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FTIR ANALYSIS OF NATURALLY AGED FeCl$_3$ AND CuCl$_2$-DOPED CELLULOSE PAPERS

FULL PAPER

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This paper shows the results of the Fourier Transform Infrared (FTIR) analysis of cellulose papers doped twenty years ago with 0.1 and 1 M solutions of FeCl$_3$ and CuCl$_2$ respectively and kept in polypropylene bags in the dark. Iron-treated samples appear today highly hydrolysed and oxidised; in particular the excess of metal (treatment with 1 M solutions) brought about the formation of iron(II) oxalate, as shown by the FTIR bands at about 1620, 1358, 1313 and 814 cm^{-1}. Washing and acid treatments removed the low-molecular weight oxidised fractions and iron oxalate, yielding the neat spectrum of oxidised cellulose. Copper-treated samples appear today only partly hydrolysed and slightly oxidised; the excess of metal (treatment with 1 M solutions) was not fully absorbed by cellulose and appears as a saline deposit of copper chloride on the surface. However, traces of copper oxalate have been detected in the FTIR spectrum.

1 Introduction

In these years the role of metals on cellulose-degradation processes has become the subject of increased attention in the field of paper conservation science. In particular, the focus on iron- and copper-induced degradation is not only confined to the study of paper decay (either in acid[1-4] or alkaline[5] media), but also concerns specific problems such as iron-gall ink corrosion[6-10] and chemical foxing.[11] Approximately 20 years ago we prepared[12] some samples of cellulose paper doped with FeCl$_3$ and CuCl$_2$ with the aim of studying the role of these ions on paper degradation by means of accelerated ageing, DP (viscometric-average degree of polymerisation) and FTIR spectroscopy. It appeared that the DP decreased to very low values after few days of accelerated ageing, while the FTIR spectra were difficult to interpret even with the second derivative technique,[13,14] so that the research was not completed and therefore not published.

More recently, Bicchieri and Pepa[3] analysed the differences in the degree of polymerisation before and after the reduction of oxidised

groups and showed that in a mildly acidic environment (pH ~6) Fe(III) promoted hydrolysis of cellulose even before accelerated ageing experiments, while Cu(II) did not. Calvini and Gorassini[4] utilised the deconvolution technique to analyse the FTIR spectra of cellulose doped with $FeCl_3$ and $CuCl_2$ and found by accelerated ageing (90 °C, sealed vessel technique) that these ions promoted the oxidation of cellulose with different mechanisms. The FTIR spectra suggested that iron(III) mainly oxidised the C6 groups, while Cu(II) oxidised the pyranose ring in the C2 - C3 position.

Recently we found small fragments of 20-years-old samples, together with the untreated reference paper, kept in polypropylene bags inside a closed paper envelope. Unfortunately, these samples were too small for an exhaustive study (a few square millimetres were available). We performed the FTIR analyses, in order to verify the degradation of Fe(III) and Cu(II) doped cellulose naturally aged in a low-oxygen and dark environment.

2 Materials and Methods

2.1 Samples

Samples of Whatman No.1 cellulose paper (chromatographic grade) were prepared in 1988, doped with $FeCl_3$ and $CuCl_2$ at medium and high content of metal ions:

1) medium content of metal ions: 1 ml of 0.1 M solution of $FeCl_3$ (or $CuCl_2$) was slowly added to 2 g of paper with the aid of a hair dryer on a warm setting, in order to evaporate the excess of water. This procedure yields a theoretical molar ratio of about 1 metal ion / 123 glucose units.

2) high content of metal ions: 1 ml of 1 M solution of $FeCl_3$ ($CuCl_2$ respectively) was added to 2 g of paper with the same procedure, in order to obtain a ten times higher ratio of metal/glucose monomer. Table 1 shows the main properties of doped samples just prepared and 20 years later.

2.2 Treatment of Samples

The FTIR analysis was first carried out without any treatment of naturally aged samples. In the second step the samples were washed with distilled water (which was utilised for the determination of pH) in order to eliminate the water soluble low-molecular weight fractions and analysed again.

In the third step the samples were treated with HCl of two concentrations (0.01 and 1 M), since it is known[17] that at neutral pH most of the carboxyl groups are in the carboxylate form. This treatment causes the shift of absorbance[18] of carboxyl groups from ~ 1600 (carboxylates) to about 1730 cm^{-1} (carboxyls).

