



FTIR (DRIFT) ANALYSIS OF SOME PRINTING INKS FROM THE 19th AND 20th CENTURIES

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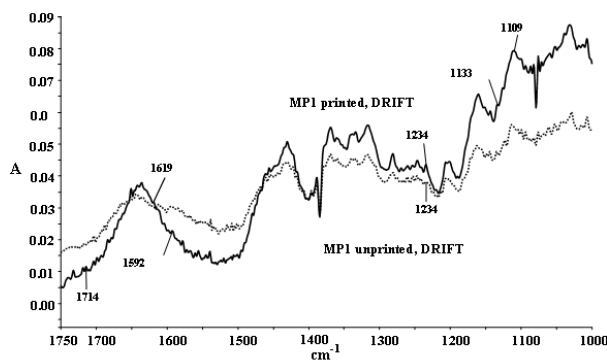
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Received September 12, 2013

Iron-gall-ink corrosion is one of the largest threats for the 'historical documents' paper. The poor quality of the used raw materials from the mid-19th century and the aggressive chemicals added to the paper pulp during its sizing (19th-20th centuries) yielded to an accelerated self-destruction process of the paper.

In this study, different historical papers dating from 1931 (Berlin, Germany) and 1867, 1937, 1930 and 1898 (Paris, France) were investigated using the Fourier-transform-infrared-spectroscopy (FTIR) diffuse reflectometry with KBr (DRIFT). The degradation mechanism of the cellulose caused by the iron-gall-ink, prepared with different ingredients including tannins and vitriol, is causing both acidic hydrolysis and Fe²⁺ catalysed oxidation of cellulose. FTIR analysis revealed few important area: peaks from 1000 cm⁻¹-1400 cm⁻¹, characteristic for cellulose, 1723 cm⁻¹ attributed to oxidation of the celluloses, the shoulder from 1648 cm⁻¹, attributed to the hydrolysis and oxidation of cellulose, typical bands at 1580 and 875 cm⁻¹ attributed to carbon-black ink, and the peaks from 1700, 1620, 1500 and 730 cm⁻¹, attributed to iron-gall ink. Some correlations with EDXRF results have been made, in order to correctly attribute the FTIR results.



INTRODUCTION

Fourier transform infrared (FT-IR) spectroscopy has extensively been used for the characterization of organic components from different materials belonging to historical documents: ink and paper. Inside of this technique, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is one of the most used techniques, being a reliable, reproducible and selective technique for the classification and identification of historical inks. Compared with conventional dispersive IR spectroscopy, DRIFTS technique provides spectra with a significantly improved signal-to-noise ratio, and therefore, it more effectively extracts data from inks.¹

In the field of art conservation, Sheare used DRIFTS to examine the surface of paint films and inks.² He identified many pigments, but specular reflection inhibited the identification of binders. Sheare used silicon carbide paper both as a sampling tool and as a DRIFTS substrate for the analysis of archaeological organic residues.² Using DRIFTS as a non-destructive tool, Hedley analyzed surfaces of paintings before and after solvent cleanings.³

Ink is any liquid or viscous substance used for writing, printing or drawing. Ink composition and consistency may be different. However, all ink types are made up of two components: a colorant and a vehicle. A colorant is also known as a

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pigment or dye, while a vehicle is defined as a liquid (i.e., water, alcohol or another solvent) into which the colorant is dispersed.

There are mentioned some types of black inks that were used for printing in the late 19th and early 20th centuries in literature.⁴

Iron gall (17th century) – brown/black colour; pigments are highly acidic, responsible for paper corrosion where ink is present.

Black ink (19th century) – carbon black ink made in Europe in the 11th century, also known as India or Chinese ink; comes from finely ground soot “lampblack” and various resins; carbon based ink is very stable and not fade.

Bistre (14th-19th century) – brown lamp black or soot brown; made from tarry soot collected in wood stove chimneys; the colour of this ink can be altered by the concentration and source of soot; colours range from dark blackish brown to brownish-saffron yellow; handmade by artist; bound and thickened with gums allowing the ink to lay on the surface instead of soaking into the paper.

Blue/black ink (19th century) – use of unstable dyes such as Prussian blue mixed with ivory black, varnish and eggs; light sensitive, fades to bluish grey or pale brown.

Sepia (19th century) – black/grey, hint of brown; made from the ink sacks of cuttlefish; used to write and produce mono-chromatic drawings; semi-stable but should be protected from ultra-violet exposure.

Aniline black ink (19th century) is probably the oldest synthetic organic pigment, it was discovered around 1860 and it is coal-tar based. It is mostly used in some special coatings where very deep blacks are required. Aniline black has a strong tinting strength, a low scattering power, a very strong light absorption capability, and its fastness properties are quite good. Aniline inks are very sensitive and may dissolve in water or other liquids or chemicals.³

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In this study, different historical papers dating from 1931 (Berlin, Germany), and from 1867, 1937, 1930 and 1898 (Paris, France) were investigated using the Fourier-transform-infrared-spectroscopy (FTIR) diffuse reflectometry with KBr (DRIFT). The degradation mechanism of the

cellulose caused by the iron-gall-ink, prepared with different ingredients including tannins and vitriol, is causing both acidic hydrolysis and Fe²⁺ catalysed oxidation of cellulose. FTIR results will be correlated with other analytical results such as EDXRF.

MATERIALS AND METHODS

Original book paper samples were from a private collection. Different historical papers dating from 1931 (Berlin, Germany), 1867, 1937, 1930 and 1898 (Paris, France) were investigated. The ink has strongly corroded the paper, yielding to large brown halos around inscriptions.

