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Research Article

Simultaneous Organic and Inorganic Analysis of Colored Oriental Lacquerware by Pyrolysis-Gas Chromatography/Mass Spectrometry

Yoshimi Kamiya,[1] Takayuki Honda,[2] Atsushi Ohbuchi,[3] and Tetsuo Miyakoshi[2]

[1] *Tokyo Metropolitan Industrial Technology Research Institute, Tama Techno Plaza, Textile and Chemical Technology Group, Department of Materials Chemistry Application, 3-6-1 Azuma-cho, Akishima-shi, Tokyo 196-0033, Japan*
[2] *Department of Applied Chemistry, Meiji University, 1-1-1 Higashi-Mita, Tama-ku, Kawasaki-shi, Kanagawa 214-8571, Japan*
[3] *Rigaku Corporation, X-Ray Research Laboratory, Application Laboratories, XRD Analysis Group, 3-9-12 Matsubara-cho, Akishima-shi, Tokyo 196-8666, Japan*

Correspondence should be addressed to Yoshimi Kamiya; kamiya.yoshimi@iri-tokyo.jp

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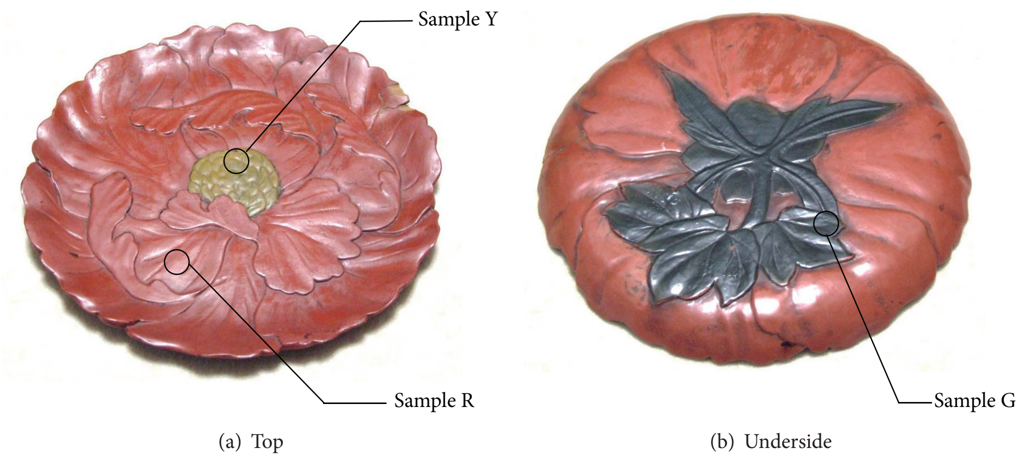
Organic analysis and inorganic analysis are generally based on different physical principles, and for this reason it is difficult to analyze resins and pigments simultaneously. For these reasons, we have performed Py-GC/MS measurements of red-, yellow-, and green-colored lacquer films applied to lacquerware items to assess the feasibility of simultaneously detecting resin ingredients together with certain pigments. We have also compared our findings to the results of SEM-EDS, X-ray fluorescence spectrometry (XRF), and X-ray diffractometry (XRD) measurements. XRD analysis yielded molecular-level information (information on binding states) regarding mercury (Hg) and iron (Fe); however, the information obtained for arsenic (As) and sulfur (S) was insufficient. In contrast, Py-GC/MS analyses simultaneously yielded molecular-level information on arsenic (As) and sulfur (S) together with detection of the primary ingredients of the lacquer. For this reason, it shows that several pieces of information is provided easily and quickly when the colored lacquer cultural heritage is measured using the Py-GC/MS method.

1. Introduction

Studies of valuable cultural heritage generally call for non-destructive methods of analysis. However, lacquered cultural heritage items are compound objects that generally incorporate a variety of distinct materials, including lacquers, wood, paper, cloth, soil, minerals, and metals. Such studies necessarily involve a combination of multiple analytical methods: observations using various microscopy techniques to assess an artifact's state of deterioration and reveal its internal structure; analysis of organic substances to assess whether or not a given object contains lacquers, oils, or similar ingredients; and elemental analysis to identify species of inorganic substances such as pigments or metals used for decoration. Most of these analytical methods involve destructive analyses, and the precious nature of cultural heritage makes it essential to restrict the quantity of measurement samples subject to destructive analyses to the absolute minimum required. This poses a challenge for methods of destructive analysis, to extract the greatest possible amount of information from the smallest possible volume and quantity of measurement samples.

The lacquer used in lacquerware is an organic substance and a resin. A general-purpose tool that has long been used to analyze organic substances of this type is *Fourier-transform infrared spectroscopy* (FR-IR). However, when the measurement sample is a mixture, or otherwise exhibits a complicated composition, FT-IR methods not only may fail to identify certain components but may also pose the risk of erroneous analysis. For this reason, the *pyrolysis-gas chromatography-mass spectrometry* (Py-GC/MS) method is increasingly being used to analyze organic substances. The use of Py-GC/MS to analyze lacquer films allows the identification of chemical species in lacquer resins that cannot be identified in analyses



(a) Top

(b) Underside

Figure 1: Photographs of a *Kamakura-bori* tray decorated with a peony design (diameter: 31 cm); (a) top, (b) underside. Locations of collected samples (○) are indicated.

using IR spectra [1]. For inorganic analysis of ingredients, such as inorganic pigments blended into paint layers or metallic powders and foils used to decorate lacquerware, many X-ray-based elemental analyses have been performed. However, the analyses of samples with multilayered structures that have been reported to date suffer from one or more of the following drawbacks. A first problem is the depth to which nondestructive X-ray analysis can probe beneath the surface layers. To remedy these difficulties, an analytical method based on *scanning electron microscopy augmented by energy dispersive X-ray spectrometry* (SEM-EDS) was proposed. This analytical method allows measurements that are pinpointed within individual layers. However, SEM-EDS requires the measurement sample to be rigidly fixed in place, and the carbon tape or other materials used to achieve this purpose may interfere with other analyses. This is the second of the problems mentioned above.

Understanding the material composition of lacquered artifacts of this sort requires the use of multiple analytical methods to gather data; full analyses can require large amounts of time and may be highly inefficient. For this reason, analytical methods that yield multiple types of information easily and rapidly from precisely targeted specific measurement sites are highly desirable. However, organic analysis and inorganic analysis are generally based on different physical principles, and for this reason it is difficult to analyze resins and pigments simultaneously. For these reasons, we have focused on analyses using Py-GC/MS, which allows analysis of tiny samples and offers outstanding ability to separate and identify sample constituents. A team of Italian researchers recently reported that Py-GC/MS could be used to detect the presence of mercury [2] and arsenic sulfide from analysis of analytical reagents [3]. According to their results, Py-GC/MS analysis can offer molecular information (information on binding states) on arsenic (As) and sulfur (S). However, although the use of Py-GC/MS to detect mercury in lacquerware has been reported [2], no report has offered evidence to support the use of Py-GC/MS to detect arsenic in lacquerware [4, 5]. Arsenic sulfide has been used since antiquity as a yellow coloring agent, and it has a history of use in painting and craftwork. In the 1970s, arsenic sulfide was determined to be poisonous for nonpharmaceutical uses; its production as a pigment for lacquerware was terminated in Japan, and arsenic-containing yellow pigments for lacquerware were destroyed. As a result, notwithstanding the use since antiquity of arsenic sulfide as a lacquerware pigment, the detailed composition of yellow pigments containing arsenic sulfide remains unclear. We have obtained yellow lacquerware pigments used in ancient times by craftsmen in the Japanese city of Wajima; after analyzing 7 varieties of these pigments, we concluded that all were sulfur compounds containing no arsenic. Among these was the yellow pigment clearly identified as orpiment, but this was not arsenic sulfide. This demonstrates that information on arsenic sulfide used as a lacquerware pigment was mixed in those days. The continuing ambiguity surrounding the characteristics of the yellow pigments used in the lacquerware production of the past is problematic from the standpoint of the preservation of lacquerware cultural heritage.

