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A procedure for identifying cellulose fibers in paper artifacts

Differentiating between flax, hemp and cotton

Maja Kostadinovska and Zorica Jakovleska Spirovska
Conservation and Restoration Laboratory
National and University Library "St. Clement of Ohrid"
Skopje, Republic of Macedonia
maja.kostadinovska@live.com, zorica@nubskedu.mk

Travis Taylor
Conservation Department
National Archives of Australia
Canberra, Australia
travis.taylor@naa.gov.au

Abstract—**A rapid and minimally interventive procedure for the identification of different cellulose fibers using a combination of optical microscopy and ATR-FTIR spectroscopy from a micro-size sample was proposed. In this study, historic paper artifacts of unknown composition (4 Islamic manuscripts, 4 Old Slavonic manuscripts, 3 printed books and 1 graphite artwork on paper) were chosen. Seven paper samples of known composition (abaca, bagasse, cotton, esparto, eucalyptus, gampi and kozo) have been taken for comparative analysis. In order to identify the cellulose fibers, samples were stained with Herzberg and Graff 'C' stain and examined with optical microscopy. The historic papers consisted mainly of rags, but ground wood, chemical softwood and oriental fibers (kozo) were also identified with microscopy. Infrared spectra were captured for rag samples in order to differentiate between flax, hemp and cotton fibers. Identification of each of the celluloses is possible with the applied vibrational method in the range of 4000 – 550 cm^{-1}. ATR-FTIR spectra on the cellulose fibers indicated that the studied sheets consisted either of flax, cotton or hemp present singly, but also in various combinations of these fibers. This agreed fully with the historical fact that the studied samples were rag papers.**

Keywords- cultural heritage, historic papers, fibers, identification, microscopic analyses, FTIR, spectroscopy

I. INTRODUCTION

Ongoing research efforts at the Laboratory for Conservation and Restoration at the University Library "St. Clement of Ohrid" in Skopje consist of developing methods for the identification of paper fibers. Knowing the fiber content in the paper support of rare manuscripts and old historic books can often enhance the understanding of an artist's work, its visual qualities, and help to select appropriate conservation treatment and techniques. The introduction and usage of some fibers, but also sizing agents, fillers and coatings in the manufacturing process are known [1,2]. Therefore, it is possible, at times, to establish the earliest date or period of the manufacture of an artifact [3]. Specific fibers and types of paper are sometimes more commonly utilized in certain countries or regions assisting in establishing the provenance of an artifact [4-6]. Different fibers have different chemical and physical properties, including, but not limited to: lignin content, morphology, color, absorbency and dimension. Knowledge of these properties may help in predicting how a paper artifact will react to specific treatments (for example: wetting, bleaching, deacidification).

In a recent literature review by Debra Carr et al. [7] on the identification methods of vegetable textile fibers (more commonly known as plant or cellulose fibers), the important implications of accurate identification (for authentication, cultural information and development of treatment protocols) for numerous conservation specializations is discussed in detail. The advantages and disadvantages of the methods, but also general and specific diagnostic features for each of the fibers, are discussed. Despite availability of different methods, distinguishing between bast fibers (flax, hemp, jute, ramie, kozo, mitsumata, gampi) is not easily done. Among the testing techniques available in a forensic lab [8,9], infrared spectroscopy equipped with an Attenuated Total Reflectance (ATR) sampling device is a very attractive method for paper characterization, especially because it allows non-destructive analyses of the sheet's surface [10]. Identification by IR is accomplished by either assigning chemical groups to the peaks in a spectrum or inferring the chemical formula of the sample, but also by comparing the spectrum to those of known compounds and making identification by the best match [11].

The aim of this study is to discriminate 12 historic paper artifacts using a combination of micro-destructive and nondestructive methods, such as microscopy and Fourier Transform Infrared (FTIR) spectroscopy. The ultimate goal of this work would be to set up an FTIR spectral database for diagnostic purposes of cellulose paper fibers.

II. MATERIALS AND METHODS

A. Materials

1) Specimens

Twelve historic paper artifacts have been chosen for this investigation: 4 Islamic manuscripts, 4 Old Slavonic manuscripts, 3 printed books and 1 graphite artwork on paper (Table I).

