

## Evaluation of the volatile organic compound emissions in modern and naturally aged Japanese paper

Dario Battistel<sup>a, b, \*</sup>

dario.battistel@unive.it

Irene Padovani<sup>a</sup>

Federico Dallo<sup>b</sup>

Carlo Barbante<sup>a, b</sup>

Elisabetta Zendri<sup>a</sup>

Leonora Balliana<sup>a</sup>

<sup>a</sup>Department of Environmental Sciences, Informatics and Statistics, University Ca' Foscari of Venice, Via Torino 155, 30170 Mestre Venezia, Venice, Italy

<sup>b</sup>Institute for the Dynamics of Environmental Processes, CNR, University Ca' Foscari of Venice, Via Torino 155, 30170 Mestre Venezia, Venice, Italy

\*Corresponding author. Department of Environmental Sciences, Informatics and Statistics, University Ca' Foscari of Venice, Via Torino 155, 30170 Mestre Venezia, Venice, Italy.

---

### Abstract

Volatile organic compounds (VOCs) can have a strong effect on cellulose degradation, contributing in decreasing the lifetime expectancy of the paper materials, widely employed in the field of conservation. In this work, we investigated several industrial and homemade Japanese papers, as well as fibers, evaluating VOCs emission by using solid-phase micro extraction coupled with gas chromatography-mass spectrometry (SPME-GC/MS). Acetic acid and 1-butanol were highly detected in industrial and homemade papers rather than fibers, suggesting that the emission of these compounds is influenced by the production process more than by the raw material itself. Conversely, N-N dimethyl formamide was peculiar of industrial processes. Ketones, aldehydes and heavier alcohols were preferentially emitted by fibers and homemade papers. The higher emission of furfural from fibers rather than on papers place new questions about the use of this compound to evaluate the degradation state of the paper material that should be carefully evaluated.

---

**Keywords:** Japanese paper; VOC emissions; SPME-GC/MS; Industrial and homemade papers; Fibers

## 1 Introduction

It has been recognized that volatile organic compounds (VOCs) can have a strong effect on degradation of cellulose, in particular for those organic compounds that contain acidic or oxidizable functions, whose removal has been estimated to positively contributing in increasing the lifetime expectancy of the paper [1,2]. It has also been observed that the main source of VOCs in libraries and archives consists in the paper itself, as a consequence of the degradation process that, in turn, depends on the stability of the paper materials, as well as the environmental conditions [3,4]. In the perspective of developing a suitable strategy to storage paper-based heritages, a wider understanding of VOCs emission by papers is desirable. However, although a few of studies were recently carried out for evaluating VOC emissions from historical papers in European libraries [3,5], to the best of our knowledge, VOCs emission from Japanese papers is still unexplored.

Japanese paper is used for conservation and intervention on a wider range of cultural heritage artifacts [6] in force of its high mechanical properties combined with a high stability, mainly due to the length of the fibers and the low presence of lignin [7,8]. Nowadays, the term 'Japanese paper' is rather ambiguous as it includes materials made using oriental fibers, chemical wood pulp as well as non-oriental fibers, such as Manila hemp, that are sometimes used by several producers for containing the production costs [9,10]. These non-oriental fibers typically contain higher amount of lignin with respect to Japanese fibers. Higher lignin content in papers used for conservation should be avoided because it can accelerate degradation processes of the paper itself as well as the restored artifacts [7].

Traditional Japanese paper, oftentimes indicated with the Japanese word '*Washi*', uses oriental fibers as Mitsumata (*Edgeworthis chrysantha*), Kozo (*Broussonetia kazinoki*) and Gampi (*Diplomorpha sikokiana*) [11], with low

lignin content [12]. *Washi* paper is traditionally produced following the so-called *Nagashi-suki* technique that includes the use of an aqueous solution containing a starchy substance (Neri) obtained from Malvaceae plants (*Abelmoschus manihot*) [13,14]. Next to the length of the fibers and the low lignin content, as previously stated, the higher mechanical and chemical quality of Japanese paper is also affected by the production process employed. For example, Uyeda et al. [15] demonstrated that the stability of papers produced with Kozo fibers can vary as a function of the type of alkaline solution used in the cooking step (i.e. sodium rather than calcium hydroxide). As a consequence, the production process could also influence the VOCs emitted by the paper materials once employed in conservation interventions. In this work, we aim to investigate several industrial Japanese papers from the VANGEROW Catalogue and two types of homemade papers made by the *Washi* paper Master Yuko Isozaki, using Mitsumata and Kozo/Gampi fibers. Since paper samples are naturally-aged and, although not declared by the manufacturers, they may differ in the raw material employed and/or in the papermaking process, we preliminarily characterized the papers using microscopy observations, attenuated total reflectance-Fourier transform infra-red spectroscopy (ATR-FTIR), thermogravimetry and differential scanning calorimetry (TG-DSC). Next to the paper samples, we also investigated the declared raw materials employed for their production (i.e. Mitsumata, Gampi and Kozo fibers). Solid-phase micro-extraction-gas chromatography/mass spectrometry (SPME-GC/MS) was also employed for detecting the VOCs emitted from the papers and the fibers considered in this study.

The availability of naturally-aged papers from the VANGEROW Catalogue (1986) and homemade papers (2005), as well as modern (2015) analogues, provides the unique opportunity also to investigate potential differences in the emission of volatile organic compounds in relation to the natural aging, the production processes and/or the raw material employed. Therefore, in view of their over the time stability and related potential conservation issues in particular for paper interventions, we evaluated the potential use of SPME-GC/MS - a totally non-invasive approach-for shedding light on the composition of Japanese paper VOCs emissions.

## 2 Materials and methods

### 2.1 Paper samples

Samples of naturally-aged industrial Japanese papers were taken from an original catalogue of VANGEROW (Bolzen, Italy) *Japanische Handapapiere* of the 1986, and kindly provided by Rosanna Chiggiato. From this catalogue, five paper samples were selected in accordance to their use in the field of conservation. New samples, sold with the same code and characteristics, were purchased from Vangerow (2015). The selected papers differentiate not only for their thickness, but also for their composition. Vangerow catalogue papers will be afterwards labeled as V where the sub- and super-scripts indicate the catalogue number (500, 508, 523, 517 and 561) and the ages, corresponding to 2015 and 1986, of these samples.

Fibers and handmade papers, both new and old, were provided by the *Washi* master Yuko Isozaki. The naturally-aged paper samples date back to 2005, while the more recent samples were produced in 2015. Homemade papers were labeled as Y-KG and Y-Mit to indicate the declared raw material used: 30% kozo/70% gampi and 100% mitsumata fibers, respectively. The sub-script refers to the age of the samples (i.e. 2015 and 2005).

### 2.2 Preliminary characterization

Paper samples were stained with Herzberg's reagent to assess the presence of lignin, following the protocol reported elsewhere [16]. The presence of lignin was detected accordingly to the coloring of the paper material [16]. Lugol's test [17] was also employed to reveal the presence of starch that turns blue due to the reaction with the reagent, in accordance with TAPPI standard T 419 OM-11. The paper samples were observed for both tests under the microscope and images were taken using a digital camera (CANON PC1049 Powershot G5) both for lignin and starch stains. pH measurements were carried out in laboratory conditions, by cutting approximately 1 g of paper in small fractions and leaving them in 70 mL of distilled water for one hour. Then, the pH value of the cold extracted was analyzed without filtration under stirring by using a Crison GLP 21 pH meter, in accordance with TAPPI standard 509 [hydrogen ion concentration (pH) of paper extracts-cold extraction method].

### 2.3 TG-DSC analysis

Thermogravimetry (TG) and differential scanning calorimetry (DSC) were performed simultaneously using a Netzsch 409/C apparatus. The temperature program was set from 30 C to 500 °C at 5 °C/min and the instrument was purged in an atmosphere containing a mixture of air and N<sub>2</sub>. The sample mass ranged between 0.5 and 2 mg and were weighted in an aluminium crucible using a TG internal balance. Alumina was used for internal calibration and data were collected with STA Netzsch software. Before analysis, samples were stored in a dessicator (20 ± 2 °C; 60 ± 5% RH) for at least 48 hours in our laboratory.