The codification of the historical book paper samples is as follows: MP1, book printed in 1931, in Berlin, Germany; MP2, book printed in 1867, in Paris, France; MP3, book printed in 1937, in Paris, France; MP6, book printed in 1930, in Paris, France; MP7, book printed in 1898, in Paris, France.

From each book sample there were scratched small pieces collected from surfaces with minimal damage. The thin layer of sample produced a reflection-absorption experiment with a spectrum similar to that obtained in transmission.

A few milligrams of scratched sample were grounded for 10 minutes in an agate mortar, by hand. From the resulting powder about 2 milligrams were mixed with a large quantity of KBr, 100 milligrams, in the agate bowl. Three spectra were recorded for each paper sample. Spectra measured this way proved a good reproducibility. The spectrum didn't need the Kubelka-Munk correction, because they were compared only with other diffuse reflectance spectra Kubelka.⁵

The FTIR 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.

A small quantity of scratched paper samples (0.5 to 1 mg), from the edges of the sheets, unwritten and uncoloured, was mixed with KBr.

Typically, all DRIFT samples should be diluted to less than 30 w/w % concentration in a non-absorbing matrix. The powder layer minimizes band broadening and poor resolution effects resulting from saturation or specular reflection problems. Additionally, the sensitivity of the measurement is improved by an increase in the depth of penetration of the beam.⁶

RESULTS AND DISCUSSION

It has been noticed that the limits and the possibilities of the different FTIR techniques for the identification of inked papers generally and of metallogallic inked paper in particular have not been explored, mainly because the interpretation of spectra is rather difficult.⁷

The diffuse reflectance spectrum depends on sample density and refractive index, as well as on particle size and morphology. For nonquantitative work, the diffuse reflectance spectra may be displayed without any Kubelka-Munk correction function. The major problem that can occur with diffuse reflectance spectra is the inclusion of a strong specular reflection component that produces slight band distortions.⁸

DRIFT gives the information about the whole semitransparent paper (due to IR light scattering inside the paper). This mixed absorption /reflection was useful outside the regions of high absorption, where the internal remission exceeds the influence of gloss. Global increase of DRIFT absorption of the paper is not caused by chemical changes, but by increase of physical surface, roughness, of historical aged paper.⁹

The comparison between the unprinted and printed paper DRIFT spectra did not reveal notable difference for this type of samples. 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, some differences in ink and in paper absorption bands could be identified.

The cellulose strong absorption region is from 1200 cm^{-1} to 900 cm^{-1} . In regions of low absorption of the cellulose and of interest for inks, from 1700 cm^{-1} to 1200 cm^{-1} and from 900 cm^{-1} to 500 cm^{-1} , based on literature reports, could be spectral absorptions bands of the functional groups from ink compounds and degraded cellulose. However it could be observed the band at 1714 cm^{-1} attributed to carboxylic group from acid and strengthened by stretch vibration band at 1234 cm^{-1} . The bands at 1108 cm^{-1} and 1155 cm^{-1} may indicate the presence of SO_4^{2-} ion which could be attributed to ferrous sulphate, Fig. 1.¹⁰ The band from 746 cm^{-1} corresponds to the symmetric out-of-plane of the aromatic ring confirmed by 870 cm^{-1} -CO from phenol symmetrical stretching vibration band.

Because of the difficulty of finding the characteristic bands of the black inks sample, the

mathematical processing of spectra was used. Computer spectral subtraction methods are used to separate spectra of components in a mixture, to remove bands due to impurities, to confirm the identity of a sample, and to detect small changes in sample. When one component is identified, its pure spectrum (in absorbance units) is multiplied by a scaling factor and subtracted out, the remaining spectral bands being examined for any differences. This is known as scaled absorbance subtraction. The auto scale subtraction computer routine estimates a scaling factor based on the integrated areas of several peaks.

Difference spectra are a result from spectrum subtraction of unprinted paper and the spectrum of printed paper. To obey the linear range covered by Beer's law, the maximum absorption bands of all samples should be no more than 0.7 Absorbance units (no less than 20% Transmittance). The difference spectra can offer some information about the fillers and binders that are present both in paper and in ink.

Results for all five pair of unprinted and printed paper are represented in Figs. 2-6.

In Fig. 1 for MP1 sample the region $1750\text{--}1600\text{ cm}^{-1}$ reveals the superposition of different bands, suggesting the apparition of several carbonyl and/or alkenes groups. Significant differences between inked and non inked areas are observed: absorption bands between $1750\text{--}1600\text{ cm}^{-1}$, at 1429 cm^{-1} , between $1400\text{--}1200\text{ cm}^{-1}$, between $1200\text{--}900\text{ cm}^{-1}$ and between $830\text{--}540\text{ cm}^{-1}$.

The band from 1492 cm^{-1} could be attributed to the ink binding substance, in good agreement with literature.¹¹

Several groups could be attributed to the frequency from 1400 cm^{-1} :

- some oxidation products of cellulose salts with inorganic cations (R-COOH or R-COOMetal), with absorption in the regions $1350\text{--}1450\text{ cm}^{-1}$ and $1550\text{--}1610\text{ cm}^{-1}$

- some azo compounds (ammonium salts, amides); protein binders may be responsible for the presence of nitrogen.¹²

The band in the range $1300\text{--}1500\text{ cm}^{-1}$ could be attributed to numerous mixed vibrations rather than to characteristic group frequencies. Thus, the bands in this range are mixtures of O-CH deformation vibrations, CH_2 bending vibrations, C-CH and C-OH bending vibrations.¹³ Also the absorptions in this region ($1350\text{--}1450\text{ cm}^{-1}$) may signify the presence of Gallic acid.¹⁴

