COMPARATIVE FTIR TECHNIQUES
APPLIED TO HISTORICAL PAPERS

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Abstract. Comparative FTIR techniques: transmission spectroscopy in KBr and diffuse reflectance spectroscopy (DRIFT) in KBr have been applied to unwritten and inked historical papers. Advantages and drawbacks of each technique have been discussed, regarded to the spectra interpretation.
In all cases the cellulose remains the major component of the samples, even in inked and damaged papers and only small discrepancies are observed between written and unwritten papers. An important parameter was the reproducibility of the measurements and the small influences have been pointed out.
Key words: FTIR techniques, historical paper, transmission spectroscopy, DRIFT

1. INTRODUCTION

Inks define a liquid or viscous substance, varied color, containing drying oils, polymerized oil, albumin and dyes and used to write, to print, to stamp, or to engrave the paper.

In the second half of the XIX-th century and early XX-th century, was used for printing iron-gall ink, carbon ink and aniline ink.

Gall ink or iron-gall ink was prepared from a mixture of vitriol ($FeSO_4 \cdot 7H_2O$), which is ferrous sulfate heptahydrate, gallic acid (extracted from galls tree), a viscous medium, with the role of a binder, gum Arabic and water.

Galls grow on the trunk of the Quercus infectoria oak which is abundant in the Middle East. Aleppo galls were most suitable for the gallotannic acid they contain, for the iron-gall inks preparation.

The reaction mechanism for obtaining gallic acid from the gallotannic acid, found in galls, is presented in the following hydrolysis reaction:
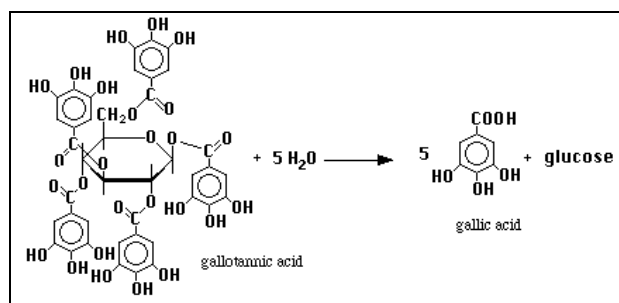
Gallic and tannic acids in solution darkens gradually becoming brown, in the presence of air, and by reacting with ferrous sulfate become black. It needs time to form a black precipitate, and to prevent this, in the ink must be added sulfuric or hydrochloric acid.

Black ink is given so the oxidation Fe^{2+} to Fe^{3+} and Fe^{3+} complex formation - gallic acid.

Historical documents written or printed with iron-gall ink present a serious conservation problem as the ink slowly oxidizes (*burns*) the paper it is written on, thereby disintegrating the document.
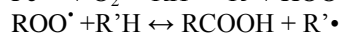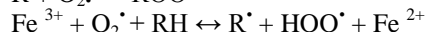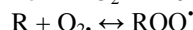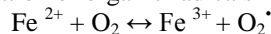
Two mechanisms are responsible for this degradation behavior of historical paper [1, 2]:
a) either the strongly acidic compounds of the ink (e.g. sulfuric acid), which hydrolyze the cellulose in the paper and lead to its disintegration,
b) or residual Fe^{2+} ions (derived from incomplete oxidation of FeSO4 in air) which reacts like catalysts for the oxidation of the organic compounds present in the paper.
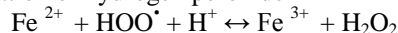
This oxidation involves the intermediate formation of radicals ($O_2^\bullet$, $HOO^\bullet$). The reaction of the Fe^{2+} in acidic medium $HOO^\bullet$ leads to the formation of H_2O_2, hydrogen peroxide, which in its turn can further oxidize the paper (and also the Fe^{2+} present in excess in the ink).

The two phases are characterized by the chemical reactions:

1) formation of organic radicals
$$Fe^{2+} + O_2 \leftrightarrow Fe^{3+} + O_2^\bullet$$
$$R + O_2\bullet \leftrightarrow ROO^\bullet$$
$$Fe^{3+} + O_2^\bullet + RH \leftrightarrow R^\bullet + HOO^\bullet + Fe^{2+}$$
$$ROO^\bullet + R'H \leftrightarrow RCOOH + R'\bullet$$
2) formation of hydrogen peroxide
$$Fe^{2+} + HOO^\bullet + H^+ \leftrightarrow Fe^{3+} + H_2O_2$$
$$Fe^{2+} + H_2O_2 \leftrightarrow Fe^{3+} + HO^\bullet + OH^\bullet$$

In the case 1) Fe^{2+} ions truly acts as a catalyst and it is not consumed during the reaction, and in the case 2) each $HOO^\bullet$ radically may lead to the oxidation of two Fe^{2+} ions.

