Review Article

Synchrotron radiation-based X-ray analysis for cultural heritage and art

1. Introduction

Today, introduction of scientific techniques has been necessary in the field of the cultural heritage. Various chemical and physical analytical techniques have been applied to archaeological sites and excavated artifacts for many purposes, e.g., identification of material and production techniques, provenancing, dating, investigation of aging degradation, and preservation and restoration. Likewise, these techniques have been utilized aggressively in the field of art as well. This is due to the efforts of curators, conservators, and scientists that we can see masterpieces of art painted hundreds of years ago in museums today. On the other hand, it is not always possible to introduce any scientific techniques into the investigation of cultural heritage and art; because of their high historical and artistic values, it is often required to choose a nondestructive and noncontact analytical technique at ordinary temperatures and pressures. The use of X-rays is a suitable solution to analyze cultural heritage and art under tight restriction. X-rays will be a good decoder for interpreting the provenance information inherent within them nondestructively. Particularly in X-ray fluorescence (XRF) analysis, a handheld XRF spectrometer has been in widespread use as an easy, quick tool for measuring chemical composition of cultural heritage and art in a nondestructive and on-site manner. Today, the application to cultural heritage and art is forming an appreciable market for X-ray instruments and related equipment in both laboratory and on-site uses.

The application of synchrotron radiation (SR) X-rays in the fields of cultural heritage and art dates to the late 1980s, but it has become widespread only recently [1] owing to the continuous development of stable light sources and measurement equipment, and close dialog among researchers in different fields: archaeologists, curators, conservators, and experts on physical and chemical techniques based on the SR. Outstanding features of the SR light sources, such as high brilliance, high directionally, and wide tunability of energy/wavelength, enable us to conduct various X-ray analyses with superior sensitivity, accuracy, and spatial resolution on cultural heritage and art without their destruction, e.g., XRF analysis, X-ray powder diffraction, X-ray absorption fine structure (XAFS) analysis, and computed tomography (CT). In addition, by shaping the size and shape of the SR-X-ray beam using optical elements, any samples from an entire painting as tall as a human to a single microscopic particle of pigment in the painting, can be a target of SR-based X-ray analysis. One of the major reasons behind the wide spread of the SR-based X-ray analytical techniques among researchers of cultural heritage and art was the investigation of a painting by Vincent van Gogh [2]. The SR-based XRF imaging of the painting successfully revealed the hidden image of a woman's head painted under Van Gogh's work "Patch of Grass." Along with a reconstructed image of this hidden face, the results of its study were widely covered by the media.

In this review, the author introduces three SR-based X-ray analytical techniques, XRF analysis, X-ray CT, and X-ray absorption edge radiography, with actual examples of application to cultural heritage and art at SPring-8.

2. High-energy SR-XRF of ceramic and glass

In the case of XRF analysis, utilizing the monochromatic SR-X-ray will improve the lower limits of detection markedly compared with bench-top XRF instruments because of the reduction in background due to the scattering of white X-rays from an X-ray source. In addition, the selection of a suitable energy of excitation X-rays enables the selective excitation of target element(s). In some SR-facilities adapted to hard X-rays, monochromated X-rays with very high energy unattainable in bench-top instruments can be utilized for XRF analysis specialized for heavy elements; this is the so-called high-energy (HE-) SR-XRF analysis. The use of 116 keV monochromated X-rays enables excitation of *K*-edges of all heavy elements up to uranium (*K*-edge: 115.6 keV). Figure 1 shows a HE-SR-XRF spectrum of NIST SRM 613, a certified standard material of soda-lime silicate glass containing 40–50 ppm trace heavy elements [3]. The spectrum was obtained at BL08W, the only wiggler beamline and the highest X-ray energy beamline in SPring-8. Lower limits of detection for elements in the lower background region of the spectrum (25–60 keV), such as Sn, Ba, and lanthanoids, were estimated to be 1 ppm or less [4]. The bench-top XRF instrument can also detect these elements using L-lines in the lower energy region, but L-line peaks of these elements overlap considerably with K-line peaks of K, Ca, and 3*d* transition metals. HE-SR-XRF analysis, therefore, is the only nondestructive multielement analytical technique for detecting trace amounts of heavy elements with sensitivity as good or better than that of the instrumental neutron activation analysis.

