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## EVALUATION OF SOLID-PHASE MICROEXTRACTION ON-FIBER DERIVATIZATION FOR THE ANALYSIS OF PAPER DEGRADATION COMPOUNDS

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### Abstract

**As a contribution to exploring non-destructive strategies for the evaluation of the state of degradation of paper documents, two SPME on-fiber derivatization methods were developed for the analysis of low molar mass carbonyl and carboxyl compounds formed during paper degradation upon ageing. The two SPME methods involved the specific extraction of carbonyl and carboxyl compounds using PFBHA and PDAM as derivatizing agents, respectively. They were first tested and validated in headspace sampling mode where the emission from a groundwood pulp paper was characterized qualitatively and quantitatively. The methods were then applied on a set of four papers of different composition and degradation state obtained by artificial ageing. The second step was aimed at extending the methodology for field application and involved the development of direct contact sampling of the VOCs emitted from four books of different composition, naturally aged, by inserting the derivatized SPME fibers inside the books core.**

**The analyses are discussed in the light of the paper's pulp composition and their degradation state related to the artificial ageing. The results showed that there was a close relation between the amount of VOCs emitted from paper and the composition of the paper, and that the general trend for both acids and aldehydes was an increase in the emissions with ageing time, or occasionally, a plateau reached at the longest ageing times. The VOCs emitted by the naturally aged books were consistent with those of the artificially aged papers. Globally the emissions of aldehydes were much lower than the emissions of acids and, for all the papers the most abundant VOC was formic acid, both in the unaged and in the aged samples. This is noteworthy as formic acid has been recently designated as highly aggressive towards cellulose.**

### 1 Introduction

For thousands of years paper has been a privileged carrier of mankind artistic expression and dissemination of knowledge. Paper is also a material that has evolved considerably in the course of the last centuries to satisfy increasing needs and specific usage requirements. These two parameters, age and composition, together with the conservation conditions aspects, are the main factors impacting paper permanence and longevity. Paper based collections housed in libraries, archives and museums across the world are thus extremely vast and varied and the need to better assess their state of degradation is an important preservation issue.

As a general consensus, the most reliable, accurate and precise methods to assess cellulose degradation are based on the measurement of molar mass (MM) and molar mass distribution (MMD) of the polymer. Interestingly it has been established that these polymer characteristics relate to the physical state of paper in a non-linear fashion<sup>1,2</sup>. However the measurement of MM or, in other words, the degree of polymerization of cellulose, is a destructive, at best a micro-destructive analysis<sup>3</sup> and sampling, even minimal, is not

always possible. Consequently it is not always possible to carry out these measurements on cultural heritage polymer materials<sup>4-6</sup>. Indirect approaches to assess paper degradation have been proposed, such as examining the end-products formed during paper degradation, mostly arising from oxidation and acid-catalysed hydrolysis reactions of cellulose, but also hemicelluloses and lignin. These compounds belong primarily to the class of low molar mass organic acids and aldehydes, but can also be sugars and aromatic compounds. They have been identified in degraded paper using gas chromatography (GC)<sup>7-9</sup>, capillary electrophoresis (CE)<sup>10</sup> and liquid chromatography (HPLC)<sup>11,12</sup>. Nevertheless, the separation techniques for their analysis also require resorting to material sampling. The non-invasive characterization of sub-products off-gassing from solid materials by solid-phase microextraction (SPME) coupled with gas chromatography and mass spectrometry (GC/MS) is a well-known and powerful tool that was developed in the early 1980s. It permits fast and solvent-free extraction and identification of volatile organic compounds (VOCs) from a wide variety of matrices with high sensitivity and reliability<sup>13-17</sup>. This static sampling method has been successfully applied in recent years in the field of cultural heritage for the screening of gas emissions from various cultural objects made of natural materials including paper<sup>18-20</sup>. This bulk of work has confirmed that low-MM aldehydes (formaldehyde, acetaldehyde, glycolaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, hexanal, benzaldehyde, furfural and other heterocyclic furanic compounds) as well as low-MM organic acids (formic, acetic, levulinic, glycolic, lactic, succinic, furoic, pyruvic, vanillic, ferulic, benzoic) from cellulose and hemicelluloses degradation can be emitted in the surrounding air. Some of these compounds have been proposed as chemical indicators of the state of degradation of paper<sup>10,18-26</sup>.

Nevertheless, adsorption phenomena on typical SPME fibers often are unspecific and result in the extraction of a wide range of compounds, including exogenous contaminants present in the atmosphere or compounds emitted by other materials in the immediate vicinity of the sample. This can prevent the identification of the compounds of interest and hinder a semi-quantitative approach. On-fiber derivatization, based on the simultaneous derivatization and extraction on a SPME fiber, offers a solution to this specificity problem by targeting the molecular specificity of key functional groups. This approach was shown to decrease detection limits and to improve the detection of compounds with low volatilities as well as to favour increased recoveries of polar molecules from the sample matrices<sup>27</sup>. SPME on-fiber derivatization targeting carbonyl and carboxyl compounds has been applied to a number of matrices<sup>28-40</sup>. However, to our knowledge, its use to analyze the specific off-gassing of paper documents has not been attempted and thus requires development and optimization. This research was aimed at exploring this approach for the non-destructive analysis of low-MM aldehydes, ketones and carboxylic acids formed upon ageing in paper. It thereby contributes to non-destructive strategies for the evaluation of the state of degradation of paper documents.

Two SPME sampling methods with on-fiber derivatization were used to characterize and quantify the most abundant compounds emitted by paper during its

degradation, namely formic acid, acetic acid, formaldehyde, acetaldehyde, acetone, hexaldehyde, and furfural. These compounds were chosen as their production in paper was previously reported to increase with ageing time<sup>10,41</sup>.

In the first method the selectivity for carbonyls extraction was increased by saturating the SPME fiber with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA). Aldehydes and ketones adsorbed are instantly derivatized on the fiber to PFBHA-carbonyl oximes which are thermally very stable. This method was first developed by Martos and Pawliszyn<sup>28</sup> and has found a wide application for the analysis of aldehydes in water<sup>29-31</sup>, alcoholic beverages<sup>32-34</sup> and indoor air<sup>35-37</sup>.

The second method involved the specific extraction of carboxyls by SPME on-fiber derivatization with 1-pyrenyldiazomethane (PDAM), where acids are derivatized to PDAM-carboxyl pyrenylmethyl esters. This method has been used to analyze short chain fatty acids in sewages, milk and faeces<sup>38-40</sup>. The two methods were first developed in headspace sampling mode where the low-MM aldehydes/ketones and acids emitted from a groundwood pulp paper were qualitatively and quantitatively characterized. The methods were then tested on a set of four papers of different composition and degradation state obtained by artificial ageing. The second step involved testing direct contact sampling of the VOCs emitted from four books of different composition, naturally aged. The qualitative and quantitative analyses of the VOCs are discussed in the light of the paper's pulp composition and their degradation state related to the artificial ageing. The VOCs of the air of the rooms and cabinet in which the books were stored were analyzed by SPME in diffusive sampling mode.

