

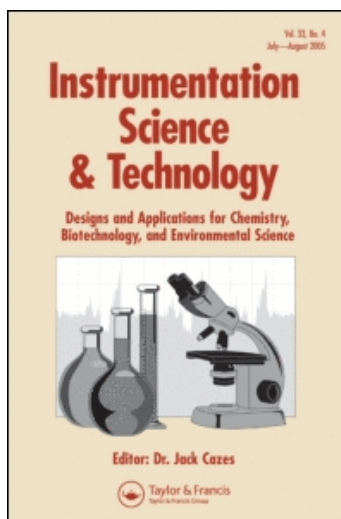
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SPECTRAL METHODS FOR HISTORICAL PAPER ANALYSIS: COMPOSITION AND AGE APPROXIMATION

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SPECTRAL METHODS FOR HISTORICAL PAPER ANALYSIS: COMPOSITION AND AGE APPROXIMATION

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□ *The research has been focusing on some connection between the chemical composition of the papers obtained by Fourier transform infrared (FTIR) spectroscopy and the nature of the fillers, determined by energy dispersion X-ray fluorescence (EDXRF) spectroscopy. The present paper corroborates the FTIR and EDXRF results obtained for some historical papers from books of the XIX-th and XX-th centuries, from private collections. These analytical results allowed a first approximation of technological paper composition and of the age determination of the samples. This analytical method can elaborate some properly methods for paper documents preservation, taking into account the aging and degradation processes of the historical paper.*

Keywords age determination, energy dispersion X-ray fluorescence (EDXRF), Fourier transform infrared (FTIR), paper composition, spectral analyses

INTRODUCTION

To understand the chemistry of a historical artifact, a restorer must analyze all of its elements, including the substrate, the fillers, the binders, and the degradation products. Knowing all the materials in a paper document can be also of great value for determining the most suitable methodology for restoring its damage or for preserving it against humidity,

This article is in memory of Professor George E. Bailuscu, Professor of Chemistry, Bucharest University, Bucharest, Romania.

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temperature, and light. Chemical analysis must be seen as a complement to the artistic study of a document.

It is well known that substances can be identified by their FT-IR spectra, typical for particular functional groups defined by specific frequencies and intensities in the spectra.^[1-4] The published results^[5-9] clearly demonstrate that FT-IR spectroscopy is an important tool for historical materials characterization.

The ageing of paper and cellulose has been extensively studied. This is not only to understand the mechanism behind the degradation, but also to develop methods for stopping or slowing it down in order to save paper-based cultural heritage world-wide. Research related to paper aging often leads to establishing new preservation activities and it also stimulates development of new analytical investigation methods.

Several years ago, voices have been raised concerning the poor quality and accessibility of papers stored in libraries, archives, and museums.^[10] One of the main causes of this fact is the change of the raw material of paper, from cotton to wood pulp.^[11,12] There are several treatises on the recipes for manufacturing traditional paper.^[13-15] Among the oldest filler compositions, ground bone ash, but also white lead, calcium carbonate, gypsum, powdered cattlebone, wax, zinc oxide, titanium dioxide, acrylic gesso, clay, kaolin, satin white, barium sulfate, calcium sulfate, calcium sulfite, and alum have been used.

These have been combined with the traditional binders such as starch, mucilage, and gums (Arabic gum), gelatin, and animal glues, such as hide glue and casein.^[16]

Until the end of the eighteenth century, white papers could only be made of white rags, as the only method of bleaching was the sun. In a sense, this was an advantage, as it prevented the deterioration of the paper by a bleaching agent, but there are other factors which had a negative effect on paper durability. After the discovery of chlorine (1774) and hypochlorite (1789), these chemicals were soon used as bleaching agents (1779), enabling colored materials to be used for the production of white papers, such as unbleached wood pulps.^[13-15]