Carbon inks were prepared, in the most cases, from the soot produced by combustion of glues, gums, etc. They contain carbon black or ground coal, in an aqueous medium of animal or vegetable glue. These were the first

liquid inks used for writing. Unlike the other inks, they do not fade, but they are very unstable to moisture [3, 4]. Documents written with this kind of ink have a good permanence, under the condition that the manuscript or the print to be kept in a dry atmosphere.

Until the seventh century, both types of inks were used simultaneous, after which prevailed iron-gall ink. The reason for this supremacy must to be searched in the fact that the iron-gall ink, unlike the carbon ink adheres better to the paper surface. However, it should be noted that although the iron-gall type of inks adhere better to the surface of the paper, they may be permanent, only if the manuscript is kept at a proper humidity and away from acidic sources, which weakens the links between the ink and paper support [5, 6, 7].

Aniline ink is an aqueous solution of aniline or coal tar and phenol or thymol and began to be produced in the second half of the nineteenth century.

2. EXPERIMENTAL PART

The paper's corrosion by iron-gall ink is one of the biggest problem in the graphics world heritage. A lot of studies have been explained the possible mechanisms of cellulose degradation and proposed the methods of its restoration and conservation [8, 9, 10].

It is well known that substances can be identified by their IR spectra, interpreted as a fingerprint for the substance. Spectra have certain bands, e.g. vibration, which are characteristic for certain functional groups or atoms which are characterized by frequencies and intensities domains in IR spectra [16, 17, 18]. Recently published results show that IR spectroscopy is an indispensable tool for material characterization. Calvin and collaborators [15, 19, 23, 24] have used infrared spectroscopy for characterization of cellulose and its derivatives, and for analysis of degraded paper, artificial aging in the laboratory.

Application of FTIR spectroscopy technique was used widely in the recent years to identify the types of cellulose, lignin and hemicellulose. Identification of the metallogallic ink or of the organic ink by FTIR spectroscopy appears very difficult because of the cellulose absorption bands, which cover other absorption bands of ink compounds [11, 12, 13].

However, in the last decade, there have been an increasing number of spectral studies to identify the types of ink.

Mosini and collaborators [14] showed by FTIR spectroscopy that the decrease of calcium carbonate and his passing into calcium sulfate is a measure of cellulose degradation due to the metallogallic ink. The FTIR spectra provide useful information to identify the metallogallic ink, although this method has not been sufficiently exploited because the interpretation of the spectra remains difficult. Therefore must carefully watched the very little influence of the inks compounds. Despite all the efforts to detect and interpret the

differences measured on the original sample composition, remains extremely difficult because the ink and the paper degradation may have combined effects [20, 21, 25].

The FTIR spectra were recorded by two spectral techniques: the transmission and diffuse reflectance spectroscopy (DRIFTS) on a Perkin-Elmer device.

The spectral transmission technique is microdestructive because the paper samples were extracted by scratching some cellulose fibers, both from unwritten and written papers. The samples thus obtained were embedded in potassium bromide pellets. As expected, the strong absorption bands of the cellulose bands mostly cover others components' bands of the fillers and of the ink. However, at a careful discrimination of spectra, it could be identify some differences in ink and in paper absorption bands. Such spectra were recorded for two samples of old books' paper, encoded MP1 and MP2, namely:

> MP1 book paper printed in 1931, in Berlin, Germany
> MP2 book paper printed in 1867, in Paris, France.

The cellulose strong absorption region is from 1200 cm^{-1} to 950 cm^{-1} and in this region can't be attributed absorption bands to the others compounds.

In regions of low absorption of the cellulose, from 2800 cm^{-1} to 1200 cm^{-1} and from 950 cm^{-1} to 600 cm^{-1}, consulting the literature and the published studies in this area, it could assigned spectral absorptions bands of the functional groups of the ink compounds and of the degraded cellulose compounds. Each sample of paper and inked paper were recorded three times and found relatively good reproducibility of spectra.

The spectra were represented versus unwritten paper and inked paper for each of the two samples.

As expected, all spectra showed a strong absorption band of the cellulose at 3346 cm^{-1}, 1158 cm^{-1}, 1111 cm^{-1}, 1061 cm^{-1} and 1036 cm^{-1}. Other representative bands that can be observed in almost all samples, but of much lower intensity than the cellulose, at 1882 cm^{-1}, 1420 cm^{-1}, 875 cm^{-1}, were assigned to the calcium carbonate. The bands at 2920 cm^{-1} and 2851 cm^{-1} found in many spectra to identified the presence of the oil in the ink composition and these were vibration bands belonging to the -CH3, -CH2 groups of linear aliphatic chains.

