PARAMETERS OF MICROSTRUCTURE AND MICROMECHANICAL PROPERTIES AS EVALUATION CRITERIA FOR COMPLIANT AND PERFORMANT PAPER MAINTENANCE

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ABSTRACT

The natural aging of paper is a complex process of chemical, physicochemical, biological and mechanical processes that are usually not independent of each other but interact with each other. These processes are accelerated or slowed down by the microenvironment of the paper (humidity and temperature), depending on the presence or not of alkaline protection $CaCO_3$ imparted by the chemical treatment. The aim of this work is to investigate for first time by X-ray Photoelectron Spectroscopy (XPS) and then by Fourier Transform Infrared Spectroscopy (FTIR) the effectiveness of these methods applied to cellulose chain decay by natural (rather than artificial) aging in archival paper and whether there is an improvement on the microstructure and micromechanical properties of paper in samples from the Historical Archive of the Communist Party of Greece. This will also contribute to a better understanding of the causes and mechanisms of wear and consequently to their more effective treatment. The analysis of the samples and the processing of the results showed that the cellulose macromolecule is stabilized in humidity and temperature conditions that do not favor its acid hydrolysis (the main mechanism of decomposition in the natural aging of paper), the endogenous and exogenous factors of its destruction (mainly acids) are weakened, neutralized after the physicochemical preservation interventions, the percentages of pure α-cellulose, hemicelluloses and lignin as well as its crystalline and amorphous regions remain stable and slightly improved in some samples.

1. INTRODUCTION

The results of "artificial aging" of paper can often be insufficient and do not reflect the phenomena that occur during natural aging (Zervos, 2010; Zou et al., 1996a; Brandis et al., 1997). The evaluation of the effectiveness of the applied methods was done with paper samples that have undergone "natural aging". Similar studies on records are not available or are rare. In the past, samples from the archive of the Communist Party of Greece were used) with the application of "artificial aging" with Scanning Electron Microscopy (SEM) – micro-analysis Energy Dispersive Spectrometer, (EDS) and through X-Ray Diffraction (XRD) and conclusions were drawn about preservation methods (Mavrantonis et al., 2022; Zervos, 2010). For the first time in the archive of the Communist Party of Greece, processed and non-archival material is examined with XPS and FTIR (Lojewska et al., 2005; Garside et al., 2003; Hajji et al. 2015). It is also one of the few times that archival material (cellulose) has been tested by XPS (Fras et al., 2005; Heijnesson et al., 2006; Fardim, 2017). It must be emphasized that the science of maintenance evolves and many times revises and abolishes previous methods and practices. Thus, the continuous monitoring of the course of applied maintenance methods in an archive with modern methods, the drawing of conclusions and the monitoring of modern literature contribute to a better understanding of the mechanism of the various chemical actions (and therefore their treatment) that cause the destruction of archives, libraries and museums (El-Saied et al., 1998; Wilson et al., 1999b; Peltikoglou, 1995; Brandis et al., 1997; Zervos, 2015).

2. MATERIALS, SAMPLING AND METHODS

2.1. Materials

The samples were sterilized with ethylene oxide, C_2H_4O (EtO). The microbiologic inactivation properties of EtO are related to its powerful alkylation reaction of cellular constituents of organisms, like nucleic acids and functional proteins, causing their denaturation. This process affects the normal cellular metabolism, leading to non-viable microbes (Mendes et al., 2007). Thanks to its high efficacy on the elimination of both insects and microbes this biocide became a very popular fumigant for libraries, archives and museums. This is also related with its great power of penetration and the possibility of use at room temperature and in the gaseous form, allowing the treatment of heat and moisture sensitive objects (Ballard et al., 1986; Hengemihle et al., 1995).

EtO was generally commercialized as a mixture with other gases, like CO_2 (10%EtO, 90%CO_2) and dichlorofluoromethane (12%EtO,88%dichlorofluoromethane). These dilutions reduce the explosiveness, flammability and toxicity of the EtO (Craig, 1986).

Deacidification is the main method of chemical stabilization of paper. It is perhaps the most important stage in paper conservation in terms of its long-term preservation prospects. The purpose of deacidification is not only to immediately neutralize the acidity of the paper, but also to deposit a substance that will be able to neutralize the acidity of the paper that may develop in the future (alkaline reserve). For this purpose, the chemical treatment is done with 4% $Ca(OH)_2$ solution, by creating an alkaline stock $CaCO_3$ (Barrow,1974; Roberson, 1981; Bansa,1998; Fengel et al.,1983). In some cases, very old documents are additionally treated with a dilute solution of 0.5-0.75% methylcellulose (MC).

In this research work will be used to characterize the paper material before and after chemical treatment with 4% $Ca(OH)_2$ solution and 0.5-0.75% MC solution, XPS and FTIR (Lojewska et al.,2005; Johansson L-S.,2022).

2.2. Sampling

Artificial aging is a method that is also used in the study of paper deterioration in order to evaluate conservation interventions on it. However, there is a risk that the results are insufficient and do not reflect the phenomena that occur during natural aging. For this reason, the life expectancy of paper obtained from kinetic experiments with artificial aging seems to be useful but may not correspond to the actual physicochemical deterioration process (Calvini P., 2012). Essentially the time after which the paper loses its properties can be estimated more closely by monitoring the rate of the natural aging reaction under storage conditions under the relatively wide range of aging parameters such as temperature, pressure and moisture content.

In this work, samples will be examined before and after chemical treatment with natural aging. All samples are kept in specific humidity and temperature conditions (T = 16 ± 2 °C and RH = 50 ± 5%) and in controlled ventilation conditions (Mavrantonis et al., 2022; Moropoulou et al., 2001). The coding of the samples, their chemical state (PH) and their chemical treatment are shown in table 1.

