FULL PAPER

EMISSION RATES
OF VOLATILE ORGANIC COMPOUNDS FROM PAPER

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Emissions of VOCs from model papers aged in closed tubes for various periods of time were quantified using an emission cell (FLEC) placed directly on the paper surface. This sampling technique is entirely non-invasive for the artefact. At the outlet of the cell, the VOCs were accumulated during 24 h on two types of sorbent packings, 2,4-dinitrophenylhydrazine (DNPH) derivatised silica and Tenax TA. Carbonyl compounds collected on DNPH/silica cartridges were analysed by liquid chromatography and UV detection (LC/UV). The other VOCs, collected on Tenax TA tubes, were thermally desorbed and injected in a gas chromatograph with dual detection by flame ionisation and mass spectrometry (TD-GC/FID/MS). Numerous VOCs produced during the degradation of the paper could be identified and quantified. For the first time, their mean emission rates were determined. The most abundant compounds, acetaldehyde, acetic acid, vanillin, furfural and other heterocyclic compounds, showed a production that increased with paper ageing time.

1   Introduction

The state of degradation of cellulose, the main polymer in paper, determines the decay in the mechanical properties of paper, which ultimately is the criterion to be related to the useful lifespan of paper. However, macromolecular characterisation of cellulose requires paper material sampling and cannot always be used.[1,2] Moreover, in order to include all aspects of paper deterioration, it is important to study the end-products resulting from oxidation and hydrolysis reactions of cellulose, hemicelluloses and lignin, the main polymers found in paper. Some of these end-products have been pointed out as likely markers of paper degradation.[3] These compounds are low-molar mass molecules, and arise mainly in the categories of aldehydes, ketones, carboxylic acids, phenolic compounds and carbohydrates. A number of them are volatile organic compounds (VOC) and can be measured in the gas phase using non-destructive sampling techniques. For instance, solid phase microextraction (SPME) coupled

with GC/MS has been proposed and has allowed the identification of several VOCs emitted by paper without resorting to material sampling.[4] However, SPME does not allow the measurement of emission rates for these VOCs.

This article presents results on the study of the emission rate of VOCs from two progressively aged model papers, obtained using the non-invasive sampling method of an emission cell.

2 Experimental

2.1 Materials

Two types of papers were used. 'Step2' was made from pure cotton linters (cold extract pH = 6.2). 'Step3' was a groundwood pulp paper (cold extract pH = 5.1). The papers were subjected to accelerated ageing following the ASTM standard method D6819-02e02.[5] One sheet of paper (4 g) was placed inside a 150 mL-glass tube (Wheaton), which was tightly closed with a heat-resistant screw-cap in the range -196 to +260 °C, and a teflon/silicon liner. The papers were aged separately, in different tubes for 2, 5, 10, 14 and 30 days. The tubes were placed in a dry heat oven (Memmert) at 100 °C. Before insertion in the tube, the papers were pre-conditioned to 23 ºC and 50% relative humidity (RH). In this type of accelerated ageing, the relative humidity in the tube at a given temperature is fully dependent on the moisture content of the paper. Once out of the oven, the tubes were left to cool and the paper samples were subsequently re-conditioned during 24 h to 23 ºC and 50% RH before analysis.

2.2 VOC Emission Measurements

The VOC emissions from the unaged and artificially aged papers were characterised using a stainless steel emission cell (field laboratory emission cell, FLEC[6]). The experiments were performed in a controlled climate room set at 23 °C and 50% RH. The emission cell was placed directly on the sheet of paper lying on a glass plate (Fig. 1). This type of cell is widely used to determine VOC emissions from building materials.[7,8]