The ink sample MP1 presented an absorption band at 2085 cm^{-1} which differed from the paper sample. The band at this wave number was assigned to specific -CN cyanide group. This was explained by the addition of a dye in ink, namely Prussian blue, which is iron iron-cyanide, $Fe_7 (CN)_{18} (H_2O) \cdot 16 H_2O$, with sixteen water molecules, to increased its blackness. In the ink spectrum it was seen an increasing band at 1750 cm^{-1} due to the cellulose oxidation.

In the written samples were seen some increasing bands at 672 cm^{-1} and 661 cm^{-1} specific to sulfates, which explained the transformation of the carbonates into

sulfates due to the degradation induced by ink in printed paper, as shown in Figure 1, Figure 2 and Figure 3.
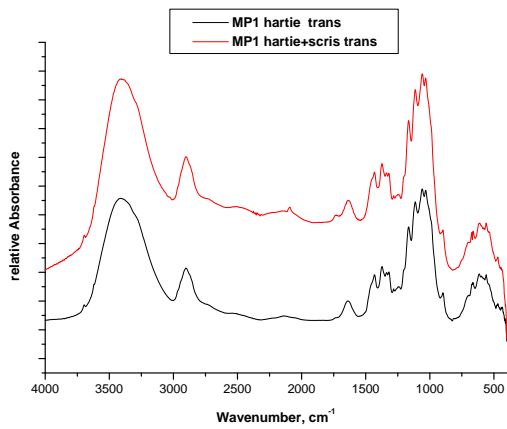
The MP2 ink sample spectrum was very similar to that of the unwritten paper MP2 and in both cases were noted the absorption band at 1621 cm^{-1} which is very sharp and specific to the inorganic cations oxalates and a band at 1686 cm^{-1} specific to the cellulose degradation, as shown in Figure 4, Figure 5 and Figure 6.
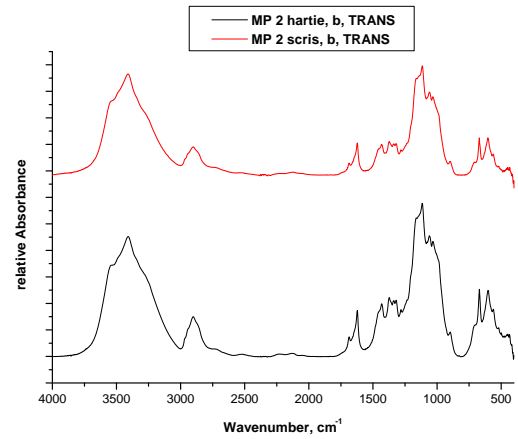

Figure 1. The FTIR spectrum, in transmission, of the MP1 paper sample and MP1 paper + writing sample
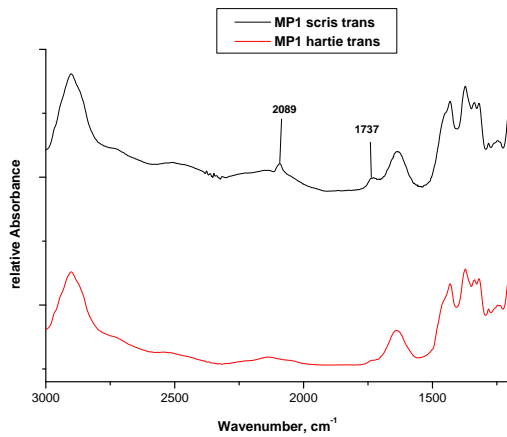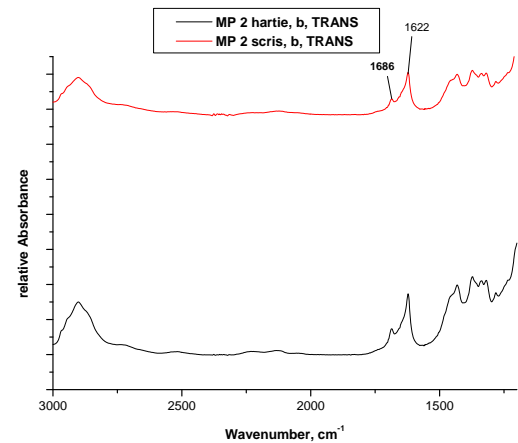

