Applied Analysis and Identification of Ancient Lacquer Based on Pyrolysis-Gas Chromatography/Mass Spectrometry

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ABSTRACT: Three lacquer samples taken from a "four-eared" pottery container, which was designated an important National Cultural Property of Japan excavated in 16–17th century ruins of Kyoto City, were analyzed by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and infrared (IR) spectroscopy to determine the source of the lacquer. It is an unexpected result that the lacquer in this pottery container is actually used by *Melanorrhoea usitata*. Alkylbenzene and alkenylbenzene as cleavage pieces of undecylbenzene (MW = 232 g/mol) and undecenylbenzene (MW = 230 g/mol), which are products of the pyrolysis of thitsiol, were detected in all three samples. Moreover, ω-phenylalkylcatechols and ω-phenylalkylphenols, which are the specific components of *M. usitata,* were also detected by Py-GC/MS, suggesting that lacquer sap of *M. usitata* was used by the Japanese people in the 16–17th centuries. In addition, Japanese lacquer culture and the advantages of the Py-GC/MS method for lacquer analysis are discussed in detail. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 897–901, 2010

Key words: cultural; lacquer; thitsiol; pyrolysis

INTRODUCTION

Lacquer has been used in Asian countries for thousands of years as a durable and beautiful coating material.[1–3] Cultural treasures coated with lacquer have maintained their beautiful surfaces without loss of their original beauty for several thousand years.[4,5] Three kinds of lacquer trees grow in the East, *Rhus vernicifera* (Japan, China, and Korea), *Rhus succedanea* (Vietnam), and *Melanorrhoea usitata* (Thailand and Myanmar), and the lacquers are named according to their place of production. The sap of lacquer trees is composed of phenol derivatives, plant gum, glycoprotein, water, and laccase enzyme. The species of lacquer tree and the growing environment are strongly affect the components of the lacquer sap.[6,7] The phenol derivative of *R. vernicifera* is urushiol (MW = 320 g/mol), of *R. succedanea* lacquer is laccol (MW = 348 g/mol), and of *M. usitata* is thitsiol (MW = 348 g/mol).[8–10]

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To better conserve and restore the valuable ancient lacquerware, identification of the kind of lacquer is important. Because lacquer films are insoluble in most solvents, only a few analytical techniques, including solid NMR, FTIR, and XPS, are appropriate. However, most of these conventional techniques are time consuming, demand large amounts of sample, and frequently require several pretreatments (such as solid NMR)[11]; further, they often do not yield clear results (such as FTIR).[12] Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) is effective for analyzing lacquer film because this method can discriminate between the pyrolysis products of a lacquer sample and that of other natural resins, as we reported previously.[13,14] Py-GC/MS analysis is not only a rapid technique but also requires only small amounts of sample and no sample preparation.

Just as "China" is a common name for Chinese ceramics, "Japan" is an old name for Japanese lacquerware, and the technique of lacquer, which sometime also called japanning, involves applying several coats of varnish, which are each subsequently dried and polished, to a substrate such as wood or bamboo. In this sense, the word of "Japan" implies the advanced lacquer culture in Japan. In this study, three lacquer samples from a four-eared jar that is Japanese National Important Cultural Property[15] obtained from 16–17th century ruins

