

Cellulose oxidative and hydrolytic degradation: In situ FTIR approach

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Abstract

This study concentrated upon refining an in-situ FTIR method to study accelerated ageing of paper under controlled conditions. The standardisation method applying the CH band at 2900 cm^{-1} allowed comparison of different samples from various experiments. To distinguish the features present in the spectra in the carbonyl region coming from carbonyl vibrations not disturbed by water vibrations, bound water present in paper was desorbed and the spectra were recorded at an elevated temperature. An oxidation index of paper defined as a ratio of integrals of bands at 1730 cm^{-1} to that at 1620 cm^{-1} has proved amenable to follow the degradation of cellulose aged under various conditions. The boundary conditions of experiments selected by us were able to discriminate between hydrolysis of glycosidic bonds and oxidation of carbon atoms in a glycopyranose anomer. Following the changes of the spectrum in the carbonyl range proceeding with oxidation time various intermediates of the cellulose partial oxidation were distinguished starting from the least oxidized monocarbonyl groups, through diketones to aldehydes and carboxyls. Assuming a parallel–consecutive mechanism of the cellulose oxidation the spectra were resolved by fitting with multiple Gaussian–Lorentzian functions.

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1. Introduction

Millions of books worldwide now are menaced by paper disintegration through malignant and inevitably progressive degradation of cellulose chains due to acidic hydrolysis of glycosidic bonds. This problem is specific to the paper produced over around 150 years between the mid-19th century and the late 20th century.

Although cellulose conformation of β -D-glycopyranose polymer is thermodynamically highly stable, it has appeared that the addition of aluminium sulphate into paper pulp acts as a catalyst of hydrolysis, which in mass exerts a detrimental effect on the cellulose durability. Long-term consequences of the modification in the paper-making technology utilising cheap ground-wood raw material and sizing additives were not recognised or ignored for years, but it was not until the past two decades that the alkaline-sized paper technology replaced the acidic one, practically eliminating acidic paper from current archivist use. In order to solve the immediate problems associated with retrospective collections, mass book deacidification programmes have been launched to protect those volumes which have

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not been completely damaged yet and to inhibit the cellulose degradation. At present, the paper preservation tasks are being aided by the research on the mechanisms of cellulose degradation which is aimed at deepening our understanding of the degradation phenomena to thus, in return, improve the existing conservation methods.

According to the most recent findings, cellulose degradation should be regarded in terms of mixed oxidative and hydrolytic mechanisms [1–3], where the two reactions are autocatalytically accelerated by active oxygen species and by protons, respectively. Presently, the paper degradation kinetics is based on formal rate laws [4,5], which with better or worse results are used to reproduce kinetic curves representing accelerated ageing of cellulose.

Typically, paper degradation is monitored by the mechanical or physical properties of paper, such as tensile strength, folding endurance, tear index [1,6], dynamic modulus or mechanical loss tangent [7]. Another parameter is the degree of polymerisation representing an average polymerisation state of cellulose chains [1]. Even though of paramount and practical importance, these parameters provide only macroscopic information on the paper condition and do not give a molecular insight into the mechanism of the degradation in cellulose-based materials. Notwithstanding numerous examples of the use of vibrational spectroscopy to resolve cellulose structure, crystalline phases [8], hydrogen bond network [9,10], vibrational spectroscopy, highly sensitive to structural changes in materials, seems still to have an unexploited potential in the modelling of kinetics of cellulose degradation. A great many sampling techniques have been used so far to study paper materials [8]: transmission spectra through KBr pellets [2,11,12], reflectance spectra using ATR [13] or DRIFT techniques [3,6,14]; each of them, however, suffers from several serious drawbacks. Various sampling techniques have also been tested by our group in the first approach to the problem of cellulose degradation [15,16]. The preparation of KBr pellets is rather time consuming as far as kinetic experiments are concerned, and not very representative of the environment in which the molecules react. The ATR and DRIFT techniques provide information restricted to the surface region of the samples, DRIFT giving high specular reflection.

Therefore what we propose herein is the application of in situ transmission FTIR measurements to directly look into the real time changes in cellulose structure during the degradation. This part of the study concentrates upon testing and refining the experimental set-up which will serve further as an effective tool for the kinetic studies involving mixed-controlled mechanisms [5]. The only example found of an interesting application of the similar in-situ method is the work by Zhou

et al. [17]. Using a combined FTIR and viscometric measurements, the authors surveyed the correlations between modifications in mechanical properties and the structure in cellulose upon temperature- and water vapour-accelerated ageing.