Figure 2. The FTIR spectrum, in transmission, of the MP1 paper sample and MP1 paper + writing sample
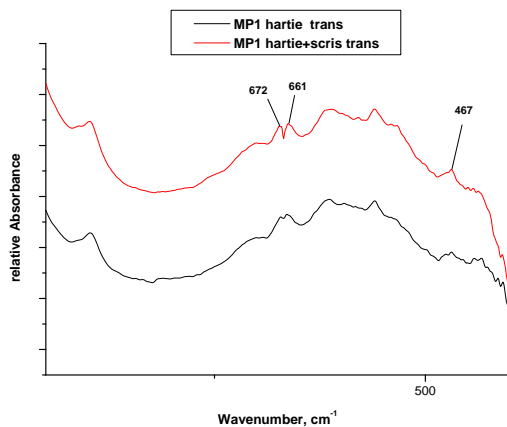
Figure 3. The FTIR spectrum, in transmission, of the MP1 paper sample and MP1 paper + writing sample

Figure 4. The FTIR spectrum, in transmission, of the MP2 paper sample and MP2 paper + writing sample

Figure 5. The FTIR spectrum, in transmission, of the MP2 paper sample and MP2 paper + writing sample
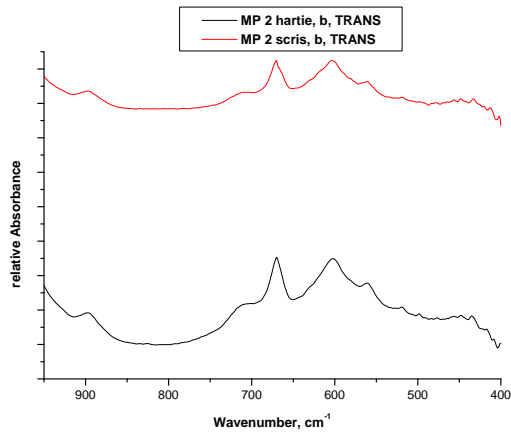
Figure 6. The FTIR spectrum, in transmission, of the MP2 paper sample and MP2 paper + writing sample

Comparative presentation of the two samples of MP1 ink and MP2 ink, in the transmission mode revealed that the two samples have absorption bands that differentiated them, namely: at 2089 cm^{-1}, at 1737 cm^{-1}, at 1636 cm^{-1} and at 467 cm^{-1}, for MP1 ink sample and at 1683 cm^{-1}, at 1622 cm^{-1}, and at 603 cm^{-1} for MP2 ink sample, as shown in Figure 7, Figure 8 and Figure 9.
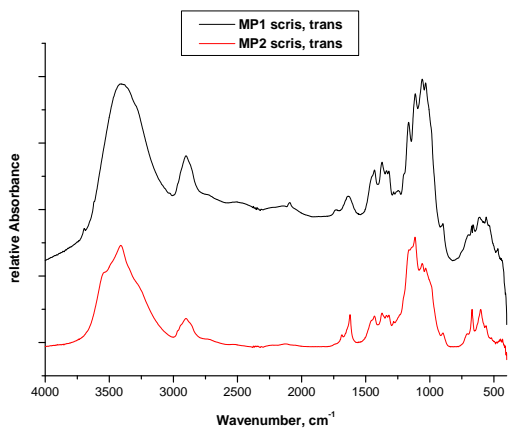

Figure 7. The FTIR spectrum, in transmission, of the MP1 paper + writing sample and MP2 paper + writing sample
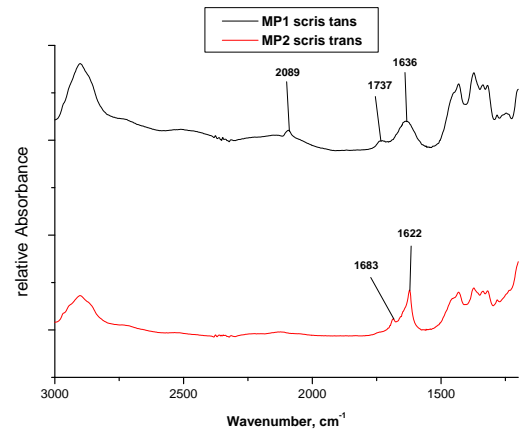

Figure 8. The FTIR spectrum, in transmission, of the MP1 paper + writing sample and MP2 paper + writing sample
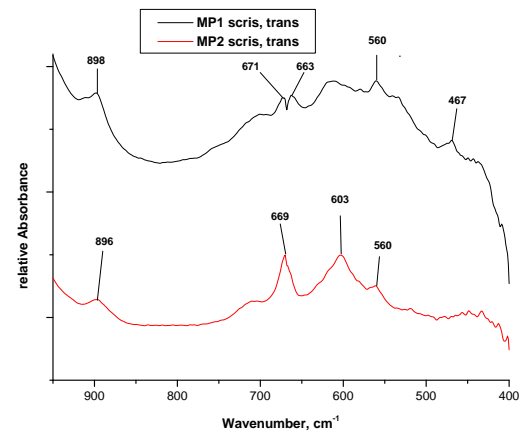

Figure 9. The FTIR spectrum, in transmission, of the MP1 paper + writing sample and MP2 paper + writing sample

Overlapping spectra of the two inked paper samples showed that the both samples MP1 and MP2 differed due to the band at 1621 cm^{-1}.