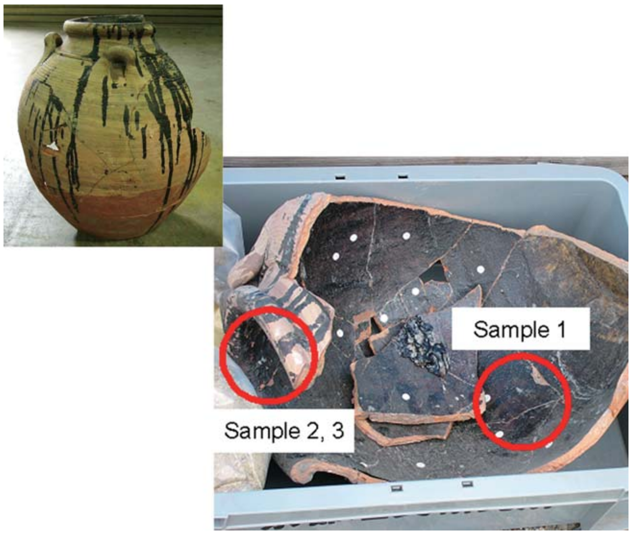

Figure 1 A "four-eared" jar and lacquer samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

(Fig. 1) in Kyoto City were analyzed by Py-GC/MS, and the results were compared with the standard natural lacquer film to determine the identity of the lacquer. In addition, the history, importation route, and technological process of lacquering in Japan are discussed.

EXPERIMENTAL

General

The Py-GC/MS measurements were carried out using a vertical microfurnace-type pyrolyzer PY-2020id (Frontier Lab, Japan), an Agilent 6890N/5975 GC/MS system (Agilent Tech., Santa Clara, CA). A stainless steel capillary column (0.25 mm i.d.× 30 m) coated with Ultra Alloy PY-1 (100% methylsilicone) was used for the separation. The sample (1.0 mg) was placed in a platinum sample cup. The cup was placed on top of the pyrolyzer at near ambient temperature. The sample cup was introduced into the furnace at 500°C, and then the temperature program of the gas chromatograph oven was started. The gas chromatograph oven was programed to provide a constant temperature increase of 20°C per min from 40 to 280°C, then held for 10 min at 280°C. The injection and interface temperature was 280°C, and the flow rate of helium gas was 1 mL/min. The mass spectrometry ionization energy was 70 eV (EI-mode). All the pyrolysis products were identified by mass spectrometry. The infrared (IR) spectra were recorded by a JASCO FTIR 460+ (Jasco, Tokyo, Japan) with the KBr method, and the spectra were acquired at 2 cm^{-1} resolution ranging from 500 to 4000 cm^{-1}.

Materials

Three pieces of lacquer taken from a four-eared jar that is a Japanese National Important Cultural Property obtained from 16–17th century Kyoto ruins were examined by Py-GC/MS. Sample 1 was a piece of lacquer obtained from the side of the vessel, Sample 2 from the mouth of the vessel, and Sample 3, with a slightly reddish black color, from the mouth of the vessel, as shown in Figure 1. The lacquer sap used as the analytical standard for *R. vernicifera* was collected in the suburbs of Aizu Wakamatsu City, Fukushima, Japan, for *M. usitata* was imported from Thailand and purchased from Dohichu Shoten (Osaka, Japan). The lacquer saps were processed by a kurome technique and coated on a glass plates using a film applicator (wet thickness: 76 μm) as we reported previously.[16,17] The Japanese lacquer was dried in a humidity-controlled chamber with a relative humidity of 70% at 20°C for 24 h, and the Thailand lacquer was dried in a relative humidity of 80% at 30°C for 3 days. The films were then removed from the chamber and stored in air for more than 3 months.

RESULTS AND DISCUSSION

Py-GC/MS analysis of standard Japanese lacquer film

The Japanese lacquer film was analyzed by pyrolysis at 500°C. The total ion chromatogram (TIC) is shown in Figure 2. Although a complex TIC was obtained, the mass chromatogram and mass spectrum confirmed that urushiol (MW = 320 g/mol) and monoene urushiol (MW = 318 g/mol) were the main components of the lacquer (Peaks 1 and 2).

