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IRON GALL INK-INDUCED DAMAGE OF CELLULOSE FROM HISTORICAL PAPERS. SPECTROSCOPIC ANALYSES

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Abstract

Degradation of cellulose in historic paper by iron gall ink is a synergistic process of both, acid hydrolysis caused by acidic ink ingredients and oxidation catalyzed by free iron and/or copper ions. The interplay of both reactions was studied for historic paper samples.

Key words: *ink, irongall, FTIR, degradation, cellulose*

1. INTRODUCTION

Cellulose is one of nature's more durable organic materials if stored at suitable conditions. This has been attested by numerous archaeological textiles, which endured the test of time for more than two millennia. Yet certain compounds, such as acids and transition metal ions, which are present in historical iron gall inks, dramatically reduce its stability, resulting in the loss of its mechanical properties. Unfortunately, iron gall ink, the most widely used ink from the Middle ages up to the 20th century, contains both corrosive transition metals and acids, and may thus inflict severe damage to paper [1] For several centuries, iron gall ink induced decay, referred to as ink corrosion, has been acknowledged as one of the major threats to the written cultural heritage. Several conservation practices have been used to stabilize endangered documents through the centuries, trying to elucidate the stability of paper containing iron gall ink. An important part of the European cultural heritage is composed of hand-written documents. Many of these documents were drawn up with iron-gall ink. This type of ink present a serious conservation problem, as it slowly oxidizes ('burns') the paper it is written on, thereby gradually disintegrating the historic document. In order to enable development of a stabilization treatment, an in-depth knowledge of the corrosion process is needed. Two mechanisms are considered to be the cause of the disintegration: (A) acid hydrolysis of the cellulose and/or (B) the oxidation of organic compounds promoted by radical intermediates that are formed due to the presence of Fe^{2+} ions.

Mechanism (B), considered to proceed independently from (A) [2-5], involves the intermediate formation of radicals (O_2•, HOO•). Reaction of Fe^{2+} with HOO• in acidic medium leads to the formation of H_2O_2, which in its turn can further oxidize the paper (and the Fe^{2+} present in the ink). In the current investigation, a strongly corroded portion 17th manuscript (Romanian Gospel 1740), featuring white, crystalline precipitates on the inked areas, next to fragment (B), without white precipitations, were studied by means of different spectral techniques: FTIR, EDXRF.

Iron gall ink corrosion of paper is one of the largest threat for our graphic patrimony. A great work has been done in this field to explain the possible mechanism of paper degradation and to propose curative methods [2-5]. The main degradation mechanism proposed in the literature is the following: iron gall ink prepared with different ingredients including tannins and vitriol causes both acidic hydrolysis and Fe^{2+} catalysed oxidation of cellulose. Paper turns brown and loses its mechanical properties. Yet the great variety of iron gall ink recipes [6, 7], and the great variety of visual aspects of manuscripts suggest that many side effects could occur and contribute to the different aspects of paper degradation (colour changes, halos, mechanical properties).

Many analytical methods have been explored to analyse original iron gall inked manuscripts: among all of these, Fourier Transform Infrared spectrsocopy (FTIR) makes it possible to identify the paper charges and the carbon inks, Gas Chromatography provides information on the evolution of gallic acid and/or the binder [8, 9], SEM analysis [10, 11] are used to measure the elementary composition of the ink and the paper. Infrared techniques have been largely used in the paper industry for identification of different types of cellulose, hemicellulose and lignin [12, 13], FTIR techniques being able to provide further informations on this types of paper and/or on the writing itself, [14], since the main signal is due to the cellulose absorption. Also, FTIR spectroscopy provides information on the cellulose oxidation stage [15]. More recently, this technique has been used successfully to observe the paper carbonate content decrease which results from the transformation of calcium carbonate into calcium sulfate [16]. Cellulose remains the major component of the sample even in inked and damaged paper and only small discrepancies are observed between inked or damaged paper spectra and pure cellulose spectra.

In this work, we measured FTIR spectra on original and Romanian Gospel probe by diffuse reflectance with KBr (DRIFT). Advantages and drawbacks of each technique will be discussed. Interpretation of spectra will be discussed and correelated with the results of others techniques: ICP-EAS, EDXRF.

2. EXPERIMENTAL

2.1. Analytical techniques

The **FTIR** spectra are recorded directly on the sample via a Perkin Elmer Spectrum GX spectrometer. A small quantity of matter (a few milligrams) is grounded, then mixed with KBr and placed in a DRIFT cell. The spectra are recorded with a Perkin Elmer. The main measurements features are the following: range 4000 to 400 cm^{-1}, 35 scan, resolution 4 cm^{-1}, gain 1.

A Varian Liberty 110 Series spectrometer was used for the **ICP-AES** analysis. Multielement, matrix matched standards were used for the quantitative determinations. Microwave assisted digestions were performed in a Berghof microwave oven with the use of high-pressure closed Teflon PFA vessels and online pressure and temperature control. In particular, 0.1 g of each sample was placed in the Teflon PFA digestion vessels and a mixture of 5 ml HF 40% and 5 ml HNO3 69.5% was added.