For these reasons, we have performed Py-GC/MS measurements of red, yellow, and green-colored lacquer films applied to lacquerware items to assess the feasibility of simultaneously detecting resin ingredients together with certain pigments. We have also compared our findings to the results of SEM-EDS, X-ray fluorescence spectrometry (XRF), and X-ray diffractometry (XRD) measurements. The results we report demonstrate that a single measurement of a small-volume sample extracted from a pinpointed region of an artifact can simultaneously yield information on organic components and some inorganic components.

2. Materials and Methods

2.1. Samples. The test item was a tray in the *Kamakura-bori* style decorated with a peony pattern colored with red, yellow, and green pigments, and samples were taken of each of the colors. Figure 1 shows the front and back surfaces of the full artifact, as well as the sampling points. The samples taken from the yellow, green, and red regions of the craft work for analysis are hereafter referred to as Samples Y, G, and R, respectively. *Kamakura-bori* is a style of Japanese craftsmanship in which lacquer coatings were painted in layers onto a design carved from wood; in this lacquerware tradition, ingredients such as *makomo* (wild rice) were used to accentuate the shading due to surface roughness in carved wood. This craft work uses both the top and the underside surfaces to express a carved image of a peony flower. The pistil at the center of the flower is colored yellow, while the leaves and other regions are colored green. Careful inspection of the leaf regions of the underside surface reveals a deep green color used to indicate the base of each leaf, which evolves gradually into a green color strongly inflected with yellow coloring as one proceeds out to the tip of the leaf; this lends the impression of a three-dimensional depiction of a leaf.

2.2. Analysis Methods

2.2.1. Surface and Cross-Section Observations. Surface observation was conducted using a digital camera attached to an optical microscope (BX51 TRF-6 [D] and DP73-CU [D], resp., Olympus Co. Ltd.). Cross-section observations were conducted using a digital camera attached to an optical microscope (KH-770 and MX (G)-10C: OL-140II, HIROX Co. Ltd.). The relevant polished cross-sections were characterized by optical microscopy in order to examine all layers comprising the tray. Each sample was embedded in epoxy resin. After the epoxy resin had completely hardened, the surfaces of the embedded samples were ground flat and polished with wet sandpaper.

2.2.2. XRF. X-ray fluorescence spectrometry (XRF) was performed using a NEX CG (polarized optics energy dispersive XRF, Rigaku Ltd.); Pd radiation was used for the X-ray tube. Secondary targets of two types were used, RX9 for sulfur (S) and molybdenum (Mo) for iron (Fe), arsenic (As), and mercury (Hg). The SDD detector was used.

2.2.3. SEM-EDS. The inorganic materials in cross-sectional samples of the three colored areas were characterized by SEM-EDS. The SEM-EDS analysis was performed using a SEM (JSM-6610LV, JEOL Ltd.) coupled with an energy dispersive spectrometer (NSS 312E, Thermo Fisher Scientific K.K.). The accelerating voltage was set at 15 kV and the working distance at 10 mm. The range of qualitative analyses included elements in the periodic table ranging from boron to uranium. Analyses of two types of small-volume samples were conducted to ensure a cross-check on the results: (1) the outermost surface and (2) cross-sectional samples for each layer. In both cases, conducting carbon tape was used to fix the sample to the sample stage and analyses were conducted without evaporative coating.

2.2.4. XRD. XRD was performed using a diffractometer (UltimaIV, Rigaku Ltd.) equipped with a sample vertical goniometer (radius of 285 mm) and Cu Kα radiation with a Ni filter operated at 40 kV and 50 mA. Conventional Bragg-Brentano focusing geometry was used in combination with a 1/3° divergence slit, an 8 mm scattering slit, and a 13 mm receiving slit. A one-dimensional silicon strip detector (D/teX Ultra, Rigaku Ltd.) was used.

Table 1: Results of surface analysis by XRF.

Sample	Color	Elements
Y	Yellow	S, Fe, As
G	Green	S, Fe, As, Hg
R	Red	S, Fe, As, Hg

2.2.5. Py-GC/MS. Very small samples were taken from each of the color regions of the craft work and analyzed by Py-GC/MS. Py-GC/MS measurements were carried out using a vertical microfurnace-type pyrolyzer (PY-2020iD, Frontier Lab. Co. Ltd.) with a 6890N/5975 GC/MS system (Agilent Technologies, Ltd.). A stainless steel capillary column (30 m, 0.25 mm I.D.) coated with 0.25 μm Ultra Alloy PY-1(MS/HT) (100% methyl silicone) was used for the separation. The sample (0.5 mg) was placed in a stainless steel sample cup (Eco-cup, Frontier Lab. Co. Ltd.). The cup was placed on top of the pyrolyzer at near ambient temperature. The sample cup was introduced into the furnace when the furnace at 500°C and the temperature of the pyrolyzer interface and injector were set at 280°C, and then the temperature program of the gas chromatograph oven was started. The gas chromatograph oven was set at 40°C and held for 2 min, then programmed to provide a constant temperature increase at 12°C/min from 40°C to 320°C, and held for 10 min at 320°C. The flow rate of the helium gas was 1 mL/min. All pyrolysis products were identified by mass spectrometry. The mass spectrometry ionization energy was 70 eV (EI-mode), the cycle time was 1.94 scans per second, and the mass range was 29–800 m/z. Collected data were processed and analyzed by MSD ChemStation Software (Agilent Technologies, Ltd.).

3. Results and Discussion

3.1. Surface Analysis

3.1.1. Observing the State of the Outermost Surface. Figure 2 shows magnified microscope images depicting the state of the outermost surface of each of the three color regions. Samples Y and R exhibited more surface roughness than Sample G, indicating that painted surfaces were in a slightly roughened state. We attribute this to the fact that, in ordinary use, the front surface of a tray receives more light illumination than the back surface. Indeed, lacquer films have the disadvantage of being vulnerable to infrared light, and lacquer films tend to decompose due to the influence of ultraviolet radiation.

