Identification of volatile organic compounds emitted by a naturally aged book using solid-phase microextraction/gas chromatography/mass spectrometry

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Abstract

Solid-phase microextraction (SPME) coupled to gas chromatography/mass spectrometry (GC/MS) has been applied to the analysis of volatile organic compounds emitted from a naturally aged groundwood pulp paper originating from an old book in order to access the products produced through the decomposition reactions occurring in paper upon ageing. Two different extraction methods were developed and compared: headspace SPME and contact SPME. The influence of few extraction parameters were tested in order to define the best extraction conditions. An optimised non-destructive contact SPME method was elaborated and allowed the characterisation of more than 50 individual constituents.
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1. Introduction and research aims

Earlier investigations using gas chromatographic-olfactory (GC sniffing technique) [1] and gas chromatographic/spectroscopy (static headspace sampling technique and gas chromatographic/mass spectrometry analysis) [2] have shown that the presence of numerous volatile organic compounds (VOCs) formed upon ageing in closed books have an influence on the complex smell of aged paper. Likewise, a recent approach to evaluate the volatile products yielded by degradation reactions occurring in stacks of paper were led using headspace solid-phase microextraction (HS-SPME) [3]. Moreover, few previous works had applied headspace sampling technique to the cultural heritage field [4–7]. These studies were focussed on materials used in the construction of storage and display cases in the museum field. They showed that wooden construction materials emit volatile compounds that are potentially harmful to art objects conserved within. Indeed, the emission of various amounts of VOCs such as acetic acid from wood and their deteriorating effects on collections have been well studied for a long time [8–10]. Particleboard and other materials such as medium density fibreboard (MDF), an engineered wood, are also known to emit a variety of acids, aldehydes and other lignocellulosic degradation products such as formic acid, acetic acid and formaldehyde. The concentration of these organic vapours were studied using SPME in order to determine the effects of the emissions on art objects [5].

Solid-phase microextraction, a new extraction technique developed in 1989 by Pawliszyn and co-workers [11–18] has gained widespread acceptance in many areas in recent years. Indeed, its use has been extended to the analysis of a wide variety of matrices (gas, liquid and solid) and to a wide range of analytes from volatile to nonvolatile compounds. For example, this technique has been successfully applied for the determination of pharmaceutical substances [19,20], environmental organic pollutants in air [21,22] and water [23,24], VOCs in packaging materials [25] and volatile flavour compounds in food [26] and beverages [27]. Nevertheless, VOCs from paper materials have not been yet much investigated and SPME seemed especially suitable for investigating volatile compounds emitted.

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The aim of the present research was to elaborate and develop an efficient SPME method to trap and identify volatile organic compounds emitted from naturally aged paper samples in order to access the products produced through the decomposition reactions occurring in paper upon ageing. To perform this work, the bulk of the analyses were carried out on a same naturally aged groundwood pulp paper originating from a book printed in 1931.

The trapping and the identification of volatile compounds were carried out by solid-phase microextraction/gas chromatography/mass spectrometry (SPME–GC/MS). Two different extraction methods were developed and compared: headspace SPME (HS-SPME) and contact SPME. The headspace SPME is based on the absorption of the analytes on a fibre coating placed in the sample's headspace volume and on the partition of the target analytes between the sampling matrix and the fibre. Headspace sampling has been widely used to analyse volatile compounds and can be envisioned as a non-destructive technique. In the present study, since the influence of several headspace sampling parameters were tested, it requires to carry out samples of paper and is considered, thus, as a destructive method which can not be always adequate for the analyses of historic books. Nevertheless, it was important, in this first step, to verify that this method was adaptable to our purpose. In a second step, it appeared necessary to elaborate a method adapted to the cultural heritage field. The contact SPME method is totally non-destructive, as opposed to the headspace extraction procedure previously reported. This is essential regarding the necessity of applying this technique on original items where sampling is not possible. It involves to place the fibre between two pages of the book kept closed. The methods used and the data obtained are presented in this paper.

In order to select the optimal extraction conditions and to ensure a good reproducibility, the influence of several SPME variables was studied. Concerning the headspace sampling procedure, two optimisation parameters such as the type of fibre and the extraction temperature were tested and discussed. Once optimised, these parameters were applied to the contact method. Concerning this method, the influence of the extraction time was evaluated and discussed.

This report presents an optimised SPME method used for the direct analysis of naturally aged paper sample. However, as opposed to other studies which focus on few compounds and considering the large amount of compounds detected, it was not possible to quantify them all. Therefore, this study was performed only on qualitative basis.

2. Experimental conditions

2.1. Samples

The sample was a naturally aged groundwood pulp paper from a 72 years old book having an aqueous extract pH of 3.6.

2.2. Standards

The identification of some of the volatile compounds was confirmed by coinjections with individual standards or comparison of their mass spectra with that of standards. Standards used to identify volatile compounds were: octanal, decanal, furfural, 2-ethylhexanoic acid, vanillin and phenol from SAS (Saint-Quentin-Fallavier, France). Benzaldehyde was purchased from VWR international (Fontenay-sous-bois, France). The quality of all standards was pro analysis.

2.3. Sampling procedures

The sampling procedure depended on the type of extraction. Two different sampling procedures, headspace SPME (HS-SPME) and contact SPME, were applied. Regardless of the extraction procedure, VOCs extracted were then identified using gas chromatography/mass spectrometry under the same conditions, as described below.