2.3 Infrared Analysis

Both in 1988 and in the published work[4] the FTIR spectra were obtained in KBr pellets. In order to minimise the amount of adsorbed water, the mixture of KBr and ground samples was heated several hours above 100 °C and the halide pellets were prepared using a warm die under vacuum. This procedure may have caused however a short accelerated ageing, particularly in the case of acid samples.[16]

In this work all the 1988 doped samples were prepared *ex novo* following the same procedure and both the reference (unaged) samples and the naturally aged samples have been analysed by FTIR in ATR mode without heating.

To this end a Perkin-Elmer Spectrum One FTIR, equipped with the Universal ATR Sampling Accessory (ZnSe cell and diamond window), was used to obtain 4 cm^{-1} resolution spectra in the 4000 - 550 cm^{-1} region, scanned 10 times (absorbance mode), in order to exploit the instrumental built-up noise reduction algorithm. FTIR spectra were normalised with the minimum between 2000 and 1800 cm^{-1} set to zero, so that no absorbance scale is given in the Figures, where the FTIR data have been shifted onto the vertical axis to permit convenient comparisons.

2.4 Data Processing

The deconvolution of FTIR data was performed over the normalised spectra by means of the sum of Lorentzian curves.[4,19] The calculated values were the peak height (H) in absorbance units, the full width at half height (w) and the centre of the peak (x°) both in cm^{-1} units. All the calculations were made with a com-

	1988		2007			
Sample	colour	pH	colour	pH	mechanical properties (observation)	Fe(II) (*)
reference (r)	white	7	white	7	unchanged	
(r) + 0.1 M $FeCl_3$	yellowish	2	brown	5	brittle	(+)
(r) + 1 M $FeCl_3$	brown	2	very brown	3	very brittle	(+)
(r) + 0.1 M $CuCl_2$	pale cyan	5	cyan	6	poor	
(r) + 1 M $CuCl_2$	greenish	6	cyan (**)	6	brittle	

Table 1: Properties of samples treated with $FeCl_3$ and $CuCl_2$.
(*) bathophenanthroline Fe(II) indicator strips[15]
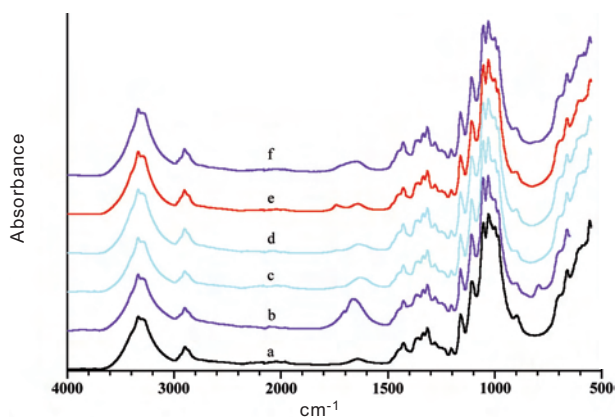(**) with deposits on the surface.

Figure 1: FTIR absorbance of reference paper (a) treated in 1988 with 0.1 M FeCl₃ (b). Other spectra refer to (b) sample after washing (c) and acidification with 0.01 M HCl for 1 h (d), 1 M HCl for 1 h (e) and 1 M HCl for 24 h (f).

mercial software (Origin 60, OriginLab Co.) which allowed the deconvolution by a non-linear curve fitting method.

The best fit between the FTIR absorbance of the samples and the weighted sum of absorbances of their components was obtained with a least squares matrix algorithm.[20] Calculations were made between 1800 and 550 cm^{-1} in order to examine the fingerprints region of cellulose and the main spectral features of the selected standards.

3   Results

3.1   Naturally Aged 0.1 M FeCl₃-Doped Paper

Figure 1b shows the FTIR spectra of naturally aged 0.1 M FeCl₃-doped sample. The main differences with the naturally aged cellulose reference (Figure 1a) are an oxidation shoulder at 1705 cm^{-1}, a strong absorbance at 1660 cm^{-1} and a new band at 793 cm^{-1}. In the fingerprints region (about 1200 - 800 cm^{-1}) the doped sample shows a sharper structure (corresponding either to the increase of the doublet at 1054 and 1031 cm^{-1} or to the decrease of the 1000 and 984 cm^{-1} bands), due to the disruption of the amorphous cellulose substrate.[4,21]

After washing most of the spectral features disappear (Figure 1c), owing to the loss of water-soluble low-molecular weight compounds. In particular, the broad band at 1660 cm^{-1} is strongly reduced (with a shift to ~1629 cm^{-1}), while the band at 793 cm^{-1} fully disappears.

