1/2013
April 2013

Introduction

Dear reader,
this is the 4th Newsletter of the European Research Centre for Book and Paper Conservation-Restoration and the first in 2013. As you might know already we publish two Newsletters per year, one in April and one in November. The concept of the newsletter is to

- Inform you about the past work
- Provide you each time with a never before published scientific article
- Inform about upcoming events

What we did for the community?

Men & Books – first results

On 1st March 2013 the second meeting in the EU Project Men and Books took place. In the symposium, which was organized by the Charles University in Prague, first results were given.

PROGRAMME

8:45 – 9:00 Registration
9:00 Opening (Zdeněk R. Nešpor)

9:15 – 10:15 Session I. Recent research on history of Silesian Protestantism

Jan Horský (Charles University, Prague): Echoes of Silesian Protestantism in the Czech lands
Veronika Chmelařová (Palacký University, Olomouc): Along with or alongside? Confessional coexistence in Teschen in the first half of the 18th century
Tomáš W. Pavlíček (Charles University, Prague): Vocation of clergymen and confessional cultures in the 19th century Silesia
Discussion

10:15 – 10:30 Coffee/tea break

10:30 – 11:30 Session II. Świdnica in history of Silesian Protestantism

Hedvika Kuchařová (Strahov Library, Prague): Franz Anton Graf Sporck und seine “Schweidnitzer Bibliothek”
Stephan Aderhold (Parafia Ewangelicko-Augsburska, Świdnica): Musikgeschichte der Friedenskirche in Schweidnitz
Zdeněk R. Nešpor & Blanka Altová (Charles University, Prague): Architecture of Restriction. Protestant church architecture in the Hapsburg lands in era of counter-reformation
Discussion

11:30 – 11:45 Coffee/tea break

11:45 – 12:45 Session III. Preservation of the cultural heritage

Piotr Oszczanowski (Uniwersytet Wrocławski, Wrocław): Glaube wie ein Herz aus Erz. Schätze aus der Friedenskirche in Schweidnitz
Patricia Engel (ERC for Book and Paper Restoration, Horn): Ethylene Oxide Residues in Fumigated Books - a First Result of the Project Men and Books
Katja Sterflinger-Gleixner (University of Natural Resources and Life Science, Vienna): Analysis of fungi on bound volumes from Swidnica - first results
Discussion

13:00 – 14:30 Lunch break

14:30 – 15:00 Move to the Strahov Monastery

15:00 – 16:00 Excursion: Treasures of the Premonstratensian Strahov Library (Hedvika Kuchařová)

16:00 End of the conference

Concerning conservation the results can be summarized as follows:

Katja Sterflinger[a] and Patricia Engel[b]
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b) European Research Centre for Book and Paper Conservation-Restoration, Wiener Straße 2, 3580 Horn, Austria

Introduction

The EU project “Men and Books” deals with bound volumes of the Archives of the Protestant Parish of the Holy Trinity in Swidnica, where 12000 individual items are stored. This archive is one of the most valuable for the history of Protestantism in Silesia, Bohemia, Moravia and Austria. Due to the climate, many of the books were attacked by fungi. During the 1990th the books in Swidnica were fumigated with ethylene oxide. In the special literature the use of ethylene oxide for book-disinfection is discussed highly controversially (see also Meyer & Petersen, 2006) and it still remains an open question whether or not ethylene oxide is a good choice for book-fumigation. It was the aim of the study (a) to analyse if there is an active fungal community on the ethylene oxide treated books and (b) to investigate possible remains of ethylene oxide that might still have an impact on the microbial community and protect the books against microbial attack but might also be health threatening for the reader of those volumes. 76 books, 44 manuscripts and 32 prints, were selected for the project. For microbiological analysis 20 samples were taken from various materials in 10 different books made of different paper types, leather and parchment, cardboard and textiles. (Table 1).
To detect off gasing ethylene oxide the books were put into a chamber of inert synthetic material of 1 qm volume and stored under closed conditions for 60 days at 20 °C and 50%rel. H.

Materials and Methods

Isolation of fungi from books

Porous membranes of different materials (nylon, polycarbonate or cellulose nitrate) with a natural electrostatic charge were used to collect fungal aerial hyphae, conidia spores and fruiting structures (Fig.2). Membranes were smoothly attached to the material surface for several seconds, removed and directly applied to cultural medium (2% MEA, DG 18) or stored in a sterile tube for DNA extraction and further molecular analysis. Plates were incubated at 20C for 7 days. Fungal cultures were purified by several transfers onto fresh medium and identified by sequencing of the ITSI-5.8S-ITSII region.

Measurement of ethylene oxide concentrations from books

The measurement was passive with ORSA-tubes filled with activated carbon. Probing lasted for 336 hours. Then the tubes were taken out of the chamber, closed and sent to gas chromatography. The analysis was made with GC/FID with retention time catalogues and quantification via external calibration function. This standard working instruction is a modified NIOSH 1612.

Results

The books from Swidnica show a severe deterioration by fungi and insects (Fig.1). However, most fungi that were isolated from the books are common species the spores of which are present in dust and in the air (Table 1). Airborne species of the genera *Cladosporium / Davidiella* were dominant on all the books. Only very few of the fungi isolated correlate with the optical phenomena like black and dark green layers, crusts and stains. Typical cellulose degrading fungi like *Alternaria*, *Acremonium* and *Phoma* were less frequent than airborne fungi. From several sampling areas no viable fungus was isolated although a fungal colony was clearly visible on the material.

Conclusions

From this results we conclude that the fungal flora in the Swidnica volumes was successfully fumigated and killed by the ethylen oxide treatment. Today, spores from airborne fungi are predominant on the books. Since no residues of the ethylen oxide could be detected, the books are now susceptible to new infections. In consequence climatic optimization of the storage conditons is highly recommended.

Acknowledgements

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References

Michaelsen, A., Pinzari, F., Ripka, K., Lubitz, W., Piñar, G., 2006. Int. Biodeterior. Biodeg. 58: 133-141
Sterflinger, Pinzari (2012): Environ Microbiol. 14(3):559-566

Innovationsscheck:

Together with WD Austria the European Research Centre for Book and Paper Conservation-Restoration developed a prototype for a humidifier, which takes into consideration the moldy environment of archival material.

ERASMUS Students – research activity

At the moment we have with us Jiri Taleva, Helsinki Metropolia University of Applied Sciences (1st March 2013-end of May 2013) and
Shirin Jacoby volunteer prior to university studies (8th May 2012 – June 2013).

More students are welcome to apply under ERASMUS – we can involve them into research on water marks, mass deacidification project and history of book binding as well as other upcoming research projects.

ARTICLE

Nanomaterials for Old Books Deacidification

Rodica Ion

NANOMATERIALS FOR OLD BOOKS DEACIDIFICATION

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Abstract

For many centuries, paper was the main material for recording cultural achievements all over the world. Historical papers represent important objects in libraries and archives as documents, manuscripts, books, herbarium and maps. Its damage is a result of different environmental factors (humidity and temperature), yield to the paper composition alteration, sometimes induced by added materials (ink, pigments or dyes). Cellulose degradation of historic paper is an undesired process for paper historical artefacts. The nano sized particles, used as non-aqueous dispersions, have been proposed particularly efficient for the preservation of cellulose-based materials that degrade through an acid-catalyzed process, which led to chemical de-polymerization. The overall effect is the shortening of the average chain length of cellulose that leads to a catastrophic loss of paper strength. This new method is based on the nanoparticles properties to penetrate into the network of the cellulose fibers, adhere to them, covering the damaged area and consolidating the paper without covering the ink. In the last few years, nanoparticles started to be used for documents recovery. It have been used $Mg(OH)_2$ and $Ca(OH)_2$ and hydroxyapatite, as restoring materials.

Special attention was paid to the positive effects of hydroxyapatite nanoparticles not only to the chemical and physical restoration of the cellulose, but also on its special property for microbiological decontamination (for fungi growth, the most frequently being Pennicillium and Aspergillus). These nanoparticles have been tested on some historical paper samples, unprinted and unwritten (from private collections), prelevated from books from 17th to the beginning of the 20th century.

Keywords: FTIR, TG, TGA, DTG; elemental analysis: ICP-AES, EDXRF, SEM, AFM, DLS, fungal decontaminating

1. Introduction

Paper consists mostly of cellulose fibres, whose molecules are linear polymers of β - D – glucopyranose monomers linked by β - 1,4 – glycosidic bonds. In addition to cellulose, paper contains also hemicelluloses, lignin and additives (inorganic fillers, dyes, pigments, metal ions, etc.) in different amounts, depending on the source of cellulose and on the final use of the material, respectively. Historical paper differs in many ways from contemporary paper [1].

Paper stability is a property related to the production processes and to the environmental conditions (temperature, humidity, presence of micro-organisms, etc.) in which the paper is stored. During the time paper undergoes unavoidable ageing processes that cause mainly the degradation of cellulose: these phenomena can involve acid substances and the moisture present in the material (acid hydrolysis), oxidative agents and the atmospheric O_2 (oxidation), micro-organisms (biodeterioration), or the light (photodegradation). All these factors act cooperatively and lead to both the progressive shortening of the polymeric chains and the variation of the crystalline content of cellulose [2].

Historical paper differs in many ways from contemporary paper. 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 [3].

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. Pollutants, light, high energy radiation and biological activity (fungi, bacteria and pests) were also found to exert a detrimental effect on paper. Studies have shown that the acidity of paper is the most important internal factor that accelerates significantly the decomposition of cellulose and the transition metal ions and other additives and impurities, from paper itself or from inks, contribute to it. Aging reduces the degree of polymerization and deteriorates the mechanical and optical properties of the paper [4].

For obtaining the best results in a restoration some principles should be obeyed:

- the treatment should be reversible so that one can go back to the original status of the work of art at any desired time;
- all the applied chemicals must ensure the maximum durability and the chemical inertness;

- applied chemicals must stop the degradation processes without altering the chemical composition of the works of art and their physicochemical and mechanical properties.

This paper deals with a new method of paper consolidation, based on the nanoparticles properties which have the ability to penetrate into the network of the cellulose fibers, to adhere to them, covering the damaged area and consolidating the paper without covering the ink. Special attention was paid to the positive effects of different types of nanoparticles not only to the chemical, physical properties on the cellulose, but also on its microbiological decontamination. Old paper in the environmental conditions is an ideal medium for fungi growth and the most frequently are Pennicillium and Aspergillus. In order to obtain good results in restoration, some physico-chemical investigations (obeying the artifact integrity), could be used: infrared spectroscopy Fourier-transformed (FTIR), Scanning Electron Microscopy (SEM), atomic force microscopy (AFM), thermal analysis, dynamic light scattering (DLS), energy-dispersive X-ray fluorescence (EDXRF) and induced coupled plasma-atomic emission spectroscopy (ICP-AES), in order to complete the elemental composition of the sample. The particles size and theirs size distribution have been measured by Dynamic Light Scattering (DLS) technique.

Nanoparticles in restoration and conservation

During the last decades, the scientists' contribution to conservation work related to cultural heritage has grown rapidly. Nowadays, conservation requires a deep knowledge of material science and nanotechnologies couldn't prevent yet all natural aging of the paper documents. Thus, chemists and physicists can contribute greatly to the *controlled death* of artifacts because they can provide useful and reliable predictions of the degradation of these works of cultural heritage [5]. The accepted idea was that these substances could be removed at any time, leaving a completely unaltered substrate.

Certain mass deacidification methods have been developed, but it can be said that none of the techniques offered fully satisfies the recommended quality criteria, such as preselection of the material to be restored, predrying, duration of the treatment, effect on ink, colours, covers, neutralisation of the paper acidity, final pH, alkali reserve, health risks to operators and readers, environmental impact, cost of the equipment and cost of treatment.

Knowing in depth of the degradation mechanisms means the decisive step in the historical paper conservation. In the last decade, on the world wide it has been started to apply the conservation of cultural heritage with nanomaterials. Among the first researches that have been applied this conservation method for the historical paper was the Wei t'o method based on the treatment with methoxy magnesium methyl carbonate, or isopropoxy magnesium isopropyl carbonate [6], creating magnesium nanoparticles. Wei T'o is less commonly used for mass deacidification treatment than for single item deacidification. Then has been followed the Ferroni-Dini method of conservation with barium hydroxide nanoparticles [7]. The so-called Ferroni–Dini method (two steps: the application of a saturated solution of ammonium carbonate, $(NH_4)_2CO_3$, and the treatment with a barium hydroxide solution, $Ba(OH)_2$, also called the 'barium' method, has long been the acknowledged method for the removal of salts that threaten paintings, reinforcing at the same time the porous structure.