TABLE I. ARTIFACTS DESCRIPTION

Artifact	Description
1	Islamic manuscript written in Arabic script "Aš-Šifā' bi / fī ta'rīf huqūq al-Mustafā" (MSA II 743), Year: 1173AH /1759AD
2	Islamic manuscript written in Arabic script "Zubdat al-I'rāb" (MSA II 909), Year: 1126AH /1714AD
3	Islamic manuscript written in Arabic script "Without Title" (OMCA II 1726), year unknown
4	Islamic manuscript written in Ottoman Turkish script "Hulviyât-ı Şerîf" (OMCT III 86), year unknown
5	Old Slavonic manuscript written in church-Slavonic and Macedonian "Liturgical Collection" (NUB Ms.165), 1880-1900
6	Old Slavonic manuscript "Kruševo Octoechos" (IMK Ms.1), 1450-1475 and restoration interventions in 1700-1800
7	Old Slavonic manuscript "Liturgical Collection of chronicles, scriptures, etc." (IMK Ms. 2), 1575-1600 and 1680-1700
8	Old Slavonic manuscript "Elected gospels of Prohor Pčinjski" (GBO Ms.1), 1575-1600 and restoration interventions in 2000
9	Printed book written in Slavonic Cyrillic script "Menology for May" (R_MM), 1705 and restoration interventions in unknown time
10	Printed book written in Slavonic Cyrillic script "The Bible" (R_BI), 1822
11	Printed book written in Slavonic Cyrillic script "Mirror" (O_MI), 1816
12	Graphite artwork "Invader", part of a series of drawings on cardboard by Borko Lazeski for the monumental work "Fresco of the NOB", 1956

2) Authentic (reference) samples

For the purpose of this investigation 7 paper samples of known composition (Table II) were obtained by Travis Taylor, paper conservator, National Archives of Australia. The authentic samples were used as reference samples for comparative analysis.

TABLE II. REFERENCE SAMPLES DESCRIPTION

Sample	Description
1	Abaca (Manilla Hemp), half stuff from Twinrocker handmade paper, Indiana, USA
2	Bagasse, from Canefields multipurpose copy paper
3	Cotton, half stuff from Twinrocker handmade paper, Indiana, USA
4	Esparto, from the 1956 book of Esparto paper produced by the Association of Makers of Esparto Papers
5	Eucalyptus, Australian from the Shoalhaven mill in NSW
6	Gampi, from a stationer in Kyoto, Japan
7	Paper mulberry (Kozo), conservation paper from Paper Nao

B. Methods

In this work all the samples were prepared following the same procedure with both the reference samples and samples that has been removed from historic paper being analyzed by optical microscopy with staining, and infrared spectroscopy.

1) Preparation of fiber samples (pulp)

In order to breakdown the specimens (paper artifacts) and reference paper samples into loose fibers, first they were cut into tiny pieces (fragments) and then placed in a small beaker with distilled water on a hot plate to heat till boiling. The water was then decanted off and the residual fibers were transferred to a 20 ml test tube with fresh distilled water and were shaken vigorously until the paper fragments were completely separated into individual fibers. Some specimens, which could not be disintegrated by distilled water, were additionally subjected to the same procedure using a solution of 1% sodium hydroxide. After decantation of the sodium hydroxide solution, the sample was washed two times with distilled water followed by the addition of 0.05 N hydrochloric acid to stand for about several minutes and then again washed with distilled water several times to remove all residual acid. After this treatment the samples were dispensed into a test tube with fresh distilled water as were the other specimens. Sodium hydroxide (pellets) and hydrochloric acid (fuming 37%) were purchased from Merck (Darmstadt, Germany) and were of analytical grade. This particular method was used because of its similarity to the TAPPI T 401 Standard Test Method for Fiber Analysis in Paper and Paperboard [12] and because fibers in most papers in this way can be separated from the binder and filler material.