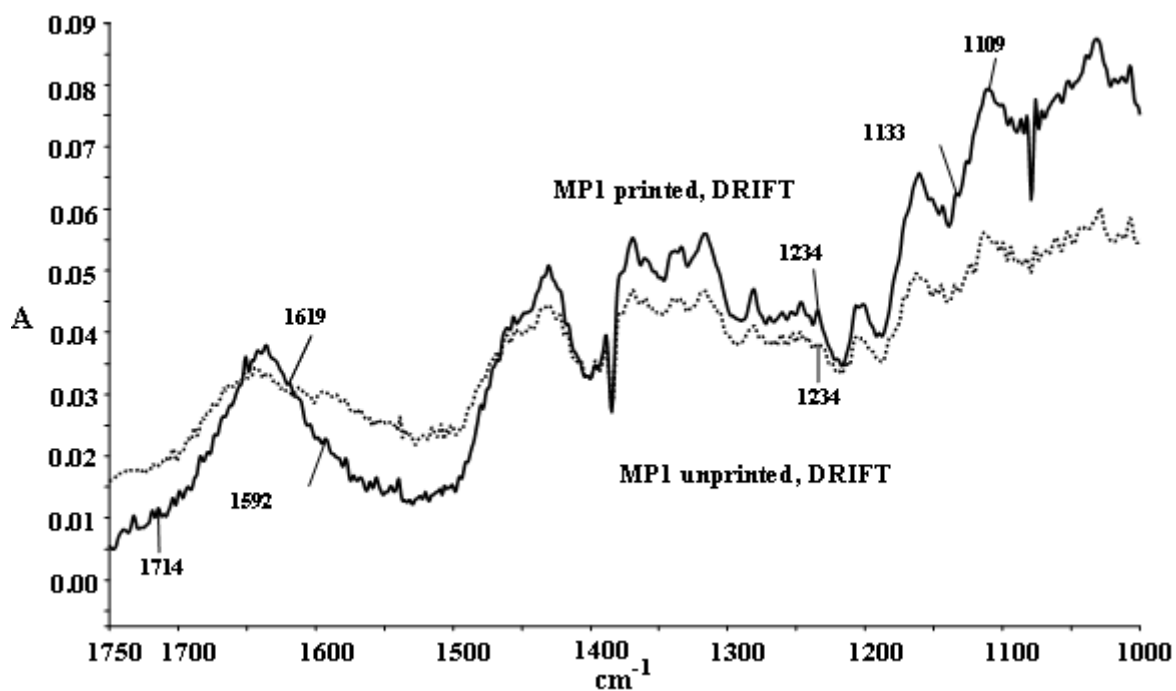


Fig. 1 – DRIFT spectra for MP1 book paper unprinted (.....) and printed (—).

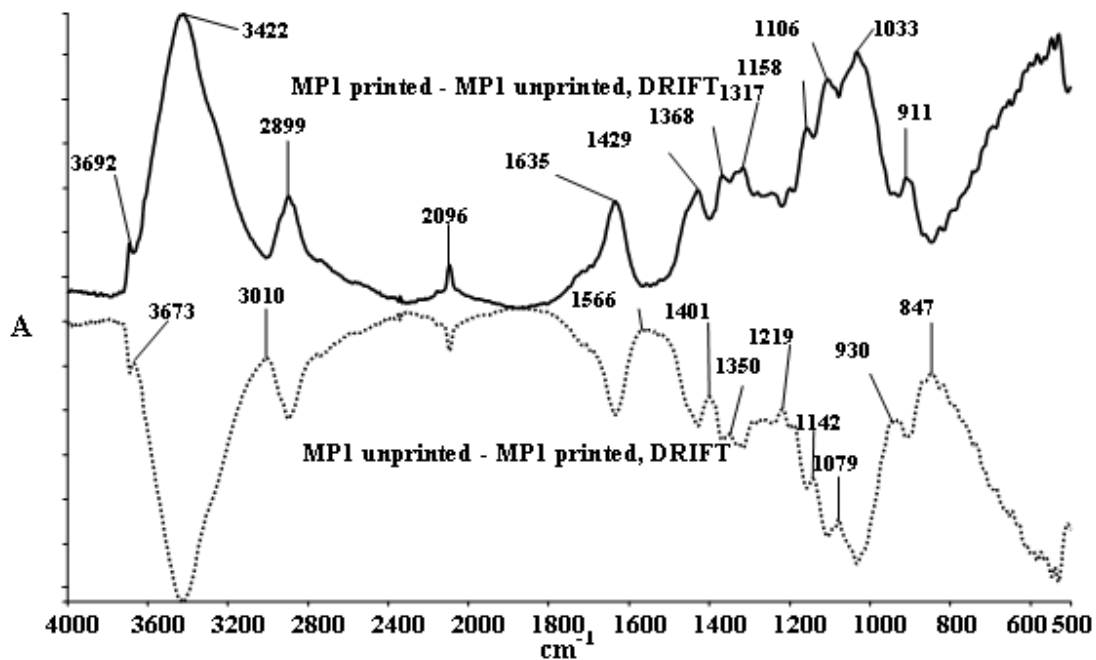


Fig. 2 – DRIFT spectra for MP1 difference spectra of book paper unprinted and printed.

