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ORIGINAL PAPER

Degradation product emission from historic and modern books by headspace SPME/GC–MS: evaluation of lipid oxidation and cellulose hydrolysis

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Abstract Volatile organic compounds emitted from a several decade series of bound periodicals (1859–1939) printed on ground wood paper, as well as historical books dating from the 1500s to early 1800s made from cotton/linen rag, were studied using an improved headspace SPME/GC–MS method. The headspace over the naturally aging books, stored upright in glass chambers, was monitored over a 24-h period, enabling the identification of a wide range of organic compounds emanating from the whole of the book. The detection of particular straight chain aldehydes, as well as characteristic alcohols, alkenes and ketones is correlated with oxidative degradation of the C_{18} fatty acid constituency of paper. The relative importance of hydrolytic and oxidative chemistry involved in paper aging in books published between 1560 and 1939 was examined by comparing the relative abundances of furfural (FUR) a known cellulose hydrolysis product, and straight chain aldehydes (SCA) produced from the oxidation of fatty acids in paper. The relative abundance of furfural is shown to increase across the 379-year publication time span. A comparison of relative SCA peak areas across the series of books examined reveals that SCA emission is more important in the cotton/linen rag books than in the ground wood books.

Keywords Paper · Cotton/linen rag · Fatty acid · Lipid · Aging · Oxidation

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Introduction

The development of sensitive sampling methods which allow the nonintrusive analysis of heritage objects is becoming critically important to these artifacts' conservation and preservation. A significant portion of our cultural heritage involves paper materials. Paper produced between 1850 and 1990 using ground wood and alum additives, which now constitutes the vast majority of circulating library collections, is undergoing fast deterioration. The acid-catalyzed hydrolysis of cellulose, leading to a lower degree of polymerization of the cellulose chain, is generally regarded as the most detrimental degradation pathway to these modern papers [1]. Historic paper produced prior to the advent of paper mills, made from cotton, linen, or hemp, is more permanent and can provide a benchmark by which modern paper is assessed.

Despite considerable progress made in the mechanistic elucidation of paper degradation, considerable gaps remain, including an understanding of the relative importance played by oxidation and hydrolysis in papers of varying composition and age. Although acid-catalyzed hydrolysis of cellulose is well understood to be one of the primary mechanisms detrimental to paper permanence, the role of paper oxidation by oxygen and reactive oxygen and nitrogen species in indoor air pollution has not been as clearly delineated [2]. Compounding the difficulty in assessing the relative importance of various paper degradation mechanisms in paper is the fact that hydrolysis and oxidation of cellulose are not mutually independent pathways, and the presence of noncellulosic constituents, such as lignin, may influence degradation pathway. When paper degrades naturally, the formation of carboxylic acid groups upon cellulose oxidation catalyzes hydrolysis, and acid hydrolysis provides new reducing alcohol groups for

oxidation. The discoloration of lignin-containing papers is mainly attributed to the oxidation of lignin which also increases the carbonyl content of the paper [3].

The degree to which minor components of paper, such as fatty acids, influence paper degradation pathway is poorly understood. Unsaturated fatty acids, including oleic, linolenic and linoleic acids, present in residual resins of wood-based papers as well as cotton/linen papers, undergo facile autoxidation resulting in the formation of monohydroperoxide radicals which further decompose, react with oxygen, or polymerize [4]. Decomposition of lipid hydroperoxides initiates a complicated free-radical process producing a myriad of aldehydes, ketones, carboxylic acids, alcohols and hydrocarbons. This oxidative chemistry likely impacts the overall degradation of cellulose due to the reactive species generated. Isolating this lipid oxidation from the various mechanisms of cellulose degradation is complicated, however, by the result that all yield an increase in carbonyl content of the paper. Nonetheless, the oxidative processes remain central to understanding paper deterioration and also generate volatile products which then become primary indoor pollutants in library atmospheres [2].

As the sensitivity of analytical instrumentation has improved, methodologies characterizing the volatile decomposition products emanating from paper have been widely employed to complement studies focused on the paper substrate itself. This telltale "smell of old books" may hold the keys to the books' original compositions, extent of aging and the array of degradation pathways traversed by the paper. The complex mixture of volatile and semivolatile paper degradation products has been interrogated using GC-sniffing [5], static headspace sampling methods [6] and, more recently, using headspace and direct-contact solid-phase microextraction (SPME) coupled with gas chromatography–mass spectrometry (GC–MS) [7–11]. Headspace SPME/GC–MS was recently demonstrated as a viable technique for the identification of volatile degradation products for well-characterized nineteenth- and twentieth-century papers, and correlating products with properties important for the preservation of historic paper using multivariate data analysis [7]. Contact SPME/GC–MS has previously been used to study papers of known compositions and a limited set of historic books [9, 12].

While headspace SPME/GC–MS has been used to assess the aging of small samples of papers through accelerated and natural aging studies, it has not been widely applied to books in circulating and special collections. These items pose unique challenges to conservators as intrusive sampling is not possible and tedious analyses which remove objects from collections for extended periods of time are not practical. We report here a systematic study using headspace SPME/GC–MS to examine the paper aging products of volumes of bound periodicals published between 1859 and 1939 and five historic books published between 1560 and 1809. Unlike in previous contact SPME/GC–MS studies, the headspace above each volume was monitored by placing the book upright in a closed chamber allowing a "fanning out" of the pages. As demonstrated below, this method allows the detection of a broad range of VOCs emanating from the whole book, including the higher molecular weight aldehydes, alcohols, carboxylic acids, and alkanes. Both the divinylbenzene carboxen/poly (dimethysiloxane) (DVB/CAR/PDMS) and carboxen/poly(dimethylsiloxane) (CAR/PDMS) SPME fiber coatings were employed to capture the widest array of low and high molecular mass compounds. A several decade series of bound periodicals published beginning in 1859 was chosen because periodicals of this genre were likely printed on inexpensive ground wood materials and are apt to show dramatic destabilization of cellulose by acid hydrolysis.