The important pyrolysis products, 3-pentadecenylcatechol (C15:1) and 3-pentadecanylcatechol (C15:0), which were obtained in mass chromatograms and mass spectra of Japanese lacquer film at m/z = 123, are shown in Figure 3(A). In this mass chromatogram, 3-heptylcatechol (C7) also was detected, and it

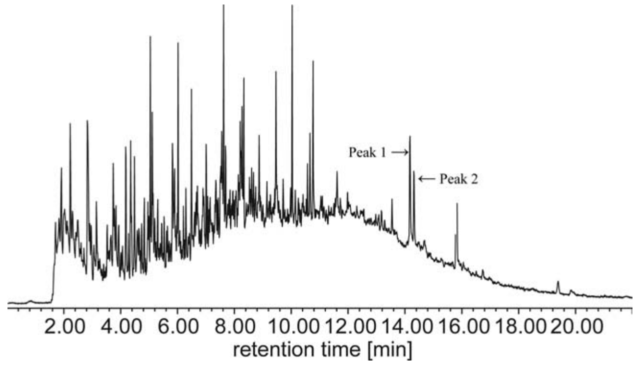

Figure 2 TIC of Japanese lacquer film.

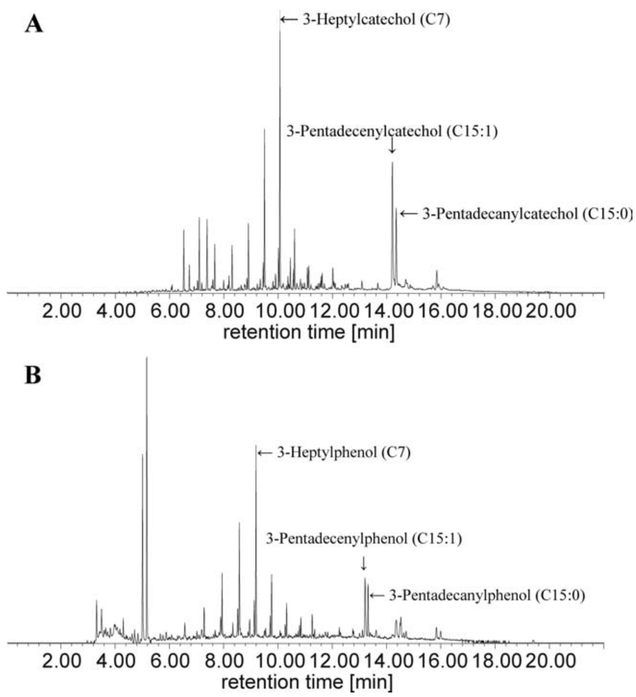

Figure 3 Mass chromatograms of Japanese lacquer film, (A) $m/z = 123$ and (B) $m/z = 108$.

had the highest relative intensity. On the other hand, 3-pentadecenylphenol (C15:1), 3-pentadecanylphenol (C15:0), and 3-pentadecenylphenol (C7) were detected in the mass chromatogram at $m/z = 108$ [Fig. 3(B)], and 3-pentadecenylphenol (C7) also showed the highest relative intensity.

It has been reported that the double bonds of the olefins at the α- and β-positions are most susceptible to thermal cleavage.[18–21] Therefore, the highest yield of 3-heptylphenol (C7) and 3-heptylcatechol (C7) can be attributed to the preferential cleavage at the α- or β-position of the double bonds of the nucleus-14th chain and/or the nucleus-8th chain by C—O couplings of the urushiol polymers.

Py-GC/MS analysis of standard Thailand lacquer film

The Thai lacquer film was analyzed by pyrolysis at 500°C like the Japanese lacquer film, and the TIC is shown in Figure 4. Although a complex TIC was obtained, the mass spectra confirmed that the main components were alkylbenzene and alkenylbenzene because undecylbenzene (MW = 232 g/mol) and undecenylbenzene (MW = 230 g/mol), which are produced by the pyrolysis of thitsiol polymer, were detected. Subsequently, 3-heptadecylcatechol (MW = 208 g/mol), 3-and 4-(10-phenyldecyl)phenols (MW = 310 g/mol), 3-and 4-(12-phenyldodecyl)phenols (MW = 338 g/mol), and 3-(10-phenyldecyl-and 12-phenyldodecyl)catechols (MW = 354 g/mol) were detected as characteristic components of Thailand

