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ORIGINAL ARTICLE

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Volatile organic compounds from wood and their influences on museum artifact materials II: inference of causal substances of deterioration based on intercomparison of laser Raman spectra of deteriorated products

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Abstract Volatile organic compounds (VOCs) from wood and their effects on artifacts are of intense interest to museum staff who must strictly manage the preservation environment. In this study, the causal substances of deterioration were inferred by comparison with laser Raman (LR) spectra of deterioration products. The artifact samples were deteriorated using VOCs from woods (WV test), and using specific substances that occur in wood VOCs (SV test). The deteriorated samples were analyzed by LR spectroscopy and the results of the WV and SV tests were compared.

Hinokitiol and acetic acid were found to be two of the main causal substances of deterioration in western red cedar. Deterioration of iron and copper by spruce did not appear to be caused by acetic acid, as is generally assumed, but by some other unknown compound(s). Sensitivity to wood-based VOC components depended on the type of artifact. In western red cedar, *mitsudasou* (litharge) was very sensitive to acetic acid, while other artifacts were sensitive to hinokitiol. The LR method used in this study is very useful for the inference of causal substances of deterioration based on the detection of small amounts of deteriorated products such as those generated by deterioration due to wood VOCs.

Key words Museum artifact material · Discoloration · Laser Raman spectroscopy · Volatile organic compounds · Hinokitiol

Introduction

In order to prevent the degradation of artifacts, museums must strictly manage the preservation environment, which includes such factors as temperature, humidity, insects, mold, and so on. Air contaminants are also an important concern. In particular, the acidification of storage rooms that use wood as an interior material is becoming a serious problem. Hence, there is intense interest in the deleterious effects of volatile organic compounds (VOCs) from wood on museum artifacts.[1–6] The relationships among wood species, artifact deterioration, and causal substances, and the development of methods for removing causal substances are very important and urgent subjects for museums and related fields.

We have been studying VOCs from four wood species that are often used as an interior material for storage rooms and/or stock cases in museums, and their effects on artifacts.[7] Our results to date point out that the effects vary greatly with wood species, and that the effects depend more on specific components such as acetic acid and hinokitiol than on the total volatile organic compounds (TVOCs). Therefore, we attempted to analyze deteriorated specimens using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). However, it was difficult to identify deteriorated products, because the deterioration was slight. Therefore, we were unable to investigate the causal substances and the mechanism of deterioration.

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In this study, the artifact material samples were deteriorated using wood VOCs, and using some specific substances which were individual components of the VOCs. The deteriorated specimens were analyzed by laser Raman (LR) spectroscopy. Then the causal substances of deterioration were inferred by comparison with LR spectra of deteriorated products.

Materials and methods

Materials and chemicals

Two species of wood samples were used in this study, namely western red cedar (*Thuja plicata* D. Don, from Canada, dried for 1 week in a chamber at 60°–70°C) and spruce (*Spruce* spp., also from Canada, air-dried for 6 months).

Metal and pigment samples were used as the artifact material samples. For the metal samples, iron (Japanese Industrial Standards, JIS: SS400) and copper (JIS: C1100P), which are specified standard samples for evaluating metal corrosivity in an air environment by the JIS, were used. For the pigment samples, special grade reagents (Kanto Chemical) commonly used as the main ingredients of pigments were used (Table 1).

The metal specimens (40 × 20 × 1 mm) were ground on both sides with emery paper in the order of No. 400, No. 600, and No. 800. Then they were cleaned with ultrasonic washing (W-115 Sanpa, Honda Electronics) in acetone for 15 min, just before use. The pigments were placed directly in the hollow (20 × 15 × 0.2 mm) of a slide glass.

Special grade volatile reagents (Kanto Chemical) of hinokitiol and acetic acid were used to investigate the effects of individual substances of wood VOCs on metals and pigments.

Methods

Influences of VOCs from wood on metals and pigments (WV test)

Each of the wood samples (5 × 4 × 1 cm, eight pieces), the metal and pigment samples, and a small glass container (10 cm^3) containing distilled water (3.0 g) were placed in a desiccator (3 dm^3) equipped with a thermohygrometer sensor (SK-L200TH, Sato Keiryoki). The desiccator was then placed in an incubator (MIR-251, Sanyo Electric) set at 30°C for 33 days. A control experiment was conducted without wood samples, that is, with only distilled water, metals, and pigments.