### 2.4 ATR-FTIR and SEM analysis

Infrared spectra were obtained by a Thermo Nicolet Nexus 670 FTIR spectrophotometer combined with a Smart Orbit Single Reflection Diamond ATR accessory, from 4000 to 400 cm<sup>-1</sup> for 128 scans with 4 cm<sup>-1</sup> resolution. Spectra were elaborated with Omnic 10.0. Surface characterization of the papers and fibres was performed using a Jeol JSM 6300 Scanning Electron Microscope operating with a Link-Oxford-Isis Energy Dispersive X-ray microanalysis system in low vacuum conditions (20 kV, back - scattered electrons, 2.10-9 A beam current and 15 mm working distance). The analysis mainly focused on the morphology of the raw fibres to highlight their characteristics and on the

paper samples for observing the possible presence of additives related to the production process.

## 2.5 SPME - GC/MS

Solid phase microextraction (SPME) was performed using 50/30  $\mu\text{m}$ , divinylbenzene/carboxen/polydimethylsiloxane (DVI/CAR/PDMS) fibers (Supelco, Bellefonte, PA). These types of fibers are suitable for a wide range of chemicals and were successfully used for studies on paper materials [18]. Before the first use, each fiber was conditioned in order to remove contaminants and to stabilize the polymeric phase. Conditioning was conducted by heating the fiber in the injection port of the GC system for 1 h at 260 °C before every extraction. The extraction was performed adapting methods available in the literature [18-20]. Briefly, contact mode SPME was used to collect the volatile compounds emitted from the papers. The holder needle was placed between two pieces of the same paper in a controlled environment (23 °C, 50% RH). The fibers were in direct contact with the sample paper for 240 minutes. After extraction, the fibers were withdrawn into the holder needle and immediately introduced into the GC-MS injector port for 10 min at 240 °C for thermal desorption. Fibers, procedural blanks and furfural standard (Sigma Aldrich) were extracted using the same conditions. The reproducibility of analyses were evaluated by extracting in triplicates each sample and the peak areas showed a variability of 20-30%, depending on the compound considered. A fiber blank chromatogram was acquired after each analysis to confirm the fiber cleanliness prior the subsequent extraction. GC-MS analysis was performed with a 6890-N GC system coupled to a quadrupole mass spectrometer 5973 (Agilent Technologies, Santa Clara CA, USA). The chromatographic analysis was carried out using a capillary column (DB-WAX, 30 m length, 0.25 mm inner diameter and 0.25  $\mu\text{m}$  film thickness). Helium flow (flow: 1 mL min<sup>-1</sup>) was used as the gas carrier. The temperature program used was as follows: 40 °C (held for 10 min) to 240 °C at 5 °C min<sup>-1</sup>. The interface temperature was 250 °C, the mass selective detector (MSD) ion source temperature was at 230 °C and MSD quadrupole was kept at 150 °C. Electron ionization was performed at 70 eV. Measurements in full scan mode (m/z from 40 to 400) were carried out for compound identification and quantification. Only for furfural determination, the detection was carried out using the selected ion monitoring (SIM) mode. The single masses m/z = 95 and m/z = 96 were chosen considering the full scan mass spectrum obtained from furfural standard.

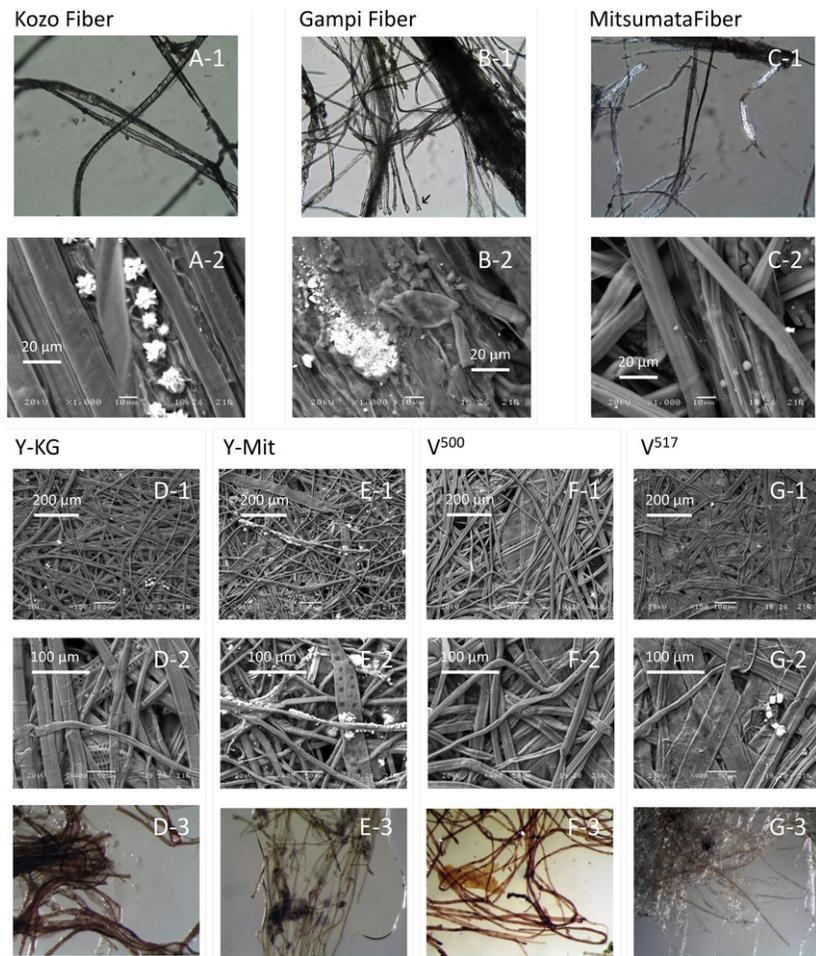
## 2.6 Statistics and data analysis

Principal component analysis (PCA) was performed to obtain correlations between variables and to analyze the data. The chemical compounds were determined with SPME-GC/MS and identified by NIST database (see Table 3 and Result section for details), the main DSC processes and the more characteristic ATR-FTIR peaks (Table 2) were used as the input variables for PCA ( $n = 13$  variables). Normality of data distribution was assessed using the Shapiro-Wilk test [21] at a 95% confidence level. Non-normal distributions were log-transformed. The dataset was then transformed into z-scores prior to PCA analysis. Statistical analysis was performed using Statistica 7.0 software and only eigenvalues larger than 1 were considered, according to the Kaiser-Gutmann criterion.

# 3 Results and discussion

## 3.1 Optic and SEM micrographs

Japanese fibers of Gampi, Mitsumata and Kozo were investigated using optic microscopy and SEM (See Fig. 1A-C). As shown, Mitsumata fibers were shorter than Kozo and Gampi, although they resulted more regular in thickness. Kozo also showed evident markings and knots all along the fiber that were almost absent in Mitsumata. All these fibers presented natural mucilaginous material and/or specific features such as phytolith assemblages (Fig. 1A-2), encrusting matter (Fig. 1B-2) or typical spherical cells due to the presence of mucilage (Fig. 1C-2) [12]. Micrographs of the homemade Japanese papers (Y-KG and Y-Mit), reported in Fig. 1D and Fig. 1E, showed a perpendicular weaving which is typical for the paper fabrication by using the *Nagazi-suki* method [22,23]. SEM images of Y-Mit in Fig. 1E-2 showed the presence of small amounts of fibers with longitudinal tracheas, typical of ligneous plants, that were likely added to the paper in order to ensure higher consistency. Fine industrial papers from Vangerow catalogue labeled as V<sup>500</sup>, V<sup>501</sup> and V<sup>508</sup> (V<sup>500</sup><sub>2015</sub> is reported in Fig. 1F as an example), showed the presence of fibers characterized by an uniform width and fine striations, probably indicating a significant load of Manila hemp fibers.



**Fig. 1** Optic and SEM images. A-C. Kozo, Gampi and Mitsumata fibers. D-E. Homemade papers. F-G. Industrial papers. D3-G3. Optic images of Herzberg test.

Micrographs of industrial papers  $V^{523}$  and  $V^{517}$  ( $V^{517}_{2015}$  is reported Fig. 1G as an example) suggested the presence of Kozo and Mitsumata fibers, respectively. However, in these two latter papers, chemical wood pulp may be present, since tracheid cells were observed in all of these samples [12]. The papers labeled as  $V^{523}$  and  $V^{517}$  were thicker and will be hereinafter indicated as ‘thick industrial papers’. Similarly, the papers labeled as  $V^{500}$ ,  $V^{501}$  and  $V^{508}$  resulted finer and will be hereinafter indicated as ‘fine industrial papers’ for simplicity.