3.1.2. XRF. Table 1 summarizes the results of XRF measurements. While sulfur (S), iron (Fe), and arsenic (As) were detected in Sample Y, sulfur (S), iron (Fe), arsenic (As), and mercury (Hg) were detected in Samples G and R. From these

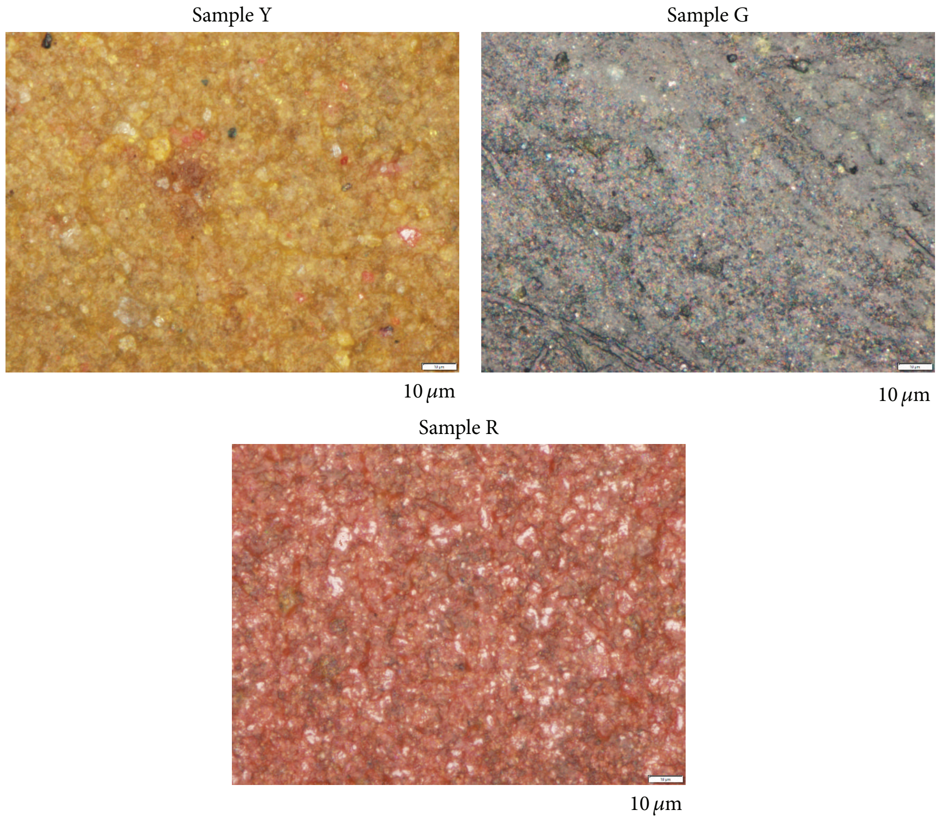


Figure 2: Microphotographs showing surface conditions of Samples Y, G, and R.

Table 2: Results of surface analysis by SEM-EDS.

Sample	Color	Elements
Y	Yellow	C, O, Al, Si, S, Ca, K, Fe, As
G	Green	C, O, Si, S, Cl, K, Ca, Fe, As, Hg
R	Red	C, O, Al, S, Fe, Cu, As, Hg

findings, we surmise that arsenic sulfide was used as a yellow pigment, while cinnabar (mercury sulfide, HgS) was used as a red pigment. However, binding information could not be obtained in cases where sulfur (S) and arsenic (As) formed compounds; thus we are unable to state definitively that the compound was orpiment (As_2S_3).

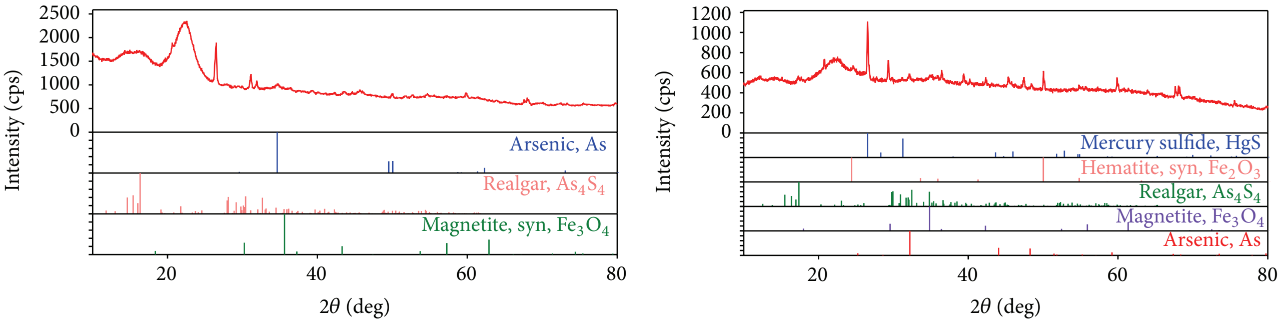
3.1.3. SEM-EDS. Table 2 lists the elements detected by SEM-EDS. It was determined with high certainty that Sample Y contained sulfur (S), iron (Fe), and arsenic (As); Sample Y was also believed to contain trace amounts of aluminum (Al), silica (Si), potassium (K), and calcium (Ca). It was determined with high certainty that Sample G contained sulfur (S), iron (Fe), arsenic (As), and silica (Si); Sample G was also believed to contain trace amounts of chlorine (Cl), potassium (K), calcium (Ca), and mercury (Hg). Sample R showed strong spectra of sulfur (S), arsenic (As), and mercury (Hg); also detected in trace amounts in Sample R were aluminum (Al), iron (Fe), and copper (Cu).

3.1.4. XRD. Qualitative analysis for elements and crystalline phases of all samples are shown in Table 3. In Sample Y, sulfur (S), iron (Fe), and arsenic (As) were detected, and realgar (As_4S_4), arsenolite (As_2O_3), and magnetite (Fe_3O_4) were identified. In Sample G, S, Fe, As, and Hg were detected, and arsenic (As), realgar (As_4S_4), arsenolite (As_2O_3), hematite (Fe_2O_3), magnetite (Fe_3O_4), and cinnabar (HgS) were identified. In Sample R, S, Fe, As, and Hg were detected; arsenic (As) and cinnabar (HgS) were identified. In Sample Y, cinnabar (HgS) occurred mainly in crystalline form/in the crystalline phase.

Figure 3 shows the results of crystal analyses of Samples Y, G, and R. The analysis of Sample R was straightforward, but the analyses of Samples Y and G were considerably more complicated. Indeed, in the crystal analysis of Samples Y and G, it was necessary to inspect the spectra with proper consideration of the possibility of ingredients that might have been used as mineral pigments in the lacquerware tradition; this makes the analysis more difficult. Kitano performed XRD analyses of arsenic sulfide contained in unearthed lacquerware items and showed that the detection rate for arsenic sulfide was lower for green lacquer than for yellow lacquer [6]. In the present case, assessing the realgar (As_4S_4) thought to be contained in Samples Y and G amounts to the question of whether or not the sample contains a very small quantity of the substance; we were unable to compare the quantities present in the two samples. A comparison with the results of Kitano's measurements is difficult because

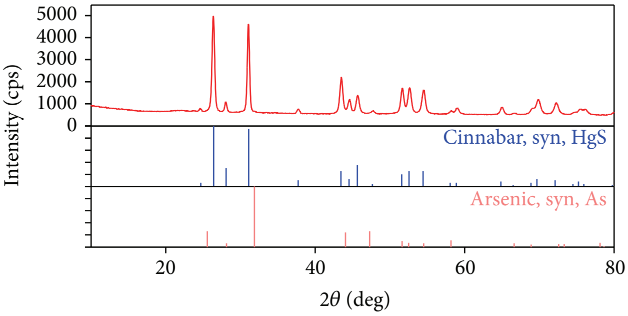
Table 3: Results of surface analysis by XRD.