Clean air, purified with particle and charcoal filters, and humidified at 50% RH is supplied continuously to the cell. The air is introduced through two diametrically positioned inlets into a circular shaped channel of 7 mm depth from where the air is distributed over the test surface through a circular air slit of 1 mm width. The weight of the cell
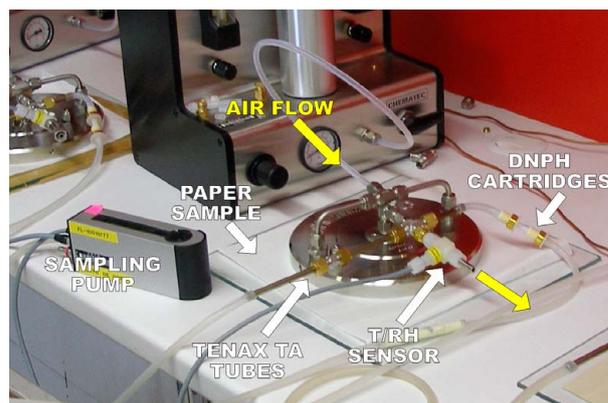

Figure 1. FLEC emission cell set-up with paper sample.

Parameters	Value
Exposed surface of paper	0.0177 m^2
Volume of the emission cell	3.5×10^{-5} m^3
Air flow rate	0.4 l min^{-1}
Loading factor L	506 m^2 m^{-3}
Air exchange rate λ	686 h^{-1}
Air velocity	0.014 m s^{-1}
Temperature	23 ± 0.5 °C
Relative humidity	50 ± 5%

Table 1. Specific parameters used to characterise VOC emissions.

Parameters	Analytical conditions
Desorption temperature / duration	260 °C /15 min
Desorption flow rate	50 mL min^{-1} nitrogen
Cold trap (Tenax)	-30 °C then 280 °C (40 °C/s)
Inlet/outlet split	0/10 mL min^{-1}
Temperature programme	40 °C, 5 min hold - 2.5/min to 170 °C - 7.5/min to 250 °C - 250 °C, 13 min hold
Capillary column	VF-5MS (60 m, 0.25 mm id, 1 µm)
Carrier gas	Helium (240 kPa, constant pressure)
FID temperature	270 °C
Mass spectrometer	Ion trap (EI mode 70 eV) - Scanning 33-425 amu
LC column	Nova-pak C18 (60 Å, 4 µm, 3.9×150 mm)
Sample temperature	4 °C
Column temperature	35 °C
Mobile phase flow rate	1.5 mL min^{-1}
Mobile phase gradient	Acetonitrile / water / tetrahydrofuran

Table 2. Analytical conditions for the measurement of VOCs.

along with a peripheral rubber seal ensures total air tightness.

The characterisation of the emissions requires that several parameters be controlled and remain constant throughout the experiments, such as air quality, humidity, temperature, air tightness, air exchange rate, air velocity, volume of the chamber, and material load. The values for these parameters are reported in Table 1. Air flow conditions in the cell have been fully described in previous studies.[9,10]

The VOCs were continuously sampled at the air outlet of the cell through two Tenax TA tubes (Perkin Elmer) in series. The second tube was used to control the VOCs breakthrough. A sampling flow rate of 50 mL min^{-1} was fixed by a mass flow controller (Brooks Inc.). Tenax TA tubes allow collecting and quantifying a wide range of VOCs with 4 to 18 carbon atoms. VOCs with 2 and 3 carbon atoms could be semi-quantified. A sampling time of 24 h was used to favour the detection of trace compounds. Under these conditions, a limit of detection of 0.02 µg m^{-3} was achieved for furfural. After sampling, the tubes were analysed with thermal desorption (ATD-400, Perkin Elmer) coupled with a gas chromatograph (3800 GC, Varian Inc.) and a double detection with flame ionization and mass spectrometry (Saturn 2000, Varian Inc.) in electronic impact mode (TD-FID-GC/MS). Quantification was performed using the FID data by external calibration for specific compounds using Tenax TA tubes doped with commercial standards of furfural, acetic acid, vanillin, hexanal, 2(5H)-furanone, γ-butyrolactone, 2-furanemethanol, all from Sigma-Aldrich. The response factor for the other compounds was estimated using both the effective carbon number concept[11] and the response factor exhibited by compounds sharing a similar molecular structure. Identification was achieved by comparing the mass spectrum to the NIST'05 library and to a homemade library of 400 spectra built from standards. The relative retention index of the compounds, originally developed by Kovats[12] was also used to help identification.