Table 1. Pigment samples

Pigment sample[a]	Color	Chemical formula
Mitsudasou (litharge)	Yellow	PbO
Enpaku (white lead)	White	$2PbCO_3 \cdot Pb(OH)_2$
Rokushou (malachite, verdigris)	Moderate green	$CuCO_3 \cdot Cu(OH)_2$

[a] Special grade reagents equivalent to principal ingredient of pigments

Individual influences of the specific substances in VOCs from wood on metals and pigments (SV test)

The metal and pigment samples and a small glass container (10 cm^3) containing the volatile reagent were placed in a sealed vessel (0.5 dm^3), then set in an incubator at 40°C. Hinokitiol (about 1 mmol) and acetic acid (5 mmol) were used as the volatile reagents. For comparison, the same experiments were conducted with distilled water (15 mmol) and no volatile reagent (control).

Laser Raman analysis

The deteriorated products of the artifact material samples that had been treated in the SV and WV tests were analyzed by LR spectroscopy (JRS-SYS1000 [D], Jeol) and their respective spectra were compared. During the analysis, the light source was an argon laser (514.5 nm), the output per sample was 0.3 mW, and the laser beam diameter was 20 μm.

Results and discussion

In this article, the metal and pigment samples treated in the SV and WV tests are notated on the basis of their treatment. For example, the sample that was treated with the

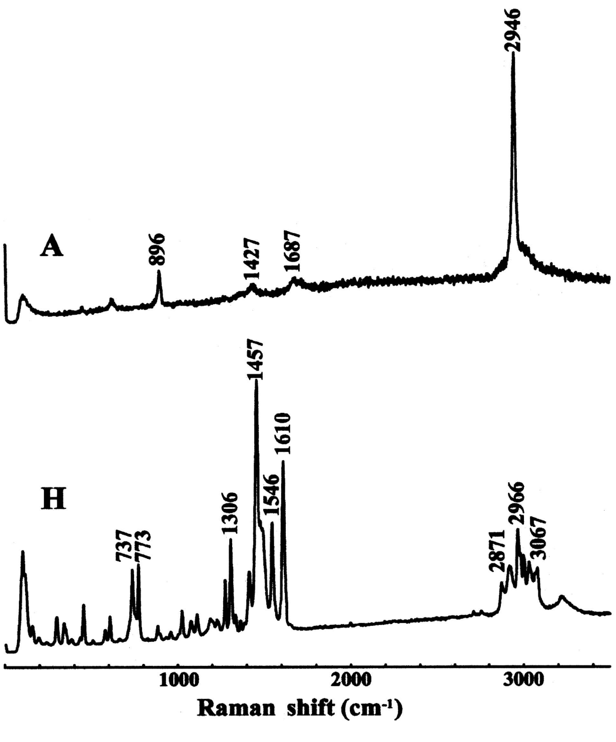

Fig. 1. Laser Ramen (LR) spectra of acetic acid standard (*A*) and hinokitiol standard (*H*)