As a sizing ingredient, alum has been known as one of the most important materials in the history of papermaking. The sizing of paper with rosin and alum was largely used since the beginning of the nineteenth century (about 1805). Then, at the beginning of the twentieth century (1900), the alum was substituted with aluminum sulfate $\text{Al}_2(\text{SO}_4)_3$, the so-called "papermaker's alum," a cheaper and more concentrated source of aluminum compounds. Alum is a potassium aluminum sulfate, $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, which contains iron, barium, magnesium, and sodium. The two major varieties employed in papermaking have not always been distinguished for their different properties. Aluminum sulfate, also called alum, often

contained varying proportions of silica, iron, and free sulfuric acid which could degrade the paper.^[13–15]

Since the late nineteenth century, alum has also been mentioned as a primary cause of paper degradation. Although both aluminum potassium sulfate and aluminum sulfate tended to introduce different impurities into paper, the negative effect of aluminum sulfate on paper degradation, overall, is more significant. The described changes in papermaking explain the poor durability of the papers.

The change from cotton to wood aggravated the problem, as wood cellulose has a lower degree of polymerization than cotton cellulose. Thus, due to degradation, chains in fact deteriorated faster according to their degree of polymerization, and wood fibers become brittle faster than cotton fibers.^[1–5]

The purpose of the present study is to use FT-IR and EDXRF spectrometry to establish the chemical composition of paper and its age. The main objective of this work is to develop a fast and accurate identification method for historic papers, reducing the sample pre-treatment, and providing direct FTIR measurement. FT-IR and EDXRF spectroscopy are very powerful analytical tools that can provide the structural and compositional information for organic and inorganic materials (components). Furthermore, for the characterization of cellulose, it is important to identify the nature of the fillers in the paper samples.

EXPERIMENTAL

Materials

Eight different types of papers from books of the XIX-th and XX-th centuries were used. The papers were delivered from private collections. The eight samples were codified as follows:

- M1 the sample from a French book, Paris, 1871;
- M2 the sample from a French book, Paris, 1913;
- M3 the sample from a Romanian book, Bucharest, 1914;
- M4 the sample from a French book, Paris, 1929;
- M5 the sample from a German book, Berlin, 1931;
- M6 the sample from a French book, Paris, 1935;
- M7 the sample from a Romanian book, Bucharest, 1888;
- M8 the sample from a Romanian book, Bucharest, 1889.

The samples were from the edges of the sheets, unwritten, and uncolored.

Different fillers were used for comparison: calcium sulfate dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; anhydrous calcium carbonate, CaCO_3 ; anhydrous barium sulfate, BaSO_4 ; kaolin, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$; aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$; zinc oxide, ZnO ; titanium dioxide, TiO_2 ; and talcum, $3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$. All the reagents were reagent grade (Merck, Germany).

Apparatus

The FT-IR sample spectra have been recorded as KBr pellets, with a Perkin Elmer Spectrum GX spectrometer while, for semi-quantitative compositional analysis of the samples, a spectrometer EDXRF PW4025 – MiniPal (Panalytical) was used.

Procedures

The FTIR spectra were recorded using a small quantity of scratched paper (0.5–1.0 mg) mixed with 150 mg KBr, in the following conditions: spectral range used was 4000 cm^{-1} to 400 cm^{-1} , the averaged spectrum was collected after 32 scans with a resolution of 4 cm^{-1} .

In order to measure the constituent elements directly by EDXRF on the edge of the sheet, the determination was carried out in a helium atmosphere, for 300 sec, at 30 kV, and automated amperage.

RESULTS AND DISCUSSION

FTIR analysis is considered “non-destructive” since the procedure does not alter the sample, thus allowing it to be used for subsequent analysis. In reality, a very small quantity of sample (0.5 up to 1.0 mg) was scratched from the edge of the papers. Furthermore, in order to better define the elemental composition of the papers, EDXRF has been performed.

Figures 1–5 present the FTIR spectra of standard microcrystalline cellulose (Figure 1), the eight paper samples (M1–M8, in Figures 2, 3, and 9), inorganic substances used as fillers (Figures 4 and 5), while Figure 6 presents an EDXRF spectrum for M3 paper.