The headspace method allowed a characterization of each book's "VOC signature". Tracer compounds were distinguished to assist in the analysis of aging pathway and the relative importance of acid hydrolysis and oxidation was examined for the books over the few century publication period. The relative amounts of the more abundant aldehydes formed via different paper degradation mechanisms were semi-quantitatively determined and compared allowing an assessment of important degradation mechanisms.

Experimental

Samples

A series of seven bound periodicals covering an 80-year period from 1859 to 1939 was chosen to investigate the effects of aging on ground wood-pulp papers. These periodicals were loaned from Pepperdine University's Payson Library circulating collection. Five rare books composed of cotton/linen rag papers published from 1560 to 1809 (1560, 1589, 1631, 1787, and 1809) and loaned from Payson Library's special collections, a rare books collection housed in a separate temperature and humidity controlled environment, were also analyzed. The fiber content of each book studied was confirmed by microscopic analysis.

The binding compositions for each of the 5 rare books were as follows: 1560, limp vellum; 1589, leather over board; 1631, leather over board; 1787, vellum; and 1809, book cloth binding. The periodicals were bound using book cloth bindings.

Standards

The identities of some of the analytes emitted from the books were confirmed by comparison of their mass spectra to that of standards. Standards (Sigma-Alrich, St. Louis, MO) used included 2-furfural, butanal, pentanal, hexanal, heptanal, octanal, nonanal, decanal, undecanal, acetic acid, propanoic acid, butanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, 2-ethylhexanol, 1-butanol, 1-heptanol, 1-octanol, 1-nonanol, 1-decanol, 1-dodecanol, benzyl alcohol, phenol, methyl isobutyl ketone, camphor, D-limonene, α-pinene, eucalyptol, vanillin, 2-methoxyphenol, 4-methoxyphenol, benzaldehyde, acetaldehyde, toluene, ethylbenzene, *p*-xylene, *m*-xylene, styrene, acetophenone, benzophenone, hexane, heptane, octane, decane, hexatriacontane, 2,3 *cis*-epoxybutane, and epoxyhexadecane.

Sampling procedures

Headspace SPME was used to sample each book. Several books were also sampled using contact SPME for comparative purposes. Volatile organic compounds extracted from the books were then characterized using GC/MS. To minimize potential contamination, extractions were performed in a newly constructed dry laboratory that was not used to store books or house chemicals.

Headspace SPME sampling procedure

Headspace SPME extraction was performed manually on each book with SPME fiber assemblies (Supelco, Bellefonte, PA). Each book was placed in a chamber for non-intrusive sampling. Sampling chambers were either (1) a modified 12 L glass desiccator (Jencons, Bridgeville, PA) or (2) a 19 L cylindrical aluminum chamber (Abbess Instruments, Holliston, MA). The glass desiccator's vacuum port was removed to accommodate a silicon plug-type septum (Suba Seal™ silicon rubber septum, Sigma-Aldrich, St. Louis, MO). The cylindrical aluminum chamber was custom designed with a Teflon Jaco septum fitting (Analytical Specialties, Elburn, IL) in the top lid which allowed SPME fiber access. In both chambers, books were placed upright with the pages fanned out to expose a maximum surface area of paper. After the book was introduced to the chamber, it was thoroughly purged with 99.999% Ar gas (Praxair, Inc., Oxnard, CA). Once purging was complete, the chamber was closed, and the SPME fiber was inserted into the chamber through the septum and exposed to the headspace above the book. All extractions were carried out at 20 °C and 1 atm pressure. The integrity of the empty chamber atmosphere was monitored each week with 24 h blank exposures.

Headspace extraction was performed for 24 h for each book. A few books were also extracted for longer time periods up to 5 days. Extraction time profiles, constructed for several of the aldehydes, revealed that the maximum detector response had not been reached for any of the aldehydes even after several days. An extraction time of 24 h was determined to be sufficient to give reproducible signal for all significant analytes. Relative standard deviations were determined for the analytes furfural, hexanal, heptanal, octanal, nonanal, and decanal (average RSD=21).

Individual extractions were performed on each book using either a 50/30 μm DVB/CAR/PDMS or a 75 μm CAR/PDMS SPME fiber (Supelco, Bellefonte, PA). Fibers were conditioned according to the manufacturer's specifications (1 h at 270 °C and 1 h at 300°, respectively) prior to use. Following the extraction, the fiber was immediately inserted into the inlet injector port of the gas chromatograph where the adsorbed analytes were thermally desorbed and transferred onto the chromatographic column for separation. The fiber remained in the injector inlet for the duration of the GC–MS analysis. Complete desorption of analytes was confirmed by immediately acquiring a fiber "blank" chromatogram after the analysis of each book.

Contact SPME analysis

The SPME fiber was placed in direct contact with the surface of two pages of the book. Extraction occurred over a 24-h time period at ambient laboratory conditions. Once the extraction was complete, the fiber was immediately transferred to the injector inlet of the gas chromatograph and thermally desorbed.

Instrumentation and chromatographic conditions

Constituents collected by the SPME fiber were separated and identified using gas chromatography–mass spectrometry by an HP 5890 Series II+gas chromatograph (Hewlett Packard, Palo Alto, CA) coupled with an HP 5972A mass selective detector (MSD). Separation was achieved using a DB-5MS fused-silica capillary column, 30 m×0.25 mm, 0.25 μm film thickness (Agilent, Santa Clara, CA). The chromatographic elution was temperature programmed as follows: isothermal hold at 35 °C for 10 min, followed by an increase of 10 °C/min up to 230 °C, ending with an isothermal hold at 230 °C for 1 min to remove any residual analyte from the column. The split/splitless injector inlet was used in splitless mode and held at 240 °C, and the helium carrier gas flow rate was constant at 0.8 mL/min. The MSD was tuned according to the highest sensitivity protocol over the mass range of 35–200 m/z. The detector temperature was set to 280 °C.

Identification of the constituents was made by comparison of retention times and mass spectra with the standard compounds or with a reference mass spectral library (National Bureau of Standards, NBS75K).