The 0.01 M HCl treatment (Figure 1d) causes only a slight change of the spectrum, while the short time (1 h) 1 M HCl treatment yields an FTIR spectrum characteristic of conjugations-free oxycellulose (Figure 1e). Further treatment with acids (24 h 1 M HCl) causes the appearance of conjugated structures, as shown by the shoulder at about 1680 cm^{-1} (Figure 1f).

The results of FTIR deconvolution in the 1400 - 1800 cm^{-1} region, shown in Table 2, allow a more in-depth analysis of the degradation.

The FeCl₃-doped sample shows the presence of both conjugated (1675 cm^{-1}) and unconjugated carboxyl groups (1710 and 1735 cm^{-1}), some of which engaged (from 1560 to 1628 cm^{-1}) in a Fe-carboxyl bond.[22] Several of these features disappear after washing, owing to the loss of low-molecular weight fragments. These findings, together with the disappearance of the band at 793 cm^{-1} shown in Figure 1, indicate that FeCl₃ partly hydrolysed the amorphous fraction of cellulose with production of oxidised and conjugated oligosaccharides. The increase of pH due to washing causes also the COOH → COO⁻ shift of some carboxyls (from >1700 to ~1600 cm^{-1}) in the insoluble residue.

Further mild HCl treatment (0.01M, 1h) does not cause an overall carboxylate - carboxyl shift, suggesting a strong COO$^{(-)}$ Fe(II, III) interaction, while higher acidity (1M HCl, 1h) recovers the carboxyl groups belon-

treatment		C-H	C-OH	COO-Fe	COO-X⁺	COO-Fe	H₂O	C=C-CO	COOH	COOH
untreated	x°	1427	1457				1641			
	w	35	31				83			
	H	0.77	0.36				0.27			
FeCl₃-doped	x°	1426	1457	1560	1607	1628	1651	1675	1710	1735
	w	39	37	66	50	57	45	41	23	60
	H	0.70	0.34	0.08	0.14	0.38	0.49	0.62	0.26	0.18
after washing (w)	x°	1427	1457		1600		1640			1748
	w	35	34		66		87			57
	H	0.74	0.36		0.21		0.40			0.04
w + 0.01 M HCl	x°	1427	1457		1598		1642			1739
	w	34	41		73		84			83
	H	0.69	0.41		0.11		0.27			0.08
w + 1 h 1 M HCl	x°	1427	1457				1641		1727	1744
	w	32	38				77		64	23
	H	0.72	0.44				0.32		0.16	0.14
w + 24 h 1 M HCl	x°	1427	1458				1636	1679	1720	
	w	34	35				55	55	41	
	H	0.75	0.39				0.26	0.21	0.12	

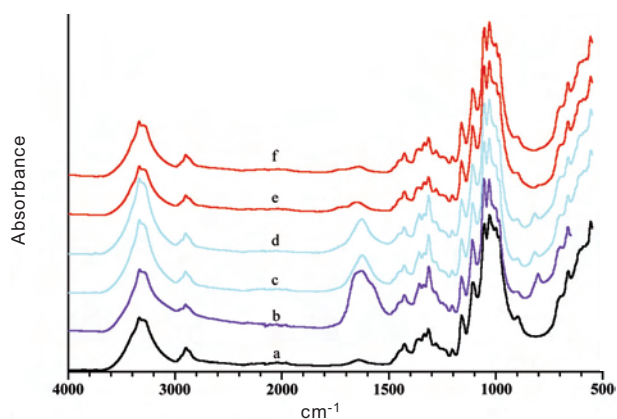Table 2: FTIR-deconvolution bands of the naturally aged 0.1 M FeCl₃ treated paper sample.

Figure 2: FTIR absorbance of reference paper (a) treated 20 years ago with 1M FeCl₃ (b). Other spectra refer to (b) sample after washing (c) and acidification with 0.01 M HCl for 1 h(d), 1 M HCl for 1 h (e) and 1 M HCl for 24 h (f).

ging to high molecular weight fraction of cellulose. Prolonged acid treatment (1M HCl, 24h) causes the appearance of some α,β-unsaturated structures (1679 cm^{-1}).

