

Evaluation of Degradation of Japanese Hanging Scrolls Using Relative Peak Area of Volatile Organic Compounds

Kang Lee¹, Michel Sablier², Toshiharu Enomae¹, Masamitsu Inaba³

¹Faculty of Life and Environmental Sciences, University of Tsukuba, Tsukuba, Japan

² Centre de Recherche sur la Conservation (CRC, USR 3224), Muséum National d'Histoire Naturelle, Ministère de la Culture, CNRS, Paris, France

³Graduate School of Fine Arts, Tokyo University of the Arts, Tokyo, Japan

Abstract

Volatile organic compounds (VOCs) generated from naturally aged Japanese hanging scrolls and their model samples were measured using solid-phase microextraction / gas chromatography-mass spectrometry (SPME / GC-MS) to clarify the effect of different painting papers and raw materials on the degradation state of hanging scrolls. VOC-based degradation markers were identified and their applicability was considered for degradation evaluations of actual Japanese hanging scrolls. The relative peak areas of different VOC groups were calculated by normalising their peak areas to the total peak area of long-chain hydrocarbons. When a painting paper was immersed in a $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution, or coated with an alum solution, the relative peak areas of furfural and carboxylic acids increased after accelerated ageing, while these relative peak areas decreased when animal glue was applied, indicating that animal glue inhibited the generation of VOCs. These results indicate that VOCs are valid degradation markers of Japanese paintings. When the painting paper containing Cu^{2+} was stacked with lining paper, furfural and carboxylic acids migrated into the lining paper with ageing. Animal glue coated on the painting paper retarded this migration into the lining paper. For the lining paper coated with wheat starch paste, the relative peak areas of furfural, carboxylic acids, and aliphatic aldehydes did not change significantly with ageing, indicating that wheat starch paste did not contribute to paper degradation, although these relative peak areas increased when aged wheat starch paste was applied. These results indicate that the targeted VOCs are valid degradation markers of Japanese hanging scrolls.

Keywords: Japanese painting, hanging scroll, volatile organic compounds, SPME GC-MS, accelerated ageing

Correspondence to: Kang Lee, University of Tsukuba, #209, Institutes of Biological and Agricultural Sciences C, 1-1-1, Tennodai, Tsukuba, Ibaraki, 305-8572, Japan. Email: nigitaz55@gmail.com

1. Introduction

Paintings for Japanese hanging scrolls (*kakejiku*) are created on a specific painting paper (*honshi*) sized with an alum-animal glue solution (*dōsa*), with brush-applied paints that contain pigments and animal glue (see Table 1 for Japanese terminologies and their English translations). For support, the paintings are bordered by mounting fabrics and lined with multiple layers of paper (Fig. 1, Ohbayashi 2015). Typically, three or four kinds of Japanese paper are used for the lining, and they are sequentially adhered on the back of the painting paper: ① First, a comparatively thin but strong lining paper (*hadaurashi*) is pasted directly on the back of the painting paper using wheat starch paste (*shinnori*). ② The subsidiary (*mashiurashi*) lining paper is then adhered with aged wheat starch paste (*furunori*) to maintain a balance between the painting paper and the mounting fabric in terms of their thickness and strength. ③ The overall lining paper (*nakaurashi*) and final lining paper (*sourashi*) are also adhered with aged wheat starch paste. The work thus mounted is rolled around a rod that is attached at the bottom of the scroll for storage (Jap. Painting Cons. Lab. 2010). However, depending on the use of inappropriate materials, poor mounting and conservation works, and improper storage environment, natural ageing of hanging scrolls is expected to proceed via various mechanisms, and conservation treatments will be carried out frequently.

The objective of this series of study is to evaluate the long-term stability of hanging scrolls. This involves considering not only a single sheet of painting paper but also the composite materials incorporated into the lining paper. Moreover, this involves clarifying the materials and potential deterioration dynamics among the painting paper, lining paper adhered to the painting paper with wheat starch paste, and other painting materials. In our previous series of studies, accelerated ageing tests using the moist heat and sealed tube methods were carried out with the painting paper immersed in a $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution, instead of copper green pigment, alum-animal glue size, animal glue, and wheat starch paste at different concentrations. The degradation rates were compared for the unlined painting paper and the painting paper from the lined complex using the moist heat ageing method. The results indicated that the presence of the lining paper improves the permanence of the painting paper both physically and chemically (Lee et al. 2021A). Degradation behaviour and rates obtained for the sealed tube ageing method, which is expected to simulate the condition of an airtight environment in a storage box and the stacked structure of a rolled paper, were compared with the results obtained for the moist heat method. This result revealed that storage of a deteriorated hanging scroll in a closed system further degraded the painting paper faster than in an open system (Lee et al. 2021B). Changes in the degree of degradation depending on the position in the rolled hanging scrolls and storage conditions were characterised for a detailed elucidation of the degradation behaviour of hanging scrolls (Lee et al. 2021C).

These results can provide information for establishing a method to extend the

preservation life of hanging scrolls. A hanging scroll is composed of several components ranging from a paper substrate to various painting materials. If the degradation state of an individual hanging scroll can be evaluated accurately and non-destructively based on an understanding of degradation behaviour, it would be possible to predict the appropriate time for conservation. However, the degradation state of paintings has been evaluated customarily by visual inspection because destructive examinations of Japanese paintings are basically prohibited under current regulations for cultural properties. On the other hand, non-destructive analytical methods for the analysis of volatile organic compounds (VOCs) using proton-transfer-reaction mass spectrometry (PTR-MS) (Lindinger et al. 1998), lithium-ion attachment-mass spectrometry (Li⁺-IAMS) (Fujii et al. 2001), direct analysis in real time time-of-flight mass spectrometry (DART-TOFMS) (Cody et al. 2005), and selected ion flow tube mass spectrometry (SIFT-MS) (Smith et al. 2011) have been used in the field of natural sciences. In particular, solid-phase microextraction / gas chromatography-mass spectrometry (SPME / GC-MS) has been shown to be highly efficient for the detection of VOCs released from artefacts, which in turn can be used to evaluate the degradation state. SPME / GC-MS does not require the use of a solvent as an extractant for sampling and can trap VOCs extensively and sensitively, leading to high reliability (Lattuati-Derieux et al. 2006). For the analysis of hanging scrolls, VOCs can be easily trapped by placing SPME fibres in gaps inside the rolled hanging scroll, on the painting paper with the hanging scroll unrolled, or in the space inside a paulownia (*Paulownia tomentosa*) storage box (*kiribako*) used to store the hanging scroll, all of which are expected to be useful to determine the comprehensive degradation state in combination with visual observation results.

There are several studies on the use of VOC measurements for book papers. Furfural has often been used as a marker of cellulose degradation, and the acidity of paper is well-correlated with the amount of furfural (Lattuati-Derieux et al. 2006; Ramalho et al. 2009; Strlič et al. 2009; Łojewski et al. 2010). Clark et al. (2011) focused on the oxidation of lipids derived from components of paper, binding agents, ground wood-pulping materials, and some glues and inks to explain the generation of aldehydes, aliphatic hydrocarbons, ketones, alcohols, and carboxylic acids. While fatty acids are minor components of paper, most of their auto-oxidation products provide a wide variety of functional groups emitted from ageing books. The degradation marker for lignin, which is one of the components of paper, includes guaiacol, vanillin, benzyl alcohol, and benzyl aldehyde (Łojewski et al. 2010; Clark et al. 2011). Moreover, Battistel et al. (2018) compared the VOCs emitted from naturally aged machine-made and hand-made Japanese papers (*mitsumata* paper and *kozo-gampi* mixed paper), in addition to their raw fibres. They detected acetic acid and 1-butanol in small amounts from raw fibres but in greater amounts from paper, indicating that the emission of these VOCs is more strongly influenced by the papermaking process than by the raw materials. Moreover, a larger amount of

furfural was detected from raw fibres than from paper, and a net difference in the amount of furfural between modern and naturally aged papers was not evident.