Results and discussion

Figure 1 compares the range of VOCs detected by SPME/GC–MS from the 1589 book during a 24-h contact study (fiber placed between two pages midway in the book) and a 24-h headspace study (fiber placed above "fanned out" pages of the book in a closed chamber) using a CAR/PDMS fiber. Figure 2 compares chromatograms of the 1589 book using the headspace and contact method over the same exposure time using a DVB/CAR/PDMS fiber. The headspace method allowed identification of a wider range of organic compounds emanating from the books than contact SPME, including the straight chain aldehydes (C_5–C_{12}), alkanes (several up to C_{36}), alcohols (C_4, C_7–C_{13}, and C_{20}), carboxylic acids, and their derivatives (C_2–C_9, C_{12}, and C_{16}), a variety of ketones and esters, and other aliphatic and aromatic hydrocarbons. Table 1 lists the range of compounds routinely identified in 24 h headspace studies of the books, including peaks annotated in the figures, as well as compounds consistently identified in longer headspace exposures (2–5 days).

Literature studies have previously reported contact SPME for natural and artificial aging of paper samples and headspace SPME for the natural and artificial aging of small paper samples, generally placed in vials [7, 8, 10, 12]. Contact SPME has also recently been applied to historic books [9]. This study represents the first to utilize headspace SPME/GC–MS to probe the emissions of whole books which span a publication range of nearly 400 years. The use of headspace SPME/GC–MS for whole book analysis reported here allows a highly representative nonintrusive examination of the entirety of the book, rather than the contact method which probes a limited area of a few pages. The "whole book" headspace method allows the identification of a wide variety of VOCs from a naturally aging book, to enable the mechanistic origin of many classes of VOCs to be proposed.

The profiles of the book emissions were fiber dependent, as also noted in previous studies of book paper [8, 9]. The CAR/PDMS fiber tended to trap the lower molecular weight species more efficiently (eluting in the first 20 min of the chromatogram) whereas the DVB/CAR/PDMS fiber

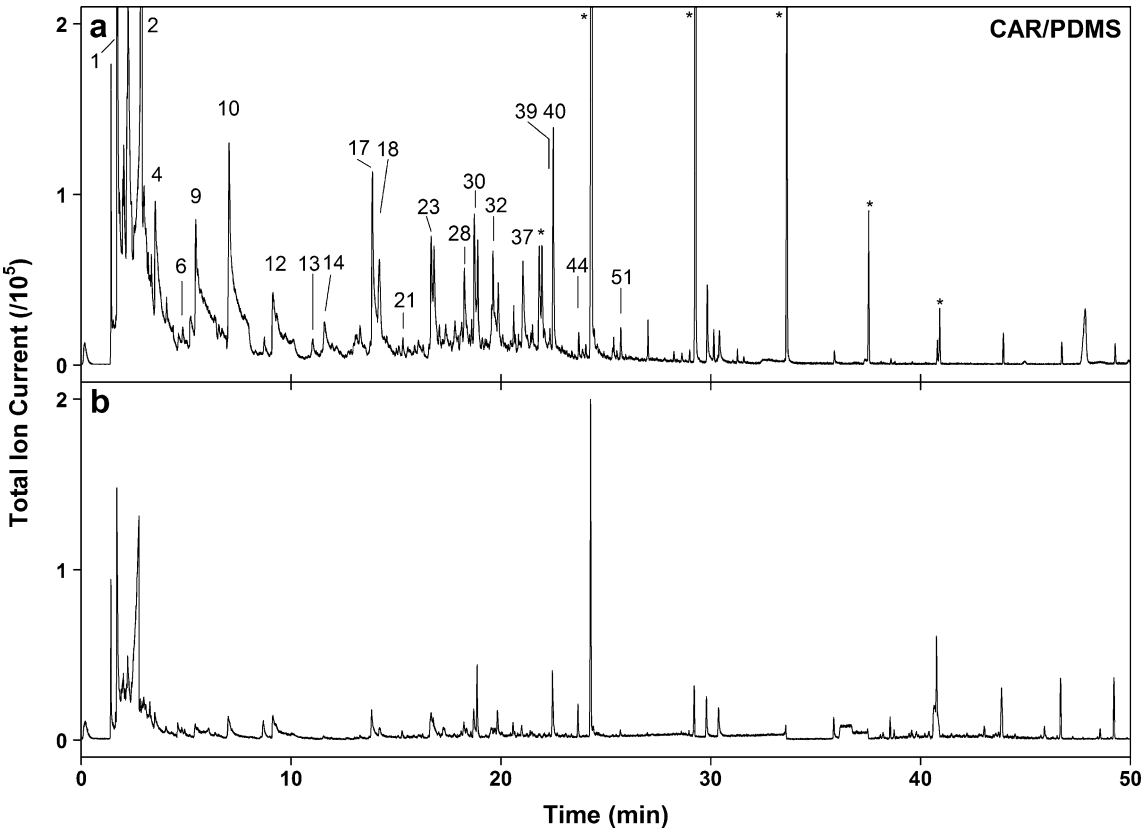

Fig. 1 **a** Gas chromatographic profile of the headspace SPME extract from the 1589 book using the CAR/PDMS fiber. Constituent compounds are listed in Table 1. Peaks marked with *asterisks* are reproducible contaminants due to outgassing septa, seals, and SPME fibers. **b** Gas chromatographic profile of the contact SPME of the 1589 book using the CAR/PDMS fiber