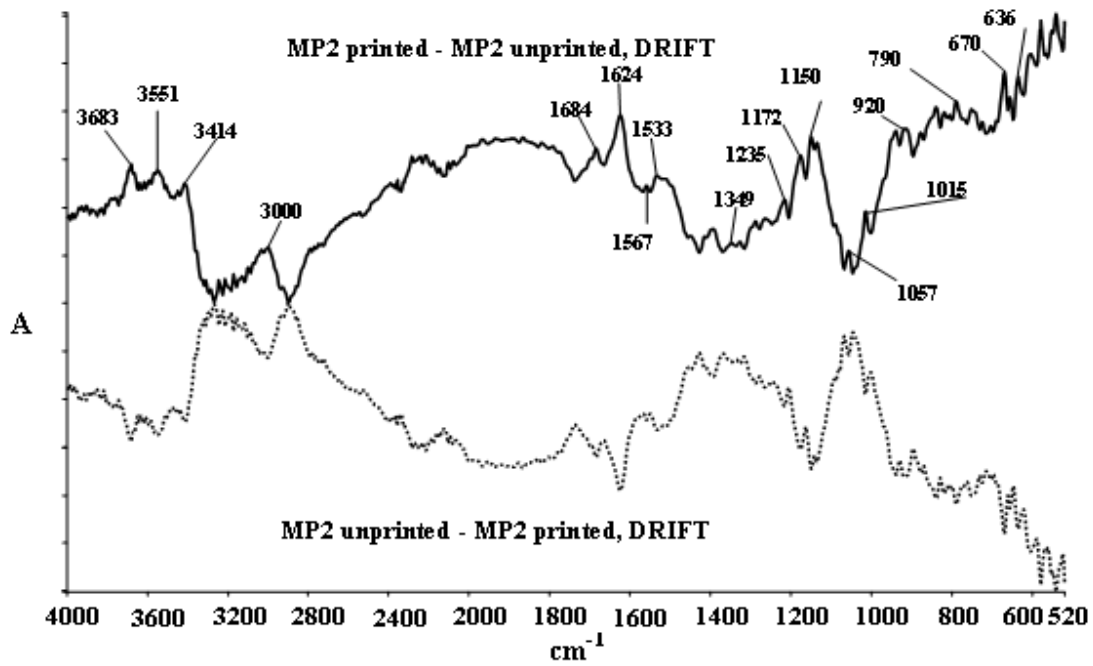


Fig. 3 – DRIFT spectra for MP2 difference spectra of book paper unprinted and printed.

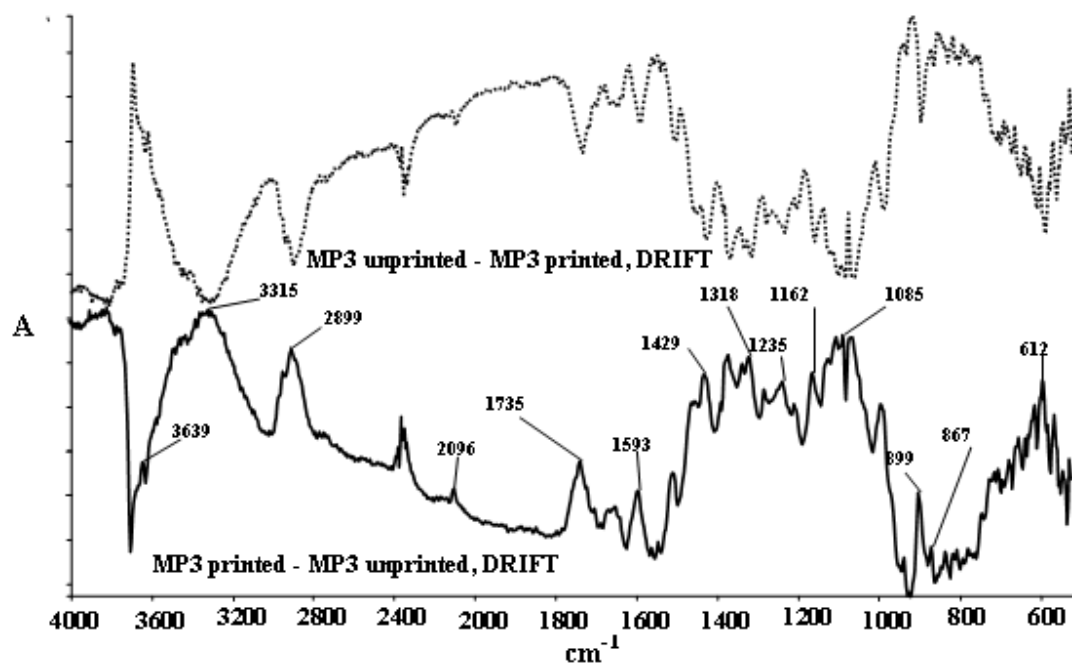


Fig. 4 – DRIFT spectra for MP3 difference spectra of book paper unprinted and printed.