2) Optical (light) microscopy

a) Staining techniques

A sample of 0.5 ml fiber suspension from each specimen and reference sample was taken for microscopic examination, placed on a microscope slide in water and then heated until dry. Iodine stains, Herzberg and Graff 'C' were applied to produce fiber specific colors on the fibers for identification.

b) Instrumentation

An optical microscope YS100 (Nikon Instruments Inc.), equipped with a mechanical stage (155 mm wide x 134 mm deep), fixed oculars of 10x and 4 achromat objectives with different magnification (4X, 10X, 40X and oil immersion 100X), was used to observe coloring of fibers produced by micro-chemical reaction. A total of 100X magnification is necessary for staining, so the operations were carried out with 4x (N.A.0.10, W.D.25mm) and 10x (N.A.0.25, W.D.5.6mm) objective lenses.

3) Infrared spectroscopy

a) Sample preparation for spectral shots

A sample of 1 ml fiber suspension was dried on clean Whatman filter paper sheets at room temperature and ambient conditions and then subjected to infrared spectroscopy analysis.

b) Instrumentation

An infrared spectrometer FTIR Perkin-Elmer 2000, equipped with a Golden Gate single reflection ATR accessory (Series Mkll) having a standard universal monoreflection composite ZnSe/Diamond crystal fixed at incident angle at 45°, was used to record pulp samples. A background scan of clean ATR crystal was acquired over the range of 4500-100 cm^{-1} with 128 scans before scanning the samples. The spectral region spanned from 4000-550 cm^{-1} with a nominal resolution of 4 cm^{-1}. Each of ATR-FTIR spectra obtained for pulp samples is the average of 64 individual scans collected at room temperature and humidity. Spectra were recorded and evaluated using Spectrum control and processing software Version 5.0.1. The ATR effect and atmospheric contributions to background noise were corrected by the Spectrum software automatically.

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The obtained experimental spectra were first manipulated in software Grams32 [13] by converting them into absorbance mode to perform multipoint baseline correction in 8 points. Normalization and peak calculations of FTIR spectra were done using Spekwin32 software [14]. Data for wavelength and peak absorbance were exported to Excel for final processing. The identification of some paper components was done by comparing the main features of the obtained spectra with those of selected standards and, in their absence, with published spectra [15-19]. This method was chosen because attenuated total reflectance is applied to samples where the composition of the surface needs to be measured and it is especially useful when the sample is soft, such as the dried pulp samples, because it can achieve good contact with the crystal of the ATR objective.

III. Results and Discussion

A. Fiber staining and microscopic examination

A total of 15 pulp samples collected from 12 original and 3 restoration paper samples were prepared and tested using the fiber staining methods. Six distinct pulps could be identified in the historic artifacts by microscopic examination: ground wood (Artifact 12), unbleached raw and well cooked softwood (Artifact 5), raw sulfate softwood (Artifact 11), bleached softwood or hardwood (restoration paper in Artifact 9), paper mulberry (kozo) mixed with unbleached softwood chemical pulp (restoration paper in Artifact 8) and pulp of rag fibers (flax, hemp or cotton) in all other samples.

Ground wood and raw softwood were easily identified by coloring of the fibers in yellow and yellow-greenish hue, respectively, whereas bleached softwood and hardwood could not be distinguished because they generally produce the same coloring of the fibers with both stains. In the case of restoration paper in Artifact 8, the oriental kozo fibers were identified with the help of reference samples (Fig.1). The coloring of the kozo with a red hue can be confused with rag fibers (flax, hemp, cotton), but the presence of long rectangular associated cells with a blue shade (Fig.1d) lead to the unambiguous identification. Fibers in all other samples (Artifacts 1, 2, 3, 4, 6, 7, 8, 9 and 10) stained in red shade color with Herzberg stain, which suggests that the papers were made of rags. The results of the fiber identification and possible fiber sources are summarized in Table III.