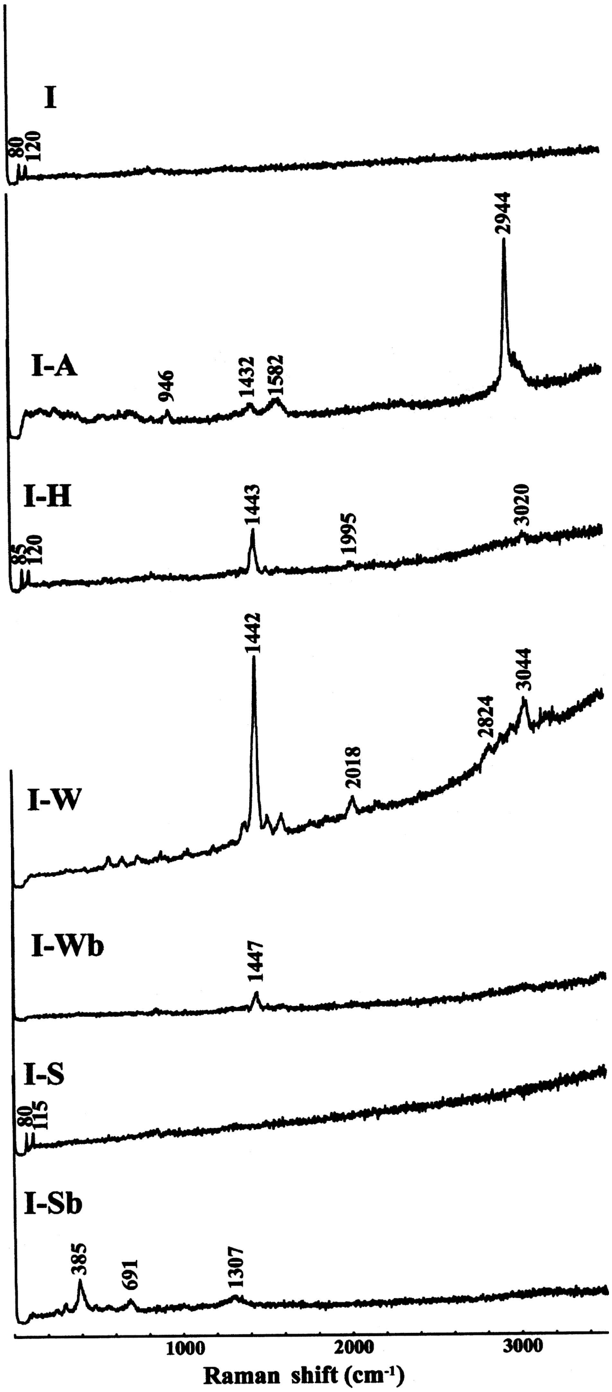

Fig. 2. LR spectra of iron. *I*, Iron (standard); *I-A*, acetic acid treatment sample; *I-H*, hinokitiol treatment sample; *I-W*, western red cedar treatment sample (tarnished part); *I-Wb*, western red cedar treatment sample (brown speckle); *I-S*, spruce treatment sample (ground metal); *I-Sb*, spruce treatment sample (dark brown deposit)

VOCs from western red cedar is denoted as the "sample treated with western red cedar".

The LR spectra of the standard acetic acid and hinokitiol samples are shown in Fig. 1.

Metals

Iron

The LR spectra of the iron samples after the SV and WV tests are shown in Fig. 2. The iron treated with acetic acid (I-A), which was covered with brown deposits, could not provide information on acetic acid products using XRD analysis,[7] but the LR spectrum showed peaks at 946, 1432, 1582, and 2944 cm^{-1}, which were attributed to the products of deterioration caused by acetic acid.

The iron treated with hinokitiol (I-H), which had rusted, had a characteristic peak at 1443 cm^{-1} and the background (BG) increased at high wave number.

For the iron treated with western red cedar, yellowish red rust (I-W) and brown speckles (I-Wb) were observed and analyzed with LR spectroscopy. Both spectra showed the characteristic peaks of 1442 (and/or 1447) cm^{-1}, and a BG increase, which were similar to the spectrum of I-H. This suggests that the products may have been produced by deterioration with hinokitiol.

The iron treated with spruce showed unique changes. Apart from the dark brown deposits (I-Sb) that were observed in places, visual inspection could find no changes (I-S). In I-S, only BG increase was observed in the LR spectrum, and there were no new peaks. In I-Sb, new peaks at 385, 691, and 1307 cm^{-1} were observed, but the spectra were different from those of I-A and I-H. This finding suggests that the causal substances of deterioration were not acetic acid or hinokitiol. Thus, it would be very interesting to investigate the products and causal substances of this deterioration. Consequently, our next study will focus on investigating this problem by screening the target substances with gas chromatography-mass spectrometry (GC-MS), subjecting them to the SV test, and analyzing the deteriorated products by LR spectroscopy, XRD, and other means.