A spectrometer **EDXRF** PW4025 – MiniPal – Panalytical was used for semi-quantitative compositional analysis of these pigments.

2.2. Archaeological material

The Romanian Gospel from 1740, has been offered for investigations by a private collectionar, and all the investigations did not damaged this piece of art. The ink has strongly corroded the paper, yielding to large brown halos around inscriptions and loss of matter in the inscriptions.



Fig. 1 – The picture of Romanian Gospel from 1740.

3. RESULTS AND DISSCUSION

The main advantage of FTIR technique remains in its totally non destructive aspect. Measurements can be carried out in a few second directly on an original sample inked area. The reproducibility of the measurements is however rather poor: figure 2 shows different spectra which are recorded on different inked and blank areas of the same document. Analysed areas were very close to each other (less than 2mm), so that the composition of the ink and the paper degradation stage are reasonably supposed to be uniform. In fact, the observed discrepancies were much larger that what was expected, especially in the cellulose high absorption region:

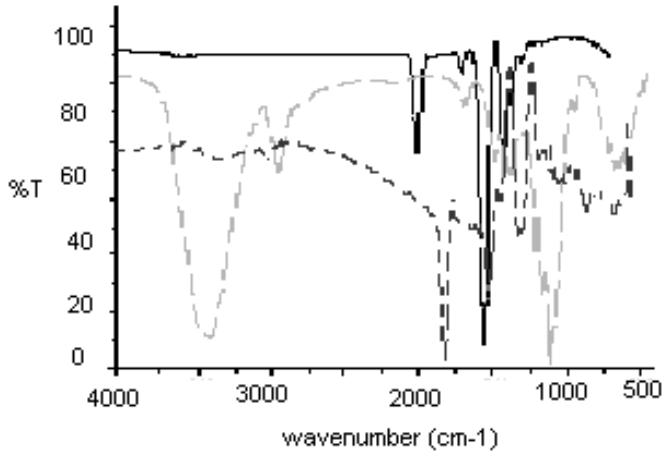

Fig 2: Reflectance microscopy on an original sample (black = paper gospel; black interrupted = evanghelia ink; grey interrupted= cellulose)

Despite the cellulose being the major component of the sample, no strong absorption band appears in the region (1200-950 cm-1)for the Gospel paper. The low absorption region (950 to 600 cm^{-1} and 1900 to 1200 cm^{-1}) of the cellulose corresponds to a low reflective index. We first notice that the paper profile is very close to the pure cellulose profile, except for the band at 1650 cm^{-1} which corresponds to the presence of water in cellulose. One can notice furthermore that inked areas are more absorbent than blank areas in the range 1750 to 1600 cm^{-1}. This increase of absorption could be attributed to the cellulose oxidation process. Finally, one can think after a careful examination, that the inked areas spectra show an increase of absorbance around 800 cm^{-1}, 1600 cm^{-1} and maybe 1400 cm^{-1}. Since these bands are rather small, we decided to explore other FTIR techniques to confirm these assumptions.

We then tried to estimate if, whether or not, this technique was reproducible enough to follow the degradation of cellulose induced by iron gall ink.

No clear distinction can be formulated between the spectra of virgin and inked paper. The concentrations of sulphate and gallic acid appear to be too low to modify the cellulose spectrum. No real information can be extracted in the cellulose strong absorption region. The cellulose oxidation appears clearly in the range 1750 to 1600 cm^{-1} and small absorption bands seem to grow up at 780 cm^{-1} and 1320 cm^{-1}.

The reflectance, R, was obtained by scanning the excitation monochromator in the adequate wavelength region. The remission function, F(R), was calculated using the Kubelka-Munk equation, defined by (1):

$$F(R) = (1-R)^2 / (2R) = K/S \quad (1)$$

The Kubelka-Munk equation applies to optically thick samples, i. e., those where any further increase in thickness does not affect the experimentally determined reflectance R. K and S are the absorption and scattering coefficients with dimensions (distance)-1 [17-19]. For an ideal diffuser, where the radiation has the same intensity in all directions, $K = 2 \varepsilon C$ (ε is the Naperian absorption coefficient, C is the concentration), K being mainly proportional to the absorption coefficient of the sample and S being mainly proportional to the scattering coefficient of the sample.

The diffuse reflectance spectra were much more comparable to transmission spectra so far a Kubelka Munk treatment was undertaken.

In the Kubelka Munk theory, the light is supposed to be scattered isotropically and the regular reflection negligible. These assumptions appear reasonable for KBr containing a small quantity of paper.

The sample consists of a little amount of paper dispersed throughout a KBr medium. The s factor should also be very closeto 1 and the k factor very close to $k=x.k_p$, x being the paper concentration of the sample and k_p the absorption coefficient of the paper. Figure 4 plots the evolution of DRIFT spectra with artificial ageing. It appears clearly that the definition of the cellulose absorption bands is rather poor for the non aged and the 7 days aged paper.