2.3 Characterization of paper with XPS and FTIR.

Paper samples 1,1A,4,4B will be tested by XPS and all samples by FTIR, (Dorris et all.,1978; Fras et all., 2005; Table 1).

Table 1. The organization of the samples

samples	sample status construction dates	chemical treatment with 4% Ca(OH)$_2$ solution	chemical treatment with 0.5-0.75% Methylcellulose solution(MC)	alkaline reserve of CaCO$_3$	XPS (X-ray photoelectron spectroscopy)	FTIR (Fourier Transform Infrared Spectroscopy)
1	PH=6, 1960				+	+
1A	PH>7	+		+	+	+
1B	PH>7	+	+	+		+
2	PH=4, 1945					+
2A	PH>7	+		+		+
2B	PH=7		+			+
3	PH=6, 1948					+
3A	PH>7	+		+		+
3B	PH>7	+	+	+		+
4	PH=4, 1940				+	+
4A	PH>7	+		+		+
4B	PH>7	+	+	+	+	+

2.4 Methods

2.4.1 FTIR, Fourier Transform Infrared Spectroscopy

The technique is based upon the identification of functional groups within molecules, where such groups vibrate (either through stretching or bending in various ways), when irradiated with specific wavelengths of light. These vibrations and their intensity (% transmission) are plotted against the frequency of light (cm^{-1}) in which the sample is exposed to produce an FTIR spectrum. The analyses were carried out at room temperature and relative humidity. All the spectra were acquired between 4000 and 400 cm^{-1} with a spectral resolution of 4 cm^{-1} and 16 scans. The FTIR spectra have been used to identify the constituents of historical paper. The IR fingerprint feature of cellulose is clearly encountered in all spectra. However, the difficulty is manifested in the more detailed interpretation of the IR chemical composition, due to the overlapping complexity of the different absorption signals of various constituents in historical papers.

The area located between 2000-700 cm^{-1} is the most complex one of all the ranges, and the results for vibrations were consistent, informing well on the cellulose profile and characterizing the structural composition (Zghari et al., 2018).

2.4.2 XPS, X-ray Photoelectron Spectroscopy

Photoelectron Spectroscopy (XPS), investigate the chemical composition of surfaces. The spectrum is obtained as a plot of the number of detected electrons per energy interval versus their kinetic energy. Each element has a unique Spectrum. The spectrum from a mixture of elements is approximately the sum of the peaks of the individual constituents. Because the, mean free path of electrons in solids is very small, the detected electrons originate from only the top few layers, making XPS a unique surface-sensitive technique for chemical analysis. Quantitative data can be obtained from peak heights or peak areas, and identification of chemical states often can be made from exact measurement of peak positions and separations, as well as from certain spectral features. The tables of energy shift data which aid in the identification of chemical states (Chastain et al., 1995). Photoelectron Spectroscopy (XPS) measurements under ultrahigh vacuum (P < 10-9 mbar). Spectra were recorded with non-monochromatized MgKa at 1253.6 eV photon energy and an analyzer pass energy of 20 eV giving a Full Width at Half Maximum (FWHM) of 0.85 eV for Ag 3d5/2 line. The analyzed area was a spot of 7x20 mm. C1s main peak was at 284.6 eV. For the deconvolution, mixed Gaussian–Lorentzian peaks and a Shirley background were used.

3. TECHNIQUES – INSTRUMENTATION

3.1. Chemical processing - deacidification of the paper

The most important mechanism that causes the chemical decomposition and aging of paper is acid hydrolysis, the rate of which directly depends on the concentration of acids in the paper (Roberson, 1981; Baty et al., 2010). Deacidification, which is done with various chemical substances of medium alkalinity, is a liquid process, mainly carried out by immersing the paper in a bath, in which water or various organic substances can be used as a solvent. It has been shown to significantly slow down the aging of paper and is the most common chemical stabilization procedure for historical documents (Barrow et al., 1959; Hey, 1979; Mihram, 1986a; Kolar et al., 1996; Moropoulou et al., 2001; Baty et al., 2010; Mavrantonis et al., 2022;

Zervos, 2010). The paper is supported during wet de-acidification with sheets of non-woven polyester (ho-litex) to prevent mechanical damage (Hey, 1979). It must be made clear that deacidification cannot restore the lost strength of aged paper. The deacidification method with calcium hydroxide Ca(OH)$_2$, for deacid-ification baths is the easiest, cheapest and most wide-spread and, moreover, has the best results (Hey, 1979; Lienardy et al., 1990b). Its disadvantage is the high pH of the washing bath (~12), which can cause color change (yellowing) in papers containing lignin (Hey, 1979) and change the color (from black to brown) of iron ink (Lienardy et al., 1990b; Reissland, 1999). The solution made is 4% Ca(OH)$_2$, the suspension is left to precipitate the insoluble calcium carbonate and the supernatant clear solution is used as is or diluted 1:1 with water. Deacidification is preceded by washing with water to eliminate the water-soluble acidity and to facilitate the penetration of Ca(OH)$_2$ into the paper fibers. The whole process takes about 45 - 60 minutes, depending on the quality of the paper. The calcium hydroxide that remains on the paper reacts with the carbon dioxide in the atmosphere as the paper dries, turning into calcium carbonate.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$
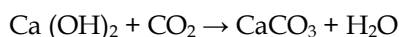
The calcium carbonate produced is the alkaline re-serve that can neutralize acids as shown by the reac-tion:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$$
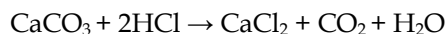
The final pH of the paper is in the neutral or slightly alkaline range (7 – 9.5). Higher pH values fa-vor other degradation mechanisms, such as alkaline hydrolysis and autoxidation (Kolar et al., 1996; Havermans et al., 1997).