In direct connection with the elemental analysis, the FTIR technique has been applied to some possible fillers (kaolin, calcium carbonate, calcium sulfate, barium sulfate, zinc oxide, titanium dioxide, talcum, and aluminum sulfate) already mentioned in the literature’s recipes for historical paper.^[14,15]

The first observation revealed that all paper samples showed similar FTIR profiles as the cellulose reference material profile.

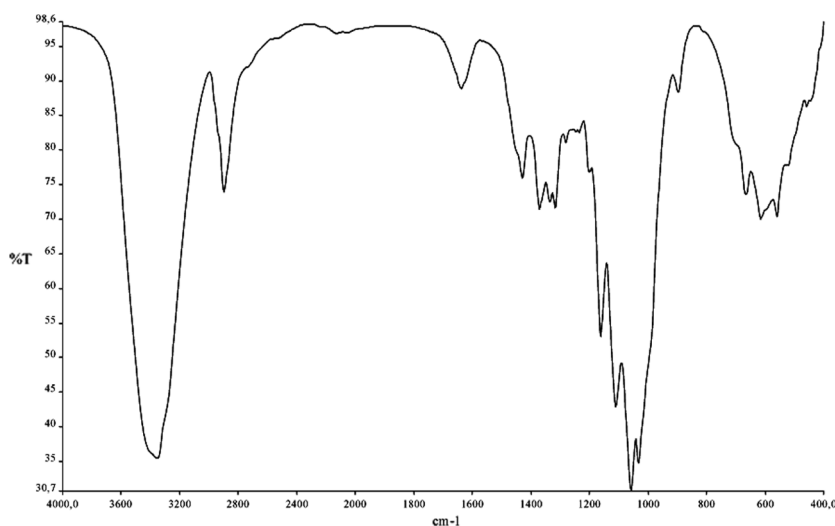


FIGURE 1 FTIR spectra of microcrystalline cellulose in KBr disk.

Cellulose's strong absorption region is between 1200 cm^{-1} and 950 cm^{-1} and the low absorption region is between 950 cm^{-1} and 600 cm^{-1} . The peaks from 900 cm^{-1} to 1200 cm^{-1} are associated with: $-\text{OH}$ absorption, 900 cm^{-1} ; $-\text{CH}$ absorption 1029 cm^{-1} ; $-\text{C}-\text{OH}$ absorption 1112 cm^{-1} ; $-\text{C}=\text{O}$ absorption 1165 cm^{-1} ; $=\text{CH}_2$ absorption 1200 cm^{-1} ; that are all groups in the glycosyl units of cellulose.^[17]

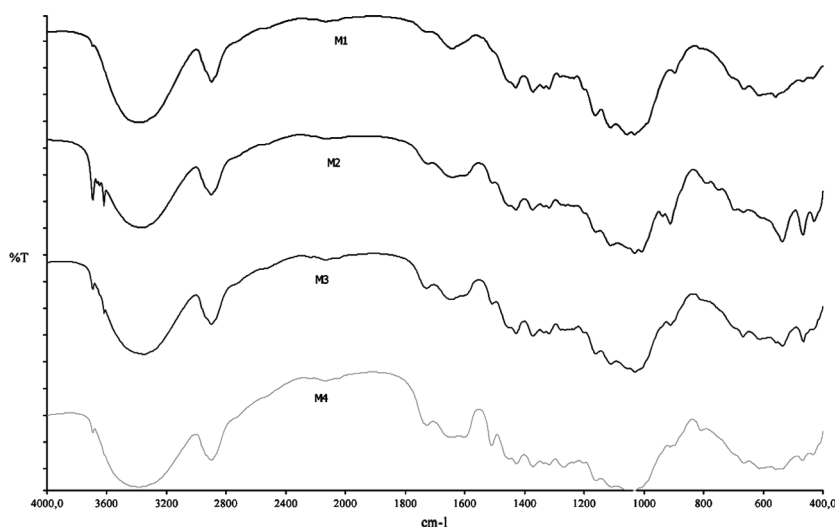


FIGURE 2 FTIR spectra of different types of papers in KBr disk. M1: M1 paper; M2: M2 paper; M3: M3 paper; M4: M4 paper.