## 2 Experimental

### 2.1 Standards and reagents

Acetaldehyde (>99.5%), furfural (99%), isobutyraldehyde (99%), formic acid (96%), 1-pyrenyldiazomethane (PDAM, C<sub>17</sub>H<sub>10</sub>N<sub>2</sub>, MW 242.27, Cas number 78377-23-8) and *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA, C<sub>6</sub>F<sub>5</sub>CH<sub>2</sub>ONH<sub>2</sub>·HCl, MW 249.57, Cas number 57981-02-9) were supplied by Sigma Aldrich (St Quentin Fallavier, France). Formaldehyde (37% in water) and valeric acid (99%) were purchased from Acros Organics (Geel, Belgium). Acetic acid (99.8%) was provided by VWR (Fontenay sous Bois, France). The gaseous isobutyraldehyde and valeric acid used as internal standards were prepared based on a previous static method<sup>42</sup>.

### 2.2 Samples and ageing

#### 2.2.1 Artificially aged model papers

Four types of papers were analysed: Whatman No.1, W1, made of pure cotton cellulose (cold extract pH = 7); P1, made of bleached sulphite softwood cellulose (cold extract pH = 6); P2, made of > 95% cotton linters with traces of softwood cellulose (cold extract pH = 7), and P3, which contains groundwood pulp (GWP) (75%) and bleached sulphite softwood pulp (25%) (*i.e.* ligno-cellulosic paper) (cold extract pH = 5.4). As opposed to

the other papers, P3 also contains fillers (~ 20% kaolin) and sizing (alum-rosin). The standard method TAPPI T509 om-02<sup>43</sup> scaled down to 0.5 g of paper, was used for determining the cold extract pH of the papers.

These papers were subjected to hygrothermal ageing at 100 °C for 2, 5, 10, 14 and 30 days in hermetically closed hybridization tubes (35 mm internal diameter (ID) × 147 mm (height), 144 mL (volume) (Wheaton) following the ASTM standard method D6819-02e2<sup>44</sup>. For each paper type, three samples of 530 mg were placed in three ageing tubes for measurements. During the ageing, the humidity in the tube is supplied and buffered by the paper, and stabilizes between 50 and 60% relative humidity (RH)<sup>45</sup>. This configuration in closed tubes has been proposed to better represent natural ageing than hygrothermal ageing in a ventilated climatic chamber in suspended sheets configuration<sup>46</sup>. It concentrates the volatile compounds produced by the paper during ageing, which thus remain in contact with the paper as they would in a closed book and accelerate the degradation. After ageing, the papers were degassed in the fumehood and left to equilibrate to ambient air for 1 hour before SPME sampling. Thereby the VOCs sampled were mostly those produced and emitted after the ageing.

### 2.2.2 Naturally aged historical papers

For contact SPME sampling, four books belonging to the Central Library of the French National Museum of Natural History (MNHN, Paris) and to CRCC (Paris) in-house collection were used. The choice for the MNHN books was guided by the fact that they had not been opened for a number of years according to the consultation room record, as opposed to the CRCC books which were opened repeatedly for analytical purposes. The VOCs in the core of the MNHN books were then most likely at the equilibrium state.

The MNHN books were:

- *Mémoires et rapports sur les matières grasses, le palmier à huile*. A periodical dated 1928, most likely partly composed of groundwood pulp. The paper was in good conservation state but groundwood pulp is known to degrade faster than pure cellulose pulps.

- *Herbarium Blackwellianum emendatum et auctum, id est, Elisabethae Blackwell collectio stirpium*, by Blackwell E., de Launoy C., Eisenberger N.F., Fleischmann I., Trew C.J., dated 1717. The book had painted illustrations of herbs and plants. It was made of rag paper and was in a very good conservation condition (slight discolouration only on the verso of the coloured areas, see: <https://archive.org/details/mobot31753000818978/>)

The CRCC in-house books were:

- *Sancti Epiphanii*, dating from the beginning of the 18th century made of linen rag (mostly flax). The book had a missing cover hence no precise printing date is available. The paper still had a good mechanical strength but was quite discoloured in the inked areas (text) and in the margins.

- *Les forces d'amour*, a paperback book dated 1931 made of groundwood pulp paper (hardwood). The paper was yellow and extremely brittle. Its cold extract pH was 3.6.

### 2.3 On-fiber derivatization and SPME sampling

Before SPME sampling, paper samples were conditioned for 24 hours to 23 °C and 50% RH (TAPPI T402 sp-03)<sup>47</sup>. Headspace SPME sampling experiments applied to all artificially aged model papers were carried out in the CRCC laboratory (23 °C and 50% RH). Simultaneously to the sampling of the papers, a blank run was obtained by sampling the laboratory air. The concentrations of VOCs in the blank were subtracted from those obtained from the paper samplings. For headspace sampling, three measurements were carried out per ageing tube by separating the mass of paper in three equal parts in headspace sampling vials. This was repeated at least twice (two ageing tubes for each paper type and ageing time) for a total of six replicate measurements for a given paper type and ageing time.

Direct contact sampling of the MNHN books was carried in the MNHN library (27 °C and 40% RH). At CRCC, the books sampling was carried out in the climate room (23 °C and 50% RH). Each book was sampled three times in three locations inside the core of the book (Figure 1). In order to obtain a fingerprint chro-

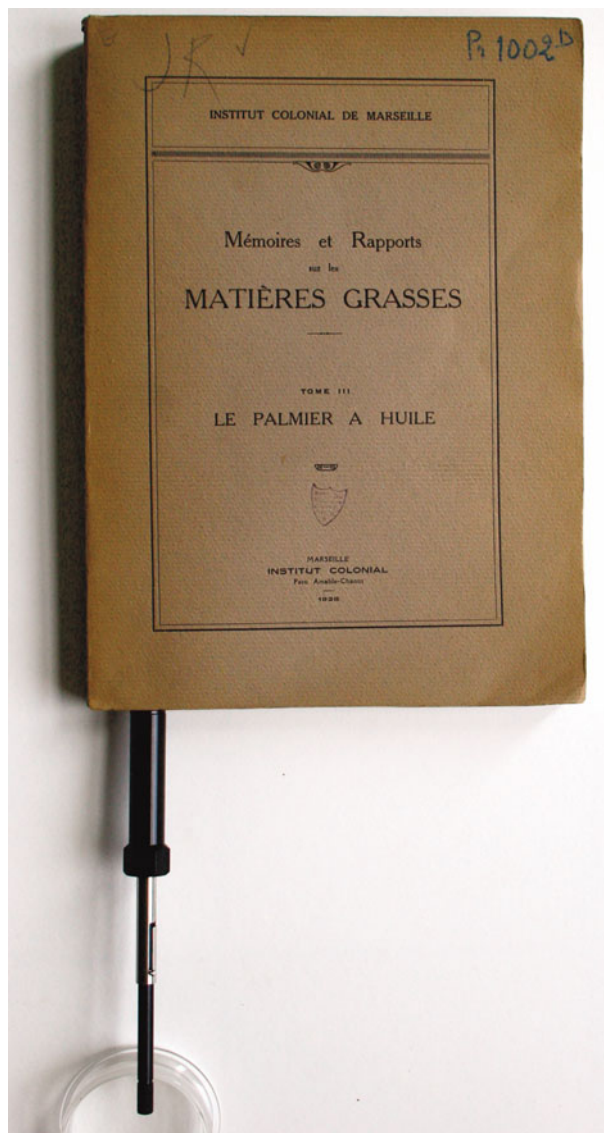


Figure 1: Direct contact sampling by insertion of the SPME fibre inside the core of the periodical *Mémoires et rapports sur les matières grasses, le palmier à huile*. © Dupont A.-L./CRCC.

matogram of the VOCs present in indoor air, diffusive gas-phase sampling was simultaneously carried out by placing fibers in various locations at CRCC: the library, the climate room and inside one of the climate room's wooden cabinets which was filled mostly with cellulosic materials.