2.3.1. Headspace SPME analysis

One hundred fifty milligrams of the paper sample cut to pieces were placed into 20 ml headspace sample vial. The open tube (Pyrex glass) and contents were conditioned, in a climatised room, at 23 °C and 50% relative humidity (RH) for a day before closing the vial with Teflon lined polypropylene caps. Twenty-three degree Celsius and 50% RH correspond to standard environmental conditions for paper physical testing and for storage areas in archives and libraries. The SPME fibre was inserted through the cap into the closed vial, a few centimetres above the sample. The vial and the fibre were placed into a heating block (Pierce biotechnology, Brebières, France) set to the desired temperature. Four extraction temperatures (room temperature, i.e. 21, 40, 60 and 80 °C) were tested. After exposure during 1 h, the fibre bearing the concentred analytes was retracted, removed from the sample vial and transferred to the sampling compartment of the analytical instrument.

The extraction of compounds was performed manually with an SPME holder (Supelco, Bellefonte, PA, USA). Several fibres of different polarity and thickness were tested, including 100 µm poly(dimethylsiloxane) (PDMS), 85 µm polyacrylate (PA), 75 µm carboxen/PDMS (CAR/PDMS) and 50/30 µm divinylbenzene-CAR/PDMS (DVB–CAR/PDMS). All these were purchased from Supelco (Bellefonte, PA, USA). According to the supplier's instructions, fibres were pre-conditioned in the GC injection port at 220, 250, 230 and 220 °C, respectively.

Comparison of the performances of four SPME coatings was carried out under the same extraction time and temperature conditions: 1 h and 80 °C.

Immediately after extractions, analytes were manually injected by insertion of the fibre into the injector port of the chromatograph. Optimal desorption time and temperature were found to be 10 min and 230 °C. This time was

enough to ensure total desorption and no memory effects were observed, which was confirmed by desorbing the same fibre a second time after the initial desorption. The VOCs were then thermally desorbed and transferred onto the chromatographic column where they were separated. Finally, the VOCs were carried to the mass spectrometer for their identification.

In order to verify the SPME–GC/MS signal reproducibility, three replicates runs of each analysis were performed.

2.3.2. Contact SPME analysis

The contact SPME fibre DVB–CAR/PDMS was placed between two pages of the book kept closed in a controlled environment room (23 °C, 50% RH). The fibre was in direct contact with the sample paper. Different extraction periods (1 h, 1, 15 and 30 days) were tested. Immediately after the extraction, organic volatiles were thermally desorbed onto the GC column (10 min, 230 °C) and characterised with mass spectrometry.

In order to verify the SPME–GC/MS signal reproducibility, three replicates runs of each analysis were performed.

2.4. Instrumentation and chromatographic conditions

The volatile compounds were identified by gas chromatography/mass spectrometry (GC/MS) analysis with an HP 6890 GC (Hewlett-Packard, Evry, France) coupled with a Finnigan Automass model mass spectrometer (Quad service, Poissy, France). The chromatographic peaks were identified either by direct analysis of the mass spectrum or/and comparison with a reference mass spectral library (US National Institute of Standards and Technology, NIST).

The chromatograph was equipped with a CP-Sil 8CB (95% dimethylpolysiloxane–5% phenyl) fused-silica capillary column, 60 m × 0.25 mm internal diameter and 0.25 μm film thickness (Chrompack, Les Ulis, France). The chromatographic elution was temperature programmed as follows: isothermal at 35 °C for 10 min, then from 35 to 250 °C at a rate of 5 °C/min, and isothermal hold at 250 °C for 30 min. The carrier gas was helium with a constant flow of 1 ml/min. The split/splitless injector was used in splitless mode and its temperature was maintained at 230 °C. The interface temperature was set at 260 °C. Mass spectra were acquired under electron ionisation mode (EI) at 70 eV and recorded from *m/z* 33 to 700 at one cycle/s.

3. Results and discussion

Generally and for both sampling procedures, considering numerous and variety of compounds trapped and since the study was limited to providing qualitative data, it appeared unnecessary to try to establish a concentration equilibrium between the sample matrix and the extraction phase. Indeed, the time required to reach the equilibrium depends on the volatility of each compound. Thus, in this work, analyses were carried out in a non-equilibrium situation as explained hereafter.

3.1. Headspace SPME

The effects of the main parameters which can affect the HS-SPME process such as SPME coating and extraction temperature were evaluated in order to find out the optimum extraction conditions.

3.1.1. Influence of the SPME coating

The influence of the type of SPME fibre on the extraction efficiency was evaluated first. Four different SPME coatings with different polarity and thickness were selected among the 27 variations of fibre coatings and sizes currently available. The first commercially available SPME fibres were coated with poly(dimethylsiloxane) (PDMS) of different thickness and polyacrylate (PA). At present, coatings with higher specificity that contain polymers such as carbowax (CWX), divinylbenzene (DVB) and carboxen (CAR) have been developed. Among fibres currently used, we decided to compare four fibres having very different properties. The following fibres were tested for trapping VOCs and compared in order to develop an optimised SPME method: 100 μm PDMS, a non-polar fibre for relatively apolar volatiles, 85 μm PA for polar semivolatiles, 75 μm CAR/PDMS a bipolar fibre for gases and low molecular weight compounds, and 50/30 μm DVB–CAR/PDMS, a dual fibre coating of divinylbenzene and carboxen suspended in poly(dimethylsiloxane) for volatile and semivolatile compounds.