3.2 Sizing

Fixation and strengthening of the paper in the sam-ples was done after deacidification, with methyllocel-lulose, by impregnation (gluing - sizing), causing at the same time "hydrophobicity" (Evetts et al., 1989; Carrapella et al., 1990; Hanus, 1994; Anders, 2013;

Hummert et al., 2013). The materials used are usually water soluble. Enhancement can be done with and with a soft animal hair brush, or by spraying, applied to moderately wet paper, or by immersing it in a sim-ilar bath, or even by spraying (Hummert et al., 2013). The preparation of the MC solution is done by gradu-ally adding methylcellulose to an increasing amount of water under constant mixing (final content 0.5-0.75%).

4. RESULTS

4.1. FTIR

-The main characteristic cellulose bands vibrations of our historical papers are: 1460, 1432, 1370, 1335, 1317, 1160, 1120, 1050, 1025, 897 cm^{-1}. Here in all our samples we see that the chemical treatment brings out the cellulose and its vibrations. The processed sam-ples have lower intensity vibrations. So, C-H bending, (*scissoring* and *wagging*-strong) at 1500-1300 cm^{-1}, the region between 1200-950 cm^{-1} corresponds to vC-O-C (strong and large with the very intense peak at 1025 cm^{-1}), and the β-(1,4)-glycosidic linkages in cellulose at 897 cm^{-1} attributed to vC1-C4 (weak and broad). In addition, the chemical treatment does not promoted the breakage of the C-O-C bonds in the β-(1,4)-glyco-sidic linkage (897 cm^{-1}) of crystalline cellulose (Gar-side et all, 2003).

- The crystalline cellulose form (strong band) ab-sorbs at 1425 cm^{-1}, and corresponds to CH$_2$ symmetric bending in crystallized cellulose I. Its empirical crys-tallinity index has been reported with a ratio of the peaks at I_{1427}/I_{897}. While the amorphous cellulose form (weak peak) shift to 1420 cm^{-1} in cellulose II. The C-H in plane bending signal at 1375 cm^{-1} is the most appropriate for indicating cellulose crystallinity in ra-tio with the peak at 2900 cm^{-1} (I_{1375}/I_{2900}). The band absorption at 1317 cm-1 is attributed to C-H bending vibration in crystallized cellulose form, while the band absorption at 1330 cm^{-1} is attributed to C-H bending vibration of amorphous cellulose (Abidi et al.,2014; Hajji et. al., 2015). In some samples (1, 1A, 1B) the chemical treatment improves the crystallinity, while in other samples (2, 2A) there is stability.

Table 2. The characteristic absorption bands of cellulose (Zghari et al., 2018)

Wave Number (cm^{-1})	Band assignments
1740	vC=O stretching vibration of carbonyl group of normal ester, acetoxy group H$_3$C–(C=O)–O–inhemicelluloses and/or cyclic ester (such as η-lactone), and/or C=O of free carboxyl acid group
1647	δ O–H in plane bending vibration of adsorbed water (*broad* and *strong*),and/or vC=O car-bonyl group in resin: 1658 cm^{-1}
1575	vC=O stretch in skeletal vibration of phenolic ring as a contribution of lignin
1539	vC=O stretch in skeletal vibration of phenolic as a contribution of lignin
1470-1472	δCH$_2$ *asym* : strong in cellulose I (in *crystalline* phase CH$_2$)
1466-1462	δCH$_2$ *sym*: in plane bending (*scissoring*) strong in cellulose I (in *crystalline* phase CH$_2$and *asym*

	in *amorphous* CH_2), δCH_3 *asym* bending in lignin (CH_3–O) and hemicelluloses (CH_3–(C=O)–)
1445	O–H in plane deformation (*shoulder*)
1430	Characteristic of cellulose I with the band at 1108 cm⁻¹ (sign of crystalline form) H–C–H and O–C–H in plane bending vibrations, V_{as}C–O in CO_3^{2-} groups of $CaCO_3$ as a contribution of calcite (inorganic filler) and $\delta_s CH_2$ at C_6 of cellulose
1425	δCH_2 symmetric bending in *crystallized* cellulose I (*strong*) and *amorphous* cellulose (*weak and* shift to 1420 cm⁻¹ in cellulose II and *amorphous* cellulose), and/or v_{as}C–O in CO_3^{2-} of $CaCO_3$ inorganic filler, with a *broad* band
1416	CH_2 (*scissoring*), *amorphous* cellulose shift to 1416 cm⁻¹ in cellulose II (*crystalline*)
1375	C–H deformation vibrations in cellulose,(most suitable for indicating cellulose, *crystallinity* in ratio with 2900 cm⁻¹ vibration)
1372, 1335, 1316	3 typical bands of *crystalline* cellulose
1330	C–H bending vibration in *amorphous* cellulose (*shoulder*) *crystalline* cellulose
1317	C–H bending vibration in *crystallized* cellulose I (CH_2 *wagging* or CH_2 rocking)
1280	Typical band of crystalline cellulose
1268	vC–O stretching vibration of carboxyl group
1230	vC–O stretching vibration of carbonyl ester group in hemicelluloses
1161	vC–O–C *asym* bridge stretching vibration in cellulose
1108	Characteristic of cellulose I with the band at 1430 cm⁻¹ (sign of crystalline form), vC–O *asym* in plane vibration valence of pyranose ring of polysaccharides CH stretching vibrations in different groups of carbohydrates
1000-900	many signals of cellulose vibrations modes
1053	vC–O bond of aliphatic C–OH vibration
1030	vC_{alk}–O–C stretching mode of skeletal vibration of polysaccharides (pyranose ring)
995	vC–O valence vibration
897	vC_1–O–C β-(1,4)-glycosidic linkages between glucose units in cellulose, *weak* and *broad* incellulose I (amorphous), *strong* and *sharp* in cellulose II (crystalline)
874	v_sC–O of $CaCO_3$ as a contribution of calcite (inorganic filler)
710	$r(CH_2)_n$ (n>4) rocking in *crystalline* cellulose I as a shoulder and/or (OCO) in CO_3^{2-} groups (in plane deformation) of $CaCO_3$
667	δ_{oop}O–H out of plane bending vibration (700-400 cm-1) of alcohol groups in cellulose, hemicelluloses and/or OH of carboxylic acid
560	(Si–O) in kaolin (inorganic filler)
430	(Al–O–Si) in kaolin (inorganic filler)
667	δ_{oop}O–H out of plane bending vibration (700-400 cm-1) of alcohol groups in cellulose, hemicellulose and/or OH of carboxylic acid
560	(Si–O) in kaolin (inorganic filler)
430	(Al–O–Si) in kaolin (inorganic filler)