Since the IR spectrum of cellulose is fairly unresolved in the finger print region due to the associated vibrations [15,16], and because the carbonyl region is relatively free from other vibrations, our focus is on the changes in the range between 1400 and 1800 cm^{-1} to finally associate them with the degradation of cellulose. A broad range of reaction conditions have been applied to distinguish between possible carbonyl vibrations and to set boundary conditions for the maximum changes in this region of the cellulose spectrum. A serious obstacle appears to be adsorbed or so called “bound” water [15], whose bending vibrations are observed around 1640 cm^{-1} and interfere with carbonyl bands, making the interpretation of the spectrum much more difficult or sometimes impossible (see examples in Refs [3,18]). Thus, another challenge is how to “clean up” the carbonyl vibrations range.

2. Experimental

2.1. Material

In this approach we decided to use the paper samples made almost exclusively of cellulose to observe the structural changes proceeding in glycopyranose rings. Model paper: bleached sulphite softwood cellulose paper with 99.5 wt% cellulose content (78 g/m^2 , BET: 1.21 m^2/g), denoted as P1 was obtained from TNO, Netherlands [19]. The same kind of paper is used in our group for the kinetic studies utilising other experimental techniques. Moisture content related to a total mass the original P1 sample is 7.47% (23 °C, 50% RH). Little impurities found in this material were assigned to lignin and oligosaccharides [20]. For reference, in selected experiments we used samples of pure cellulose (JNO Pine 90, bleached softwood craft pulp) obtained from Botnia, Finland. The samples used for temperature tests were thinned mechanically to reduce the paper grammage by around 50 wt% thus allowing the satisfactory transmittance through the paper sheets.

2.2. Equipment

The spectra were recorded on a Bruker Equinox 55 spectrometer with an MCT detector at an optical resolution of 2 cm^{-1} and two level zero-filling. For the accelerated ageing tests a quartz reaction chamber with ZnSe optical windows was placed in the sample compartment of the spectrometer. The chamber was equipped with an electric furnace enabling heating in the

broad temperature range (to 900 °C) and with a gas supply and evacuating system.

2.3. In situ FTIR analyses

The temperature tests at (100, 150 and 250 °C) were performed in situ in the reaction chamber using the following gas mixtures:

- dry air atmosphere – moisture was evacuated from the chamber using liquid nitrogen to freeze out the residual water vapour;
- humid atmosphere – water vapour was introduced to the evacuated reaction chamber at 20 °C to achieve the partial pressure around 10 Torr.
- humid air atmosphere – water vapour was introduced into the evacuated reaction chamber in the same way as above (resulting partial pressure 10 Torr) and next filled up with air to attain 1000 Torr. 10 Torr of H₂O corresponds to 60% relative humidity at 20 °C.

Prior to experiments the samples were evacuated and the temperature was raised to 100 °C at which the samples were conditioned for 30 min to remove “bound” water. Next, the reaction was initiated by introducing the gas mixture of a content given above at the temperature of 100 °C. During the experiments, the temperature was step-wise increased and the reaction proceeded for 2 h at a given temperature. Then the sample, if necessary, was cooled down and the spectra were recorded each time at 100 °C.

The experiments with isotopic exchange were performed using D₂O. The D₂O vapour was gradually introduced from a glass tube at room temperature through a vacuum valve into the evacuated reaction chamber with a sample inside. All in all four exchange cycles were applied within 24 h.

Except temperature short-time ageing tests in various atmospheres, prolonged isothermal experiments were performed in the dry air atmosphere at 150 °C. This time, air was dried up by the system of zeolite traps kept in cooling baths at 0 °C. The spectra were collected every 30 min at 150 °C.

2.4. Data processing

The spectra obtained were preprocessed. The procedure included water rotational spectrum subtraction, if necessary, smoothing by the adjacent averaging method, a base line correction and standardisation. The standardisation procedure and its validation are described in the next section. It consisted of dividing the absorbances by the integral of the CH 2900 cm⁻¹ band of the initial sample at 100 °C.

3. Results and discussion

3.1. Internal standard

The most obvious advantage of the in situ FTIR measurements is that the information on the sample instantaneous composition comes from the same area thereby allowing to keep up with the problem of the paper inhomogeneity (different paper thicknesses, variation in composition and crystallinity) and to treat the results semi-quantitatively. Since the band at around 2900 cm⁻¹, whose main intensity comes from the CH stretching vibrations, almost does not change with time and temperature of the reaction at various conditions used, it was regarded as a good candidate for an internal standard. An example of the band evolution with temperature in the more robust atmosphere used (the humid air atmosphere) is presented in Fig. 1 illustrating a slight decrease in the area occurring after 2-h reaction at 250 °C. Thus, an integral of the CH band in the arbitrary chosen range between 3000 and 2800 cm⁻¹ from the first IR spectrum recorded under vacuum at 100 °C after water desorption (30 min) but prior to the reaction, will be a normalisation factor and a benchmark to compare the spectra from different samples. To do this the results were recalculated to the standardised absorbance or standardised integrals (abbreviated as std. absorbance or std. integrals, respectively).