3.2 Naturally Aged 1 M Fe(III)-Doped Paper

Figure 2b shows the FTIR spectrum of the naturally aged 1M FeCl₃ doped sample. The main differences with naturally aged cellulose reference (Figure 2a) are a broad, strong band at about 1625 cm^{-1} with a shoulder at ~1570 cm^{-1}. Another feature is the increase of the 1358 and 1313 cm^{-1} bands, while a shoulder at ~817 cm^{-1} changes the structure of the 793 cm^{-1} band observed in the 0.1 M FeCl₃ doped sample (compare with Figure 1b). As in the previous sample, the fingerprints region shows a sharper structure, due to the disruption of the amorphous domain.

After washing (Figure 2c) and further mild acid treatment (Figure 2d) the strong band at about 1625 cm^{-1} diminishes, the 1358 and 1313 cm^{-1} bands slightly change and the disappearance of the oligosaccharide band at 793 cm^{-1} reveals a small peak at 814 cm^{-1}. Further treatments with 1 h and 24 h 1 M HCl (Figure 2e and 2f) yield a spectrum of oxidised cellulose.
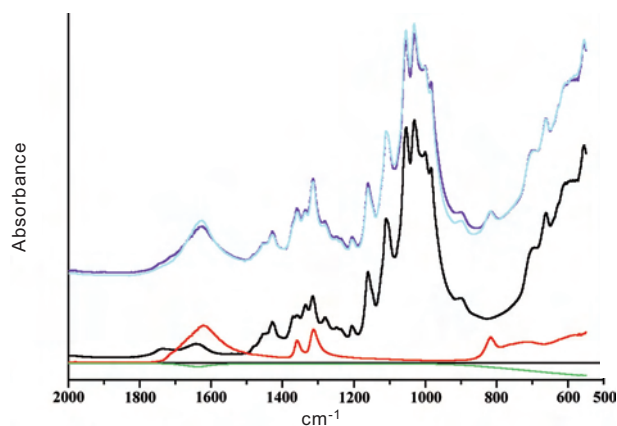

Figure 3: FTIR spectra of water (green), Fe(II) oxalate bi-hydrate (red) and naturally aged 1 M FeCl₃ doped sample treated with 1 M HCl (black). Their weighted sum yields a FTIR spectrum (blue) which corresponds to the naturally aged 1 M FeCl₃ doped sample treated with 0.01 M HCl (cyan), where oxalate was not fully removed.

These findings suggest that this sample was hydrolysed and oxidised by iron in the same way of the 0.1 M Fe(III)-doped sample, with production of low-molecular weight fragments, but a third component contributes to the overall spectrum. It may be possible to hypothesise that this component, characterised by the bands at ~1620, 1358, 1313 and 814 cm^{-1}, is iron(II) oxalate[9]. To confirm this hypothesis, the FTIR spectra of FeCl₃ doped sample treated with 1 M HCl, of iron(II) oxalate bi-hydrate and of water have been numerically added by means of the least squares matrix algorithm[20] and compared with the spectrum of doped sample treated with 0.01 M HCl (Figure 3).

treatment		C-H	C-OH	(*) Fe(II) oxalate and COO-Fe	(*) Fe(II) oxalate	H₂O	C=C-CO	COOH	COOH
untreated	x°	1427	1457			1641			
	w	35	31			83			
	H	0.77	0.36			0.27			
FeCl₃-doped	x°	1426	1458	1570	1603	1629	1666		
	w	42	44	76	38	65	48		
	H	0.60	0.31	0.87	0.22	1.15	0.96		
after washing (w)	x°	1427	1459	1565	1607	1635			
	w	41	47	89	59	94			
	H	0.64	0.36	0.16	0.34	1.15			
w + 0.01 M HCl	x°	1426	1442	1530	1616	1633			1738
	w	18	80	156	87	92			25
	H	0.30	0.62	0.13	0.34	0.97			0.03
w + 1 h 1 M HCl	x°	1427	1457			1642	1670	1714	1740
	w	33	27			79	35	40	41
	H	0.81	0.35			0.45	0.12	0.10	0.13
w + 24 h 1 M HCl	x°	1427	1456			1640	1693		1737
	w	30	33			82	86		73
	H	0.81	0.42			0.34	0.07		0.14