Copper

The LR spectra of copper samples after the SV and WV tests are shown in Fig. 3. For the copper treated with acetic acid (C-A), which turned a reddish color, a new, very small peak of 2939 cm^{-1} was observed. However, except for the new peak there was no large difference between the LR spectra of C-A and standard copper (C).

For the copper treated with hinokitiol (C-H), which had gray deposits, the characteristic peaks at 1443, 1455, 1596, and 2863–3050 cm^{-1} were observed. They were attributed to the products of deterioration caused by hinokitiol.

For copper treated with western red cedar, yellowish orange tarnish (C-W) and dark brown speckles (C-Wb) were observed, and both were analyzed by LR spectroscopy. The LR spectra of C-W and C-Wb were similar both to each other, and to that of C-H. This suggests that they may be the same substance that arose from deterioration by hinokitiol.

Copper treated with spruce showed signs of discoloration to reddish brown (C-S) and dark brown speckles (C-

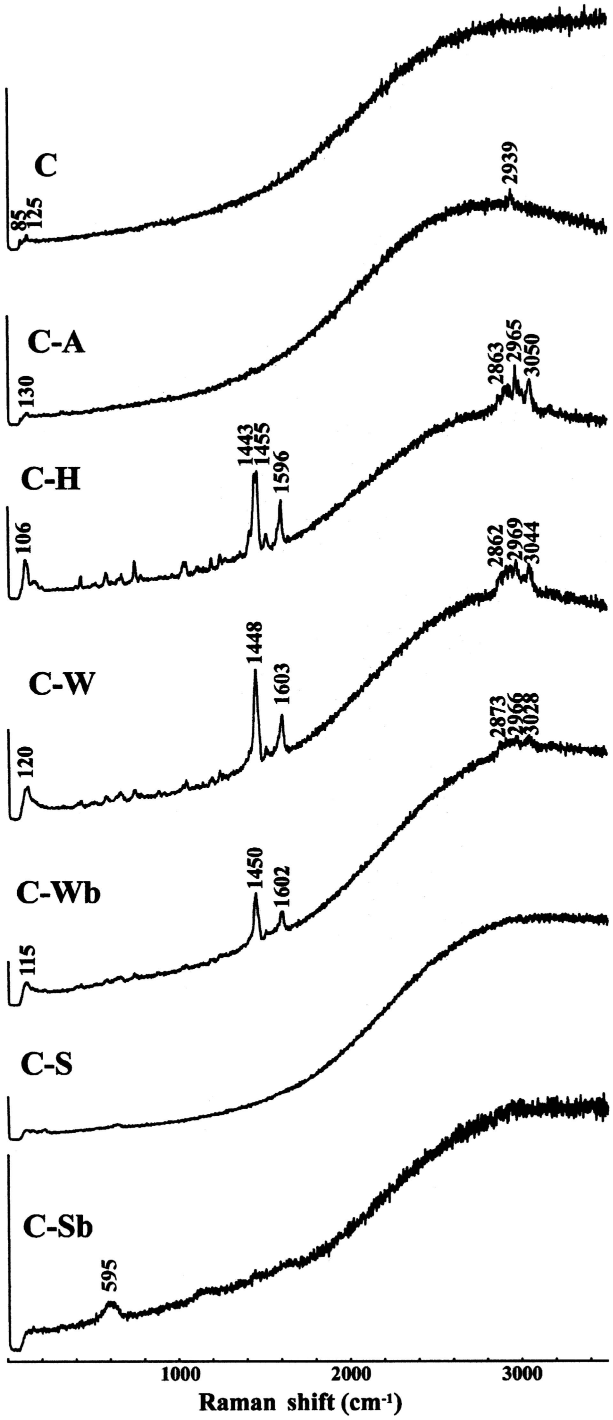

Fig. 3. LR spectra of copper. *C*, Copper (standard); *C-A*, acetic acid treatment sample; *C-H*, hinokitiol treatment sample; *C-W*, western red cedar treatment sample (discolored part); *C-Wb*, western red cedar treatment sample (dark brown speckle); *C-S*, spruce treatment sample (discolored part); *C-Sb*, spruce treatment sample (dark brown speckle)