On-fiber derivatization and sampling of low-MM carbonyls and carboxyls were performed according to a three step-procedure: (1) loading of the derivatizing reagent on the fiber, (2) exposure of the fiber to the sample, and (3) exposure of the fiber to the internal standard.

O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) was used as derivatizing reagent for aldehydes. A 65  $\mu\text{m}$  divinylbenzene/polydimethylsiloxane (DVB/PDMS) fiber coating (Supelco, Bellefonte, USA) was used. This coating was selected for its ability to retain PFBHA and for its high extraction efficiency with PFBHA-oximes<sup>28</sup>. The fibers were loaded by exposure to the headspace of a 1 mL stirred solution of aqueous PFBHA (17 mg/mL) in a 4 mL vial at 23 °C during 5 minutes. It was determined that the equilibrium loading time was 20 minutes (data not presented here). Nevertheless, equilibrium conditions are not necessary if excess PFBHA is loaded to compensate for the depletion that occurs during the derivatization. A loading time of 5 minutes, which allowed reaching the excess reagent condition was thus applied as it was less time consuming. The fiber loaded with PFBHA was then placed for 2 hours either in the headspace of the hybridization tube containing the artificially aged model papers or was directly inserted between two pages of the naturally aged book kept close. Optimal derivatization efficiency (signal-to-noise ratio, S/N) was investigated by testing several extraction times performed at 23 °C. Afterwards the fiber was exposed to an internal gaseous standard, isobutyraldehyde (27.3  $\mu\text{g/L}$ ) in a 120 mL vial at 23 °C for 2 minutes. The fiber was then inserted for 2 minutes into the injector port of the GC heated at 270 °C. As confirmed by a second desorption run, this time allowed a complete desorption of PFBHA-carbonyl oximes and unreacted PFBHA.

A 85  $\mu\text{m}$  polyacrylate (PA) fiber coating (Supelco, Bellefonte, USA) was used for the analysis of carboxylic acids. 1-pyrenyldiazomethane (PDAM) was used as derivatizing reagent. The coating phase was dipped in a PDAM/hexane solution (2.5 mg/mL) in a 2 mL conical vial at 23 °C for 15 minutes<sup>38-40</sup>. The fiber loaded with PDAM was then placed for 1 hour either in the headspace of the hybridization tube containing the artificially aged model papers or inserted directly into the naturally aged book. Different extraction times were tested to optimize S/N ratios of the target compounds. The loaded fiber was then exposed to gaseous valeric acid in a 9 mL vial at 23 °C for 2 minutes, which was used as internal standard (11.7 mg/L). Lastly, the fiber was inserted for 1 minute into the injector port of the GC heated at 270 °C. As confirmed by a second desorption run, this time allowed a complete desorption of PDAM-carboxyl pyrenylmethyl esters and unreacted PDAM.

## 2.4 Instrumentation and chromatographic conditions

GC analyses were carried out using a HP 5890 gas chromatograph equipped with a flame ionization detection system (Agilent, Evry, France). Separation was performed using a CP-Sil 8 CB fused-silica capillary column, 60 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$  (length  $\times$  internal diameter  $\times$  film thickness) (Chrompack, les Ulis, France). Helium was used as carrier gas at a constant flow rate of 1 mL/min. The split/splitless injector was used in splitless mode at 270 °C and the FID temperature maintained at 300 °C for both procedures. The GC temperature program for PFBHA-carbonyl oximes was 45 °C (1 min) to 270 °C (10 min) at 10 °C/min. The GC temperature program for PDAM-carboxyl pyrenylmethyl esters was 100 °C (2 min) to 280 °C (1 min) at 20 °C/min, then 0.5 °C/min to 290 °C (1 min) and finally 2 °C/min to 310 °C (2 min).

GC-MS analyses were performed on a Thermo Trace gas chromatograph coupled with a Thermo DSQ quadrupolar mass spectrometer (Thermo Fisher Scientific, les Ulis, France). Chromatographic conditions were the same as above. The interface temperature and the ion source temperature were set at 270 °C and 200 °C, respectively. Mass spectra were acquired under electron ionization (EI) mode at 70 eV and recorded from  $m/z$  50 to 500 with a cycle time of 1 s. VOCs identification was performed by analyzing the mass spectra and/or comparing the retention times and mass spectra with entries from a reference mass spectra library (NIST, Mass Spectral Search Program Version 2.0 a, 2002).

## 3 Results and discussion

### 3.1 Method development: low-MM carbonyls and carboxyls in aged model paper P3

#### 3.1.1 Low-MM carbonyls

Aldehydes/ketones derivatization with PFBHA led to two geometrical isomers (Figure 2) which appeared as two peaks on the chromatograms, except for formaldehyde which is symmetrical and therefore presented a single peak. On the mass spectra, PFBHA-carbonyl oximes were identified by the presence of a main ion fragment at  $m/z$  181 which is characteristic of methyl pentafluorobenzene.

Figure 3 shows the GC profile of the headspace SPME extract with the PFBHA derivatized fiber from the model paper P3 aged 5 days. The chromatogram is dominated by three main carbonyl compounds: formaldehyde, acetaldehyde and acetone. These compounds have been reported as compounds released by aged papers<sup>9,41,48</sup>, but they can also arise from widespread exogenous sources. Blank measurements allowed distinguishing between the amounts emitted by the paper and the baseline concentration of these VOCs in the air of the room. In a context where measurements are carried out on-site, where it can be problematic to distinguish the emission source for these carbonyl VOCs, it is important to perform simultaneous blank air samples. The most common exogenous sources of these carbonyl compounds in libraries and archives repositories, especially concerning formaldehyde, are the pressed wood products made

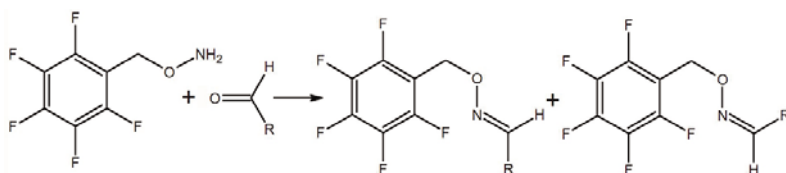


Figure 2: Reaction between carbonyls and PFBHA leading to PFBHA-carbonyl oximes.