- The phenomenon of natural aging cellulose degradation is firstly associated with the appearance and increase of a new absorption signal between 1800-1500 cm⁻¹ and second, from changes in the crystalline / amorphous content ratio in the 1500-1100 cm⁻¹ range. The appearance of new bands can be attributed to the carbonyl groups (1740, 1575 and 1539 cm⁻¹). In samples 2 and 4 (poor quality paper, figs 2 and 4) such absorption bands appear, but they disappear in chemically treated 2A and 4A. No carbonyl bands appear in sample 3 (rice paper, very good quality, fig. 3, Table 1).

- The $CaCO_3$ product of chemical processing was investigated and identified by the broad stretching asymmetric absorption peak at 1425 cm⁻¹ (V_{as}C–O in CO_3^{2-}), and two weak peaks at 874 (stretching symmetric vsC–O of $CaCO_3$) and 710 cm⁻¹, in plane deformation δ(OCO) in CO_3^{2-} groups of $CaCO_3$,(Hajji et al.,2015;Zghari et all,2018;Table 2.).

Peaks are characteristically high in the treated samples, samples 1,1A, 1B, 2, 2A, 2B, 3, 3A, 3B, 4, 4A, 4B, Fig. 1-4). Peak intensity drops in MC treated samples.

- Drastic changes have not occurred in the wide range of 1200-850 cm⁻¹. This shows us that there are no changes in cellulose and especially in the C-O-C bridge bond of cellulose (1161 cm⁻¹), and in the C_{alk}-O-C bond of the skeletal vibration of the polysaccharide ring (1030 cm⁻¹, pyranose). Therefore, the chemical treatment does not affect the C_1-O-C_4 β-(1,4) - glycosidic bonds (897 cm⁻¹) between cellulose pyranose sugar units, resulting in almost disappearance of the band at 874 cm⁻¹. Glycosidic bonds (897 cm⁻¹) are present and strong in all treated samples, (Abidi et al., 2014; Zghari et al., 2018; Figs 1-4).
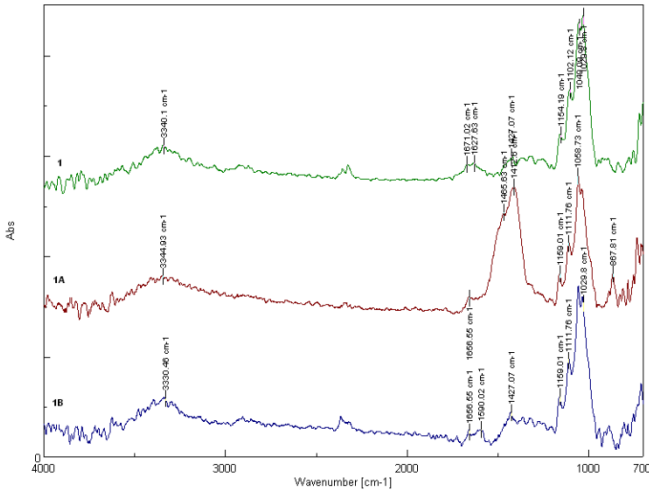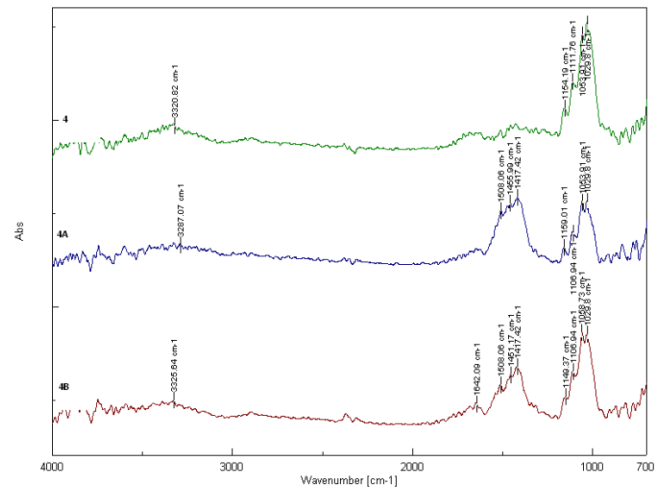
Figure 1. Comparative FTIR spectrum for samples 1, 1A, 1B. Samples 1A and 1B have been chemically treated and Processed , see Table 1
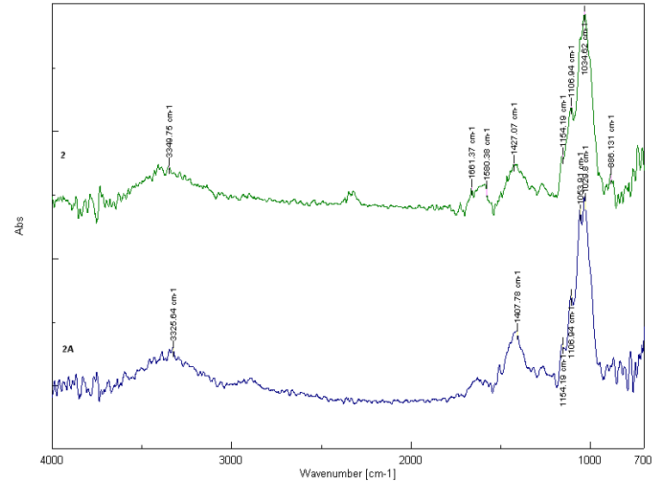
Figure 2. Comparative FTIR spectrum for samples 2, 2A. Sample 2A has undergone chemical treatment, see Table 1
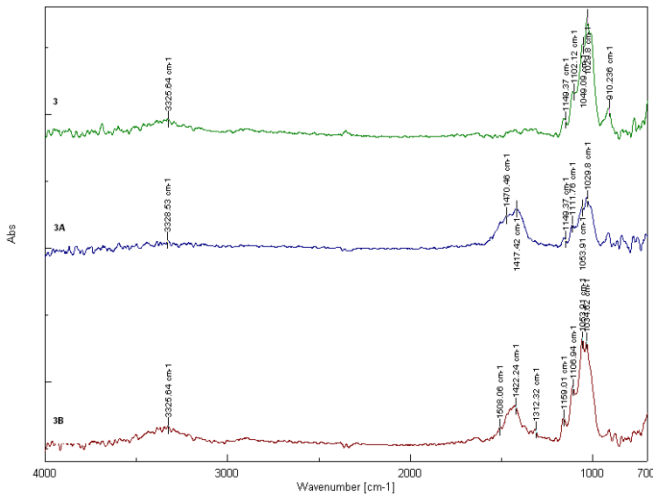
Figure 3. Comparative FTIR spectrum for samples 3, 3A, 3B. Samples 3A and 3B have been chemically treated and processed, see Table 1