Sb). There was no characteristic peak in the LR spectrum of C-S, although a peak at 595 cm^{-1} was observed in the C-Sb spectrum, suggesting that C-S and C-Sb were different substances. Furthermore, there was no peak at 595 cm^{-1} in either C-A or C-H; therefore, the causal substances of

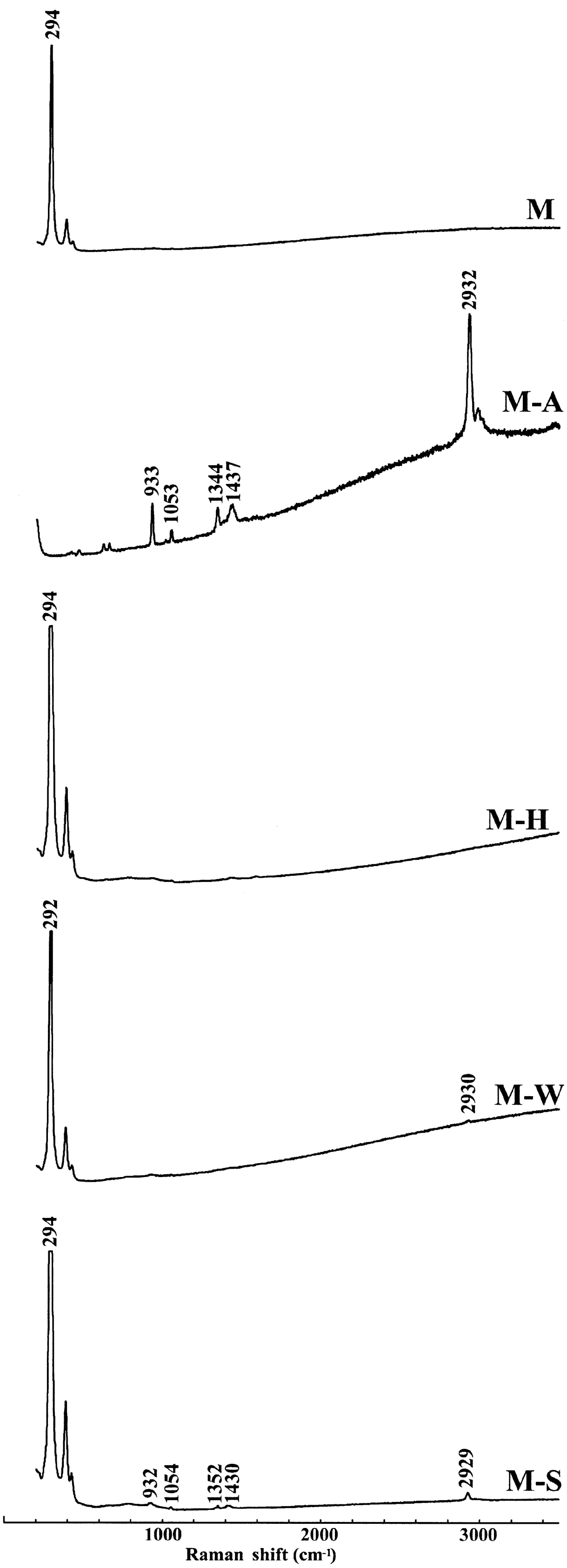

Fig. 4. LR spectra of *mitsudasou*. *M*, *Mitsudasou* (standard); *M-A*, acetic acid treatment sample; *M-H*, hinokitiol treatment sample; *M-W*, western red cedar treatment sample; *M-S*, spruce treatment sample

deterioration may have been some compound(s) other than acetic acid and hinokitiol.

Pigments

Mitsudasou

Figure 4 shows the LR spectra of *mitsudasou* samples after the SV and WV tests. For *mitsudasou* treated with acetic acid (M-A), which turned white, the large peak at 294 cm^{-1} disappeared and new peaks (933, 1053, 1344, 1437, and 2932 cm^{-1}), which were attributed to the products of deterioration caused by acetic acid, were observed. The result of XRD analysis, which identified the lead compound $3[Pb(CH_3COO)_2] \cdot PbO \cdot H_2O$,[7] supports this inference.