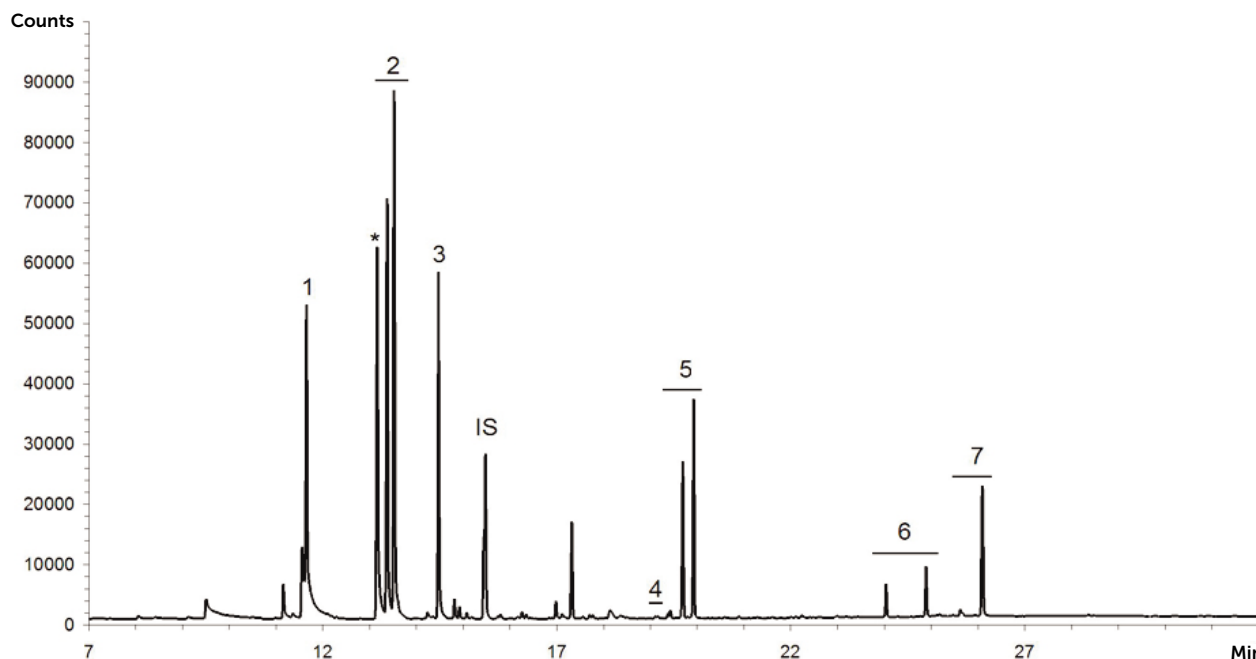


Figure 3: Gas chromatographic profile of the headspace SPME extract with PFBHA on-fiber derivatization (DVB/PDMS, 2 hours at 23 °C and 50% RH) from the model paper P3 artificially aged 5 days. 1. Formaldehyde, 2. Acetaldehyde, 3. Acetone, 4. Hexaldehyde, 5. Furfural, 6 and 7. Dimethylglyoxal and its conformer, \* PFBHA, IS. Internal standard (isobutyraldehyde).

with urea formaldehyde resins, such as particle board or hardwood plywood paneling used in the furniture<sup>49-51</sup>. Furfural is a common compound found in paper emissions and results from acid catalyzed hydrolysis via glucose dehydration and rearrangement via 3-deoxyglucosone<sup>21,52</sup>. As such, it is representative of a major degradation pathway occurring in paper during ageing and is often considered as a chemical marker of paper degradation<sup>11,18,19,23</sup>. Hexaldehyde has been reported in previous studies as a specific degradation product in paper, which contributes to its characteristic odor<sup>53-55</sup>. It is also supposed to arise from the oxidation of linoleic acid which is a fatty acid present in wood. Lastly,  $\alpha$ -dicarbonyl compounds have also been proposed as degradation products of glucose via breakdown of 3-deoxyglucosone. Unfortunately, the PFBHA-derivatization of dimethylglyoxal was not complete, and partially derivatized compounds were present on the chromatogram (retention time near 17.5 minutes, Figure 3). Thus its quantitation was not investigated.

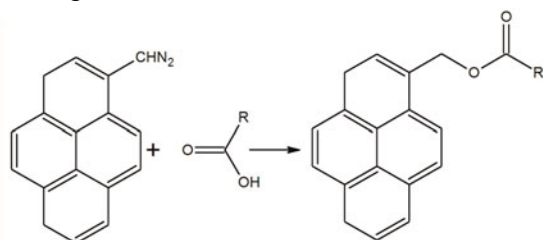


Figure 4: Reaction between low molar mass acids and PDAM leading to PDAM-carboxyl pyrenylmethyl esters.

### 3.1.2 Low-MM carboxyls

Carboxylic acid derivatization with PDAM led to pyrenylmethyl esters (Figure 4), the mass spectra of which showed a base peak at  $m/z$  215, characteristic of the cleavage between the pyrenylmethyl group and the fatty acid moiety.

The two major peaks on the GC profile of the headspace SPME extract with PDAM on-fiber derivatization from the model paper P3 artificially aged 5 days were those corresponding to derivatized formic and acetic acids (Figure 5). Both acids are well known degradation products from paper and wood polysaccharides. Formic acid results directly from the scission of 5-hydroxymethylfurfural, coming itself from glucose dehydration via acid catalyzed hydrolysis<sup>21</sup>. They have been identified in several types of paper and their concentrations have been proposed to indicate the level of paper degradation<sup>10,23</sup>. Nevertheless, as for small straight chain aldehydes, formic and acetic acids are also common compounds in the atmosphere of museum and storage rooms arising from the paper collections themselves but also from other wood products<sup>9,56</sup>. Their emissions from construction or display materials are suspected to be a plausible cause of metal and mineral museum objects deterioration (lead and bronze corrosion and efflorescence of calcareous materials)<sup>57-60</sup>.