Figure 4. Comparative FTIR spectrum for samples 4, 4A, 4B. Samples 4A and 4B have been chemically treated and processed see Table 1

4.2 XPS

For the comparison of the 1, 1A and 4, 4B samples, the entire XPS (XPS wide scan) spectra are shown below, in order to first make a quick identification of the elements present on the surface (Figs 5,6). It is reasonable that the overall XPS spectrum (XPS wide scan) for both samples is dominated by the peaks of C and O_2. In sample 1 A and 4 B there is additionally the Ca $(OH)_2$ peak.
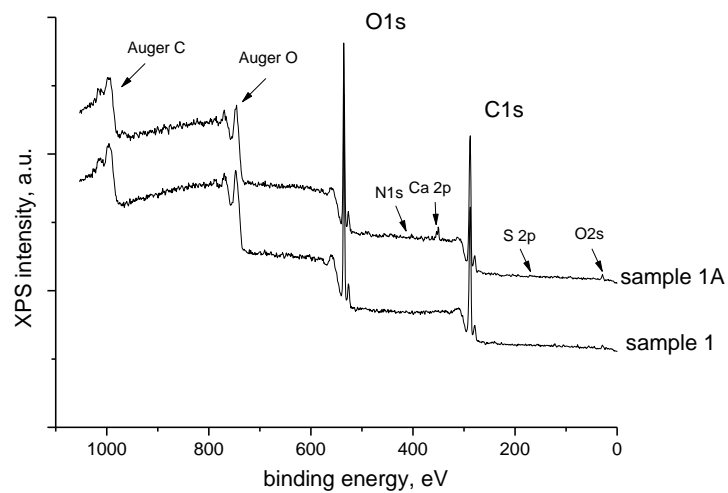
Figure 5. Comparative XPS wide scan for samples 1, 1A. Sample 1A has undergone chemical treatment, see Table 1
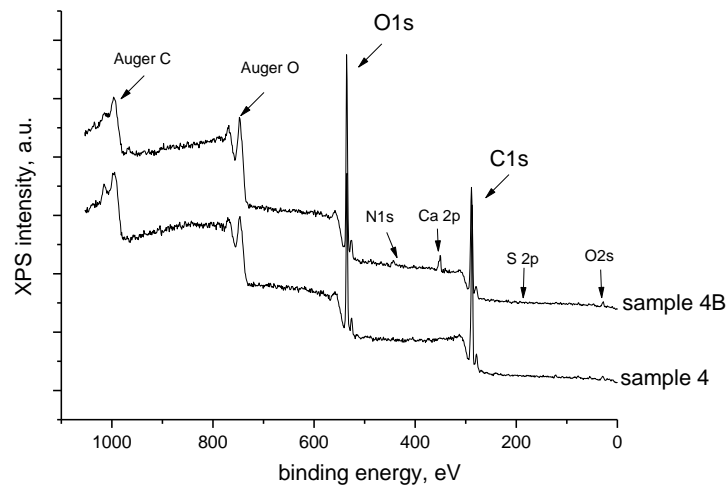

