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FTIR Technique Used to Study Acidic Paper Manuscripts Dating from the Thirteenth to the Sixteenth Century from the Archive of the Crown of Aragón

ABSTRACT

Fourier transform infrared spectrometry (FTIR), using a range of different accessories, was applied to the analysis of manuscripts. Diffuse reflection (DRIFT), a microscope with an attenuated total reflection (ATR) objective, and a microscope with a diamond cell were compared. This technique has proved to be useful to determine whether gelatin was used as a sizing in the paper and to identify remnants of lignin in early Arabic and Italian paper (circa 1350). With FTIR, cellulose in acidic papers which have been degraded by iron-gall inks exhibits a carbonyl band around 1720 cm^{-1}, which changes its shape depending on the pH of the paper. Samples also show different behavior according to the aqueous deacidifying solutions used: calcium hydroxide, calcium bicarbonate, or magnesium bicarbonate. The carbonyl band disappears completely with calcium hydroxide. Using a microscope with a diamond cell permits us to identify several oxalates in the ink composition: iron (III) potassium oxalate trihydrate in the most acidic inks, and iron (II) oxalate dihydrate when inks are nonacidic. Other compounds such as iron sulfate, calcium oxalate, calcium sulfate, and calcium carbonate were also identified in the samples.

INTRODUCTION

Degradation of paper and parchment has been studied because of its devastating effects on library and archive materials. Determining the composition of papers and inks is important in order to understand the reaction mechanisms involved in the damage to these materials. Knowledge of the compounds used to manufacture the paper and ink, their acidity, and their degradation products allows us to try to describe the degradation mechanisms and consequently to avoid them (Kolar 2006). Corrosion in manuscripts involves acidity and oxidation processes. Iron ions also play an important role in the oxidation of cellulose (Reissland 2000; Richly 2006; Strlič 2003).

Deacidification and counteracting the activity of iron ions are two of the usual practices in the conservation of manuscripts, though improvements to this process are still being discussed. Nowadays, information about compounds involved in the composition of degraded inks—as well as the influence of oxidation in cellulose when using different deacidifying solutions (Malesie 2002; Sistach 1999) such as calcium hydroxide, calcium bicarbonate, or magnesium bicarbonate—can be very useful when studying the degradation of paper or manuscripts (Bukosky 2001; Kolar 1998; Strlič 2005). Because these samples are, in many cases, unique and valuable, specific methodologies must be applied in order to minimize the amount of sample to be used and, consequently, to avoid any damage to manuscripts.

Infrared spectroscopy has been successfully applied to the analysis of papers and inks (Ferrer 2005; Calvini 2002; Lojewska 2005). Different methodologies and accessories can be used depending on the amount of sample, destruction, and information required. In this study we have used two different methods: diffuse reflection and microscopy. The microscope can be used either in transmission mode with a diamond cell or with an attenuated total reflectance (ATR) objective.

We applied FTIR in three different steps and with three different aims:

1. to identify gelatin and lignin in paper samples from the middle of the thirteenth century to the end of the fourteenth century;
2. to check the differing degree of cellulose oxidation linked to different levels of acidity in manuscripts and the different behavior of these oxidized or nonoxidized samples when using calcium hydroxide, calcium bicarbonate, or magnesium bicarbonate for deacidification;

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3. to identify compounds in inks.

EXPERIMENTAL

Apparatus

Microanalysis was performed on a Bomem MB120 infrared spectrometer with a coupled Spectra Tech IR Plan Microscope. The spectrometer has a KBr beamsplitter and a glowbar source. The microscope has an MCT detector refrigerated with liquid nitrogen and an ATR objective of ZnSe. Infrared spectra were measured at a resolution of 4 cm^{-1} in transmission mode and 8 cm^{-1} in ATR mode. The range measured was between 4000 and 720 cm^{-1}. The spectral data were processed with GRAMS/32 software.