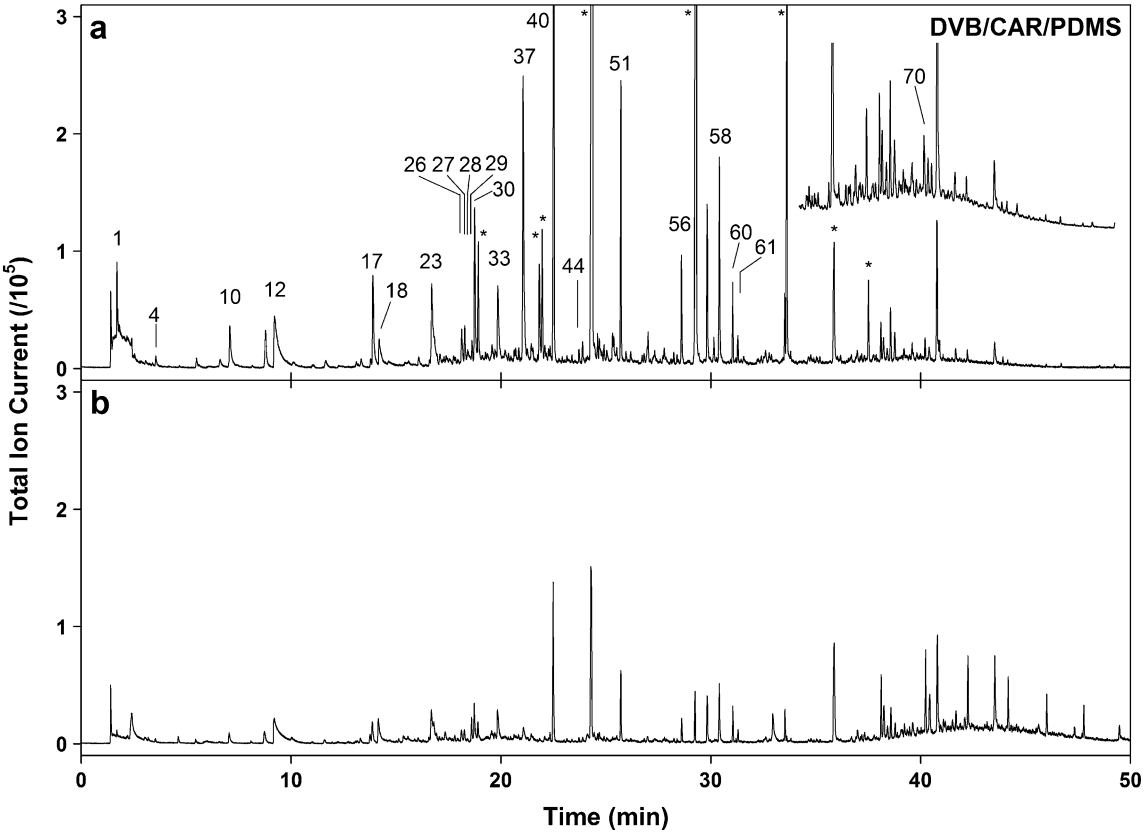

Fig. 2 **a** Gas chromatographic profile of the headspace SPME extract from the 1589 book using the DVB/CAR/PDMS fiber. Constituent compounds are listed in Table 1. **b** Gas chromatographic profile of the contact SPME of the 1589 book using the DVB/CAR/PDMS fiber

extracted more aromatic and higher molecular mass compounds. In the contact studies, the broad hump in the chromatogram near 40 min results from many unresolved peaks corresponding to high mass hydrocarbons and alcohols residing close to the surface of the page. With this group of heavy analytes, which includes alkanes containing over 30 carbon atoms, longer exposure times (72 h) were sometimes necessary using the headspace method to accumulate a sufficient amount of analyte on the fiber for detection (see Fig. 1 inset). The low abundance of these heavier analytes made unequivocal spectral identification difficult, so many were not identified in Table 1. Although the blend of compounds emanating from aging books has commonly been categorized as "VOCs", many of the higher molecular weight compounds observed in this study exhibit room temperature vapor pressures well below 0.100 Torr and normal boiling points over 300 °C.

The headspace SPME method utilized in this study enables compounds emanating from the bulk of the book to be trapped, unlike contact SPME which preconcentrates compounds only within a fraction of the volume of two compressed pages. This provides a more representative examination of the organics emitted during the aging of paper (as well as binding materials) than the contact method. In historic books, the edges of the paper sheets are likely more degraded than the center of the sheets because of their increased exposure to the library atmosphere and other external degrading processes. Studies exploring paper degradation in stacks of sheets have also suggested that interior pages age at an accelerated rate relative to the top most sheets, presumably due to slow diffusion of moisture, acids, and oxidizing volatiles through the stack [13]. In centuries-old books containing hundreds of pages, such as the 1589 book (a Bible) examined in this study, individual pages are likely at varying stages of degradation. Placement of the fiber in direct contact with the page presumably samples best the small area of those pages intimately exposed to the fiber as well as nearby pages. Placing the fiber in the headspace above an upright book with the pages "fanned out" samples a greater surface area of paper and may allow a truer examination of the book's overall conservation state. While headspace studies of entire volumes also necessarily sample binding materials, contact studies have revealed the presence of glues and resins likely originating from the binding as well. Contact studies may also show an increased tendency toward early fiber saturation by the major volatile species, such as acetic acid and formaldehyde, which easily desorb from the book. Finally,

Table 1 Compounds identified in the headspace of the historic and modern books in the study using headspace SPME–GC/MS

Compound	Identification
1	Acetone
2	Acetic acid
3	1-Butanol
4	Pentanal
5	Heptane
6	Propanoic acid
7	Epoxybutane
8	Methyl isobutyl ketone
9	Toluene
10	Hexanal
11	Butanoic acid
12	Furfural
13	Ethylbenzene
14	*p*-Xylene
15	2-Hexenal
16	*m*-Xylene
17	Heptanal
18	2-Butoxyethanol
19	Nonane
20	Butyrolactone
21	α-Pinene
22	Pentanoic acid
23	Benzaldehyde
24	1-Heptanol
25	5-Methylfurfural
26	6-Methyl-5-hepten-2-one
27	2-Octanone
28	Phenol
29	Decane
30	Octanal
31	Hexanoic acid
32	D-Limonene
33	2-Ethyl-1-hexanol
34	Benzyl alcohol
35	2-Hydroxybenzaldehyde
36	2-Octenal
37	Acetophenone
38	1-Octanol
39	Undecane
40	Nonanal
41	2-Nonanone
42	2-Methoxyphenol
43	Heptanoic acid
44	Camphor
45	(E)-2-nonenal
46	Naphthalene
47	2-Decanone
48	1-Nonanol
49	2-Undecanone
50	Octanoic acid
51	Decanal
52	Dodecane
53	(E,E)-2,4-nonadienal
54	1-Decanol
55	(E)-2-decenal
56	Undecanal
57	Nonanoic acid
58	Butyl butanoate
59	Eucalyptol
60	Tetradecane
61	Dodecanal
62	Vanillin
63	6,10-dimethyl-(E)-5,9-undecadiene-2-one
64	1-Dodecanol
65	Phytol
66	Nonadecane
67	Benzophenone
68	Dotriacontane
69	Squalane
70	Hexatriacontane

Peaks are sequentially numbered according to retention time

there are practical aspects discouraging the use of contact SPME in books; the thin polymeric coating of the fibers are easily damaged or stripped from repeated contact, particularly considering the mass of a closed volume on the fragile fiber.