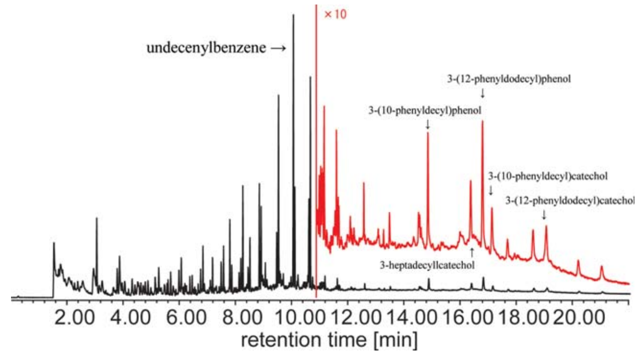

Figure 4 TIC of Thai lacquer film. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

lacquer. However, the intensity peaks of these materials were very weak compared with those of alkanes and alkenes because of undecylbenzene and undecenylbenzene, as shown in Figure 4.

The main pyrolysis products in the mass chromatogram at $m/z = 123$ of Thailand lacquer film are 3-heptylcatechol (C7) and 4-heptylphenol (C7), as shown in Figure 5(A). ω-Phenylalkylcatechols and ω-phenylalkylphenols, specific components of *M. usitata* lacquer, also were detected in the mass chromatogram at $m/z = 123$. These compounds are not found in Japanese lacquer (*R. vernicifera)* or Vietnamese (*R. succedanea*) lacquer films.[9,10] Rather, the main pyrolysis products in the mass chromatograms at $m/z = 108$ of Thai lacquer film are 3-heptylphenol (C7) and 3-pentadecylphenol (C15), as shown in Figure 5(B). Meanwhile, 3-(10-phenyldecyl)phenylalkylcatechol and 3-(12-phenyldodecyl)phenol, which are the

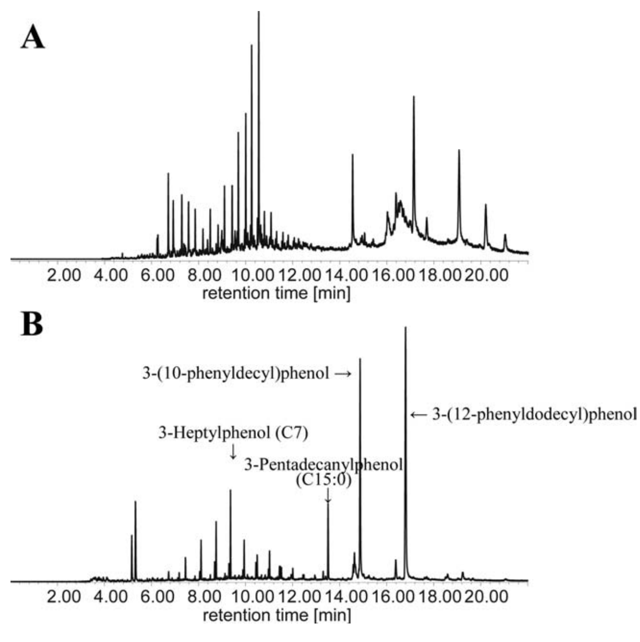

Figure 5 Mass chromatograms of Thai lacquer film, (A) $m/z = 123$ and (B) $m/z = 108$.