The last elaborate method by the Proffesor Baglioni and collaborators was the treating with carbonates of the papetar objects [8]. Baglioni's group was among the first to synthesize nanoparticles in non-aqueous solvents with the optimal properties for application to cultural heritage conservation. Nano-sized particles, used as non-aqueous dispersions, have been proposed particularly, in this study, for their efficiency in the preservation of cellulose-based materials that degrade through an acid-catalyzed process, which leads to chemical disruption of the cellulose polymer. It has been shown that acid-catalyzed hydrolysis is the main chemical route for cellulose de-polymerization. The overall effect is the shortening of the average chain length of cellulose that leads to a catastrophic loss of paper strength [9, 10]. Dispersions of kinetically stable $Ca(OH)_2$ nanoparticles in non-aqueous solvents solved most of the drawbacks of the microsized powders. Each method has advantages and disadvantages and for this reason there are been looking new and new performance methods.

During the last years, a new type of material has been synthesized and applied for paper restoration. In the patent RO126570 (A2) it is presented for the first time in the literature the preparation and application of a suspension of hydroxyapatite nanoparticles in isopropylic alcohol, in a concentration of 0.08 ... 0.8% for chemical restoration and biological desinfection (for Aspergillus şi Penicillium fungi) for the surface of a deteriorated paper [11].

Hydroxyapatite (HA), $[Ca_{10}(PO_4)_6(OH)_2]$, nanoparticles dispersions in isopropylic alcohol applied on paper by spraying or by impregnation. Hydroxyapatite was used in many applications such as surgical and prosthetic bone implant, separation of proteins and as a vehicle for different drugs, obviously led to the conclusion that this substance has antibacterial properties [12]. This is a great advantage in handling paper-based artifacts that applied material also inhibits development of microorganisms in general, such as fungi and bacteria in particular.

The biological disinfection means the destruction and removal of bacteria, fungi and/or mold (or of their traces) from the paper support. In addition to these advantages, there are also two more, that the application of hydroxyapatite as hydroalcoholic solution allows nanoparticles a deep penetration into cellulose fibril structure so that its strength is improved and it creates a reservoir to neutralize the paper's acidic reaction. A possible mechanism reaction that occurs between the cellulose fibers and HAp takes place mainly at the primary OH group of cellulose, which is the most reactive of the three existing, and which has enough energy to form calcium phosphate cellulose with a free OH group involved in the neutralization of the paper acidity.

All these techniques have been tested on some small pieces of paper prelevated from Romanian books (delivered from private collections).

PAPER MATERIALS

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

The Romanian Gospel from 1740, has been offered for investigations by a private collectionary, 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.

ANALYTICAL TECHNIQUES

The **FTIR** spectra have been recorded directly on the sample with a Perkin Elmer Spectrum GX spectrometer, in the following conditions: range 4000 to 400 cm^{-1}, 32 scan, resolution 4 cm^{-1}, gain 1. A small quantity of matter (1 or 2 milligrams) was grounded, then mixed with KBr and placed in a DRIFT cell.

Induced coupled plasma-atomic emission spectroscopy (ICP-AES) analysis has been achieved with a Varian Liberty 110 Series spectrometer. Multi-element, matrix matched standards were used for the quantitative determinations. Microwave assisted digestions were performed in a Berghoff 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.

Energy dispersion X-ray fluorescence spectroscopy (EDXRF) has been achieved with a spectrometer **EDXRF** PW4025 – MiniPal – Panalytical. It was used for semi-quantitative compositional analysis of the paper samples, for determination the inorganic elements.

Thermal analysis have been performed on a Mettler Toledo Thermogravimetric Analyser TGA/ SDTA 851^e, in the range of temperature 25^{0}C to 1000^{0}C, in dynamic air, with 60 ml/min, at a heating rate of 10^{0}C/min, in alumina crucible, for all the paper samples, of 3mg to 5mg .

The particles size and theirs size distribution have been measured by **Dynamic Light Scattering (DLS) technique.** A measurement system of particles dimensions by Dynamic Light Scattering, Molecular Weight and Z Potential comprises the Zetasizer instrument and a computer with the Zetasizer software. The software is used to control the measurement of the sample

The Quanta 200 Scanning Electron Microscope (SEM) was used to produce enlarged images of a variety of specimens, achieving magnifications of over 100000x providing high resolution imaging in a digital format. This important and widely used analytical tool provided exceptional depth of field, with no samples preparation. The morphological structure of paper fibers can be investigated through the images collected by SEM and allows a direct observation of paper.

Atomic force microscopy (AFM) investigations were carried out with an Agilent 5500 SPM system, described by PicoSPM controlled by a MAC Mode module and interfaced with a PicoScan controller from Agilent Technologies, Tempe, AZ, USA (formally Molecular Imaging). A multipurpose large scanner and Point Probe Plus Silicon SPM Sensor cantilevers (PPP-FM cantilevers), n^+- silicon material and none coating, of about 227 µm length, 1.8 N m^{-1} spring constants, with the tips oscillated near their resonant frequencies (NANOSENSORS) in air, of about 64 kHz were used for all measurements. All AFM measurements (256 samples/line × 256 lines) were done by scanning the surface at a rate of 0.8-1.2 lines per second and were done at room temperature in tapping mode. The original images for the samples, the 3D topographical images and section analysis over the magnetite particles were performed using the PicoView SPM Software, version 1.6.2, Molecular Imaging. Height image data obtained by the AFM is three-dimensional. The usual method for displaying the data is by using a color mapping for height, for example black for low features and white for high features. The images were processed by first order flattening in order to remove the background slope and the contrast and brightness were adjusted

Acoustic AC Mode (AAC mode, tapping mode) is an oscillating technique that is less sensitive than MAC Mode, but gentler and less destructive than contact mode. The AAC mode option includes an AAC mode controller and an AAC mode scanner module. The piezo causes the probe tip to oscillate, typically at or near one of its resonance frequencies, such that it taps gently on the surface. The tip is then raster-scanned over the region of interest while the amplitude of oscillation is monitored to produce images. Through this method, lateral forces on the tip are virtually eliminated, enabling higher resolution imaging than is possible with Contact Mode.

BIOLOGICAL DECONTAMINATION OF PAPER

STOCK CULTURE

These cultures of Aspergillum sp. and Penicilium were cultivated on potato dextrose agar Petri dish and in gelose, respectively.

Stock cultures were then obtained by standard spread plate microbial techniques. It was inoculated into a growth medium comprised of KH_2PO_4 1g/L; $NaH_2PO_4.H_2O$ 1g/L; MgSO4 0,2g/L; MnSO4 0,002g/L; NH4NO3 0,5g/L; CaCl2 0,02g/L; FeCl3.6H2O 0,002g/L and glucose 2g/L as sole carbon source and 100 ml of these medium was transferred to 500 mL conical flasks. The flasks were placed on a rotary shaker operating at 150 rpm, where Aspergillus sp. was cultured aerobically. All culture work was conducted under aseptic conditions at room temperature (30ºC). The pH of the medium obtained was about 5.1. Growth of the fungus was observed after two days and it grew as pellets. The biomass was then washed thoroughly with deionized water to remove the growth medium sticking on to its surface.

CULTIVATION

Cultures set up using fungal structures sampled from the book with the aid of cotton swabs and inoculated directly on to agar plates resulted in the development of a few colonies of fungi (eight colonies randomly distributed over 20 agar plates). The two colonies developed were identified as belonging to the species, Penicillium chrysogenum and Aspergillus niger.

The same swabs, following immersion in sterile Gelose broth, developed the same colonies of fungal strains as mentioned above.

3. ANALYTICAL METHODS FOR OLD BOOKS INVESTIGATION

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.

3.1. Thermal analysis

Generally, thermal analysis represents a reproducible and practically convenient method to characterize heterogeneous organic material, as paper. Thermogravimetric analysis (TGA) provides a method for the determination of mass change in the polymer as a function of time and temperature: thus, this technique reflects reactions which occur at the molecular level of the polymeric material. In the case of paper, the thermal behaviour of its main components, as cellulose, hemicelluloses, lignin and additives can be well investigated with TGA and DTG [13, 14]. Also the presence of some filler influences the behaviour of paper during the thermal degradation.

A relationship between the chemical composition of the paper sample obtained by EA, EDXRF, thermal analysis TGA and DTG, with determination of the history of the paper samples and the method of manufacturing of the historical paper, has been achieved and published [15].

The TGA and DTG analysis have 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.

From analytical point of view, a thermal analysis of historical book papers is a first step in their degradation process evaluation. From the literature it is known that during the ageing of the paper can be identified the following processes:

- 20–100◦C—water desorption, recrystallization, glycosides bonds cleavage;
- 100–150◦C for functional groups formation;
- 150–250◦C, where occur new degradation products;
- 250◦C, specific for pyrolysis and dehydration process, with the formation of CO, CO_2 and water.

All these processes are exothermic, but basically the degradation of the cellulose in the gaseous combustion stage is endothermic.

The thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) curves for the paper are shown in Figure 1. No degradation takes place until 200 °C. Above this temperature thermal stability gradually decreases and the cellulose decomposition occurs. Generally, at temperatures less than 100 °C the water loss in all the samples takes place. Moreover, TG analysis gives an insight into the presence of inorganic fillers compounds in the sample by detection, in the derivatives curves, of their decomposition at temperatures usually higher than the decomposition temperature of cellulose. In a first approximation it can be assumed that cellulose does not interact with the fillers. Thus, it can be considered the decomposition of cellulose and the fillers independently.

First peak of the DSC curves represents the dehydration process; the second one represents the oxidative combustion of cellulose, each type of paper being characterized by different degradation velocity, at different temperatures. All kind of samples have the third peak of combustion that represents the oxidative degradation of lignin. The oxidative degradation of the inorganic fillers occurs above 700-750 ^{0}C.

From the literature it is known that the combustion of cellulose comprise two stages – gaseous combustion in which the gaseous degradation products catch fire, and then glowing combustion in which the carbonaceous residue pyrolysis with the evolution of CO, CO_2 and water [16-19].

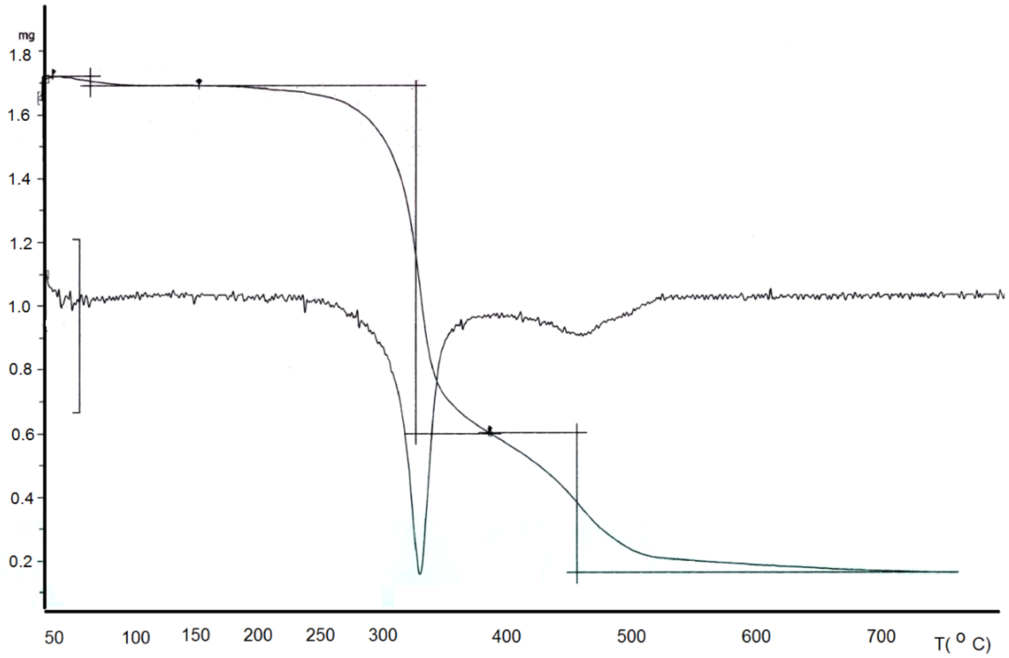


Fig. 1: TG and DSC curves for paper samples

Both these processes are exothermic but basically the degradation of the cellulose in the gaseous combustion stage is endothermic. It is only that the exothermic character of the combustion of the gases produced overwhelms the endothermic character of the basic reaction that produces the exothermic observed in DTA plots [20,21].

A significant influence present the organic additives or the cellulose from the paper, because they can increase the carbonaceous residues and alter the combustion-temperature ranges associated with the gaseous and glowing combustion.