Visual inspection of *mitsudasou* treated with hinokitiol (M-H) found no change, nor was there a characteristic peak in the LR spectrum. For *mitsudasou* treated with western red cedar (M-W), which turned yellowish gray, only a very small peak at 2930 cm^{-1} and a small BG increase were observed. Although the peak was small, the LR spectrum of M-W was similar to that of M-A, suggesting that a small amount of acetic acid product(s) might have been produced.

Mitsudasou treated with spruce (M-S), which turned white, showed peaks at 932, 1054, 1352, 1430, and 2929 cm^{-1}, which were similar those of M-A. This suggests that some acetic acid product(s) might have been produced.

Enpaku

Figure 5 shows the LR spectra of *enpaku* samples after the SV and WV tests. For *enpaku* treated with acetic acid (E-A), which was not noticeably discolored, a trace of deliquescence appeared to have occurred. In the LR spectrum, several new peaks (932, 1344–1479, 2933, and 2983 cm^{-1}), which were attributed to the products of deterioration caused by acetic acid, were detected.

For *enpaku* treated with hinokitiol (E-H), which turned yellow, a BG increase was observed, but there was no large difference in the LR spectra between E-H and standard *enpaku* (E). For *enpaku* treated with western red cedar (E-W), which turned yellow, there was no new characteristic peak, but there was a BG increase. The similarity of this result with that of E-H suggests that hinokitiol is a causal substance; however, further examinations by other methods are required before a definitive conclusion can be drawn. For *enpaku* treated with spruce (E-S), which was not noticeably discolored, there was no new characteristic peak, but there was a BG increase.

Rokushou

Figure 6 shows the LR spectra of *rokushou* samples after the SV and WV tests. *Rokushou* treated with acetic acid (R-A), which turned blue, showed some new peaks (1353, 2730, 2810, and 2947 cm^{-1}), which were attributed to the products of deterioration caused by acetic acid. For *rokushou* treated with hinokitiol (R-H), which turned yellowish green, characteristic new peaks (1448, 1595, and 2866–3053 cm^{-1}), which were assigned to the products of deterioration caused by hinokitiol, were observed.