3.2. Water deformation zone

The disappearance of adsorbed water from the samples was monitored by the vanishing of the 1640 cm⁻¹ band, characteristic of bending vibration of water molecules. Such an effect has already been observed by Hatakeyama et al. and Zhou et al. [12,17]. To prevent the readsorption of water which shields the important carbonyl/carboxyl bands, all the spectra were

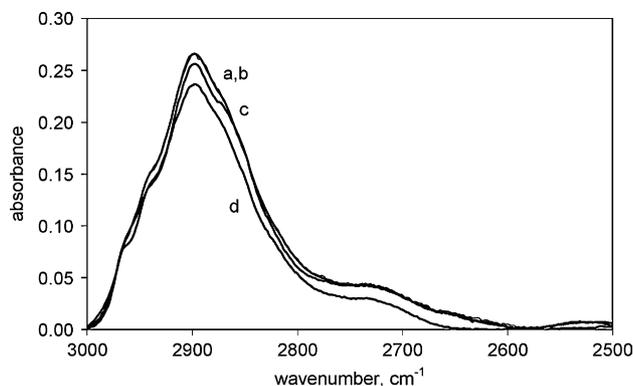


Fig. 1. CH region of the PI sample spectrum in the FTIR in situ experiment in humid air atmosphere at various temperatures: (a) reaction initiation at 100 °C, (b) 2-h reaction at 100 °C, (c) 2-h reaction at 150 °C, and (d) 2-h reaction at 250 °C.

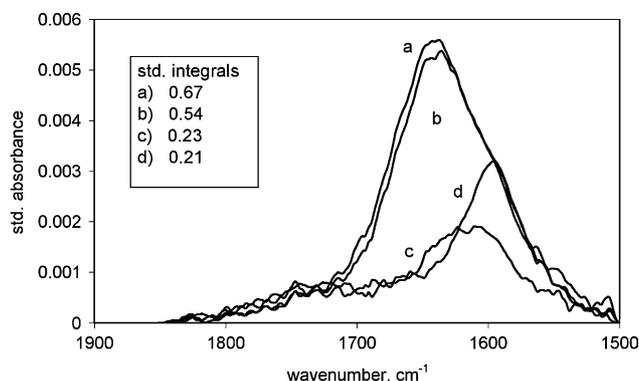


Fig. 2. Water desorption from P1 sample monitored by in situ FTIR: (a) an initial sample of P1 at ambient conditions, (b) after 15 min evacuation to 10^{-3} Torr, (c) after 30-min heating in dry air at $100\text{ }^{\circ}\text{C}$, and (d) another P1 sample exchanged with D after 30 min heating in dry air at $100\text{ }^{\circ}\text{C}$.

collected at $100\text{ }^{\circ}\text{C}$. As it was checked by independent studies (to be published in the forthcoming paper [21]), the water desorption at this temperature is practically irreversible. Fig. 2 illustrates the water desorption progress. The spectrum of the initial sample in air (curve a) is compared to that obtained after the sample was exposed to vacuum for 15 min (curve b) at $20\text{ }^{\circ}\text{C}$ and after the 30-min evacuation at $100\text{ }^{\circ}\text{C}$ (curve c). The desorption proceeded until no further decrease in the 1640 cm^{-1} vibration was detected. Such a temperature treatment of the P1 sample revealed the trace vibrations at ca. 1620 cm^{-1} most evidently originating from the carbonyl groups [11,18] indicating that the initial sample had already been slightly oxidized. The broadening of this remaining band, on the other hand, might suggest that there was a little contribution of the residual water, more strongly bonded to the cellulose fibrils, which could not be desorbed under the conditions used. However, similar vibrations from carbonyl groups with a sharper maximum at 1595 cm^{-1} (curve d) appeared on the H/D-exchanged sample and next treated in the same way, which suggests that this band and the band at 1620 cm^{-1} were from the same carbonyl groups. The shift of the band in the exchanged sample towards lower frequencies may be accounted for by the formation of different hydrogen bonds on replacing H with D atoms. Additional though indirect evidence is that the standardised integrals of these two bands are almost alike (see inset in Fig. 2). Carboxyl or aldehyde absorptions which could be expected in cellulose above 1700 cm^{-1} as arising from the opened terminal glycopyranose rings or oxidation of the C–OH groups are practically indiscernible. Thus performed desorption treatment defines the initial state of the samples surveyed.