Table 3: FTIR-deconvolution bands of the naturally aged 1 M FeCl₃-treated paper sample. (*) Assignments after deconvolution of the FeC₂O₄·2H₂O standard (main peak at 1603 cm-1).
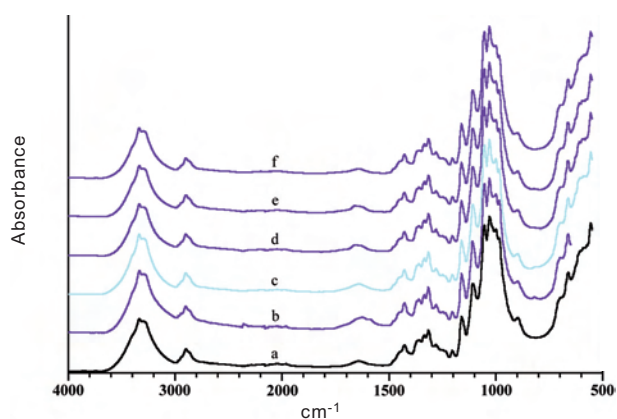
Figure 4: FTIR absorbance of reference paper (a) treated 20 years ago with 1M CuCl$_2$ (b). Other spectra refer to (b) sample after washing (c) and acidification with 1h 0.01M HCl (d), 1h 1M HCl (e) and 24h 1M HCl (f).
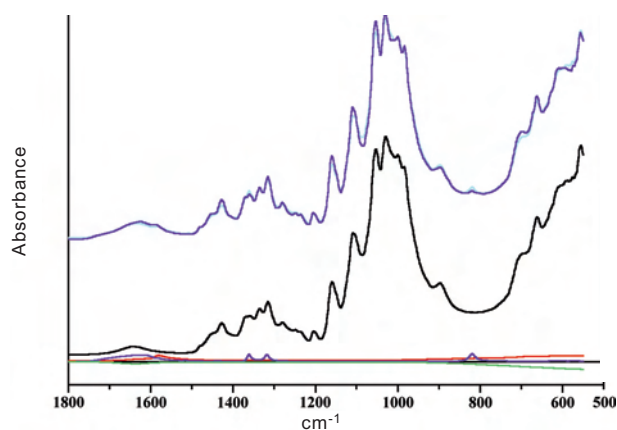

Figure 5: FTIR spectra of water (green), Cu(II) oxalate bi-hydrate (violet), copper chloride (red) and naturally aged reference Whatman paper (black). Their weighted sum yields a FTIR spectrum (blue) which corresponds to the naturally aged 1M CuCl$_2$ doped sample (cyan).

The good fit indicates that iron oxalate contributed to the FTIR spectrum of high molecular weight fraction of iron-oxidised cellulose, the small differences in the 1800 - 1500 cm^{-1} region being due to the pH-dependent carboxyl - carboxylate shift. It is worth noting that the matrix algorithm assigned a *negative* absorbance to water, possibly owing to the hydration state of the oxalate standard.

Table 3 shows the results of deconvolution of the 1 M FeCl$_3$-doped paper sample. It confirms the presence of iron oxalate and shows some conjugated carbonyl groups at 1666 cm^{-1}. The absorbance at 1570 cm^{-1}, higher than the main peak of iron oxalate, suggests the presence of some masked carboxylates that can be hardly detected by the deconvolution technique.

After washing the low-molecular weight conjugated carbonyls (1666 cm^{-1}) and some carboxylates (1570 cm^{-1}) disappear. The strong bands of iron oxalate remain after mild acid (0.01 M HCl) treatment, making it difficult to evaluate the presence of carboxyl and carboxylate groups. In any case further treatments with 1 M HCl eliminate the oxalate salt and recover many unconjugated carboxyls (bands at 1740 and 1714 cm^{-1}) as well as some conjugated oxidised structures (band at 1670 cm^{-1}).

3.3 Naturally Aged CuCl$_2$-Dope Cellulose

Rather surprisingly, the FTIR spectra of naturally aged Cu-doped samples show only faint signs of oxidation. While the 0.1 M CuCl$_2$ doped paper shows a small shoulder at about 1615 cm^{-1} leaning against the water band at 1636 cm^{-1} (possibly due to copper carboxylate), which does not disappear after washing (data not shown in the Figures), the 1 M CuCl$_2$-doped sample shows a whitish-cyan saline deposit on its surface, identified as CuCl$_2$, which absorbs at 1581 cm^{-1} (Figure 4b) and disappears after washing (Figure 4c). Another small band at 820 cm^{-1}, that resists to washing but disappears after HCl treatment (Figure 4d), is compatible with the presence of low amounts of copper oxalate.