Sample	Color	Crystalline phases
Y	Yellow	Arsenic (As), realgar (As_4S_4), magnetite (Fe_3O_4)
G	Green	Arsenic (As), realgar (As_4S_4), hematite (Fe_2O_3), magnetite (Fe_3O_4), cinnabar (HgS)
R	Red	Arsenic (As), cinnabar (HgS)



(a) Sample Y

(b) Sample G



(c) Sample R

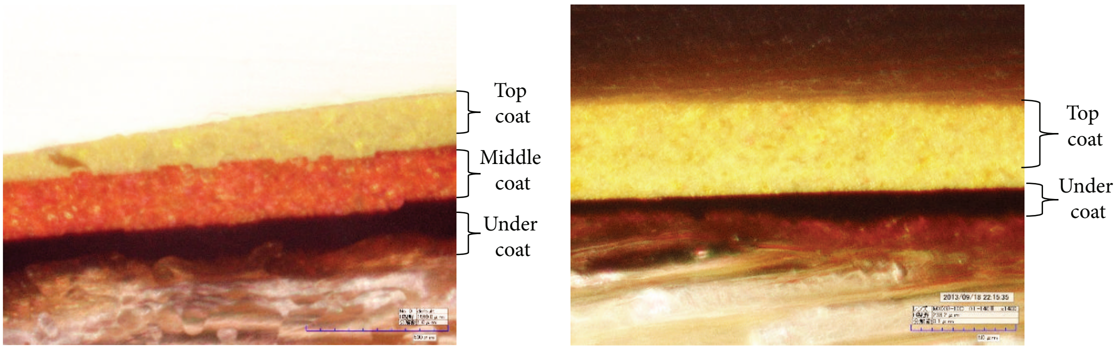
Figure 3: XRD crystal diffraction experiments.

the detailed methods of those measurements are unclear; it is possible that the measurement sample was ground into a powder to enable the measurements. The present study is concerned with nondestructive measurements, and hence we do not grind measurement samples into powders; still, our finding that XRD spectra are more complicated when the lacquer sample contains arsenic sulfide is in good agreement with the findings reported by Kitano. In XRD measurements, determining the presence of arsenic sulfide is more difficult for samples of lacquer mixtures than for individual samples of arsenic sulfide (single-body mineral samples). Thus, although the question is somewhat dependent on the quantity of arsenic sulfide contained in the sample, in general it is best to avoid reliance on XRD measurements alone when determining whether or not oriental lacquer films contain arsenic sulfide.

3.2. Cross-Sectional Analysis

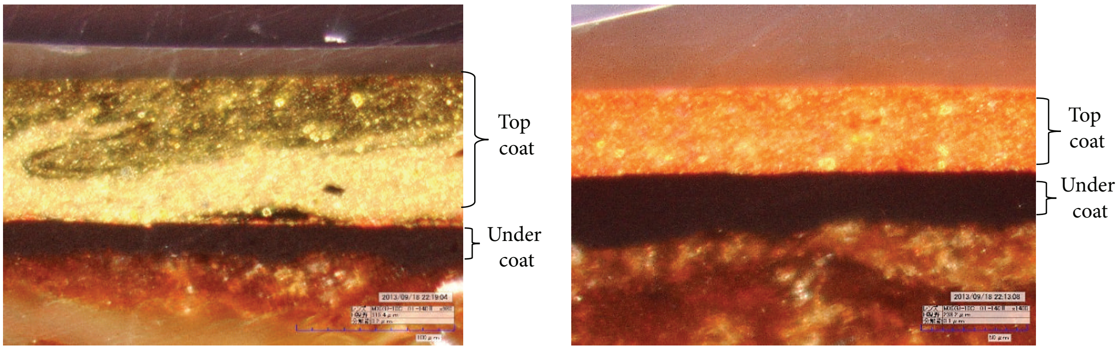
3.2.1. Cross-Sectional Observations. Figure 4 shows microscope images of cross-sectional samples from the various color regions. Images (a) and (b) are both of cross-sectional samples taken from Sample Y, while images (c) and (d) are cross-sectional samples of Samples G and R, respectively. All of these samples included an underlayer of black paint.

Comparing the two images of cross-sectional samples taken from Sample Y (Figures 4(a) and 4(b)), we see that although the uppermost painted layer in the Sample Y region is yellow in color, some samples taken from this region—depending on the site from which the sample was collected—contain red paint films as well. No red paint film lying beneath the yellow paint film was observed for the sample collected from the point closer to the center. We conclude that samples exhibiting red paint films were those taken from regions corresponding to petals of the peony; these regions surround the central region of the flower, which is covered in yellow paint. Presumably the artist was not excessively meticulous when painting the artifact, resulting in a coating of yellow paint. Inspection of the image of Sample G in Figure 4(c) reveals a yellow-painted region lying above a black paint film and marbled with regions of strong green and dark green coloration. This indicates that two shades of green paint were blended on the artifact before the wet paint solidified to form paint films. As seen in Figure 1, the dark green color present at the petiole of the leaves turns gradually into a green color with a strong yellow tint as one traces the leaf to its tip, conveying



(a) Sample Y

(b) Sample Y



(c) Sample G

(d) Sample R

FIGURE 4: Cross-sectional photos of Sample Y (a) and (b), Sample G (c), and Sample R (d).

a sense of the three-dimensional nature of the leaf; we believe that this explains the cross-sectional structure observed in Figure 4(c). The image of Sample R in Figure 4(d) shows a red paint film lying atop a black paint film. The upper paint layer (the red layer) is dotted with yellow particles large in size compared to the red particles, suggesting the possibility that red and yellow pigments were blended. This was most likely done to yield a bright orange color for the petals of the peony that this tray seeks to depict.

3.2.2. SEM-EDS. Figure 5 shows the results of elemental mappings conducted via SEM-EDS on the cross-sectional samples. Analysis of the red-colored layers observed in Figures 4(a) and 4(d) revealed that the same elements were detected in these two samples. For this reason, Figure 5(a) shows the results of analysis of the cross-sectional sample of Figure 4(a). Figure 5(b) shows the results of analysis of the cross-sectional sample of Figure 4(c). No elements originating from pigments were detected in the black-painted underlayers. The yellow-, green-, and red-painted layers observed in Figure 4 were all observed to contain elements believed to originate from pigments.

Inspecting the element mapping of the Y layer in Figure 5(a), we see that the points at which arsenic (As) is present roughly coincide with the points at which sulfur (S) is present, strongly suggesting the presence of arsenic sulfide. In contrast, in the R layer of Figure 5(a), the points at which arsenic (As) and sulfur (S) are present do not agree to the same extent; on the other hand, the points at which mercury (Hg) and sulfur (S) are present agree quite well. We thus conclude that the R layer of Figure 5(a) contains only small quantities of arsenic sulfide; instead, mercury sulfide constitutes the majority of the pigment in this region. Looking at the element mapping of the G layer in Figure 5(b), we see a lesser presence of arsenic sulfide than in the Y layer of Figure 5(a). Mercury (Hg) is also scattered throughout this region.

