A preliminary study on the relation between camphor wood volatile matters and corrosion of museum metallic objects

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Abstract. Camphor wood is a traditional storage material used in Chinese museums for repelling insects and inhibiting moulds. Since camphor wood continuously emits volatile matters, it leads to potential risks to museum collections on the other hand. Oddy test was conducted in this study to evaluate the reliability level of four different camphor wood samples for museum use. The samples were put into water and the pH values were measured in order to learn the acidity of each sample preliminarily. Modern instrumental methods including gas chromatography – mass spectrometry, X-ray diffraction and X-ray photoelectron spectroscopy, were employed to identify the volatile matters emitted by each sample and the corresponding corrosion products, respectively. The identification results were discussed together to infer possible corrosion mechanisms and evaluate the effects of aging time and species. The results showed that compared with the Cinnamomum camphora samples, the Cinnamomum glanduliferum sample led to higher risk to the metallic objects, while the reserve of acetic acid tended to decrease along with continuous aging of the Cinnamomum camphora sample but the risk did not decline significantly.

1. Introduction
As a natural product, wood has been employed by human beings as a storage material since long ago [1]. Wood is also widely used as a museum storage and display material due to rich source, nice appearance, good mechanical behavior and favorable breathability [2]. In China, camphor wood is a common material traditionally applied to making furniture [3]. It is welcomed by many Chinese museums because of its insect repelling and mould inhibiting effects as well. However, the strong smell implies that camphor wood contains a high amount of volatile matters which mean a potential risk to museum collections from the perspective of preventive conservation. It is necessary to evaluate the reliability level of camphor wood as a museum storage material by using modern analytical methods so that the conservators can come to rational judgments when camphor wood is included in the sample list.

Oikawa et al. found that when metals and pigments are influenced by different types of wood, changes in the samples vary significantly, which depends on the amount of specific compounds like Hinokitiol or acetic acid rather than total volatile organic compounds [4]. The work provides the route for studying the responsible volatile components causing corrosion. In the present study, four camphor wood samples were employed as the potential materials for museum use. The samples were evaluated by using the Oddy test. Volatile matters emitted by the samples and corrosion products emerging from the metallic coupons were identified by solid-phase micro-extraction – gas chromatography – mass spectrometry (SPME-GC-MS), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS),
respectively. The results were applied to explaining the judgments of reliability. The corrosion mechanisms were discussed also by considering both the volatile matters and the corrosion products.

2. Experimental section

2.1. Materials
The camphor wood materials originated from China have not been processed through boiling. The species included *Cinnamomum camphora* (aged for 30, 50 and 100 years, originated from Jiangxi Province) and *Cinnamomum glanduliferum* (aged for 30 years, originated from Yunnan Province). The raw wood materials were cut into the same shape using an electric saw. The saw dusts were also collected for later use. The sample appearances are shown in Figure 1.

![Figure 1](image1.png)

**Figure 1.** Camphor wood samples prepared. (a) *Cinnamomum camphora* (aged for 30 years). (b) *Cinnamomum camphora* (aged for 50 years). (c) *Cinnamomum camphora* (aged for 100 years). (d) *Cinnamomum glanduliferum* (aged for 30 years).

Isooctane (analytical grade), and copper, silver and lead foils (99.9 %), were purchased from Sinopharm Chemical Reagent Company, China. Metallic coupons used in this study were obtained by cutting the raw metallic foils into the same size (3.5 cm × 1.0 cm) according to the reference [5]. Isooctane was used without further purification. Deionized water was used throughout this work.

2.2. Separation and identification of volatile matters by SPME-GC-MS
Volatile matters emitted by the camphor wood samples were separated and identified by using an Agilent 7890B-5977B GC-MS. First, volatile matters were extracted from the saw dusts by SPME. The saw dust amounts for the *Cinnamomum camphora* samples aged for 30, 50 and 100 years and the *Cinnamomum glanduliferum* sample were 0.1044, 0.1021, 0.1002 and 0.1090 g, respectively. SPME conditions were as follows. Device: CTC 3-in-1 automatic sampler; fibre: 50/30 μm CAR/DVB on PDMS; temperature: 50 °C; time: shaking for 15 min and extracting for 30 min; shaking rate: 250 rpm; desorption time: 5 min; GC cycling time: 50 min. Then, GC-MS conditions were as follows. Column: DB-wax (30 m × 0.25 mm × 0.25 μm); inlet temperature: 260 °C; split ratio: 5:1; carrier gas: helium (99.999 %); flow: 1 mL min⁻¹; column temperature: held at 40 °C for 5 min, then increased to 220 °C at 5 °C min⁻¹, and then increased to 250 °C at 20 °C min⁻¹ and held for 2.5 min; interface temperature: 260 °C; ionization temperature: 230 °C; quadrupole temperature: 150 °C; ionization mode: EI⁺, 70 eV; scanning mode: full scan; mass range: 20 – 400; spectra database: NIST 2014.

