SPECTRAL METHODS FOR THE AGE APPROXIMATION AND MANUFACTURING CLASSIFICATION OF HISTORICAL PAPER DOCUMENTS

Sanda Maria DONCEA[1], Rodica Mariana ION[2],
Radu Claudiu FIERASCU[3], Elena BACALUM[4]

Abstract. *The present review corroborated the infrared Fournier transform spectroscopy (FTIR) with energy dispersion X-ray fluorescence spectroscopy (EDXRF) both applied for some historical paper samples, unprinted and unwritten, from books of the end of the XIXth century and of the beginning of the XXth century, delivered from private collections. The research has been focusing on some connection between the chemical composition of the paper samples obtained by FTIR spectroscopy and the fillers nature (that find in the papers), determined by EDXRF spectroscopy. These analytical results allowed a first approximation of the age determination and of technological manufacturing classification of the paper samples. Prospective, this analytical tackling, create the premises to elaborate some properly methods for paper documents preservation taking account to ageing and degradation processes of the historical paper.*

Key words: paper, spectral analyses; FTIR; EDXRF; age determination

1. Introduction

The ageing of paper and cellulose has been studied for about last hundred years. 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 word-wide.

Research related to paper ageing often leads to establishing new preservation activities. It also stimulates development and application of new analytical tools. At present, many studies focusing on research of paper ageing and deterioration due to internal and external factors.

Since 150 years ago, voices have been raised concerning the poor quality and accessibility of papers stored in libraries, archives and museums. One of the main causes of this fact is attributed to the change of the raw material of paper, from cotton pulp to wood pulp [2,18]. There are several treatises on the recipes for creating traditionally prepared paper. Among the oldest fillers compositions is

---

[1] Valahia University of Targoviste
[2] Eng., Prof., PhD, Valahia University of Targoviste, Roumania, Senior Researcher ICECHIM, Roumania
[3] Valahia University of Targoviste
[4] Valahia University of Targoviste

ground bone ash, but also white lead, calcium carbonate, gypsum, powdered cuttlebone, 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 (like gum Arabic), gelatin and animal glues, such as hide glue and casein [2,18].

There is a great deal of literature on the history and technology of papers manufacturing.

Until the end of the XVIIIth 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. Other factors which had a negative effect on paper durability followed. 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 as, for example, unbleached wood pulps.

As a sizing ingredient, alum has been of the most important materials in the history of papermaking. The sizing paper, with rosin and alum, was largely used since the beginning of the XIXth century (approximately 1805) and then at the beginning of the XXth century (1900) the alum was substituted with aluminum sulfate $Al_2(SO_4)_3$, the so called “papermaker’s alum”, a cheaper and more concentrated source of aluminum compounds. Alum is a potassium aluminum sulfate, $KAl(SO_4)_2 \cdot 12H_2O$, that also 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, was often contained varying proportions of silica, iron and free sulfuric acid, which could deteriorate the paper [18].

Since the late XIXth century, the 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 lower degree of polymerization that 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.

But the main degradation mechanism of paper is due to different ink ingredients, causing acidic hydrolysis or cellulose catalysis [1,2,3,4,5].

2. Materials and methods. Experimental part

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 also be of great value for determining the most suitable methodology for restoring its’ damage or for preserving it against humidity, temperature and light. Chemical analysis must be seen as a complement to the artistic study of a document.

FTIR and EDXRF spectroscopy are very powerful analytical tools that can provide the structural and compositional information of organic and inorganic materials (components). Beside the characterization of the cellulose, it is important to know the fillers’ nature in the paper samples.

The research has been focusing on same connections between the chemical composition of the paper sample obtained by FTIR spectroscopy and fillers nature determinate by EDXRF spectroscopy.

It’s well known, that substances can be identified by their IR spectra, which show certain bands, i.e. characteristic vibrations, typical for particular functional groups defined by specific frequencies and intensities in IR spectra [8,9]. The published results [10,11,12,13,14], clearly demonstrate that FT-IR spectroscopy is an important tool for the historical materials characterization.