3.3. Chemical Analysis

3.3.1. Analysis of Resins via Py-GC/MS. To identify the resins used as paints, we performed Py-GC/MS data analysis. Figure 6 shows an ion chromatogram (m/z 108)—extracted from the *total ion chromatogram* (TIC)—that originates from alkylphenol and is used in the principle component analysis of oriental lacquer. Essentially identical pyrolysis products were observed from all samples (Samples Y, G, and R). Our identification of these pyrolysis products allows us to determine [7, 8] the substance in question as *Toxicodendron vernicifluum* (the academic name for a tree) for which urushiol is a primary component. *T. vernicifluum* is an oriental lacquer tree cultivated in Japan, China, and Korea. It shows that the paint applied to all colored regions of the *Kamakura-bori* tray used sap tapped from *T. vernicifluum*. The substance detected with the greatest intensity camphor may be used as a diluting agent when applying coats of oriental lacquer. Because the wood carving of our sample exhibits surface roughness, the application of only an impasto coat of oriental lacquer would create a high risk of paint defects. We surmise

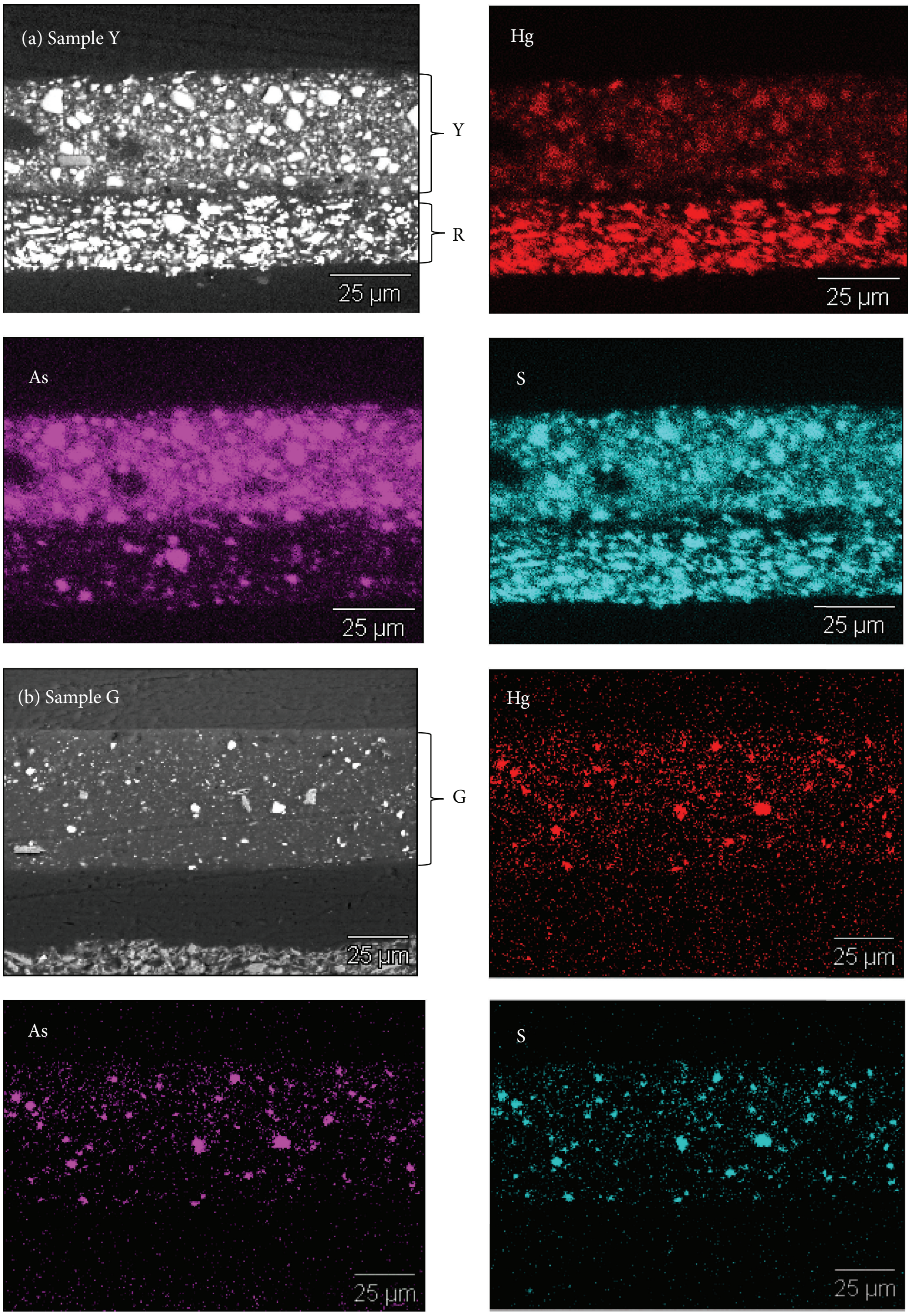


Figure 5: Cross-sectional element mapping experiments. (a) Sample Y, (b) Sample G.

that camphor was used to dilute the oriental lacquer applied to the item to mitigate this risk.

3.3.2. Py-GC/MS Analysis of Pigments. To investigate the ways in which S, As, and Hg—which may have been used as pigments—were present in our samples, we analyzed the results of Py-GC/MS analyses.

(1) Investigation of Sulfur (S) and Arsenic (As). Samples Y and G gave nearly identical results by Py-GC/MS analysis; the results of Sample R were also similar but of weaker intensity. Figure 7 collects the results for Sample Y. Figure 7(a) shows the TIC, while Figures 7(b), 7(c), and 7(d) show the mass spectra near the high-intensity Peaks B, C, and D labeled in Figure 7(a). The mass spectrum of Peak B is consistent with

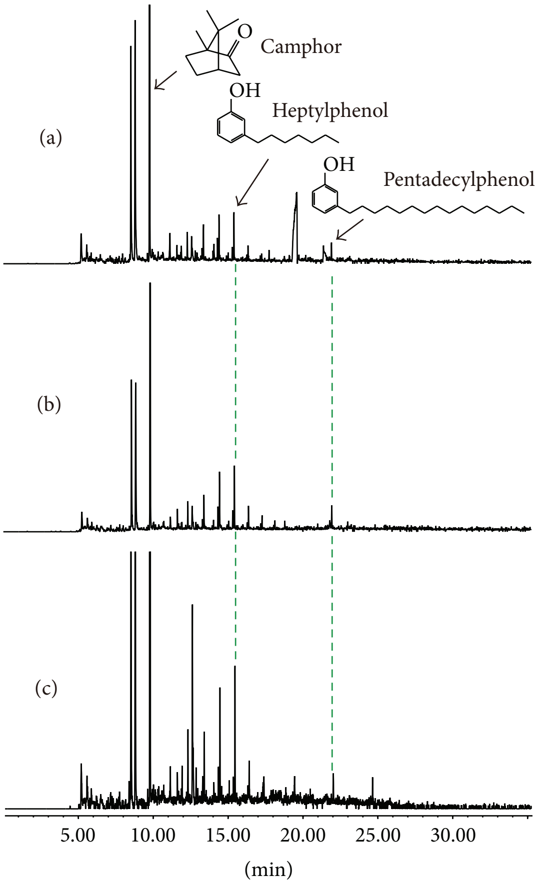


Figure 6: Ion chromatograms of the m/z 108 fragment ion of the alkylphenol of Sample Y (a), Sample G (b), and Sample R (c).