Fig. 1 shows the distributions of the compounds of the headspace SPME extract from the selected paper with the four different SPME fibres. It illustrates the influence of different SPME coatings on the VOCs extracted. Extractions were performed at 80 °C because this temperature provided the largest amount of analytes extracted, as discussed further in Section 3.1.2. Extraction time was set to 1 h. Although 1 h is a non-equilibrium situation, this time was chosen as a good compromise among the several extraction times tested because it is long enough to trap and identify a large amount of VOCs and it does not affect the reproducibility of the whole procedure without lengthening the experimental procedure.

Individual components were characterised by GC/MS and arranged according to eight classes of organic compounds likely to be degradation markers as follows: carboxylic acids, aldehydes, alcohols, benzenic derivatives, alkylbenzenes, esters, aliphatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) (see Fig. 1). The relative abundance of each compound is given in percentage of total compounds and peak assignments is provided in Table 1.

The PDMS fibre shows a particular affinity with hydrocarbons and PAHs and thus no particular interest in our study.

The PA fibre traps acids, aldehydes, benzenic derivatives, isopropylic esters, hydrocarbons and PAHs. The interest of
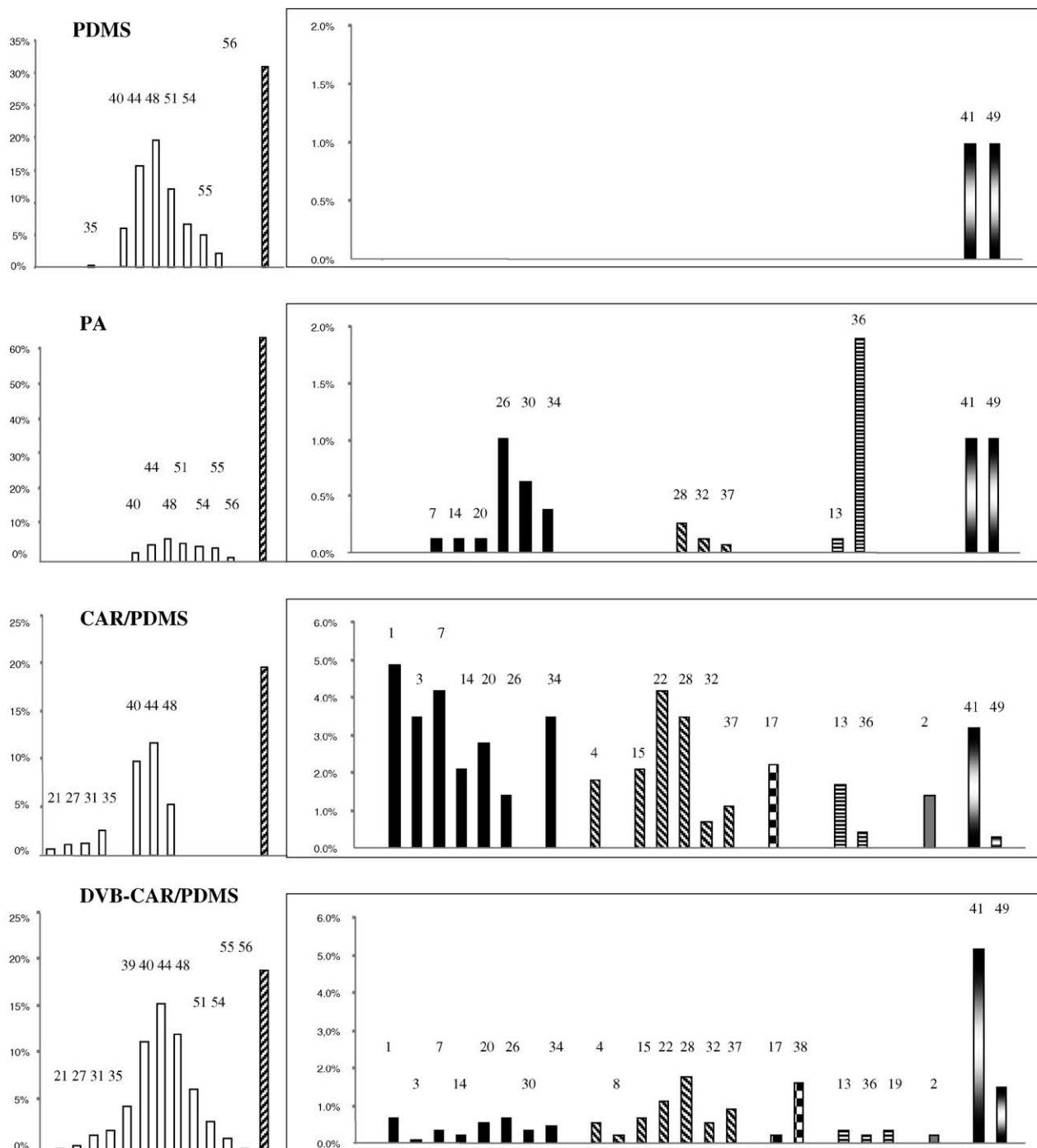
Fig. 1. Comparison of the performance of four SPME coatings. Distributions of the compounds of the headspace SPME extract from the selected naturally aged paper (extraction temperature: 80 °C, extraction time: 1 h). Individual components were characterised by GC/MS (for HS-SPME and GC/MS conditions, see Section 2) and ordered in eight classes of organic compounds. The relative abundance of each compound is given in percentage of total compounds. Peak assignments are in Table 1.