Macroanalysis was performed on a Bomem DA3 infrared spectrometer. The spectrometer has a KBr beamsplitter, a glowbar source, and an MCT detector refrigerated with liquid nitrogen. The accessory used was a diffuse reflection (DRIFT). The instrument works under vacuum. The range measured was between 4000 and 450 cm^{-1} with a resolution of 4 cm^{-1}. The spectral data were processed with GRAMS/32 software.

Samples

Samples were chosen according to the three purposes of the analysis:

1. *Content analysis of paper*

Some Italian and Arabic papers with gelatin, starch, and lignin content were used when searching for these components.

2. *Acidity of paper*

We used eleven manuscripts with different acidity (pH 3.5 to 6.5) and several deacidifying solutions were applied: calcium hydroxide, calcium bicarbonate, and magnesium bicarbonate. These samples showed three different levels of degradation depending on their pH:

a. very acidic: pH lower than 4.5;
b. acidic: pH between 4.5 and 5.5;
c. nonacidic: pH higher than 6.

The aqueous solutions used in this study were calcium hydroxide (semi-saturated, pH = 12), calcium bicarbonate (pH = 5.4–5.8), and magnesium bicarbonate (pH = 6.4).

Samples were soaked in aqueous deacidifying solutions for 15 minutes according to their volume to weight ratio (1 mL of solution:1 mg of paper).

3. *Content analysis of inks*

We used sixteen paper and two parchment manuscript samples with different types of ink and different levels of degradation. The sixteen samples were classified in four groups according the type of ink:

a. light ink;
b. dark ink without corrosion;
c. black ink with weak corrosion;
d. black ink with strong corrosion.

Sample Handling

The diamond cell is one of the most frequently used tools in analysis of valuable samples. It is normally used when samples are very small but can be separated from the matrix. The particle or fiber, which can be as small as 5 mm, is removed from the matrix with the help of tungsten needles. It is then placed in a diamond window and put under pressure with the help of another diamond window. The pressure of the cell allows the sample to spread over the diamond, increasing its surface area while decreasing its thickness. In this way, the infrared radiation is able to pass through the sample and, therefore, its infrared spectrum can be obtained by transmission.

Attenuated total reflectance (ATR) is applied to samples where the composition of the surface needs to be measured. This is especially useful when the sample is either too thick or cannot be destroyed, separated, or manipulated. It is applied to soft samples, which can achieve good contact with the crystal of the attenuated total reflectance objective. The only consideration to be kept in mind is the ability to obtain good optical contact between the surface of the sample and the ZnSe crystal.

When the sample is big enough and it is not necessary to focus on small areas, it is possible to use diffuse reflection accessories in the macro sample compartment. These accessories give us information on a large area of the surface (about 2 mm).

The configuration of the diffuse reflection accessory has some limitations when the samples are too big. The size of the sample, 2.5 x 2 cm, is the maximum size in order to avoid a loss of energy.

RESULTS AND DISCUSSION

Initially, we compiled information about probable differences between Arabic papers used before 1350 and early Italian papers from between 1350 and 1450. Differences in sizing were found: gelatin was identified as the usual size used in early Italian paper, whereas starch was used in Arabic paper. We first applied microscopic analysis to characterize fibers and sizing in order to identify remnants of lignin and gelatin in each sample (fig. 1). The lignin was also identified as originating from straw in this early paper from Arabic production and from Italian production (figs. 2–3). Samples with significant degradation and acidity (pH = 3–4.5) exhibit oxidation of cellulose, with a clear shoulder for carbonyl groups placed around 1720 cm^{-1}. This carbonyl band is smaller when the initial pH increases (fig. 4).