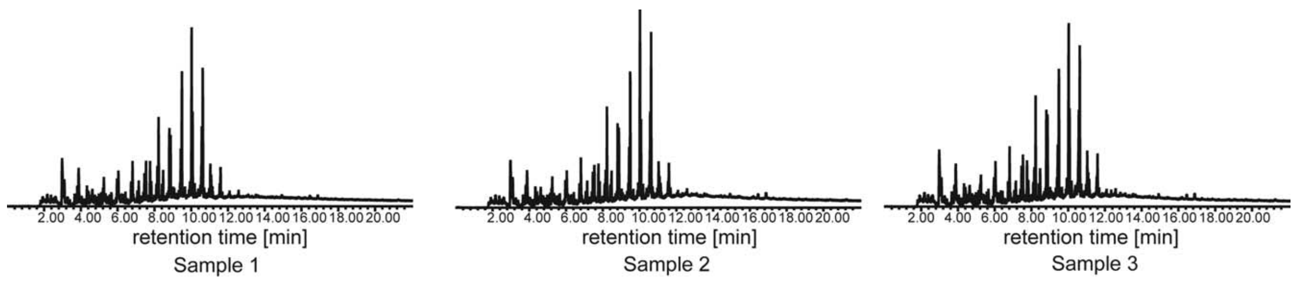

Figure 6 TIC of Samples 1, 2, and 3.

specific pyrolysis components products of *M. usitata* lacquer, were also detected in the mass chromatograms at $m/z = 108$.

Py-GC/MS analysis of lacquer samples

Samples 1, 2, and 3, taken from a four-eared jar obtained from 16–17th century ruins in Kyoto City, were analyzed by pyrolysis at 500°C using the same protocol as the standard Japanese and Thai lacquer films, and the TIC results are shown in Figure 6. Because the three samples have quite similar TIC resolution patterns, it was judged that they were all a material of the same character. Figure 7 is the mass chromatogram at $m/z = 123$ (A) and $m/z = 108$ (B) of Sample 1. The peak at the retention time of 17.3 min ($m/z = 123$, Peak 1) is 3-(10-phenyldecyl)-catechol and at 20.4 min ($m/z = 123$, Peak 2) is 3-(10-phenyldodecyl)catechol, respectively, according to the results of analysis of the mass chromatogram (Figure not shown).

IR analysis

The IR spectra of the Japanese and Thai standard lacquer films and Sample 1 are shown in Figure 8. Although the peaks at 2960–2850 cm^{-1} due to the absorption of the C—H stretching vibration and at 1480 cm^{-1} due to the absorption of C—H bending vibration in a side chain showed similar absorption patterns, peaks at 698 cm^{-1} belonging to the C=C bending vibration of the substituted aromatic group and at 748 cm^{-1} belonging to the C—H bending vibration of thitsiol were observed. The peak at 3040 cm^{-1} is the stretching vibration of C=C bond and only observed in the Sample 1 and Thai lacquer. These results suggest that the material of Sample 1 may be derived from *M. usitata*. Moreover, peak at 1714 cm^{-1} is the stretching vibration of C=O group, which belong to the oxidation degradation of lacquer film,[22,23] and because the oxidation degradation is progressing, this peak becomes stronger than the Thai standard lacquer.

As described above, after comparing the Py–GC/MS and IR results of the standard lacquers and lacquerware samples, it can be concluded that the Samples 1, 2, and 3 taken from different places on a four-eared jar found in 16–17th century ruins in Kyoto City were made from *M. usitata*.

The Py-GC/MS method can not only to distinguish the lacquer species but also to discriminate between lacquer and other resins (such as epoxy or wax) for the conservation and restoration of lacquer objects. As the research results in this article revealed the lacquer found in a four-eared jar excavated from 16–17th century ruins in Kyoto City was made from the lacquer sap of *M. usitata*. In general, *Rhus verniciflua* lacquer is usually used in Japanese lacquerware because the lacquer tree grows in Japan. However, the present analytical results revealed that Thailand lacquer was used at Kyoto in the 16–17th century. Japan traded with foreign countries