### 3.2 Herzberg test

Herzberg test showed a purplish-red (P-R) and purplish-yellow (P-Y) turning for Y-KG and a greenish-yellow (G-Y) turning for Y-Mit (see Fig. 1D-3 and Fig. 1E-3), suggesting the presence of Kozo/Gampi and Mitsumata fibers, respectively, in agreement to what declared by the manufacturer. It must be noted that only thick industrial papers turned red (R) that suggests the presence of Manila hemp [24].

### 3.3 Lugol test

Lugol reagent was used to test the presence of starch both in fibers than in paper samples. The Lugol test provided a blue-black color tone in all fibers (except for Mitsumata) and in all homemade papers. The fine industrial papers (both recent rather than naturally-aged) resulted in a negative Lugol test, suggesting that starch was not added during the papermaking processing of these papers. Conversely, thick industrial papers were positive to Lugol test (except for  $V^{523}_{1986}$ ). Overall observations are summarized in Table 1, where the presence of starch is indicated. Starch is commonly used in Japanese paper production (up to 10%) [25] as well as other chemical fillers [11]. A higher

amount of starch is used to maintain strength and printing properties. Surface starch also works as a binder and primer. The discrepancy between recent and naturally-aged V<sup>523</sup> papers may suggest that the production papermaking technique has changed during the last decades, where starch was added to improve the mechanical or printing properties.

**Table 1** List of fiber and paper samples and basic characterization parameters.

alt-text: Table 1

Type	Samples	Label	Age	Microscopy					ATR-FTIR Peak (cm <sup>-1</sup> )		TG-DSC								
				Manila hemp	LigneousFibers	Lugol Test	Herzberg Test	pH ± 0.02	810	1730 Pectine	Type	Levoglucosan <sup>a</sup>		CHAR <sup>b</sup>		Residue <sup>c</sup>		<sup>d</sup>	
												T (°C)	Wg <sup>-1</sup>	T (°C)	W g <sup>-1</sup>	T (°C)	W g <sup>-1</sup>	T (°C)	W g <sup>-1</sup>
Fiber	Gampi	Gampi <sub>2015</sub>	2015			Starch	P-Y	n.a.	n.d.	10.0	(A)	n.d.	n.d.	337	-1.45	423	-1.08	n.d.	n.d.
Fiber	Gampi	Gampi <sub>2005</sub>	2005			Starch	P-Y	n.a.	n.d.	10.3	(A)	n.d.	n.d.	337	-1.46	423	-1.09	n.d.	n.d.
Fiber	Kozo	Kozo <sub>2015</sub>	2015			Starch	P-R	n.a.	n.d.	3.8	(B)	n.d.	n.d.	342	-0.71	455	-2.02	n.d.	n.d.
Fiber	Kozo	Kozo <sub>2005</sub>	2005			Starch	P-R	n.a.	n.d.	4.5	(B)	n.d.	n.d.	342	-0.73	455	-2.05	n.d.	n.d.
Fiber	Mitsumata	Mit <sub>2015</sub>	2015			n.d.	G-Y	n.a.	n.d.	1.3	(A)	n.d.	n.d.	342	-0.86	452	-1.06	n.d.	n.d.
Fiber	Mitsumata	Mit <sub>2005</sub>	2005			n.d.	G-Y	n.a.	n.d.	0.8	(A)	n.d.	n.d.	342	-0.86	452	-1.02	n.d.	n.d.
Ind. paper	C500	V <sup>500</sup> <sub>2015</sub>	2015	Present		n.d.	R	6.94	n.d.	n.d.	(C)	324	0.06	345	-1.40	420	-7.16	n.d.	n.d.
Ind. paper	C500	V <sup>500</sup> <sub>1986</sub>	1986	Present		n.d.	R	6.65	n.d.	n.d.	(C)	n.d.	n.d.	341	-1.59	420	-8.05	n.d.	n.d.
Ind. paper	C561	V <sup>501</sup> <sub>2015</sub>	2015	Present		n.d.	R	6.98	n.d.	n.d.	(C)	324	0.05	349	-1.27	420	-7.32	n.d.	n.d.
Ind. paper	C561	V <sup>501</sup> <sub>1986</sub>	1986	Present		n.d.	R	6.65	n.d.	n.d.	(C)	n.d.	n.d.	345	-1.41	420	-7.33	n.d.	n.d.
Ind. paper	C508	V <sup>508</sup> <sub>2015</sub>	2015	Present		n.d.	R	7.13	n.d.	n.d.	(C)	324	0.03	347	-1.18	420	-7.24	n.d.	n.d.
Ind. paper	C508	V <sup>508</sup> <sub>1986</sub>	1986	Present		n.d.	R	6.80	n.d.	n.d.	(A)	n.d.	n.d.	347	-1.45	420	-1.81	n.d.	n.d.
Ind. paper	C517	V <sup>517</sup> <sub>2015</sub>	2015		Present	Starch	G-Y	5.95	0.70	n.d.	(A)	n.d.	n.d.	337	-1.22	439	-1.08	n.d.	n.d.
Ind. paper	C517	V <sup>517</sup> <sub>2005</sub>	1986		Present	Starch	G-Y	7.35	0.75	n.d.	(B)	n.d.	n.d.	340	-1.57	450	-0.62	416	-0.27
Ind. paper	C523	V <sup>523</sup> <sub>2015</sub>	2015		Present	Starch	P-R	6.88	1.48	n.d.	(A)	325	0.19	344	-1.07	455	-0.74	n.d.	n.d.
Ind. paper	C523	V <sup>523</sup> <sub>2005</sub>	1986		Present	n.d.	P-R	5.84	0.39	n.d.	(A)	n.d.	n.d.	337	-0.24	452	-0.63	n.d.	n.d.
Homemade	30%K 70%G	Y-KG <sub>2015</sub>	2015			Starch	P-R/P-Y	6.50	n.d.	n.d.	(B)	n.d.	n.d.	344	-1.48	445	-1.33	413	-0.16
Homemade	30%K 70%G	Y-KG <sub>2005</sub>	2005			Starch	P-R/P-Y	6.27	n.d.	n.d.	(B)	n.d.	n.d.	342	-1.36	455	-1.94	418	-0.21
Homemade	100%Mit	Y-Mit <sub>2015</sub>	2015			Starch	G-Y	7.38	n.d.	n.d.	(B)	n.d.	n.d.	344	-1.62	435	-1.62	408	-0.23
Homemade	100%Mit	Y-Mit <sub>2005</sub>	2005			Starch	G-Y	7.19	n.d.	n.d.	(C)	n.d.	n.d.	334	-1.61	416	-6.25	n.d.	n.d.

P-Y: purplish-yellow; G-Y: greenish-yellow; P-R: purplish-red; R: reddish; n.d.: not determined (below detection limit); n.a.: not available.

<sup>a</sup> Thermal process individuated (see text).

<sup>b</sup> Thermal process individuated (see text).

<sup>c</sup> Thermal process individuated (see text).

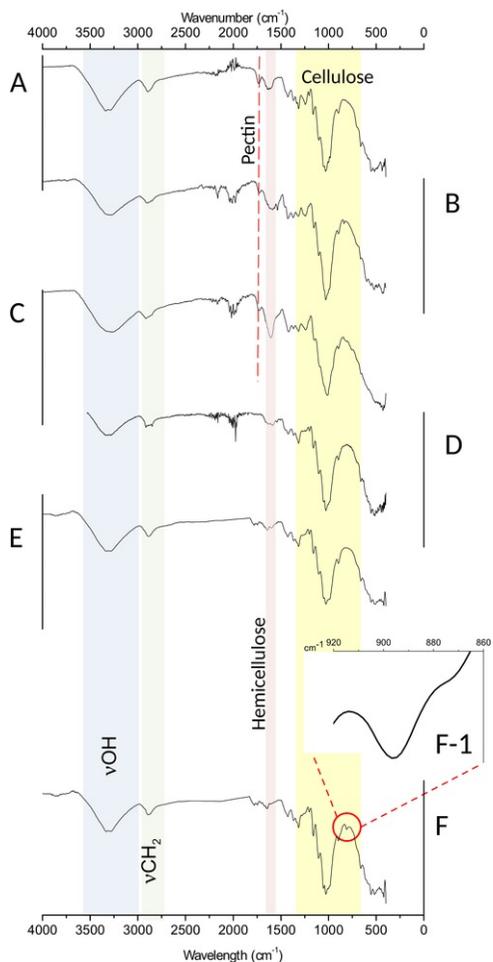
<sup>d</sup> Thermal process individuated (see text).