As_4 (MW 300) and shows a typical fragmentation by sequential loss of As atoms (Figure 7(b)). This agrees with the results reported by Chiavari et al. [3, 9]. In the mass spectrometry analysis of Sample Y, elemental As was detected at m/z 74.9 for 1x As, m/z 149.8 for 2x As, m/z 224.7 for 3x As, and m/z 299.6 for 4x As. Chiavari et al. reported that the presence of As_4 indicates the use of orpiment (As_2S_3) as a yellow pigment [3]. We performed Py-GC/MS measurements of orpiment (As_2S_3) and realgar (As_4S_4) from commercial suppliers. Measured results for the mineral samples of orpiment reveal mass spectra identical to those observed near Peaks B and C (Figures 7(b) and 7(c)). However, the As_3S_3 and As_4S_4 features observed near Peak D (Figure 7(b)) were not seen for the orpiment mineral sample. In contrast, the mass spectra detected for the mineral sample of realgar contained the As_3S_3 and As_4S_4 features seen near Peak D (Figure 7(b)). On the other hand, none of the samples we measured indicated As_2S_3 (MW 246) in their mass spectra. Chiavari et al. did not perform measurements with As_2S_3 as a standard reagent [3], while the mass spectra reported by Ma et al. [4] were not able to confirm a mass spectrum of As_2S_3 but nonetheless identified the substance as orpiment (As_2S_3). In the future, further analyses focusing on the binding states of arsenic (As) and sulfur (S) are necessary to investigate the detailed composition of yellow pigments containing arsenic sulfide.

Figure 8 shows ion chromatograms with m/z 300 (solid curves) and m/z 427.6 (dashed curves). Results for Sample Y are shown in Figures 8(a) and 8(b), and results for Sample G are shown in Figures 8(c) and 8(d). Samples Y and G both contained As_4, corroborating the results obtained by both XRD analysis and SEM-EDS mapping analyses, which suggested the presence of isolated arsenic (As). As_4 was also strongly detected in Sample R. While As_4S_4 was strongly detected in Sample Y, irrespective of the position on the artifact from which the sample was collected for analysis, the intensity of the As_4S_4 that was detected was variable in Sample G. The reason for this disparity may be due to the varying amounts of differently colored lacquer that were blended together when the artifact was made; for example, in order to elicit stronger coloration in the green-colored region of Sample G, yellow-green lacquer containing a strong yellow tint was blended with a deep green lacquer containing a weak black-inflected yellow tint to produce the two distinct lacquer layers that are visible in the cross-section shown in Figure 4(c). Consequently, the intensity with which As_4S_4 was detected varied depending on the precise location from which the material was collected for Py-GC/MS analysis.

Most reports of scientific investigations involve the use of X-ray techniques to confirm the presence of the elements arsenic and sulfur—findings which are habitually attributed to As_2S_3 (orpiment) despite the absence of molecular-level information. Many studies in the field of cultural artifact research have used methods of Raman spectroscopy to identify molecular-level signatures of arsenic sulfide [10]. However, in the case of lacquerware artifacts, the existence of light emission from lacquer-coating layers prevents the collection of analyzable spectra, and thus Raman spectroscopy cannot be used for such objects. On the other hand, these findings showed that information on binding states, which is difficult to infer based on XRD analysis, can easily and rapidly be obtained from Py-GC/MS analysis. Indeed, depending on the analytical methods employed, a single measurement can yield a variety of information regarding the use of pigments.

(2) Investigation of Mercury. Many naturally occurring elements are composed of multiple stable isotopes of different mass numbers [11]. For mercury, there are 7 stable isotopes, and the use of Py-GC/MS allows the stable isotopes of mercury to be detected with ease [2]. The total ion chromatography (TIC) and the m/z 202 ion chromatograms of standard HgS powder are shown in Figure 9 together with mass spectra and isotope ratios inset. The values listed in the table of isotope ratios were derived as follows. Following the literature by taking the ^{198}Hg isotope to be 100, the isotope ratios of ^{196}Hg, ^{198}Hg, ^{199}Hg, ^{200}Hg, ^{201}Hg, and ^{204}Hg were each computed from the mass spectra, and the measured values were compared to values available in the literature. From the TIC peak in Figure 9, a total of 6 isotope peaks were detected, with m/z 202 being the primary peak (Figure 9 inset). The isotope ratios are close to those reported in the literature, whereupon we conclude that these mass spectra originate from mercury [12].

The TIC and the m/z 202 ion chromatograms of Sample R are shown in Figure 10. Because the mercury isotope peaks

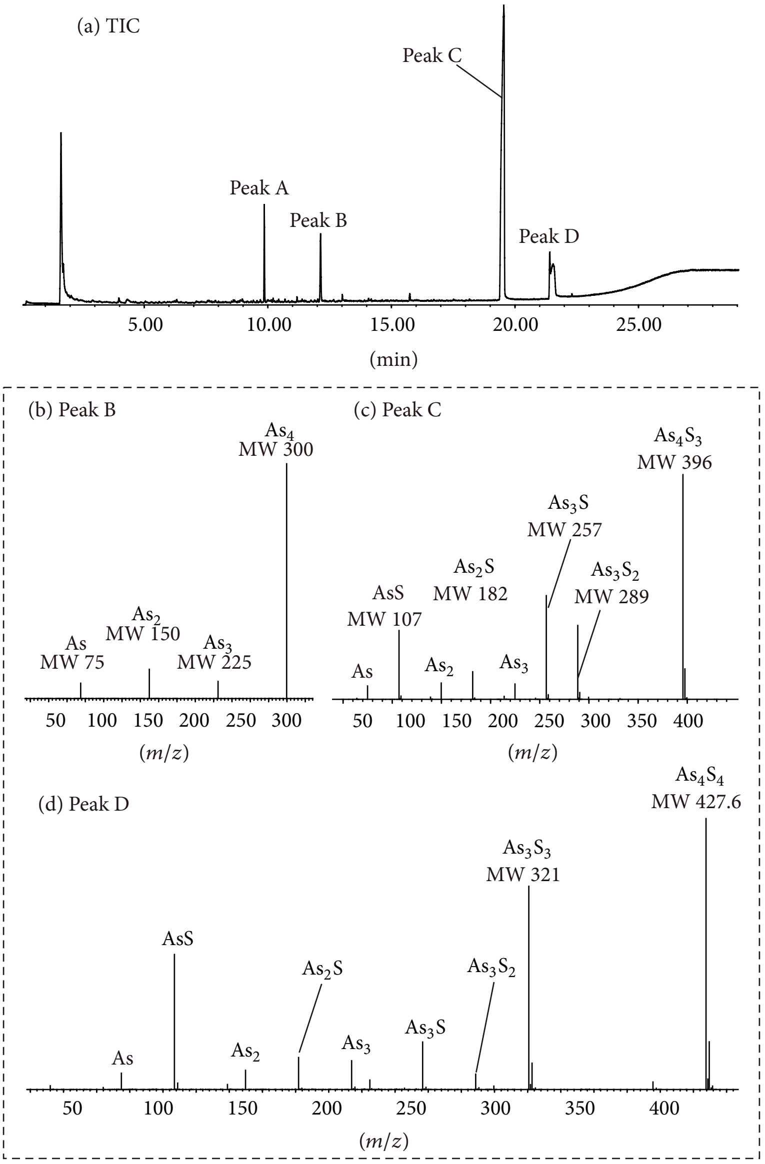


Figure 7: Py-GC/MS analyses of Sample Y. (a) TIC, (b) ion chromatograms of Peak B, (c) ion chromatograms of Peak C, and (d) ion chromatograms of Peak D.

were detected with greatest intensity in Sample R, Figure 10 shows results of measurements on Sample R. Isotope peaks were not detected for Sample Y. On the other hand, for Sample G, isotope peaks similar to those of Sample R but of weaker intensity were detected. The results of these measurements agree well with the results of XRF, SEM-EDS, and XRD analyses. Inspecting the table of isotope ratios in the inset of Figure 10, we see results that lie closer to literature values than the measured values in the inset of Figure 9. However, in Figure 9, which measured powders of a mercury sulfide (HgS) reagent, a strong spectrum was observed at 7 minutes and 30 seconds; in contrast, for Sample R, a strong spectrum was observed at 11 minutes and 30 seconds. Because we did not make any significant modifications to the state of the measurement apparatus, the origin of this discrepancy in the retention time is unclear and remains a question for future work.