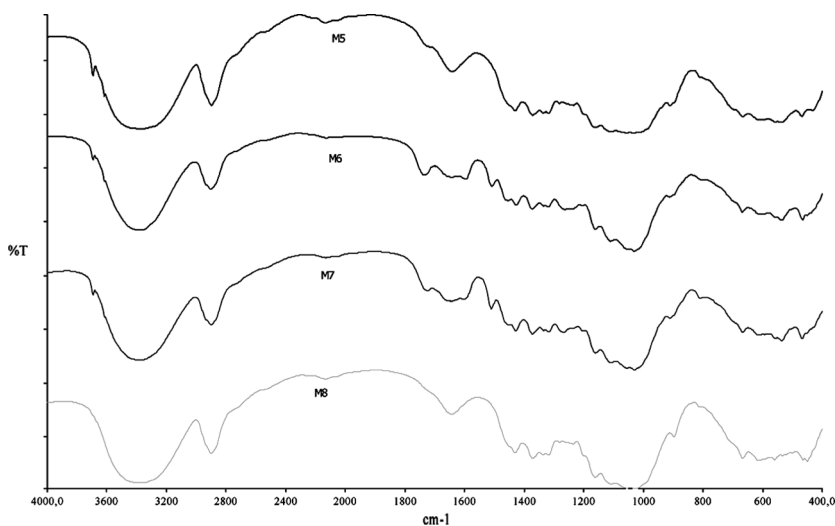


FIGURE 3 FTIR spectra of different types of papers in KBr disk. M5: M5 paper; M6: M6 paper; M7: M7 paper; M8: M8 paper.

At a fixed chemical structure, cellulose-based materials and their derivatives can differ from a physicomechanical, technological, and operational characteristics point of view. This is fully determined by the peculiarities of their physical structures. A change in the physical structure – the spatial arrangement of macromolecules and their components, intra- and

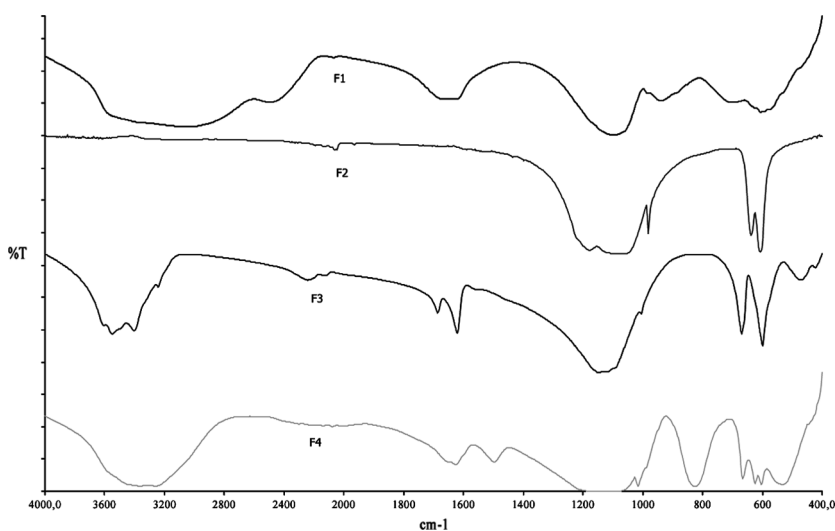


FIGURE 4 FTIR spectra of different types of sulfate fillers in KBr disk. F1: Aluminium; F2: Barium; F3: Calcium; F4: Ferrum.