In order to test this hypothesis, the matrix algorithm[20] was applied to the system naturally aged paper + copper chloride + copper oxalate + water = naturally aged 1 M CuCl$_2$-doped paper with a good fit and Figure 5 shows the low contribution of these compounds to the overall spectrum (notice again the *negative* absorbance of water).

treatment		C-H	C-OH	CuCl$_2$	COO-Cu	H$_2$O	C=C-CO	COOH *
untreated	x°	1427	1457			1641		
	w	35	31			83		
	H	0.77	0.36			0.27		
1 M CuCl$_2$	x°	1427	1456	1589	1623	1642	1661	1717
	w	30	37	70	33	55	89	41
	H	0.75	0.37	0.26	0.13	0.12	0.21	0.04
washed (w)	x°	1427	1456		1601	1635	1664	1706
	w	29	36		61	56	63	72
	H	0.73	0.41		0.09	0.22	0.15	0.06
w + 0.01 M HCl	x°	1427	1457		1603	1641	1663	1721
	w	32	31		41	70	27	66
	H	0.79	0.38		0.04	0.29	0.12	0.06
w + 1 h 1 M HCl	x°	1427	1457			1639	1658	1738
	w	35	26			46	48	38
	H	0.79	0.34			0.15	0.12	0.13
w + 24 h HCl 1 M	x°	1427	1457			1633	1661	1744
	w	36	28			59	47	92
	H	0.79	0.34			0.18	0.08	0.04

Table 4: FTIR deconvolution bands of naturally aged 1M CuCl2 doped paper. * the low oxidation of the sample makes this attribution uncertain.

Table 4 shows the results of the deconvolution of FTIR spectra. Before any treatments this sample shows the presence of some $CuCl_2$ into the fibres, together with copper carboxylates, α,β unsaturated groups and low amount of carboxyls.

The presence of $CuCl_2$ can be inferred from its absorbance at 1589 cm^{-1}, while the copper oxalate band in the 1800 - 1400 cm^{-1} region contributes to the overall absorbance at 1623 cm^{-1}.

After washing, the Cu-doped sample loses the $CuCl_2$ salt, but retains most of its spectral features, indicating the presence of very low amounts of low-molecular weight compounds. However, this sample shows the presence of some conjugated groups (at about 1660 cm^{-1}) which partly disappear after acid treatments.

4   Discussion

The FTIR spectra of naturally aged samples before any treatment clearly show extensivedegradation brought about by iron(III) chloride (Figure 1b and Figure 2b), as compared with that of copper(II) chloride (Figure 4b). This peculiarity of $CuCl_2$ has been already observed[23] in contrast with the strong degradation induced by copper acetate[23,], and this finding should be further analysed in order to ascertain the influence of anions[1,2,24-26] (chlorides, sulphates, acetates with their own pH values) on the metal-catalysed degradation of paper.

The limited amount of samples did not allow further chemical analyses and the attribution of oxidation bands of the insoluble residue after washing and acid treatments is somewhat speculative, owing to the variety of structures that can be obtained by means of hydrolysis and oxidation of cellulose.

Referring to iron-doped samples, the high oxidation that led to the formation of oxalates makes it unlikely that the insoluble residue contains high amounts of either aldehyde or ketone groups. The increase of absorbance in the carbonyl region (>1700 cm^{-1}) and the simultaneous decrease of the carboxylate bands (~1600 cm^{-1}) after acid treatments suggests the presence of carboxyl groups. Although we could not analyse the degree of polymerisation (DP) of these samples before and after reduction (in order to avoid the alkaline β-alkoxy fragmentation in the viscometer[3]), their poor mechanical properties (Table 1) indicate an extensive hydrolysis toward the levelling-off degree of polymerisation (LODP ~200) typical of the crystalline regions of cellulose.[27] The height of the oxidation bands (Figures 1e and 2e) corresponds to that of alkaline hypochlorite oxidised cellulose

with similar LODP values and suggests a side oxidation along the chains other than the possible formation of C1 carboxyls at the reducing ends. Both hypochlorite-oxidised and our washed samples showed the (~1600) - (>1700) - (~1600) - (>1700) cm^{-1} shifts typical of carboxylate - carboxyl - carboxylate - carboxyl groups after sequential acid and alkaline treatments.