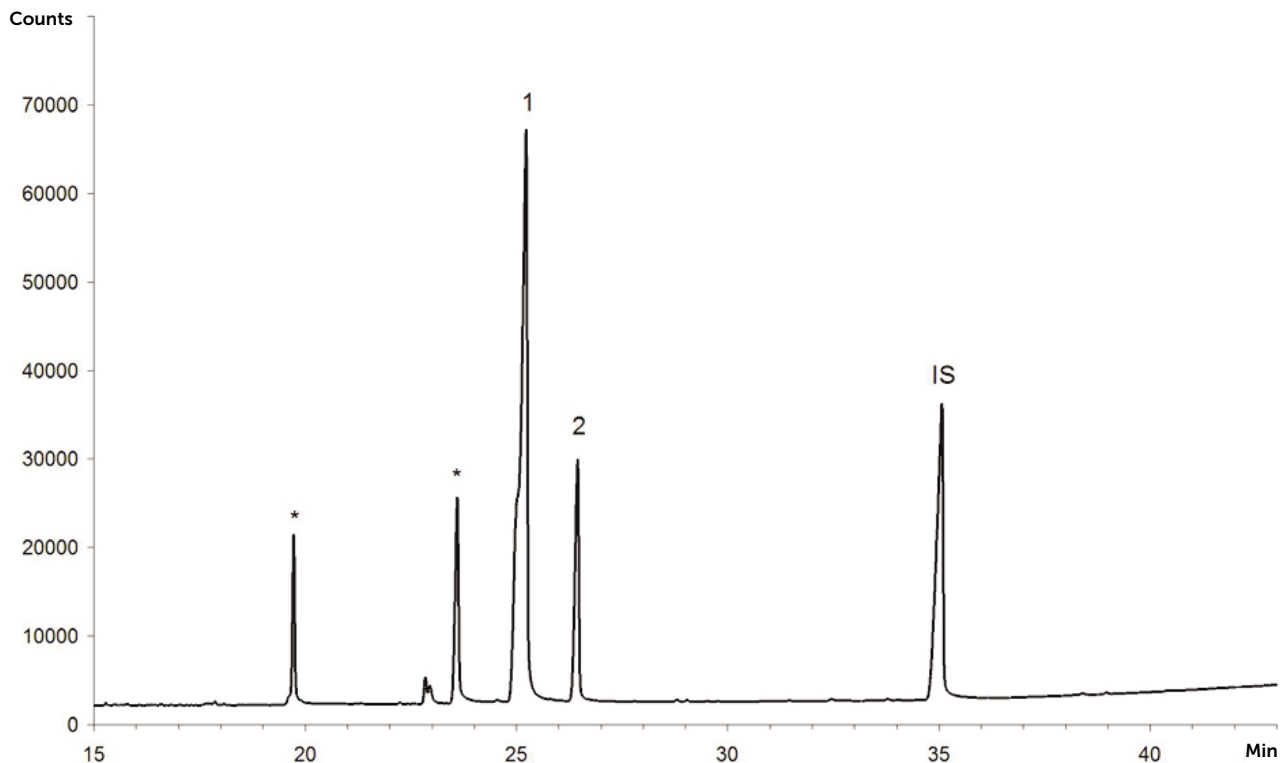


Figure 5: Gas chromatographic profile of the headspace SPME extract with PDAM on-fiber derivatization (PA, 1 hour at 23 °C and 50% RH) from the model paper P3 artificially aged 5 days. 1. Formic acid, 2. Acetic acid, \* Pyrenyl pollutants, IS. Internal standard (valeric acid).

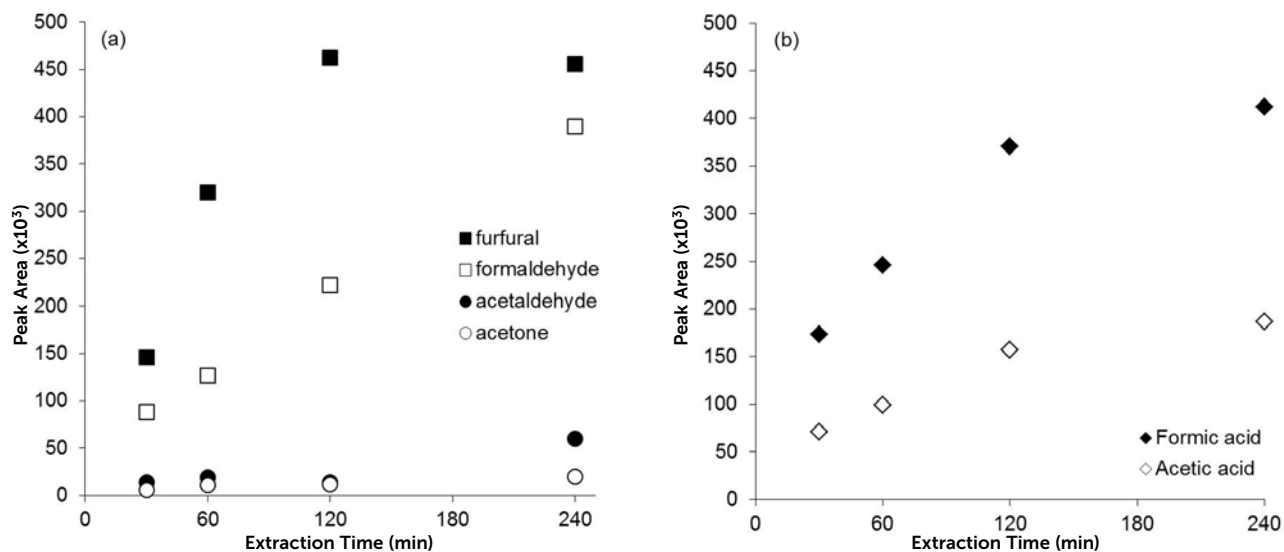


Figure 6: (a) Extraction time profiles for carbonyls emitted by artificially aged model paper P3 using headspace SPME with on-fiber PFBHA derivatization. (b) Extraction time profiles for carboxyls emitted by artificially aged model paper P3 using headspace SPME with on-fiber PDAM derivatization. Sample mass was 530 mg and vial volume was 22 mL. SPME extractions were performed at 23 °C and 50% RH.

### 3.1.3 Optimization and evaluation of the two derivatization headspace sampling procedures

#### 3.1.3.1 Exposure time of the fibers

In order to optimize the extraction time for the two SPME methods, the fibers impregnated with the derivatizing reagents were exposed to the headspace of paper samples (530 g) in a 22 mL tube for 30, 60, 120 and 240 minutes at 23 °C. Figure 6 presents the peak area of the selected compounds from the SPME-

GC/MS profiles. Except for formaldehyde that did not reach the equilibrium, a concentration plateau was reached for most PFBHA-carbonyl oximes and PDAM-carboxyl pyrenylmethyl esters within the time range tested, which indicated complete derivatization of the analytes. This behavior of formaldehyde has been previously reported in research dealing with sorption of aldehydes in water<sup>30-32</sup> and was explained by its higher affinity with the aqueous phase than with the gas phase. As paper is a hygroscopic material, with equilibrium moisture content usually between 5 and 8%, formaldehyde is assumed to preferentially dissolve in

the water sorbed in the paper. The non-equilibrium extraction time that yielded the best compromise with sensitivity was defined as 120 minutes for the aldehydes and 60 minutes for the acids.

### 3.1.3.2 Quantitation and performance

Volatile carbonyl and carboxyl compounds were quantified using internal calibration. Isobutyraldehyde and valeric acid were chosen as internal standards for aldehydes/ketones and acids quantitation, respectively, for several reasons. They belong to the same chemical families, their MM are close to those of the targeted compounds, and they were not present in the samples volatile fractions. Proceeding in a stepwise fashion according to the method employed by Xiong and co-workers<sup>42</sup>, the fibers were first exposed to the sample and then to the internal standard. Calibrations were performed by determining response factors for the targeted VOCs in relation with their respective internal standard. This procedure allowed minimizing variations due to sampling and analysis, which was confirmed by the linear calibration curves obtained (Table 1).