There are two concerns that inspired our study. First, there have been few reports on VOC studies using SPME / GC-MS for hanging scrolls and Japanese paintings. If information on VOCs can be obtained from hanging scrolls, it is possible to acquire more detailed information for the degradation behaviour and deterioration dynamics in hanging scrolls. In this study, to examine the applicability of VOCs for the assessment of the degradation state of Japanese hanging scrolls, VOCs from model samples of Japanese hanging scrolls before and after ageing were measured using SPME / GC-MS to clarify the effect of different painting papers and painting materials on the degradation state of hanging scrolls.

Another concern that inspired our study was the relationship between natural ageing and accelerated ageing. Shahani et al. (2001) found that the generation and decomposition of organic acids in book papers by natural ageing are more similar to those of sealed tube ageing than those of moist heat ageing and, furthermore, that organic acids can be used to distinguish the degradation mechanism between natural and accelerated ageing sensitively. Lee et al. (2017) also found that sealed tube ageing provided better simulation results of natural ageing than moist heat ageing because the composition ratio of oxalic and glycolic acids, the primary and secondary products in book papers, were similar to those before accelerated ageing. This result confirms that natural ageing can be simulated in terms of organic acid generation. In this respect, if each VOC amount changes at the same rate between natural ageing and accelerated ageing, then that VOC detected in accelerated ageing must be generated and removed by the same mechanism as that of the natural ageing. To this end, naturally aged hanging scrolls were additionally aged by the moist heat and sealed tube methods, and VOCs were measured before and after accelerated ageing to evaluate the correlation between natural ageing and accelerated ageing.

2. Experimental

2.1. Samples

Samples were prepared to acquire information on VOCs separately not only from the painting paper but also from the painting materials contained in the painting paper—lining paper complex. As untreated samples, two kinds of Japanese paper were used. One was *kumohada-mashi* (produced by Iwano-Heizaburou Seishisho; paper mixed with hemp [*taima*] and *kozo* fibres; cooked with sodium carbonate not wood ash as typical for historical paper; approx. 75 g/m²). The other was unbuffered *kozoshi* (produced by Kashiki Seishi; only *nasu-kozo* fibres; cooked with sodium carbonate; approx. 33 g/m²). Moreover, *senshi* (*Menryo-tansen*; produced by China Xuan Paper Group Corporation; paper mixed with *seitan* [*Pteroceltis tatarinowii*] and rice straw fibres; approx. 12 g/m²), popularly used as a general Japanese painting, was prepared, although it is not Japanese paper. In addition, buffered *kozoshi*

(produced by Kashiki Seishi; only *nasu-kozo* fibres; cooked with sodium carbonate and loaded with calcium carbonate; approx. 12 g/m²) used as the lining paper was also prepared. The dimensions of the samples were 100 × 240 mm².

Model samples of the painting paper using *kumohada-mashi* were treated with different solutions of materials listed below to investigate the effect of different conditions on the generated amount of each VOC (see Fig. 2 and Table 2).

- Sample C: The painting paper was immersed in a copper (II) sulphate pentahydrate (CuSO₄ · 5H₂O, Fujifilm Wako Pure Chemical Industries; coated amount: approximately 0.8 g/m²; hereafter referred to as Cu²⁺) solution instead of the copper green pigment.
- Sample CG: An animal glue (Asahi Gelatine Industrial, Asuka[®]) solution was uniformly applied on the front and backside of sample C using an applicator bar (RK Print Coat Instruments, K-Lox proofer) instead of a Japanese sizing brush (*dōsabake*). This sample had the purpose of clarifying any inhibiting effect of animal glue on the copper-induced degradation.
- Sample A: An alum (AlK(SO₄)₂ · 12H₂O, Fujifilm Wako Pure Chemical Industries) solution was uniformly applied on the front and backside of the painting paper using an applicator bar.
- Sample AG: An alum-animal glue mixed solution was uniformly coated on the front and backside of the painting paper using an applicator bar.

Normally, to support the painting paper, the lining paper is pasted onto the painting paper with wheat starch paste. However, in this study, the lined painting paper—lining paper complex was not prepared for the purpose of considering the painting paper and lining paper separately. Therefore, unadhered single samples were prepared by applying the adhesives only to the lining paper.

- Sample W: Wheat starch paste (starch was produced by Kagoshima Denpun, starch concentration of 12%) was coated on the front of the lining paper using a paste brush (*noribake*).
- Sample AW: Aged wheat starch paste (*furunori*), which was fermented for more than 10 years, was coated on the front of the lining paper using a paste brush. The same starch concentration as that for sample W was used for comparison.

The aged wheat starch paste has a lower adhesiveness and viscosity than fresh wheat starch paste, which leads to a soft texture during the process of preparing hanging scrolls in which several kinds of lining papers are adhered together (Hayakawa et al. 2002). In fact, wheat starch paste is used to adhere the first lining paper to the painting paper, and the aged wheat starch paste is used to adhere the rest of the lining papers; however, in this case, the same type of first lining paper was used to compare the emission behaviour of VOCs in the same type of substrate.

To characterise the VOCs not only from paper but also from raw materials, samples of animal glue, wheat starch paste, and aged wheat starch paste were also prepared.

Table 1 Japanese technical terms used in this study and their English translations

Japanese terms	English translations
<i>kakejiku</i>	Japanese hanging scroll
<i>Honshi</i>	Painting paper
<i>Hadaurashi</i>	First lining paper
<i>Mashiurashi</i>	Subsidiary lining paper
<i>Nakaurashi</i>	Overall lining paper
<i>Sourashi</i>	Final lining paper
<i>Dōsa</i>	Alum-animal glue size
<i>Shinnori</i>	Wheat starch paste
<i>Furunori</i>	Aged wheat starch paste
<i>Kiribako</i>	Paulownia wooden box
<i>Taima</i>	Hemp
<i>Dōsabake</i>	Sizing brush
<i>Noribake</i>	Paste brush