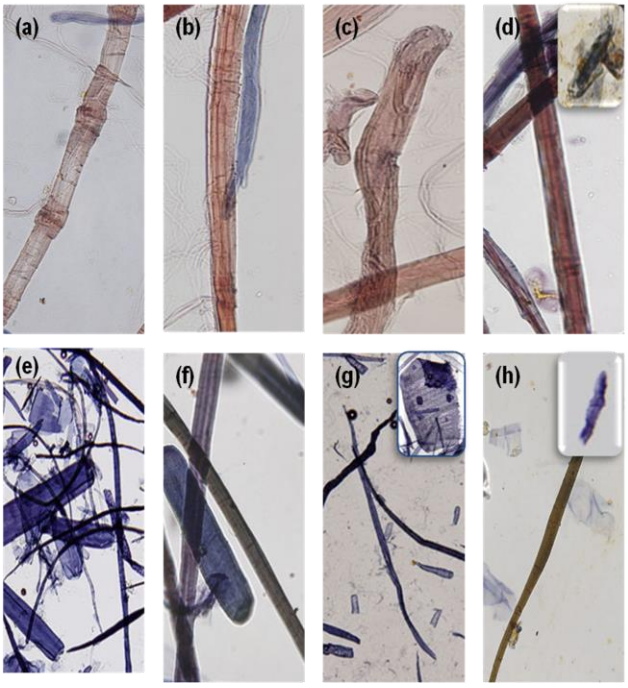

Figure 1. Microscopic morphological features and associated cells of the stained fibers in reference samples: (a) Flax, (b) Hemp, (c) Cotton, (d) Kozo, (e) Bagasse, (f) Abaca, (g) Eucaluptus and (h) Gampi. Available from Oriental Papermaking Fibres online database (http://www.culturalconservation.unimelb.edu.au/PapermakingFibres/)

According to historical records, the raw materials used in papermaking through the centuries (1276 until 19th century) were rags from used textiles exclusively. Thus, our expectations, based on artifacts dating (for those we had information), that most of the samples (at least 7) will turn out to be rag papers was confirmed.

In order to identify whether the origin of the textile fiber was flax, hemp or cotton, microscopic slides with reference cotton fibers (Sample 3, Table II) were examined with both stains. Conclusive results could not be produced by color

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TABLE III. RESULTS OF FIBER IDENTIFICATION BY STANING METHODS

Artifact No.	Pulp Sample	Date (AD)	Stained Color		Possible Fiber Sources
			Herzberg	Graff 'C'	
1	MSA II 743	1173AH /1759AD	Carmine Red	Peach Red	Flax, Hemp or Cotton Rags
2	MSA II 909	1126AH /1714AD	Carmine Red	Peach Red	Flax, Hemp or Cotton Rags
3	OMCA II 1726	Unknown	Carmine Red	Peach Red	Flax, Hemp or Cotton Rags
4	OMCT III 86	Unknown	Carmine Red	Peach Red	Flax, Hemp or Cotton Rags
5	NUB Ms.165	1880-1900	Blue Gray	Yellow and Purple Gray	Unbleached raw and well cooked softwood
6	IMK Ms. 1 (original)	1450-1475	Carmine Red	Carmine Red	Flax, Hemp or Cotton Rags
	IMK Ms.1 (restoration)	1700-1800	Carmine Red	Peach Red	Flax, Hemp or Cotton Rags
7	IMK Ms. 2	1575-1700	Carmine Red	Peach Red	Flax, Hemp or Cotton Rags
8	GBO Ms.1 (original)	1575-1600	Carmine Red	Peach Red	Flax, Hemp or Cotton Rags
	GBO Ms.1 (restoration)	2000	Carmine Red (Type 1)	Dark Red (Type 1)	Kozo (Type 1)
			Blue Purple (Type 2)	Pale Orange Green (Type 2)	Unbleached softwood (Type 2)
9	R_MM (original)	1705	Carmine Red	Peach Red	Flax, Hemp or Cotton Rags
	R_MM (restoration)	Unknown	Orange Red	Purple Red	Bleached softwood or hardwood
10	R_BI	1822	Carmine Red	Peach Red	Flax, Hemp or Cotton Rags
11	O_MI	1816	Olive Grey	Pale Yellow Green	Raw sulfate softwood
12	Invader	1956	Yellow	Yellow	Ground wood

comparison as they all color in red shades and their morphological features (Fig.1a, b and c) may have disappeared after basic treatments in manufacturing of cloths, and thereafter of paper. A trial to differentiate between flax, hemp and cotton has been made by undertaking further analysis of the paper samples by FTIR spectroscopy.