Figure 3 displays chromatograms of the emission profiles from the historic volumes (1560 to 1809) in the study. Figure 4 includes chromatograms of the emissions from some of the ground wood book series (1859 to 1939). Prominent emission products common to both modern and historic books, irrespective of paper composition, were acetic acid, furfural, and the straight chain aldehydes hexanal, heptanal, octanal, nonanal, and decanal. Furfural is an established marker for the acid-catalyzed hydrolysis of both glucose and pentose units of cellulose and hemicellulose [7, 8]. Emission of furfural from papers has been directly correlated with a higher acidity of paper [7]. The acidity of paper, generally measured by the pH of its aqueous extract, arises from the natural degradation of paper and from acids introduced if the paper was alum-sized. The straight chain aldehydes are convenient markers for the autoxidation of fatty acids in paper, as are the longer chain alcohols, carboxylic acids, some esters and hydrocarbons, as further detailed below. Acetic acid, acetaldehyde, and acetone, present in the chromatograms of each

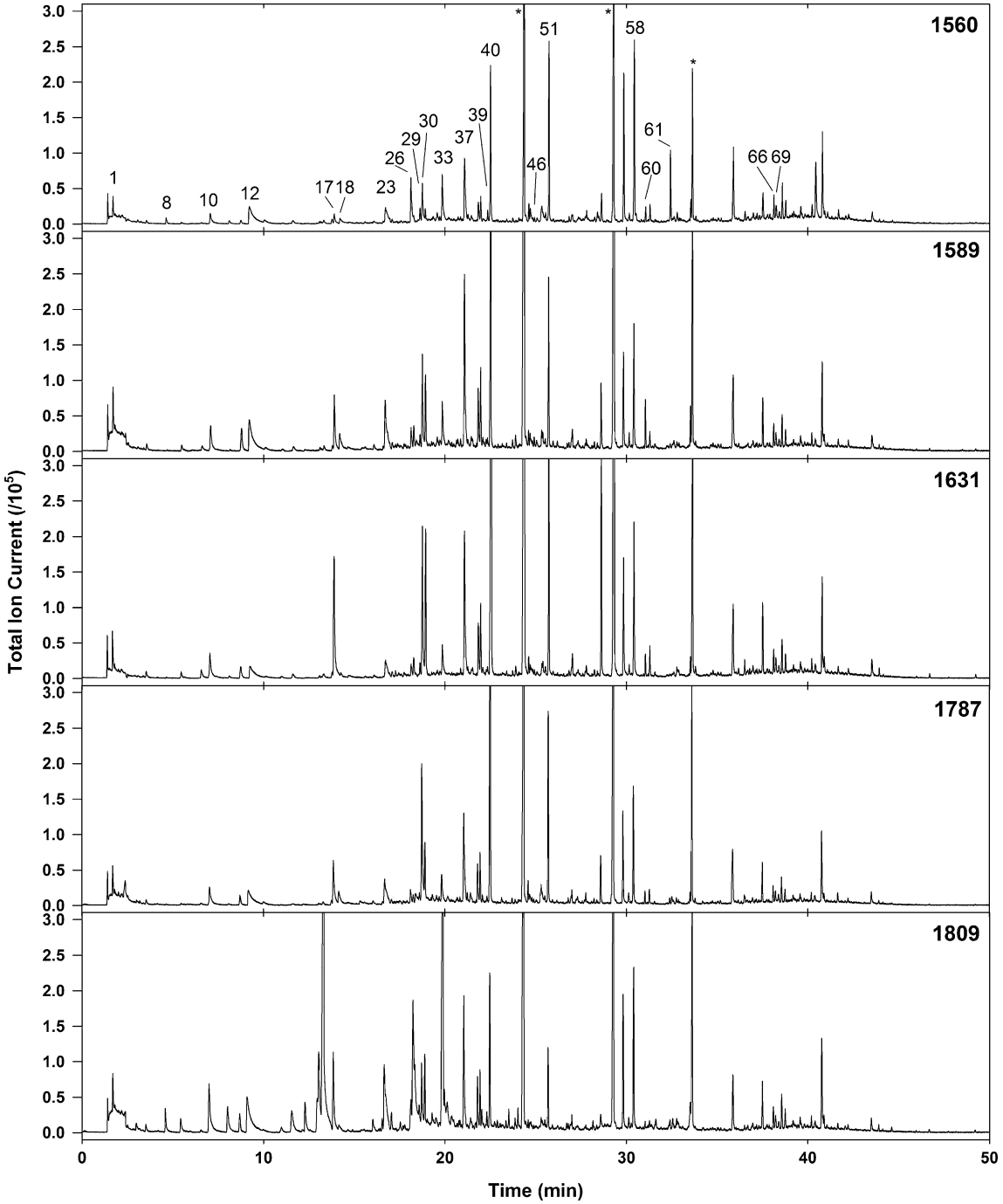

Fig. 3 Gas chromatographic profiles of the cotton/linen rag historic books in the study. Peak annotations are given in Table 1

volume studied, are suspected tracers of cellulose oxidation. Lignin oxidation was suggested by the presence of vanillin, benzyl alcohol, benzaldehyde and substitutions of these compounds.

The homologous series of straight chain aldehydes resulting from fatty acid oxidation serve as convenient tracer compounds to assess the relative importance of oxidation, while furfural emission is evidence of acid-catalyzed hydrolysis. The formation of straight chain aldehydes is an established gauge of oxidative stress in both plant and animal tissue [14].