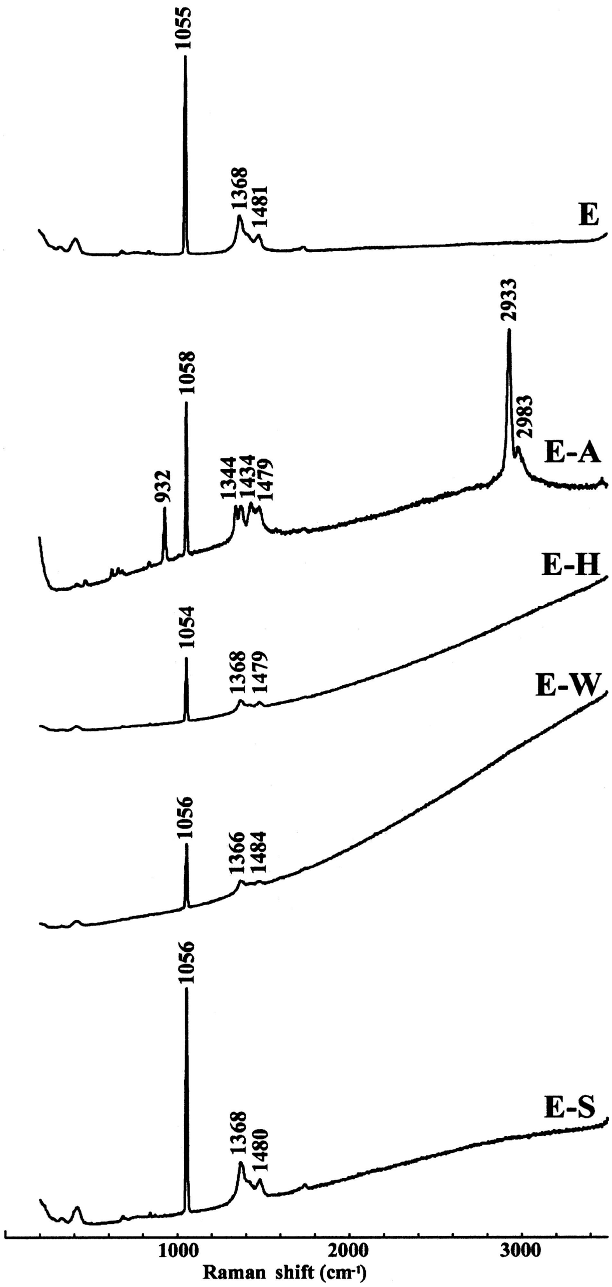

Fig. 5. LR spectra of *enpaku*. *E*, *Enpaku* (standard); *E-A*, acetic acid treatment sample; *E-H*, hinokitiol treatment sample; *E-W*, western red cedar treatment sample; *E-S*, spruce treatment sample

Rokushou treated with western red cedar (R-W), which turned yellowish green, showed some new peaks at 1449, 1597, and 2873–3051 cm^{-1}, which were similar to those of the R-H spectrum. This suggested that the deterioration was caused by hinokitiol. *Rokushou* treated with spruce (R-S) showed no obvious discoloration, and there was no large difference between the LR spectra of R-S and standard *rokushou* (R). The experiments conducted in this study yielded no results that indicate deterioration.

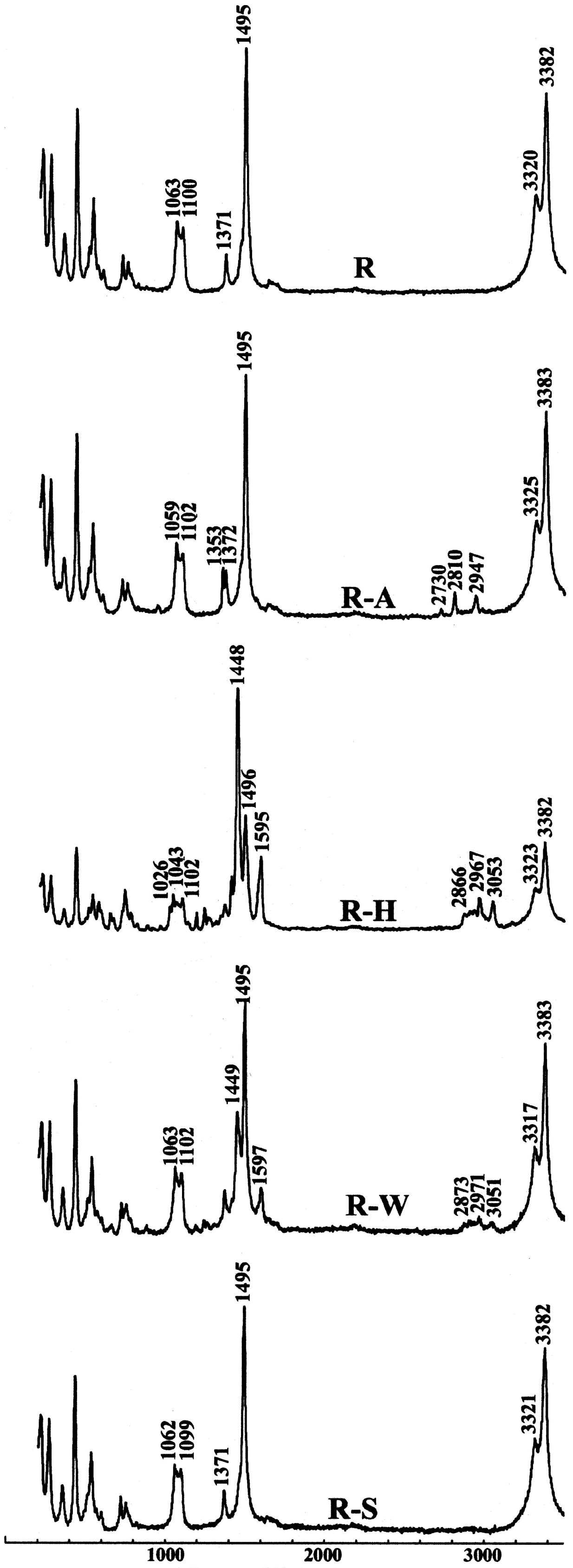

Fig. 6. LR spectra of *rokushou*. *R*, *Rokushou* (standard); *R-A*, acetic acid treatment sample; *R-H*, hinokitiol treatment sample; *R-W*, western red cedar treatment sample; *R-S*, spruce treatment sample