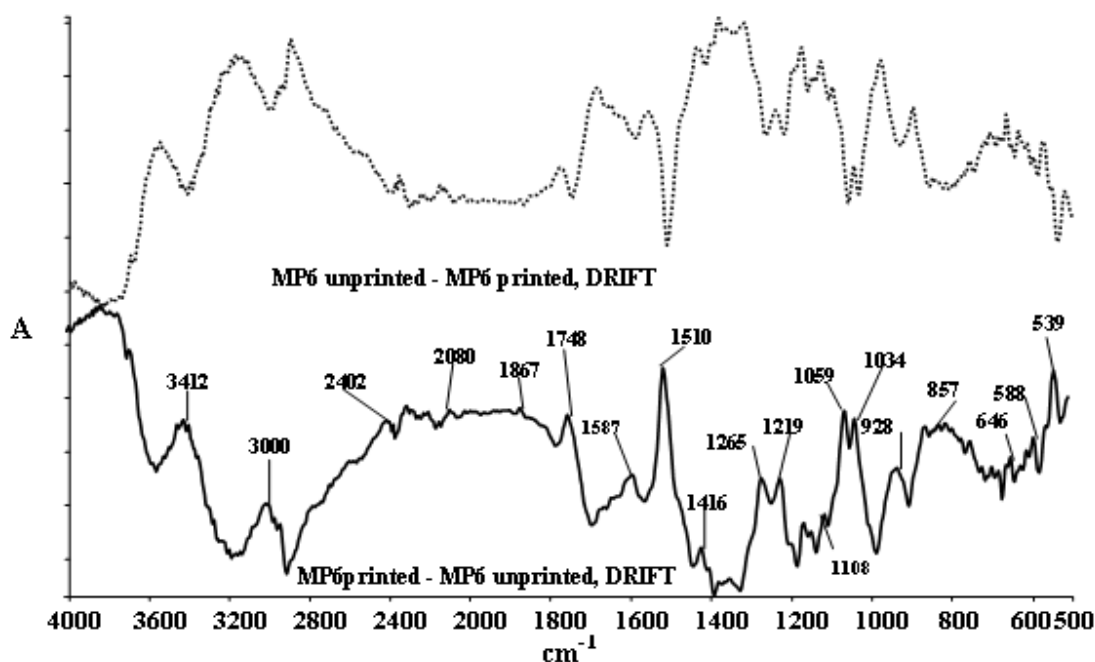


Fig. 5 – DRIFT spectra for MP6 difference spectra of book paper unprinted and printed.

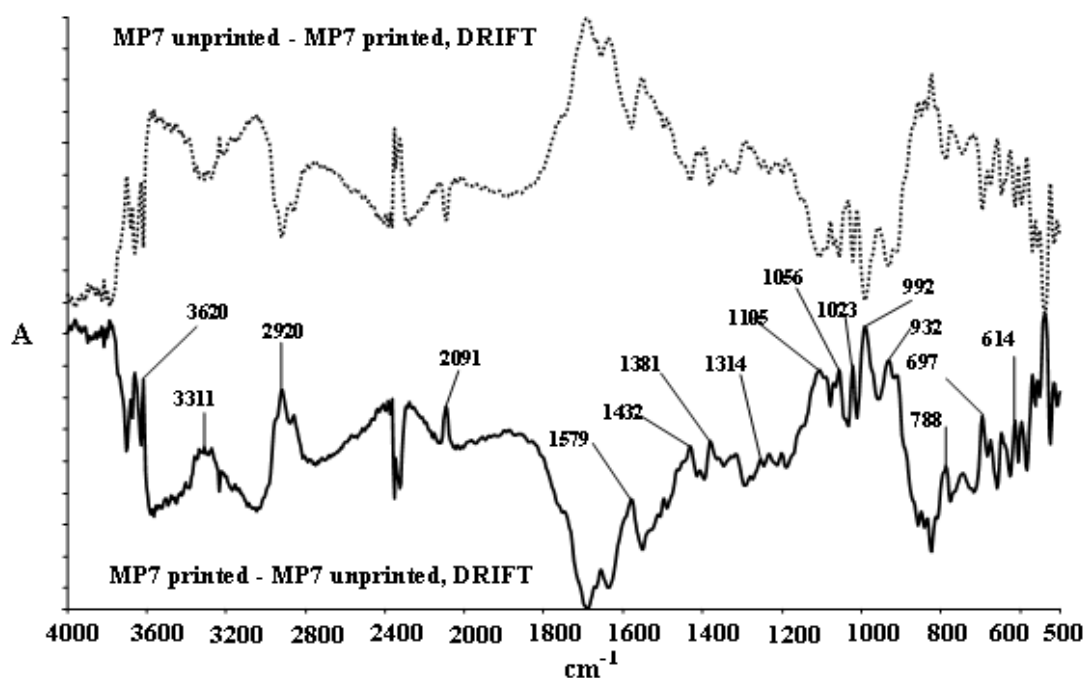


Fig. 6 – DRIFT spectra for MP7 difference spectra of book paper unprinted and printed.

The bands at 1106 cm^{-1} and 1158 cm^{-1} may indicate the presence of SO_4^{2-} ion which comes from ferrous sulphate.¹⁰

The band at 1429 cm^{-1} may be due to H-C-H and O-C-H in plane bending vibrations while the band at 1317 cm^{-1} may be attributed to C-O-H and H-C-C bending vibrations. Also, the absorptions in this region ($1350\text{--}1450\text{ cm}^{-1}$) may signify the existence of Gallic acid used in the inks applied to paper samples.¹¹

In MP1 sample ink Prussian blue is also present, identified by 2089 cm^{-1} absorption band, attributed to $\text{C}\equiv\text{N}$ vibration.¹⁵

The presence of iron gall ink in sample MP1 was previously confirmed by EDXRF, in our previous work.¹⁶

We should take into account that both samples MP1 and MP3 have been printed in the same period of time (~ 1930), so could be expected that the printing technology to be the same.

The intensive band from the MP3 spectrum in the region between 1200 and 1800 cm^{-1} can be explained by the oxidation reaction of cellulose in the presence of excess iron (II) sulphate, since free Fe^{2+} ions acts as a catalyst for the formation of hydroxyl radicals, Fig. 4.¹⁷

The sample MP3 gives a more intense band at 1735 cm^{-1} compared to sample MP1. This can be attributed to gallic acid excess that acts as a reducing agent for ferric pyrogallate complex. It can reduce the soluble Fe^{2+} ions, then being removed from the complex and becoming free.¹⁸

The sulphate bands were observed 1108 cm^{-1} and 1162 cm^{-1} , could rise from ferrous sulphate in both samples.

The absorption bands in the region 3500-3400 cm^{-1} are assigned to OH functional groups of carboxyl or of phenols from gallic structure.