All FTIR analysis is considered technically, “non-destructive” since the procedure does not alter the sample, allowing it to be used for subsequent analysis. In reality, very small quantity of sample (0.5 or 1 milligram) was scratched out from the edge of the sheets, unwritten and uncolored.

The FT-IR technique has been first tested on eight different types of paper samples from books of the end of the XIXth century and of the beginning of the XXth century, delivered from private collections. The eight samples were codified as fallows:

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

Furthermore, for identification and semi-quantitative determination of the elements from the samples, energy dispersion X-ray fluorescence spectroscopy (EDXRF) has been used, in order to better define the elemental composition of the papers.

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, aluminum sulfate) already mentioned in the literature's recipes for historical paper (references) [2,3,12,13].

The **FT-IR** samples spectra have been recorded as KBr pellet, with a Perkin Elmer Spectrum GX spectrometer, in the following conditions: range 4000 cm^{-1} to 400 cm^{-1}, 32 scan, resolution 4 cm^{-1}, gain 1. A small quantity of scratched paper samples (0,5 to 1 mg), from the edges of the sheets, unwritten and uncolored, was mixed with KBr.

A spectrometer **EDXRF** PW4025 – MiniPal – Panalytical was used for semi-quantitative compositional analysis of the paper samples, for determination the constituent elements, directly on the edge of the sheet of the paper, unwritten and uncolored, in helium atmosphere, 300 sec, 30 kV, automated amperage.

The **FT-IR** spectra of the above mentioned fillers' etalon, have been recorded as KBr pellet, with the same Perkin Elmer Spectrum GX spectrometer, in the same conditions: range 4000 cm^{-1} to 400 cm^{-1}, 32 scan, resolution 4 cm^{-1}, gain 1. The quantity of fillers' etalon (0,5 to 1 mg), was mixed with KBr.

3. Results and discutions

The first observation revealed that all paper samples showed similar FTIR profiles with the cellulose reference material profile. Cellulose strong absorption region lies between 1200 cm^{-1} and 950 cm^{-1} and the low absorption region is between 950 cm^{-1} and 600 cm^{-1}.

FT-IR analysis of papers exhibited a typical carbohydrate type spectrum for all the eight studied samples. The peaks from 900 cm^{-1} to 1200 cm^{-1} were associated with: – OH absorption, 900 cm^{-1}, – CH absorption 1029 cm^{-1}, C– OH absorption 1112 cm^{-1}, C = O absorption 1165 cm^{-1}, = CH_2 absorption 1200 cm^{-1}, that are all groups in the glycosyl units of cellulose.

At a fixed chemical structure, cellulose-based materials and its derivatives can differ from physico-mechanical, technological and operational characteristics point of view. This is fully determined by the peculiarities of their physical structure. A change in the physical structure – the spatial arrangement of macromolecules and their components, intra- and 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 CH_2-OH has strong absorbance and also the typical features of the aromatic rings belonging to lignin are present. It is well-known that lignin accompanied the cellulose in the paper samples [20].

In addition 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}, were attributed to an aluminum silicate component that might be kaolin.

b) the bands from 1450-1320 cm^{-1} and 900-800 cm^{-1} [11] were attributed to carbonates compounds.

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 (Schrader, 1995; Zotti et al., 2008), as shown in Figure 1.

Meanwhile, EDXRF analysis of the M1 to M8 papers, showed the presence of different metals: Al, Ca, Na, Fe and K being the most representative. Also, Cu, Zn, Mn and Ti are present in the samples [20].

The metals like: Ba, Mg, Co and Ni are characteristic only of some of the samples. All the papers contained Si as metalloid and Cl, S and P as nonmetals. These components are reported as percent, but these are just relative percents, because the elemental analysis of organic C, H, N and O was not effectuated yet.