Table 2 gives an overview of the changes (corrosion or discoloration) in artifact material samples that were caused by VOCs from wood and the likely causal substances of the deterioration suggested by the LR analyses. Sensitivity to components of wood VOCs differed among the artifact materials. For example, for western red cedar, *mitsudasou* was sensitive to acetic acid, while other materials were more affected by hinokitiol. For spruce, *mitsudasou* was also sensitive to acetic acid, but the LR spectral analysis suggested that contrary to expectations, iron and copper were affected by some other, unidentified, substance(s).

The method used in this study was very useful for detecting subtle changes such as those caused by VOCs present in wood and for identifying causal substances. With LR spectroscopic analysis, the changes of C-H were detected, which was not possible with XRD. This is because XRD requires a relatively large measurement area (about 3 cm^2) and depth (several tenths of a millimeter) for measurements such as those reported in our previous article,[7] and similarity with C-W and C-Wb was also clearly shown.

LR spectroscopic analysis revealed a BG increase in E-S, even though no change was observed by visual inspection. This led us to infer that some sort of changes were occurring, and if the BG increase detected is truly indicative of actual changes, the LR spectroscopic analysis is considered to be promising for use in preventing deterioration of artifact materials. Observation of changes with time will be an interesting theme to pursue.

At the moment, it is often difficult to identify substances by LR analysis alone because of the insufficient amount of accumulated spectral data. In such cases, it may be effective to use the new method in conjunction with previously prepared control samples, such as those obtained from SV tests.

Conclusions

The findings from the present study can be summarized as follows:

1. The main VOCs in western red cedar causing deterioration appear to be hinokitiol and acetic acid.
2. In the VOCs of spruce, as expected, acetic acid was the substance that caused the deterioration of *mitsudasou*; however, contrary to expectations, the deterioration of iron and copper may have been caused by compound(s) other than acetic acid or hinokitiol.
3. The sensitivity of artifact materials to wood VOC components differed greatly. *Mitsudasou*, for example, was easily deteriorated by minute concentrations of acetic acid from western red cedar and spruce.
4. Other materials, however, were sensitive to other components, such as hinokitiol in western red cedar.
5. The LR spectroscopic method used in this study is very useful for the identification of causal substances of deterioration based on the detection of small amounts of deteriorated products such as those generated by deterioration due to wood VOCs.

Table 2. Corrosion or discoloration of artifact material samples caused by volatile organic compounds from wood and the likely substances causing deterioration

Materials	Western red cedar		Spruce	
	Visual inspection	Causal substance[a]	Visual inspection	Causal substance[a]
Iron	Yellowish red	Hinokitiol	NC	UC (BI)
	Brown speckles	Hinokitiol	Dark brown deposit	UC (385)
Copper	Yellowish orange	Hinokitiol	Reddish brown	(–)[b]
	Dark brown speckles	Hinokitiol	Dark brown speckles	UC (595)
Mitsudasou	Yellowish gray	Acetic acid	White	Acetic acid
Enpaku	Yellow	(Hinokitiol?)	NC	UC (BI)
Rokushou	Yellowish green	Hinokitiol	NC	–

Values given in parentheses for unknown compounds are Raman shifts (cm^{-1}) of specific peaks
NC, No change; UC, unknown compounds; BI, background increasing
[a] One of the causal substances as indicated by similarities in Laser Raman (LR) spectra and visually noticeable changes
[b] The LR spectrum did not differ remarkably from the standard sample

Only a few of the multitude of wood VOCs that cause deterioration were examined in this report. The investigation of other causal substances is an urgent subject. Museums have so far been concerned with acetic acid from wood that is used for interior materials in storage rooms. However, they should also be concerned with other substances, such as hinokitiol in western red cedar or unknown caustic substances in spruce.

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