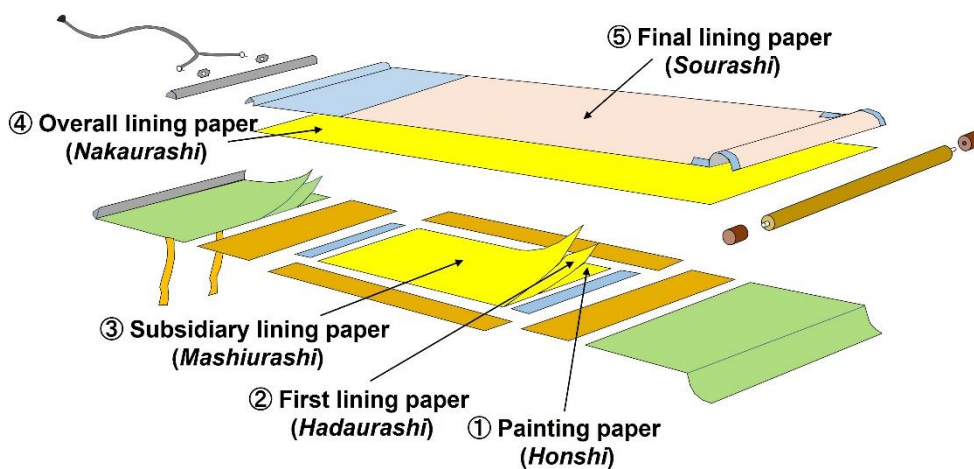


Fig. 1 Structure of disassembled hanging scroll from the back-side

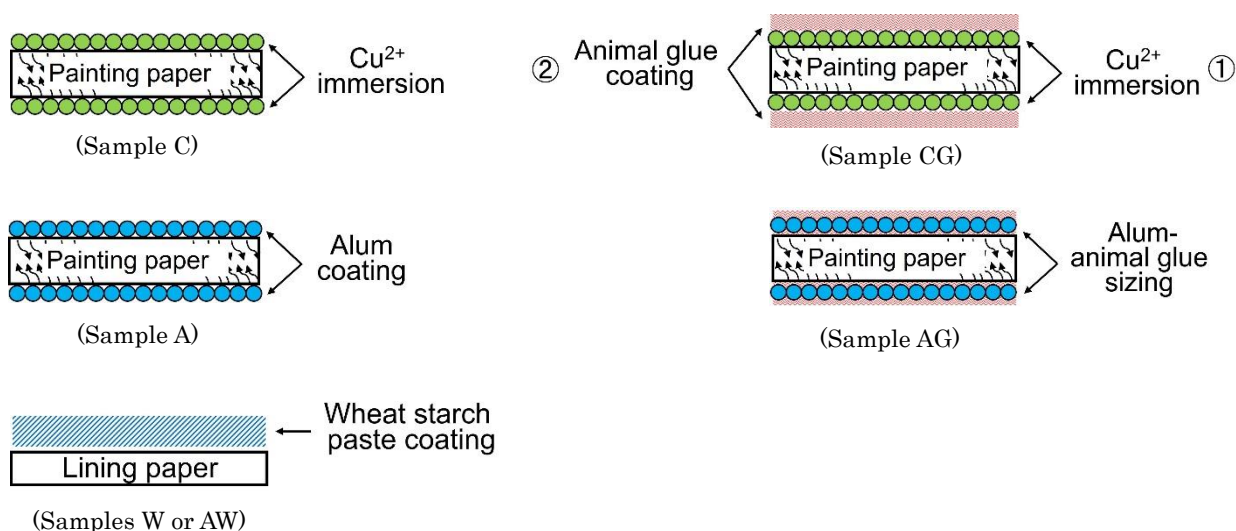


Fig. 2 Structures of model samples

Table 2 List of model samples

Symbol	Sample	Concentration of aqueous solutions				
		Cu^{2+} (mmol/L)	Alum (w/v %)	Animal-glue (w/v %)	Wheat starch (w/v %)	Aged wheat starch (w/v %)
-	<i>Unbuffered kozoshi</i>	-	-	-	-	-
-	<i>Kumohada-mashi</i>	-	-	-	-	-
-	<i>Senshi</i>	-	-	-	-	-
-	<i>Buffered kozoshi</i>	-	-	-	-	-
C	Cu^{2+} -immersed <i>kumohada-mashi</i>	6	-	-	-	-
CG	Animal glue coated <i>kumohada-mashi</i> after Cu^{2+} immersion	6	-	0.6	-	-
A	Alum coated <i>kumohada-mashi</i>	-	0.3	-	-	-
AG	Alum-animal glue sized <i>kumohada-mashi</i>	-	0.3	0.6	-	-
W	Wheat starch paste coated <i>buffered kozoshi</i>	-	-	-	12	-
AW	Aged wheat starch paste coated <i>buffered kozoshi</i>	-	-	-	-	12

To correlate the relative peak areas of the detected VOCs between natural ageing and accelerated ageing of paper, we obtained three naturally aged hanging scrolls (scrolls A, B, and C), although the production years of the scrolls are unknown. Scrolls A and B are the same samples used in our previous study (Lee et al. 2021C). Scroll B showed significant discolouration towards the peripheral positions of the roll, while scrolls A and C showed significant discolouration towards the central positions in the vertical direction. VOC extraction of the three hanging scrolls was conducted near the periphery of the painting paper.

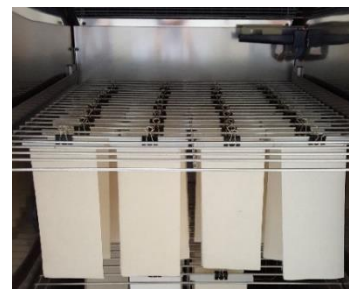
2.2. Accelerated ageing test

The model samples were aged using the sealed tube method (ISO 5630-5: 2008). The paper samples (5.3 g / 194 mL) and raw materials (5 g / 194 mL), i.e., animal glue, wheat starch paste, and aged wheat starch paste, were inserted in separate glass tubes. After 24 h of conditioning at 23°C and 50% RH, the samples were sealed in the glass tubes. The temperature was set to 80°C, the same temperature used in the moist heat method, rather than the standard temperature of 100°C. The ageing test was carried out for a maximum of eight weeks.

To examine VOC migration between the non-adhered painting and lining papers, one sheet of each was stacked in close contact between two glass plates clamped together tightly and aged at 80°C and 65% RH for two weeks (stack method). On the other hand, naturally aged hanging scrolls were aged using both the moist heat method at 80°C and 65% RH (ISO 5630-3: 1996) and the sealed tube method (80°C) for two weeks (Fig. 3).



(sealed tube method)



(moist heat method)

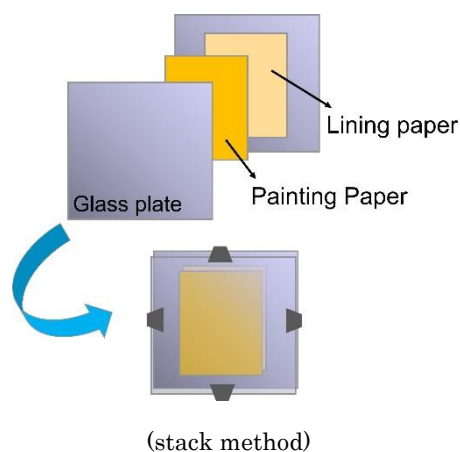


Fig. 3 Accelerated ageing methods

2.3 Analytical methods

2.3.1 SPME / GC-MS

To collect VOCs from the samples, 50/30 μm of divinylbenzene / carboxen / polydimethylsiloxane (DVI / CAR / PDMS) fibre (Supelco) was used for solid phase microextraction (SPME). To remove the fibre contaminants and stabilise the polymer phase, conditioning was carried out at 270°C for 30 min in the GC injector port every time prior to collecting the VOCs from the sample. The needle of the holder equipped with the fibre was inserted into the vial (30 mL) containing the sample (paper: 0.1 g, raw material: 3g), and the fibre was then slowly pushed out and left at ambient temperature (approx. 23°C) for 24 h without contacting the sample for collecting VOCs. After extracting the VOCs, the fibre was returned to the inside of the needle of the holder and immediately inserted into the GC-MS injection port, and the VOCs were desorbed at 250°C for 1 min. Prior to each sample analysis, a blank run was performed under the same measurement conditions to remove residual VOCs and contaminants in the GC injection port or the GC column.

For the GC-MS (Shimadzu, GC2010, GCMS-QP2010plus) analysis, a capillary column (Agilent J&W, DB-WAX, length: 30 m, inner diameter: 0.25 mm, film thickness: 0.25 μm) was used. The mobile phase was helium gas (flow rate: 1 mL/min), and the temperature was held at 40°C for the first 2 min and then increased to 250°C at a rate of 5°C/min. The interface temperature was 300°C, and the ion-source temperature of the mass selective detector was 200°C. The paper samples were run in the splitless mode (sampling time: 1 min), and the raw material samples were run in the split mode (sampling time: 0.5 min). The split ratio applied after injection was 1:10 and 1:20, respectively. The NIST 11 database was used to identify the VOCs. Because the amount of acetic acid reached the saturation level of the MS detector before other VOCs were detected, the MS measurement was started after the acetic acid peak was detected (at approx. 2 min of retention time). In calculating the total peak area, the detected siloxane derivatives were excluded because they were regarded as a system-derived component, such as septum, capillary column, and SPME fibre.

2.3.2 pH

The pH of the paper surfaces was measured following TAPPI 529 om-04: 2009. To measure the pH of the sample, 60 μL of 0.1 mol/L potassium chloride solution was dropped onto the surface of the paper placed on a silicon plate, and the sample was left for 2 min in contact with a flat surface electrode (Extech Instruments, pH100). An average of 8 measurements for each sample was collected.