In accordance with the literature, it has been established that no degradation takes place until 200 ^{o}C. Above this temperature thermal stability gradually decreases and the cellulose decomposition occurs. Generally, at temperatures less than 100 ^{o}C the water loss in all the samples takes place.

Moreover, TGA analysis gives an insight into the presence of inorganic fillers compounds in the sample by detection, in the derivatives curves, of their decomposition at temperatures usually higher than the decomposition temperature of cellulose. In a first approximation it can be assumed that cellulose does not interact with the fillers.Thus, it can be considered the decomposition of cellulose and the fillers independently.

In the TGA and DTG results discussion, coming from the recorded weight loss curves and their correspondent derivative curves, are reported in terms of:

1. Dehydratation Temperature of paper- peak 1
2. Decomposition Temperature of cellulose (Td_{cell})- peak 2
3. Decomposition Temperature of lignin (Td_{lignin})- peak 3
4. Decomposition Temperature of fillers ($Td_{fillers}$)
5. Residual weight (RW %) - at 1000 °C.

This value includes the amount of chairs, unburned components (i.e. inorganic fillers) and final decomposition products produced during the analysis.

All the paper samples show the cellulose decomposition in the range 310-350 °C, also when fillers are present in the material. Paper sample M2 shows the highest thermal stability.

Probabely due to the high ratio of heating, respectively 10^0C/ min, no peaks related to the inorganic fillers are revelated for all the paper samples.

The data are tabulated for all paper samples investigations in Table 1: sample type, initial temperature T_i [^{0}C], peak temperature T_p [^{0}C], final temperature T_f [^{0}C] of the DTG plot and the mass % of residue of inorganic salts and oxides, at 1000°C.

First peak of the DTG curves represents the dehydration process; the second one represents the oxidative combustion of cellulose, each type of paper being characterized by different degradation velocity, at different temperatures. All kind of samples have the third peak of combustion that represents the oxidative degradation of lignin. In the case of the paper M4 and M8, there is one more peak of oxidative degradation. This peak could not be assigned to the fillers because in the literature reports the oxidative degradation of the inorganic fillers occurs above 700-750^0C. The fourth peak appears at 490-505^0C.

Comparable results for the value of the residue of inorganic salts and oxides at 1000^0C are obtained for the M4, M5, M6 and M7 book paper samples that mean they have approximately the same amount of filler agents in their composition.

There are the M1 and M8 paper samples that have the smallest mass % of residue of inorganic salts and oxides, at 1000°C, 3,52% respectively 0,16%. At the opposite side, M2 paper sample, has the biggest mass % of residue at 1000^{o}C, namely 55,91%, and M3 sample has also a very high mass % of residue at 1000^{o}C, respectively 27,97%, that means the amount of fillers is very high .

A great importance has the second oxidative degradation step from the TGA curve that represents the oxidative combustion of cellulose, for all samples.

As the peak temperature corresponding to the second peak of the DTG curve is higher, the thermo destructive resistance of the paper is higher, and in this case is M2. That means that the paper resists better to thermal variations of the environment, so it presents the advantage of a better conservation. Very close values of the maximum temperatures of the second peak means that the cellulose from the studied papers is of the same type.

Table 1. TGA results for the paper samples: M1, M2, M3, M4, M5, M6, M7, M8

Samples	peak	T_i [^{o} C]	T_p [^{o} C]	T_f [^{o} C]	mass % of residue of inorganic salts and oxides at 1000 ^{o}C.
M1 French book, Paris, 1871	1	30	80	115	-
	2	172	328	396	-
	3	402	421	549	-
					3.52%
M2 French book, Paris, 1913	1	30	68	110	-
	2	180	345	413	-
	3	413	560	770	-
					55.91 %
M3 Romanian book, Bucuresti, 1914	1	30	64	130	-
	2	182	327	368	-
	3	368	470	510	-
					27.97 %
M4 French book, Paris, 1929	1	30	64	120	-
	2	185	320	370	-
	3	370	426	465	-
	4	465	503	545	
					8.44 %
M5 German book, Berlin, 1931	1	30	58	120	-
	2	160	328	387	-
	3	387	459	529	-
					9.63 %
M6 French book, Paris,	1	30	69	120	-

1935	2	171	315	394	-
	3	394	477	574	-
					12.21 %
M7 Romanian book, Bucuresti 1888	1	30	63	108	
	2	160	318	350	
	3	350	467	542	
					12.65 %
M8 Romanian book, Bucuresti, 1889	1	30	67	120	
	2	140	316	387	
	3	387	448	477	
	4	477	491	510	
					0.16 %

3.2. FTIR

As a direct connection with these results, FTIR technique has been applied to some possible filler already mentioned in the literature’s recipes for historical paper. 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.

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, $3MgO \cdot 4SiO_2 \cdot H_2O$, could be identified concluding that the historical artifacts contained this kind of fillers, in good agreement with the literature references. The entire FTIR spectrum indicates that the paper profile is very close to the pure cellulose profile even if the paper is highly damaged.

The main advantage of FTIR technique remains in its totally non destructive aspect. By comparison with cellulose standard, provided by Merck, could be observed that Romanian Gospel shows similar FTIR profiles with the cellulose 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}.

In the FTIR spectrum of Romanian Gospel there are two peaks at 1723 cm^{-1} and at 1236 cm^{-1} which are associated with the C=O and C-O stretching of the carboxyl group respectively. These two peaks indicate the presence of the acetyl group. The peak at 1723 cm^{-1} indicates the oxidation of the cellulose the shoulder near the water absorption belong to the C = O band, at 1648 cm^{-1}, which can be explained by hydrolysis and oxidation of cellulose. This is associated with reduction in the –OH band at 3430 cm^{-1}. 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 strong absorbance and also is present the typical features of the aromatic rings belonging to lignin, which accompanied the cellulose in the paper samples.

From the FTIR spectra, it was possible to put into evidence the degraded cellulose present in the analyzed spectra, too. By comparison between the high damaged samples and the pure cellulose suggested us that the absorption increasing from the range 1750 to 1600 cm^{-1} and 780 cm^{-1} is a relevant proof for the degradation of cellulose induced by the artificial ageing. Also, the bands from 1450-1350 cm^{-1} and 1610-1550 cm^{-1} have been attributed both to carboxylic salts and to C=O representing a possible way to put into evidence the carboxylic components. SO_2 asymmetric stretching from 670-640 cm^{-1} and 1690-1620 cm^{-1} have been reported, too, as a proof for the presence of sulfates in the samples.

In this review, the FTIR spectra from database spectra of Inorganic Art Materials [22] have been compared 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 (1430cm^{-1}), calcium sulfate (665cm^{-1}, 1621cm^{-1}, 1685 cm^{-1}) kaolin (468 cm^{-1}, 912cm^{-1}, 3620cm^{-1}, 3696 cm^{-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 [23, 24,25].

For a better knowledge of the paper's structure, it was done, as a first step, the size analysis of the different types of fillers, whose presence was confirmed by FTIR and EDXRF analysis on the paper samples. This dimensional analysis was performed with a transmission electron microscope, TEM, and was found that the most fillers are nanosize, e.g.: TiO_2 80-155 nm, ZnO 1.9 nm, $BaSO_4$ 24.3 nm, $CaCO_3$ 100 nm, $CaSO_4$ 30 nm, $Al_2(SO_4)_3$ from 0.2 to 50 nm. The others fillers, as was natural, had larger sizes: talcum 0.6 µm and kaolin 6 µm. This thing is of major importance in terms of preservation for these paper documents with nanoparticles.

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. Because of these two fillers, the ratio between Al percents and Si percents and the S contents, are so different in all samples. A similar remark could be done about Cl content. 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.

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 a sample to another. 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.

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 the fiber. 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}.

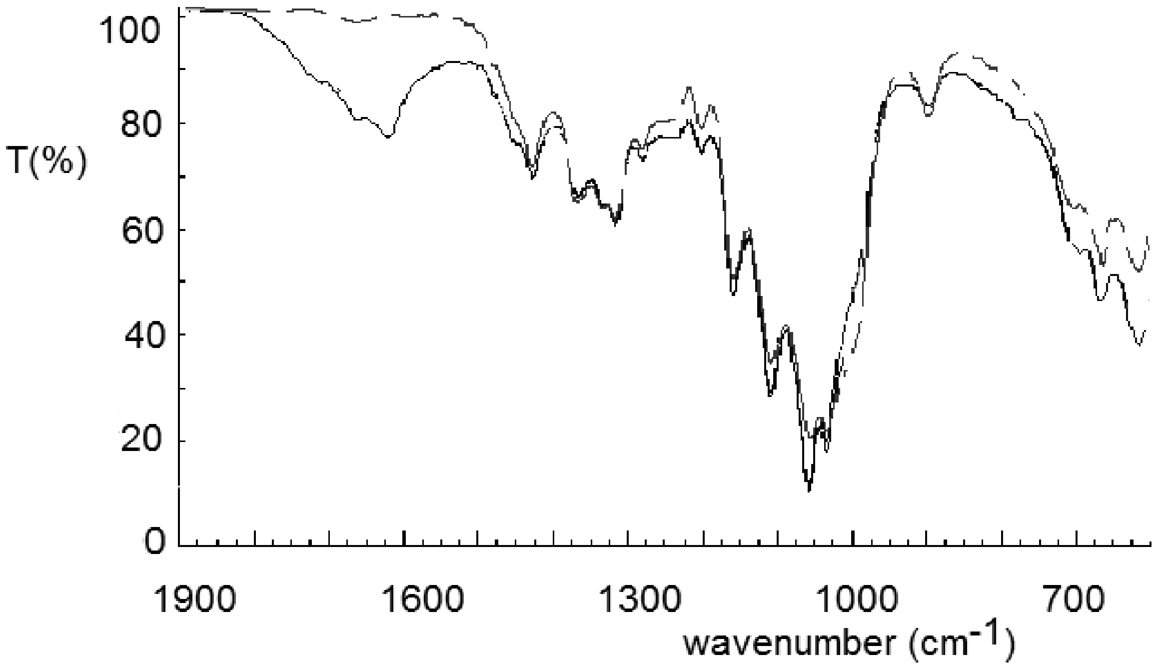


Fig. 2: Diffuse reflectometry with KBr (DRIFT) of Romanian Gospel paper

3.2.1. Cellulose crystallinity by FTIR

Cellulose crystallinity changes during ageing of paper, so variation in intensities and shifts of the individual bands at 3350 cm^{-1}, 3415 cm^{-1}, 3466 cm^{-1} in different spectra can be assessed. The peak at 2900 cm^{-1} is associated with the C-H stretching of non-aromatic compounds.

FT-IR can allow us to estimate the cellulose crystallinity (CI). The infrared crystallinity index has been already developed in 1960s by Nelson and O'Connor [26] and is based on the absorption ratio of two bands in the infrared spectrum of cellulose, 1372 cm^{-1} /2900 cm^{-1}. They found that the band at 2900 cm^{-1}, C-H and CH_2 stretching is relatively invariant while the absorption at 1372 cm^{-1} attributed to C-H bending, is quite sensitive to crystallinity changes. In both spectra in Romanian Gospel and in Liturgical Book papers there are two peaks at 1723 cm^{-1} and at 1236 cm^{-1} which are associated with the C=O and C-O stretching of the carboxyl group respectively. These two peaks indicate the presence of the acetyl group. The region 1750-1600 cm^{-1} reveals the superposition of different bands, probably due to several carbonyl and/or alkene groups. The small band 780 cm^{-1} (C-H out of plane vibration) is attributed to the C-H out of plane vibration in conjugated molecules. Anyway, definitive interpretation of theses absorption bands remains difficult. The peak at 1723 cm^{-1} indicates the oxidation of the cellulose and it isn't a clear band, it is a shoulder near the water absorption belonging to the C = O band, at 1648 cm^{-1}, which can be explained by hydrolysis and oxidation of cellulose. This is associated with reduction in the –OH band at 3430 cm^{-1} [27-28].

The band at 2370 cm^{-1} occurring in the spectrum belongs to the adsorbed carbon dioxide from the atmosphere. 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 strong absorbance and also is present the typical features of the aromatic rings belonging tolignin, which accompanied the cellulose in the paper samples [29-32].

Same remarks could be valuable for Liturgical Book. Also, we compare their FTIR spectra to those of Merck fillers as: calcium sulfate dehydrate, anhydrous calcium carbonate, barium sulfate Such samples show specific absorption bands for calcium carbonate (1430cm^{-1}), calcium sulfate (665 cm^{-1}, 1621 cm^{-1}; 1685 cm^{-1}) kaolin (468 cm^{-1}, 912 cm^{-1}, 3620 cm^{-1} 3696 cm^{-1}), concluding that our historical artifacts contain this kind of fillers, in good agreement with the literature data [33].