B. ATR-FTIR

Figure 2 shows the spectra of all pulp samples of the historic papers, which microscopically have been found to contain either flax, hemp or cotton fibers. A general study of the spectra confirms that the papers are made up of pulped rags, shown by the presence of the absorption bands in the fingerprint region of cellulose (~ 897, 1030, 1055, 1105, 1155 and 1200 cm^{-1}, [20]) and by the low absorbency at 1505–1510 cm^{-1} and ~ 1595 cm^{-1} for lignin (a polymer that indicates the use of ground wood, [21]). A further indication that the use of ground wood is ruled out in these samples was that all spectra did not contain bands at 1730 cm^{-1} produced by oxidation of cellulose (oxicellulose), but also because bands around 1735 cm^{-1}, indicative of non-conjugated carboxyl groups of cellulose, were present in some spectra [15,22].

Although we expected sizing material and fillers to be washed out by the preparation procedure, two types of fillers were identified: sulfates (~ 1150 and 670 cm^{-1}) [23], in some cases present singly, and calcium carbonate (~ 1425, 874, 712 cm^{-1}) [24], the latter particularly evident in artifacts 2, 3, 4 and 7, but also present in artifacts 6 and 8. Regarding the sizing in these samples, bands of Amide I, II and III (~ 1644, 1550, 1316 cm^{-1}) [25] are present in all of the artifacts, which indicates the use of gelatin. Alum escapes FTIR analysis because the most intense peak around 1105 cm^{-1} overlaps with cellulose bands in the fingerprint region [26], but still the use of alum is not excluded as the presence of sulfates was confirmed.

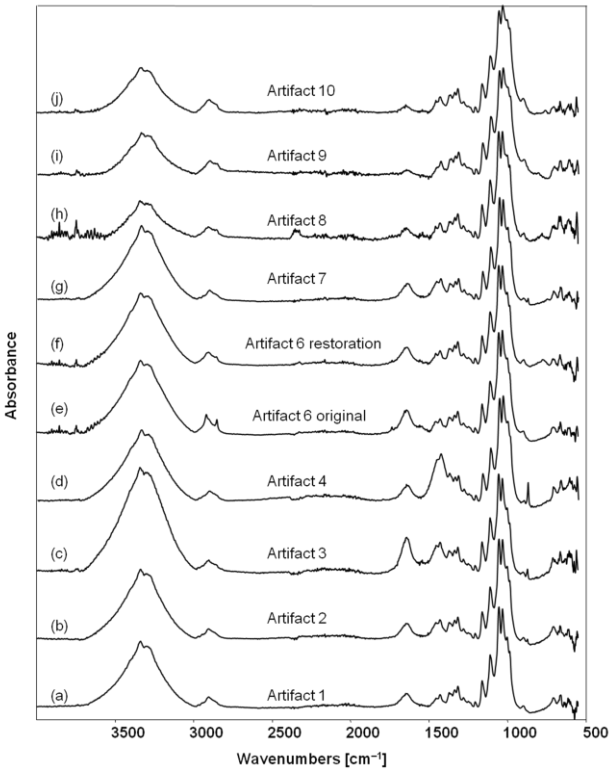

Figure 2. ATR-FTIR spectra of pulp samples from historic paper artifacts

The study of cellulose bands in FTIR spectra in order to differentiate between flax, hemp and cotton fibers in analyzed historic paper artifacts has shown that possible differing fiber source can be predicted through variations of the following assignments in spectra:

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(1) Asymmetric out-of-phase ring stretch in β-glycoside (C_1–O–C_4) bond (895–900 cm^{-1})
(2) C–O stretch in primary (~ 1030 cm^{-1}) and secondary (~ 1055 cm^{-1}) alcoholic groups of cellulose
(3) C=C stretch in lignin aromatic rings at 1505–1510 cm^{-1} and ~ 1595 cm^{-1}.
(4) Asymmetric (~ 2918 cm^{-1}) and symmetric (~ 2850 cm^{-1}) CH_2 stretch in long alkyl chains for waxes and pectin.