Table 1
Constituent compounds of SPME extracts from the naturally aged paper (both headspace and contact sampling procedures) and of the laboratory environment

Peak number	Structural identification
1	Acetic acid
2	Toluene
3	Butanoic acid
4	Furfural
5	Benzene, ethyl-
6	Xylene
7	Pentanoic acid
8	Heptanal
9	Cyclohexane, propyl-
10	Benzaldehyde
11	Benzene, trimethyl-
12	Furfural, 5-methyl-
13	Phenol
14	Hexanoic acid
15	Octanal
16	Decane
17	1-Hexanol, 2-ethyl-
18	Cyclohexane, butyl-
19	Acetophenone
20	Heptanoic acid
21	Undecane
22	Nonanal
23	Hexanoic acid, 2-ethyl-
24	Cyclohexane, pentyl-
25	Decamethylcyclopentasiloxane
26	Octanoic acid
27	Dodecane
28	Decanal
29	Cyclohexane, hexyl-
30	Nonanoic acid
31	Tridecane
32	Undecanal
33	Cyclohexane, heptyl-
34	Decanoic acid
35	Tetradecane
36	Vanillin
37	Dodecanal
38	1-Dodecanol
39	Pentadecane
40	Hexadecane
41	Dodecanoic acid, 1-methylethyl ester
42	Naphthalene derivative
43	Naphthalene derivative
44	Heptadecane
45	Naphthalene derivative
46	Naphthalene derivative
47	Naphthalene derivative
48	Octadecane
49	Tetradecanoic acid, 1-methylethyl ester
50	Phthalic acid, dibutyl ester
51	Nonadecane
52	Phenanthrene derivative
53	Phenanthrene derivative
54	Eicosane
55	Heneicosane
56	Docosane
57	Siloxane derivative

Individual components were characterised by GC/MS (GC/MS conditions, see Section 2).

this fibre is its relative strong affinity with vanillin (compound no. 36). Indeed, this compound has been reported in the literature [28] as a degradation product of lignin and, as such, can be considered as a degradation marker of paper. The CAR/PDMS fibre provided a large range of components in each class of compounds selected and significantly enhanced the extraction of low molecular weight analytes compared to the others. Its main interest is its good affinity for acids, aldehydes and more especially furfural (compound no. 4). Concerning aldehydes and acids, their relative abundances are two to five times larger compared to those obtained with the other fibres. Therefore, CAR/PDMS-coated fibre should allow to follow the formation of these degradation products. This is important to better understand their formation and their role in the ageing process of cellulose-based papers. Indeed, it is well known that significant concentrations of several carbonyls and especially low mass organic acids are generated by oxidative and hydrolytic reactions in the natural ageing of all cellulose-based papers under ambient storage conditions [29]. Concerning furfural, it is well established that it results from the acid hydrolysis combined with a dehydration reaction of cellulose [30,31] and was found also in naturally aged paper at room temperature [2] and, could be a potential good ageing marker of paper. Moreover, as reported [28], furfural is also a characteristic product emanating from oxidised cellulose. This fibre seems thus interesting to identify polar compounds. In order to improve GC separation, MS identification and limits of detection of carbonyl compounds, various derivatisation techniques recently developed could be implemented in combination with SPME [32–34]. Generally, these derivatisation methods aim at preparing less polar, relatively volatile, e.g. higher molecular weight derivatives and thermally stable derivatives of polar analytes.

The DVB–CAR/PDMS fibre yields numerous headspace constituents and a few lignocellulosic degradation markers, such as furfural and vanillin in lower abundance compared to the CAR/PDMS coating. Moreover, polar compound classes (e.g. alcohols, aldehydes and acids) were distinctly less represented in this SPME extract than apolar constituents (e.g. hydrocarbons and terpenes). Nevertheless, this fibre provided the largest qualitative distribution of compounds in each class selected and thus it appeared to us that the possibility of trapping and of identifying compounds likely to be degradation markers was larger. Since our study was perform only on qualitative basis this fibre was thus chosen as the most suitable to pursue this study.

3.1.2. Influence of the extraction temperature

The effect of the temperature on the extraction efficiency was also investigated. This is one of the most important variables in the HS-SPME process. On the one hand, the temperature affects the distribution constants of the fibre-gas and sample-gas equilibria. Indeed, the Henry's constant increases with the increased temperature. An increase in the temperature results in an increase in the concentration of
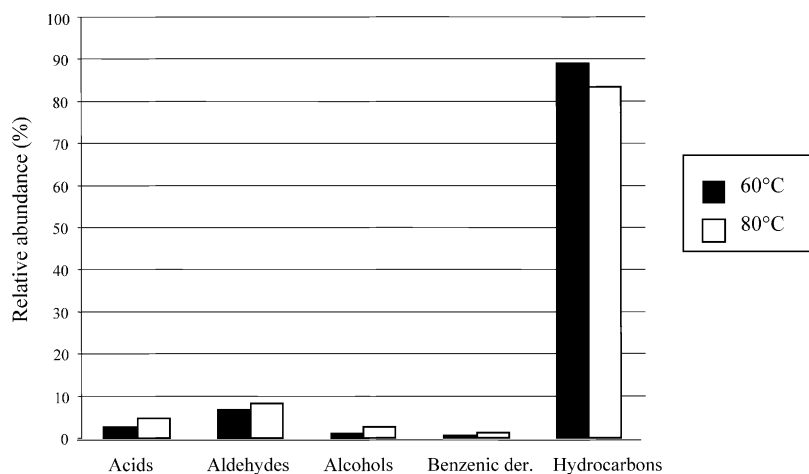
Fig. 2. Influence of the extraction temperatures, 60 and 80 °C (extraction time: 1 h), on the HS-SPME of VOCs from the selected naturally aged paper. Individual components were identified by GC/MS (for HS-SPME and GC/MS conditions, see Section 2) and ordered by class of organic compounds. The relative abundance of each class is given in percentage of total compounds considered.