3.2.2. Ink identification by FTIR

For many centuries ago, paper was the main material for recording cultural achievements all over the world. The historical papers constitute important objects in libraries and archives (documents, manuscripts, maps), and their damages as a result of different environmental factors (humidity and temperature), yield to the paper composition alteration, sometimes induced by added materials (ink, pigments or dyes). The destruction mechanism is not yet fully understood.

In order to preserve the historical paper, some effective treatments are imposed but only after the identification of the ink composition [34, 35].

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 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 [36].

- 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 [37].
- 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-19 th century and the aggressive chemicals added to the paper pulp during its sizing (19 th – 20 th centuries) yielded to an accelerated self-destruction process of the paper.

It’s well known, that chemical substances can be identified by their IR spectra, which show certain bands, i.e. characteristic vibrations, typical for particular chemical groups defined by specific frequencies and intensities in IR spectra [38, 39].

The recently published results [40-44], clearly demonstrate that FT-IR spectroscopy is an important tool for the historical materials characterization.

The composition and degradation of historical paper has been investigated by FT-IR spectroscopy. This technique allows the identification of the cellulose origin and the chemical composition of some additives used in the papermaking [45].

Sampling of historical artifacts, for analysis, is rarely permitted, and for this reason, only non-destructive or at least micro-destructive analytical techniques are allowed. Infrared spectroscopy is suitable for all these demands and shows great potential for conservation and restoration of surface materials studies [46, 47].

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, Figure 3.

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 [48], which could be attributed to ferrous sulphate. 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, it was used the mathematical processing of spectra. 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.

The difference spectra can offer some information about the fillers and binders that are present both in paper and in ink.

Results for unprinted and printed paper are represented in Figures 4,5.

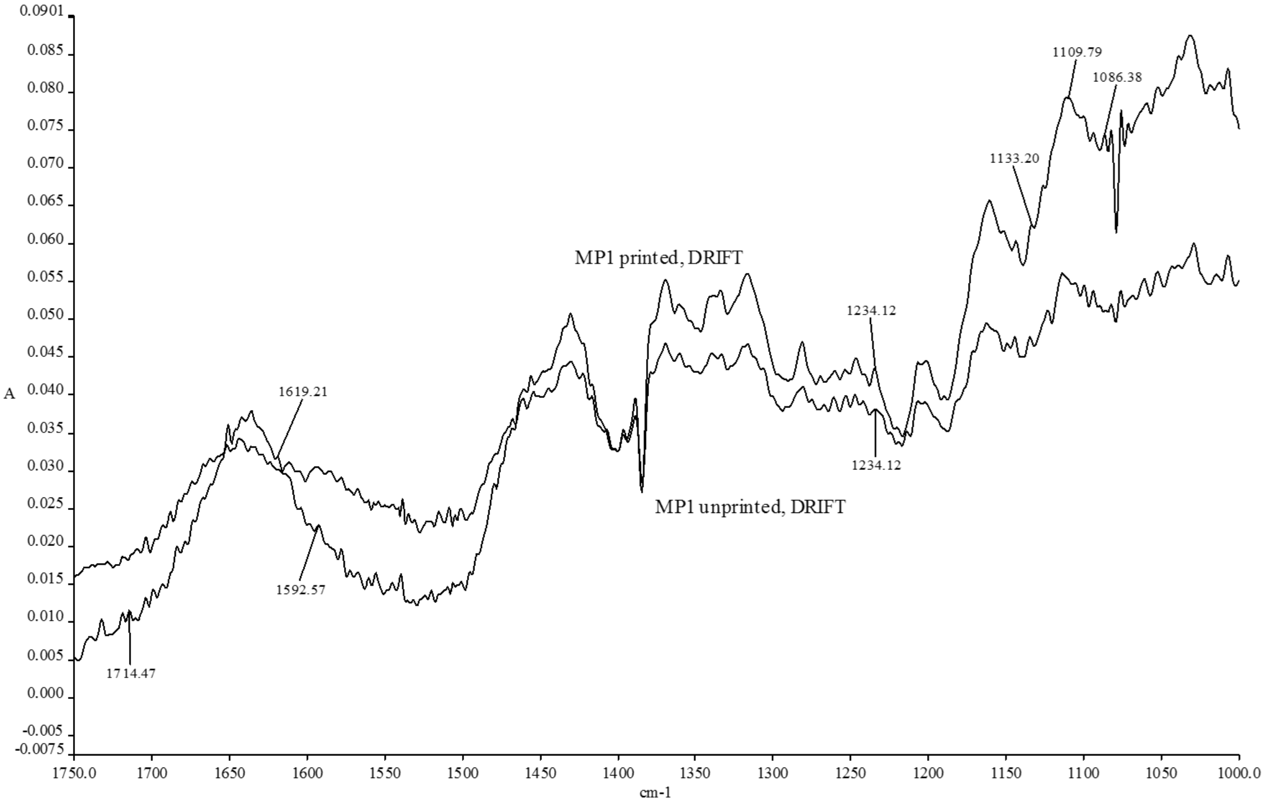


Figure 3. DRIFT spectra for MP1 book paper unprinted and printed

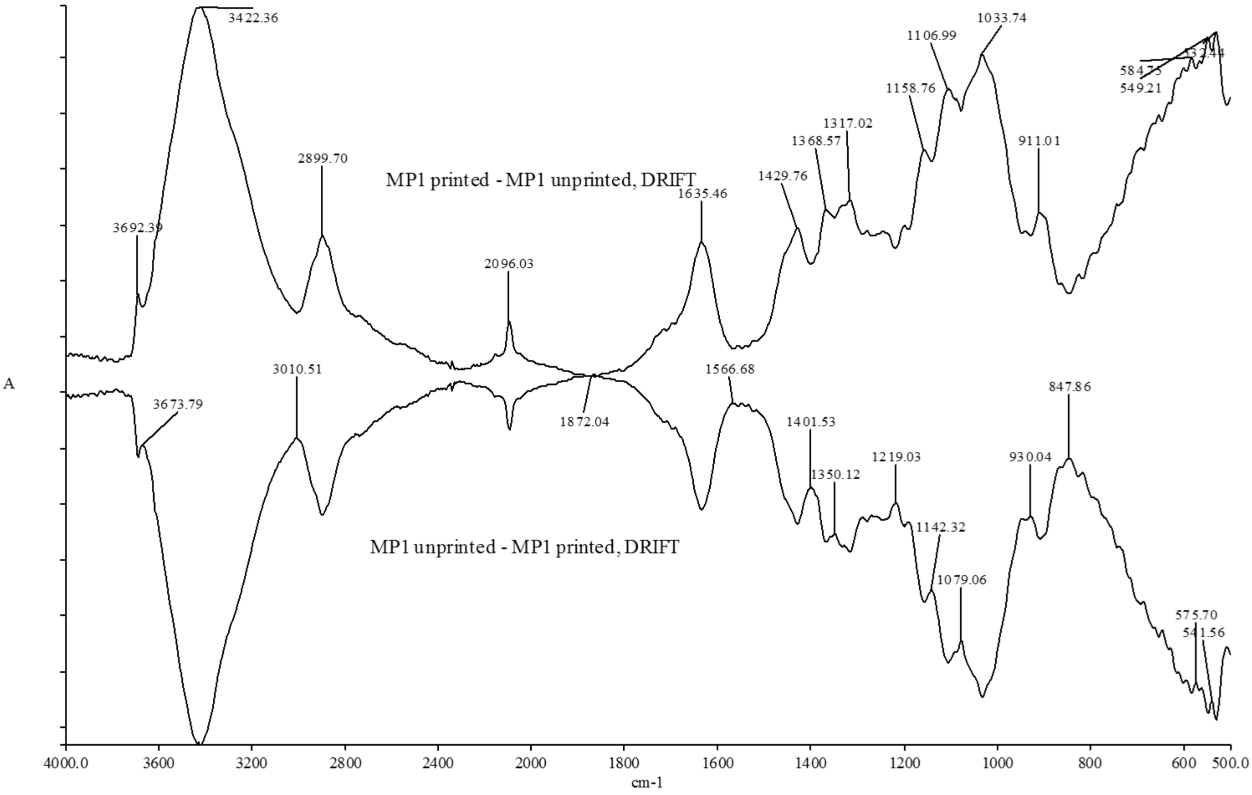


Figure 4. DRIFT spectra for MP1 difference spectra of book paper unprinted and printed

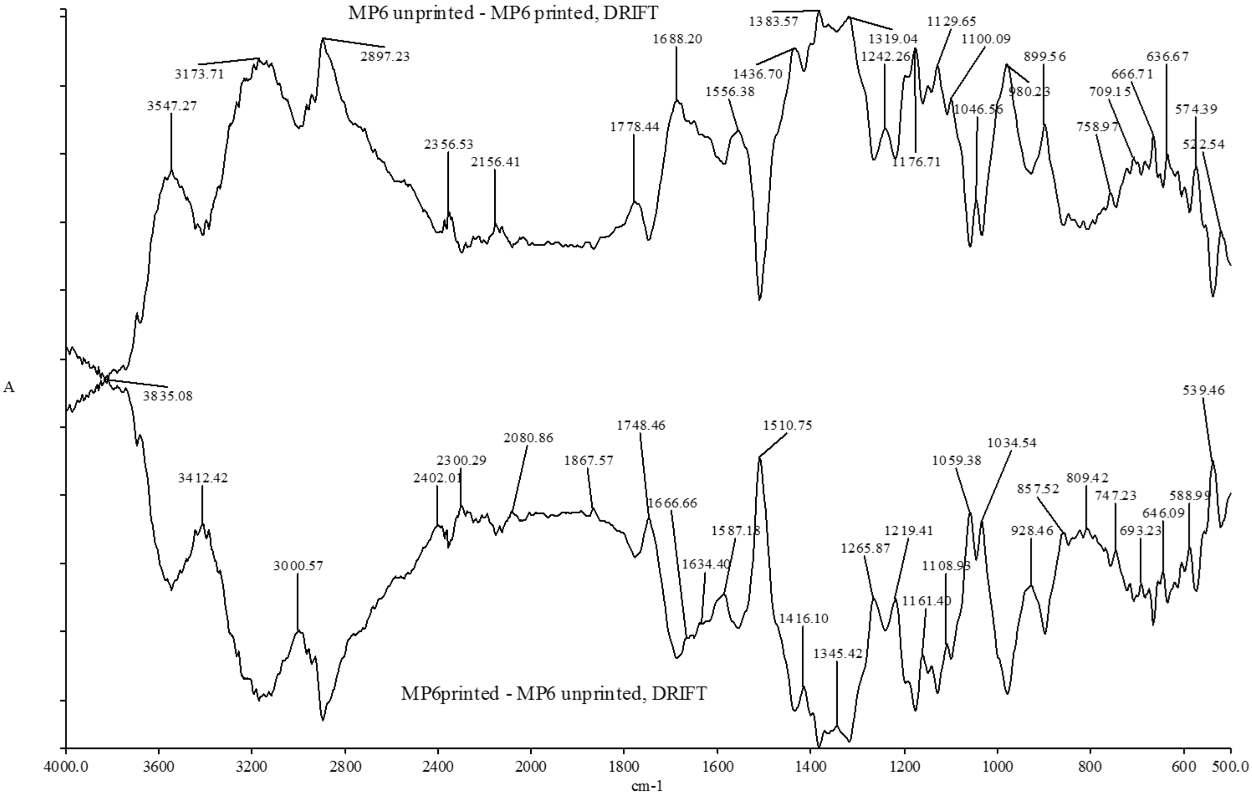


Figure 5. DRIFT spectra for MP6 difference spectra of book paper unprinted and printed

In Figure 4 for MP1 sample the region 1750-1600 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 1750-1600 cm^{-1}, at 1429 cm^{-1}, between 1400-1200 cm^{-1}, between 1200-900 cm^{-1} and between 830-540 cm^{-1}.

The band from 1492 cm^{-1} could be attributed to the ink binding substance, in good agreement with literature [48].

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 1350-1450 cm^{-1} and 1550-1610 cm^{-1}
- some azo compounds (ammonium salts, amides). Protein binders may be responsible for the presence of nitrogen.

The band in the range 1300 - 1500 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 [49]. Also the absorptions in this region (1350-1450 cm^{-1}) may signify the presence of Gallic acid [50].