The advantages of the transmission technique are that the reproducibility of the samples' spectra is relatively high and quantity of the taken sample is small, 1-2 mg. The disadvantage is that the absorption bands aren't too sharp and there are many overlapping which makes them assignment more difficult.

Then we analyzed samples of ink and paper by diffuse reflectance spectroscopy technique (DRIFT), which can't be considered a nondestructive testing technique, because each measurement requires a few milligrams of sample. The KBr diffuse reflectance spectroscopy was used in connection with the idea of having a direct measurement of the ink sample.

The MP1's sample revealed the absorption band at 2090 cm^{-1} specific cyanide group,-CN, and the band at 1639 cm^{-1} specific to oxalates, as shown in Figure 10, Figure 11 and Figure 12.
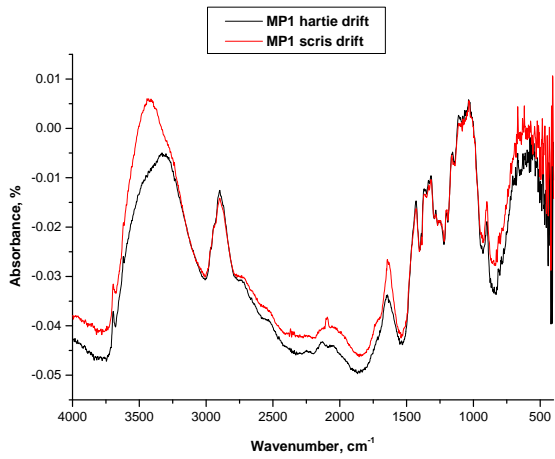
Figure 10. The FTIR spectrum, by DRIFT, of the MP1 paper sample and MP1 paper + writing sample
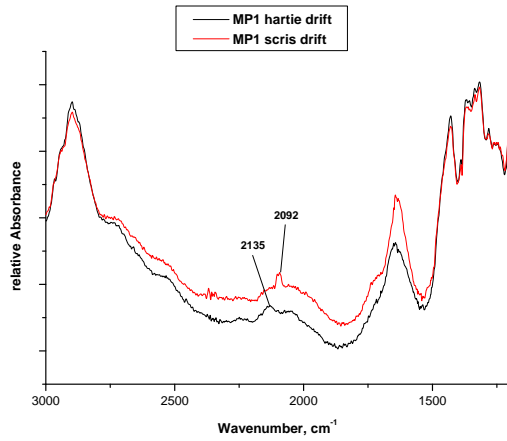

Figure 11. The FTIR spectrum, by DRIFT, of the MP1 paper sample and MP1 paper + writing sample
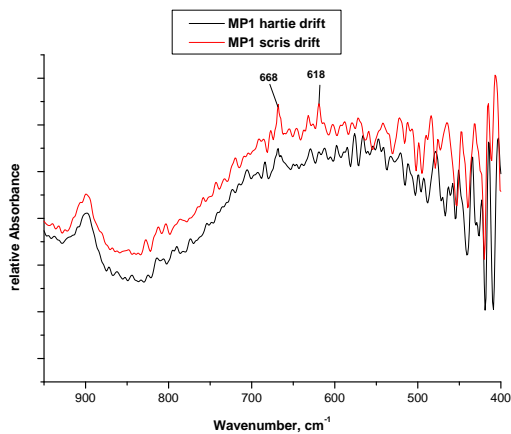

Figure 12. The FTIR spectrum, by DRIFT, of the MP1 paper sample and MP1 paper + writing sample

The MP2 ink sample recorded by DRIFT, differed not from the MP2 unwritten sample, but again there was a strong absorption band at 1621 cm^{-1} specific to the inorganic cations oxalates.