### 3.4 Paper acidity

The paper acidity (pH values in [Table 1](#)) was determined for evaluating the state of conservation of the papers. All the samples (except for V<sup>517</sup>) showed slightly lower pH values for aged papers that may indicate the occurrence of degradation that resulted in the formation of more acidic functionalities. It is interesting to observe that pH difference between modern and naturally aged papers were ~ 0.2-0.3 pH units, except for V<sup>523</sup> and V<sup>517</sup>, where an increase/decrease of 1.0 and 1.4, respectively, was observed. This marked difference suggests that a possibly different production technique was employed for these two types of paper during the years, as previously observed for V<sup>523</sup>. However, the use of V<sup>517</sup><sub>2015</sub> and V<sup>523</sup><sub>1986</sub> should be avoided in intervention for conservation, since they showed pH values below the threshold (pH = 6) commonly allowed for this kind of action [\[25\]](#).

### 3.5 ATR-FTIR analysis

The ATR-FTIR analysis allowed the identification of raw materials as well as fillers employed for paper production. [Fig. 2A-F](#) shows the ATR-FTIR spectra of Japanese fibers as well as homemade and industrial papers. As expected, the fingerprint region of cellulose (850-1500 cm<sup>-1</sup> [\[26-31\]](#)), the broad peak related to the stretching vibration of the intra and inter-molecular of alcohol-bonded hydroxyl group ( $\nu$  OH; between 3650 and 3100 cm<sup>-1</sup>, centered at 3300 cm<sup>-1</sup> [\[32\]](#)) and the CH stretching region (3000-2850 cm<sup>-1</sup> assigned to the  $\nu$  CH<sub>2</sub> stretching vibrations [\[33-36\]](#)) were clearly evident in all samples.



**Fig. 2** ATR-FTIR spectra of fibers of Kozo (A), Gampi (B) and Mitsumata (C). FTIR spectrum of the Y-Mit<sub>2015</sub> homemade paper (D);  $\nu^{500}_{1986}$  thin industrial paper (E);  $\nu^{523}_{1986}$  thick industrial paper (F). Inset F-1: zoom of  $\nu^{523}_{1986}$   $\nu^{523}_A$  in the 860-920  $\text{cm}^{-1}$  region.

The absorption band at 1650-1600  $\text{cm}^{-1}$ , attributable to the presence of hemicellulose [37], was more evident in Japanese fibers than in industrial or homemade papers. The amount of these polysaccharides in Japanese fibers ranged between  $\sim 8$  (in Kozo) to  $\sim 20\%$  (in Gampi and Mitsumata) [38], while a considerable amount of hemicellulose could have been removed as a result of papermaking processing [33].

Peaks due to the bending of methoxy (1430  $\text{cm}^{-1}$ ) and aromatic groups (1595 and 1505  $\text{cm}^{-1}$ ) can be attributed to the presence of lignin [26-29]. Japanese papers contain small amounts of lignin (from 3 to 6% [12,38]). Although small peaks were observed in several samples corresponding to or close to these wavelengths, they could not be unequivocally assigned by the ATR-FTIR spectra obtained in this study, because they were not significantly higher than the background.

The peak at 1730  $\text{cm}^{-1}$  suggested the presence of pectin [26-31]. In contrast to the methoxy and aromatic groups in lignin, the 1730  $\text{cm}^{-1}$  peak was clearly evident in all fiber spectra (Fig. 2A-C). However, in industrial and homemade papers, pectin was almost absent, suggesting that also this compound may have been removed during the papermaking process.

It is also interesting to note that small but detectable peaks were observed at  $\sim 810$   $\text{cm}^{-1}$  in  $\nu^{523}$  and  $\nu^{517}$  papers in both modern and naturally aged samples (Fig. 2-F and inset). Although we did not unequivocally assign this peak, several authors observed similar features due to pentose sugars (D-ribose) [39] and it cannot be excluded that it is related to papermaking processing. Here, we just report this evidence, where this aspect deserves further investigations that are out of the scope of this work. The IR band and peak assignment and the main observations are summarized in Table 2. As it is evident from the table, IR analysis mainly discriminates fibers from papers, where

papermaking process removes hemicellulose and pectin in the fibers. However, the presence of lignin is not easily to detect, due to the spectrum background and the low content in Japanese papers.

**Table 2** ATR-FTIR bands assignment.

alt-text: Table 2

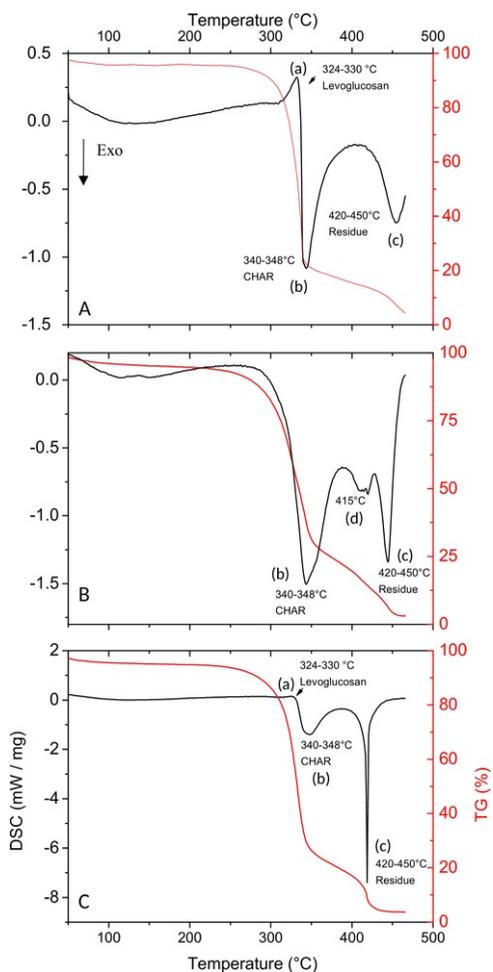
Compound	Assignment	IR bands	Samples
Cellulose [26–31]	Fingerprint region	850–1500 $\text{cm}^{-1}$	All samples
Cellulose [32]	Stretching vibration ( $\nu$ OH)	3000–2850 $\text{cm}^{-1}$	All samples
Cellulose [33–36]	Stretching vibration ( $\nu$ CH <sub>2</sub> )	3650–3100 $\text{cm}^{-1}$	All samples
Hemicellulose [37]		1650–1600 $\text{cm}^{-1}$	More evident in Japanese fibers
Lignin [19–22]	Aromatic Groups Bending of methoxy groups	1595–1505 $\text{cm}^{-1}$ 1430 $\text{cm}^{-1}$	Not unequivocally assigned
Pectine [31–36]		1730 $\text{cm}^{-1}$	Clearly evident in Japanese fibers and almost absent in industrial and homemade papers
D-ribose (?) [39]		810 $\text{cm}^{-1}$	Observed in thin industrial papers

### 3.6 TGA-DSC analysis

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out in all samples. From the analysis of all the thermograms, we recognized the following four main processes (a-d):

- (a)** endothermic pyrolysis of cellulose with the formation of levoglucosan (1,6 anhydro  $\beta$ -D-glucopyranose) and volatile organic compounds at 330–335 °C [40];
- (b)** exothermic charring and oxidation of the by-products from thermal decomposition (CHAR) at 340–348 °C [40];
- (c)** exothermic oxidation of the unburned solid residue at 420–450 °C (residue) [40]. It must be noted that the sharpness of this latter peak is likely affected by the previous decomposition processes. Thus, shape and peak temperature also depend on the composition and structure of the material;
- (d)** a faint exothermic reaction between process (b) and (c) was occasionally observed at  $\sim$  430 °C. The attribution of this process is not easy. Although this process may be due to lignin decomposition that occurred at temperatures higher than cellulose [41], this hypothesis is not always well-supported by the following evidence reported in this study.

