identify all of them by measuring 20–7 μm particles for 30–90 minutes[5]. Table 2 summarizes the identification results.

5. Suitable equipment for micro-XRD of cultural properties

In addition to the D/MAX RAPID II MM007 used in the above analysis examples, the following systems are also suitable for micro-XRD of cultural properties.

5.1. D/MAX RAPID II

This is an X-ray diffractometer equipped with a curved IP detector and sealed tube X-ray generator (Fig. 12). There are two types of tubes: a high-brilliance microfocus tube and an ordinary fine focus tube. The microfocus tube type can generate high-brilliance X-rays in combination with a multilayer mirror, even though output is a low 30 W. Therefore, the system is effective for trace and micro samples. The fine focus tube type uses a graphite monochromator and can handle X-ray sources from Ag to Cr, so various tubes can be selected. In addition, replacement of the tube and alignment of the graphite monochromator due to the tube replacement is very easy, and thus an optimal wavelength can be used depending on the sample.

5.2. D/MAX RAPID II MM007DW

This is an X-ray diffractometer equipped with a curved IP detector and a dual-wavelength (DW) rotating anode X-ray generator. X-ray intensity is about 10 times that of a microfocus sealed tube. The DW type can use different wavelengths without changing the target[6].

5.3. ELement ANalyzer (element analysis attachment)[7]

In combination with the RAPID series, this attachment enables elemental analysis (qualitative analysis) with a RAPID X-ray generator (Fig. 13). Shooting the X-ray at same position where the XRD experiment was performed, elemental information is provided by fluorescent X-rays. The elemental information helps to carry out more accurate structure analysis.

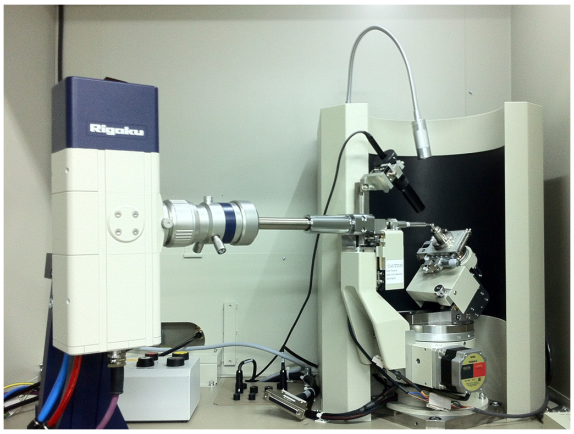

Fig. 12. D/MAX RAPID II (example of combination with microfocus type MM003).

Fig. 13. ELement ANalyzer (element analysis attachment).

6. Conclusion

In addition to micro-XRD instruments, the MiniFlex series of benchtop X-ray diffractometers, SmartLab fully-automatic multi-purpose X-ray diffractometers, and other X-ray diffraction instruments are used at museums and archaeology research sites. Among X-ray diffractometers, the D/MAX RAPID II micro-XRD instrument is currently used at museums throughout the world due to the above features. It is also frequently used for forensic investigations and at earth/planetary research laboratories for the measurement of cosmic dust and estimation of structure in the deep earth. In the future, this equipment is expected to be used in an even wider range of fields.

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