As shown on Fig. 1, silica cartridges with 2,4-dinitrophenylhydrazine (DNPH) as the derivatizing agent (Waters) were also placed at the outlet of the cell. They were used to sample the low molar mass carbonyl compounds (formaldehyde, acetaldehyde and acetone) at a flow rate of 150 mL min^{-1}. The derivatised carbonyl compounds were then eluted with 2 mL acetonitrile, from which 20 µL were injected in the high performance liquid chromatograph (Alliance 2690, Waters). Detection was performed in UV mode at 360 nm (HPLC/UV).

Fifteen targets were quantified by external calibration using a mix of derivatised standards (TO-11/IP-6A, Supelco). Analytical conditions for the two types of analysis are in Table 2.

Assuming that interactions with the cell walls are negligible, the concentration of a given VOC emitted in the emission cell varies according to the mass balance equation (1). This assumption is correct for most VOCs but is not applicable to low vapour pressure compounds.

$$V \frac{dC_{(t)}}{dt} = V \cdot L \cdot R_{(t)} - \lambda \cdot V \cdot C_{(t)} \qquad (1)$$

Where C is the concentration of a given VOC (µg m^{-3}), V the volume of the cell (m^3), L the loading factor (m^2 m^{-3}), R the emission rate at a given time (µg m^{-2} h^{-1}), λ the air exchange rate (h^{-1}) and t the time (h). From equation (1) R can be expressed as:

$$R_{(t)} = \frac{1}{L}\left(\frac{dC_{(t)}}{dt} + \lambda C_{(t)}\right) \qquad (2)$$

The mean emission rate $\bar{R}_{(t)}$ over the measuring period (0 to n) is obtained by integrating equation (2) between initial and final concentrations and dividing by the difference between final and initial times (t_n-t_0):

$$\bar{R}_{(t)} = \frac{1}{(t_n - t_0)} \int_{t=0}^{t=n} R_{(t)} = \left(\frac{1}{L}\frac{C_n - C_0}{t_n - t_0}\right) + \left(\frac{\lambda}{L}\frac{\int_{t=0}^{t=n} C}{t_n - t_0}\right) \qquad (3)$$

The left hand side in equation (3) represents the mean emission rate over the measurement duration. The first term on the right hand side is related to the difference between final and initial concentrations. The second term on the right hand side corresponds to the mean concentration in the cell. The first term can be neglected as the concentration in the cell after 24 h is very low and close to the initial concentration. This assumption was verified with an additional experiment using a photoionisation detector (PID ppbRAE) that monitored in real time the total concentration of all the compounds with an ionisation energy below 10.6 eV. After 15 h, the concentration in the cell measured by the PID was equal to the initial concentration. In this condition, the mean emission rate of a given VOC can be directly determined from the integrated concentration measured in the cell. Results are expressed in nanograms per gram per hour, taking into account the basis weight of the papers, which was measured after each ageing period. The moisture content (MC) of each unaged and aged paper equilibrated at 23 °C/50% RH was measured and found to be of 6.7±0.3% for Step2, and 7±0.3% for Step3. MC decreased slightly with ageing time, however the resulting value of $\bar{R}_{(t)}$ did

not change significantly whether these values were or were not included in the calculations. Consequently this parameter could be neglected.