The EDXRF results for M1 to M8 samples are summarized in the Table 1a and Table 1b.

Table 1a. The chemical EDXRF composition of paper samples M1 …… M8 in %

	Paris	Paris	Bucuresti	Paris	Berlin	Paris	Bucuresti	Bucuresti
	1871	1913	1914	1929	1931	1935	1888	1889
	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

Table 1b. Comparative presentation of chemical EDXRF composition for paper samples M1….M8

	M1	M2	M3	M4	M5	M6	M7	M8
Ba	■							
S	■	■	■	■	■	■	■	■
Al	■	■	■	■	■	■	■	■
Si	■	■	■	■	■	■	■	■
P	■	■	■	■	■	■	■	■
K	■	■	■	■		■	■	
Cl	■	■	■	■	■	■	■	■
Ca	■	■	■	■	■	■	■	■
Fe	■	■	■	■	■	■	■	■
Na	■	■	■	■	■	■	■	■
Mg	■							
Ti		■	■		■	■	■	■
Cu	■	■	■	■	■	■		■
Mn	■		■	■	■	■	■	■
Zn	■			■	■	■		
Co					■			
Ni					■			

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, $Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$ or $Al_2(OH)_4{\cdot}Si_2O_5$, calcium carbonate, $CaCO_3$, calcium sulfate dihydrate $CaSO_4{\cdot}2H_2O$, barium sulfate, $BaSO_4$, zinc oxide, ZnO, titanium dioxide, TiO_2, talcum, $3MgO{\cdot}4SiO_2{\cdot}H_2O$, aluminum sulfate, $Al_2(SO_4)_3{\cdot}18H_2O$) already mentioned in the literature's recipes for historical paper [15,16,19].

Also, we compared their FTIR spectra from database spectra of Inorganic Art Materials [22], to those of Merck, Darmstadt, Germany, filler etalons as: calcium sulfate dihydrate, $CaSO_4{\cdot}2H_2O$, anhydrous calcium carbonate, $CaCO_3$, anhydrous barium sulfate, $BaSO_4$, kaolin, $Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$, aluminum sulfate, $Al_2(SO_4)_3{\cdot}18H_2O$, zinc oxide, ZnO, titanium dioxide, TiO_2, talcum, $3MgO{\cdot}4SiO_2{\cdot}H_2O$. Such substances showed specific absorption bands: calcium carbonate (2515cm^{-1}, 1795 cm^{-1}, 1430 cm^{-1} and 875 cm^{-1}), calcium sulfate (3406cm^{-1}, 1685cm^{-1}, 1621cm^{-1} 1135 cm^{-1}, 1114 cm^{-1} and 665 cm^{-1}) kaolin (3696cm^{-1}, 3620cm^{-1}, 912cm^{-1}, 468cm^{-1}), barium sulfate (982 cm^{-1}), zinc oxide (438 cm^{-1}), titanium dioxide (539 cm^{-1}), talcum (1032cm^{-1}, 669 cm^{-1}) and aluminum sulfate (3620 cm^{-1}, 1022 cm^{-1}), concluding that the historical artifacts contained this kind of fillers, in good agreement with the literature references [21], as shown in Figure 2.

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

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

Calcium carbonate, which is an 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 doesn't decreasing the mechanical properties of the paper, like the others fillers do.

The M1 sample has an high content of Ba, corroborate with the presence of the S, suggested that the barium sulfate is one of the filler, which doesn't confer strength but is important to whitening the paper, because its degree of whiteness. The presence of this filler, also suggest that the paper was manufactured before the ending of the XIX th century. In that period of time, alum was used of paper manufacturing, facts that explain 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, fact that means talcum isn't present as filler. Talcum is soft and greasy, and was used to confer opaqueness and smooth 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 XIXth 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 should be the explication 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 XXth century the alum was substituted with aluminum sulfate $Al_2(SO_4)_3$, 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 percents varies from 3,2 to 9,6%.