HE-SR-XRF at SPring-8 was originally developed for a forensic application by Nakai *et al*. [5] in the late 1990s. As the first application to a cultural heritage, Miura *et al*. [6] applied this technique to porcelain clay bodies of china wares excavated from old kilns in Kutani and Arita districts in Japan and showed that Kutani and Arita wares can be clearly distinguished on the basis of the trace heavy element composition. The author has recently applied the technique to ancient glass products found in Japan to identify where they were manufactured. Because no evidence of primary glass production from raw materials prior to the late 7th century was previously found in Japan, it is believed that all earlier glass products were imported from overseas. In contrast to the thousands of glass beads excavated from a number of ancient tombs in Japan, only a few glass vessels imported to ancient Japan remain today. The author conducted the HE-SR-XRF analysis of fragments of two glass vessels excavated from a tumulus in Nara prefecture and revealed that these precious glass vessels were originally manufactured at workshops located in the Sasanian Empire (West Asia) and Roman Empire (Mediterranean region) [4,7]. As an example, Fig. 2 shows the chemical compositions of Specimen A, a fragment of a glass bowl excavated from the tumulus, and glassware manufactured in the Sasanian Empire, namely, Sasanian glass; the compositional feature of the fragment closely matches that of one of the three compositional groups identified in Sasanian glass, that is, the Sasanian 2 group. The results of this study thus demonstrated scientifically the extent of East-West trade through the Silk Road in ancient times.

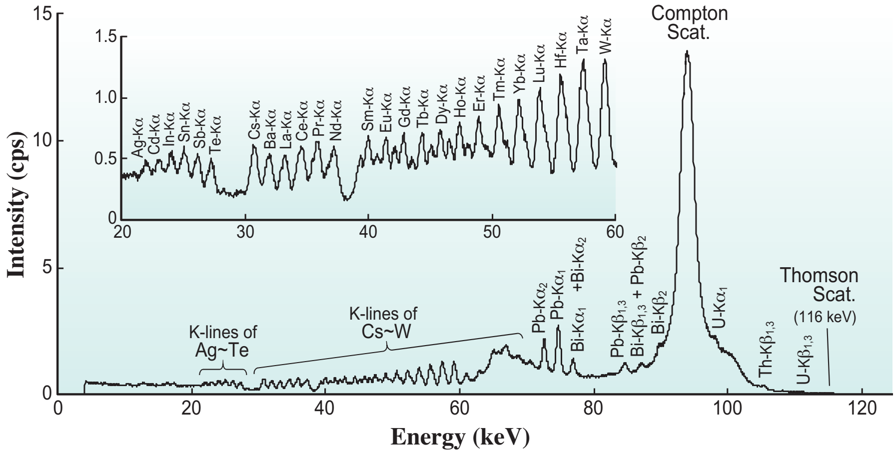

Fig. 1. HE-SR-XRF spectrum of NIST SRM613, a certified standard material of soda-lime silicate glass containing trace heavy elements, obtained by the author using SPring-8 BL08W [3].

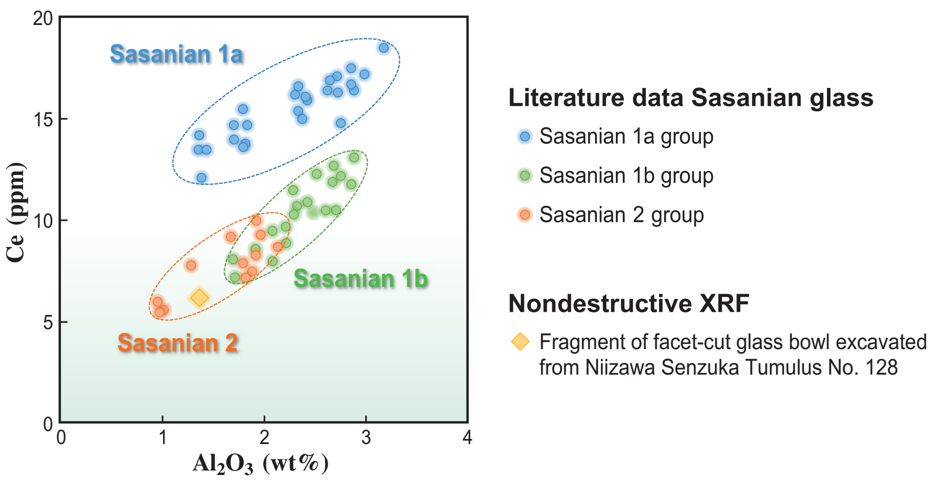

Fig. 2. Chemical composition of a fragment of a facet-cut glass bowl excavated from Niizawa Senzuka Tumulus No. 128 in Nara prefecture and literature data of three compositional groups of Sasanian glass [4,7].