2.3.3 Degree of polymerisation (DP)

The degree of polymerisation (DP) was measured using the viscosity method with a copper ethylenediamine solution (CuED) (ISO 5351: 2010). The painting paper was

rinsed thoroughly with warm water (50°C) to remove the animal glue or wheat starch paste on the painting paper and then shredded in a blender for 3 to 5 min. The shredded paper was then filtered and reduced for 1 h using 10 mL of a borane *tert*-butylamine complex solution (0.2 mol/L). A 25-mg sample of the dried paper was weighed and dissolved in a 0.5 mol/L CuED solution (GFS Chemicals). The limiting viscosity number $[\eta]$ was determined from a measurement of one concentration solution using a Cannon–Fenske viscometer (Sibata, No.100) at 25.0±0.1°C. Martin’s equation (according to the table in the ISO 5351: 2010) was used for the calculation:

$$\log \frac{\eta_{sp}}{c} = \log[\eta] + k[\eta] \cdot c \quad (\eta_{sp} = \frac{\eta}{\eta_0} - 1),$$

where η is the viscosity of the solution, η_{sp} is the specific viscosity, $[\eta]$ is the limiting viscosity number, and c is the concentration. The viscosity-average degree of polymerisation (DP_v) was calculated using Mark–Houwink–Sakurada’s equation (Santucci et al. 2001):

$$[\eta] = K_m \cdot DP_v^a,$$

where m is the molecular weight and K and a are the Mark–Houwink constant and exponent, respectively. In this study, $K_m = 1.33$ and $a = 0.905$ were used (Brandrup et al. 1998). The degradation rate constant (k) of the degree of polymerisation was calculated according to the method of Sharples (1971):

$$\frac{1}{DP_n} = kt + \left(\frac{1}{DP_{n0}}\right),$$

where DP_{n0} is the degree of polymerisation before accelerated ageing, which was determined by converting the viscosity-average degree of polymerisation (DP_v) into the number-average degree of polymerisation (DP_n), and the difference of its reciprocal ($1/DP_n$) is considered the number of chain cleavages (Whitmore et al. 1994).

3. Results and Discussion

3.1. VOCs detected from model samples

Łojewski et al (2010) showed that the generation rate of long-chain hydrocarbon compounds (LHCs) of VOCs does not change significantly as degradation progresses. In this paper, we report the total peak area of each target group, i.e., furfural, carboxylic acids, alcohols, aldehydes, ketones, and terpenes, relative to that of LHCs because LHC emissions were also observed to remain stable throughout the experiments. This normalisation enables quantitative evaluation of the VOCs emissions of the samples.

VOCs from untreated paper samples, i.e., unbuffered *kozoshi*, *senshi*, *kumohada-mashi*, and buffered *kozoshi*, were quantified (Fig. 4). Because the physical strength of “*senshi*” and “*unbuffered kozoshi*” changed relatively small compared with those of “*kumohada-mashi*” and “*buffered kozoshi*” during the ageing test over four weeks, the ageing span was set separately for the SPME analysis to determine VOC changes clearly during the degradation process. Fig. 4-A shows the changes in the relative peak areas of furfural, which was the smallest among all the VOC components prior to accelerated ageing. The generation rate of furfural increased with ageing according to previous studies (Lattuati-Derieux et al. 2006; Ramalho et al. 2009; Strlič et al. 2009; Łojewski et al. 2010); however, the relative peak area decreased for the untreated samples. Battistel et al. (2018) attributed this behaviour of furfural to raw fibres. Because the untreated samples possibly have marginal internal degradation factors such as acids, it was thought that the furfural amount decomposed by internal factor is larger than that of generated with ageing.

Carboxylic acids are generated by oxidative degradation of cellulose, hemicellulose, and lignin in paper and are known to accelerate acid hydrolysis by accumulating in the paper (Shahani et al. 2001). Fig. 4-B shows the changes in the relative peak areas of carboxylic acids, including C₄ - C₁₂ acids. The relative peak area of these acids tended to increase with ageing, although it did not change in the buffered *kozoshi* during the ageing time. This inhibition is attributable to calcium carbonate in buffered *kozoshi* used as filler.

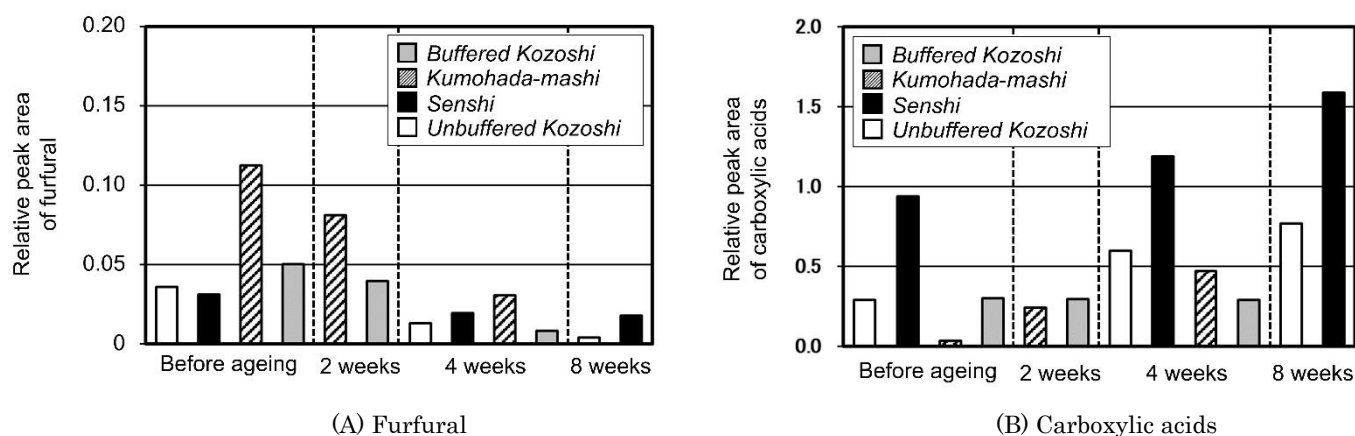


Fig. 4 Changes in the peak area of each group relative to the peak area of hydrocarbons in the untreated paper samples with ageing

Fig. 5 shows a comparison of the behaviour of different VOCs in the presence of painting materials that accelerate acid hydrolysis and / or oxidation, mainly attributable to Cu^{2+} , organic acids, and alum in the painting paper. The concentrations of Cu^{2+} from the copper green pigment and alum used in the actual paintings have some variations, and therefore it is difficult to determine the effect of Cu^{2+} or alum on the degradation of each paper object. However, to examine how the differences in the degree of degradation of these samples because of acid hydrolysis and oxidation clarified in our previous study (Lee et al. 2021A) are reflected in the relative peak areas of the VOCs, changes in the peak areas due to the materials added to the painting paper were compared.

Fig. 5-A shows that the relative peak areas of furfural and carboxylic acids were larger in all the treated samples than in the untreated paper. Samples CG and AG containing animal glue tended to have lower peak areas of furfural and carboxylic acids than samples C and A. As described in our previous study (Lee et al. 2021A), because Cu^{2+} in sample C gives rise to oxidation reactions in the painting paper and co-occurring organic acids and, additionally, alum in sample A dissociates sulphate ions, these effects further accelerate the acid hydrolysis and oxidation of cellulose and hemicellulose to form furfural and carboxylic acids. However, when animal glue was applied, because it can chelate Cu^{2+} and buffer the acid dissociated from alum, degradation reactions and, thus, the generation of furfural and carboxylic acids were inhibited.

Fig. 5-B shows that the relative peak area of aldehyde was larger in samples C and A than in untreated paper while the relative peak area of alcohol was smaller in samples C and A than in untreated paper, indicating that the oxidation of alcohol to aldehyde proceeded, and therefore aldehyde can be used as a marker of the oxidative degradation of Japanese paintings. However, the relative peak area of aldehydes was larger in samples CG and AG than in their counterpart samples C and A. Because the oxidation reaction rate at each stage is not necessarily identical, the transformation of aldehyde to carboxylic acid can be suppressed by applying animal glue.