VOCs in the gas phase. Therefore, it determines the amounts of analytes extracted. On the other hand, the temperature affects the kinetics of the process since the diffusion rates of headspace constituents in the polymer matrix and the fibre coating increase with the increase in temperature.

The effect of four temperatures, 21, 40, 60 and 80 °C, on peak areas were measured for the same 1 h exposure time. As has been previously described, 1 h extraction is a non-equilibrium situation. Therefore, the increase of temperature may have a noticeable effect on the sensitivity since extrac-

tion kinetics is temperature dependent. VOCs extracted from the selected naturally aged paper were identified by GC/MS and arranged according to the main classes of organic compounds likely to contain degradation markers: acids, aldehydes, alcohols, benzenic derivatives and hydrocarbons.

Extractions performed at 21 °C and 40 °C provided components detected as trace. Relative abundance of individual components could not be evaluated. Fig. 2 illustrates the effects of extraction temperatures and shows the relative abundance of the main classes of compounds obtained at
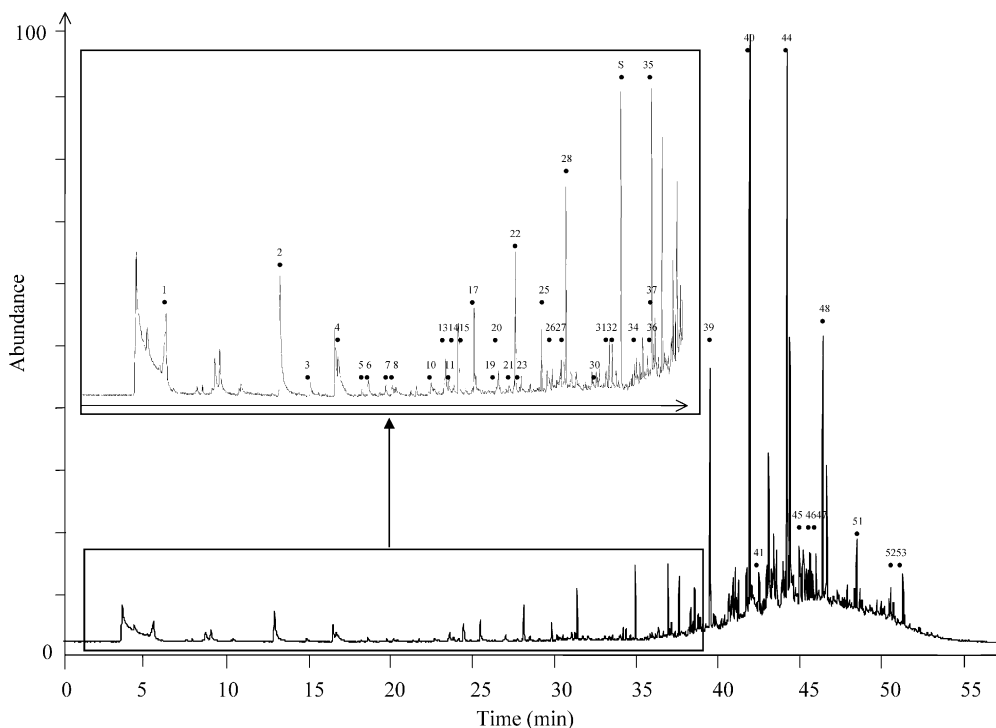

Fig. 3. Gas chromatographic profile and expansion of the headspace SPME extract (extraction temperature: 60 °C, extraction time: 1 h) from the selected naturally aged paper. Individual components were identified by GC/MS (for HS-SPME and GC/MS conditions, see Section 2). Constituent compounds are listed in Table 1.

60 and 80 °C. Except in the case of hydrocarbons, peak areas obtained at 80 °C are only marginally higher than those achieved at 60 °C. Therefore, increasing the extraction temperature from 60 to 80 °C did not lead to a significant improvement of the abundance of VOCs trapped on fibre. The temperature of 60 °C was thus selected for the subsequent experiments since this value is relatively closer to room temperature and prevents potential generation of artefacts.