An alternative way to remove the adsorbed H_2O from the carbonyl region is the isotopic exchange by D_2O . A similar technique was applied by Ali et al. to study paper

oxidation effects in the same range of the spectrum but without giving the details on the exchange procedure [13]. In this study, the exchange progress was monitored with FTIR by a decrease in OH (3344 cm^{-1}) and an increase in OD bands (2514 cm^{-1}); the results being shown in Fig. 3. There is practically no difference in the OD intensity at 2514 cm^{-1} between the third cycle performed after 4 h and the fourth cycle after 24 h, implying that a shorter procedure is sufficient to eliminate the adsorbed H_2O from this region of the spectrum.

The efficiency of the isotopic exchange performed under vacuum at $20\text{ }^{\circ}\text{C}$ is only about 40% as calculated from the decrease in the area of OH bands at 3344 cm^{-1} measured before and after the exchange. This indicates that under the conditions used only a part of OH groups is prone to the exchange; these being probably adsorbed water molecules and the most exposed OH groups in cellulose fibrils.

We would like to point out that the use of D-exchanged samples in kinetic studies involving long ageing experiments is rather doubtful because an original paper sample and a D-exchanged sample seem not the same in terms of their reactivity.

3.3. Hydrolysis and oxidation in carbonyl region vibrations

The experiments were designed in an attempt to distinguish the products of cellulose hydrolysis and partial oxidation, starting from monocarbonyls as the least oxidized products to carboxylates as the final oxidation stage. This was achieved using three experimental variables: gas composition, temperature and time. Thus, in the humid atmosphere at $100\text{ }^{\circ}\text{C}$ cellulose is expected to mainly undergo hydrolysis of glycosidic

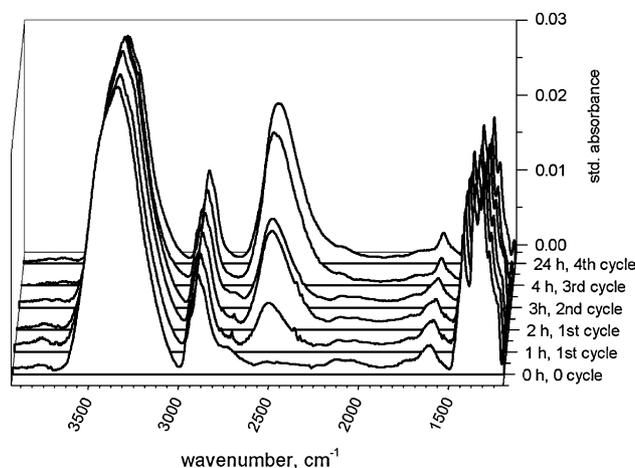


Fig. 3. Progress of isotopic exchange of P1 sample with D_2O monitored by in situ FTIR measurements.

bonds, while in the oxygen-rich atmosphere at 150 °C, oxidation of functional groups is presumed to progress slowly with a variety of transitional products, and to accelerate significantly at 250 °C where cellulose pyrolysis begins. For the maximum effect we decided to work under extreme reaction conditions that are not the typical of cellulose ageing procedures which, according to the recent reports, should apply temperatures lower than 100 °C [1].

Fig. 4 shows the results of the short-term ageing experiments performed at 100, 150 and 250 °C at various gas contents. Irrespective of the gas composition the 2-h ageing at 100 and at 150 °C did not affect the spectrum of either P1 or cellulose used as a reference sample. The most profound effects occurred in the studied range of the cellulose spectrum at temperature as high as 250 °C.

The adsorbed water amount differed among various samples (compare curves a in Fig. 4A–D), although they were maintained in moisture-free atmosphere in a desiccator. Most evidently, the materials are able to response quickly to various atmospheric conditions to which they were exposed when transferred to the reaction chamber. The general trend is common for all the samples: on increasing temperature two broad overlapped bands evolve with maxima at around 1730 and 1620 cm^{-1} .

The smallest changes were observed in water vapour (humid atmosphere) at 250 °C giving residual vibrations between 1670 and 1770 cm^{-1} with a maximum around 1730 cm^{-1} (Fig. 4B). These can be assigned as arising from hydrolysis of hemiacetal bonds which may eventually generate aldehyde groups on opening the

terminal rings. At such a high temperature, cellulose may also undergo dehydration stimulated by vacuum and accompanied by the formation of various unsaturated C–C bonds or enolic groups, as suggested by Calvini and Gorassini [18] and Ali et al. [13].