For MP3 sample a decrease was observed in the bands at 3330-3350 cm^{-1} which corresponds to –OH stretching vibrations on ageing due to the loss of moisture on ageing. The band at 1735 cm^{-1} and the shoulder of 1707 cm^{-1} indicates the presence of carboxylic group from acid and 1235 cm^{-1} confirms this thing. The aromatic character of the compounds is confirmed by the absorption bands at 1660-1600 cm^{-1} and the absorption band at 867 cm^{-1} . The bands between 1270 cm^{-1} and 1200 cm^{-1} represent the C-O deformation vibration of phenols and carboxyl. An increased absorption bands at 1430, 1318, and 899 cm^{-1} and broadening peaks at \approx 1370, 1267, 730 cm^{-1} , an indication of possible interactions between the functional groups of acids. The sulphate bands at 1108 cm^{-1} and 1162 cm^{-1} were observed in both samples.

In receipt of MP3 sample ink Prussian blue is also present, which was identified by 2089 cm^{-1} absorption band, corresponding to $\text{C}\equiv\text{N}$ vibration.

From the literature, as Reissland mentioned, the iron (III)-gallic acid binary complex has the following absorption bands 3550-3150 cm^{-1} represented –OH stretching vibration band, 1590 cm^{-1} represent a weak –COO asymmetrical stretching vibration band, 1700 cm^{-1} represented a weak –COO symmetrical stretching vibration band, 1609 and 1252 cm^{-1} represent a weak –CO phenol symmetrical stretching vibration bands, 863 and 770 cm^{-1} represent –C=C bending vibration bands, 1119, 1105, 1089 and 624 cm^{-1} represented –C-H bending vibration band that are in good agreement with the MP1 and MP3 samples.^{15, 19, 20}

For sample MP2 as seen in Fig. 3, the absorption bands present in the IR spectrum couldn't be attributed to any specific functional groups from the studied inks, except the 1568 and 876 cm^{-1} IR bands that are characteristic to carbon black ink.

Sample MP6 presented the following absorption bands 3412 cm^{-1} represented –N-H stretching vibration band, 1587 cm^{-1} represented a shift of a weak –NH₂ scissor vibration band, 1510 cm^{-1} represent a shift of a strong –CH₃ stretching vibration band, 809 cm^{-1} represent –NH₂ wagging vibration bands, Fig. 5. These bands are characteristic for aniline black ink spectrum from the data bases of the spectrometer library.

MP7 inked sample presented the following absorption bands 3550-3150 cm^{-1} represented –OH stretching vibration band, 1579 cm^{-1} represent a –COO asymmetrical stretching vibration band, 1579 and 1252 cm^{-1} represent –CO phenol symmetrical stretching vibration bands, 770 cm^{-1} represent –C=C bending vibration band, 1105, 1056 and 615 cm^{-1} represented –C-H bending vibration bands, Fig. 6. These bands are characteristic for iron gall ink. In receipt of MP7 sample ink Prussian blue is also present which was identified by 2089 cm^{-1} absorption band, corresponding to $\text{C}\equiv\text{N}$ vibration.

The comparative spectrum of MP1 sample and spectrum of Pyrogallol and gallic acid from data base spectrometer library, confirm that the nature of the ink is iron gall ink.

Another analytical FTIR DRIFT method for paper samples, consisted in scanning of unprinted paper (as reference) sample being its pair of printed paper. In Figs. 7-11, are shown comparative spectra obtained by the two mentioned DRIFT methods.

It has been noted that both methods offer important information about the spectra. In the case of spectrum subtraction of unprinted paper from the spectrum of printed paper the absorption bands are sharper and their number in cellulose absorption area (1200 to 900 cm^{-1}) is greater.¹⁶ It is important that in this region the SO_4^{2-} components and –C=C bending vibration bands present characteristic absorptions. The unprinted background method is less sensitive and many overlapped bands are present in spectra.

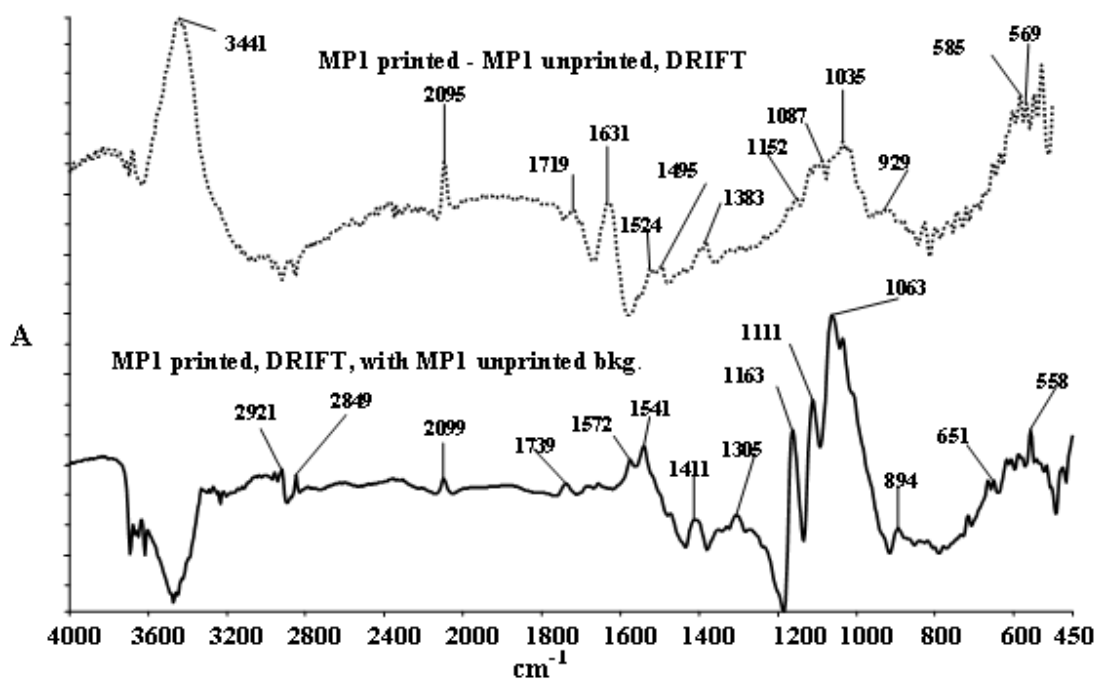


Fig. 7 – Comparison between two DRIFT measurement methods for MP1 sample.