4. Conclusions

Upon comparing the results of the XRF and XRD analyses, SEM-EDS measurements of the outermost layers and the cross-sectional layers, and Py-GC/MS measurements, we arrive at the following conclusions.

(1) Observations regarding Arsenic Sulfide. The results of elemental analyses conducted via XRF and SEM-EDS afford knowledge of the presence of As and S. By further combining the SEM-EDS-based elemental mapping analyses for As and S, we may determine whether or not the sites at which these

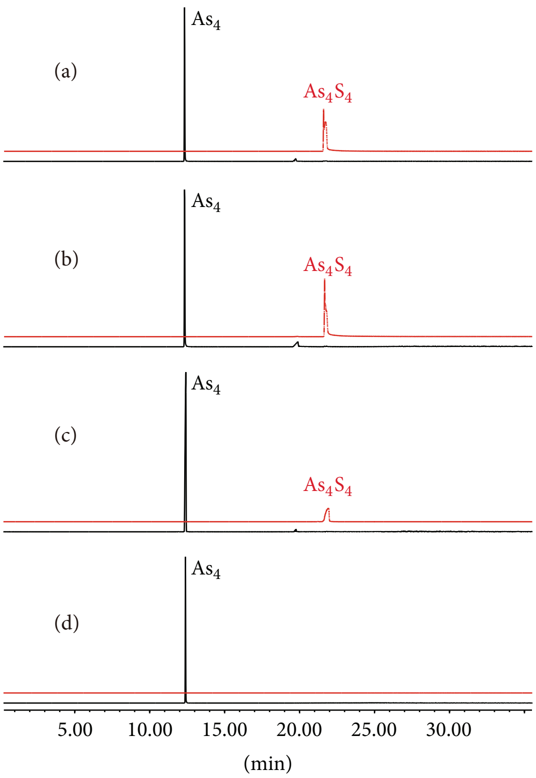
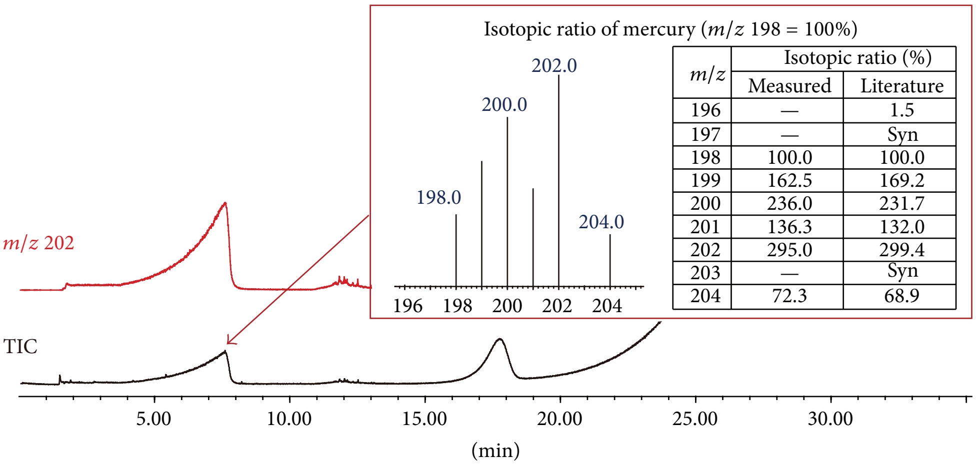


FIGURE 8: Ion chromatograms of the m/z 300 and m/z 427.6 fragment ions of Sample Y (a) and (b), Sample G (c) and (d).

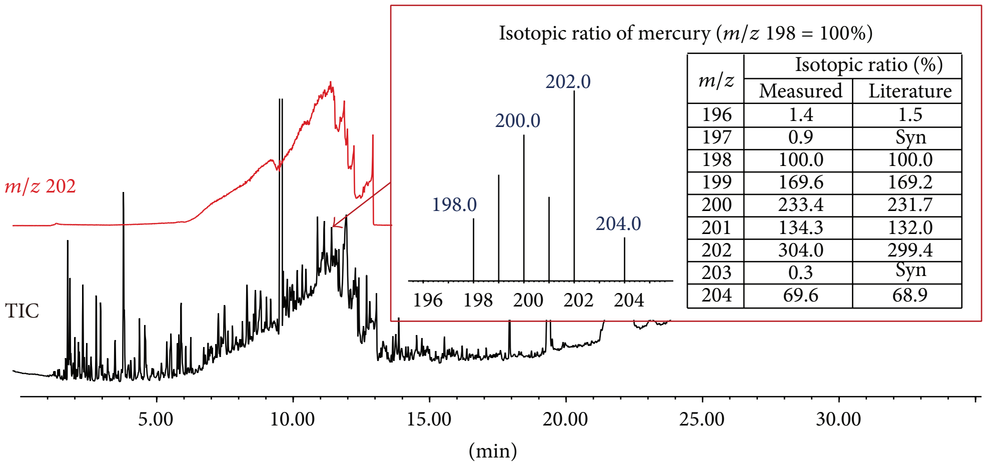


m/z	Isotopic ratio (%)	
	Measured	Literature
196	—	1.5
197	—	Syn
198	100.0	100.0
199	162.5	169.2
200	236.0	231.7
201	136.3	132.0
202	295.0	299.4
203	—	Syn
204	72.3	68.9

FIGURE 9: TIC and ion chromatograms of the m/z 202 fragment ion of standard HgS powder.

two elements are present coincide. However, it is difficult to pinpoint the binding configuration of the As and S atoms. The use of XRD measurements allows determination of the binding states of As and S; however, in cases involving mixtures with lacquer, the peaks that allow detailed analysis are difficult to observe, and it is challenging to confirm the presence of substances. In contrast, the use of Py-GC/MS readily allows determination of specific binding states of As and S—such as As_4S_4—whereupon the presence of such substances may be rapidly discovered.

(2) Observations regarding Substances Other Than Arsenic Sulfide. We were able to verify the presence of mercury via elemental analyses using XRF, SEM-EDS, and XRD, while Py-GC/MS identified mercury by detecting the mass spectra of its isotopes. We were able to verify the fact that mercury was present in the form of cinnabar (mercury sulfide) from the results of XRD analyses. The presence of iron was confirmed by XRF, SEM-EDS, and XRD. The results of XRD analyses indicated the possibility that iron was present in the form of hematite (Fe_2O_3) or magnetite (Fe_3O_4).



m/z	Isotopic ratio (%)	
	Measured	Literature
196	1.4	1.5
197	0.9	Syn
198	100.0	100.0
199	169.6	169.2
200	233.4	231.7
201	134.3	132.0
202	304.0	299.4
203	0.3	Syn
204	69.6	68.9

Figure 10: TIC and ion chromatograms of the m/z 202 fragment ion of Sample R.