Fig. 3 presents the gas chromatographic profile and the expansion of the HS-SPME extract from the naturally aged paper obtained at 60 °C. From this HS-SPME extract, 41 components belonging to a wide variety of organic classes have been identified by GC/MS. The constituent compounds identified are listed in Table 1. Several attributions were confirmed by coinjections with standards. As described in the literature, acids, aldehydes, alcohols, benzenic derivatives and hydrocarbons, all derive from lipids degradation, and are formed during the ageing of groundwood pulp paper. The presence of isopropylic esters, however, which to the best of our knowledge have not been reported as paper emanations, is unexplained. They could arise from materials used in the manufacture of papers such as, for instance, glues or resins [1]. Future investigations will try to elucidate their presence. Benzene, toluene, ethylbenzene and xylene isomers and alkylbenzenes (BTEX compounds) are low molecular mass, volatile and non-polar organic compounds which are found in environmental pollution. In order to confirm the origin of these mononuclear aromatics, a DVB–CAR/PDMS fibre was exposed for 1 h, at room temperature, in the laboratory environment. Fig. 4 shows the chromatogram obtained after the exposure and highlights several compounds

with low to high relative abundance which correspond for the majority to hydrocarbons and alkylbenzene-BTEX, with a clear predominance of toluene. Acetic acid was found in the blank chromatogram, but it is not clear where it stems from. In order to control atmospheric pollutants and to subtract the blank chromatogram to the sample chromatogram in the subsequent analyses, this test was regularly repeated. Finally, polycyclic aromatic hydrocarbons such as naphthalene and phenanthrene derivatives are substances present at various concentrations in the atmosphere, soil and water, and commonly considered as organic pollutants. As they have been identified in the extracts, we believe them to be constituents of the groundwood in the paper. This was also proposed in a recent study in which these compounds were also identified [1]. Moreover, as described in the literature, these polyaromatic compounds can also be used to produce whitening agents for paper [26] and are known to be found in the extracts of heat-treated softwoods [35].

The identification of these 41 components allows to highlight well-known olfactive volatile compounds in the aged papers. Low molecular mass carboxylic acids and aldehydes, for instance, impart odour. Indeed, low concentrations of these were reported to cause the off-flavours in low concentrations in paper were identified mainly as carbonyl compounds and as aldehydes while alkanes and alkenes rarely impart odour [36,37]. As described in a previous work which identified numerous compounds in the complex mixture of smell-causing compounds of old books [1], benzaldehyde, ethylbenzene and toluene, 2-ethyl hexanol, and vanillin are responsible for almond-like, sweet, slightly floral and vanilla-like odours, respectively.
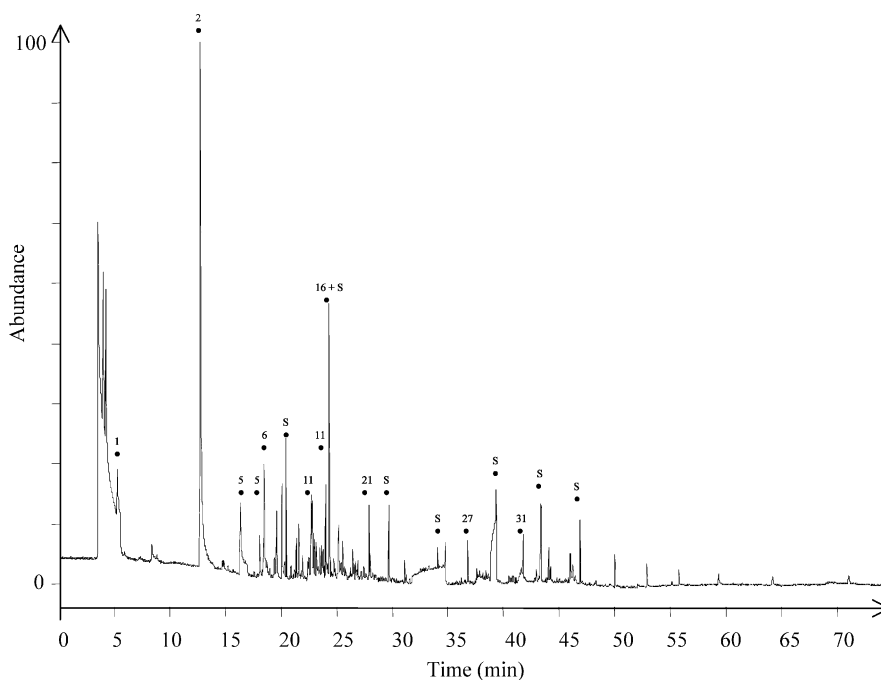

Fig. 4. Gas chromatographic profile of the headspace SPME extract (extraction temperature: 21 °C, extraction time: 1 h) of the laboratory environment. Individual components were characterised by GC/MS (for HS-SPME and GC/MS conditions, see Section 2). Constituent compounds are listed in Table 1.