3. SR-X-ray CT of ancient metallic sword

Since humans have long been using metals, there are many historic and archaeological artifacts and works of fine art made of metal. For such studies, X-ray CT is an indispensable tool because it allows us to investigate the inner structure of samples nondestructively. In such studies, high-energy X-rays are required to penetrate a metal object with high density. Hoshino *et al*. [8] applied a CT imaging system using the high-energy (200 keV peak energy) non-monochromatized X-rays from a bending magnet at SPring-8 BL28B2 to visualize the inner structure of an ancient bimetallic sword consisting of both bronze and iron. The sword is part of a collection at Okayama Orient Museum. It is 86 cm long and its blade is bronze. The hilt is also bronze on the surface, but unusual in that it has an iron core, thus bimetallic. It is considered to be from northern Iran dated 10th–8th century BC, which is a transition period from the Bronze Age to the Iron Age. As shown in Fig. 3, the inner structure of this bimetallic sword made of iron and bronze was visualized successfully by SR-based high-energy high-resolution X-ray tomography without destruction. Although the beam hardening of a 2.5% difference in density was observed, inner structures of the ancient sword were clearly visualized. This work demonstrated the feasibility of the high-energy, high-resolution imaging of metallic objects.

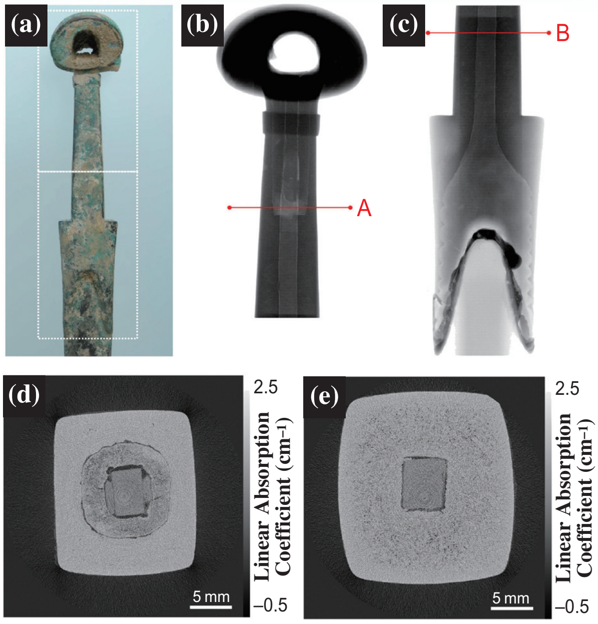

Fig. 3. **(a)** Photograph of a bimetal sword stored at Okayama Orient Museum, Japan. **(b, c)** X-ray projection images of the hilt (handle) and pommel (knob) of the sword indicated by dotted rectangles in (a). **(d)** CT cross section at the solid line A shown in (b). **(e)** CT cross section at the solid line B shown in (c). All data were obtained at SPring-8 BL28B2 and reprinted from the article by Hoshino *et al*. [8].

4. SR-X-ray absorption edge radiography of oil painting

Large-area XRF elemental mapping, the so-called scanning macro (MA)-XRF imaging, is one of the most effective tools for investigating paintings in a nondestructive and noncontact manner, as introduced at the beginning of this review. Although the utilization of the SR-X-ray beam was, in the past, the only way to carry out the MA-XRF imaging of a large painting, some portable analytical instruments specialized for nondestructive on-site MA-XRF imaging have recently been developed and are now in practical use. Today, MA-XRF imaging has become a standard method of investigating paintings nondestructively, but note that a long measurement time is necessary to analyze an entire painting; it sometimes takes all hours of the night. In addition, the same as conventional XRF analysis, the result of MA-XRF imaging will be influenced to no small extent by the presence of other elements that may be present as a major component of the painting.

As a rapid and element-selective imaging technique applicable to cultural heritage and art, SR-based X-ray absorption edge radiography is introduced here. Similarly to conventional X-ray radiography, the technique irradiates a large-area X-ray beam onto the object and records a transmission X-ray image using a two-dimensional (2D) X-ray detector. What is different from the conventional X-ray radiography is that two transmission images are recorded simultaneously using two different energies of monochromatic X-rays above and below the absorption edge energy of the target element. The distribution of only the target element can be visualized by calculating the difference between these two images. Similar X-ray imaging techniques using contrast between above and below the absorption edge were, in principle, utilized since the early stage of the application of SR-X-rays in the healthcare field. For the application to cultural heritage and art, Wallert *et al*. [9] applied the technique to an early modern painting as "dual-energy *K*-edge absorption radiography." They successfully visualized the distributions of Pb and Hg on the painting by measuring their *K*-edge absorptions, but only the high-energy X-rays over 80 keV were used in consideration of the strong absorption of X-rays by the pigments containing these heavy elements and the lack of sensitivity of the 2D X-ray detector in the lower energy region.