Thus, maximum 19 variations based on the type and quantity of fiber contained in the sample are possible. In this study, eight patterns become apparent:

- Pattern 1: Cotton (~ 896, 1054, 1506 and 2902 cm^{-1});
- Pattern 2: Cotton > Hemp (~ 901, 1055, 1506 and 2902 cm^{-1});
- Pattern 3: Hemp > Cotton (~ 897, 1031, 1506 and 2901 cm^{-1});
- Pattern 4: Flax (~ 898, 1032, 1511, 2850 and 2917 cm^{-1});
- Pattern 5: Flax = Cotton (~ 896, 1056, 1511, 2853 and 2903 cm^{-1});
- Pattern 6: Flax = Cotton > Hemp (~ 896, 906, 1056, 1511, 2852 and 2905 cm^{-1});
- Pattern 7: Flax > Hemp (~ 898, 1031, 1512, 2854 and 2897 cm^{-1});
- Pattern 8: Hemp (~ 900, 1030, 1506, 2889 cm^{-1}).

The mathematical symbol ">" denotes that the individual fiber content falls in the order from left to right, where as the symbol "=" denotes equal content of fiber species.

The most important ATR bands detected for flax and hemp fibers in the IRUG database [27] and pulp sample of reference sample 3 (Cotton, Table II) [28] are presented in Table IV.

All the bands discussed above and their assignments related to the components and possible fibers present in the analyzed historic paper artifacts are summarized in Table V.

TABLE IV. ATR-FTIR BANDS FOUND FOR FLAX, HEMP AND COTTON

Flax[a]	*ATR Band [cm^{-1}]*	3350	2906	2849	1511	1155	1109	1057	1035	/	897
	Ai/At	0,710	0,140	0,100	0,020	0,350	0,680	1,000	0,800	/	0,040
Hemp[b]	*ATR Band [cm^{-1}]*	3336	2892	/	1505	1155	1100	1059	1034	/	901
	Ai/At	0,640	0,170	/	0,060	0,450	0,650	1,000	0,820	/	0,080
Cotton[c]	*ATR Band [cm^{-1}]*	3339	2902	/	1506	1161	1110	1055	1032	1001	898
	Ai/At	0,964	0,128	/	0,096	0,315	0,573	1,000	0,972	0,731	0,053

a. ICB00058 Flax fiber; Cargille; 2-E; PMA; tran; reference material. Available at: http://www.irug.org/jcamp-details?id=606
b. ICB00054 Hemp fiber; Cargille; 3-E; PMA; tran; reference material. Available at: http://www.irug.org/jcamp-details?id=1107
c. Pulp sample from reference sample No.3 (Table II)

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TABLE V. ATR-FTIR BANDS AND THEIR ASSIGNMENTS RELATED TO COMPONENTS AND POSSIBLE FIBERS PRESENT IN HISTORIC PAPER ARTIFACTS