Integrated peak areas (ion current) of the furfural (FUR) peak and the straight chain aldehyde peaks (area underneath hexanal, heptanal, octanal, nonanal, and decanal, denoted SCA) were measured in the chromatograms for each book. The FUR peak area (ratioed to the

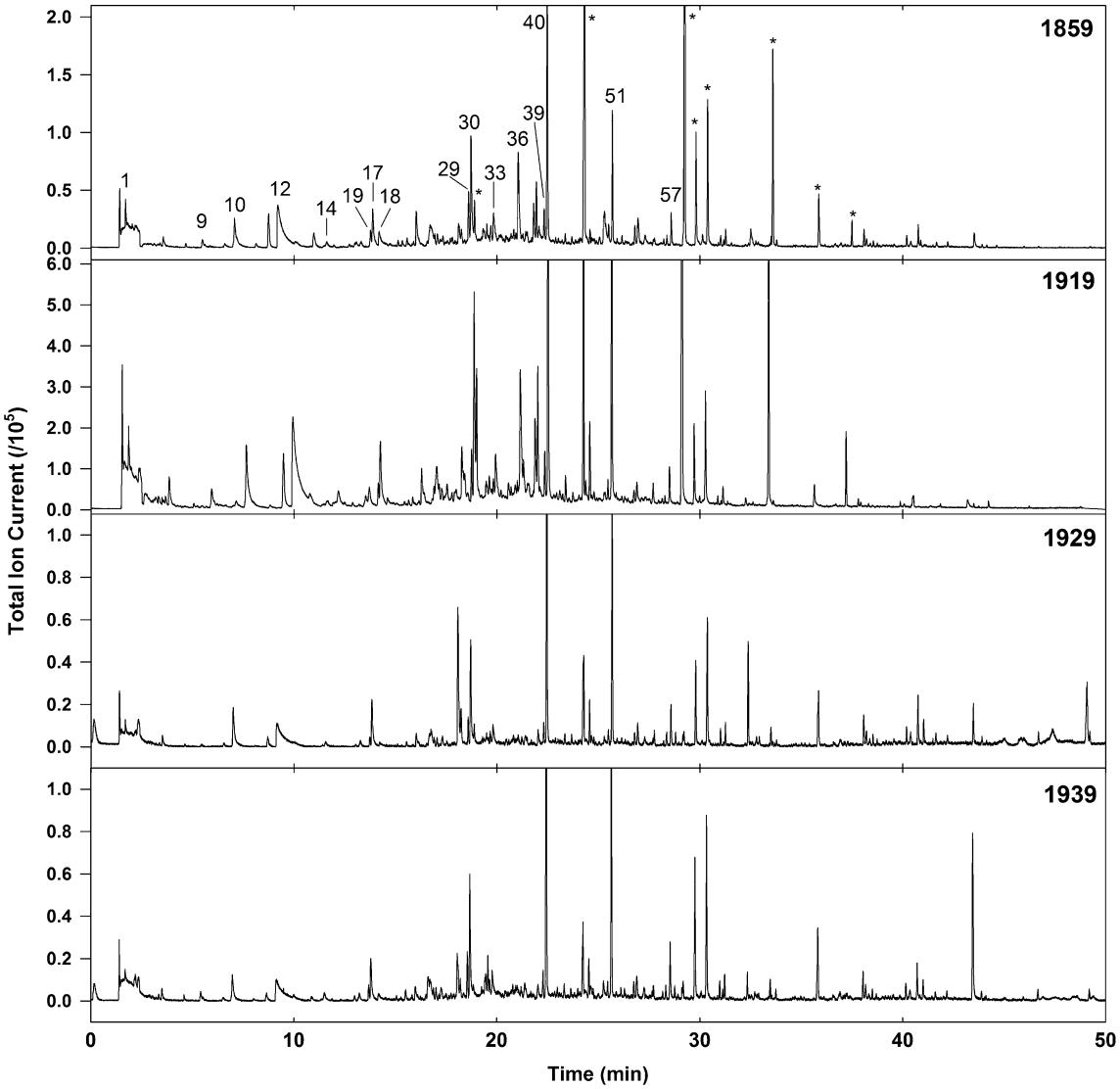

Fig. 4 Gas chromatographic profiles of some of the bound periodical volumes in the study. Peak annotations are given in Table 1

total ion current (TIC) across the chromatographic area) was compared with the SCA total peak area (ratioed to the TIC across the same chromatographic time span). Peaks due to reproducible contaminants outgassing from silicon-based septa to seals were removed from the TIC across the chromatographic area. As shown in Fig. 5, FUR emission is more important in the ground wood volume series (published 1859 and after) than the cotton/linen rag books and increases in importance as publication year increases. The time dependence of FUR production from the acid hydrolysis of five- to six-carbon sugars in cellulose over centuries of degradation is not known, but it likely is an ongoing process that proceeds as long as the sugar moiety is available. Although only 11 volumes were examined in this comparison, these data suggest that acid hydrolysis is of more consequence for books containing ground wood papers.

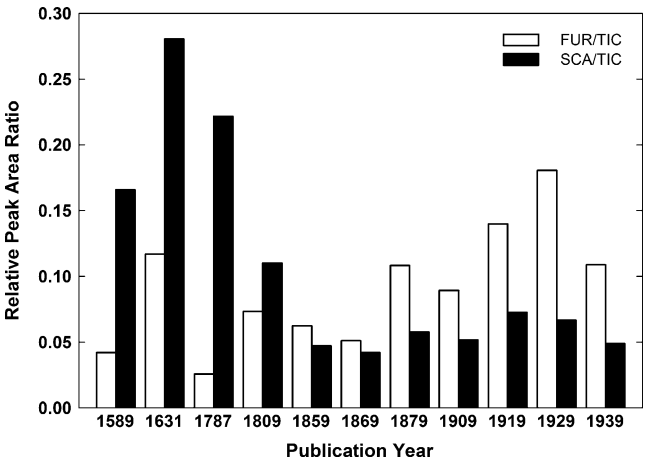

Fig. 5 Comparison of the relative peak areas of the furfural (*FUR*) and straight chain aldehyde (*SCA*) constituents. SCA refers to the sum of peak areas of C_6–C_{10} straight chain aldehydes. Both FUR and SCA peak areas are ratioed to the TIC of the chromatogram

Data provided in Fig. 5 suggest that SCA emission is more significant than FUR for the cotton/linen rag books. These data do not include the volume published in 1560, since its FUR peak could not be resolved. The enhancement in SCA emission relative to ground wood books could imply that oxidative degradation of fatty acids is more important in cotton/linen rag papers which tend to be more alkaline. However, these data do not exclude the possibility that the cotton/linen books studied here simply have greater fatty acid content than the wood-pulp books. The enhanced SCA emission noted in the cotton/linen rag papers, while not the result of cellulose oxidation, could initiate cellulose oxidation through an autoxidative mechanism. The prominence of the SCA peaks in the TIC compared with other VOCs is also likely due to their volatility and hydrophobic tails which may strongly adsorb to the nonpolar DVB/CARB coating.