To ensure that furfural and carboxylic acids are valid degradation markers, the peak areas of furfural and carboxylic acids were compared with the pH and the degradation rate index of degree of polymerisation of cellulose (I_D : degradation rate constant k divided by the value of DP_0 , before accelerated ageing), as shown in Figs. 6 and 7. At low pH, cellulose chains were decomposed and I_D tended to be large, which indicated that the generation of furfural and carboxylic acids was exponentially correlated with low pH and large I_D . Moreover, the peak area was larger for samples C and CG, wherein Cu^{2+} causes oxidation reactions and co-occurring organic acids to promote acid hydrolysis, than samples A and AG, which contain acid dissociated from alum.

From the above results, among the VOCs released from the treated painting papers,

the relative peak areas of furfural and carboxylic acids correspond to the oxidation and acid hydrolysis reactions of paper attributed to the presence of Cu^{2+} or alum. Because of these correlations, furfural and carboxylic acids are thought to be valid degradation markers of Japanese paintings.

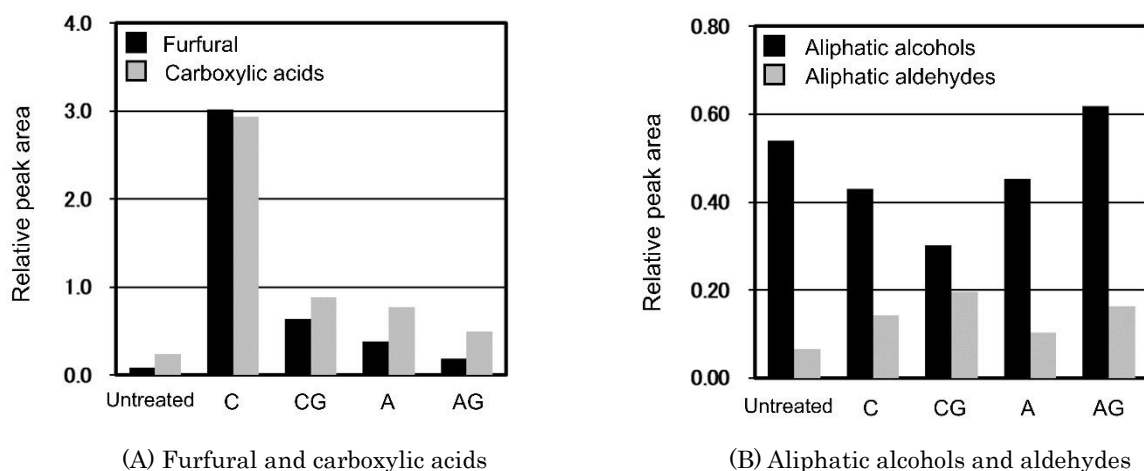


Fig. 5 Comparison of the peak area of each group relative to the peak area of hydrocarbons in the treated samples after ageing for two weeks

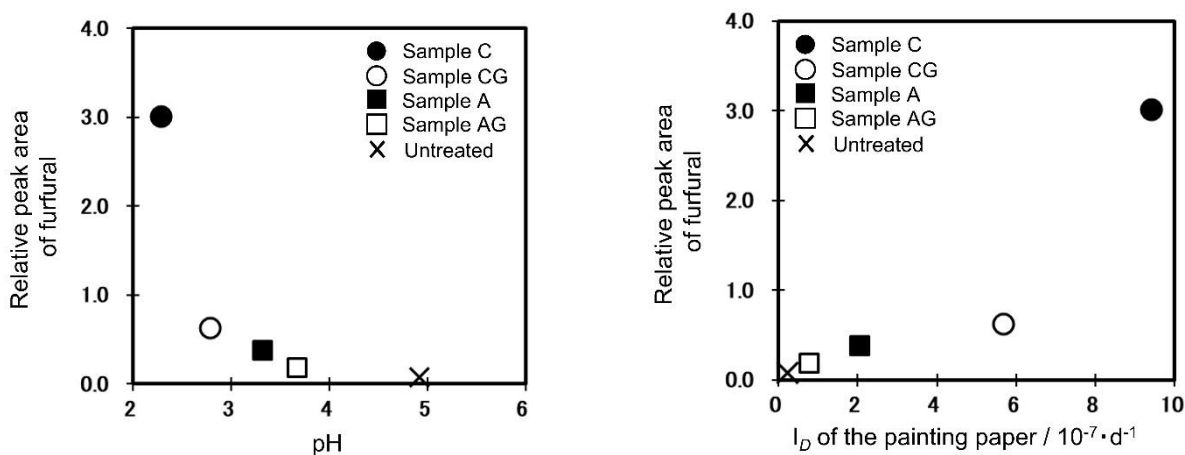


Fig. 6 Comparison of the pH and degradation rate index of degree of polymerisation (I_D) with the peak area of furfural relative to the peak area of hydrocarbons detected from the treated samples after ageing for two weeks

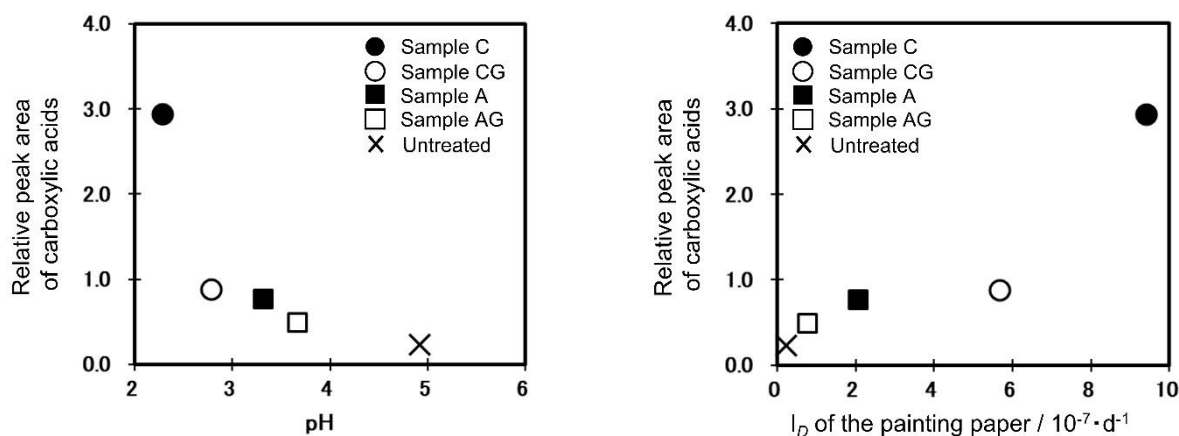


Fig. 7 Comparison of the pH and degradation rate index of degree of polymerisation (I_D) with the peak area of carboxylic acids relative to the peak area hydrocarbons detected from the treated samples after ageing for two weeks

To examine the migration of VOCs generated in the painting paper into the lining paper, the painting papers (samples C and CG) underwent accelerated ageing in a stack with unadhered lining papers. As shown in Fig. 8, the relative peak areas of furfural and carboxylic acids were larger in both samples C and CG than in the aged untreated lining paper. Lee et al. (2021A) previously reported that organic acids generated by the oxidation of Cu^{2+} in the painting paper, in addition to Cu^{2+} itself, can migrate into the lining paper. In this case, the furfural and carboxylic acids generated in the painting paper or Cu^{2+} migrated into the lining paper, generating those VOCs. In sample CG, the peak areas of furfural and carboxylic acids were smaller in each lining paper than in sample C, indicating that animal glue partially inhibited the generation and migration of furfural and carboxylic acids in addition to the migration of Cu^{2+} into the lining paper.