Wavenumber [cm^{-1}]	Assignment	Component	Artifact No.	1		2		3		4		6		6		7		8		9		10	
				MSA II 743		MSA II 909		OMCA II 1726		OMCT III 86		IMK Ms 1 Original paper		IMK Ms 1 Restoration paper		IMK Ms 2		GBO Ms.1		R_MM		R_BI	
				ATR band [cm^{-1}]	Ai/At [ab]	ATR band [cm^{-1}]	Ai/At	ATR band [cm^{-1}]	Ai/At	ATR band [cm^{-1}]	Ai/At	ATR band [cm^{-1}]	Ai/At	ATR Band [cm^{-1}]	Ai/At	ATR band [cm^{-1}]	Ai/At	ATR band [cm^{-1}]	Ai/At	ATR band [cm^{-1}]	Ai/At	ATR band [cm^{-1}]	Ai/At
3500-3100	H-bonded OH stretch	Cellulose, free H_2O		3336	0,6622	3335	0,7019	3340	1,0000	3335	0,6765	3337	0,7429	3336	0,7544	3337	0,7322	3340	0,4201	3338	0,3932	3330	0,4411
~ 2918	Asym. CH_2 stretch in long alkyl chains	Waxes / Pectin		**2902**[c]	**0,1130**	**2902**	**0,1151**	**2902**	**0,1380**	**2901**	**0,0989**	**2917**	**0,2788**	**2903**	**0,2253**	**2903**	**0,1148**	**2905**	**0,2018**	**2897**	**0,1299**	**2899**	**0,1552**
~ 2850	Sym. CH_2 stretch in long alkyl chains											**2850**	**0,2351**	**2853**	**0,1852**			**2852**	**0,1777**	**2854**	**0,1048**		
~ 1735	C=O vibration in C(O)OH groups	Nonconjugated carboxyl groups of cellulose										1735	0,1715	1734	0,1532			1734	0,1322	1735	0,0208	1735	0,0490
1730	C=O vibration	Oxidation of cellulose																					
~ 1705-1710	Carbonyl/carboxyl vibration	Nonconjugated carboxyl groups of rosin; ageing band										1716	0,1658	1715	0,1553			1716	0,1288	1716	0,0152	1722	0,0505
~ 1644	Typical peptide C=O (Amide I band)	Animal glue or gelatin		1648	0,1482	1645	0,1685	1641	0,3491	1648	0,1620	1642	0,3185	1640	0,2694	1641	0,1786	1644	0,1947	1648	0,0487	1648	0,1080
~ 1635	Absorbed H_2O in cellulose	Intramolecular H_2O, conjugated C=O		1637	0,1468													1631	0,1816	1635	0,0413		
~ 1595	C=C stretch in aromatic rings	Lignin																1594	0,1363				
1546-1559	Typical peptide N–H (Amide II band)	Animal glue or gelatin		1550	0,0414	1558	0,0551	1542	0,1382	1563	0,0458	1559	0,1872	1558	0,1580	1558	0,0597	1541	0,1567			1542	0,0648
1525	Unassigned	/						1529	0,1138					1522	0,1380			1529	0,1300			1527	0,0530
1505-1510	C=C stretch in aromatic rings	Lignin		**1506**	**0,0300**	**1506**	**0,0752**	**1506**	**0,1323**	**1506**	**0,1488**	**1511**	**0,1527**	**1511**	**0,1368**	**1506**	**0,0832**	**1511**	**0,1339**	**1512**	**0,0276**	**1506**	**0,0460**
~ 1455	OH in plane bending	Cellulose		1455	0,1012	1456	0,1775	1455	0,2739	1455	0,3937	1456	0,2183	1457	0,2160	1456	0,1999	1458	0,2066			1456	0,1475
~ 1425	CH_2 bending ; asym. C-O stretch in $CaCO_3$	Cellulose; $CaCO_3$ (Calcite)		1429	0,1364	1430	0,2043	1429	0,3036	1427	0,4502	1429	0,2412	1429	0,2395	1428	0,2247	1430	0,2334	1426	0,1251	1428	0,1792
~ 1365	CH bending (deformation stretch)	Cellulose		1370	0,1565	1370	0,1786	1371	0,2247	1372	0,2668	1371	0,2559	1371	0,2581	1370	0,1790	1371	0,2452	1361	0,1506	1362	0,1973
~ 1335	OH in-plane bending	Cellulose		1335	0,1830	1335	0,2001	1335	0,2291	1336	0,2307	1337	0,2717	1335	0,2880	1335	0,1985	1335	0,2796	1335	0,1759	1335	0,2205
1315-1320	CHwagging; Typical peptide N–H (Amide III band)	Cellulose, Animal glue or gelatin		1315	0,2182	1316	0,2308	1316	0,2576	1316	0,2437	1316	0,3056	1316	0,3201	1316	0,2260	1316	0,3103	1316	0,2117	1316	0,2526
~ 1280	CH twisting (deformation stretch)	Cellulose		1280	0,1066	1280	0,1161	1280	0,1460	1280	0,1180	1280	0,2048	1280	0,2131	1280	0,1194	1280	0,2110	1279	0,1050	1279	0,1352
~ 1247	OH out-of-plane bending	Cellulose		1248	0,0704	1249	0,0771	1248	0,1044	1248	0,0726	1247	0,1747	1248	0,1795	1247	0,0814	1248	0,1717				
~ 1200	OH in-plane bending	Cellulose		1205	0,0653	1205	0,0704	1206	0,0869	1206	0,0583	1206	0,1651	1206	0,1730	1205	0,0761	1206	0,1623	1206	0,0540	1205	0,0881