A similar remark could be done about Cl content that 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 indicated as filler ground bone ash, which is primarily composed of calcium phosphate, and that 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. There are metals like: Ca, Fe, Na and Mn that are present in all type of samples. Contrariwise, there are metals like: K, Ba, Mg, Cu, Zn, Ti, Co and Ni that are present only in same papers.

The ZnO was used as whitening agent, and is interesting to remark that it isn’t present in samples M3, M7 and M8, the papers manufactured in Romania.

The Cu is present in all samples except M7, and its concentration varies from 0,17% in M2 to 1% in M1. The most efficient filler dew to its small particles dimensions, about 80 to 155 nm, is TiO_2 and although it was expensive, it was used because its highest degree of whiteness, 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 one paper sample M5, in small amounts 0,2% for the first, respectively 0,2% for the second.

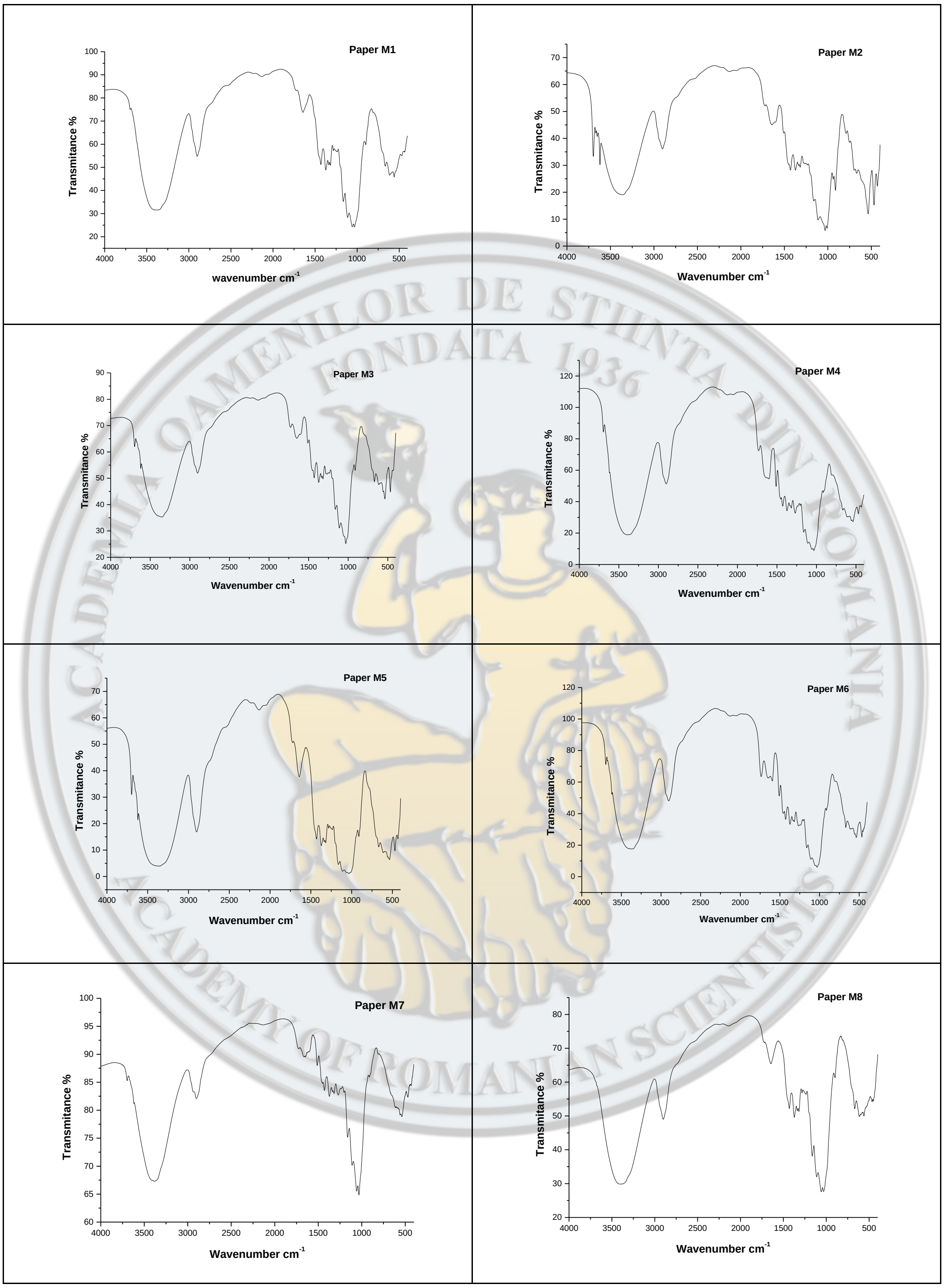
Paper M1
Transmitance %
100
90
80
70
60
50
40
30
20
4000
3500
3000
2500
2000
1500
1000
500
wavenumber cm^{-1}
Paper M2
Transmitance %
70
60
50
40
30
20
10
0
Wavenumber cm^{-1}
Paper M3
Transmitance %
90
80
70
60
50
40
30
20
Wavenumber cm^{-1}
Paper M4
Transmitance %
120
100
80
60
40
20
0
Wavenumber cm^{-1}
Paper M5
Transmitance %
70
60
50
40
30
20
10
0
Wavenumber cm^{-1}
Paper M6
Transmitance %
120
100
80
60
40
20
0
Wavenumber cm^{-1}
Paper M7
Transmitance %
100
95
90
85
80
75
70
65
60
Wavenumber cm^{-1}
Paper M8
Transmitance %
80
70
60
50
40
30
20
Wavenumber cm^{-1}