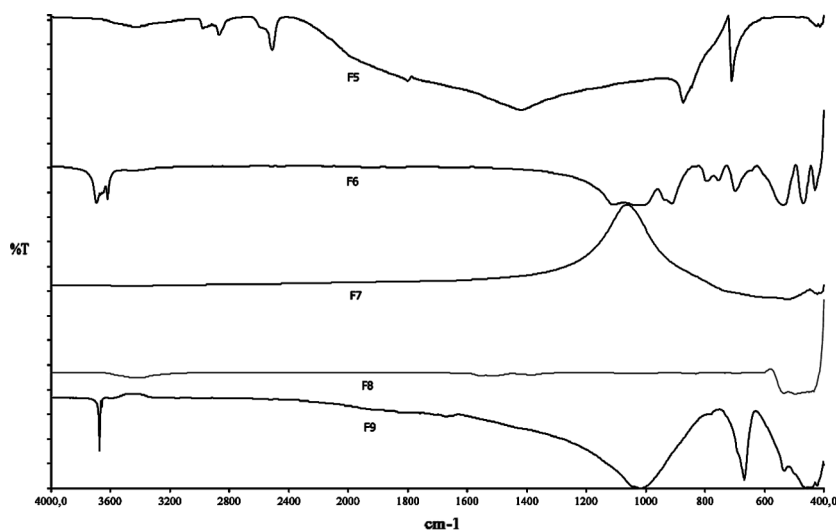


FIGURE 5 FTIR spectra of different types of fillers in KBr disk. F5: CaCO₃; F6: Kaolin; F7: TiO₂; F8: ZnO; F9: Talc.

inter-molecular interaction – is the main source of knowing the nature and the quality of the cellulose. For this reason, the intensity of the bands and the ratio among them are so different and they are different in the two examined paper samples.

Particularly interesting is the so called “fingerprint region” between 1000 cm⁻¹ and 1400 cm⁻¹ because this is the region characteristic of the cellulose, which is the main substance from the paper. In this area, the –CH₂–OH has strong absorbance and also the typical features of the

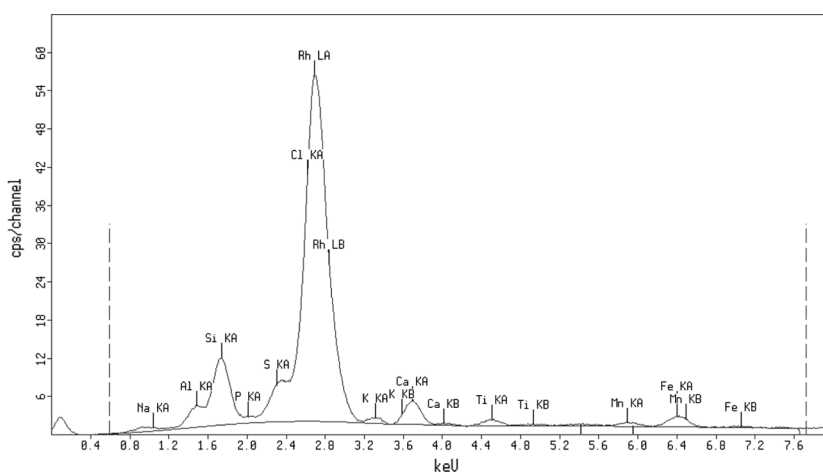


FIGURE 6 EDXRF spectra for M7 paper (similar results were obtained for all the samples).

aromatic rings belonging to lignin are present. It is well known that lignin accompanied the cellulose in the paper samples.^[18]

Also, FT-IR analysis exhibited a typical carbohydrate type spectrum for all the eight studied samples.

Additionally, with the fillers' nature, from the FTIR spectra of the book papers, it was possible to put into evidence the following remarks:

- a) the bands from 3690–3620 cm^{-1} and the strong band 469 cm^{-1} are attributed to an aluminum silicate component that might be kaolin.
- b) the bands from 1450–1320 cm^{-1} and 900–800 cm^{-1} are attributed to carbonate compounds.^[6]
- c) SO_4^{-2} strong asymmetric stretching from 1210–1040 cm^{-1} and 680–570 cm^{-1} has been a proof for the presence of sulfates in the samples.^[6,19]

Meanwhile, EDXRF analysis of the M1 to M8 papers showed the presence of various metals: Al, Ca, Na, Fe, and K being the most representative. Also, Cu, Zn, Mn, and Ti are present in some of the samples.^[18] Metals such as Ba, Mg, Co, and Ni are characteristic only of some of the samples. All of the papers contained Si as metalloid and Cl, S, and P as nonmetals. These components are reported as percents, but these are just relative percents, because the elemental analysis of organic C, H, N, and O was not effectuated yet. There are metals such as: Ca, Fe, Na, and Mn that are present in all types of samples. Contrarily, there are metals, for example, K, Ba, Mg, Cu, Zn, Ti, Co, and Ni that are present only in some papers.