Fig. 9 compares the VOCs (the relative peak areas of furfural, carboxylic acids, and aliphatic aldehydes) generated in samples W and AW, respectively. Sample AW showed larger peak areas than sample W. Sample W showed slightly larger peak areas than the aged untreated lining paper. This result agrees with our previous result (Lee et al. 2021A) in that wheat starch paste has a marginal effect on the degradation of paper. Aged wheat starch paste is produced by fungal microbial activity and the ageing of starch with long-term storage, wherein starch is converted into smaller molecules and organic acid by-products are produced by micro-organisms.

Ageing reduces the molecular weight of the starch paste, which contributes to an increase in the crystallinity of the paste (Hayakawa et al. 2002; Belard et al. 2010). This yields an adhesive with desirable working properties and low viscosity, giving rise to the soft texture in the hanging scroll made of several kinds of lining papers. This reduces the stress on the paper when the rolled scroll is opened or closed. However, the organic acids produced in aged wheat starch paste induce acid hydrolysis of the paper. Therefore, the relative peak areas of furfural and carboxylic acids were larger than in the case of wheat starch paste. In fact, the pH before and after ageing for 2 weeks was respectively 5.6 and 5.2 in the untreated lining paper sample, 5.5 and 5.2 in sample W, and 4.9 and 4.5 in sample AW. Moreover, aliphatic aldehydes can be used as a marker of the oxidative degradation of the adhesive in hanging scrolls.

From the above results, migration of VOCs into the lining paper corresponds to degradation of the painting paper. Animal glue inhibited the generation of VOCs, which reduces the amount of VOCs that can migrate into the lining paper. Sample W was not significantly different from the untreated lining paper, wherein the VOCs were released, indicating its stability during degradation. By contrast, aged wheat starch paste led to larger peak areas of VOCs, thus contributing to paper degradation.

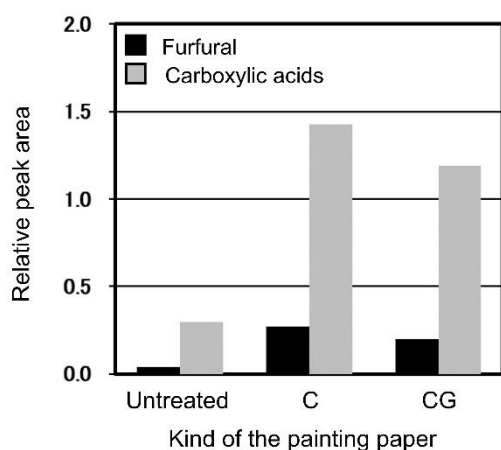


Fig. 8 Peak areas of furfural and carboxylic acids relative to the peak area of hydrocarbons detected from the lining paper stacked with the painting paper after ageing for two weeks

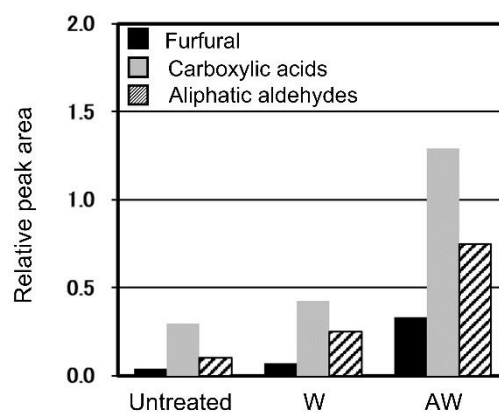


Fig. 9 Peak areas of furfural and carboxylic acids relative to the peak area of hydrocarbons detected from the lining paper after ageing for two weeks

3.2. VOCs detected from raw material samples: animal-glue, wheat starch paste, and aged wheat starch paste

Table 3 compares the relative peak areas of the VOCs in the accelerated ageing for the raw materials, i.e., animal glue, wheat starch paste, and aged wheat starch paste, from each paper sample before and after accelerated ageing. The relative peak area of furfural did not change in the animal glue and increased only slightly in the wheat starch paste after ageing, although it increased dramatically in the aged wheat starch paste. Similarly, the relative peak area of carboxylic acids was not significantly different in the animal glue and wheat starch paste before and after ageing, although it increased greatly in the aged wheat starch paste. These results are consistent with the tendency discussed in the previous section. The decomposition of starch produces organic acids, which in turn induces the acid hydrolysis of starch, thus lowering the molecular weight of starch and resulting in the production of furfural and carboxylic acids.

For aliphatic alcohols and aliphatic aldehydes, C₅–C₁₀ aldehydes were detected in the fresh and aged wheat starch pastes, and C₉–C₁₀ aldehydes were detected in the animal glue. The relative peak area of aldehyde was larger than the alcohol from all three materials after sealed tube ageing, particularly from aged wheat starch paste, indicating that oxidation occurred to a greater extent in this sample. In animal glue and wheat starch paste, oxidation occurred only to a slight extent. A small amount of aromatic aldehyde was detected, and in all samples, the relative peak area of aromatic aldehyde increased slightly after ageing. Furthermore, terpenes whose source includes trees and the indoor environment (Cincinelli et al. 2016) were detected in animal glue. The relative peak area of terpenes increased slightly after ageing, presumably because terpenes were absorbed from the environment. Ketones were detected only in wheat starch paste and aged wheat starch paste. Ketones are known to be produced from the oxidation reactions of carboxylic acids and lipids

(Strlič et al. 2009). From the above results, it can be concluded that animal glue and wheat starch paste are stable materials, and furfural, carboxylic acids, and aldehydes can be considered as markers of the degree of degradation of aged wheat starch paste.

Table 3 Peak areas of each group relative to the peak area of hydrocarbons in raw materials after ageing for two weeks

Degradant	Animal-glue		Shinnori		Furunori	
	before ageing	2 weeks	before ageing	2 weeks	before ageing	2 weeks
Furfural	0	0	0.01	1.32	0.01	47.46
Aliphatic alcohols	0.55	0	1.83	1.24	1.37	15.49
Aliphatic aldehydes	0.22	0.32	0.14	0.55	0.16	23.79
Aromatic aldehydes	0.20	0.91	0.07	0.34	0.00	0.25
Carboxylic acids	0.59	0.41	1.00	1.06	1.32	21.35
Ketones	0	0	0.24	0.40	0.75	6.46
Terpenes	0.53	1.48	0.04	0	0	0

3.3. VOCs detected from naturally aged hanging scrolls

The relative peak areas of VOCs, such as furfural, carboxylic acids, and aldehydes, emitted before and after ageing using the moist heat and sealed tube methods were evaluated as degradation markers in the previous sections, and these peak areas were compared among the three naturally aged hanging scrolls (samples A, B, and C). Fig. 10 shows the results of a comparison of the peak areas of these VOCs before and after ageing. Here, the relative peak area (%) was calculated, i.e., the total area of the furfural or aldehyde peak relative to the total area of all the detected peaks. In this graph, the relative peak area of furfural and aldehydes before and after ageing lie on the 45° line, indicating that no change occurred in the relative peak area before and after ageing and suggesting that the mechanism of generation and decomposition of VOCs by accelerated ageing is identical to that of natural ageing.

For sample B, the moist heat method provided peak areas that were more similar to those of natural ageing before and after ageing than the sealed tube method. By contrast, for samples A and C, the sealed tube method provided peak areas that were more similar to those of natural ageing before and after ageing than the moist heat method. These results possibly indicate that the different storage conditions (open or closed systems) of the hanging scrolls are reflected in the ageing conditions. Sample B, which was stored open in the rolled state, showed significant discolouration (Fig.11-B) towards the peripheral positions with a larger amount of sulphate ions, which was possibly affected by the external atmosphere (Lee et al. 2021C). This condition reflects an environment where air circulates, such as for the moist heat method. For samples A and C, which were stored in wooden storage boxes, the difference in discolouration between the first and third turns from the outer side of the scroll cannot be distinguished (Figs.11-A and C). This reflects the sealing

environment in the box and the tightness of the rolled scrolls as in the sealed tube method.