It is interesting that both the sample paper and ink had bands at 1690 cm^{-1} and at 1621 cm^{-1}, first corresponding to the oxidation of cellulose, and the second to the inorganic cations oxalates, as shown in Figure 13, Figure 14 and Figure 15.
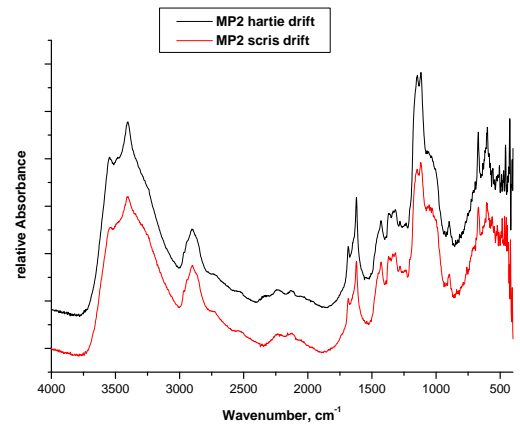

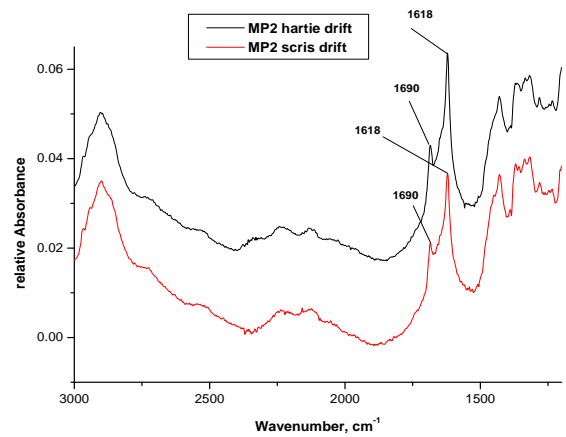**Figure 13. The FTIR spectrum, by DRIFT, of the MP2 paper sample and MP2 paper + writing sample**

Figure 14. The FTIR spectrum, by DRIFT, of the MP2 paper sample and MP2 paper + writing sample
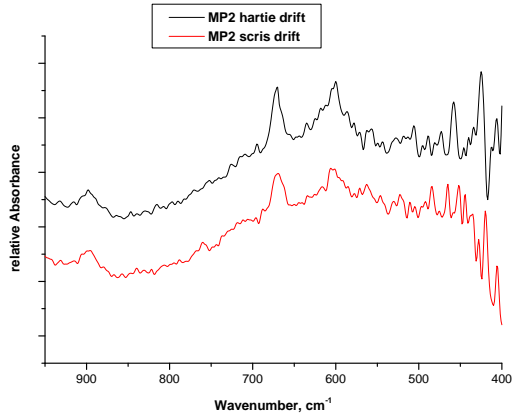
Figure 15. The FTIR spectrum, by DRIFT, of the MP2 paper sample and MP2 paper + writing sample
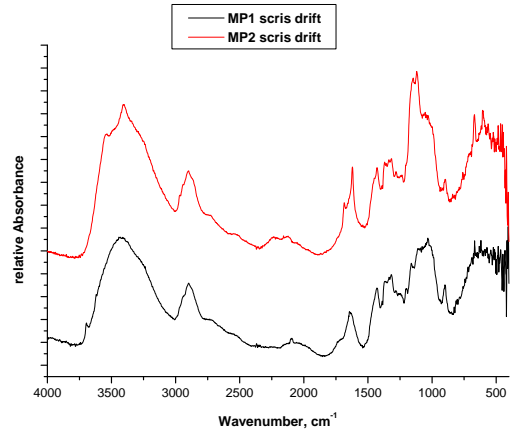

Figure 16. The FTIR spectrum, by DRIFT, of the MP1 paper + writing sample and MP2 paper + writing sample

The DRIFT overlap spectra of both MP1 and MP2 inks samples had highlighted the difference between them, as well as for the transmission spectra, as shown in Figure 16, Figure 17 and Figure 18.

In the case of the method by DRIFT, the bands of absorption spectra of both samples of paper and ink were better defined and symmetrical, so they were easily assigned. But because the background noise was much higher than in the DRIFT spectra case than in the transmission spectra and because a fairly large quantity of sample for each determination was required, which meant more profound damage to leaf book, it couldn't say that the DRIFT technique had more advantages than transmission technique.

The reproducibility of the transmission technique was higher than that of the DRIFT technique, but both methods gave satisfactory results in this regard.

To confirmed the presence of iron, and of the others components of the functional groups assigned to the ink it was also used the of X-ray fluorescence spectrometry after energy dispersion technique (EDXRF).
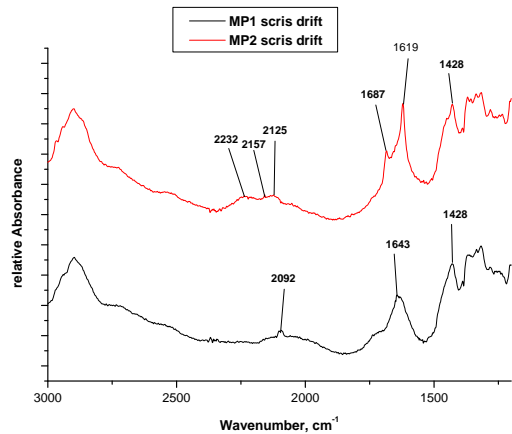