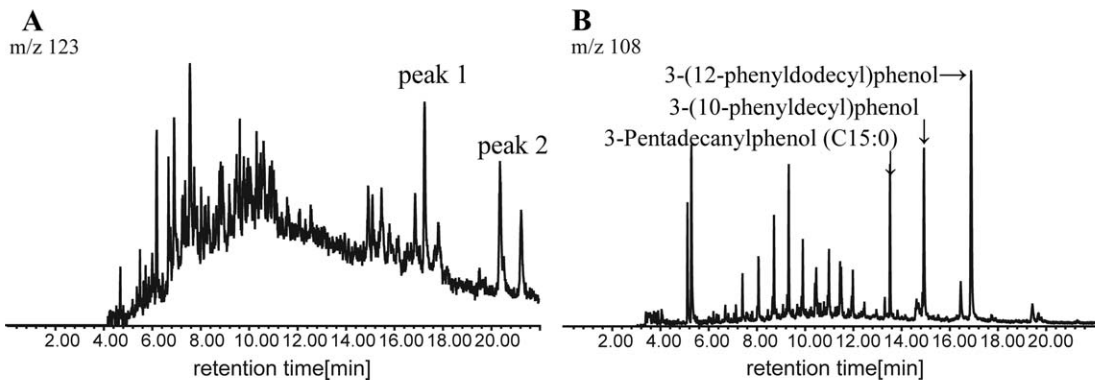

Figure 7 Mass chromatograms of Sample 1 at (A) $m/z = 123$ and (B) $m/z = 108$.

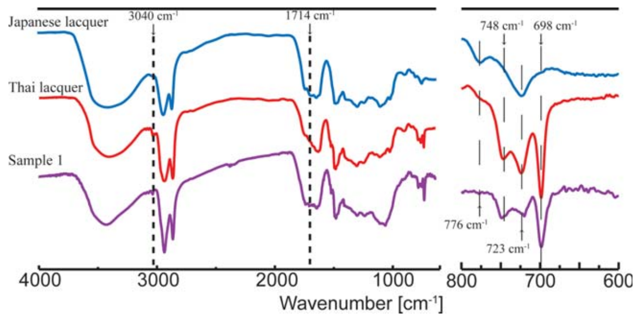

Figure 8 IR spectra of standard Japanese, Thai lacquer, and Sample 1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

according to the historical literature, although the trade was limited to Port Nagasaki and Port Hirado in the 16th century. Large quantities of the imported Thai lacquer were used on lacquer objects and wooden buildings such as the castles and Shinto shrines that were constructed during the Momoyama cultural period (A.D. 1573–1615) in Japan. The "Diary of the Nagasaki Dutch trading house,"[24] which contains documents concerning lacquer imports in the 16–17th century, records that a large amount of lacquer sap (~50–100 tons/year) was imported to Japan from Thailand between 1636 and 1643. However, because the "Diary of the Nagasaki Dutch trading house" is only established since 1633, and the samples from the "four-ear" jar on this study were constructed during the Momoyama cultural period, according to the dating, we estimated that the imports of Thai lacquer can probably back to more than 100 years ago. We had previously suspected that the lacquer sap produced in Japan was insufficient for Japanese market and that a large amount of lacquer sap was imported from Thailand; we are interested in where such a large amount of lacquer was used. These exciting results make us eager to continue our search for 16–17th century buildings and lacquerware to distinguish the species of lacquer and to aid the protection of important cultural properties.

CONCLUSIONS

The lacquer fragment extracted from the four-eared pottery jar, which was discovered in National Important Cultural Property in the 16–17th century ruins in Kyoto City, was *M. usitata*. Moreover, the "four-eared" style vessels used to store the lacquer are the same as pottery currently being used as containers for various things in Thailand. Thus, the lacquer stored in the excavated pottery was actually imported from Thailand during the Momoyama cultural period and used in Kyoto. However, neither buildings nor lacquer wares made of the Thai lacquer have been excavated till now. We are continuing our search for the buildings and lacquer wares in which Thai lacquer sap was used.

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