Oxygen-rich conditions gave rise to an intense growth of carbonyl vibrations at 250 °C with the two broad maxima appearing at 1730 and 1620 cm^{-1} . At this temperature oxidation runs partly through pyrolysis accompanied by the rotational spectrum from gaseous products: CO_2 and CO . Addition of water vapour did not produce any remarkable changes in the spectra after 2-h oxidation as compared to the dry air atmosphere (Fig. 4C). Long-term effects of water presence should, however, be much more harmful to cellulose since water molecules act twofold: as a plasticizer on cellulose polymer and as carriers of protons, which catalyse hydrolysis of hemiacetal bonds. For comparison, the spectrum of pure cellulose having been subjected to the same treatment was obtained, giving a picture similar to that of the P1 samples (compare Fig. 4C and D).

To check if the isotopic exchange method can be applied to capture the changes in the carbonyl region of the paper spectrum, the reaction in the humid air atmosphere was repeated on the H/D-exchanged P1 sample, according to the previous experimental procedure; the results being presented in Fig. 5. The spectroscopic picture is similar to that obtained for the unexchanged P1 sample (Fig. 4C), the only difference being that the two broad bands observed before around 1730 and 1620 cm^{-1} at 250 °C shifted towards lower wavenumbers: 1724 and 1595 cm^{-1} , together with the rotational spectrum of D-exchanged water vapour.

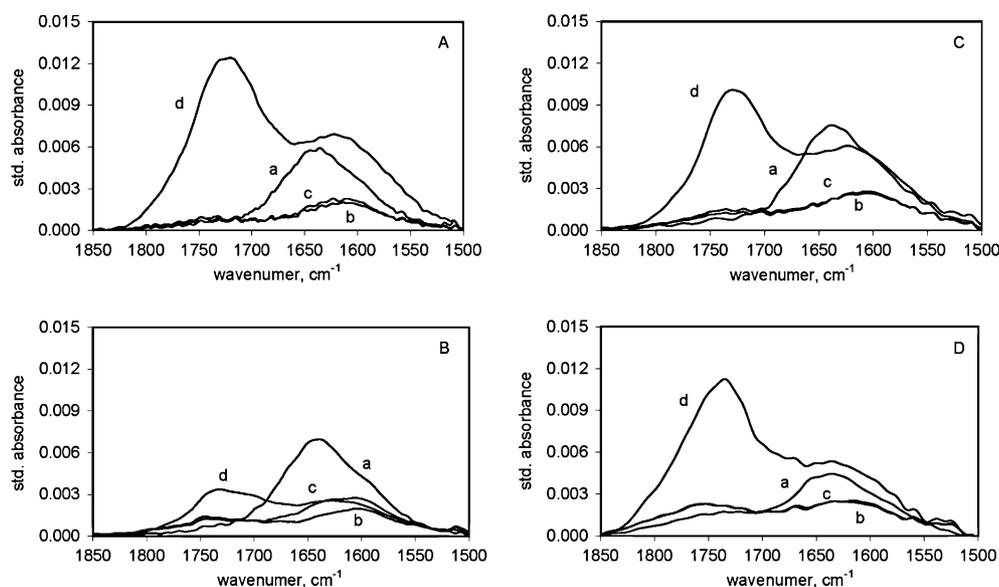


Fig. 4. FTIR in situ spectra of the CO region of the P1 sample studied at various gas content and temperatures. A – dry air atmosphere; B – humid atmosphere; C – humid air atmosphere; and D – reference sample of cellulose in humid air atmosphere. Curves in A–D: (a) under vacuum at 20 °C, (b) 2-h reaction at 100 °C, (c) 2-h reaction at 150 °C, and (d) 2-h reaction at 250 °C.

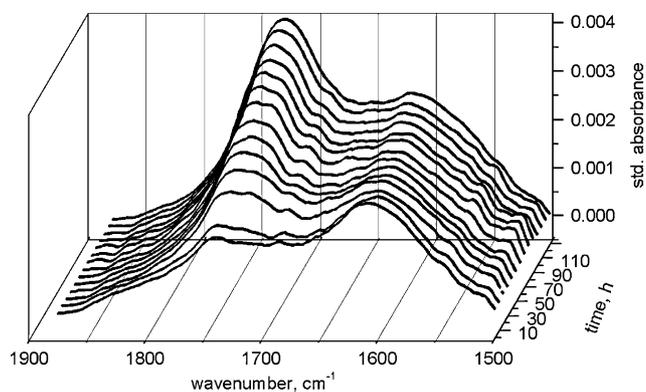


Fig. 5. FTIR in situ spectra of the CO region of the P1 sample exchanged with D₂O studied in the humid air atmosphere: (a) 2-h reaction at 100 °C, (b) 2-h reaction at 150 °C, and (c) 2-h reaction at 250 °C.