Figure 6. Comparative XPS wide scan for samples 4,4B. Sample 4B has undergone chemical treatment, see Table 1
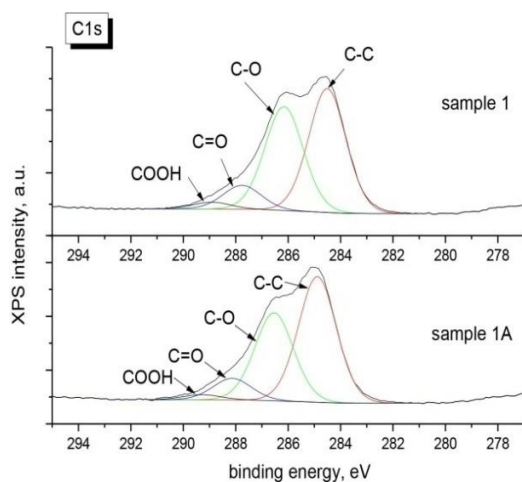

Figure 7. Comparative XPS spectrum for C in samples 1, 1A. Sample 1A has undergone chemical treatment, see Table 1

Then we take the spectra of the individual elements with greater clarity so that we can do a quantitative analysis and see the various oxidation states of the elements, especially the carbon that interests us in this particular case. For samples 1 and 1A the carbon spectra are shown in Fig. 7.
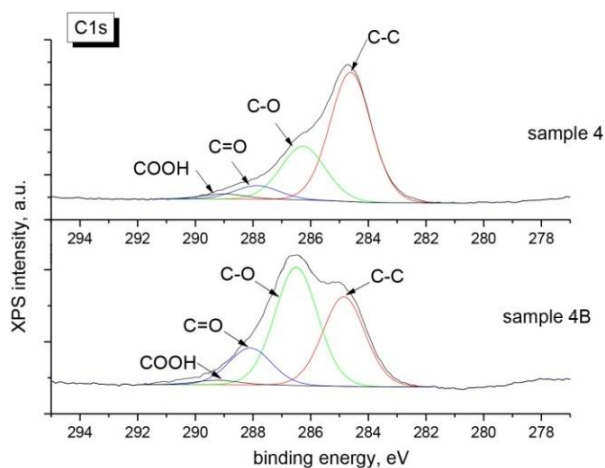
Figure 8. Comparative XPS spectrum for C in samples 4, 4B. Sample 4B has undergone chemical treatment, see Table 1

The corresponding spectra for samples 4 and 4B are shown in Fig. 8 (Fras et al., 2005; Beamson et al, 1992; Chastain et al., 1995; Ruigang et al., 2005). Below is Table 3 with the percentages of the different types of carbon in the 4 samples.

From Fig. 9 and Table 3, there is a reduction of oxidized carbon species (C-O, C=O, COOH) in sample 1A, where it has been treated with Ca(OH)₂, compared to sample 1, which has not has been processed.

On the contrary, in sample 4B the peaks of the oxidized carbon species, C-O and C=O, increased significantly because this sample has been treated with methylcellulose (in addition to Ca(OH)₂) and so these peaks dominate the carbon spectrum corresponding to methylcellulose (Fig. 8 and Table 3). The above is also confirmed by Table 3 (quantitative analysis of the data), where the ratio of oxygen to carbon (O/C) decreases in the case of sample 1A compared to sample 1, but increases significantly in sample 4B due to the treatment with methylcellulose. The –COOH peak is noticeably reduced in chemically treated samples 1A and 4B. XPS spectra of oxygen, sulfur, nitrogen and calcium elements for samples 1 and 1A are given below, (Heijnesson et al., 2006; Fardin et al., 2005; Figs 9-12).

Table 3. The percentages of the different types of carbon in the samples 1, 1A, 4, 4B.

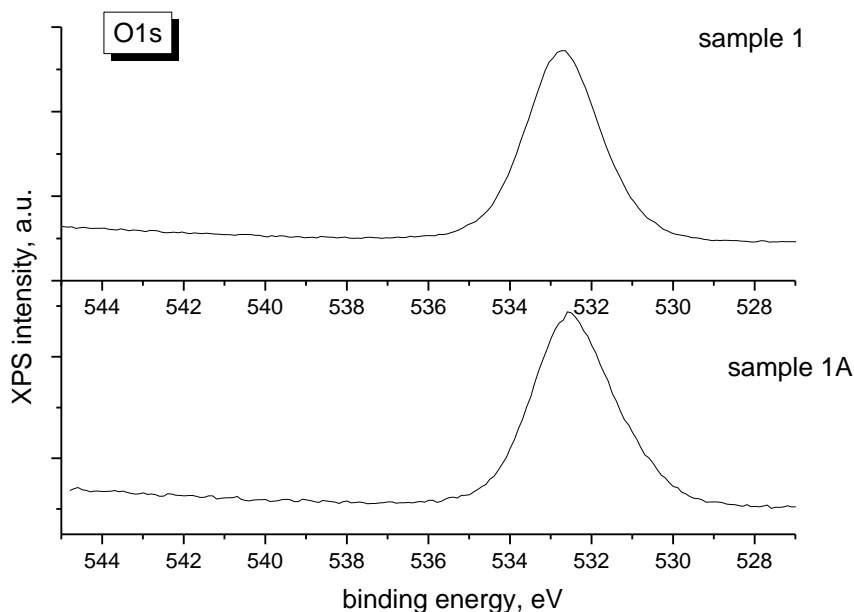| Sample	Peak C-C, %	Peak C-O, %	Peak C=O, %	Peak COOH,%
1	47,26	40,7	9,38	2,66
1A	51,88	36,9	9,06	2,16
4	62,56	27,83	7	2,6
4B	35,66	47,72	14,83	1,79