Considering the intensity and the shape of the peaks corresponding to the thermal processes previously individuated, we identified three main peculiar thermograms (Fig. 3 A-C and Table 1) that were recorded in the overall set of samples. Gampi and Mitsumata fibers were characterized by TG-DSC thermograms type A (see Fig. 3A), although the process (a) was not well evident. In contrast, Kozo fibers thermograms (type B) showed the presence of process (d), while process (b) is more intense than (c). We did not observe any significant difference between modern and naturally aged fibers.



**Fig. 3** Three different types of TG-DSC thermograms obtained from fibers, homemade and industrial papers.

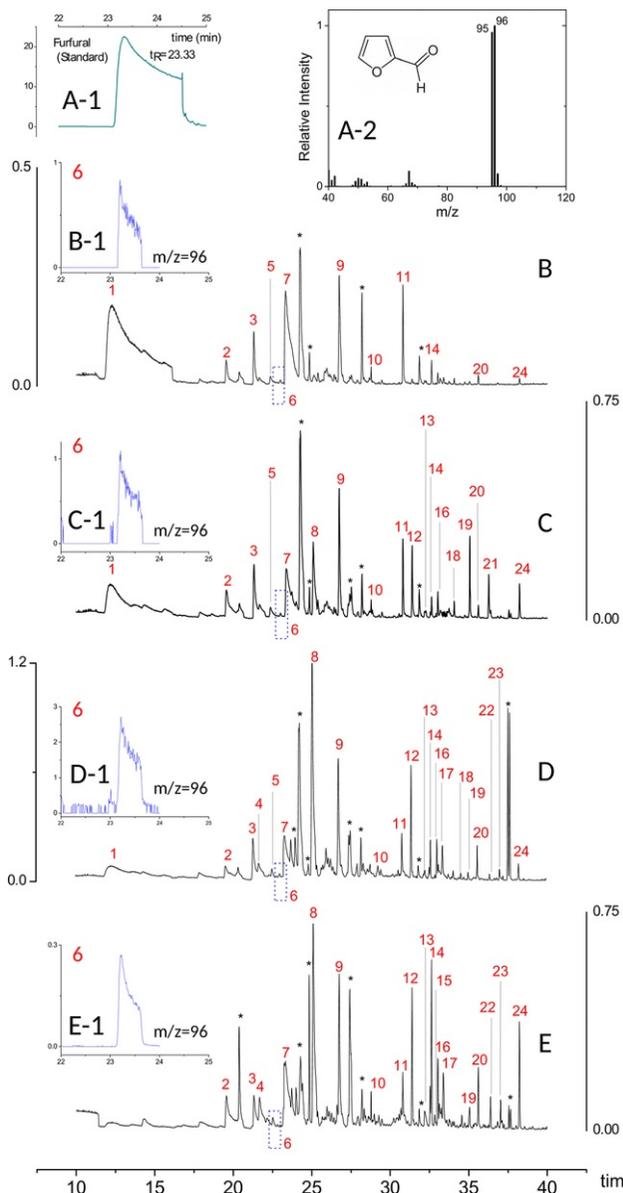
Modern and naturally-aged fine industrial papers showed thermograms characterized by a sharp (c) process (type C in Fig. 3C) where a weak levoglucosan oxidation peak is observed only in naturally aged papers (except for  $V_{1986}^{508}$ ) (Table 1). Once again, the results from thick industrial papers differed from fine papers. Thermograms from these latter papers were similar to Gampi fiber (type A), except for  $V_{2015}^{523}$  where levoglucosan oxidation is more evident (see Fig. 3A). Both modern and naturally aged homemade papers Y-KG showed a behavior similar to  $V^{517}$  and Gampi fiber (type A), while Y-Mit showed consistent differences between modern (type B) and naturally aged papers (type C). The TG-DSC behavior observed in fine industrial papers and Y-Mit<sub>2005</sub> is very similar to *Kraft* paper thermograms [40], where *Kraft* process reduces the amount of lignin and avoid cellulose degradation. Thus, the occurrence of *Kraft* paper-like thermograms may be diagnostic of higher elasticity and resistance of the paper achieved during production processing.

From Table 1, the levoglucosan peak (a), was observed only in modern industrial papers. Here, the combustion of cellulose takes place with an initial dehydration step, followed by endothermic reactions that competes for the depolymerization of the residual cellulose, where levoglucosan (1,6-anhydro- $\beta$ -D-glucopyranose) is an intermediate product [42,43]. Several authors showed that the endotherm process disappeared entirely when the paper was heated prior to DSC analysis [42,43]. The heat treatment formed high quantities of anhydrocellulose, which, in turn, enhanced the exotherm reaction. Thus, the heat involved exceeds the heat absorbed during depolymerization and the endothermic peak was not observed. In our view, naturally aged paper combustion may follow the same mechanism proposed by Arsenau (1971) [43]. Natural aging, instead of heating, may induce slow dehydration that, in turn, leads to the production of more-than-usual amounts of anhydrocellulose. Therefore, endothermic reactions (a) were not evidenced in all naturally-aged but in the majority of modern industrial papers.

TG-DSC analyses showed a very similar behavior between modern and naturally-aged fibers. The main differences observed in paper thermograms are likely due to the raw material and/or to the papermaking process employed that must be taken into account when evaluating VOC emissions, especially for industrial papers  $V^{508}$ ,  $V^{517}$  (modern and naturally-aged) as well as Y-Mit (modern and naturally-aged).

### 3.7 SPME-GC/MS analysis and VOCs emissions

Solid-phase micro-extraction was carried out following a non-invasive analytical method previously proposed for the determination of VOCs in paper samples [18-20]. In Fig. 4B-E typical chromatograms obtained in fibers, industrial and homemade papers were reported. The peak identification was performed by using the corresponding mass spectra compared with NIST database. A set of 23 compounds were clearly identified (Table 3) by comparison with blank chromatograms ( $n = 3$ ) where these compounds were not detected. The peaks labeled with asterisks in Fig. 4 were identified as siloxane derivatives that resulted as contaminants likely deriving from the SPME fibers, as well as methoxy-phenyl-oxime (peak 11), as reported by other investigators [44]. A particular attention was paid for furfural, since several authors [45] suggest that this aldehyde is a potential marker for cellulose degradation. However, since this compound was not easily detected in full scan-mode mass spectrometry, we extracted the single-ion chromatograms ( $m/z = 95$  and  $m/z = 96$  from mass spectrum reported in Fig. 4A-2) and we used the retention time of standard compound for identification (see chromatograms in Fig. 4A-1). Peak areas of each compound were normalized by the total contribution of the compounds considered, and more complex alcohols (i.e. except 1-Butanol) and ketones + aldehydes (RC = O, except furfural) were reported as a sum (see Fig. 5). Although the peak area is proportional to the concentration of the selected compound, without a response factor correction, the comparison between compounds is only semi-quantitative. Nevertheless, the comparison of the relative amounts of each compound between samples is instead quantitative because, in this case, a response factor correction is not required. Following the indications obtained from previous observations, we individuated four groups of samples: fibers (A), fine industrial papers (B), thick industrial papers (C) and Yuko homemade papers (D) (see Fig. 5 bottom). As is evident from Fig. 5, VOCs individuated in all samples were not uniformly distributed. It is interesting to note that 1-Bu was not present in fibers and in Y-Mit, while it resulted very abundant in all industrial papers. Similarly, N-N dimethyl formamide (DF) was completely absent in fibers and its contribution increases from homemade to industrial papers. This result is not surprising, since 1-Bu and DF are widely used as delignificant agents in industrial paper processing [46-48]. It must be noted that the use of these chemicals is strongly limited in homemade papers.



**Fig. 4** SPME-chromatograms (A-1) and mass spectrum (A-2) from standard furfural. Full scan chromatogram from: (B)  $V^{500}_{1986}$ ; (C)  $V^{500}_{2015}$  (D) Y-Mit<sub>2015</sub>; (E) Mitsumata fiber. Insets (B-1-E-1) Selected ion ( $m/z = 96$ ) chromatograms for furfural detection.