Figure 17. The FTIR spectrum, by DRIFT, of the MP1 paper + writing sample and MP2 paper + writing sample
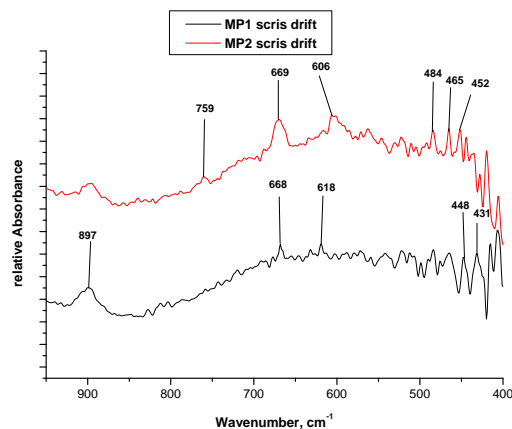

Figure 18. The FTIR spectrum, by DRIFT, of the MP1 paper + writing sample and MP2 paper + writing sample

Radiative intensity response of an element is a measure of radiation emitted by that element and it is considered directly proportional to its amount found in the sample, as shown in Figure 19 and Figure 20.
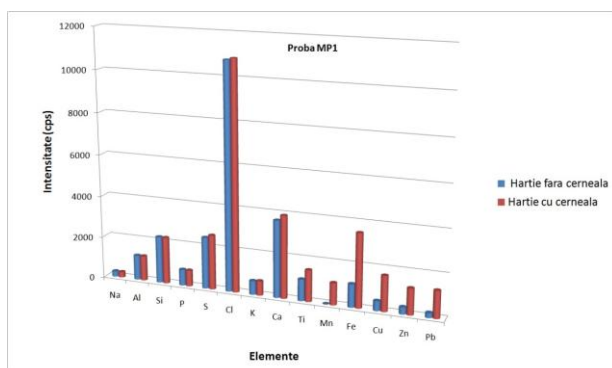

Figure 19. The EDXRF analysis of MP1 paper sample and of MP1 written paper sample
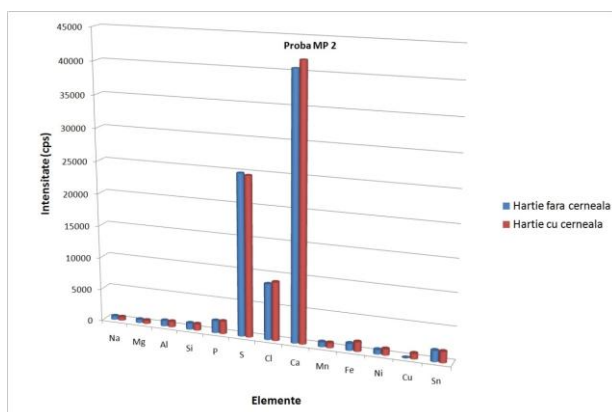

Figure 20. The EDXRF analysis of MP2 paper sample and of MP2 written paper sample

Same samples were analyzed by X-ray fluorescence spectrometry after dispersion energy and the energy intensity measured on the written and unwritten paper sample, gave the following results: in the case of MP1 ink sample the energy intensity of iron was approximately 2.5 times greater than in the case of the unwritten paper samples, which in conjunction with the presence of cyanide group in the spectrum, leaded to the conclusion that the ink is an iron-gall ink. Also in the ink sample there were present Cu, Zn, Pb, Mn and Ti, and the energy intensity of sulfur was slightly higher in the ink sample and the same situation was encountered to the K.

In the case of MP2 ink sample, which had an absorption band at 1621 cm^{-1}, corresponding to the inorganic cations oxalates, it was demonstrated by energy intensities, that comparable equal Fe quantity found in the paper and in the ink. This fact leaded to the conclusion that the ink was not an iron-gall ink. Also the

ink sample had a little more Cu than the paper, but Sn, Mn and S were less than in the paper. All these things meant that the MP2 ink was a carbon ink, or, with an extremely low probability, an aniline ink.

3. CONCLUSIONS

To determine the type of ink used to print books from the late nineteenth century and early twentieth century, FTIR spectroscopy method was used.

The FTIR spectra of both unprinted paper samples and printed paper samples with blacks inks were recorded in two spectral techniques: the transmission and the diffuse reflectance.