Figure 9. Comparative XPS spectrum for O in samples 1, 1A. Sample 1A has undergone chemical treatment, see Table 1.
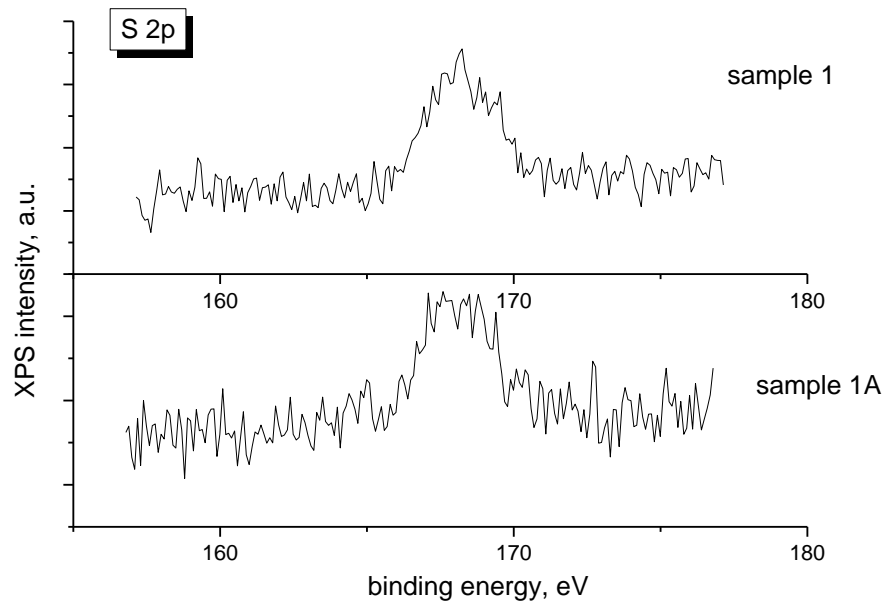
Figure 10. Comparative XPS spectrum for S in samples 1, 1A. Sample 1A has undergone chemical treatment, see Table 1.
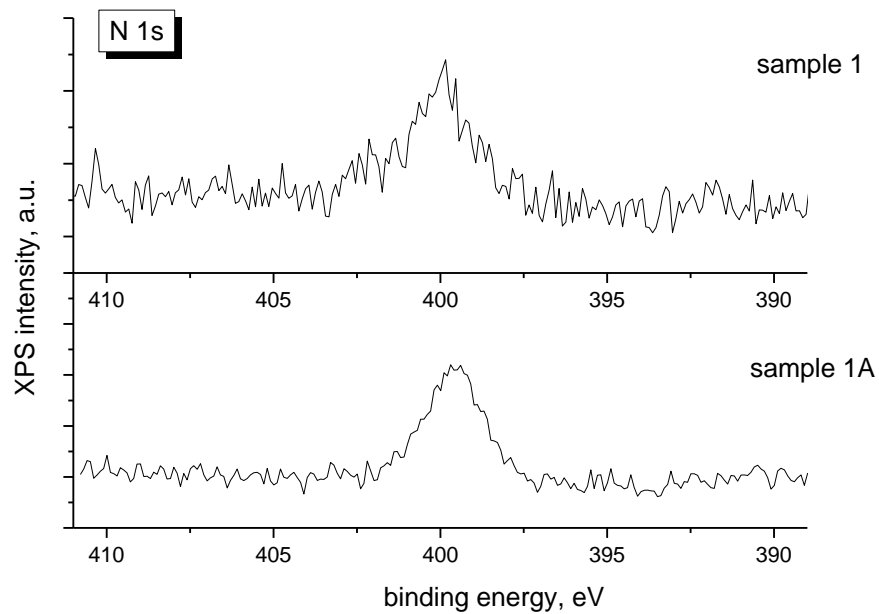

Figure 11. Comparative XPS spectrum for N in samples 1, 1A. Sample 1A has undergone chemical treatment, see Table 1
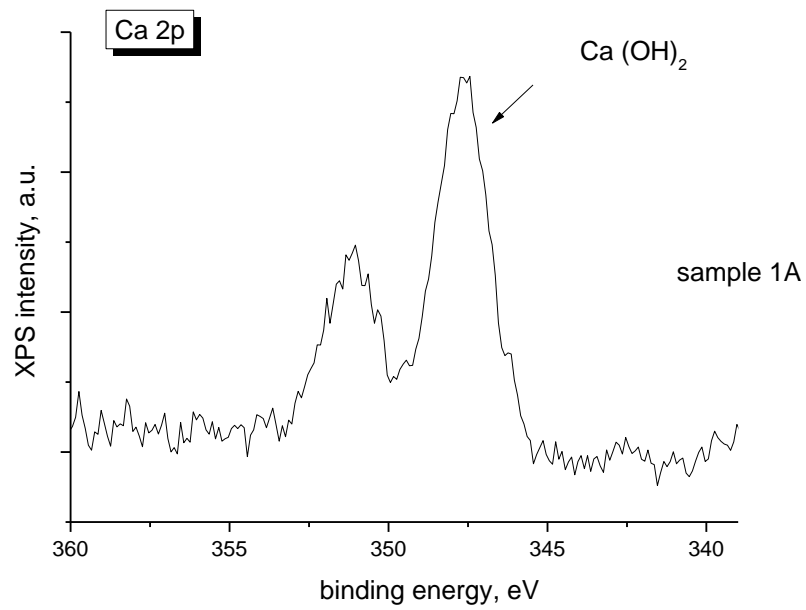
Figure 12. XPS spectrum for Ca in sample 1A. Sample 1A has undergone chemical treatment, see Table 1. The corresponding spectra for samples 4 and 4B are shown in Figures 13-16.
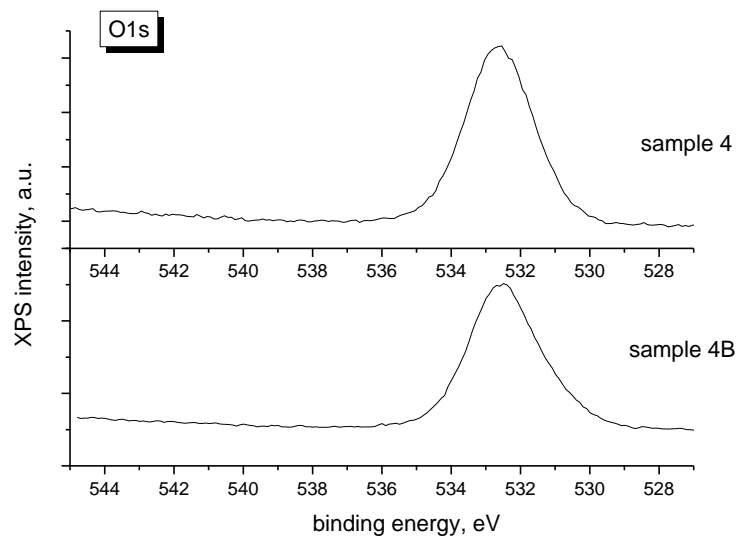