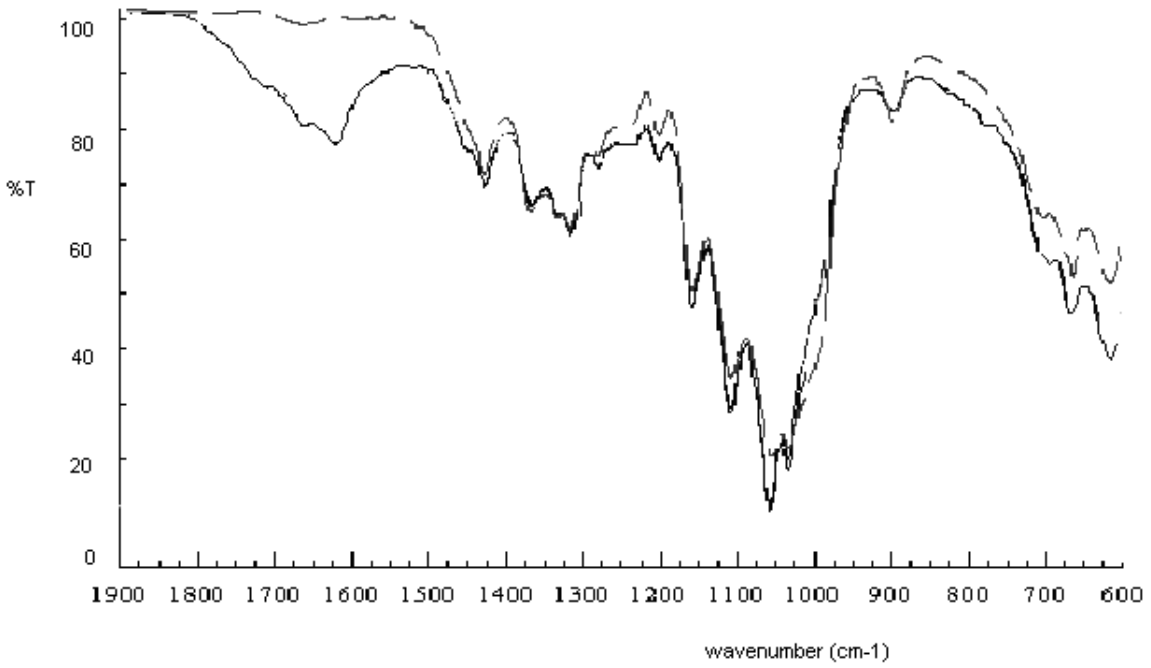

Fig 3: Diffuse reflectometry with KBr (DRIFT).
(interrupted line= pure cellulose; continuous line= degraded cellulose)

The comparison between the high damaged samples and the pure cellulose suggests the following comments :

- the increase of absorption in the range 1750 to 1600 cm^{-1} and at 780 cm^{-1} is confirmed. In conclusion, these absorption bands are relevant to the degradation of cellulose induced by the artificial ageing.

The region 1750-1600 cm^{-1} reveals the superposition of different bands, suggesting the apparition of several carbonyl and/or alkene groups. The apparition of a small band at 780 cm^{-1} (C-H out of plane vibration) is attributed to the C-H out of plane vibration in conjugated molecules. Still, further interpretation of theses absorption bands remains difficult.

Significant differences between inked and non inked areas are observed: absorption bands appear respectively between 1750-1600 cm^{-1}, at 1400 cm^{-1} and between 830-780cm^{-1}.

Several groups may correspond to the frequency1400 cm^{-1}:

-salts of cellulose oxidation products with inorganic cations (R-COOH ↔R-COOMetal). These salts absorb in the regions 1350-1450 cm^{-1} and 1550-1610 cm^{-1} [12]. Carboxylic salts may also be present in gums.

-SO_2 asymmetric stretching of sulphates ($(RO)_2SO_2$) [18]. But no equivalent band was found in laboratory probes.

EDXRF analysis of the Romanian Gospel paper coroborated with ICP-AES, data showed the presence of Fe, Ca, Mn, Zn, Ba, Si, Al, Na, K, Fe_2O_3, $CaCO_3$, ZnO, $BaSO_4$, $SrCrO_4$, K_2O, Na_2O, Al_2O_3, $Ca_3(PO_4)_3$.

4. CONCLUSION

Our first purpose was to investigate the possible application of FTIR techniques for the analysis of original manuscripts. The main difficulty of this kind of analysis consists in the great variety of possible ingredients and the influence these ingredients may have on paper degradation. The work presented above on laboratory probes indicates that the paper profile is very close to the pure cellulose profile even if the paper is highly damaged. Diffuse reflectance microscopy performed directly on the sample is of limited use, because of regular reflection. DRIFT spectroscopy with KBr offers a better reproducibility than transmission microscopy and is also preferentially used for laboratory probes. On the contrary, transmission microscopy is preferred for original samples, because of it's non destructive aspects. In this work, we showed that the two techniques give similar results on an original manuscript, which presents great discrepancies between inked and non inked areas.

Still the interpretation of the measured effects remains difficult and should be related to the comparison of laboratory probes and original manuscripts. We showed that the presence of iron gall complex can not be detected by FTIR The great differences observed in the spectra should also be attributed to the ink binding substance, and/or to the degradation state of cellulose in the paper.

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