3 Results and Discussion

Several VOCs were identified in the gas phase emission of both types of papers studied. Only those which were considered as the most significant, in terms of abundance and emission rate are reported. Step2 paper was mostly characterised by emissions of furanic compounds, such as furfural, 2-furanemethanol, 2(5H)-furanone, γ-butyrolactone, with emission rates which increased with ageing time (Figs. 2 and 3). Each point on the graphs represents the mean value of three replicates. Error bars represent one standard deviation and include analytical uncertainty, sample heterogeneity and differences in the ageing effect. As the three replicate samples were aged separately, the degradation process may differ slightly from sample to sample. For Step2, the emission of carboxylic acids -mainly acetic acid- reached a plateau at 5 days of ageing (Fig. 4). On the other hand, the VOC emissions of Step3 were dominated by furfural and acetic acid with increasing emission rates up to 10-14 days, after which a limiting value was reached. It has to be noted that the emission of acetic acid - and other organic acids - will depend on the pH of the paper. The acetate form which predominates at pH > pKa (= 4.76) is preferably sorbed in the paper while the acid form which predominates at pH < pKa is preferably released in the environment. For Step2, pH was 6.2 at t_0 and decreased regularly to reach 5.7 at t_{30}, while for Step3, pH values were in the range 5.1 at t_0 to 4.2 at t_{30}. These pH values, although mostly slightly above, were close to the pKa value. It was thus assumed that the ratio between acetate and acetic acid would not affect significantly the emission rate.

Some VOCs emissions were characteristic of one type of paper or the other. For instance, 2-furanemethanol, which increased in Step2, was found to decrease progressively in Step3 with the ageing duration. The opposite observation was made for the emission of 5-methyl-2-furfural. Vanillin, which is a degradation compound of lignin, was found only in Step3 and also showed increasing emission with ageing (Fig. 4).

The emissions of carbonyl compounds were in general considerably higher in Step3 than in Step2. The emission of formaldehyde remained almost constant over the entire ageing period (initial value excluded) as shown in Fig. 5. Thus formaldehyde cannot be used as a reliable marker of cellulose degradation. Acetaldehyde (as well as
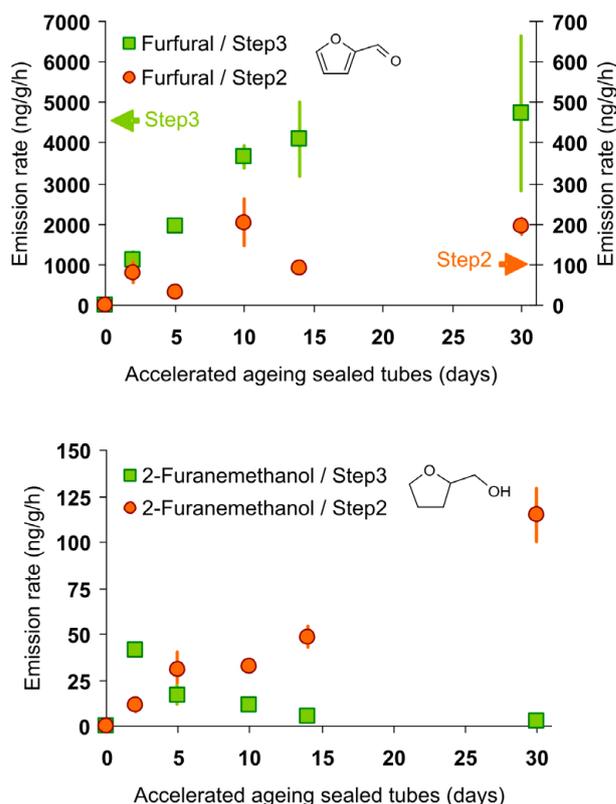