Figure 13. Comparative XPS spectrum for O in samples 4, 4B. Sample 4B has undergone chemical treatment, see Table 1.
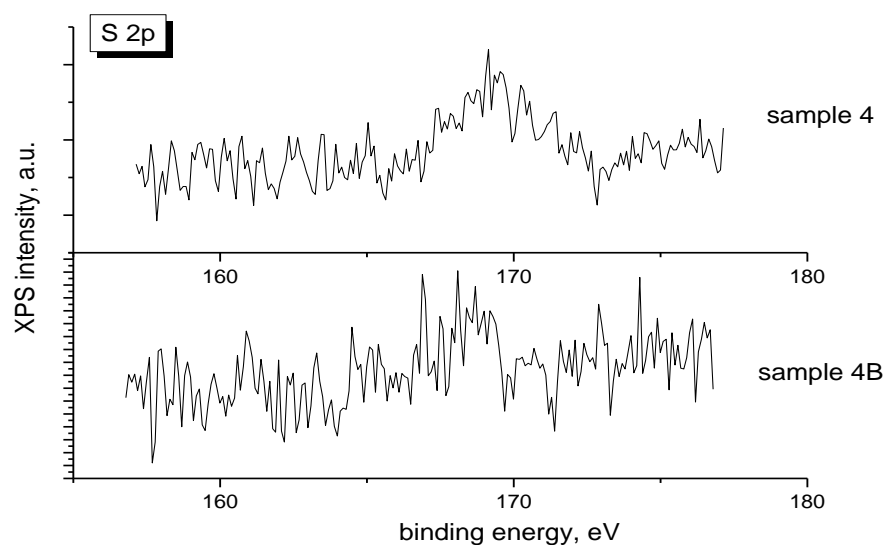
Figure 14. Comparative XPS spectrum for S in samples 4, 4B. Sample 4B has undergone chemical treatment, see Table 1

Table 4 shows the quantitative analysis of the data for all samples (1, 1A, 4, 4B). The ratios given above are atomic ratios (not mass ratios), i.e. ratio of atoms or moles. With the XPS technique the absolute amount of an element is not given, but just a ratio relative to some other reference elements.

Table 4. Quantitative analysis by XPS for samples 1, 1A, 4, 4B as elemental ratios.

Sample	Ca/C	N/C	S/C	O/C
1	---	0.0062	0.004	0.506
1A	0.02	0.0142	0.0032	0.416
4	---	0.0027	0.0025	0.346
4B	0.031	0.0083	---	0.562

5. DISCUSSION & CONCLUSION

First of all, we must note that the humidity percentages in all the samples are satisfactory (around 3440 cm^{-1}), which means that the storage conditions of the archival material ensure the humidity of 2%-3% that the international literature for preservation provides of records (Mavrantonis et al., 2022; Moropoulou et al., 2001). The treatment with $Ca(OH)_2$ leads to a small increase in the crystalline area (1111 cm^{-1}) and a decrease in the amorphous (900 cm^{-1}) area (Figs. 1-4). Lignin does not show strong peaks in the 1.1A samples, 1B; 3, 3A, 3B, Fig. 1,3 (good quality papers) while there are peaks in samples 2, 2A, 4, 4A, 4B, Fig. 2,4

(poor quality papers) of lower intensity in the processed samples. Calcium carbonate ($CaCO_3$) appears with very intense peaks in the treated samples (less intense in those treated with MC (Fig. 1-4, 12, 16, Table 4). This means that the treated material has acquired a strong alkaline reserve, which is maintained for many years, able to deal with endogenous and exogenous agents degrading the cellulose chain. FTIR measurements are confirmed by XPS measurements.

The oxidized species of carbon, -CO, -C=O, -COOH, which play a dominant role in the degradation of the cellulose chain, are reduced in the samples treated with $Ca(OH)_2$, while in the samples treated with $Ca(OH)_2$ and MC there is a reduction only in terms of –COOH (Zghari et al., 2018; Zou et al., 1996a). And here there is agreement of FTIR and XPS measurements.

Of interest are the measurements in the XPS of nitrogen and sulfur (and by extension their oxides), two exogenous main degradation factors, whose peaks are very weakened, a fact that can be interpreted by the controlled preservation conditions of the archival material. Based on all of the above, we can say that the chemical treatment contributes to improving the chemical composition of the cellulose, inactivating several degradation factors, strengthening its crystalline areas, consequently improving the micromechanical properties of the archival paper material (Brandis et al., 1997; Zervos et al., 2010; Moropoulou et al., 2001).

ACKNOWLEDGEMENTS

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