However, the relative peak area of carboxylic acids (Fig. 12), one of the degradation markers, was larger after ageing using the moist heat and sealed tube methods than before ageing in all the samples. Although all the relative peak areas of aliphatic alcohols were reduced after ageing, thus contributing to the formation of carboxylic acids by oxidising aldehydes, carboxylic acids were possibly volatilised more easily in the two ageing methods than in naturally aged scrolls regardless of the storage method. This suggests neither of these two accelerated ageing methods accurately simulated the natural ageing conditions for generating and decomposing volatile carboxylic acids, although they tended to simulate those for generating and decomposing furfural and aliphatic aldehydes.

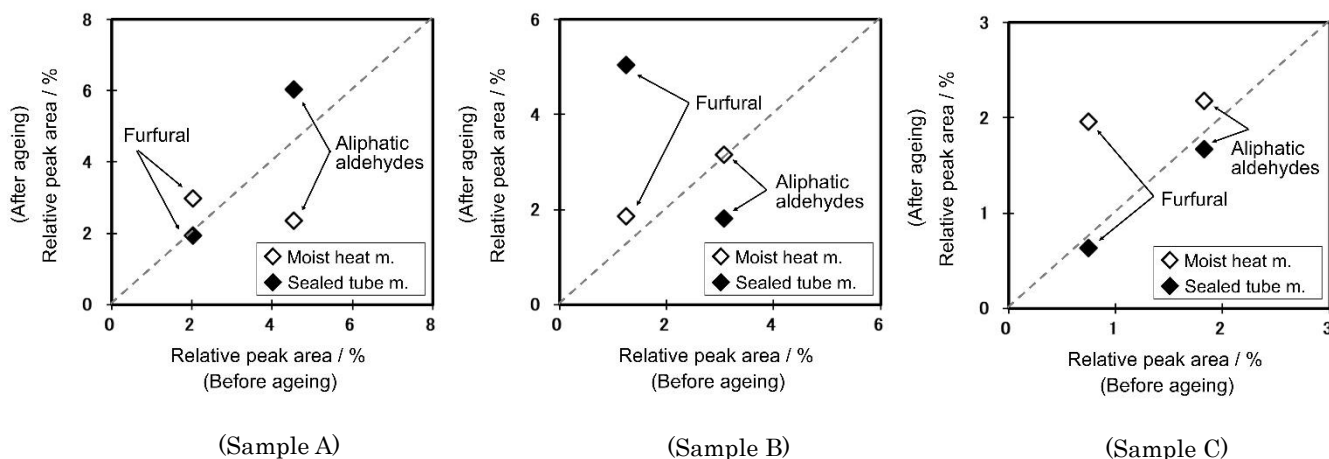


Fig. 10 Relationship between the peak areas of furfural and aliphatic aldehydes relative to the total peak before and after accelerated ageing

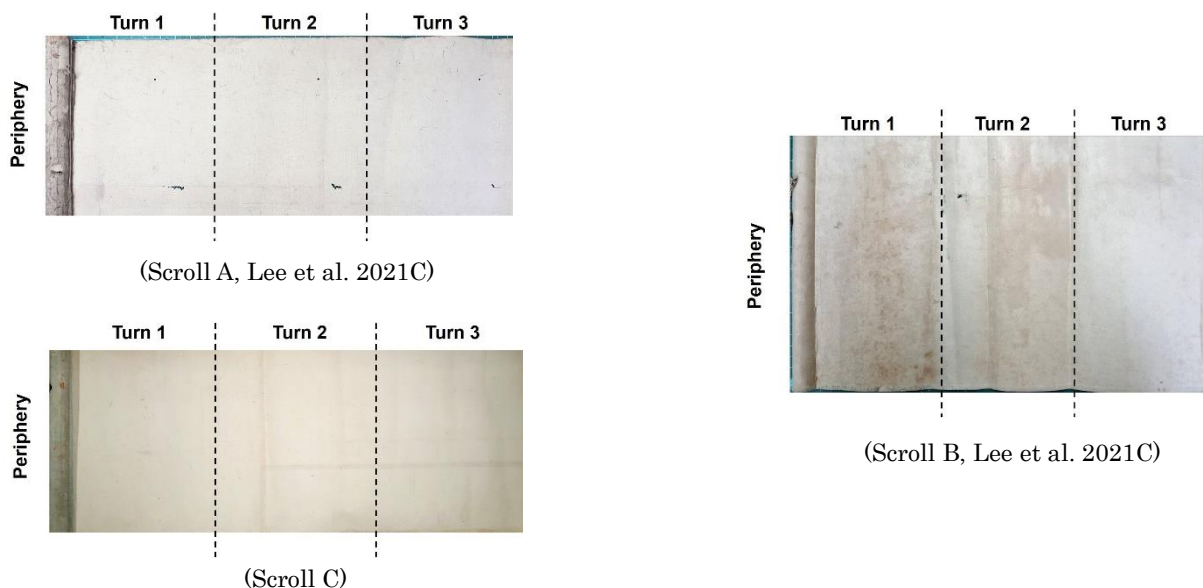


Fig. 11 Monitoring of discolouration from each turn of backside of the outermost lining papers

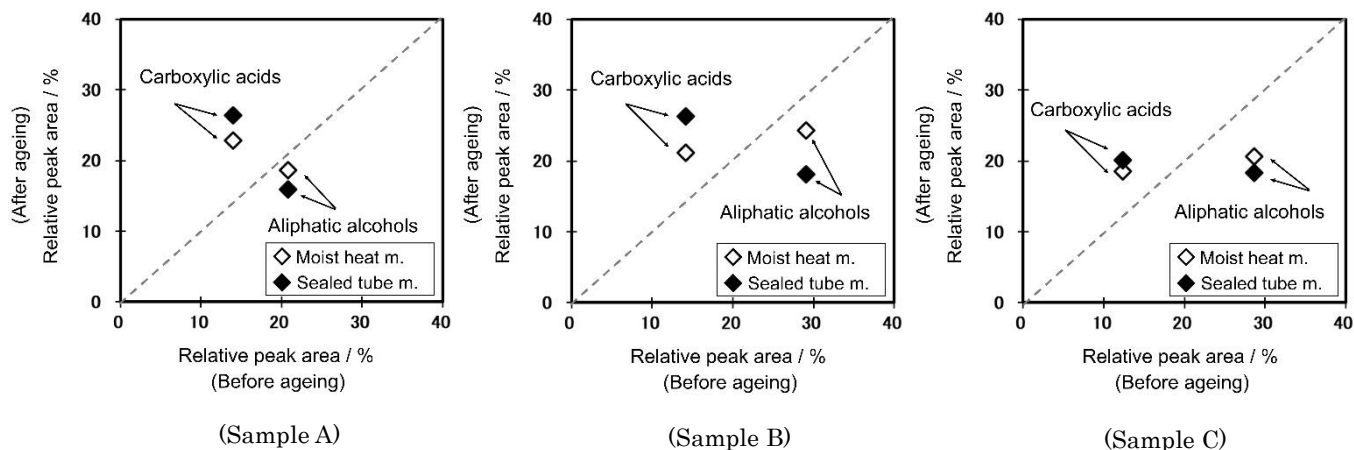


Fig. 12 Peak areas of carboxylic acids and aliphatic alcohols relative to the total peak before and after accelerated ageing

4. Conclusion

VOCs from various aged model samples composed of different Japanese papers and painting materials representing Japanese hanging scrolls were measured using SPME / GC-MS, and the applicability of VOCs as degradation markers was determined. The relative peak areas of the target VOC groups (furfural, carboxylic acids, alcohols, aldehydes, ketones, and terpenes) were calculated by normalizing their peak areas to the total peak area of the long-chain hydrocarbons in VOCs.