2.3. Measurement of pH in camphor wood aqueous extractions
The pH values of camphor wood aqueous extractions were measured by a Sartorius PB-10 pH meter. The measurement procedures were according to the reference [5].
2.4. The Oddy test
The assembling of experimental devices and the detailed process of test were described in the previous work [6]. However, the deposited metal films applied to that work were not used in the present study. The whole experimental device is shown in Figure 2.

![Diagram](image)

**Figure 2.** Typical device for the Oddy test conducted in this study.

2.5. Identification of corrosion products by XRD and XPS
Corrosion products on the metallic coupons were analysed using a Rigaku SmartLab X-ray diffractometer (Cu Kα, 40 kV, 100 mA) in situ. Possible phases were identified according to the database ICDD PDF-2 (2004). Corrosion products on the metallic coupons affected by the *Cinnamomum glanduliferum* sample were also analysed using a Kratos AXIS Ultra DLD system (Al Kα, 105 W) in situ. The XPS spectra were referenced to C 1s at 284.8 eV (binding energy).

3. Results and discussion

3.1. Volatile matters emitted by the camphor wood samples
Major volatile matters identified by SPME-GC-MS are listed in Table 1. It was found that the predominant volatile matters emitted by the camphor wood samples were terpenes or their derivatives. L-(-)-Camphor (or (±)-Camphor), α-Terpineol and Terpinen-4-ol were found in all the cases, but their relative contents differed a lot. L-(-)-Camphor (or (±)-Camphor) occupied the primary position in all the three *Cinnamomum camphora* samples with similar relative contents, while in the *Cinnamomum glanduliferum* sample it just occupied the third place and the peak area was much smaller. Both the relative contents of α-Terpineol and Terpinen-4-ol presented an unconspicuous decline during the 30 – 50 years aging period for the *Cinnamomum camphora* sample, while a sharper decline was found during the 50 – 100 years aging period. Compared with the *Cinnamomum camphora* sample aged for 30 years, the *Cinnamomum glanduliferum* sample contained almost the same relative content of α-Terpineol and a fewer relative content of Terpinen-4-ol.

On the other hand, acetic acid was also detected in all the samples, but it did not occupy a dominant position. According to the measurements, the relative contents of acetic acid were 0.61 %, 0.09 %, 0.04 % and 1.13 % for *Cinnamomum camphora* samples aged for 30, 50 and 100 years and the *Cinnamomum glanduliferum* sample, respectively, while the absolute concentrations were 119.50, 63.35, 50.48 and 327.50 μg g⁻¹, respectively. These results indicate that the reserve of acetic acid continuously decreases along with the aging of the *Cinnamomum camphora* sample, while the *Cinnamomum glanduliferum* sample is more dangerous to metallic objects.
In a word, the individual contents of terpenes, their derivatives and acetic acid emitted by different wood samples varied greatly, which was probably a major factor leading to the various corrosion appearances and corrosion products [4].

Table 1. Major compounds emitted by the camphor wood samples and their relative contents.

| No. | Compound (30a C. camphora) | Peak area (%) | Reliability value (%) | Compound (50a C. camphora) | Peak area (%) | Reliability value (%) |
|-----|----------------------------|---------------|------------------------|-----------------------------|---------------|------------------------|
| 1   | L(-)-Camphor               | 35.01         | 97                     | (±)-Camphor                 | 29.78         | 97                     |
| 2   | α-Terpineol                | 16.98         | 90                     | α-Terpineol                 | 16.83         | 91                     |
| 3   | Terpinen-4-ol              | 12.15         | 96                     | (-)-α-Santalene             | 11.59         | 98                     |
| 4   | Safrole                     | 6.85          | 97                     | Terpinen-4-ol               | 10.98         | 97                     |
| 5   | Nerolidol                  | 4.75          | 91                     | Eucalyptol                  | 4.11          | 98                     |
| 6   | Eucalyptol                 | 3.29          | 97                     | (-)-β-Santalene             | 3.82          | 93                     |
| 7   | p-Menth-1(7)-en-8-ol       | 1.55          | 47                     | trans-α-Bergamotene        | 3.22          | 98                     |
| 8   | D-Piperitone               | 1.01          | 96                     | Safrole                     | 2.25          | 97                     |
| 9   | m-Cymen-8-ol               | 0.87          | 90                     | p-Menth-1(7)-en-8-ol        | 2.09          | 72                     |
| 10  | Geranylacetone             | 0.80          | 91                     | Nerolidol                   | 1.31          | 91                     |