This created a noise around 1500 cm⁻¹ which could be removed by the subtraction of neither H₂O rotational spectrum nor D₂O rotational spectrum (Fig. 5). Therefore, quantitative interpretation or fitting the spectra of H/D-exchanged samples is more ambiguous.

The values of the standardised integrals of the two bands observed under various conditions are presented in Table 1. The integrals are calculated in a relatively broad range ignoring the fact that the spectra are most evidently composed of many overlapping bands. The congruity between the values of the integrals amongst the P1 samples treated with air additionally supports the standardisation procedure proposed here. If we assume that the highest contribution to the 1730 cm⁻¹ band comes from carboxyl or aldehyde groups, and to the 1620 cm⁻¹ band – from carbonyl groups, the ratio of these two integrals can serve as an index defining an oxidation state of cellulose (oxidation index). Even though there were traces of water vibrations in the 1620 cm⁻¹ integral absorbance, they would only slightly underestimate the value of the oxidation index. Accordingly, the lowest oxidation state can be attributed to the water vapour-treated P1 sample, the intermediate – to the oxygen-treated P1 samples, while the highest – to the cellulose sample. The latter observation seems

Table 1
Standardised integrals of 1730 and 1620 cm⁻¹ bands observed after 2 h reaction at 250 °C as in Fig. 4A–D

Figure number	Sample and reaction conditions	Standardised integrals		
		<i>I</i> ₁₇₃₀ , 1664–1837 cm ⁻¹	<i>I</i> ₁₆₂₀ , 1500–1664 cm ⁻¹	<i>I</i> ₁₇₃₀ / <i>I</i> ₁₆₂₀
4A	P1 – dry air	0.46	0.14	3.3
4B	P1 – humid	0.12	0.07	1.7
4C	P1 – humid air	0.39	0.13	3.0
4D	Cellulose – humid air	0.53	0.10	5.3

slightly surprising because the cellulose sample shows also the highest crystallinity in comparison with the P1 samples as inferred from the ratio of the integrals of the band at 1370 cm⁻¹ to that at 2900 cm⁻¹, commonly accepted as the paper crystallinity factor [6,12].

In an attempt to capture the intermediate products of the paper partial oxidation, the time dependence was obtained in the dry air atmosphere at 150 °C (Fig. 6). The overall oxidation index, defined above (Table 2), shows a growing tendency with oxidation time, however, not reaching the values obtained at 250 °C. Although the general tendency is similar to that observed at 250 °C with two most developed maxima at 1730 and 1620 cm⁻¹, more bands can be distinguished in the spectrum as shoulders or little maxima emerging from the saddle between the two strong bands. Indeed, the presence of carbon atoms in various oxygen environments (–COOH, –CHO, –CO) was confirmed by XPS spectra of the C_{1s} and O_{1s} electrons obtained for the naturally aged samples [11]. This is not surprising though because partial oxidation, a parallel–consecutive type reaction occurring on C–OH groups in glycopyranose rings, is expected to give a variety of products whose vibrations, to make the matter more complicated, are tuned by hydrogen bond network also changing with time. This is the reason why the characteristic group vibrations may appear at the frequencies higher than typically described in the group frequencies databases.

Following the algorithm described by Calvini and Gorassini [18], the bands were resolved by fitting the multiple mixed Gaussian–Lorentzian functions to the overlapping bands observed at 150 °C (Table 3). Briefly, the constraints imposed on the fitting algorithm were: the number of fitted bands, full width in half maximum (FWHM) of a band, and the range of frequency in which the minima were searched. The contribution of the Lorentzian function in the generated bands was, however, negligibly small, except the band at 1685 cm⁻¹ (peak 4) which was composed almost of pure Lorentz's

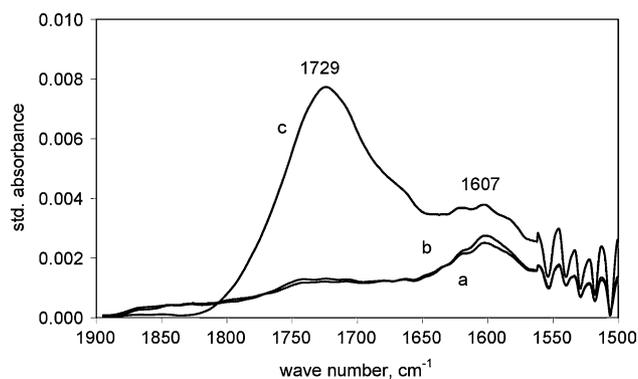


Fig. 6. Isothermal oxidation of P1 sample in the dry air atmosphere at 150 °C monitored every 10 h by in situ FTIR measurements.