The bands at 1106 cm^{-1} and 1158 cm^{-1} may indicate the presence of SO_4^{2-} ion [51] which comes from ferrous sulphate. 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 (1350-1450 cm^{-1}) may signify the existence of Gallic acid used in the inks applied to paper samples [52]. In MP1 sample ink there is present also Prussian blue, identified by 2089 cm^{-1} absorption band, attributed to C≡N vibration [53]. 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, [54]. The sample MP1 gives a more intense band at 1735 cm^{-1} that 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 [55].

The sulphate bands were observed 1108 cm^{-1} and 1162 cm^{-1}, could be 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.

From the literature [56], 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 [57] that are in good concordance with the MP1 and MP3 samples.

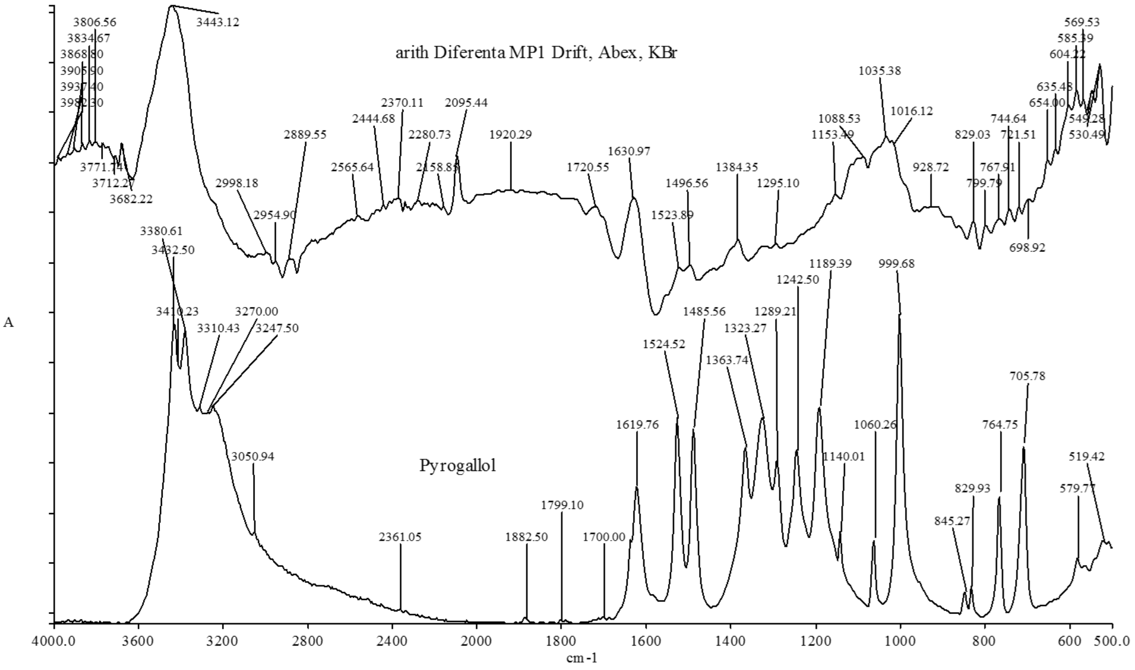


Figure 6. The comparative spectrum of MP1 sample and spectrum of Pyrogallol

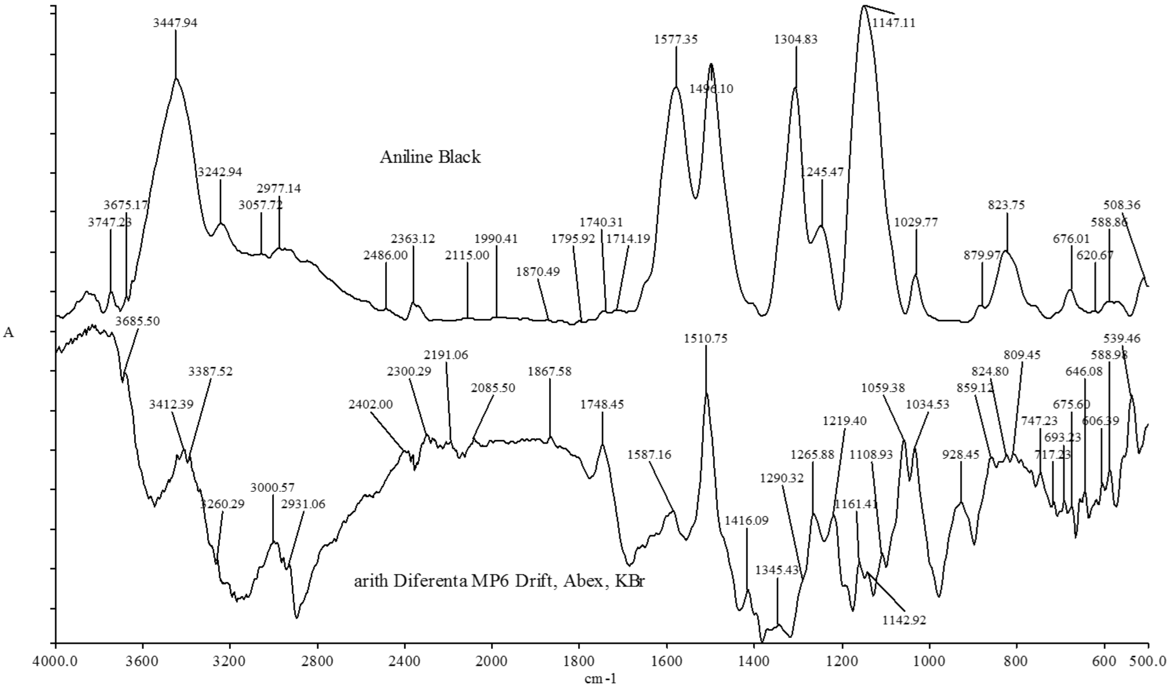


Figure 7. Comparative spectrum of MP6 printed sample and the spectrum of aniline black ink

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 –NH$_2$ wagging vibration bands, Figure 6. These bands are characteristic for aniline black ink and in Figure 7 there are comparative represented the spectrum of MP6 printed sample and the spectrum of aniline black ink. The comparative spectrum of MP1 sample and spectrum of Pyrogallol from data base spectrometer library are shown in Figure 6, and this fact is to confirm the nature of the ink.

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. 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.

Also, Si, Al, Na Fe, Mn could be present in the sample as secondary fillers. By comparing FTIR spectrum of Romanian Gospel with to those of Merck fillers as: calcium sulfate dehydrate, anhydrous calcium carbonate, barium sulfate, could be observed specific absorption bands for calcium carbonate (1430cm^{-1}), calcium sulfate (665cm^{-1}, 1621cm^{-1}; 1685 cm^{-1}) kaolin (468 cm^{-1}, 912cm^{-1}, 3620cm^{-1} 3696 cm^{-1}), concluding that our historical artifacts contain this kind of fillers, in good agreement with the literature data [58-65].

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.

3.3. EDXRF

Although no peaks related to the inorganic fillers are revealed for the paper samples, it is important to note that EDXRF analysis detected the presence of the inorganic fillers in all the paper samples. In order to better define the elemental composition of the papers, EDXRF spectroscopy has been used for analysed the historical 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 [32].

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 2.

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.

Table 2. The chemical EDXRF composition of paper samples M1, M2, M3, M4, M5, M6, M7, M8 in relative %

	Paris	Paris	Bucharest	Paris	Berlin	Paris	Bucharest	Bucharest
	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

EDXRF analysis of the Romanian Gospel paper corroborated 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, $Ca_3(PO_4)_3$.

Meanwhile, EDXRF analysis of the Romanian Gospel paper corroborated with ICP-AES, showed the presence of different metals, Ca and Ba being the most representative [66].

3.4. ICP-AES spectroscopy

In order to define the elemental composition of the papers, ICP-AES spectroscopy has been used for small pieces detached from the book showing 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. EDXRF analysis of the Romanian Gospel paper corroborated 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, $Ca_3(PO_4)_3$. These results are in good agreement with some literature reports, where alum represents a class of chemical compound, usually added to the gelatin size or, alternatively, applied to paper separately after gelatin sizing [67]. 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. The specific compound is the hydrated potassium aluminum sulfate (Potassium alum) with the formula $KAl(SO_4)_2.12H_2O$, or even $FeAl_2(SO_4)_4.22H_2O$, $MgAl_2(SO_4)_4.22H_2O$, $NaAl(SO_4)_2.6H_2O$, $MgSO_4.7H_2O$ and $Al_2(SO_4)_3.17H_2O$. Any contamination with iron sulfate was greatly disliked as this darkened and dulled dye colors [68,69].

3.5. Elemental analysis

Elemental analysis, EA, and EDXRF spectroscopy are very powerful analytical tools that can provide the compositional information of organic and inorganic materials (components). Beside the organic components of the paper samples, consist in cellulose, hemicelluloses, lignin and binders, it is important to know the fillers' nature in the paper samples [70, 71].

To determine the percentual composition of the organic components from all the eight paper samples, elemental analysis, EA, has been applied. The results are sumarised in Table 3, and they represent an average of three measurements.

Table 3. Elemental analysis of organic compounds from paper samples: M1, M2, M3, M4, M5, M6, M7, M8

Sample	C %	H %	O %

M1	37.34	5.99	56.67
M2	32.63	5.61	61.76
M3	38.53	5.87	55.60
M4	42.90	6.39	50.71
M5	38.84	6.26	54.90
M6	40.51	6.03	53.46
M7	40.22	6.08	53.70
M8	38.46	6.28	55.26

After recalculation the percentual composition of the samples, taking account of the organic material, the results are given in Table 4.

Table 4. Elemental analysis of organic and inorganic compounds, after the percentage redistribution, for paper samples: M1, M2, M3, M4, M5, M6, M7, M8

Sample	C%	H%	O%	Residual weight %, at 1000 ^{0}C
M1	36.03	5.78	54.67	3.52
M2	14.39	2.51	27.19	55.91
M3	27.75	4.19	40.09	27.97
M4	39.28	5.85	46.43	8.44
M5	35.10	5.66	49.61	9.63
M6	35.57	5.29	46.93	12.21
M7	35.23	5.42	46.70	12.65
M8	38.40	6.27	55.17	0.16

6. SEM/AFM and treatment with nanocrystals

Electron microscopy became one of the most important techniques to characterize the materials morphology on the nanometer and nowadays even on the atomic scale. Scanning electron microscopy (SEM) produces high resolution images of a sample surface. SEM images have a characteristic 3-D appearance and are therefore useful for judging the surface structure of the sample. The primary electrons coming from the sources strike the surface and they are inelastic scattered by atoms in the sample. The electrons emitted are detected to produce an image. The micro-architecture of cellulose pellicles was investigated for untreated paper, unwritten and uncolored, as reference. Micrographs obtained for this sample revealed a densely packed network of cellulose fibers which, within the sheet of paper, appeared to be random in orientation at the micron length scale, with no indication of microfiber directionality. The fibers are homogeneous and seem to originate from rags, probably cotton or linen. The fiber sizes are different and some seem to be broken. Some fibers exhibit encrustations which could be salt crystals. The presence of minerals in paper can often be the consequence of the way it was produced. The light part of the image can be the consequence of the presence of a thick part of sizing material or of a rupture in the paper. This important and widely used analytical tool provided exceptional depth of field, with no samples preparation. The morphological structure of paper fibers can be investigated through the images collected by SEM and allows a direct observation of paper [72].

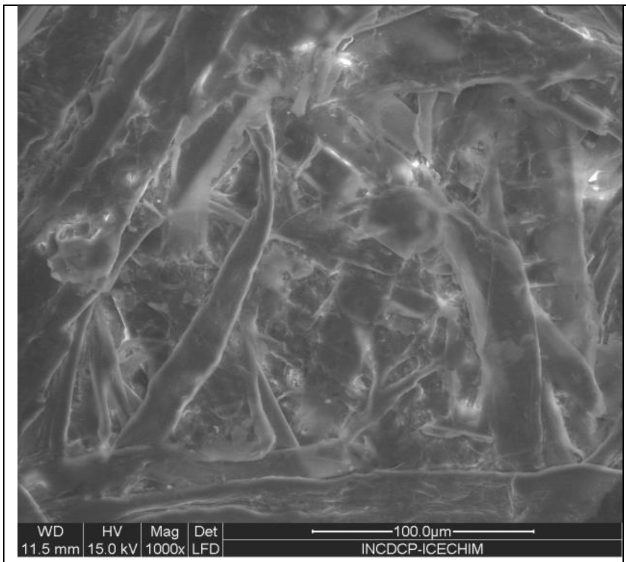


Fig. 8 - SEM micrograph of a reference sheet of paper of a magnified of 5000X.