| No. | Compound (100a C. camphora) | Peak area (%) | Reliability value (%) | Compound (C. glanduliferum) | Peak area (%) | Reliability value (%) |
|-----|----------------------------|---------------|------------------------|----------------------------|---------------|------------------------|
| 1   | (±)-Camphor                | 32.73         | 97                     | α-Terpineol                | 16.97         | 90                     |
| 2   | (-)-α-Copaene              | 9.18          | 97                     | α-Humulene                 | 9.28          | 97                     |
| 3   | Eucalyptol                 | 9.11          | 98                     | L(-)-Camphor               | 7.53          | 97                     |
| 4   | α-Terpineol                | 8.85          | 95                     | Eucalyptol                 | 6.96          | 98                     |
| 5   | Terpinen-4-ol              | 6.76          | 95                     | Terpinen-4-ol              | 6.78          | 96                     |
| 6   | (+)-Borneol                | 4.47          | 91                     | β-Elemene                  | 3.11          | 91                     |
| 7   | (+)-δ-Cadinene             | 2.96          | 97                     | Germacrene D               | 2.94          | 99                     |
| 8   | Germacrene D               | 2.57          | 91                     | Safrole                    | 2.39          | 96                     |
| 9   | α-Humulene                 | 2.51          | 98                     | α-Cubebene                 | 2.37          | 98                     |
| 10  | β-Elemene                  | 1.58          | 91                     | (−)-Humulene epoxide II    | 1.98          | 98                     |

3.2. Acidity of camphor wood aqueous extractions

According to the measurement results, pH values of camphor wood aqueous extractions were 6.28, 6.83, 6.87 and 6.21 respectively for *Cinnamomum camphora* samples aged for 30, 50 and 100 years and the *Cinnamomum glanduliferum* sample. The results were in accord with the acetic acid concentrations measured above. The weak acidity indicates the potential risk when metallic objects contact with the camphor wood materials.
3.3. Coupon appearances and material reliability levels

![Figure 3. Coupon appearances. (a) Initial. (b) Control coupons at Day 28. (c) Coupons affected by *Cinnamomum glanduliferum* sample aged for 30 years. (d) Coupons affected by *Cinnamomum camphora* sample aged for 30 years. (e) Coupons affected by *Cinnamomum camphora* sample aged for 50 years. (f) Coupons affected by *Cinnamomum camphora* sample aged for 100 years.](image)

As shown in Figure 3, the control coupons generally maintained the gloss during the Oddy test. Silver and lead control coupons did not seem to have changes compared with their initial appearances, while the copper coupon was slightly oxidized to a carmine color, which is regarded as a natural oxidation in the Oddy test [5]. Compared with the control coupons, the affected silver coupons were still in good conditions in general, while the affected lead and copper coupons were corroded significantly. Yellow particles emerged from the surface of all the lead coupons, which was more significant in the case of the *Cinnamomum glanduliferum* sample. The copper coupons showed another phenomenon, as a generally darkened appearance. According to the evaluation standard [5], all the four camphor wood samples were evaluated as unusable. In a previous daily test also concerning the reliability level of camphor wood for using in museums, the author tested the *Cinnamomum camphora* samples and judged them temporarily usable for which aged for 30 and 50 years and unusable for which aged for 100 years. The difference between judgment results in these two tests is related to the sampling method. Since the volatile matters are not always emitted evenly in different parts of a big wood block, sampling at different sites may lead to quite different judgment results. Considering that the mass of each sample is only 2.0 g in the Oddy test [5], mixing tiny pieces obtained from several different parts of a big wood block, or even testing the mixed saw dusts, may be a more reasonable and effective way to get the real situation. However, in this way the experimental conditions deviate a lot from the practical conditions of wood materials for using in museums. Therefore, it is necessary to develop a
more reasonable sampling method for big block materials, which will be helpful for getting objective results rather than arriving at the judgments on the basis of particular cases.

3.4. XRD and XPS analyses of the deteriorated materials

It was not found in Figure 4 that any new phase had occurred significantly on the control coupons during the Oddy test. Also, nearly no change occurred on the silver coupons affected by the camphor wood samples, which was in accord with the coupons’ appearances. However, patterns of the affected copper coupons showed a higher slope in the 5° – 40° (2θ) interval compared with that for the control coupon. Several tiny peaks were found on the patterns of the affected copper coupons, which corresponded to tenorite (JCPDS 05-0661) according to the database. On the other hand, pattern baselines for the lead coupons were generally similar, but new diffraction peaks were obviously found on the patterns of the affected lead coupons, while the original peaks for lead were significantly weakened, especially on that related to the *Cinnamomum glanduliferum* sample. The new peaks corresponded to plumbonacrite [Pb₁₀(CO₃)₆(OH)₆O] (JCPDS 19-0680) according to the database.