The efficiency of both VOC extraction methods was evaluated in terms of precision, sensitivity and linearity of response. The precision, expressed in terms of relative standard deviation (RSD) was assimilated to the reproducibility (R) and was determined by analyzing the headspace of six different samples of the same paper (same type and ageing). The limit of detection (LOD), which represents sensitivity, was calculated as three times the signal to noise ratio. The linearity of the response was determined individually for each compound by building a calibration curve with five concentration levels. As showed in Table 1, both methods indicated relatively good reproducibility with RSD comprised between 10 and 23%. The differences were mainly attributed to the sample heterogeneity due to the artificial ageing which is a well-known fact in aged and degraded samples. The repeatability, based on six successive injections from sampling the same headspace of a paper sample, showed even greater variations than the reproducibility for carbonyl-oxime PFBHA (results not shown). However, this was expected and was explained by the depletion over time of carbonyl compounds in the sample headspace upon the repeated sampling (six replicates). Repeatability was thus not studied for the PDAM based-derivatization method since it was also expected to be poor because of sample depletion. For both methods, LOD values were in the order of nmol/L, which represents good sensitivity, except in the case of formaldehyde

COV	RSD (%)	LOD (nmol/L)	Calibration <sup>a</sup>	R <sup>2</sup>
Formaldehyde	10	0.09×10 <sup>3</sup>	y = 4.8741x	0.9898
Acetaldehyde	23	1.78	y = 8.5065x	0.9912
Acetone	15	0.65	y = 7.3972x	0.9663
Hexaldehyde	20	0.57	y = 15.2905x	0.9986
Furfural	23	1.2	y = 9.0550x	0.9926
Formic acid	18	0.56×10 <sup>3</sup>	y = 42.1044x	0.9549
Acetic acid	15	13.92	y = 66.9676x	0.9886

Table 1: Performance of both PFBHA and PDAM methods.

<sup>a</sup> calibration curve equation with y = peak area (counts) ratio (VOC / internal standard) and x = concentration ratio (VOC / internal standard) in  $\mu\text{mol}$  and in  $\text{mmol}$  for PFBHA and PDMA methods respectively

and formic acid. The two compounds coeluted with impurities, which interfered with the integration of the peaks. Nevertheless and particularly for acids, LODs were higher than values previously reported in the literature (high pmol/L to low nmol/L)<sup>39</sup>. The response factors in the calibration curves increased with the length of the carbon chain of the compounds. Coefficients of determination R<sup>2</sup> close to 0.99 for the quantitation of aldehydes demonstrated a good linearity of the method. R<sup>2</sup> were slightly lower for the quantitation of the acids (between 0.95 and 0.98) due to impurity interference and indicated a good to moderately good linearity.

These results showed that SPME on-fiber derivatization can be used as a completely non-destructive method for the sampling of low-mass aldehydes and acids emitted by paper. Nevertheless, despite good reproducibility, LOD values remained high - although being acceptable for most compounds (e.g. 0.57 nmol/L for hexaldehyde) - especially for formic acid (0.56×10<sup>3</sup> nmol/L). The overall medium performance of the methods as applied to aged paper was however hardly perfectible as it was predominantly attributed to the sample heterogeneity inherent to the ageing methodology.

## 3.2 SPME headspace sampling of artificially aged model papers

The methods were applied to the headspace sampling and identification of low-MM volatiles emitted by artificially aged model papers. Both methods yielded consistent results both qualitatively and quantitatively. Figure 7 shows the concentrations calculated for the various VOCs in the different unaged and aged papers. All the papers emitted measurable amounts of all the VOCs during their degradation, except hexaldehyde which was below LOD in the cotton linters papers W1 and P2 over the whole ageing period. The quantities of acids and aldehydes were consistent with their expected concentrations based on their emission rates. The latter have been quantified using an emission cell (field laboratory emission cell, FLEC) in dynamic mode, data that was published in a separate article<sup>41</sup>. For instance, for acetic acid, formaldehyde and furfural in P2 and P3, the calculated concentrations based on the emission rates were in average two times higher than the concentrations directly measured with SPME. The observed variation is explained by differences in the sampling mode, *i.e.* static headspace diffusive sampling with SPME and dynamic headspace active sampling with the FLEC. With SPME, the amount of VOC collected on the fiber depends on the gas/paper equilibrium (related to the vapor pressure of each compound), possible interactions with the inner walls of the tube and air/fiber diffusion coefficient. The first two vary with the volume of the tube. With the FLEC, the amount of VOC emitted by the paper is controlled by the linear air velocity above the surface of the paper, which remained constant, as well as possible sorption on the inner walls of the cell. Thus, in the latter case, the emission of VOCs from paper is less restrained and should result in higher amounts of VOCs, which was confirmed. Despite these differences, this result clearly shows the applicability of SPME for identifying and semi-quantifying VOCs emitted from paper.



P3 emitted the highest amount of VOCs, followed by P1. Both papers are made from wood but cellulose is purified by totally removing the lignin from the pulp through a bleaching process in P1, while lignin is still largely present in P3. W1 and P2 presented much lower amounts in their emissions for most VOCs. This was expected as both are made of cotton and hence do not contain hemicelluloses (nor lignin), which is more prone to degradation than cellulose. Thus, in the experimental conditions of this study, the amount of VOCs emitted from paper as a function of their ageing time depended mainly on the paper composition. With a few exceptions (mostly for P2), the general trend for both acids and aldehydes was an increase in the emissions with ageing time or a plateau reached between 14 and 30 days. This asymptotic behaviour could be partly due to a bias in the ageing method. It has been shown that during prolonged ageing periods at high temperature, moisture tends to leak through the seal of the tubes. This has been observed by other researchers too<sup>45</sup>. As moisture inside the tube comes exclusively from the paper, the relative humidity to which the papers are exposed during the ageing may have slowly decreased over time. Water is the main reactant in the degradation path of paper under high humidity and temperature. Thus a shortage thereof could explain a decrease in the degradation rate of cellulose over time.

Globally the emission rate of aldehydes was much lower than those of the acids, below 10 nmol/g of paper for the papers exempt of lignin (W1, P1 and P2) and up to 50 nmol/g of paper for P3.