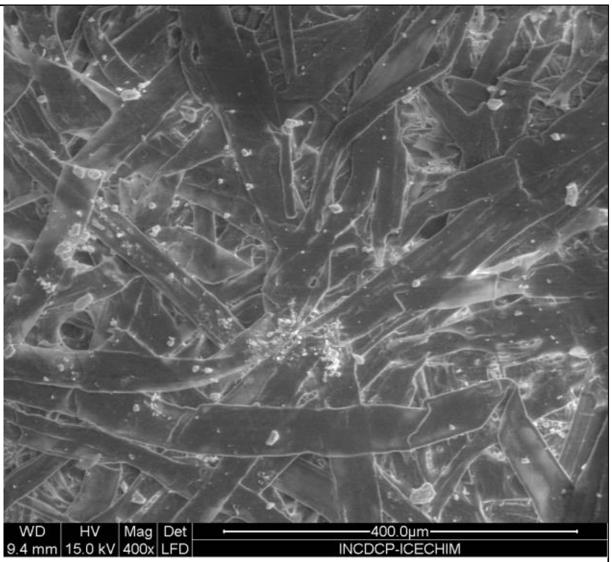


Fig. 9 - SEM micrograph of a sheet of paper sprayed with HAp synthesized nanoparticles in 2-propanol of a magnified of 5000X.

Nanoparticles were habitually shaped, hexagonally plated as were mentioned in literature [73]. It has been observed that no foxing process, not fading, or not white deposits appears at a macroscopic examination. But at SEM examination it has been observed that white deposits were formed and not the entire quantity of HA sprayed reacted to neutralize the acidity of the paper. The de-acidification dispersion doesn’t alter the macroscopic optical properties of the sample after spraying and drying. Printed paper, from the same book, was analyzed by SEM, in Fig.10. Previous ink analysis showed that the printed ink is iron gall ink [74, 75]. The two major mechanism of degradation of the paper caused by iron gall ink are hydrolysis of cellulose and its oxidation, a mechanism that is catalyzed by the presence of Fe^{2+} ions. For this reason, the conservation of paper carrying iron gall ink must first focus on the neutralization of acids and second on the inhibition of cellulose oxidation that is enhanced by the catalytic action of Fe^{2+} ions. Deacidification of inked paper by HA nanoparticles didn’t cause observable ink dissolution, as shown in Fig. 11.

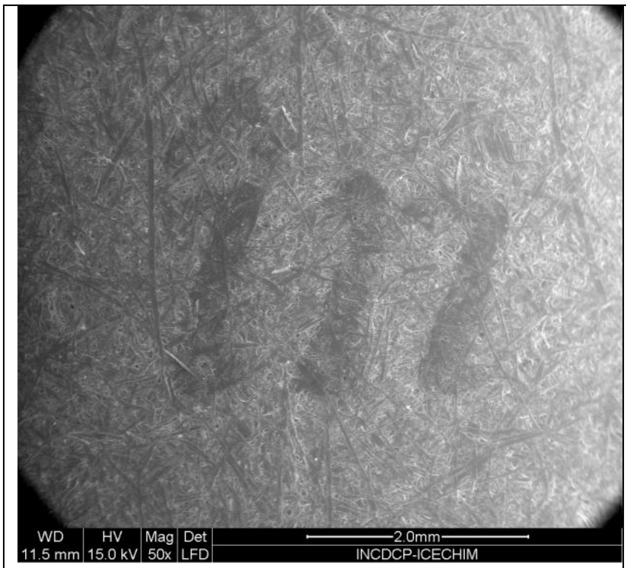


Fig. 10 - SEM micrograph of a sheet of printed paper of a magnified of 50x.

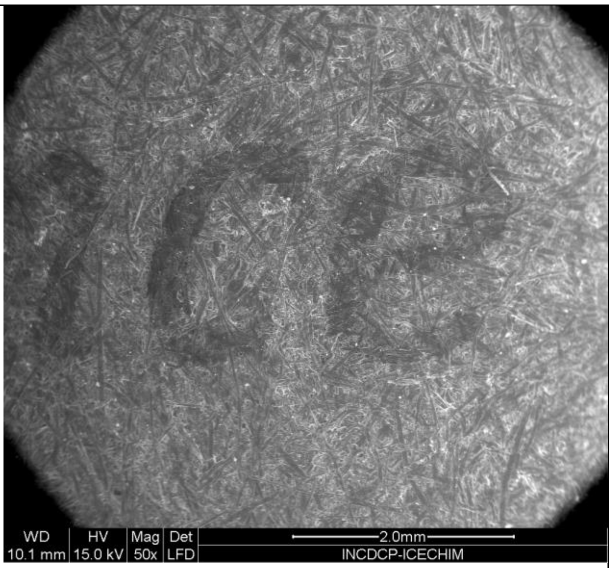


Fig. 11 - SEM micrograph of a sheet of paper sprayed with HA synthesized nanoparticles in 2-propanol of a magnified of 50x

The AFM has several advantages over SEM and TEM such as true 3D imaging, working under atmospheric pressure and the possibilities to scan in controlled environmental and under liquids. Also, no special preparation of the samples is required. Besides detail structural features AFM can provide important information on surface forces (adhesion, friction, electrostatic, van der Waals, etc). Also, the measurements can be done in situ, i.e., in real time to see the reaction developing during scanning. This makes AFM indispensable tool that can shed light on the nanostructures comprising paper and cellulose. Analyzing a typical image (Fig. 12) the basic paper morphology features can be seen: cellulose fibers are long (characteristic libriform cells in gymnosperms), with a rounded section (diameters between 15 and 22 µm) and are organized in a random way in the paper; partially degraded primary cell wall during the refining produces debris and separated macro fibrils that bind neighboring fibers thus increasing the paper strength. It is possible, using standard microscope software, to calculate the paper surface roughness (one of the basic paper surface characteristic) among others parameters.

By **AFM**, 3-D surface topography has been recorded on a 0.5-0.5 mm^2 surface area. AFM revealed a rough surface architecture for HA, the predominant size of grains being in the range of 90-100nm. At higher temperature the de-agglomeration of bulk phases and agglomeration of nano phases leads to the nano crystalline HA in this present study.

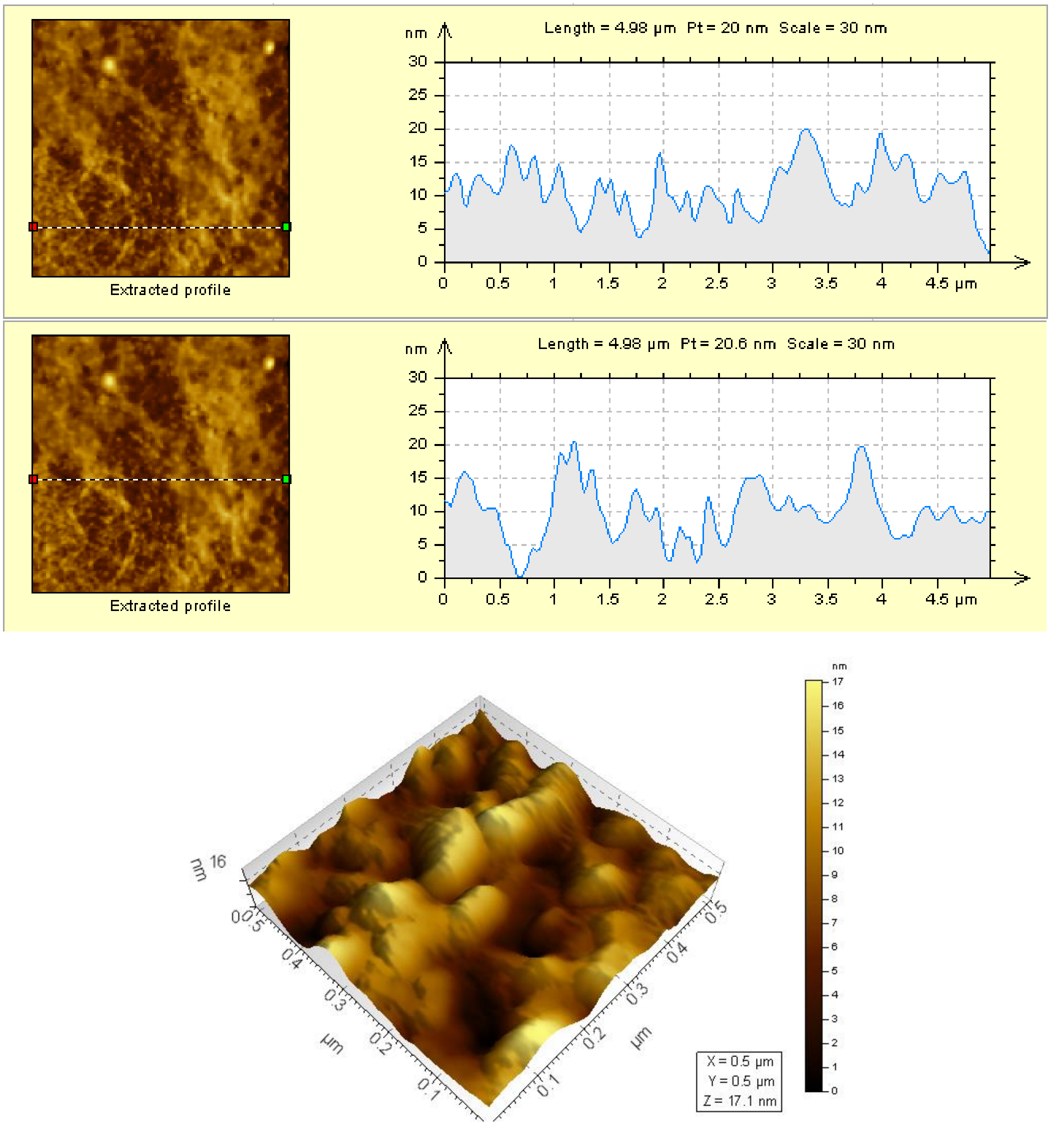


Fig.12. The AFM morphology (up) and topology (down) of paper treated with HA

7. *Dynamic Light Scattering (DLS) technique*

The particles size and theirs size distribution have been measured by Dynamic Light Scattering (DLS) technique. A measurement system of particles dimensions by Dynamic Light Scattering, Molecular Weight and Z Potential comprises the Zetasizer instrument and a computer with the Zetasizer software. The software is used to control the measurement of the sample. The basic way to make a measurement was:

- a manual measurement where all the measurement parameters were set immediately before the measurement was performed.

The Zetasizer Nano series performs size measurements using a process called DLS – Dynamic Light Scattering. DLS measures Brownian motion and relates this to the size of the particles. It does this by illuminating the particles with a laser and analyzing the intensity fluctuations in the scattered light. The Zetasizer Nano system measures the fluctuation in scattering intensity and uses this to calculate the size of particles within the sample. If large particles are being measured, then, as they are moving slowly, the intensity of the speckle pattern will also fluctuate slowly. And similarly, if small particles are being measured, as they are moving very quickly, the intensity of the speckle pattern will also quickly fluctuate.

The HA nanoparticles were used for paper treatment, at a concentration of 0.8% in 2-propanol, and the historical papers were sprayed manualy. HA showing a size distribution around of 30 nm.

By comparison with HA, it has been examined the size distribution of $Ca(OH)_2$ and $Mg(OH)_2$. $Mg(OH)_2$ and $Ca(OH)_2$ nanoparticles dispersions in alcohols, may be applied on paper by spraying or by impregnation in a chamber similarly to Bookkeeper, Battelle and Wei t'o methods (worldwide used methods for deacidification) [6, 76-78].

The used solvents are volatile, environmentally friendly and with low surface tension so that they properly work as carrier for solid particles, ensuring a homogeneous and penetration depth within the paper fibers. The task of preserving the historic paper entrusted to the libraries and archives, the conservation scientists have studied the influence environmental factors on the stability of cellulose. The main process responsible for natural cellulose aging is the random hydrolysis of the glycosidic linkage between the glucose residues in the macromolecule of cellulose. The oxidation and the crosslinking also contribute to the deterioration process. It has been shown that the temperature and the relative humidity of the repositories play a crucial role in the longevity of paper.

The size for $Ca(OH)_2$ nanoparticles dispersed in 2-propanol was 183 nm, and for the size distribution by light intensity was 100%, Fig 13.

The size for $Mg(OH)_2$ nanoparticles dispersed in 2-propanol was 188,2 nm, and for the size distribution by light intensity was 100%, Fig 14.