The FTIR deconvolution bands detected at about 1670 cm^{-1} (Tables 2 and 3) in the insoluble residue of iron doped samples indicate the presence of other structures, possibly conjugated, but without further analyses it is impossible to state the nature of these groups. Similar features have been observed in the intermediate stages of alkaline hypochlorite oxidation in an on-going research project, but the acidity of iron-doped samples makes it unlikely the occurrence of a β-alkoxy elimination. Another possibility is the presence of α-diketones in a keto-enol tautomery, the extent of which may depend upon the interactions with iron ions, removed by the acidic washing treatments. In that case, the formation of α-diketones in the C2-C3 position may occur only at the dangling ends of chains or in the low-molecular weight fractions of cellulose, because the required change of hybridation of carbon atoms (from sp^3 to sp^2) of anhydroglucose units in the middle of long chains implies a strong conformational rearrangement of the remaining ribbons of the chain, largely inhibited in a solid network of hydrogen-bonded structures as cellulose fibres naturally degraded by iron in a non aqueous environment. A third possibility is the formation of furan derivatives, that have been observed as volatile organic compounds from paper degraded by iron-gall inks.[28]

Referring to the copper-doped samples, the low interaction with the cellulose fibres (appearance of a saline deposit on the surface) and the low amount of oxidative degradation has been already underlined. However, copper ions are known oxidising agents, stronger than iron[29] at neutral-alkaline pH, largely utilised in the chemical analyses of cellulose (copper number[30]). The initial pH of our samples was not low (compare with iron in Table 1), so that it is unlikely that copper ions lost their oxidising properties. On the other hand copper ions experienced the same cellulose environment of iron, with the large C6-OH groups easily available on the surface of fibres.[31] A reasonable hypothesis is therefore that copper ions prefer to interact with the C2-C3 groups of anhydroglucose (with formation of α-diketones) other than with the C1 reducing end groups, rather than with C6 groups. The low amount of hydrolysis at slightly acidic pH (see Table 1) does not favour the increasing formation of low molecular weight fragments and may have slowed down the C2-C3 oxidation.

5   Conclusions

The FTIR analysis of naturally aged iron and copper-doped cellulose shows that iron(III) chloride degrades the paper samples even in low-oxygen and dark environments, while copper(II) chloride acts at reduced rate, perhaps with a different mechanism. Hydrolysis and oxidation occur in a synergistic way and the difference of the initial pH may be a key factor for the degradation brought about by different iron and copper salts. These results call for a deeper analysis, in particular for the degradation of ancient manuscripts due to metal-gall inks, because our results suggest that the formation of oxalates[9,32] may occur in few decades rather than in centuries as implicitly assumed until now. Even though copper ions degrade cellulose at reduced rate, it is known that these ions catalyse the oxidation of Fe(II) to Fe(III) under anoxic and low acid conditions[33] and their presence may speed up the degradation brought about by ancient mixed recipes of metal-gall inks.

Zooming out in a wide-angle view, the FTIR analysis poses some new questions, related to the predictive value of accelerated ageing tests. Zou et al.[34,35] showed that accelerated ageing (closed vessel technique) adequately describes the long-term hydrolytic degradation of paper. Although some different results obtained in different experimental conditions suggest that the reaction kinetics requires a better understanding,[36-38] it appears that this technique mimics in a satisfactory way the decrease of degree of polymerisation of naturally aged paper.

A different picture emerges in the case of a co-operative action of oxidation and acidity. Our results clearly show that the final products are low-molecular weight oxidised fragments, relatively high molecular weight partly oxidised cellulose and often oxalates. Although signs of oxidation are normally found in degraded paper documents, to our knowledge neither ageing in humid climate chambers nor the sealed vessels technique mimic the formation of oxalates. It is likely that these modes of ageing enhance the hydrolytic mechanism at the expense of oxidation. A deeper analysis is beyond the limits of this paper, but our suggestions for future works are to re-evaluate both dry and UV/daylight ageing, which are known to give rise to hydrolysed and oxidised products of degradation.[39,40]

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