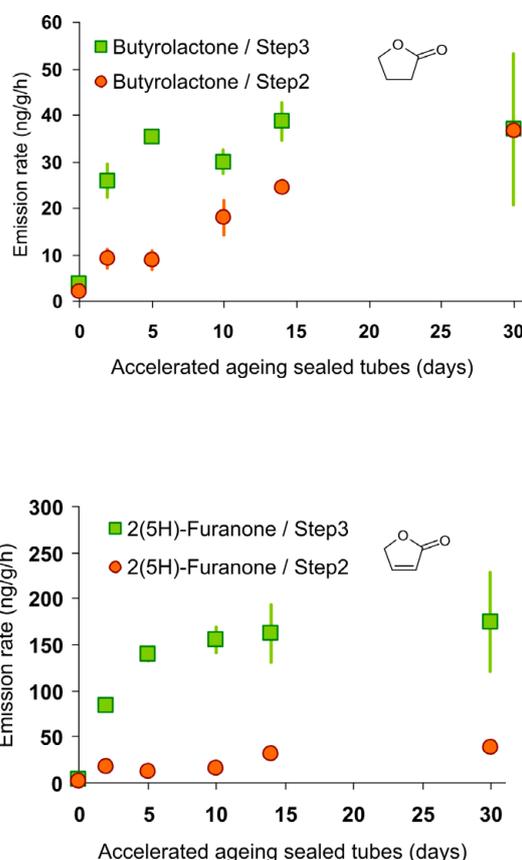Figure 2. Emission rate of furfural and 2-furanemethanol.

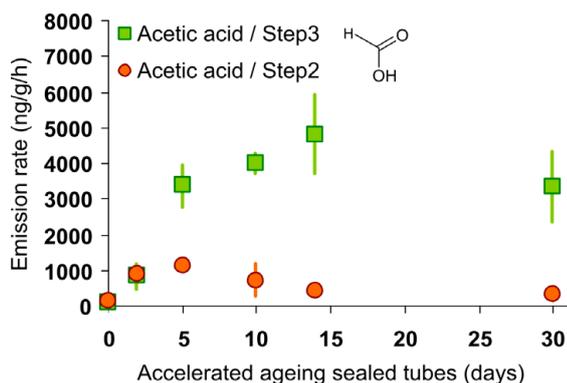Figure 3. Emission rate of γ-butyrolactone and 2(5H)-furanone.

Figure 4. Emission rate of acetic acid and vanillin (only present in Step3).

Figure 5. Emission rate of formaldehyde and acetaldehyde.

acetone) showed an increase in emission rate up to 14 days, followed by a decrease at 30 days.

The maximum emission rates observed for the major compounds are presented in Table 3. In addition to the compounds listed, numerous other VOCs, mostly furanic compounds were found in both papers. Among them were 2(3H)-furanone, 3-furaldehyde, furfuryl formate, 2-acetylfuran, 5-methyl-2(5H)-furanone, 3-methyl-2(5H)-furanone, γ-hexalactone, γ-octalactone, 2-formylpyrrole, carboxylic acids up to C9, ketones and diketones, aliphatic hydrocarbons (mainly hexa- and heptadecane), and terpenes (*e.g.* longifolene). More compounds were found in the emissions from aged Step3, *e.g.* methyl 2-furoate, furan 2,5-dicarboxaldehyde, methyl 3-hydroxypropanoate, methyl 4-oxopentanoate, 4-hydroxybenzaldehyde, guaiacol, and 4-isopropylbenzaldehyde.

The compounds identified are in agreement with previous experiments on naturally and artificially aged papers and books.[4,13,14] Most of the furanic compounds have also been reported as cellulose pyrolysis products.[15,16]

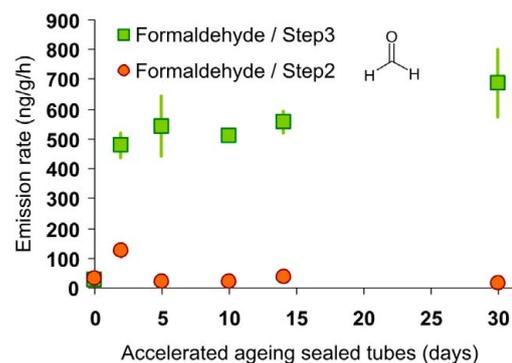The asymptotic behaviour of most emissions was attributed to the ageing method. It has to be noted