The author has recently developed this technique for the lower energy region using a large-area monochromatic SR-X-ray beam at BL20B2 in the Medium-length Beamline Facility of SPring-8 with a 2D-flat panel X-ray sensor suitable for the detection of X-rays with an energy higher than 12 keV [10]. The verification using model paintings prepared by the author demonstrated that it is possible to rapidly perform the elemental imaging of paintings by this method: ~5 min per element for an area of 10×10 cm^2. The analysis of a modern oil painting showed that this technique is useful for the elemental imaging of elements with absorption edge energies above 12 keV (see Fig. 4) with a spatial resolution of ~100 μm. Because the technique utilizes the absorption of X-rays, it is expected that the technique will enable the mapping of the difference in the chemical state of the same element by combined use of XAFS analysis. While there is still some room for improvement before practical realization, this new SR-based analytical technique could become an alternative for the investigation of the cultural heritage and art instead of the MA-XRF imaging technique in the future.

5. Conclusion

SR-based X-ray analytical techniques are highly suitable for the investigation of cultural heritage and art because of the strong demand for nondestructive and noncontact techniques. In contrast to the increasing activity concerning cultural heritage and art at SR facilities in the US and Europe, only a few researchers apply SR-X-rays to these fields at a limited number of beamlines available for these fields in Japan. It is hoped that the usefulness of the SR-based X-ray analytical techniques will gain increasing recognition among researchers in the fields of cultural heritage and art in this country. At the same time, we scientists utilizing the techniques based on SR should not forget to make compromises with researchers in different fields. On the other hand, we should understand that there are drawbacks to using the SR-based X-ray analysis in the investigation of cultural heritage and art. Needless to say, to use SR-X-rays, all samples for analysis must be transported into the SR facility. For cultural heritage and art, transport between their depository and the SR facility poses a risk of unnecessary damage or destruction. In particular, in the case of objects designated as important cultural heritage or national treasures by the government, it will be more difficult to remove them from their depository even for scholarly purposes. Thus, for researchers working in the fields of cultural heritage and art, the use of SR-X-rays is a "last resort". In other words, researchers exhaust other options before taking the cultural heritage or art into the SR facility.

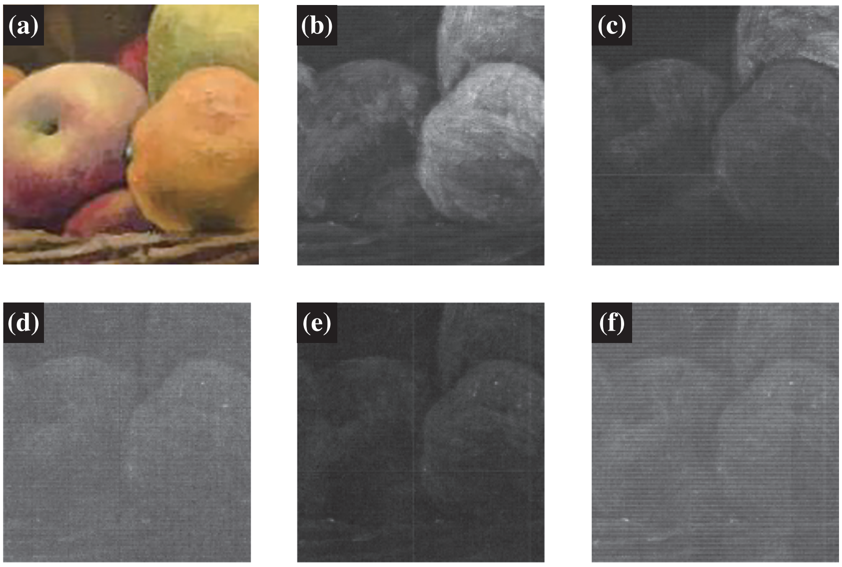

Fig. 4. **(a)** Photograph of modern oil painting analyzed in this study. Representative elemental distributions visualized by SR-X-ray absorption edge radiography: **(b)** Pb L_3-edge, **(c)** Cd *K*-edge, **(d)** Ba *K*-edge, **(e)** Sr *K*-edge, and **(f)** Se-*K* edge. All data were obtained at SPring-8 BL20B2 by the author [10].

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