TABLE 1 The chemical EDXRF composition of paper samples (%)

Element	M1	M2	M3	M4	M5	M6	M7	M8
Na	5	4	4	7	5	6	3	1
Mg	2	0	0	0	0	0	0	0
Al	17	29.6	19	17	11	14	16	7.3
Si	22.3	44.4	33	17	14	23.3	36.5	17.8
P	1.4	0.81	1.9	1.5	1.8	1.8	2.7	2.3
S	3.6	3.2	6.3	4.5	6.51	5.9	7.54	9.61
Cl	24	9.6	23.5	28.5	38.5	37.1	29	41.4
K	3.6	3.7	2.2	2.6	0	2.5	0.2	0
Ca	4.2	1.4	4.3	17.7	15.4	2.2	3.9	18
Mn	0.1	0.07	0.1	0.31	0.3	0.2	0.23	0.72
Fe	5.2	3.17	3.42	3.06	3.1	5.04	0.53	1.1
Cu	1	0.17	0.29	0.56	0.61	0.31	0	0.3
Zn	0.25	0.062	0	0.24	0.1	0.1	0	0
Ba	10.8	0	0	0	0	0	0	0
Ti	0	0.16	1.9	0	3.1	0.71	0.61	0.1
Co	0	0	0	0	0.2	0	0	0
Ni	0	0	0	0	0.2	0	0	0

The EDXRF results for M1 to M8 samples are summarized in Table 1.

As a direct connection with the elemental analysis, the FTIR technique has been applied to some possible fillers (kaolin, which is a hydrated aluminum silicate, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ or $\text{Al}_2(\text{OH})_4 \cdot \text{Si}_2\text{O}_5$; calcium carbonate, CaCO_3 ; calcium sulfate dihydrate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; barium sulfate, BaSO_4 ; zinc oxide, ZnO ; titanium dioxide, TiO_2 ; talcum, $3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$; aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), already mentioned in the literature's recipes for historical papers.^[6,19]

Also, we compared their FTIR spectra, shown in Figures 4 and 5, with database spectra of inorganic art materials.^[20] Such substances showed specific absorption bands: calcium carbonate (2515 cm^{-1} , 1795 cm^{-1} , 1430 cm^{-1} , and 875 cm^{-1}), calcium sulfate (3406 cm^{-1} , 1685 cm^{-1} , 1621 cm^{-1} , 1135 cm^{-1} , 1114 cm^{-1} , and 665 cm^{-1}), kaolin (3696 cm^{-1} , 3620 cm^{-1} , 912 cm^{-1} , and 468 cm^{-1}), barium sulfate (982 cm^{-1}), zinc oxide (438 cm^{-1}), titanium dioxide (539 cm^{-1}), talcum (1032 cm^{-1} , 669 cm^{-1}), and aluminum sulfate (3620 cm^{-1} , 1022 cm^{-1}), concluding that the historical artifacts contained these kinds of fillers, in good agreement with the literature references.^[6,19]

The assignment of the absorption bands specific for barium sulfate and aluminum sulfate to the paper samples was inconclusive because of the strong absorption of the organic groups from the cellulose.

These analytical results allowed a first approximation of the age and of technological manufacturing classification of the paper samples.

Calcium carbonate, which is a universal filler, is present in all eight samples, and it was used not only for its degree of whiteness, but also for its gloss. Its main advantage is that it does not decrease the mechanical properties of the paper, as the other fillers do.