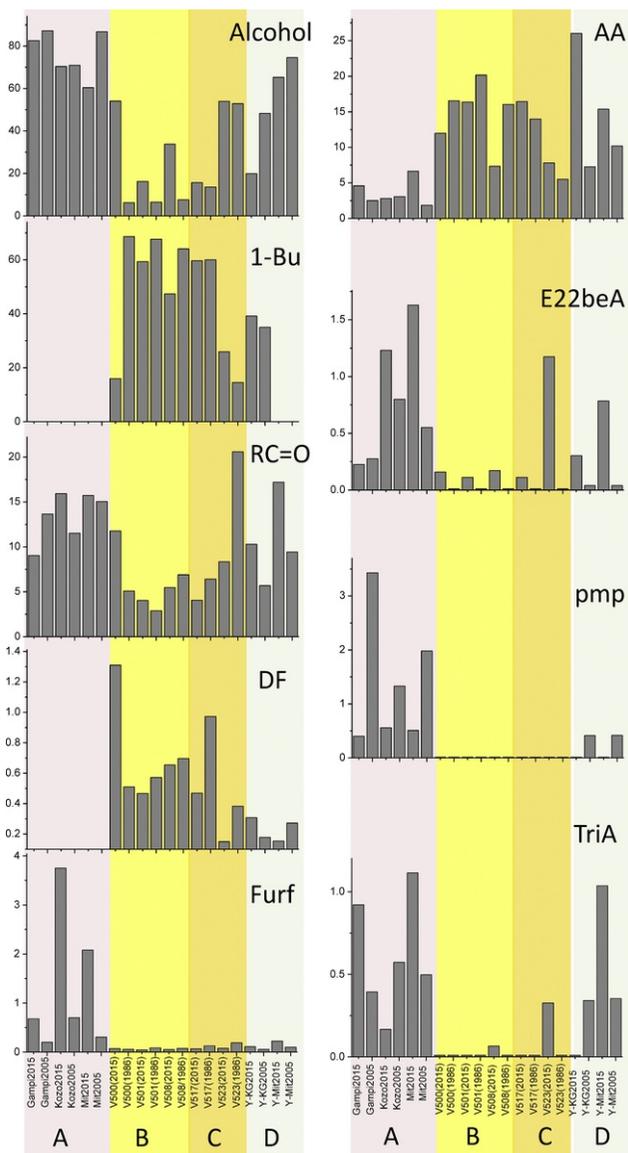
**Table 3** List, abbreviation, retention time (minutes) and % NIST match of the chemical compounds detected in all the samples (see chromatograms in Fig. 4).

alt-text: Table 3

Peak	Compound	Classification	Abbreviation	Retention Time (min)	NIST match (%)
1	1-butanol	Alcohol	1-Bu	12.13	91-95

2	5-hepten-2-one-6-methyl	Ketone	5h2o-6 m	19.60	94-96
3	Nonanal	Aldehyde	NN	21.31	91-95
4	Ethanol-2-butoxy	Alcohol	E2b	21.67	82-85
5	N-N, diethyl-formamide	Amide	DF	22.37	91-93
6	Furfural <sup>a</sup>	Aldehyde	Furf	23.21	-
7	Acetic acid	Acid	AA	23.40	84-86
8	2-propanol, 1(2-methylpropoxy)	Alcohol	2p12mp	25.10	83-86
9	Propylen glycole	Diol	PG	26.75	80-84
10	2-pyrrolidinone 1-methyl	Heterocyclic Amine	2p1 m	28.78	74-81
11	Oxime methoxy phenyl	Imine	ox-mp	30.80	91-93
12	Ethanol 2 (2-butoxy-ethoxy)	Alcohol	E22be	31.42	86-88
13	Ethanol 2 (2-butoxy-ethoxy) acetate	Ester	E22beA	32.54	83-87
14	5,9 undecadien 2-one, 6-10 dimethyl	Ketone	59u-one	32.62	80-85
15	Pyridine 3-1 methyl 2-pyrrolidinyl	Heterocyclic Amine	pmp	32.82	94-96
16	Benzyl alcohol	Alcohol	BA	33.05	91-95
17	1,2 - hexanediol	Diol	12h-OH	33.37	80-82
18	2,6 bis (1,1) dimethyl ethyl 4,1 - oxopropyl phenyl	Alcohol	26Ph	34.07	89-91
19	Ethanol 2,2' oxy bis	Diol	E22oxb	35.06	83-86
20	Phenol	Alcohol	Ph	35.60	94-95
21	2-pyrrolidinone	Heterocyclic Amine	2py	36.33	91-95
22	1-phenoxy-propan-2-ol	Alcohol	pp2ol	36.40	96-97
23	Triacetin	Ester	TriA	37.01	83-87
24	Ethanol 2-phenoxy	Alcohol	e2p	38.20	95-96

<sup>a</sup> Furfural was determined using standard compounds.



**Fig. 5** Compound distribution from fibers, homemade and industrial paper detected by SPME-GC/MS.

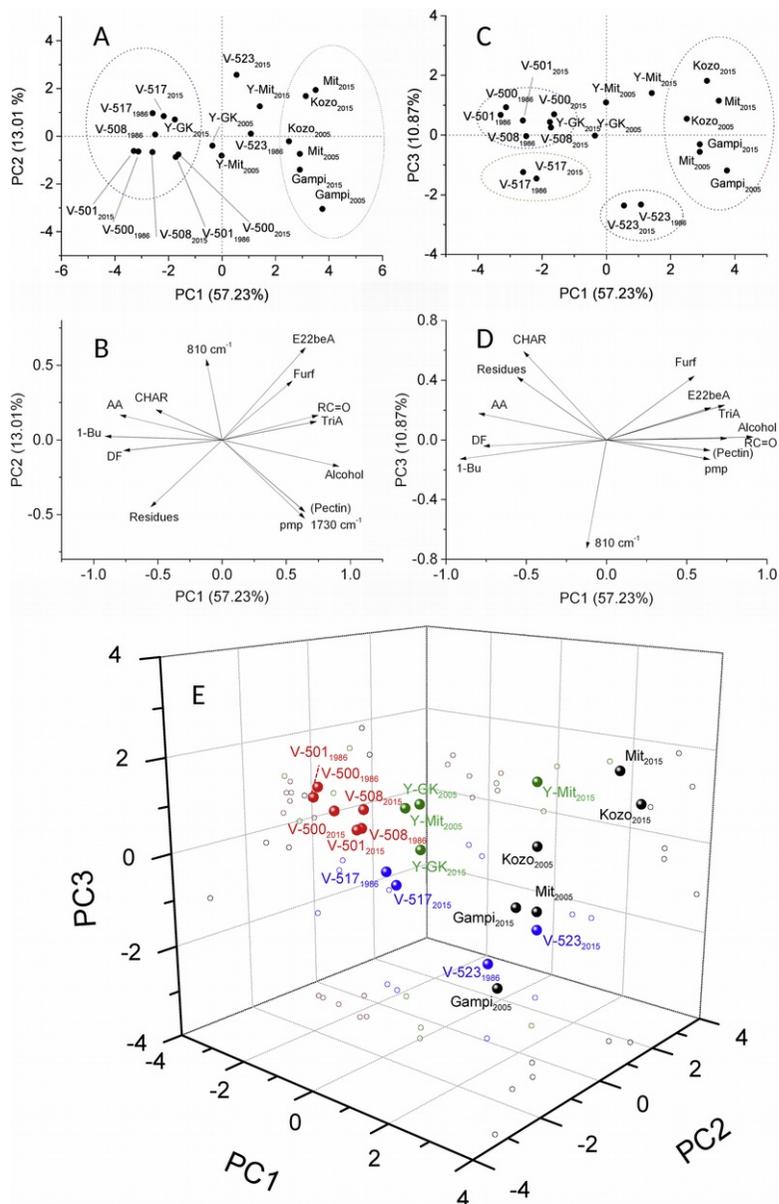
A different behavior was observed for furfural (Furf) that resulted relatively much more abundant in fibers than in papers, while a net difference between modern and naturally aged papers was not evident. This occurrence is rather unexpected, based on previous studies [48], where furfural was proposed as a possible marker for degradation. Although lower furfural emissions in papers may be due to production processing that stabilize the paper with respect to fibers, the presence of acetic acid (AA), often attributed to cellulose oxidation processes, resulted generally higher in papers than in fibers. Moreover, higher values in AA were evident only in naturally aged fine industrial papers (Fig. 5) with respect to modern, while in the thick industrial papers the opposite occurred. It must be noted, however, that, differently from fine industrial papers, the production processing may have changed during the years for thick industrial and Yuko papers investigated in this work, making the comparison not completely reliable. Nevertheless, 2-(2-butoxy-ethoxy) ethyl acetate (E22beA) was detected at significant amounts in all modern papers, while it was undetected in naturally aged. This occurrence suggests that E22beA could be used as a marker for distinguishing modern from naturally-aged papers, although the reason of the presence/absence of this compound results still

unclear.