After ageing, the relative peak areas of furfural and carboxylic acids increased in the painting paper containing Cu^{2+} or alum, which can induce the degradation of paper. However, the relative peak areas of furfural and carboxylic acids decreased in the sample coated with animal glue, which possibly also reduced the amount of all generated VOCs. Furfural and carboxylic acids showed good correlations with pH variations and the degradation rate index of the degree of polymerisation of the painting paper. Moreover, when the painting paper containing Cu^{2+} was stacked with the lining paper, furfural and carboxylic acids migrated into the lining paper with ageing, whereas for the painting paper coated with animal glue, generation and migration of those VOCs were inhibited. By coating the lining paper with wheat starch paste, the relative peak areas of furfural, carboxylic acids, and aliphatic aldehydes changed marginally after accelerated ageing, while a coat of aged wheat starch paste increased those peak areas, which indicates that those VOCs are valid degradation markers for Japanese hanging scrolls. These results demonstrate that facile SPME / GC-MS measurements can help elucidate the degradation state of the painting papers and painting materials in hanging scrolls. This also indicates that the long-term stability of hanging scrolls can be evaluated with VOCs.

The correlation between natural ageing and accelerated ageing was evaluated by comparing the relative peak areas of VOCs from three naturally aged hanging scrolls before and after moist heat and sealed tube ageing. The relative peak areas of furfural and aliphatic aldehydes were similar before and after ageing, indicating that the

accelerated ageing conditions reflected the actual storage conditions (open or closed systems). However, the relative peak areas of carboxylic acids were not evidently similar before and after ageing using both methods. This indicates that neither of the two ageing methods accurately simulated the conditions for the generation and decomposition of volatile carboxylic acids.

Acknowledgment

The authors thank Professor Kei Arai, Laboratory of Japanese Painting Conservation, Tokyo University of the Arts for offering aged wheat starch paste.

References

- Battistel, D., Padovani, I., Dallo, F., Barbante, C., Zendri, E., Balliana, E.: *Evaluation of the Volatile Organic Compound Emissions in Modern and Naturally Aged Japanese Paper*. Journal of Cultural Heritage 33 (2018): 18-29
- Belard, R., Higuchi, H., Perry, J.: *Furunori (Aged wheat starch paste): Challenges of Production in Non-Traditional Settings*, Journal of the Institute of Conservation 32 (2009): 31-51
- Brandrup, J., Immergut, E. H., Grulke, E. A.: *Viscosity Molecular Weight Relationship*. In: *Polymer Handbook*, 2nd edition (Brandrup, J. ed.), New York: Wiley-Interscience (1998): 103-110.
- Cincinelli, A., Martellinia, T., Amore, A., Dei, L., Marrazza, G., Carretti, E., Belosi, F., Ravegnani, F., Leva, P.: *Measurement of Volatile Organic Compounds (VOCs) in Libraries and Archives in Florence (Italy)*, Science of the Total Environment 572 (2016): 333–339.
- Clark, A. J., Calvillo, J. L., Roosa, M. S., Green, D. B., Ganske, J. A.: *Degradation Product Emission from Historic and Modern Books by Headspace SPME/GC-MS: Evaluation of Lipid Oxidation and Cellulose Hydrolysis*. Anal Bioanal Chem 399 (2011): 3589-3600
- Cody R.B., Laramée J.A., Dupont Durst H.: *Versatile New Ion Source for the Analysis of Materials in Open Air under Ambient Conditions*, Anal. Chem. 77 (2005): 2297-2302.
- Fujii, T., Selvin, P. C., Sablier, M., Iwase, K.: *Lithium ion attachment mass spectrometry for on-line analysis of trace components in air: direct introduction*, Int. J. Mass Spectrom. 209 (2001), 39-45.
- Hayakawa, N., Kigawa, R., Kawanobe, W., Higuchi, H., Oka, Y., Oka, I.: *Basic Research of "Aged Paste" (Aged wheat starch paste) – Traditional Japanese Restoration Material-by GPC and HPLC for Organic Acid Analysis*. Hozonkagaku 41 (2002): 15-28.
- Japanese Painting Conservation Laboratory, Tokyo University of the Arts, ed.: *"Mounting / Sōkō", An illustrated dictionary of Japanese-style painting terminology*, Tokyo: Tokyo Bijutsu (2010): 122-133.

Lattuati-Derieux, A., Bonnassies-Termes, S., Lavédrine, B.: *Characterisation of Compounds Emitted during Natural and Artificial Ageing of a Book. Use of Headspace-Solid-Phase Microextraction / Gas Chromatography / Mass Spectrometry*. Journal of Cultural Heritage 7 (2006): 123-133

Lee, K., Inaba, M.: *Accelerated Ageing Test of Naturally Aged Paper (Part4): Effect of Humidity, Amount of Oxygen and of Organic Acids on the Degradation of Paper in Sealed Tube Method*, Japan Tappi 71 (2017): 90-99. (English translation 100-110).

Lee, K., Enomae, T., Inaba, M.: *Effect of Lining Papers on the Permanence of Painting Papers in Japanese Scroll Paintings During Moist Heat Ageing*. Studies in Conservation. Doi: 10.1080/00393630.2020.1870363 (2021A).

Lee, K., Enomae, T., Inaba, M.: *Comparison of Degradation Behaviour of the Painting Paper in Japanese Scrolls for Moist Heat and Sealed Tube Ageing Methods*, Studies in Conservation. Doi: 10.1080/00393630.2020.1846931 (2021B).

Lee, K., Enomae, T., Inaba, M.: *Changes in the Degree of Degradation with Position of Painting Papers in Japanese Hanging Scrolls by Accelerated Ageing Using Open and Sealed Tube Methods*, Studies in Conservation. Doi: 10.1080/00393630.2021.1956185 (2021C).

Lindinger W., Hansel A., Jordan A.: *Proton-transfer-reaction mass spectrometry (PTR-MS): on-line monitoring of volatile organic compounds at pptv levels*, Chem. Soc. Rev. 27 (1998): 347-354.

Łojewski, T., Sawoszczuk, T., Łagan, J M., Zieba, K., Baranski, A., Łojewska, J.: *Furfural as a Marker of Cellulose Degradation. A quantitative approach*. Appl Phys A 100 (2010): 873-884.

Ohbayashi, K.: *Soukou Bunkazai no Hozon-Syuri: Touyou-Kaiga · Syoseki-Syuri no Genzai*, Kyoto: Kokuhou-Shuri-Soukousi-Renmei (2015): 74. (*Preservation & Conservation of East Asian Mounted Paintings: Up to Date with Conservation of East Asian Paintings and Manuscripts*)

※ The figure1 presented herein is a modification of the figure on page 74.

Ramalho, O., Dupont, A L., Egasse, C., Lattuati-Derieux, A.: *Emission Rates of Volatile Organic Compounds from Paper*. e-Preservation Science 6 (2009): 53-59.

Santucci, L., Zappala, M. P.: *Cellulose Viscometric Oxidometry*. Restaurator 22 (2001): 51-65.

Shahani, C. J., Lee, S. B., Hengemihle, F. H., Harrison, G., Song, P., Sierra, M. L., Ryan, C. C., Weberg, N.: *I. Chemical Analysis of Degradation Products, In: Accelerated Aging of Paper* (Shahani, C. J ed), Washington: Library of Congress (2001): 11-32.

Sharples, A.: *Degradation of cellulose and its derivatives. A. Acid Hydrolysis and Alcoholysis, In: High Polymers, Cellulose and Cellulose Derivatives, Part5*, 2nd Edition (Bikales, N. M., Segal, L. eds.), New York: Wiley-Interscience (1971): 991-1006.

Smith D., Španěl P.: *Ambient analysis of trace compounds in gaseous media by SIFT-MS*, Analyst 136 (2011): 2009-2032.

Strlič, M., Thomas, J., Trafela, T., Csefalvayova, L., Cigic, I K., Kolar, K., Cassar, M.: *Material Degradomics: On the Smell of Old Books*. Anal. Chem 81 (2009): 8617-8622.

Whitmore, P. M., Bogaard, J.: *Determination of the cellulose scission route in the Hydrolytic and Oxidative Degradation of Paper*. Restaurator 15 (1994): 26-45.