Although many SCAs and FUR, as well as a wide variety of organic compounds have been previously noted in the emissions of old books and paper samples [5, 7–9, 12], the precise origin of most of these species, including the SCAs, has not been proposed. To account for the array of aldehydes, alkanes, alkenes, ketones, alcohols, and carboxylic acids observed in Table 1, lipid oxidation must be taken into account, as lipids are components of paper, binding agents, ground wood-pulping materials, and some glues and inks. While fatty acids are not a major component of paper, the plethora of reactive species generated from their autoxidation provides the wide variety of functional groups noted in the emissions of aging books and their olfactory properties. Residual resins in wood fiber are known to be dominated by the 18 carbon unsaturated acids oleic, linoleic and linolenic acids, although the C_{16}, C_{20}, C_{22}, and C_{24} acids are also abundant [15]. The fiber of flax stem, the source of the linen textile and the rags used to make linen papers, also contains these acids as well as a host of C_{14}–C_{52} aldehydes, alcohols, esters and hydrocarbons [16]. The waxy component of cotton fiber, also derived from fatty alcohols to acids, generally contains even numbers of carbon atoms from C_{28}–C_{34} [17]. In historic books, convenient rags of many materials were often pressed together in papermaking; thus the precise lipid content of these papers is difficult to assess without sample destruction.

It is conceivable that fatty acids may emanate from the leather binding and cover materials of the books sampled in this study yielding some of the VOCs noted in Table 1, especially given that librarians and book collectors may have applied oils to leather bindings of the rare books. However, contact studies carried out on a few of the leather bindings, including the vellum bindings, and on the book covers, yielded very low ion signal counts, even when extracted over periods of several days. This was in contrast to contact studies of the book pages, which showed degradation product emission patterns similar to those seen in the headspace studies of the whole volumes, albeit at much lower signal intensities. It was not possible to separate the pages of loaned historic books from their bindings or covers. Fingerprint oils deposited on the books' pages over years of handling could also play a role in VOC generation. To address the role of human contamination, we noted that similar VOC emission profiles (including the prominence of SCAs) arose from newly opened reams of cotton to linen papers and from recently published cloth bound cotton books.

In the autoxidation of a monounsaturated fatty acid, an allylic hydrogen is first lost resulting in a conjugated allylic radical. Depending upon the position of H-abstraction, two different conjugated allylic radicals may be formed and oxygenation can occur at either end of each allylic radical (Fig. 6). This results in four types of hydroperoxides being formed which are isomers of each other, differing only in the placement of the –OOH group [4]. These lipid hydroperoxides are the fundamental primary products of autoxidation, and have recently been reported as paper degradation products [18]. A new chromatographic method for their determination in cellulose, after dispersion in aqueous solution and trapping via a hydroxyl radical scavenger, was recently reported [19].

Monohydroperoxides decompose via homolysis of the hydroperoxide group yielding an alkoxy and hydroxy radical (Fig. 6). The alkoxy radicals can undergo radical elimination by β-scission of a C–C bond to form an oxo compound and an alkyl or alkenyl radical [4]. Mechanistically, the possible monohydroperoxide degradation products from particular free fatty acids to their esters have been proposed and detected in oxidation studies at room and elevated temperatures [4]. The preponderance of 5, 6, 8, 9, 10, and 11 carbon aldehydes, alkanes, alkenes, and alcohols

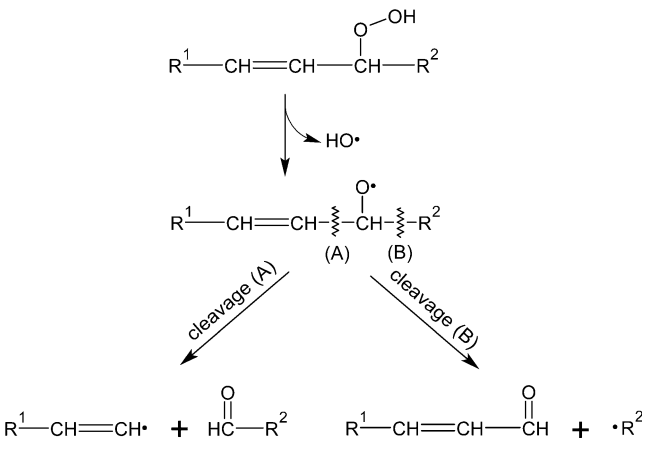

Fig. 6 Generalized mechanism of fatty acid oxidation. R^1 and R^2 may either be the alkyl or carboxyl end of the fatty acid

noted in the emissions of the books is explained by the autooxidation of the 18 carbon mono-, di-, and tri-enic fatty acids from the fragments obtained by β-scission.