Therefore, Py-GC/MS analyses simultaneously yielded molecular-level information on arsenic (As) and sulfur (S) together with detection of the primary ingredients of the lacquer. We were also able to confirm the presence of mercury (Hg), in agreement with the results of previous work [2]. These findings demonstrate that Py-GC/MS is capable of identifying the presence of arsenic (As), sulfur (S), and mercury (Hg), even when mixed together in a lacquer film; thus Py-GC/MS may be used for simultaneous analysis of organic and inorganic substances.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References

[1] R. Lu, Y. Kamiya, and T. Miyakoshi, “Applied analysis of lacquer films based on pyrolysis-gas chromatography/mass spectrometry,” *Talanta*, vol. 70, no. 2, pp. 370–376, 2006.

[2] G. Chiavari and R. Mazzeo, “Characterisation of paint layers in Chinese archaelogical relics by pyrolysis-GC-MS,” *Chromatographia*, vol. 49, no. 5-6, pp. 268–272, 1999.

[3] G. Chiavari, D. Fabbri, and G. C. Galletti, “Pyrolysis/gas chromatography/mass spectrometry of arsenic inorganic compounds,” *Rapid Communications in Mass Spectrometry*, vol. 9, no. 7, pp. 559–562, 1995.

[4] X. M. Ma, R. Lu, and T. Miyakoshi, “Application of pyrolysis gas chromatography/mass spectrometry in lacquer research: a review,” *Polymers*, vol. 6, no. 1, pp. 132–144, 2014.

[5] T. Honda, R. Lu, M. Yamabuki et al., “Investigation of Ryukyu lacquerwares by pyrolysis-gas chromatography/mass spectrometry,” *Journal of Analytical and Applied Pyrolysis*, 2014.

[6] N. Kitano, *The Industrial Technique and the Organization of Modern Lacquer Ware*, Yuzankaku, 2005, (Japanese).

[7] N. Niimura and T. Miyakoshi, “Characterization of natural resin films and identification of ancient coating,” *Journal of the Mass Spectrometry Society of Japan*, vol. 51, no. 4, pp. 439–457, 2003.

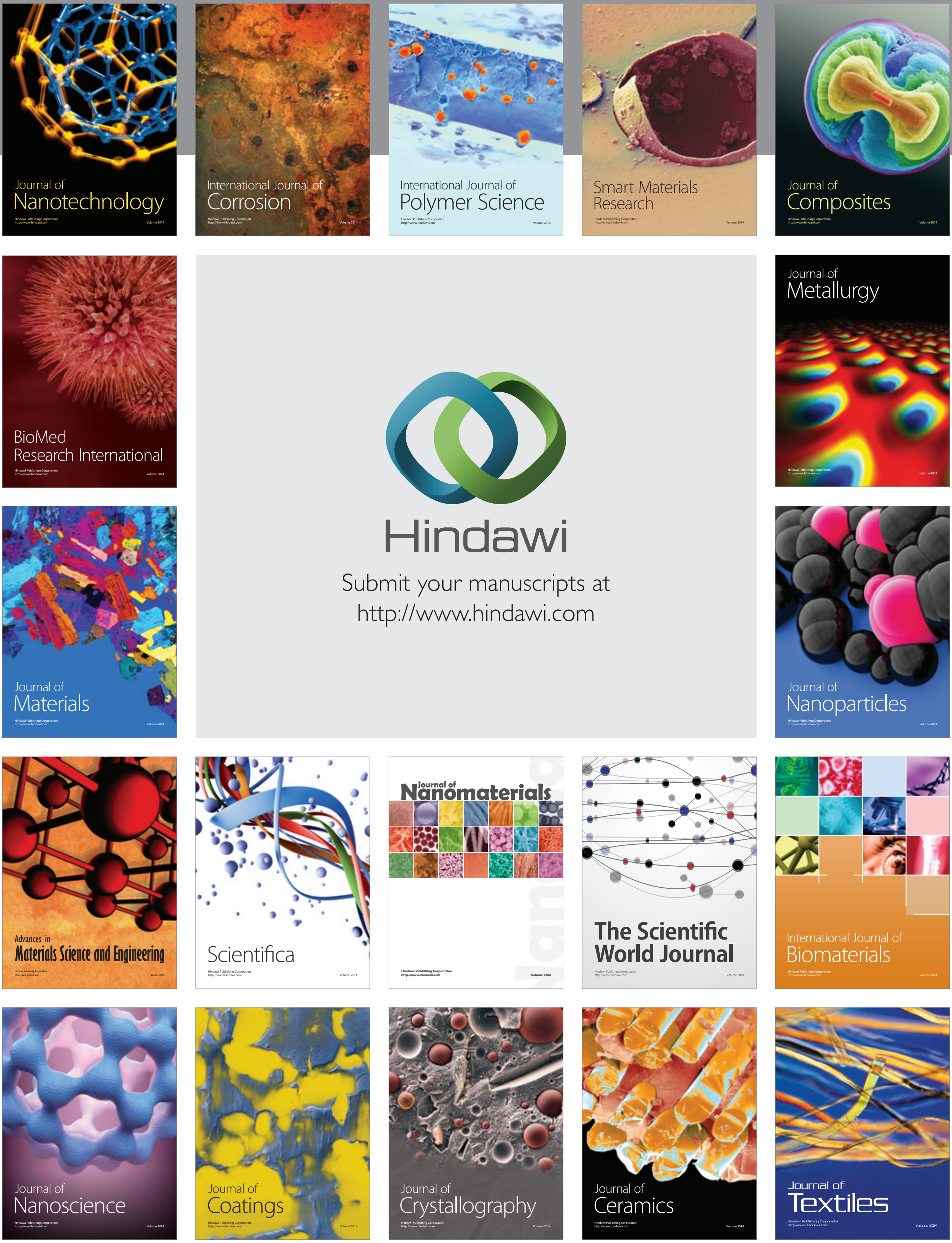
[8] R. Lu, Y. Kamiya, and T. Miyakoshi, “Preparation and characterization of *Melanorrhoea usitata* lacquer film based on pyrolysis-gas chromatography/mass spectrometry,” *Journal of Analytical and Applied Pyrolysis*, vol. 78, no. 1, pp. 172–179, 2007.

[9] G. Chiavari, D. Fabbri, G. C. Galletti, and R. Mazzeo, “Use of analytical pyrolysis to characterize Egyptian painting layers,” *Chromatographia*, vol. 40, no. 9-10, pp. 594–600, 1995.

[10] I. M. Bell, R. J. H. Clark, and P. J. Gibbs, “Raman spectroscopic library of natural and synthetic pigments (pre-~1850 AD),” *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 53, no. 12, pp. 2159–2179, 1997.

[11] J. D. Blum and B. A. Bergquist, “Reporting of variations in the natural isotopic composition of mercury,” *Analytical and Bioanalytical Chemistry*, vol. 388, no. 2, pp. 353–359, 2007.

[12] A. Takeuchi, Y. Shibata, and A. Tanaka, “Mercury (Hg) isotope biogeochemistry,” *Journal of Environmental Chemistry*, vol. 19, no. 1, pp. 1–11, 2009 (Japanese).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