The M1 sample has a high content of Ba in the presence of S, suggesting that barium sulfate is one of the fillers, which doesn't confer strength, but is important to whitening the paper because its degree of whiteness. The presence of this filler also suggests that the paper was manufactured before the end of the nineteenth century. In that period of time, alum was used for paper manufacturing; such fact explains the presence of Fe, Ba, Mg, Na, and K as impurities of alum. It is interesting to remark that the rest of the paper samples, M2 to M8, did not contain Mg, which indicates that talcum is not present as a filler. Talcum is soft and greasy, and was used to confer opaqueness and smoothness to the paper.

In sizing practice, alum was added to the gelatin size or, alternatively, was applied to paper separately after gelatin sizing. Both of these sizing methods are recorded in the early nineteenth century literature. The quality of the alum (as mainly determined by the extent of its contamination especially by Fe) and of the gelatin probably was more important in influencing the aging properties of papers than was the method of application.

Aluminum ammonium sulfate was an occasional substitute for aluminum potassium sulfate in paper sizing. This would be the explanation when elemental analysis of paper shows the presence of Al, but not of K, like in the samples M5 and M8.

At the beginning of the twentieth century, alum was substituted with aluminum sulfate $\text{Al}_2(\text{SO}_4)_3$, the so called “papermaker’s alum,” a cheaper and more concentrated source of aluminum compounds, but contaminated with great concentration of alumina, Al_2O_3 , silica, SiO_2 , Fe, and free sulfuric acid, H_2SO_4 . The presence of kaolin, which was the most used filler, with a high degree of whiteness, in all samples is put into evidence by FT-IR spectra. Because of these two fillers, the ratio between Al percents and Si percents and the S contents are so different in all samples. For instance, the S percent varies from 3,2 to 9,6%.

A similar remark could be made about Cl content, which varies from 9.6% for M2 to 41.4% for M8 (as relative percents). The presence of Cl isn’t only from chlorinated compounds, but also from hypochlorite used as bleaching agent.

The treatises on recipes for creating traditionally prepared paper indicate as filler, ground bone ash, which is primarily composed of calcium phosphate; this explains the presence of P in all papers. The amount of P varies from 0.81% in sample M2 to 2.7% in sample M7.

ZnO was used as whitening agent, and it is interesting to remark that it isn’t present in samples M3, M7, and M8, the papers manufactured in Romania, because in Romanian technology used TiO_2 for this purpose.

Cu is present in all samples except M7; its concentration varies from 0.17% in M2 to 1% in M1.

The most efficient filler due to its small particle dimensions, about 80 to 155 nm, is TiO_2 and although it was expensive, it was used because of its high degree of whiteness, i.e., over 98%. This filler is present only in M2, M3, M5, M6, and M7 papers.

The two metals, Co and Ni, are both present only in paper sample M5, in small amounts, 0.2%.

CONCLUSIONS

The FT-IR analysis of the samples from the ancient manuscripts clearly shows cellulose to be the major component of the sample. Despite the main goal of the IR characterization, few vibrations are identified rather approximately. Therefore, some comments regarding interpretation of IR spectra presented are fairly speculative. Consequently, the exact origin or history of same grouping is not exactly known. Though an exact identification of an artifact paper can not be entirely possible, due to the similarity of

spectra of different compounds, the general classification still remains the principal topic for investigation. The next goal is to identify as many types of fillers as possible, for historical paper, to establish a reliable method of preservation, and to evaluate the age of the paper.