3.2. Contact SPME

In the first step, we showed that the HS-SPME method allowed the sampling and the identification of numerous VOCs from the selected naturally aged paper. Nevertheless, in a second step, it appeared necessary to define a SPME method adapted to the analyses of historic books and we decided thus to elaborate a non-destructive contact extraction. This method involves to place the fibre between two pages of the book kept closed and, proceeds, thus, at room temperature,
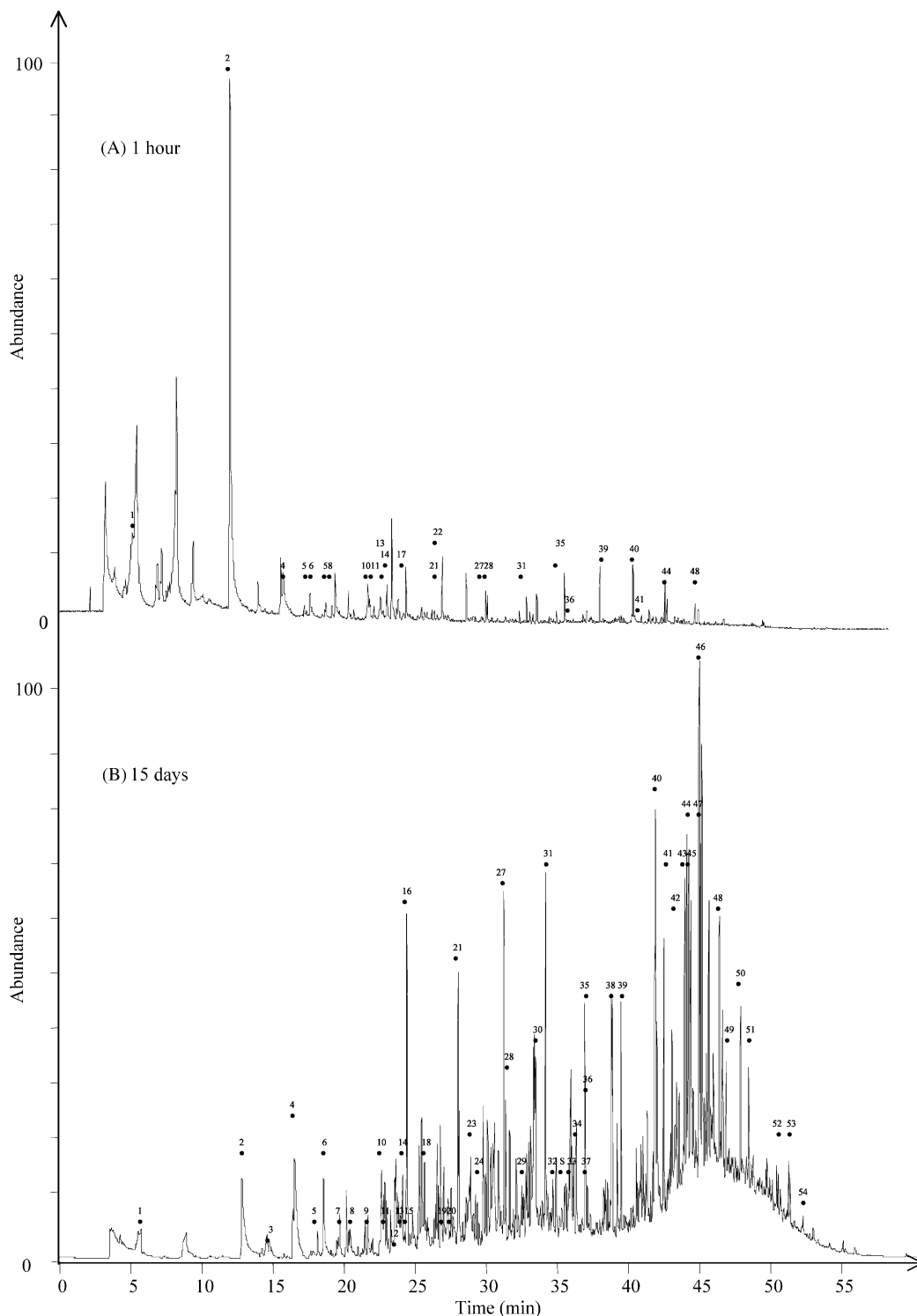

Fig. 5. Gas chromatographic profiles of the contact SPME extracts (extraction temperature: 21 °C, extraction time: (A) 1 h, (B) 15 days) from the selected naturally aged paper. Individual components were characterised by GC/MS (for contact SPME and GC/MS conditions, see Section 2). Constituent compounds are listed in Table 1.

i.e. 21 °C. According to the results exposed in the previous section, only one fibre was tested for contact SPME which is the DVB–CAR/PDMS-coated fibre. The influence of exposure time which corresponds to the most significant parameter in the contact process is studied to optimise this SPME procedure.

3.2.1. Influence of the extraction time

It appeared interesting to evaluate the influence of the exposure time on the extraction efficiency. Extractions were performed during 1 h, 1, 15 and 30 days, at 21 °C. After 1 h and 1 day, the total ionic currents of the contact SPME extracts obtained were very similar. It was thus decided to significantly prolong the extraction time to 15 days. This time extension from 1 h to 15 days was found to increase considerably the abundance of the products extracted. The extraction was far more efficient by applying longer sorption times. Increasing the sampling time from 15 to 30 days led to a similar chromatogram profile. Indeed, the time necessary to establish the equilibrium was likely reached already in 15 days and, exposing the fibre for a longer time did not allow to accumulate a larger number of analytes. The qualitative distribution of individual components in the extract does not change with longer extraction times either and the variation of the signal intensity between 15 and 30 days was very small for most analytes, as the GC/MS analyses showed (chromatograms not presented here). To conclude, 15 days exposure time provided the highest extraction yield and was chosen as a compromise between sensitivity and analysis time.