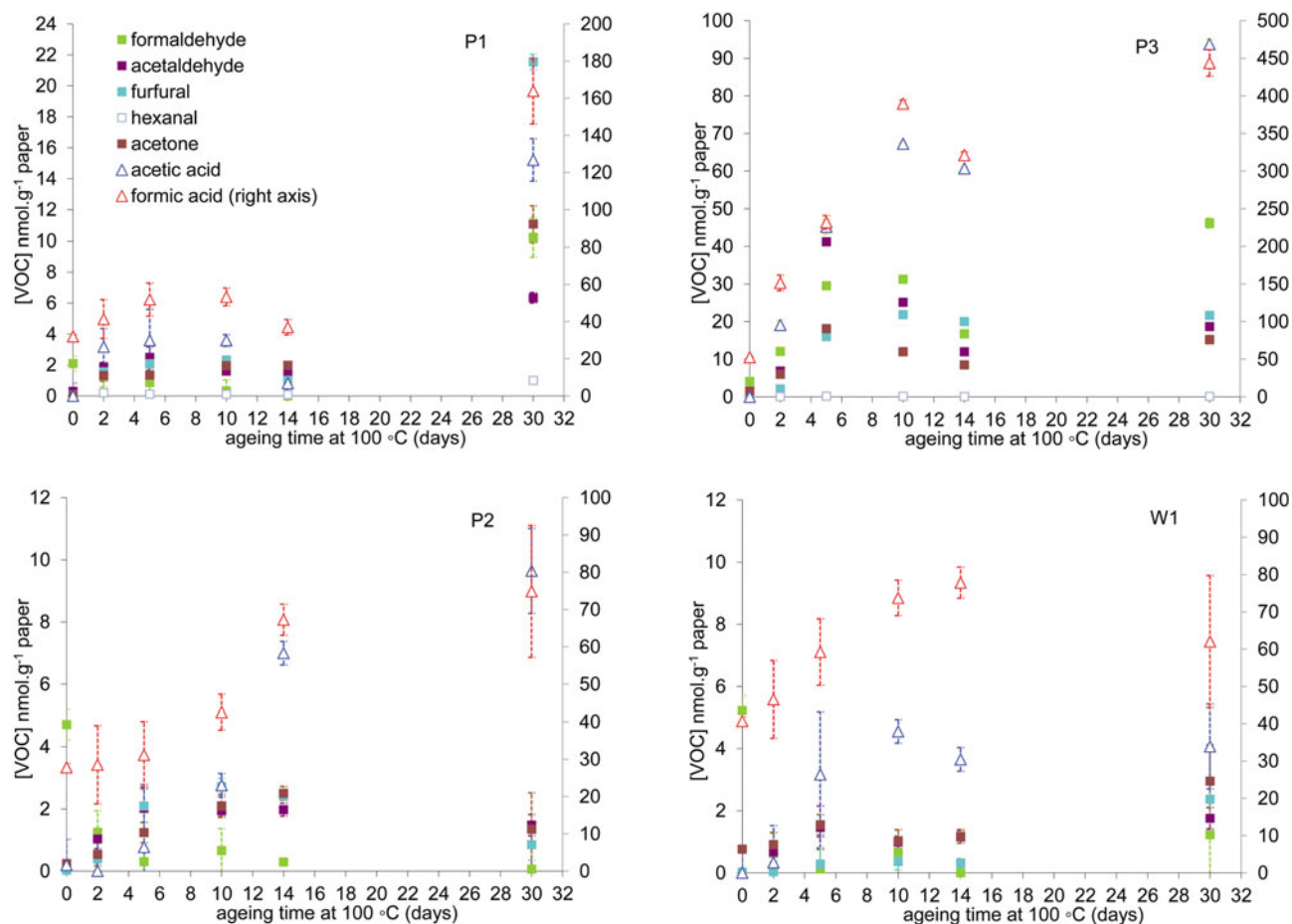


Figure 7: Quantitation of carbonyl and carboxyl compounds emitted (aged model papers P1, P2, P3 and W1) as a function of ageing time in closed tubes at 100 °C (nmol/g of paper). Standard deviations are indicated by the error bars. SPME extractions were performed at 23 °C and 50% RH.

For all papers the most abundant VOC emitted was by far formic acid. It was emitted in appreciable amount both by the unaged samples, in the range of 28 (P2) to 52 nmol/g of paper (P3), and by all the aged samples (after 14 days P1 produced 37, W1 produced 67, P2 produced 77 and P3 produced 321 nmol/g of paper). Unlike acetic acid, formic acid in volatile form has not been preferentially looked at as a VOC emitted from paper documents. This is partly due to analytical limitations as being the lowest MM organic acid, it is not easily detected. The advantage of the method proposed is that the derivatization with PDAM increases the compound MM, which then becomes more easily detectable using GC/MS instrumentation. Formic acid has been designated as a major degradation compound of paper and was found in aqueous extracts of aged papers in micromolar amounts per gram using capillary electrophoresis<sup>10,61</sup>.

Way behind formic acid, acetic acid was the second most abundant VOC, and as formic acid it was also more abundant in the woodpulp papers P1 and P3 (and much more so in the latter). Interestingly, formic acid has been recently shown to be significantly more aggressive towards cellulose than acetic acid, with a much larger depolymerisation effect, while the aldehydes showed no adverse effect<sup>62</sup>. Although several studies indicate that acetic acid is more abundant than formic acid in paper-based documents repositories<sup>63,64</sup>, the present study shows that the emissions from the paper itself largely favour the release of formic acid over acetic acid and over most VOCs. A possible explanation is that formic acid may have a

higher diffusion coefficient than acetic acid and the other carbonyl compounds. This should result in higher amounts of formic acid collected on the fiber compared to the other compounds despite lower concentration in the gas phase. However, Gibson and co-workers found slightly higher experimental diffusion coefficient for acetic acid than formic acid when sampling on Palmes diffusion tubes (0.13 and 0.12 cm<sup>2</sup>/s)<sup>65</sup>, which was also confirmed by the work of Hodgkins<sup>66</sup> and Stranger and co-workers<sup>67</sup>. On the other hand, acetic acid, and in a lesser way formic acid, were shown to efficiently deposit on glass surfaces<sup>68</sup>. The high surface to volume ratio of the glass tube may favour a stronger deposition of acetic acid to the inner glass walls and result in a lower gas-phase concentration. Added to the fact that emission rates were expressed in nmol/g and not in ng and thus independently of MM, these assumptions could explain slightly higher amounts of formic acid than acetic acid but not the large differences observed in this study. Another assumption to explain the higher formic acid concentration is an increase of the oxidation in aqueous phase of formaldehyde<sup>69</sup>, glyoxal<sup>70</sup>, methylglyoxal<sup>71</sup> and glycolaldehyde<sup>72</sup> to form formic acid during the ageing of paper. Formaldehyde and dimethyl glyoxal were indeed observed, but not glyoxal, methylglyoxal and glycolaldehyde. Moreover, the ageing conditions are different than those used in these studies which focused on atmospheric chemistry. Thus, there is no evidence that such oxidation occurred during the ageing of paper. On the other hand, formic acid may react with hydroxyl radicals and ozone<sup>73</sup> in real environments which may explain the lower formic acid concentrations found in the repositories. The diffusion coefficient of carbonyl compounds decreases more or less with MM, e.g. the uptake rate of formaldehyde and hexaldehyde in radial diffusive tubes was found to be 99 mL/min and 18 mL/min<sup>74,75</sup>, respectively. The amount of carbonyl compounds collected on the SPME fiber may more likely reflect the difference in diffusion coefficient rather than the difference in gas-phase concentration.

### 3.3 SPME direct contact sampling of naturally aged papers and diffusive air sampling

Carbonyls and carboxyls detected with the loaded fibers inserted in the core of the books kept closed were the same as those detected in the artificially aged papers albeit in amounts sometimes approaching LOD values. The results are presented in Figure 8a. The VOCs emissions were consistent with those of the artificially aged papers. Formic acid was found clearly the most abundantly produced VOC by all the books tested, between 13 and 16 nmol. The production of formaldehyde, acetic acid, and acetaldehyde was three times to an order of magnitude lower. The VOCs detected in lowest amount were furfural, acetone and hexaldehyde. As with headspace sampling, the most abundant VOCs were the lowest MM compounds. The previous assumptions made for the headspace sampling could also explain this observation. Contact SPME combines both diffusion between the fiber and gas-phase from the pores of the paper and between the fiber and the solid phase paper material. Standard SPME sampling enhances collection of high-MM VOCs due to competition effect on the available sites of the fiber with long duration time<sup>16</sup>. However, due to derivatizing reagents adsorbed on SPME, low-MM carbonyl and carboxyl compounds are bound to the high-MM reagents and remain on the fiber. According to the previous assumptions, the observed results suggest that pore/fiber diffusion is the predominant mechanism. Therefore, the same VOC profiles were observed for headspace SPME and contact SPME.