Table 2
Standardised integrals of 1730 and 1620 cm^{-1} bands developed with time in the dry air atmosphere at 150 $^{\circ}\text{C}$ as in Fig. 5

Time, h	Standardised integrals		
	I_{1730} , 1664–1837 cm^{-1}	I_{1620} , 1500–1664 cm^{-1}	I_{1730}/I_{1620}
0	0.48	1.29	0.4
10	0.88	1.20	0.7
20	1.02	1.17	0.9
30	1.08	1.06	1.0
40	1.14	1.01	1.1
50	1.48	1.29	1.1
60	1.44	1.08	1.3
70	1.50	1.06	1.4
80	1.59	1.06	1.5
90	1.62	1.01	1.6
100	1.64	0.98	1.7
110	1.79	0.99	1.8
120	1.76	0.96	1.8

function. This suggests that the origin of this maximum is different from the rest of the bands, which maintain the Gaussian shape. The prevailing Gaussian character of the bands can be accounted for by the heteromorphic structure of paper material. The number and positions of fitted peaks (all in all nine bands were fitted) were set-up based on the frequencies of the expected products of cellulose oxidation described in the literature [2,3,8,22,23] and on our spectral analysis, namely, the presence of the additional shoulders and maxima (Fig. 6). The number of fitted curves may seem overestimated and unreliable because undoubtedly the larger is the number of fitted curves the better is the fitting statistics; however, the fitting involving a lower number of bands (<9) was not able to reproduce the spectrum shape giving lower convergence.

The question thus arises, what are the underlying scientific issues behind this complex vibrational pattern.

The literature does not provide any systematic and consistent results on the band assignment in the carbonyl region whatsoever. Mosini et al. and Calvini et al. [11,18] ascribed the two most intense maxima to aldehyde/carboxyl groups (1730 cm^{-1}) and conjugated carbonyl groups (1620 cm^{-1}), respectively, though in the other paper partly by the same authors [2], quite reverse band assignment is supposed, similar to that made by Ali et al. [13]. This is why it seems essential to consider the band assignment in conjunction with both the mechanism of cellulose degradation and the results of complementary experiments.

The C atoms which are most prone to oxidation occupy the 2, 3, 6 positions in glycopyranose anomer inside the cellulose chain; and the 1, 4 positions in terminal anomers whose number increases upon hydrolysis and which can exist as opened or closed rings. On oxidizing they give a variety of products schematically envisaged in Fig. 7 as functional groups which may appear on the glycopyranose ring at various positions. In Fig. 7, these groups were associated with the vibration frequencies taken from the literature reports presented below. They may appear at various positions in the ring giving, as a consequence, broad bands composed of many vibrations coming from one functional group in various environments.

The assignment of the resolved bands is supportive of the consecutive character of the reaction mechanism presumed: the carboxyl vibration around 1745 cm^{-1} (peak 2) representing a final oxidation stage of carbon atoms in glycopyranose rings, increases with time, while carbonyl bands at 1710 cm^{-1} (peak 3) and at around 1618 cm^{-1} (peak 6) arising from the oxidation intermediates, show small maxima. A similar behaviour exhibits the band at 1660 cm^{-1} (peak 5) assigned to an enolic group [11,13,18], being in equilibrium with its

Table 3
The results of fitting mixed Lorentzian–Gaussian functions to the spectra obtained in the dry air atmosphere at 150 $^{\circ}\text{C}$ as in Fig. 5

Time, h	Fitting parameters	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6	Peak 7	Peak 8	Peak 9
0	Center	1778	1743	1707	1685	1663	1618	1574	1538	1513
	FWHH	65	40	40	23	40	58	55	28	20
	Std. integral	0.0251	0.0454	0.0362	0.0096	0.0309	0.1004	0.0653	0.0109	0.0064
10	Center	1780	1745	1713	1685	1665	1617	1571	1538	1513
	FWHH	50	40	40	26	48	63	60	32	19
	Std. integral	0.0251	0.0645	0.0536	0.0185	0.0419	0.1044	0.0654	0.0102	0.0066
40	Center	1773	1738	1710	1686	1662	1612	1564	1536	1511
	FWHH	55	40	31	25	47	65	51	37	16
	Std. integral	0.0454	0.0795	0.0505	0.0283	0.0530	0.1220	0.0446	0.0149	0.0071
80	Center	1770	1743	1715	1686	1662	1616	1569	1540	1512
	FWHH	55	35	38	29	45	60	66	30	17
	Std. integral	0.0484	0.0777	0.0864	0.0409	0.0531	0.1046	0.0741	0.0091	0.0081
110	Center	1770	1743	1716	1685	1661	1619	1571	1539	1514
	FWHH	54	39	41	36	41	59	58	23	19
	Std. integral	0.0456	0.0917	0.0990	0.0598	0.0435	0.1120	0.0744	0.0080	0.0069