Z-Average (d.nm): 673.8
PdI: 1.000

Intercept: 0.999

	Diam. (nm)	% Intensity	Width (nm)
Peak 1:	183.0	100.0	13.62
Peak 2:	0.000	0.0	0.000
Peak 3:	0.000	0.0	0.000

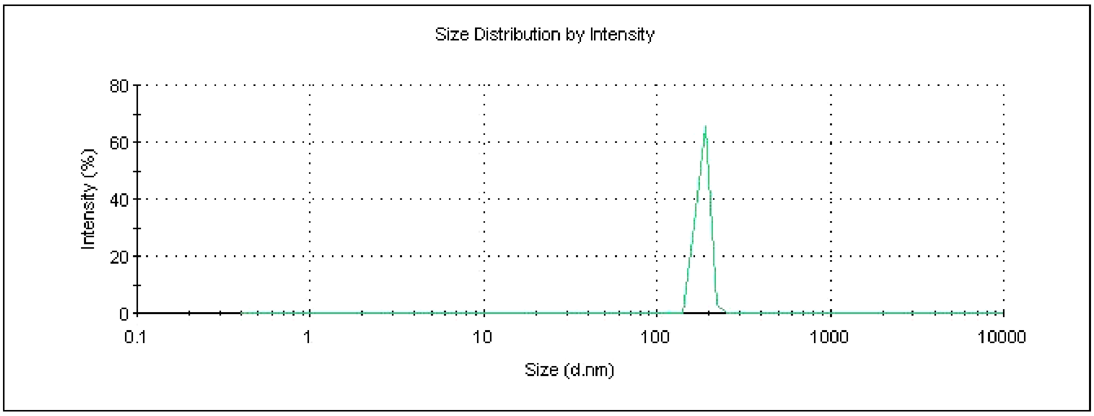


Fig.13 Size distribution for $Ca(OH)_2$ nanoparticles dispersed in 2-propanol

Z-Average (d.nm): 1622
PdI: 1.000

Intercept: 1.55

	Diam. (nm)	% Intensity	Width (nm)
Peak 1:	188.2	100.0	6.766
Peak 2:	0.000	0.0	0.000
Peak 3:	0.000	0.0	0.000

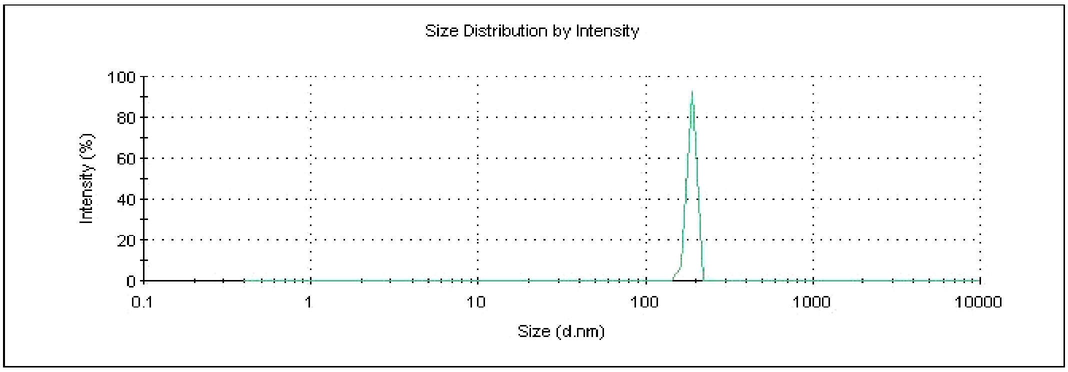


Fig. 14 Size distribution for $M(OH)_2$ nanoparticles dispersed in 2-propanol

SEM examination of a paper treated with $Ca(OH)_2$ nanoparticles, as a suspension in 2-propanol, and after dried, reveals habitualy shaped, hexagonally plated nanoparticles, as were mentioned in literature [79].

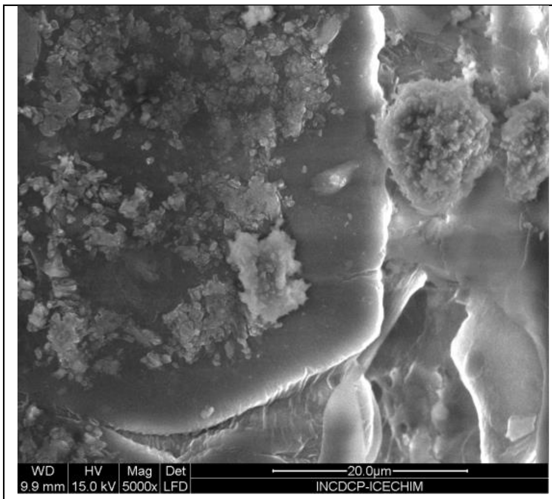


Fig. 15. SEM micrograph of a sheet of paper sprayed with $Ca(OH)_2$ synthesized nanoparticles in 2-propanol of a magnified of 5000X

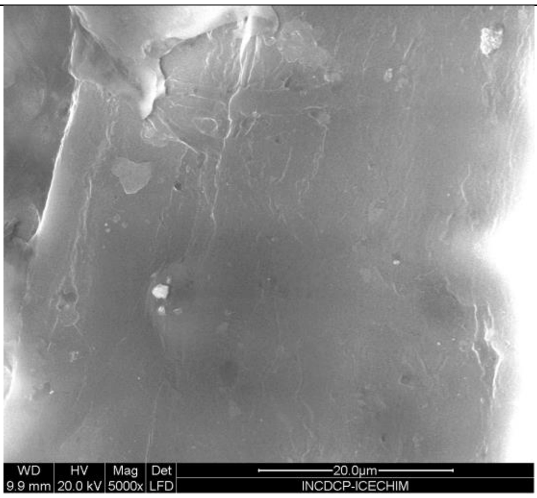


Fig. 16 SEM micrograph of a sheet of paper sprayed with $Mg(OH)_2$ synthesized nanoparticles in 2-propanol of a magnified of 5000x.

It has been observed that no foxing process, not fading, or not white deposits appears at a macroscopic examination. But at SEM examination it has been observed that white deposits were formed and not the entire quantity of $Ca(OH)_2$ sprayed reacted to neutralized the acidity of the paper. The de-acidification dispersion doesn't alter the macroscopic optical properties of the sample after spraying and drying.

For the other sheet of paper, sprayed with synthesized $Mg(OH)_2$ nanoparticles, as a suspension in 2-propanol, and after dried, at the macroscopic examination of the sample sprayed with $Mg(OH)_2$ nanoparticles, did not indicated a negatively influence the optical parameters of paper. At SEM examination it has been observed that less white deposits of $Mg(OH)_2$ were formed than in the case of $Ca(OH)_2$, although the same concentration and the same volume of suspension has been applied on the same type of paper. The possible explanation of this fact is that $Mg(OH)_2$ has an stronger basic character then $Ca(OH)_2$, so it neutralizes greater the acidity from the paper. It is also known that magnesium is less visible on the scanning microscopy because it has a smaller contrast, and it seems to cover the most part of the cellulosic fibers. Not the entire quantity of sprayed $Mg(OH)_2$ nanoparticles reacted to neutralized the acidity of the paper and it will be carbonated, in time in the presence of atmospheric CO_2. A better SEM micrograph, which can illustrate the previous arguments is of a magnified of 2000x is Figs. 17,18.

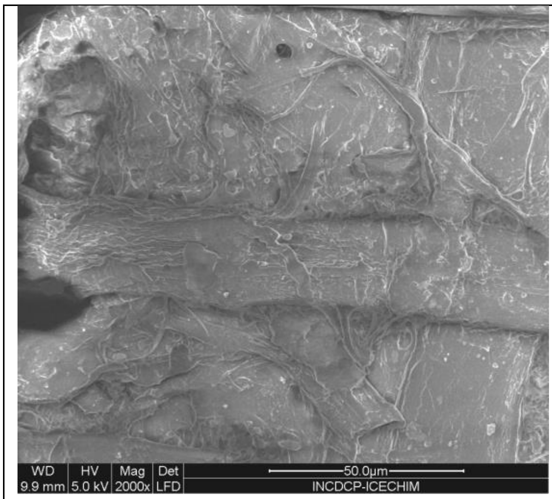


Fig. 17 SEM micrograph of a sheet of paper sprayed with $Mg(OH)_2$ synthesized nanoparticles in 2-propanol of a magnified of 2000x

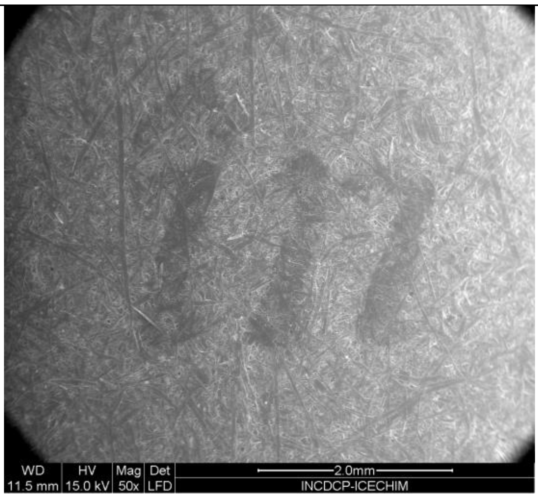


Fig.18 SEM micrograph of a sheet of printed paper of a magnified of 50x

Printed paper, from the same book, was analyzed by SEM, Figs. 17, 18. Previous ink analysis showed that the printed ink is iron gall ink [80].

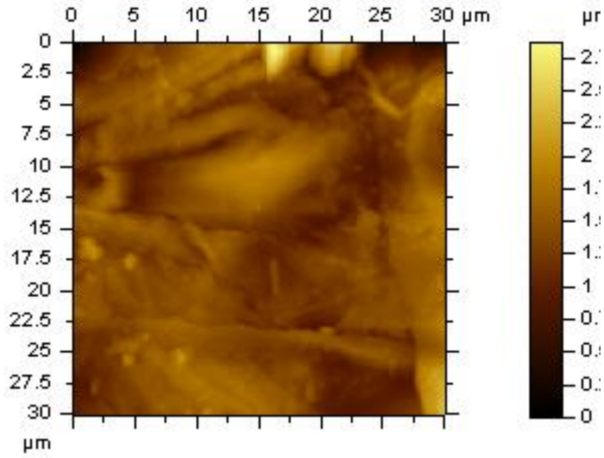
The two major mechanism of degradation of the paper caused by iron gall ink are hydrolysis of cellulose and its oxidation, a mechanism that is catalyzed by the presence of Fe^{2+} ions. For this reason, conservation of paper carrying iron gall ink must first focus on the neutralization of acids and second on the inhibition of cellulose oxidation that is enhanced by the catalytic action of Fe^{2+} ions. Deacidification of inked paper by $Ca(OH)_2$ or $Mg(OH)_2$ nanoparticles, didn’t cause observable ink dissolution, as shown in Figs. 17, 18.

Alcohols nanoparticles dispersion have a great advantage in deacidification process due to their lower surface tension compared to aqueous systems, that ensures a faster and more homogenous penetration of the deacidifying into the paper matrix [81-84].

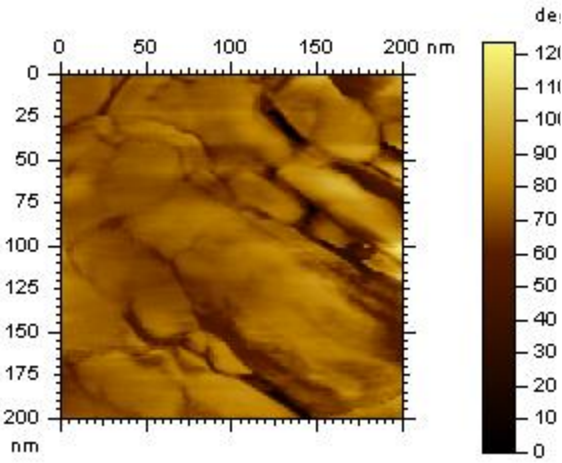
The proposed deacidification method simultaneously slows down cellulose oxidation and decreases the formation of the byproducts of cellulose decomposition through acid hydrolysis.

Figure 19 shows a collection of 3-D surface topographies recorded on a 0.5-0.5 mm^2 surface area. AFM revealed a rough surface architecture for HA, the predominant size of grains being in the range of 90-100nm. Also, the AFM microgrammes are compared with $Ca(OH)_2$ and $Mg(OH)_2$.

Could be observed that HA is able to cover quite homogneously the paper surface, by comparison with $Ca(OH)_2$, where the covering is partially, and $Mg(OH)_2$ where a mica-covering model is obeyed.