Finally, pyridine 3-(1-methyl-2-pyrrolidinyl), also known as nicotine, was observed in fibers and in naturally aged homemade papers. This compound is clearly an external contamination. However, its presence is indicative of the environment where these samples were stored before the analysis.

### 3.8 Principal component analysis

All previously reported results were synthesized by using principal component analysis (PCA). The PCA explained a total variance of 81.1% with 3 principal components. The score plot of PC1 vs PC2 in [Fig. 6](#) shows a major discrimination from fibers to industrial Japanese paper (except V<sup>523</sup>) mainly due to the first component. The loadings of the first component ([Fig. 6B](#)) showed a higher correlation between 1-Bu, DF and AA that are, in turn, anti-correlated with the total amount of complex alcohol, RC = O, triacetin (TriA) and the presence of pectin (1730 cm<sup>-1</sup> peak in ATR-FTIR analysis). As previously observed, 1-Bu and DF are widely used in the papermaking processing to break down lignin, thus this main discrimination indicates a sort of index related to the transformation from fibers to paper. Interestingly, homemade papers as well as V<sup>523</sup> are not endmembers, where modern Y-Mit and Y-GK are closer to pure Japanese fiber and industrial paper groups, respectively. Moreover, in homemade papers, a significant difference between modern and naturally-aged papers was also observed in TG-DSC thermograms (CHAR and Residue), corroborating a difference in the production processing, resulting in less invasive processing for Mitsumata homemade paper with respect to Gampi-Kozo. The second component (PC2), characterized by a contribution of E22beA in the loading plot ([Fig. 6B](#)), only partially discriminates modern (more positive PC2) from naturally aged fibers and homemade paper.



**Fig. 6** Principal component analysis. A, B. PC1-PC2 score and loading plots. C, D. PC1-PC3 score and loading plots. E. 3D plot of the PC1-PC2-PC3 scores.

Although PC3 explains slightly less variance (11%) than PC2 (13%), the comparison between PC1 vs PC3 score results are particularly interesting (Fig. 6C). In fact, PC3 is able to differentiate thick from fine industrial papers and fibers. Loadings of PC3 (Fig. 6D) suggested that this difference occurred mainly because both types of thick industrial papers are characterized by the 810 cm<sup>-1</sup> peak in ATR-FTIR spectra. However, since this peak was detected only in thick papers, it cannot be excluded that it might be due to the papermaking process.

Although the statistical analysis could be significantly improved by including more observations, this multi-analytical approach provides useful indications for understanding the characteristics of the homemade papers obtained

from Japanese fibers related to the raw material employed (i.e. Japanese fibers rather than Manila hemp). We demonstrated that paper processing widely affects the characteristics of the final product, even more than the type of fiber used. Indeed, although Y-GK homemade papers were surely made with Japanese fibers, the final product contains characteristics similar to industrial papers, where a significant load of Manila hemp was observed. Conversely, Y-Mit<sup>2015</sup> resulted closer to natural fibers than industrial papers.

The higher release of AA was mainly observed in industrial papers rather than fibers and homemade papers (except Y-KG<sub>2015</sub>) and it is associated with 1-Bu and DF, thus suggesting that the use of delignificant agents may promote the release of acetic acid. Moreover, it seems possible that paper treated with delignificant agents still release these compounds.

## 4 Conclusion

In this paper, we proposed a non-invasive multi-analytical approach that can be successfully used for characterizing Japanese paper materials. Several papers (industrial and homemade) were analyzed together with the Japanese fibers Kozo, Mitsumata and Gampi. The volatile organic compounds were detected by SPME/GC-MS and information on the structure and the raw materials used in the paper making process were obtained from ATR-FTIR, complemented by TG-DSC analysis and supported by microscopy observations. The emission of acetic acid and 1-butanol resulted very low in pure fibers, differently from industrial and homemade papers where these compounds were highly emitted, suggesting a strong influence of the papermaking process. However, although the presence of non-oriental fibers (e.g. Manila hemp) strongly differentiate industrial from homemade papers, it does not influence the emission of these compounds. Nevertheless, homemade papers presented a high variability that mainly depends on the process employed for their production that may have changed during the last 10 years, probably in relation with the choices of the paper-making master. E22-beA was significantly detected only in modern papers and, although the reason of the presence/absence of this compound is not completely clear, we propose this compound as a possible marker for distinguishing modern to naturally-aged papers. N-N dimethyl formamide was peculiar of industrial processes, while ketones, aldehydes (furfural) and heavier alcohols were preferentially emitted by fibers and homemade papers. Surprisingly, the higher content of furfural in fibers rather than in papers places new questions about the use of this compound to evaluate the degradation state of the paper materials [48] that should be carefully evaluated.

## Funding

The research did not receive any specific grant from funding agencies in the public, commercial nor not-for-profit sectors.

## Acknowledgments

The authors would like to thank the *Washi* paper Master Yuko Isozaki for the hand-made papers and the professor and paper conservation restorer Rosanna Chiggiato for her interest in the research and for providing samples. Finally, we would like to thank Dr. Natalie M. Kehrwald for grammar checking and comments, which improved the quality of the manuscript.

## References

- [1] A.L. Dupont and J. Tetreault, Cellulose degradation in an acidic acid environment, *Stud. Conserv.* **45**, 2000, 201.
- [2] M. Strlic, I. Kralj Cigic, M. Alenka, G. de Bruin, J. Kolar and M. Cassar, The effect of volatile organic compounds and hypoxia on paper degradation, *Polym. Degradation Stabil.* **96**, 2011, 608-615.
- [3] L.T. Gibson, A. Ewlad-Ahmed, B. Knight, V. Horie, G. Mitchell and C.J. Robertson, Measurement of volatile organic compounds emitted in libraries and archives: an inferential indicator of paper decay?, *Chem. Cent. J.* **6**, 2012, 42-64.
- [4] M. Strlic, E. Menart, I. Kralj Cigic, G. de Bruin, J. Kolar and M. Cassar, Emission of volatiles and reactive oxygen species during degradation of iron gall ink, *Polym. Degradation Stabil.* **95**, 2010, 66-71.
- [5] C. Bembibre and Matija Strlic, Smell of heritage: a framework for the identification, analysis and archival of historic odours, *Herit. Sci.* **5**, 2017, 2.
- [6] R. Koestler, N. Indictor and B. Fiske, Characterization of Japanese papers using energy-dispersive x-ray spectrometry, *Restaurator* **13**, 2009, 58-77.
- [7] C.H. Stephens and P.M. Whitmore, Comparison of the degradative behavior of cotton, linen and kozo paper, *Cellulose* **20**, 2013, 1099-1108.
- [8] S. Margutti, G. Conio, P. CALVINI and E. Pedemonte, Hydrolytic and oxidative degradation of paper, *Restaurator* **22**, 2001, 67-83.
- [9] T. Kurosawa and T. Hashino, From the Non-European tradition to a variation of Japanese model of competitiveness: the Japanese modern paper industry since 1870s, 2010, Springer.
- [10] J. Lamberg, J. Ojala, M. Peltoniemi and T. Särkkäthe, Evolution of global paper industry 1800-2050: a comparative analysis, 2012, Springer.
- [11] T. Barrett, Japanese papermaking, 1983, Weatherhill; New York, 145-149.