~ 1155	Asym. ring breathing in β-glycoside (C_1–O–C_4) bond; Sulfates asym. valence vibration	Cellulose, Sulfates (SO_4^{2-})		1160	0,2741	1160	0,2832	1161	0,3073	1160	0,2636	1161	0,3691	1161	0,3725	1160	0,2941	1161	0,3876	1160	0,2972	1161	0,2969
~ 1105	Asym. in-plane ring stretch in β-glycoside (C_1–O–C_4) bond	Cellulose, Alum		1110	0,5285	1110	0,5276	1110	0,5307	1110	0,5058	1110	0,5637	1110	0,5866	1110	0,5268	1110	0,5935	1110	0,5442	1109	0,5475
~ 1055	C–O stretch in 2° alcoholic groups of cellulose	Cellulose		**1054**	**1,0000**	**1054**	**1,0000**	**1056**	**0,9384**	1054	0,9760	1056	0,9811	**1056**	**1,0000**	**1054**	**1,0000**	**1056**	**1,0000**	1055	0,9730	1053	0,9512
~ 1030	C–O stretch in 1° alcoholic groups of cellulose	Cellulose		1031	0,9803	1031	0,9942	**1032**	**0,8976**	**1031**	**1,0000**	**1032**	**1,0000**	1032	0,9965	1031	0,9806	1032	0,9994	**1031**	**1,0000**	**1030**	**1,0000**
~ 1000	C–O, C-H stretch	Cellulose, Starch		1001	0,7034	1001	0,7317	1001	0,6238	1001	0,7583	1001	0,7627	1001	0,7599	1001	0,7161	1001	0,8024	1000	0,8216	1001	0,8727
~ 985	C–O, C-H stretch	Cellulose		985	0,5676	985	0,5963	985	0,4833	985	0,6183	986	0,6355	986	0,6437	985	0,5821	985	0,7175	985	0,7339	984	0,9773
895-900	Asym. out-of-phase ring stretch in β-glycoside (C_1–O–C_4)bond	Cellulose		**896**	**0,0292**	**897**	**0,0338**	**900**	**0,0258**	**897**	**0,0093**	**898**	**0,1362**	**896**	**0,1593**	**902**	**0,0384**	**906**	**0,1401**	**898**	**0,1420**	**900**	**0,1654**
																		896	**0,1495**				
~ 875	Sym. C-O stretch of $CaCO_3$	$CaCO_3$ (Calcite)				873	0,1055	872	0,0530	872	0,1791					873	0,0354	875	0,1039				
~ 712	O-C-O bending (in-plane deformation)	$CaCO_3$ (Calcite)						711	0,1589	711	0,1388	712	0,1703			710	0,1066	712	0,2068				
~ 670	Sulfates bending vibration	Sulfates (SO_4^{2-})		659	0,1326	665	0,1450	663	0,2168	662	0,2011	663	0,2149	666	0,2043	667	0,1438	672	0,2887	665	0,1310	664	0,1382
	Possible Fiber Sources			Pattern 1 Cotton		Pattern 1 Cotton		Pattern 2 Cotton/Hemp		Pattern 3 Hemp/Cotton		Pattern 4 Flax		Pattern 5 Flax/Cotton		Pattern 2 Cotton/Hemp		Pattern 6 Flax/Cotton/Hemp		Pattern 7 Flax/Hemp		Pattern 8 Hemp	

a. Ai – Internal transmittance (energy loss by absorption of the medium itself)
b. At – Total transmittance is due to absorption, scattering, reflection, etc.
c. The ATR bands demonstrating different patterns are highlighted

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IV. CONCLUSION

The analyses performed on the pulp samples made it possible to conduct a complete characterization of the paper fibers in the historic artifacts at our disposal.

Microscopic analysis with staining techniques is useful in identifying the fibers in several classes: ground wood, chemical pulps, rag pulps and oriental papermaking fibers. The techniques are useful when fibers can be differentiated by their morphological characteristics, but at the same time complicated when it comes to distinguish fibers which have undergone treatments or are difficult to differentiate morphologically, such as between flax and hemp.

The ATR-FTIR analysis allowed the identification of the type of sizing and fillers as well as the raw materials used, thus making it possible to differentiate between rag paper from different origin (flax, hemp and cotton fibers) by revealing some characteristic FTIR patterns.

Good correlations between these two analytical methods were found for the studied samples. The methods are evaluated with respect to their capability to discriminate between celluloses and to the ease and feasibility of sample preparation.

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