A comparison of results for samples representing different deacidification compounds shows spectra with relevant differences depending on the initial pH of the paper. These differences are most evident when the solutions used have high alkaline pH, such as calcium hydroxide, and react with oxidized cellulose. The initial

Fig. 1. Image of remnant straw on the surface of the paper

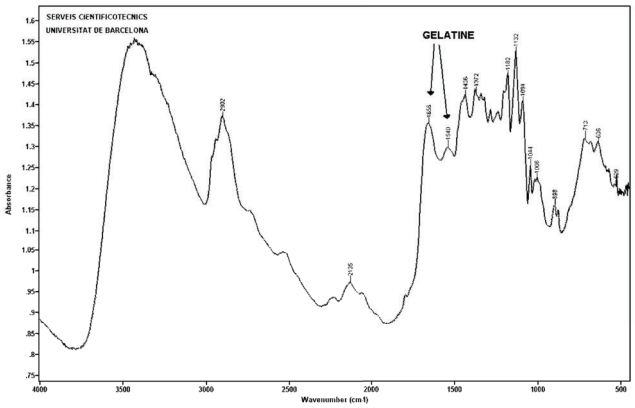

Fig. 2. FTIR-DRIFT spectrum of gelatin in early Italian paper

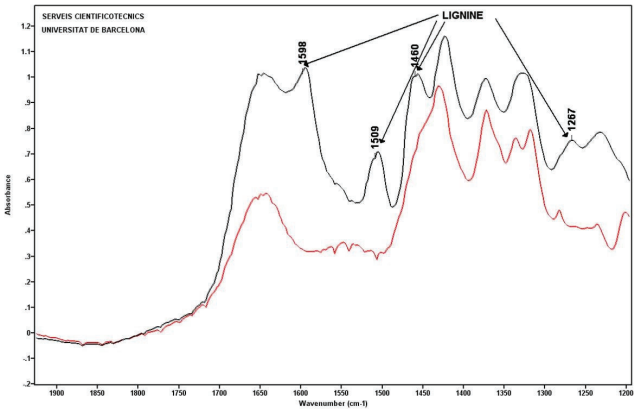

Fig. 3. FTIR spectrum with microscope and diamond-cell of lignin from remnants of straw in Arabic paper

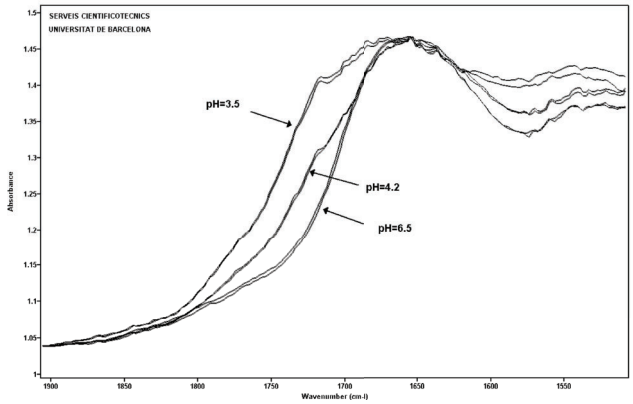

Fig. 4. FTIR-DRIFT spectra of samples with different acidity

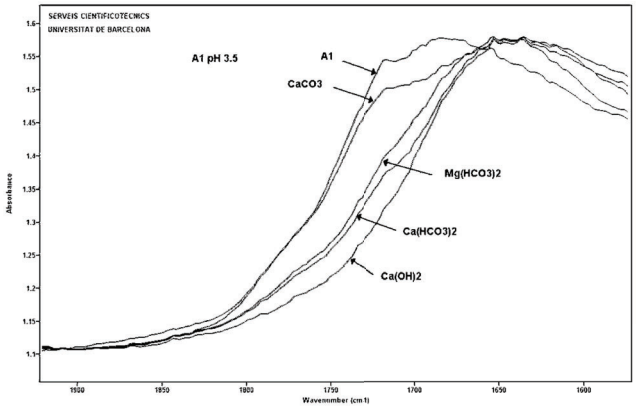

Fig. 5. FTIR-DRIFT spectra of an acidic sample A1 (pH=3.5) before deacidification and after soaking in calcium hydroxide, calcium bicarbonate, or magnesium bicarbonate

oxidation degree of the paper seems to be linked to acidity; therefore, the most acidic samples are those which show the most important changes in the carbonyl band depending on the pH of the aqueous solution used for deacidification.