Fig. 1.

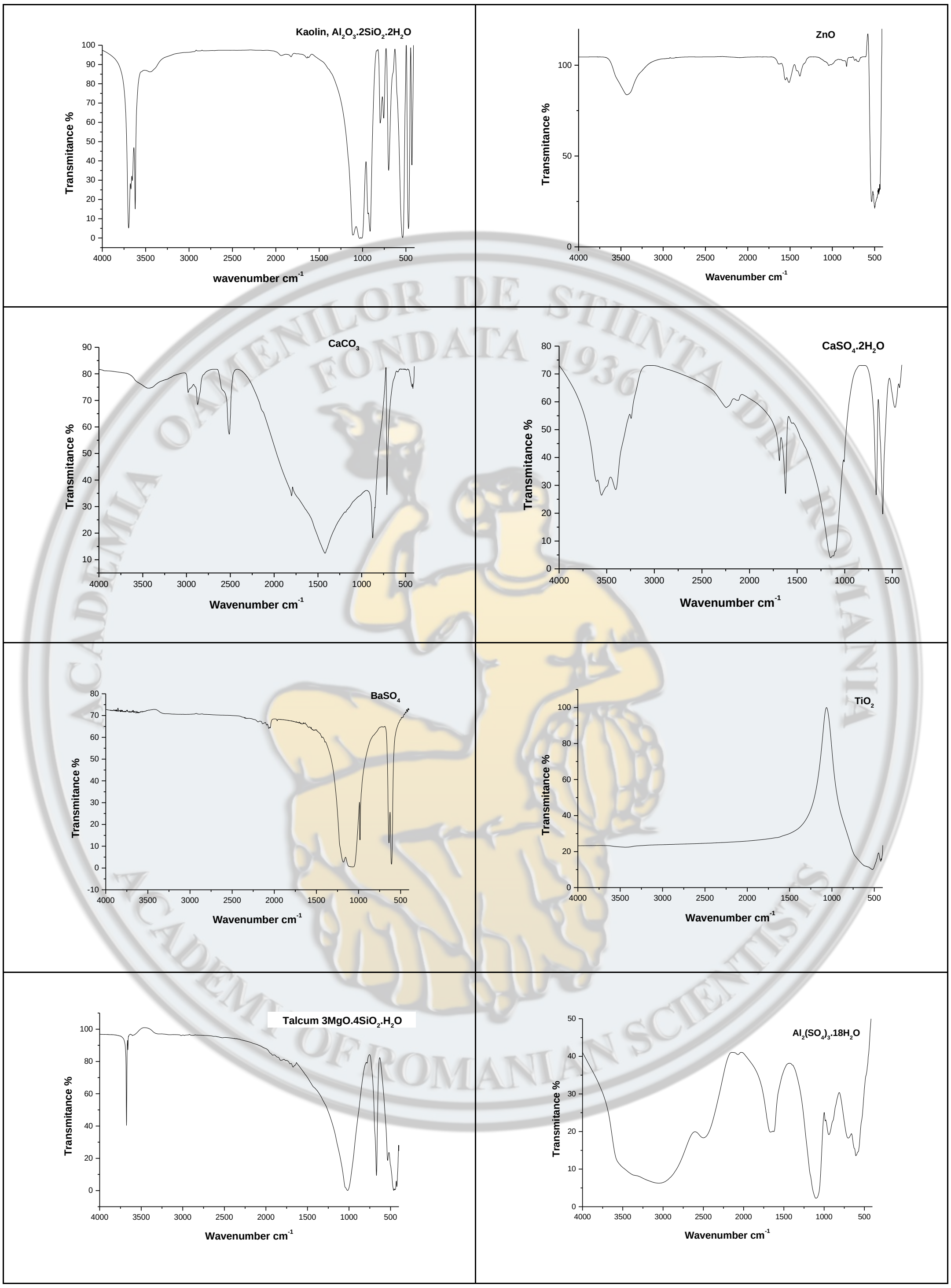
Kaolin, Al_2O_3.2SiO_2.2H_2O
Transmitance %
wavenumber cm^{-1}
ZnO
Transmitance %
Wavenumber cm^{-1}
$CaCO_3$
Transmitance %
Wavenumber cm^{-1}
$CaSO_4$.2H_2O
Transmitance %
Wavenumber cm^{-1}
$BaSO_4$
Transmitance %
Wavenumber cm^{-1}
TiO_2
Transmitance %
Wavenumber cm^{-1}
Talcum 3MgO.4SiO_2.H_2O
Transmitance %
Wavenumber cm^{-1}
$Al_2(SO_4)_3$.18H_2O
Transmitance %
Wavenumber cm^{-1}
4000
3500
3000
2500
2000
1500
1000
500

Fig. 2.

Conclusions

The FT-IR analysis of the samples from the ancient manuscript clearly shows the cellulose being the major component of the sample. Despite the main goal of the IR characterization was achieved, few vibrations are identified rather approximately. Therefore some comments regarding interpretation of IR spectrum 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 the conservation. The next goal is to identify as many types of filler as possible, for historical paper, and to establish a reliable method of preservation.

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

REFERENCES

[1] MacInnes, A., Barron, A. R., 1992, A spectroscopic evaluation of the efficacy of two mass deacidification processes for paper, Journal of Materials Chemistry, 2 substrates A: 1049.

[2] Calvini, P., Franceschi, E., Pallazi, D., 1996, Spectra of Paper Documents. A FTIR – Deconvolution Analysis, Science and Technology for Cultural Heritage, 5: 1-5

[3] Sistach, M. C., Ferrer, N., Romero, M. T., 1998, Fourier Transform Infrared Spectroscopy Applied to the Analysis of Ancient Manuscripts, Restaurator, 19: 173-186

[4] Ramezeilles, C., Quillet, V., Calligaro, T., Dran, J. C., Pichon, L., Salomon, L., 2001, PIXE elemental mapping on original manuscripts with an external microbeam. Application to manuscripts damaged by iron-gall ink corrosion, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, Volume 181, No. 1,: 681-687.