In papers containing oleic acid, the decomposition of the four possible isomeric hydroperoxides yields a variety of volatile carbonyl compounds including 2-undecenal, 2-decenal (by "B" bond scission in Fig. 6), octanal, and nonanal (by type "A" scission). These products have been detected in the autoxidation of oils containing oleic acid [20]. Octanal and nonanal were detected in the headspace of all the books in the study (components 30 and 40). The monounsaturated aldehydes were detected in some of the books at low levels (2-decenal, component 55) and likely undergo further autoxidation forming shorter chain saturated aldehydes. Linoleic acid, a 1,4 dienoic acid, is more labile with respect to oxidation and yields deca-2,4-dienal by type B scission and hexanal by type A scission. Deca-2,4-dienal was not observed in the book chromatograms. A study examining the oxidation of linoleic acid has suggested that decadienal undergoes even more facile oxidative cleavage than its fatty acid precursor, forming hexanal and 2-octenal [21]. 2-Octenal was noted in several of the cotton/linen rag books, but only after longer exposure times (component 36). Nona-2,4-dienal (component 53) was observed in a few of the books and is a well-characterized dehydration product of hydroxynonenal [22], which is a tracer of lipid oxidation in biological systems. Nona-2,4-dienal has also been reported as a linoleic and linoleic acid oxidation product [4]. Other 2-alkenals, 2-alcohols, and 2-alkanones (C_8–C_{11}), especially prevalent in the historic books, but also detected in the modern book series, are characteristic fatty acid oxidation products resulting from β-scission of the possible isomeric hydroperoxides.

Of these tracers, hexanal has previously been suggested as a useful guide substance for the assessment of lipid oxidation in paperboard [23], and since it can be formed via multiple autoxidation pathways from different fatty acids, its presence in the headspace of aging paper materials is ubiquitous. In general, the manifold of hydroperoxide decomposition pathways for C_{16}, C_{18}, C_{20}, and C_{22} unsaturated fatty acids likely leads to the homologous series of C_6–C_{12} aldehydes, providing the prominent aldehyde features noted in each book's chromatogram. While the oxidation of the cellulose backbone also produces aldehydes, the longer chain aldehydes cannot arise from simple oxidation mechanisms of hexose/pentose units and result from lipid oxidation. The waxy content of both linen and cotton fiber is the source of numerous fatty alcohols and high molecular weight alkanes emitted from the cotton/linen rag books (Table 1). Lower molecular weight alkanes, including heptane and nonane (components 5 and 19) are also decomposition products of unsaturated hydroperoxides, according to the mechanism in Fig. 6. The higher molecular weight alkanes, also noted in a previous contact SPME study of historic books [9], may be the result of lipid peroxidation if the alkyl radical product of cleavage "B" in Fig. 6 recombines with another alkyl radical, or may simply be primary emanations from the waxes found in cotton, linen and wood rosin.

The homologous series of straight chain carboxylic acids were present in several of the books, and according to the mechanism in Fig. 6 their origin also includes fatty acid oxidation processes. These acids may also form as secondary products from the oxidation of the corresponding alcohols, produced via monohydroperoxide decomposition, or from oxidation of the fatty acid by another oxidant such as ozone. Nonanoic acid, for example, is a well known ozonolysis product of oleic acid [24]. Indoor ozone concentrations measured in southern California museums have been reported to be as high as 143 ppb [25], and in urban areas experiencing many sunny days per year, oxidation of heritage items by ozone and reactive oxygen and nitrogen species in the photochemical smog cycle deserves careful consideration [26]. Indoor levels of NO_2 and nitric acid in several southern California museums were comparable to outdoor levels showing measurements as high as 120 ppb NO_2 and 10 ppb for nitric acid [26]. Although concentrations of these pollutants inside libraries and archives in areas experiencing high ozone and NO_x levels quality have not been as widely studied, typical diurnal urban pollution patterns of O_3, NO, and NO_2 were recently reported [2] in indoor repository environments of The National Archives, London, with measured pollutant levels in the low parts per billion.

The ground wood books (1859–1939) showed a wider variety of volatile aromatic compounds possibly resulting from lignin oxidation, including vanillin, benzaldehyde, 2-hydroxybenzaldehyde, benzyl alcohol, acetophenone, and benzophenone. Only a few aromatic species, including benzyl alcohol, acetophenone, and benzaldehyde, were detected in the historic cotton/linen rag books at lower relative amounts than in the ground wood books. Many BTEX compounds and other mononuclear aromatics observed in contact studies as well as a few of the chamber studies were laboratory/chamber air contaminants and not significant constituents of book emissions. Lignin oxidation tracers in historic books have not been widely studied, but promising marker compounds recently identified in a sample of historic ground wood and rag books using capillary zone electrophoresis [27] included acetosyringone, 4-hydroxyacetophenone, 4-hydroxybenzaldehyde, vanillin, vanillic acid, furoic acid, and 4-hydroxybenzoic acid. These species are quite polar and have a high affinity for paper. Thus, much longer exposure studies using headspace SPME/GC–MS would likely be required to

quantify the importance of lignin oxidation, particularly in rag papers having trace lignin content.

Conclusions

The results of this study demonstrate headspace SPME/GC–MS to be a viable method for studying the aging characteristics of modern and historic books. The headspace method offers advantages over the contact method, including the ability to probe the conservation state of the bulk of the volume at once. The enhanced peak areas noted from sampling many pages of a book enable the identification of a wide variety of acids, aldehydes, alcohols, hydrocarbons and aromatic species, and the origin of particular C_6–C_{11} constituents is traceable to fatty acid precursors. The richness of the chemistry underlying monohydroperoxide radical decomposition leads to an array of both low and high molecular weight oxidation products observed including aldehydes, alcohols, carboxylic acids, ketones, alkenes and alkanes. The aldehydes and alcohols derived from this autoxidation have low odor thresholds and provide much of the olfactive nature of old books [5].

A semi-quantitative assessment of the importance of cellulose degradation via acid hydrolysis in books published over a 379 year range was provided by comparison of relative furfural abundances. Books published after the mid-1800s emitted relatively more furfural, a known cellulose acid hydrolysis product, than the historic books printed on cotton/linen papers, and furfural emission generally increased with the publication year of the volume sampled. The relative importance of hydrolytic and oxidative chemistry involved in paper aging was examined by determining the relative emission yields of furfural and straight chain aldehydes produced from the oxidation of fatty acids in paper. Furfural emission was favored in the more modern wood pulp books (1859–1959) relative to the historic cotton/linen rag books. The straight chain aldehydes hexanal, heptanal, octanal, nonanal, and decanal, were prominent features in all the book chromatograms, but were more abundant in the cotton/linen rag books, possibly suggesting that oxidative pathways are more important in these papers.

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