To detect the differences between the spectrum of the paper, of which the major component is cellulose, and the inks, special attention was paid to the absorption regions from 2800 cm^{-1} to 1200 cm^{-1} and from 950 cm^{-1} to 600 cm^{-1}. Comparing data from published literature and studies in this area, it could be assigned the spectral bands of the functional groups such as the degraded cellulose and ink.

To confirm the presence of iron, and also of the others elements of functional groups assigned from ink, was used and the X-ray fluorescent spectrometry after energy dispersion technique (EDXRF).

Radiative intensity response of an element is a measure of radiation emitted by that element and is considered directly proportional to its quantity in the sample.

The MP1 ink sample was found to be an iron-gall ink, while the MP2 ink sample was a carbon ink, or with a very low probability, an aniline ink.

The historical paper and ink studies will continue and will focus on the preservation with the nanoparticles.

REFERENCES

[1] JG Neevel, "Phytate: a Potential Conservation Agent for the treatment of ink corrosion caused by irongall inks", restaurateur, 16, 1995, 143-160.

[2] JG Neevel, CTJ Mensch, "The behavior of sulfuric acid, iron and iron gall ink corrosion During», ICOM CC triennal 12th Meeting, Lyon, 1999, vol II, 528-533.

[3] B. Reissland, "Ink Corrosion Aqueous and Non Aqueous Treatment of Paper Objects - state of the art", restorer 20, 1999, 167-180.

[4] Reissland B., De Groot S, "Ink corrosion: comparison of Currently used aqueous treatments for paper objects", goatling, Copenhagen, 1999, 121-129.

[5] M. Zerdoun "Les noires encres have Moyen Age (jusqu'au 1600)» Editions du CNRS 1983.

[6] CH Wunderlich, "Geschichte und Chemie des Eisengallustinte", Restauro, 6, 1994, 414-421.

[7] M. Darbour, Bonnassies S., Flieder F. "Les encres métallogalliques: Etude from degradation of acidic

gallique et l'Analyse du complex ferrogallique» ICOM CC 6th Triennal Meeting, Ottawa 1981, 3-14.

[8] J. Bleton, Coupry C. J. Sansoulet "Approche d'Etude des Anciennes encres" Studies in Conservation 41, 1996, 95-108.

[9] MC Sistach, Espadaler I. "Organic and Inorganic Components of Iron Gall Inks', ICOM CC Tiennal 10th Meeting, 1993, Vol II, 485-489

[10] Duval A. "PIXE Analysis of Pisanello's drawings" 5th International Conference on Non-destructive Testing Microanalytical Methods and Environmental Evaluation for Study and Conservation of Works of Art (Budapest, 24 to 28 September 1996)

[11] Zhbankov RG, "Infrared Spectra of cellulose", Consultant Bureau, New York, 1966

[12] Havermans J.B.G.A. "Environmental Influences on the deterioration of Paper", Barjesteh, Meeuwes and Co., Rotterdam, 1995, 43-76.

[13] J. Burandt, "An Investigation toward the identification of traditional drawing inks", The Book and Paper Group, 1994, 9-16.

[14] V. Mosin, Calvin P., Mattogno G. Righini G. "Derivatives infrared spectroscopy and electron spectroscopy for chemical analysis of ancient paper documents", cellulose Chemistry and Technology, 24, 1990, 263-272.

[15] C. Sistach, N. Ferre, MT Romer, "Fourier Transform Infrared Spectroscopy applied to the Analysis of Ancient Manuscripts", restorer n ° 19, 173-186, 1998.

[16] K. Pandey, "A Study of Chemical Structure of Soft and Hardwood and Wood Polymer by FTIR Spectroscopy", Journal of Applied Polymer Science, 71, 1999, 1969-1975.

[17] G. Socrates, "Infrared Group Chracteristic frequencies", Wiley and Sons New York, 1994.

[18] A. MacInnes, A. R. Barron, J. Mater. Chem. 2, 1992, 1049

[19] P. Calvin, E. Franceschi, D. Palazii Sci. Tehnolit. Worship. Heritage 5, 1996

[20] MC Sistach, N. Ferre, MT Romero, restorer 19, 1998, 173

[21] C. Remazeilles V. QuiletT. Calligaro, J. C. shingle, et al. Nuclei. Tools. Methods Phys. 181, 2001, 681

[22] P. Clavini, A. Gorassini, Restorer 23, 2202, 205

[23] P. J. Gibbs, K. R. Seddon et al. Anal. Chem. 69, 1997, 1965

[24] J. R. Mansfield, M. Attas, E. Cloutis vibrate. Spectrosc. 28, 2002, 59

[25] J. Thompson, Manuscript Inks The Caber Press, Portland, Oregon, 1996

[26] P. Arpino, JP Moreau, F. Flieder, J. Chromatogr. A 134, 1977, 433