Fig. 5 presents the gas chromatographic profile of the contact SPME extract from the naturally aged paper obtained after 1 h (Fig. 5A) and 15 days (Fig. 5B). From this 15 days extraction time, 54 components in each class of organic compounds detected in the previous section have been characterised. This result validates the extraction contact method. The constituents compounds identified are listed in Table 1. Fig. 5 shows that if the extraction period is extended from 1 h to 15 days, all peaks, especially hydrocarbons and isopropylic esters, appeared, at longer retention times, with enhanced intensity. Absorption and desorption from the fibre both are much slower processes for less volatile than for highly volatile compounds. With increasing extraction time, semi and low volatile compounds accumulate on the SPME fibre. In the same way, the baseline displaying a broad hump which represents a large number of unresolved peaks corresponding to a series of polycyclic aromatic hydrocarbons. It is also interesting to note that when the extraction proceeds for a prolonged time, BTEX pollutants from the laboratory atmosphere, originally adsorbed on the fibre, are displaced by components given off by the paper. Thus, for instance, the prominent signal due to toluene (compound no. 2) in the Fig. 5A appeared very reduced in the Fig. 5B and therefore can be disregarded in discussing the constituents of the paper extract.

Degradation products of paper previously identified, vanillin and furfural were observed with a low intensity on the 1 h-SPME extract and appeared with higher intensity on the 15 days-extract. Longer exposure time have strongly influenced their extraction efficiency and their characterisation by GC/MS were thereby facilitated. Moreover, the 15 days extraction time chromatogram highlighted an additional main degradation product: furfural, 5-methyl- (compound no. 12). Indeed, as described in previous work [28], this compound results from both cellulose and hemicellulose degradation and can be regarded as an ageing marker of paper. This method appeared extremely interesting in that helping to identify this compound. Its presence can help to
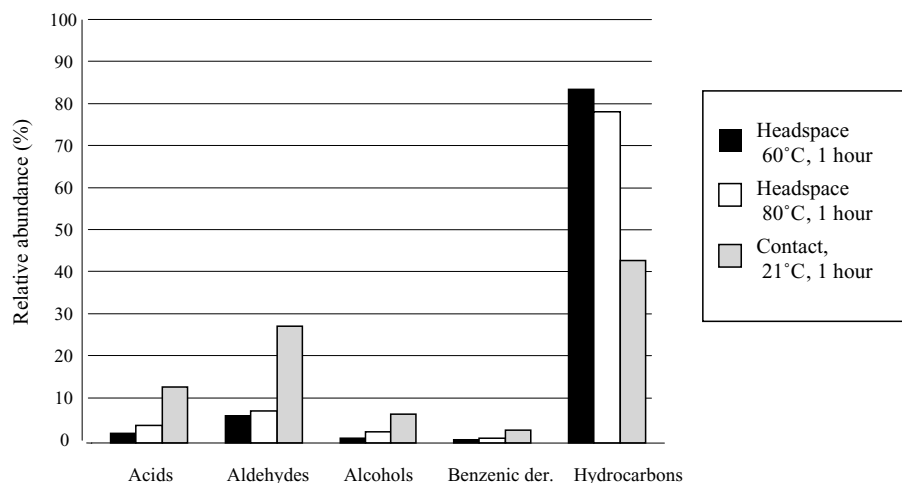

Fig. 6. Influence of the sampling procedures: headspace SPME (extraction temperatures: 60 and 80 °C, extraction time: 1 h) and contact SPME (extraction temperature: 21 °C, extraction time: 1 h) on VOCs extracted from the selected naturally aged paper. Individual components were identified by GC/MS (for HS-SPME, contact-SPME and GC/MS conditions, see Section 2) and ordered by class of organic compounds. The relative abundance of each class is given in percentage of total compounds considered.

understand better the processes of degradation of papers, and to evaluate better the state of degradation of an old paper.

3.3. Influence of the sampling method

The efficiency of contact extraction in comparison with headspace method is compared. Fig. 6 presents the effect of the sampling procedure—headspace SPME or contact SPME—on the extraction efficiency, for a same exposure time. The relative abundance obtained for the main classes of compounds shows that the contact method is more sensitive than the headspace method. Indeed, except for hydrocarbons, peak areas measured with contact SPME at 21 °C are higher than those obtained with HS-SPME at 60 or, 80 °C, the latter being the temperature of optimal extraction yield (see Section 3.1.2). After evaluation of the main factors affecting the analysis, the best condition to extract compounds from the selected old paper was found to be the contact sampling procedure, at 21 °C.

4. Conclusions

The main goal of this research was to elaborate an efficient method to trap and identify VOCs emitted from a naturally aged groundwood pulp paper. Two different extraction methods were developed and compared: headspace SPME and contact SPME. In the first step, we verified that headspace SPME was adapted to our purpose. In the second step, we elaborated the contact method which complies with the requirements of working on art objects. In order to select the optimal extraction conditions, the influence of the fibre coating, the extraction temperature and the time was studied. The non-destructive contact extraction time of 15 days at room temperature with the DVB–CAR/PDMS coating was successfully applied to the analysis of the aged paper selected and could be considered such as the best conditions. Indeed, we identified 56 individual components and contributed, thus, to a better knowledge of VOCs emitted from naturally aged paper sample and of the smell-causing volatile compounds in the aged papers. Moreover, we highlighted three compounds which can be considered as potential good ageing markers of cellulose-based paper. The results obtained are very promising and represent the potential scope of success in future researches concerning the characterisation of the degradation state of historic documents. Indeed, a way to assess the degradation state of aged paper could be based on the determination of compounds such as volatile organic compounds produced through the decomposition reactions occurring in paper upon ageing. This approach could make it possible to meet the undeniable need to develop other chemical methods for evaluating and characterising the conditions of papers or their potential endangerments, especially when working with degraded paper, as is most often the case for historic documents.

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