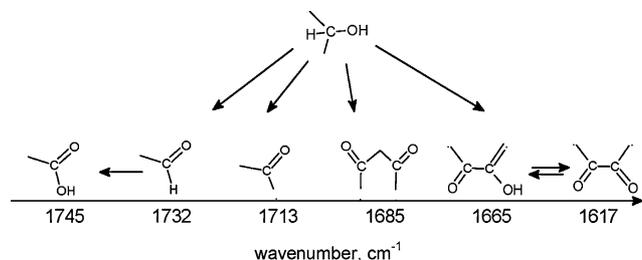


Fig. 7. Possible products of cellulose partial oxidation presented as functional groups associated with frequencies of their vibrations.

tautomer, a conjugated carbonyl group. Furthermore, other possible configuration of carbonyl groups, β -diketones, could be attributed to the band at 1685 cm^{-1} similar to quinone-type vibrations described by Agarwal [24], if it had not been for their Lorentzian shape. Therefore, this maximum should be regarded more as an artefact generated during data preprocessing than a material property. A fairly intense band at around 1570 cm^{-1} (peak 7), showing minimum after 40-h oxidation, is difficult to classify though according to the authors of the cited references [11,18], this band may arise from aryls or conjugated aryl groups of lignin, which, if this is so, may be merely a coincidence. Other less intense vibrations (peaks 1, 4, 8, and 9) not changing markedly with time supposedly come from the P1 sample impurities. Among them, the band at 1510 cm^{-1} (peak 9) is said to be characteristic of the lignin present in the sample, which complies with the band at 1570 cm^{-1} [8,11,18]. Indeed, small amounts of lignin impurities together with oligosaccharides were found previously in the P1 samples [20].

Our fitting results support the results presented by Calvini et al. [18], however, the width values (FWHM) obtained in this work are much more reasonable, though they still exceed the typical values. Additionally, according to our findings, the spectrum of cellulose is more complex in the carbonyl region than was assumed by the cited authors who did not solve the problem of the water shielding effect at around 1640 cm^{-1} . Taking all these into account, the bands generated from deconvolution in the cited reference seem not to represent pure vibrations.

The authors must admit that fitting mixed Gaussian–Lorentzian function to the overlapped bands (often called, not quite precisely, spectral deconvolution) is somewhat arbitrary even though the most strict fitting procedures were applied and obeyed. For this reason the same algorithm applied to the results obtained at $250\text{ }^\circ\text{C}$ did not give consistent fitting parameters showing many local minima in the space of fitted parameters with comparable statistical estimators (Chi^2 and R^2). Therefore, spectral deconvolution without a solid complementary experimental basis allowing to verify band positions seems hardly reliable.

4. Conclusions

The transmission in situ FTIR method proved to have advantages over other techniques in the studies of paper ageing, because it provides information from the same sample area and allows observing real time structural changes of material under controlled conditions. Benefiting from these we have proposed methods of paper spectra standardisation which consist of:

- (1) Spectral normalisation by an internal standard defined as an integral absorbance of the CH 2900 cm^{-1} band in the range $3000\text{--}2800\text{ cm}^{-1}$;
- (2) Water vibration removal from the carbonyl vibrations region by preliminary H_2O desorption from the samples and by recording the spectra at elevated temperatures;
- (3) Introduction of an oxidation index, defined as a ratio of integrals of bands at 1730 cm^{-1} to that at 1620 cm^{-1} .

These allow for semi-quantitative interpretation of the paper spectra, regardless of the sampling technique used. Such standardisation is a preparation stage to obtain kinetic curves representative of ageing. However, for less advanced studies, for conservators applications to evaluate paper condition both from recent and ancient collections we propose the oxidation index derived from a narrow paper spectrum range.

Using various experiment variables (gas mixture composition, temperature, and time) different carbonyl vibrations have been recognised starting from the least oxidized monocarbonyl groups, through diketones to aldehydes and carboxyls. The band assignment has been supported by the spectral fitting by mixed Lorentzian–Gaussian function optimization. The band evolution upon paper oxidation has been found to correspond to a parallel–consecutive mechanism.

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