Furfural and acetic acid have been previously proposed to be of particular diagnostic value for the assessment of cellulose degradation from papers under conditions of natural or accelerated degradation<sup>18,57</sup>.

The VOCs identified upon sampling the atmosphere of the rooms were consistent with those of the papers, being mostly the same ones (Fig 8b) as well as a few additional ones (not presented): straight chain saturated aldehydes (C1 to C10), nonanal being predominant among them (0.49 ± 0.04 nmol). Nonanal is known as an oxidation product from the heterogeneous reaction of various materials (wood, paper, paint, PVC, etc.)

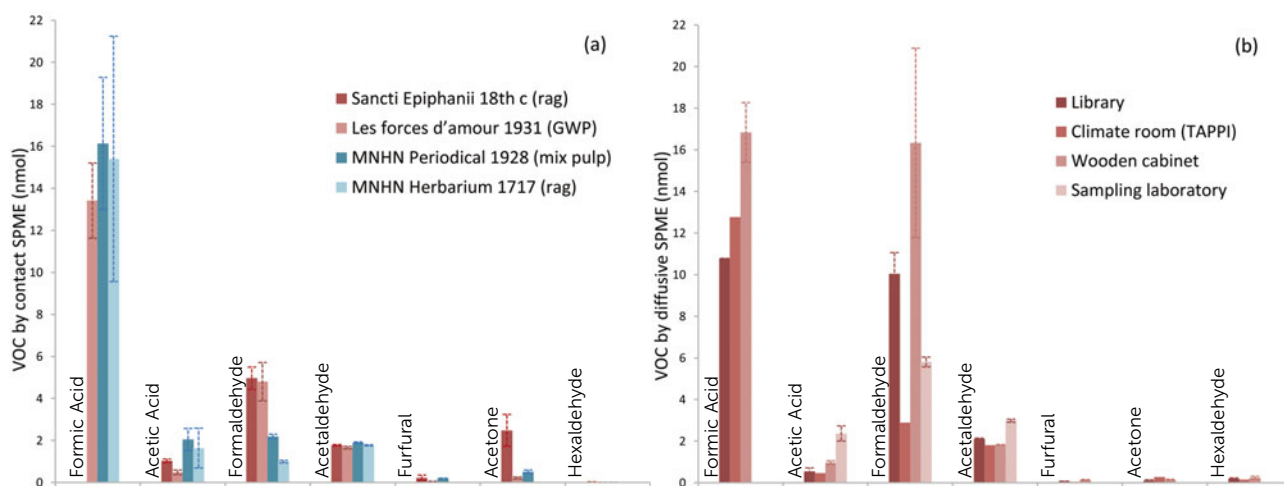


Fig 8: (a) VOCs samples inside the closed books sampled by contact SPME. Each book was sampled three times in three locations inside the core of the book. (b) VOCs present in the air of the rooms at CRCC sampled by diffusive SPME. Standard deviations are indicated by the error bars. Books sampling was performed at 27 °C and 40% RH. Air sampling was performed at 23 °C and a 50% RH (climate room, wooden cabinet and sampling laboratory) and in unmonitored conditions (library).

with ozone<sup>76</sup>. The amounts of VOCs in the air of the rooms were roughly consistent with those of the books, qualitatively, with formic acid being predominant (10.8-12.8 nmol), except in the CRCC sampling laboratory where it was below LOD. Formaldehyde was found in higher amount than in the books, especially inside the wooden cabinet (16.3 nmol). Formaldehyde is ubiquitous of almost every indoor atmosphere because of its numerous sources. It is reported as the most abundant aldehyde VOC in specific indoor environments<sup>37</sup> such as in libraries, where concentrations up to 106 µg/m<sup>3</sup> have been measured<sup>63</sup>. Regarding acidic VOCs in libraries and archives, previous work focused mostly on acetic acid which has been found in the concentration range 10 to 200 µg/m<sup>3</sup><sup>49,57,63</sup>. As the air/fiber diffusion coefficient for the different VOCs was not available the concentration of VOCs in the air could not be calculated from the amount collected by diffusion on the fiber. Therefore, these qualitative results could not be compared to other studies such as the one based on passive direct sampling during fourteen days with the same SPME polymeric phases which found high concentration of furfural in locations filled with paper-based collections<sup>57</sup>.

#### 4 Conclusion

This research was dedicated to exploring SPME on-fiber derivatization for the non-destructive analysis of low molar mass carboxyl and carbonyl volatile compounds formed upon natural and artificial ageing in papers, and to relating the emissions with their state of degradation. The benefit of assessing VOCs emissions using totally non-destructive tools suitable to cultural heritage documents is undeniable. Most often non-destructive or non-invasive approaches in this field are only qualitative. We showed here that by using SPME, a relative quantitation dimension can be added to the measurement, which is a key aspect when degradation state appraisals need to be made. Compared to other analytical techniques, SPME differs by providing results expressed in terms of amount of VOCs rather than concentrations. However, this study showed that they were related to the degradation state of paper and books. This global approach allowed to target the molecular specificity of key functional groups and thus contributed to a better knowledge of the evolution of the emission of the main degradation compounds by aged papers. The results obtained on the four model papers yielded new and exploitable results which were consistent with those obtained, by direct contact sampling of the VOCs emitted from four historic naturally aged books. The analyses of the VOCs discussed in the light of the paper's pulp composition and their degradation state related to the artificial ageing pointed out that for a given experimental condition (i) a close relation was found between the amount of VOCs emitted as a function of ageing time and the composition of the paper and, (ii) the general trend for both acids and aldehydes was an increase in the emissions with ageing time or, in some cases, a plateau reached between 14 and 30 days. Globally the emissions of aldehydes by the papers were much lower than those of the acids and, in all cases, the most abundant VOC emitted was by far formic acid, even in the unaged samples. This is noteworthy as formic acid has been recently designated as highly aggressive towards cellulose. This result,

which is different than previous studies which propose acetic acid as the major carboxyl VOC in paper-based documents, was discussed in the light of the sampling mechanism on the SPME fiber, the diffusion coefficients differences and the possible various sources of production of formic acid. A similar profile for VOC amounts was found in the air of the rooms and in the books, with formic acid being largely predominant in all the rooms containing wooden cabinets and paper materials. However, formaldehyde was more abundant in the air of the rooms than in the papers where it was found in very low amount. If present data would be worth expanding with a larger sample panel, the results obtained fully validate that SPME on-fiber derivatization is a completely non-destructive, relevant and simple tool for the sampling of paper degradation compounds.

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