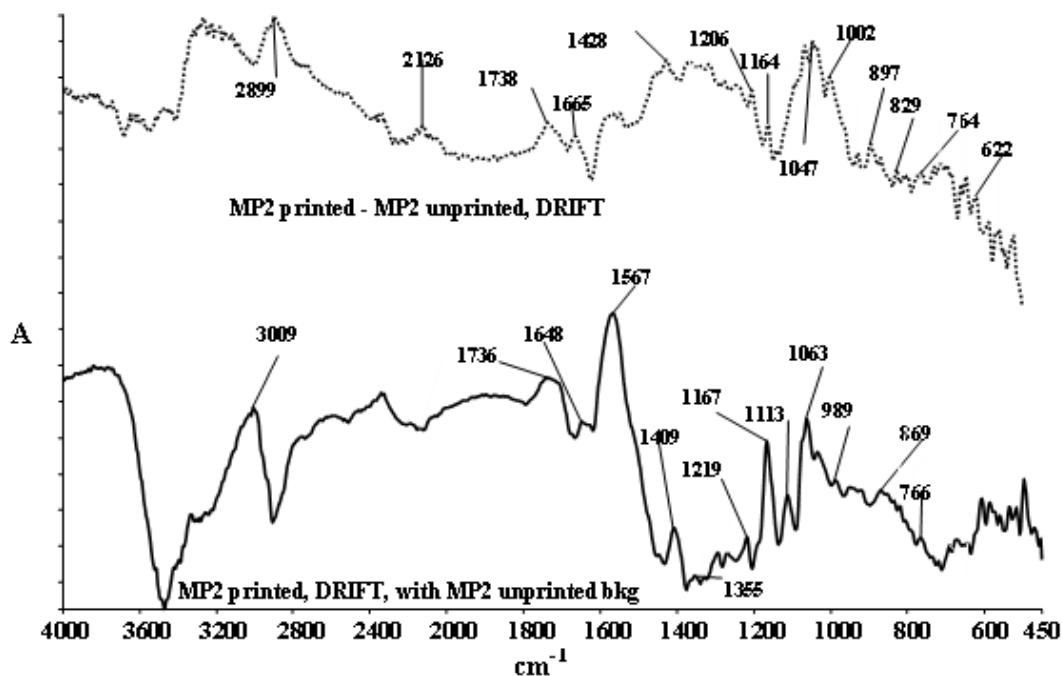


Fig. 8 – Comparison between two DRIFT measurement methods for MP2 sample.

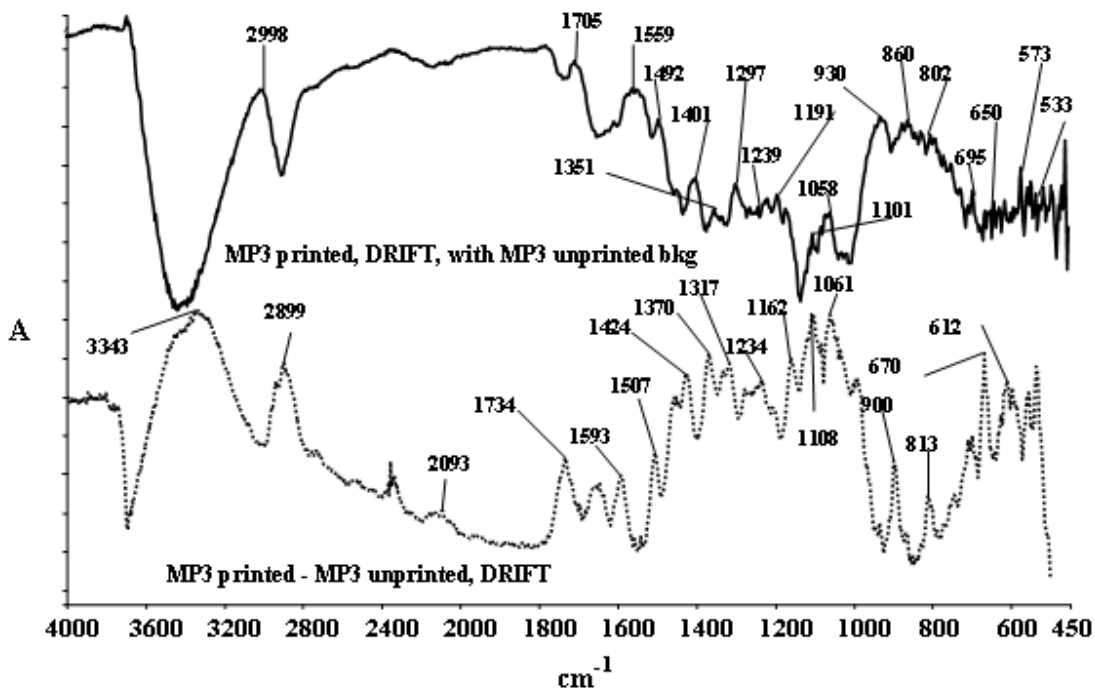


Fig. 9 – Comparison between two DRIFT measurement methods for MP3 sample.