- [12]** M.-S. Ilvessalo-Pfäffli, Fiber atlas: identification of papermaking fibers, 1995, Springer, 348-350.
- [13]** Y.-H. Han, M. Yanagisawa, T. Enomae, A. Isogai and T. Ishii, Analyses of mucilaginous compounds used in making traditional handmade paper, *Japan TAPPI J.* **59**, 2005, 121-130.
- [14]** T. Oshibuchi and Y. Owada, Studies on the mucilage of the root of "Tororo-aoi" (*Abelmoschus manihot*), *Nippon Nōgeikagaku Kaishi* **28**, 1954, 558-562.
- [15]** T. Uyeda, Y. Tanya, K. Saito, M. Inaba and A. Osawa, The effect of cooking agent on Japanese paper, *Restaurator* **20**, 1999, 119-125.
- [16]** L. Micheli, C. Mazzucca, A. Palleschi and G. Palleschi, Development of a diagnostic and clearing tool for paper artworks: a case of study, *Microchem. J.* **126**, 2016, 32-41.
- [17]** N. Odegaard, S. Carroll and W.S. Zimmt, Material characterization tests for objects of art and archaeology, 2000, Archetype Publications.
- [18]** E.M. Gaspar, J.C. Santana, J.F. Lopes and M.B. Diniz, Volatile organic compounds in paper; an approach for identification of markers in aged books, *Anal. Bioanal. Chem.* **397**, 2010, 369-380.
- [19]** M. Strlic, J. Thomas, T. Trafela, L. Cse Falvayova, I.K. Cigic, J. Kolar and M. Cassar, Material degradomics: on the smell of old books, *Anal. Chem.* **81**, 2009, 8617-8622.
- [20]** A.J. Clark, J.L. Calvillo, M.S. Roosa, D.B. Green and J.A. Ganske, 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.
- [21]** S.S. Shapiro and M.B. Wilk, An analysis of variance test for normality (complete samples), *Biometrika* **52**, 1965, 591-611.
- [22]** H.G. Wiedemann, J.R. Giinter and H.R. Oswald, Investigation of ancient and new Japanese papers, *Thermochim. Acta* **282-283**, 1996, 453-459.
- [23]** J. Shi and T. Li, Technical investigation of 15th and 19th century Chinese paper currencies: fiber use and pigment identification, *J. Raman Spec.* **44**, 2013, 892-898.
- [24]** M. Goodway, Fiber identification in practice, *J. Am. Inst. Conserv.* **26**, 1987, 27-44.
- [25]** A. Ansalone, C. Di Majo, L. Federici and Mita, La connotazione dei materiali impiegati per il restauro: le carte giapponesi, *Bollettino Istituto Centrale della Patologia del Libro* **40**, 1986, 7-40.
- [26]** P. Garside and P. Wyeth, Identification of cellulosic fibres by FTIR spectroscopy: thread and single fibre analysis by attenuated total reflectance, *Stud. Conserv.* **48**, 2003, 269-275.
- [27]** L. Liu, T. Jiang and J. Yao, A two step chemical process for the extraction of cellulose fiber and pectin from mulberry branch bark efficiently, *J. Polym. Environ.* **19**, 2011, 568-573.
- [28]** P. Calvini, A. Gorassini and R. Chiggiato, Fourier transform infrared analysis of some Japanese papers, *Restaurator* **27**, 2006, 81-89.
- [29]** P. Sannigrahi, D.H. Kim, S. Jung and A. Ragauskas, Pseudo-lignin and pretreatment chemistry, *Energy Environ. Sci.* **4**, 2011, 1306-1310.
- [30]** S. Ouajai and R.A. Shanks, Composition, structure and thermal degradation of hemp cellulose after chemical treatments, *Polym. Degrad. Stab.* **89**, 2005, 327-335.
- [31]** U. Muller, M. Ratzsch, M. Schwanninger, M. Steiner and H. Zobl, Yellowing and IR-changes of spruce wood as result of UV-irradiation, *J. Photochem. Photobiol. B: Biol.* **69**, 2003, 97-105.
- [32]** M. Schwanninger, J.C. Rodriguez, H. Pereira and B. Hinterstoisser, Effects of short-time vibratory ball milling on the shape of FT-IR spectra of wood and cellulose, *Vibr. Spec.* **36**, 2004, 23-40.
- [33]** J. Kiuberis, S. Tautkus, R. Kazlauskas, I. Pakutinskiene and A. Kareiva, Protective coating for paper: new development and analytical characterization, *J. Cult. Herit.* **6**, 2005, 245-251.
- [34]** M.A. Abeer, Z. Abd El-Wahab, A.A. Ibrahim and T.M. Al-Shemy, Characterization of microcrystalline cellulose prepared from lignocellulosic materials. Part II: physicochemical properties, *Carbohydr. Polym.* **83**, 2011, 676-687.
- [35]** A. Boukir, E. Aries, M. Guiliano, L. Asia, P. Doumenq and G. Mille, Subfractionation, characterization and photooxidation of crude oil resins, *Chemosphere* **43**, 2000, 279-286.
- [36]** M. Polovka, J. Polovkova, K. Vizarova, S. Kirschnerova, L. Bielikova and M. Vrska, he Application of FTIR spectroscopy on the characterization of paper samples, modified by bookkeeper process, *Vib. Spectrosc.* **41**, 2006, 112-117.
- [37]** L. Hajji, A. Boukir, J. Assouik, H. Lakhiari, A. Kerbal, P. Doumenq, G. Mille and M.L. De Carvalho, Conservation of Moroccan manuscript papers aged 150, 200 and 800 years. Analysis by infrared spectroscopy (ATR-

FTIR), X-ray diffraction (XRD) and scanning electron microscopy energy dispersive spectrometry (SEM-EDS), *Spectrochim Acta Part A: Mol. Biomol. Spectrosc.* **136**, 2015, 1038-1046.

**[38]** T. Collings and D. Milner, The identification of oriental paper-making fibres, *Paper Conservat.* **3**, 1978, 51-79.

**[39]** E. Wiercigroch, W. Szafraniec, K. Czamara, M.Z. Pacia, K. Majzner, K. Kochan, A. Kaczor, M. Baranska and K. Malek, Raman and infrared spectroscopy of carbohydrates: a review, *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc* **185**, 2017, 317-335.

**[40]** S. Soares, G. Caminot and S. Levchik, Comparative study of the thermal decomposition of pure cellulose and pulp paper, *Polym. Degrad. Stab.* **49**, 1995, 275-283.

**[41]** S. Bourbigot, S. Chlebicki and V. Mamleev, Thermal degradation of cotton under linear heating, *Polym. Degrad. Stab.* **78**, 2002, 57-62.

**[42]** N. Berkowitz, On the differential thermal analysis of coal, *Fuel* **36**, 1957, 355-373.

**[43]** D.F. Arsenau, Competitive reactions in the thermal decomposition of cellulose, *Can. J. Chem.* **49**, 1971, 632-638.

**[44]** Analysis of volatile compounds in the headspace of rice using SPME/GC/MS in R. Marsili, In: C.C. Grimm, E.T. Champagne and K. Oktsuba, (Eds.), *Flavour, fragrance and odor analysis*, 2002, M. dekker; New York, 229-248.

**[45]** T. Lojewski, T. Sawoszczuk, J.M. Lagan, K. Zieba, A. Baranski and J. Lojewska, Furfural as a marker of cellulose degradation. A quantitative approach, *Appl. Phys. A* **100**, 2010, 873-884.

**[46]** B. Gross, A. Gallois, H. Spinnler and D. Langlois, Volatile compounds produced by the ligninolytic fungus *Phlebia radiata* Fr. (Basidiomycetes) and influence of the strain specificity on the odorous profile, *J. Biotechnol* **10**, 1989, 303-308.

**[47]** J.H. Hui wang and X. Chun, Two new 2-phenylethyl alcohol derivatives and one new lignan derivative from the root of *Ilex pubescens*, *Helv. Chim. Acta* **91**, 2008, 1244-1250.

**[48]** M.H. Ekthera, M. Azdadfallah, M. Barhami and J.M. Rovshandeh, Comparative studies of pulp and paper properties of canola stalks prepared by using dimethyl formamide or diethylene glycol, *Bioresurces* **4**, 2009, 214-233.

---

## Highlights

- Non-invasive multi-analytical approach for characterizing Japanese papers.
- SPME-GC/MS provides information on the organic substances emitted by papers and fibers.
- Acetic acid and 1-butanol emission are related to the papermaking process.
- N-N dimethyl formamide was emitted exclusively by industrial papers. Ketones, aldehydes and heavier alcohol were preferentially emitted by fibers and homemade papers.
- Higher furfural emission from fibers place further question about the use of this compound for evaluating degradation of the paper.

---

## Queries and Answers

**Query:** Please provide the given name of authors.

**Answer:** I included the given names in the text.

**Query:** The author names have been tagged as given names and surnames (surnames are highlighted in teal color). Please confirm if they have been identified correctly.

**Answer:** Yes

**Query:** Please check the following sentence: He flow (1mL min<sup>-1</sup>) was used as a carrier.

**Answer:** I changed the sentence in to be clearer.