[5] Calvini, P., Gorassini, A., 2002, The Degrading Action of Iron and Copper on Paper. A FTIR – Deconvolution Analysis, Restaurator, 23: 205-221

[6] Gibbs, P.J., Seddon, K.R., Brovenko, N.M., Petrosyan, Y.A., Barnard, M., 1997, Identification of Indigoid Natural Dyestuffs Used in Art Objects by HPLC, Analytical Chemistry, 69: 1965–1969

[7] Mansfield, J. R., Attas, M., Majzels, C., Cloutis, E., Collins, C., Mantsch, H. H., 2002, Near infrared spectroscopy reflectance imaging: A new tool in art conservation, Vibrational Spectroscopy, 28: 59-66

[8] Neevel, J., 1995, Phytate: A Potential Conservation Agent for the Treatment of Ink Corrosion caused by Iron Gall Inks, Restaurator, 16: 143-160

[9] Thompson J., 1996, Manuscript Inks, The Caber Press, Portland, Oregon, 343 p

[10] Arpino, P., Moreau, J. P., Oreuzbal, C., Flieder, F., 1977, Gas chromatographic-mass spectrometric analysis of tannin hydrolysates from the ink of ancient manuscripts (XIth to XVIth century), Journal of Chromatography A Elsevier, 134: 433-439

[11] Espadaler, I., Sistach, M.C., Cortina, M., Eljarrat, E., Alcaraz, R., Cabañas, J., Rivera, J., 1995, Organic and inorganic components of manuscript inks, Anales de Quimica, 91: 359-364

[12] Bulska, E., Wagner, B., Sawicki, M. G., 2001, Investigation of complexation and solid-liquid extraction of iron from paper by UV/VIS and atomic absorption spectrometry, Microchimica Acta, 136: 61-66

[13] Sistach, M. C., Gibert, J. M., Areal, R., 1999, Ageing of Laboratory Irongall Inks Studied by Reflectance Spectrometry, Restaurator, 20: 151-166

[14] Wagner, B., Bulska, E., Hulanicki, A., Heck, M., Ortner, H. M., 2001, Topochemical investigation of ancient manuscripts, Fresenius' Journal of Analytical Chemistry, 369: 674-679

[15] Righini, G., Segre, A. L., Mattogno, G., Federici, C., Munafo, P. F., 1998, An X-ray photoelectron spectroscopic study of ancient paper , Natturwiesenschaften, 85: 171-175

[16] Nakamoto, K., 1986, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley-Interscience, p 390, New York

[17] Schrader, B., 1995, Infrared and Raman Spectroscopy: Methods and Applications, Wiley-VCH, p 7-61, Weinheim

[18] Brückle, I., 1993, The Role of Alum in Historical Papermaking, Abbey Newsletter, Vol. 17, No. 4: 53-57.

[19] Zotti, M., Ferroni, A., Calvini, P., 2008, Microfungal biodeterioration of historic paper: Preliminary FTIR and microbiological analyses, International Biodeterioration and Biodegradation, 62 (2) : 186-194

[20] Ion, R. M., Ion, M. L., Niculescu, V. I. R., Dumitriu, I., Fierascu, R. C., Florea, G., Bercu, C., Serban, S., 2008, Spectral analysis of original and restaurated ancient paper from a Romanian Gospel, Romanian Journal of Physics, 53: 781-791, Bucharest

[21] Zhbankov, R. G., Firsov, S. P., Buslov, D. K., Nikonenko, N. A., Marchewka, M. K., Ratajczak, H., 2002, Structural physico-chemistry of cellulose macromolecules. Vibrational spectrum and structure of cellulose, *Journal of Molecular Structure*, 614: 117-125

[22] e-VISART database