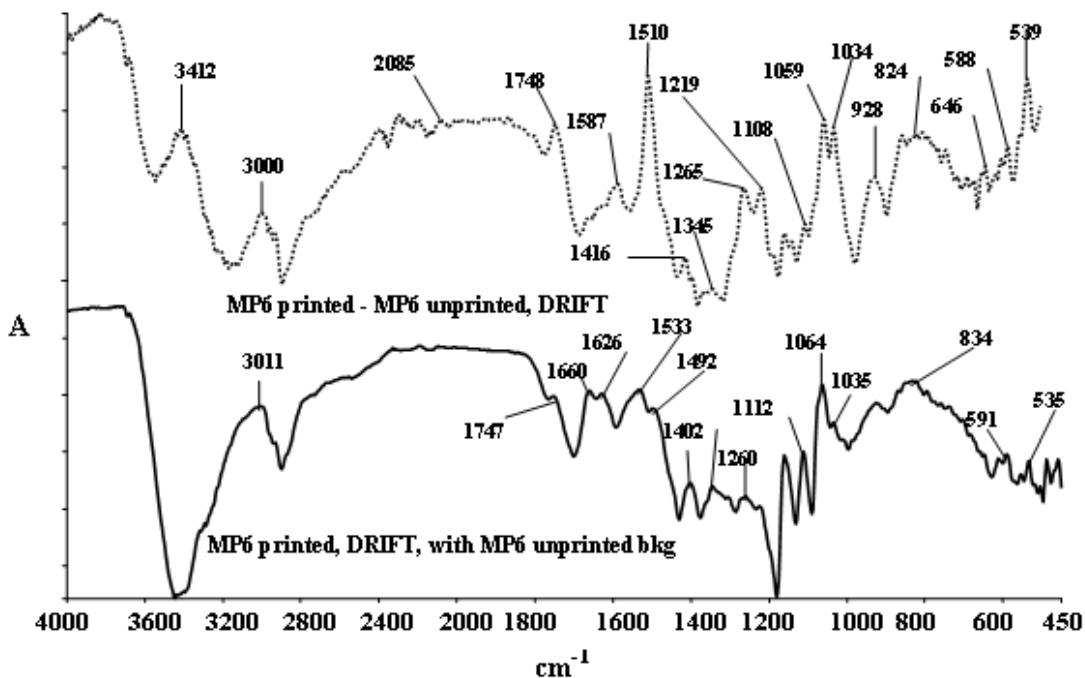


Fig. 10 – Comparison between two DRIFT measurement methods for MP6 sample.

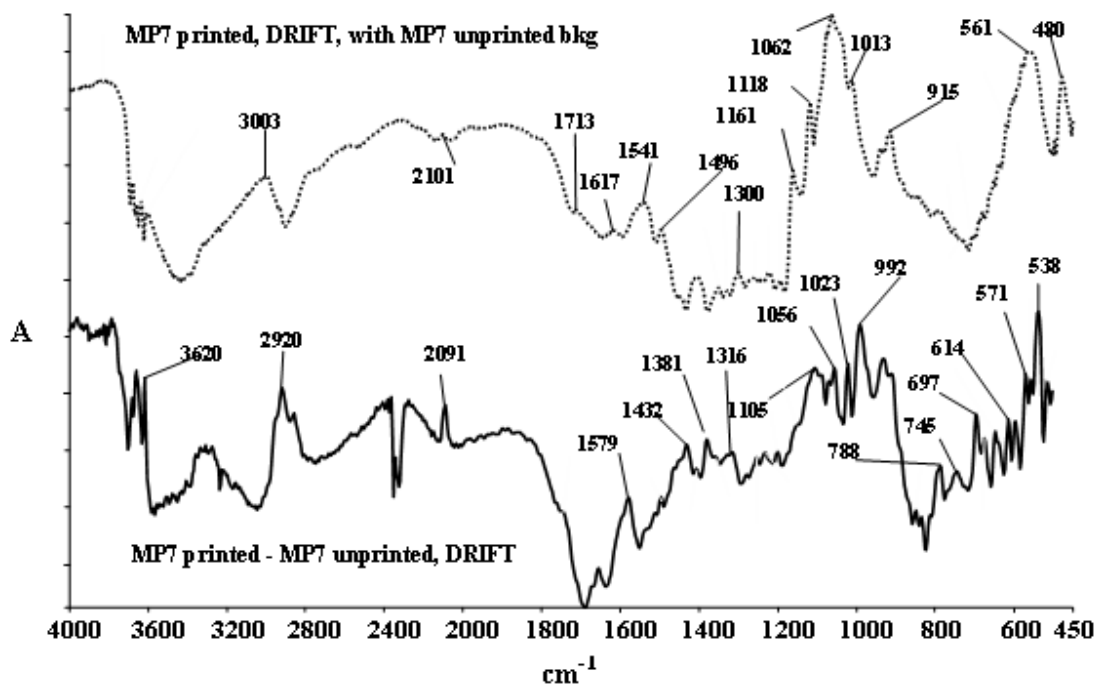


Fig. 11 – Comparison between two DRIFT measurement methods for MP7 sample.

CONCLUSIONS

To identify the type of ink used for books printing in the late nineteenth century and early twentieth century, FTIR spectroscopy method was applied. FTIR spectra of both unprinted paper samples and samples of blacks were recorded in two spectral techniques: the transmission and diffuse reflection. To detect differences between the spectrum of paper (the major component is cellulose) and inks, special attention was paid to absorption regions from 2800 cm^{-1} to 1200 cm^{-1} and 950 cm^{-1} to 600 cm^{-1} .

Comparing published data and our present studies in this area, spectral bands of functional groups, such as degraded cellulose and ink, could be identified. To confirm the presence of iron, but also other elements, components of functional groups of ink, X-ray fluorescent spectrometry after energy dispersion (EDXRF), was used.

MP1, MP3 and MP7 were found to be iron gall ink while MP2 is a carbon black ink. Sample MP6 was identified as aniline black ink.

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