Compound	Step2 ($ng\ g^{-1}\ h^{-1}$)	Step3 ($ng\ g^{-1}\ h^{-1}$)
Furfural	193 ± 19	4720 ±1900
Acetic acid	887 ± 216	4820 ±1120
2(5H)-Furanone	38 ± 2	174 ± 54
5-Methyl-2-furfural	7 ± 1	55 ± 24
γ-Butyrolactone	37 ± 0.2	39 ± 4
2-Furanemethanol	115 ± 14	41 ± 5
Vanillin	-	38 ± 5
Formaldehyde	125 ± 22	685 ± 118
Acetaldehyde	58 ± 6	850 ± 66
Acetone	109 ± 10	396 ± 57

Table 3. Maximum observed emission rate for the major compounds identified (± standard deviation).

that the ASTM standard method D6819-02e02 recommends the duration of 5 days at 100 °C or 14 days at 90 °C. The reason for extending the ageing period beyond was to obtain a wider span in the degradation state of the papers. However, in the case of a small leakage of air from the tube, the conditions during the ageing would probably change from t_0 to t_{30}. This was verified by monitoring the RH inside tubes containing pure cellulose

paper (Whatman No.1) during 30 days at 80 °C, using a small 2 cm diameter T/RH sensor (HygroBouton, Proges Plus); 85 °C being the specified maximum temperature that the sensor can resist. A monotonous decrease was recorded: 50% RH at t_0, 48% at t_2, 45% at t_5, 37% at t_{10}, 33% at t_{14}, and 15% at t_{30}. At low RH, the MC of paper decreases and, as a consequence the rate of hydrolysis of cellulose also decreases[17]. This loss of water during ageing in closed tubes has also been observed by Sawoszczuk et al[18]. On the other hand, oxidation can progress normally as long as oxygen is available. The level of oxygen was measured at t_{30} using a handheld oxygen analyser (Visciano Vigaz, canal 111). It was 20.8% and 19.8% inside the tubes containing Whatman No.1 and Step3, respectively, which corroborates the hypothesis of unhampered oxidation reactions. Furanic compounds being mostly secondary products from hydrolysis,[19,20] a slower formation of these degradation products at longer ageing times is consistent with a slower rate of hydrolysis. This can explain the plateau values of the emission rates for these compounds in both papers. On the other hand, degradation products arising exclusively from oxidation reactions should show increasing emission rates over the whole ageing period. As this was not observed for compounds such as formaldehyde, acetic acid and acetaldehyde, which show a plateau in emission rate, it implies either that at least one production or reaction path for these compounds from cellulose include water-dependent steps or that the production and reaction paths lead to an equilibrium concentration for these compounds reached after 5 days in the tubes.

4   Conclusion

Numerous VOCs, especially furanic compounds, aldehydes and carboxylic acids, have been identified in the analysis of gas phase emissions of the two artificially aged model papers. For the first time, the emission rate of the major VOCs has been characterised. The dynamic sampling method with the FLEC emission cell is a non-invasive sampling technique. The evolution of the emission rate of VOCs with ageing time was shown to differ according to the type of compound and the type of paper, especially in terms of abundance. However, the general trend was an increase of the emissions with ageing time, with an asymptotic behaviour towards 14 - 30 days of ageing, which is most likely due to the ageing procedure.

The study of the emission rate of VOCs from artificially aged model papers allows a better understanding of paper degradation, and helps targeting those compounds which show growing emissions during accelerated ageing such as furfural, and other furanic compounds, as markers of the extent of degradation of paper, as well as potential harmful compounds for the paper through re-absorption. This work shows the potential of the technique used for the non-destructive assessment of degradation of paper documents. In order to understand the evolution of the emission rate of specific VOCs and draw comparisons with the degradation state of the papers, it is important to understand the kinetics of the emission rates through the application of models, and relate the data with the macromolecular characterisation of cellulose. This is beyond the scope of the present paper but the work is currently in progress.

5   Acknowledgements

6   References

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