REFERENCES

1. Neevel, J. Phytate: A potential conservation agent for the treatment of ink corrosion caused by iron gall inks. *Restaurator* **1995**, *16*, 143–160.
2. Thompson, J. *Manuscript Inks*; The Caber Press: Portland, Oregon, 1996; 343.
3. Calvini, P.; Franceschi, E.; Pallazi, D. Spectra of paper documents. A FTIR – deconvolution analysis. *Sci. Technol. Cult. Heritage* **1996**, *5*, 1–5.
4. Sistach, M.C.; Ferrer, N.; Romero, M.T. Fourier transform infrared spectroscopy applied to the analysis of ancient manuscripts. *Restaurator* **1998**, *19*, 173–186.
5. Arpino, P.; Moreau, J.P.; Oreuzbal, C.; Flieder, F. Gas chromatographic-mass spectrometric analysis of tannin hydrolysates from the ink of ancient manuscripts (XI-th to XVI-th century). *J. Chromatogr. A* **1977**, *134*, 433–439.
6. Espadaler, I.; Sistach, M.C.; Cortina, M.; Eljarrat, E.; Alcaraz, R.; Cabañas, J.; Rivera, J. Organic and inorganic components of manuscript inks. *Anales de Quim.* **1995**, *91*, 359–364.
7. Bulska, E.; Wagner, B.; Sawicki, M.G. Investigation of complexation and solid-liquid extraction of iron from paper by UV/VIS and atomic absorption spectrometry. *Microchim. Acta* **2001**, *136*, 61–66.
8. Sistach, M.C.; Gibert, J.M.; Areal, R. Ageing of laboratory iron-gall inks studied by reflectance spectrometry. *Restaurator* **1999**, *20*, 151–166.
9. Wagner, B.; Bulska, E.; Hulanicki, A.; Heck, M.; Ortner, H.M. Topochemical investigation of ancient manuscripts. *Fresenius' J. Anal. Chem.* **2001**, *369*, 674–679.
10. MacInnes, A.; Barron, A.R. A spectroscopic evaluation of the efficacy of two mass deacidification processes for paper. *J. Mater. Chem.* **1992**, *2*, 1049–1056.
11. Ramezeilles, C.; Quillet, V.; Calligaro, T.; Dran, J.C.; Pichon, L.; Salomon, L. PIXE elemental mapping on original manuscripts with an external microbeam. Application to manuscripts damaged by iron-gall ink corrosion. *Nuclear Instrum. Meth. Phys. Res., B: Beam Interact. Mater. Atoms* **2001**, *181*, 681–687.
12. Mansfield, J.R.; Attas, M.; Majzels, C.; Cloutis, E.; Collins, C.; Mantsch, H.H. Near infrared spectroscopy reflectance imaging: A new tool in art conservation. *Vibr. Spectros.* **2002**, *28*, 59–66.
13. Brückle, I. The role of alum in historical papermaking. *Abbey Newslett.* **1993**, *17*, 53–57.
14. Hunter, D. *Papermaking, The History and Technology of an Ancient Craft*; Dover Publications: New York, 1978.
15. Rudin, B. *Making Paper, A look into the History of an Ancient Craft*; Rudins, Vallingby: Sweden, 1990.
16. Calvini, P.; Gorassini, A. The degrading action of iron and copper on paper. A FTIR – deconvolution analysis. *Restaurator* **2002**, *23*, 205–221.
17. Zhabankov, R.G.; Firsov, S.P.; Buslov, D.K.; Nikonenko, N.A.; Marchewka, M.K.; Ratajczak, H. Structural physico-chemistry of cellulose macromolecules. Vibrational spectrum and structure of cellulose. *J. Molec. Struct.* **2002**, *614*, 117–125.
18. Ion, R.M.; Ion, M.L.; Niculescu, V.I.R.; Dumitriu, I.; Fierascu, R.C.; Florea, G.; Bercu, C.; Serban, S. Spectral analysis of original and restaured ancient paper from a Romanian Gospel. *Romanian J. Phys.* **2008**, *53*, 781–791.
19. Zotti, M.; Ferroni, A.; Calvini, P. Microfungal biodeterioration of historic paper: Preliminary FTIR and microbiological analyses. *Intl. Biodeter. Biodegrad.* **2008**, *62*, 186–194.
20. Kepa, C.; Maite Pérez, M.D.; Rodríguez-Laso, G.; Madariaga, J.M. Peer Reviewed: FTIR Spectra Database of Inorganic Art Materials. *Anal. Chem.* **2003**, *75*, 214A–221A.