Samples soaked in calcium hydroxide show the most significant decrease in the carbonyl band together with the simultaneous formation of carboxylates. When samples are soaked in calcium bicarbonate, a diminution of the carbonyl group is also evident, whereas magnesium bicarbonate results in smaller changes (fig. 5). Less acidic samples (pH > 5.5) show smaller decreases of the carbonyl band when soaking them in calcium hydroxide, calcium bicarbonate or magnesium bicarbonate. Spectra of samples whose pH is around 6.5 show no differences when using different deacidifying solutions.

The different behavior indicates that several factors have to be taken into account: the initial pH of the sample (together with oxidation of cellulose), the pH of the aqueous solution (the pH of calcium hydroxide in solution is between 10.5 and 12), and the use of magnesium or calcium bicarbonate. One explanation could be linked to the hydrolysis of oxidized cellulose (in C2 and/or C3) when using solutions with highly alkaline pH at room temperature, because the cellulose chain is broken at the ß-glycoside bond. Mg^{2+} ions can stabilize oxidized cellulose by contributing to the complex between

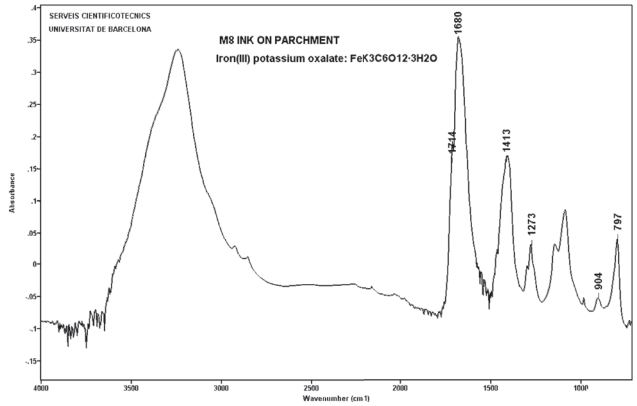

Fig. 6. FTIR spectrum with microscope and diamond cell of the iron (III) potassium oxalate trihydrate.

glucopyranoside units and the coordination of Mg^{2+}. This enodiol structure stabilizes the glycosidic bond and prevents later depolymerization.

Identification of compounds in inks shows several oxalates which were found in ink used on both paper and parchment. Compounds identified include calcium oxalate, iron (II) oxalate dihydrate, iron (III) potassium oxalate trihydrate (fig. 6), iron (II) sulfate, calcium sulfate, calcium carbonate, and ammonium-ferrous sulfate sixhydatate (Mohr salt). Bands were clearly identified using both microtransmission and the microscope with the ATR objective.

CONCLUSIONS

The techniques described allow us to distinguish between Arabic paper produced on the Spanish Mediterranean coast from the middle of the thirteenth century to the middle of the fourteenth century and early Italian paper. Starch sizing was normally used for Arabic paper, and gelatin was used for the Italian paper. Lignin was the other important component that was also found in remnants of straw in early papers.

Analysis of original acidic manuscripts using the DRIFT accessory can give us information about the oxidation characteristics of cellulose. Manuscripts that have a pH lower than 5.5 show different behavior depending upon the alkalinity of the solution used to deacidify and the type of compound used.

This technique also allows us to compare results after using calcium bicarbonate, magnesium bicarbonate, and calcium hydroxide. According to the spectra, it seems that magnesium ions contribute to the stabilization of glycosidic bonds. This study should be extended by testing different mixtures of calcium and magnesium bicarbonate in order to take the best advantage of calcium solutions and to improve results when using magnesium bicarbonate.

Gelatin and starch can also be identified with using the DRIFT accessory.

The analysis of papers and inks using a microscope with a diamond cell or ATR objective is useful in identifying compounds such as lignin, gelatin, and starch in papers, or oxalates and other inorganic salts in inks.

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