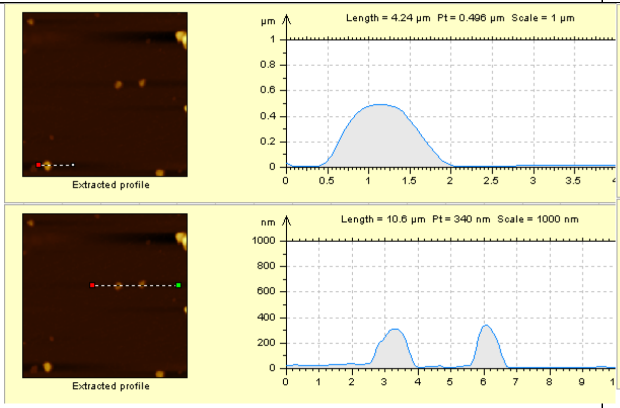


AFM morphology of $Ca(OH)_2$ sprayed on the paper

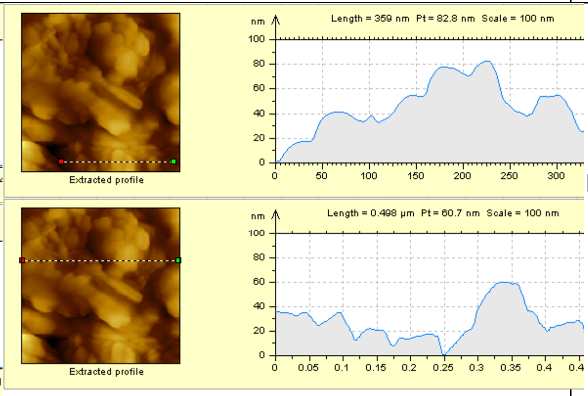


AFM morphology of $Mg(OH)_2$ sprayed on the paper

A

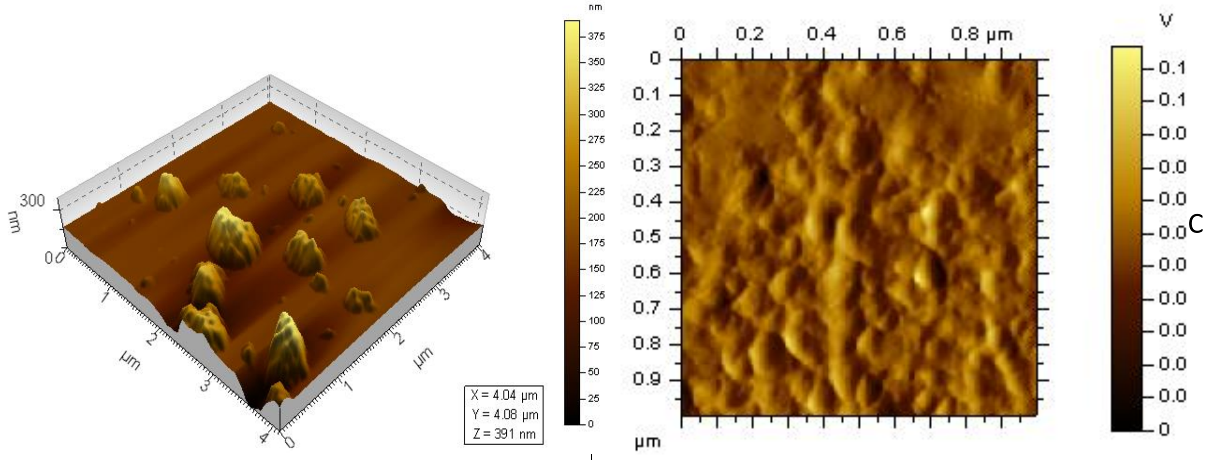


AFM topology of $Ca(OH)_2$ sprayed on the paper



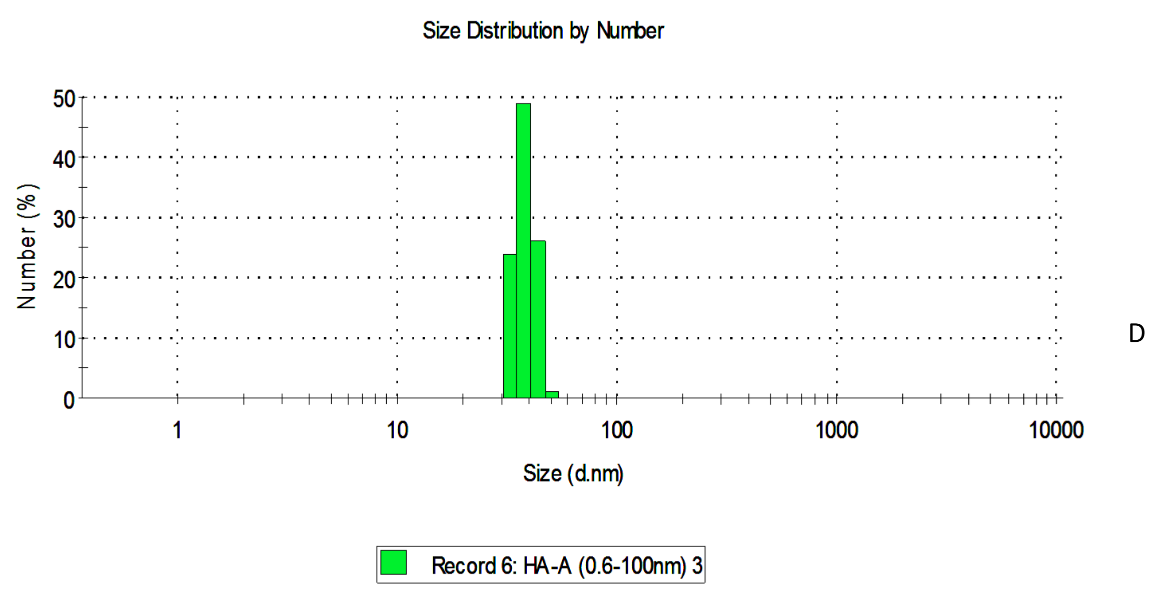
AFM topology of $Mg(OH)_2$ sprayed on the paper

B



C

AFM morphology for HA nanocrystals (left) and HA sprayed on the paper (right)



DLS sizes distribution of HA nanocrystals

Fig.19. AFM images (morphology and topography) collection (a-c) and DLS sizes distribution (d) for sprayed $Ca(OH)_2$, $Mg(OH)_2$ and HA nanocrystals

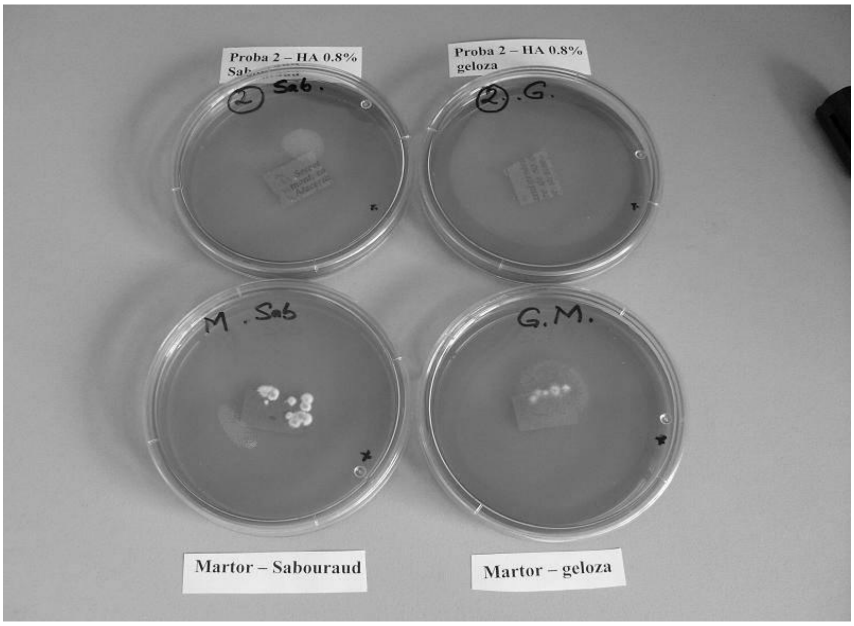
8. BIOLOGICAL DESINSECTION OF OLD PAPER

Special attention was paid to the positive effects of nanoparticles not only to the chemical, physical and mechanical properties on the cellulose, but also on its microbiological decontamination. Historic paper in the environmental conditions is an ideal medium for fungi growth and the most frequently are Pennicillium and Aspergillus.

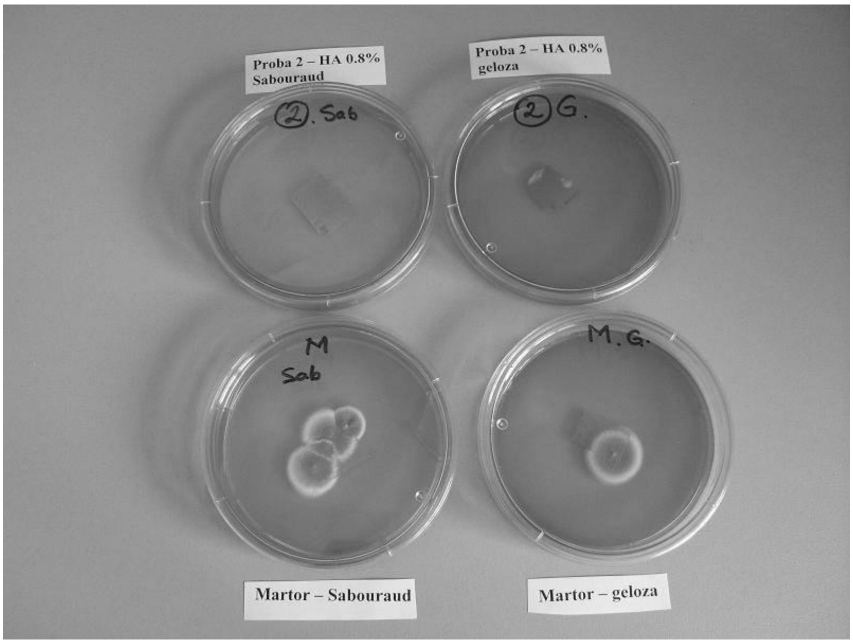
Microbiological deterioration is one of the most important factors determining the durability of paper, which can be chemically assimilated (treated as a nutriment for microorganisms) or dissimilated (destroyed by metabolites produced by them). Most archaeological documents stay in the soil, where a variety of microorganisms can be found, such as bacteria, actinomycetes, fungi, algae and protozoa. Microbes emit acid radicals causing chemical processes typical for corrosion. Very important factors are the properties of the environment in which decay takes place – humidity, pH, light, temperature, ventilation and material properties – the chemical constitution, structure and other compounds of the object, such as mordents, dyes, adhesives and finishes, which can slow down accelerate the biodeterioration processes. Microbial deterioration of heritage materials occurs primarily through the formation and growth of biofilms—microorganisms attached to a surface and embedded within a microbial produced polymer matrix.

Natural fibres are especially susceptible to bio-corrosion due to the content of chemical individuals being a nutrient for microorganisms, among which the most dangerous for paper being fungi: *Aspergillus and Penicilium.* Cellulosic fibres include cotton, flax, hemp and other vegetable fibres. Cellulose is decomposed in enzymatic hydrolysis by both fungi (*Penicilium, Aspergillus.*For example, Aspergillus nidulans and its cultures can secrete a purple–brown pigment. For different species of *Aspergillus* and *Penicillium*, produces cellulases while growing on cellulose as a carbon source, and is able to induce hydrolysis of lignocelluloses materials, and presents high glucosidase activity. More than that, Anita Srivastava and Rita Kar explained that *Aspergillus Niger* could degrade gallic acid and intermediates of this degradation could be *cis*-aconitic, - ketoglutaric and citric acids. In addition, Saxena et al. (1995) determined species of *Aspergillus* and *Penicillium that* could use catechin, gallotannin and gallic acid as carbon sources [85-88].

The restoration of the Romanian Gospel was carried out according to the ‘‘in situ repair’’ method, which calls for limited operations to treat limited damage. Partial interventions are based on the theory of non-invasive restoration strategies aimed at safeguarding every original component forming a book. In this way all the historical and technical information contained in the original binding of the book was preserved. A full disinfection procedure was performed because agar cultures of samples obtained from the book developed a small number of fungal and bacterial colonies.



(a)



(b)

Fig. 20: The Petri dishes with Aspergillus (a) and Penicilium (b) before (down) and after 48 h of incubation with HA (up)

The suspension of nanoparticles sprayed on the paper book, did not affect the paper integrity and destroyed the fungal and bacterial colonies. Also, a slight discoloration of the paper has been observed, Fig. 21.

Fig. 21: The picture of Romanian Gospel from 1740, before (left) and after (right) treatment with HA

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Abstract:

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REFERENCES

We would like to thank the peers for their great work in double blind reviewing the article.

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