![Figure 4. Phases identified by XRD.](image)

(a) Copper coupons. (b) Silver coupons. (c) Lead coupons. Patterns from the bottom to the top respectively correspond to the initial coupons, the control coupons at Day 28, and the coupons affected by *Cinnamomum camphora* samples aged for 30, 50 and 100 years, and by *Cinnamomum glanduliferum* sample aged for 30 years.

![Figure 5. Detailed XPS spectra for coupons affected by the *Cinnamomum glanduliferum* sample.](image)

(a) O 1s spectrum for copper. (b) O 1s spectrum for silver. (c) O 1s spectrum for lead. (d) Cu 2p spectrum for copper. (e) Ag 3d spectrum for silver. (f) Pb 4f spectrum for lead.
On the other hand, the XPS results provide further information about the corrosion. Since different camphor wood samples led to similar corrosion products (reflected by the XRD patterns), it is feasible to collect the XPS spectra for coupons affected by one sample (Cinnamomum glanduliferum) only. As shown in Figure 5, for the affected silver coupon only a single O 1s peak was found, which was centred at 531.1 eV. According to the reference [7], the single peak indicates the adsorbed oxygen on metallic silver rather than the Ag-O bond, which was in accord with the XRD results. For the affected lead coupon, two extremely asymmetric O 1s peaks centred respectively at 530.8 and 533.1 eV were fitted from the raw spectrum, between which the former indicates the structure of lead carbonate-hydroxide as well as its predominance [8]. For the copper, two O 1s peaks were observed correspondingly, which were respectively centred at 529.9 and 531.4 eV. The calculated area ratio (0.71:1) indicates that the contents of copper oxide and surface hydroxide are close to equilibrium on the coupon surface [9]. Moreover, the appearance of Cu 2p_{3/2} and 2p_{1/2} peaks (centred at 932.3 and 952.2 eV, respectively) and the presence of a strong shake-up satellite band located between the two peaks fitted the feature of CuO very well [10], while the Ag 3d_{5/2} peak (centred at 367.7 eV) and the Pb 4f_{7/2} peak (centred at 138.5 eV) suggest the form of Ag\(^{0}\) [11] and Pb\(^{2+}\) salt [12], respectively.

3.5. Corrosion mechanisms

Compared with cuprite (Cu\(_2\)O), tenorite is a scarcer corrosion product of copper in the nature. Tenorite is traditionally regarded as produced under special conditions like combustion or seawater immersion [13], and is secondary to cuprite in occurrence order [14]. The results obtained indicate that mild non-contact heating together with high humidity also leads to the occurrence of tenorite provided that certain volatile matters are coexisted in the system. On the other hand, plumbonacrite is an intermediate corrosion product during the carbonation of lead [15]. Carbon dioxide and water are required for the formation of plumbonacrite [16]. Although this process tends to occur in air, the rate is not high enough to reflect that on the control coupon. This fact also implies the effect of certain volatile matters. Acetic acid, as detected by GC-MS, was considered in the first place. However, acetates were not found in XRD results, implying that either acetic acid was only a less important contaminant affecting the coupons, or the acetates were converted into stabler products. Since the acetic acid amount reserved in the camphor wood samples was very limited compared with the mass of any coupon or corrosion product, two different assumptions can be made. One is that the limited acetic acid may play a catalytic role in the transformation processes and the acetates were not the final products; the other is that the predominant neutral terpenes may have been converted into reactive carboxylic acids through certain paths [17,18], and the carboxylates were just intermediate products as well. It can be inferred from the above discussion that the emitted contents of L-(−)-Camphor (or (±)-Camphor), α-Terpineol and Terpinen-4-ol were greatly correlated to the corrosion level of coupons. Besides acetic acid, the three components may be regarded as the causal matters, just like the role of Hinokitiol described in the reference [4]. However, the corresponding carboxylic acids were not detected by GC-MS in this study. Therefore, the real mechanisms need further and deeper studies.

4. Conclusions

Camphor wood samples tested in this study are unsuitable to be used as museum storage materials, especially for the storage of metallic objects. Volatile matters emitted by the samples are mainly composed of terpenes and their derivatives. Acetic acid does not occupy a significant content in the volatile matters, but it may play a catalytic role in the corrosion processes. The reserve of acetic acid continuously decreases along with the aging of the Cinnamomum camphora sample, while the Cinnamomum glanduliferum sample contains a higher concentration of acetic acid. Aqueous extraction pH value of the Cinnamomum camphora samples increases along with the aging of sample, while the Cinnamomum glanduliferum sample presents stronger acidity in aqueous extraction. The corrosion products include CuO and Pb\(_{10}(\text{CO}_3)_{6}(\text{OH})_6\)O respectively for copper and lead coupons, while the silver coupons are resistant to the volatile matters. It is necessary to further study the
corrosion mechanisms, such as the role of specific volatile components, so that the manufacturers and the conservators will be clearer about the modification strategy for the camphor wood materials.

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