ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

An Infrared, SEM and XRF study of the Paper of a 1588 Spanish Book.

Juan S Gómez-Jeria[1]*, Ernesto Clavijo[1] and Sebastián Gutiérrez[2]*.

[1]Department of Chemistry, Faculty of Sciences, University of Chile. Las Palmeras 3425, Santiago 7800003, Chile.
[2]Instituto de Alta Investigación, Laboratorio de Análisis e Investigaciones Arqueométricas, Universidad de Tarapacá, Antofagasta 1520, Arica, Chile.

ABSTRACT

An infrared, scanning electron microscopy and X-ray fluorescence study was performed on the Spanish book entitled *Treated of the True and False Prophecy* printed in Segovia during 1588. Three small samples were taken from the margins of three pages. Two of them belong to the original book while the third one is from a page added later during the binding of the book. The first result is that the paper is contaminated with numerous metallic elements. The distribution of these contaminants in the three samples suggests that this process began after the binding of the book. The carbonate moiety of the calcium carbonate seems to have disappeared with the passing of time transformed in carbon dioxide. Al, K and S, components of potassium alum are detected by SEM and XRF analyses. Gelatin seems to be present because some IR bands of proline suggest that. There is an unsolved problem with some IR bands because of the fact that they can be ascribed to two different entities.

Keywords: Cellulose, infrared spectra, archeology, paper analysis, Spain, XRF, SEM, gelatin, rags, potassium alum, conservation.

Corresponding authors

ISSN: 0975-8585

INTRODUCTION

Recently we have been focusing our research interest in the infrared (IR) characterization of the papers used to print postage stamps [1-3]. Besides this immediate goal we intend to build a method allowing classifying in some way the many IR spectra we are accumulating. We found that it is necessary to expand our work to obtain results from other kinds of papers.

Paper manufacture originated in China (hemp paper around eight century BC, paper made with mulberry, fishnets, old rags and hemp waste around year 105, toilet paper by the 6th century, square bags to preserve the flavor of tea during the Tang Dynasty and paper-printed money during the Song Dynasty). It seems that when the armies of the Abbasid Caliphate and the Tibetan Empire won the Battle of Artlakh (on the border of present-day Kazakhstan and Kyrgyzstan) against the army of the Tang dynasty, some Chinese prisoners brought paper-making technology to the Middle East. Paper production began in Samarkand (751), Baghdad (793), Damascus, Cairo (10th century), Morocco and then Muslim Spain (Al-Andalus, Caliphate of Cordoba, 11th century). The technique of papermaking remains virtually unchanged from the end of the 13th century to the 18th century [4]. The paper employed for printing books during the Renaissance is a potential source of information. The raw material for making paper at those times was rags and linen.

They were collected and transported it to the mill, where they were organized. The rags were cut into small parts and left to ferment. Throughout this process the fatty components were separated from the cellulose. At the end of the process sizing agents such as gelatin and alum were added. Calcium carbonate should be also present (coming from hard water and other sources). We recommend the reader the excellent article of María Del Carmen Hidalgo Brinquis [5] and an excellent book about paper making [6].

Here we present the results of infrared, scanning electron microscopy (SEM) and X-ray fluorescence (XRF) analysis of some samples of the paper used to print, at the end of XVI century, a book in Spanish language. The book is entitled *Tratado de la verdadera y falsa prophecia* (*Treated of the true and false prophecy*) and was written by Don Iuan de Horozco y Couarruuias. It was printed in Segouia by Iuan de la Cuesta during the year 1588 (size: 4^0). The copy is in a regular state of conservation. The author of this text, Juan de Orozco Covarrubias y Leiva, was born was born in Toledo, Spain in 1544. He was the son of the poet Sebastián de Orozco and brother of the lexicographer Sebastián de Covarrubias. He was ordained a priest on 12 May 1573. He became bishop of Agrigento (in Sicily, a possession of the Aragon Crown) and then of Guadix (in the province of Granada, Spain). Problems with some of his publications obliged him to go to Rome to explain himself, thing he did. He died in Guadix in 1608. His treatise on True and False Prophecy rejects astrology as a source of knowledge. During January 5 1586, Pope Sixtus V issued a papal bull (*Coeli et terrae* or *Heaven and Earth*) condemning magic and all forms of divination, including judiciary astrology, and establishing the competence of Inquisitors, even in the illusionistic practices. For this reason the book is complemented at its end with the Pope's bull. This text is included in the book under study in Latin and Spanish languages (pages 155 and 161 respectively). Note that this bull not only penalizes the practitioners but also anyone reading or possessing a book about these topics. An example of its application is the Italian mathematician, physician, biologist, physicist, chemist, astrologer, astronomer, philosopher, writer and gambler Jerome Cardan (Gerolamo Cardano), who was arrested and held under house arrest by the Inquisition under suspicion of violating Sixtus' bull.The printer, Juan de la Cuesta (?-1627), is known for printing the first edition of Don Quixote de la Mancha.

SAMPLES AND METHODS

Figure 1 shows the title page (from Biblioteca Virtual del Patrimonio Bibliográfico, http://bvpb.mcu.es/es/ consulta/ registro.cmd?id=397076).

ISSN: 0975-8585

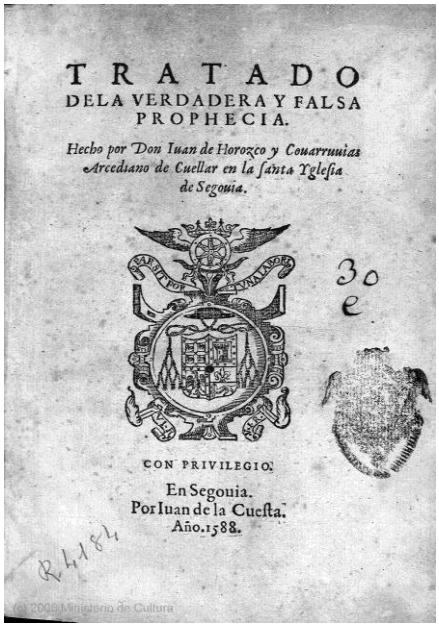
TRATADO
DELA VERDADERA Y FALSA PROPHECIA.
Hecho por Don Iuan de Horozco y Couarruuias Arcediano de Cuellar en la santa Yglesia de Segouia.
CON PRIVILEGIO.
En Segouia.
Por Iuan de la Cuesta.
Año. 1588.

Figure 1: Title page.

Title page and page 1 (Folio 1) are repaired. The pages' thickness varies: 0.07 mm for title page, 0.06 mm for page 157, 0.12 mm for page 154 and 0.08 mm for page 1. Small variations of thickness can be found inside a page. The book was bound at a later time.

Very small samples were extracted from the title page (sample 1, S1), page 154 (sample 2, S2) and a white page following the page containing the phrase '*En Segouia. Por Iuan de la Cuesta. Año. 1588*' (sample 3, S3). The page corresponding to sample 3 does not to belong to the original edition and was incorporated later during the binding of the book (this information was provided by Biblioteca Pública del Estado en Maó in Maó, Minorca, Spain, NIC 72706). The IR spectra were recorded with a Perkin Elmer Systems 2000 spectrophotometer. The standard technique of disk pressing in KBr was employed. Briefly, 0.5-1.0 milligrams of sample and 80-100 mg of IR grade KBr were used. The mixture was submitted to a pressure of 15 t /cm^2 for 30 seconds to form a 13 mm diameter disk.The XRF analysis was carried out with a Bruker III-SD equipment. The target area was the center of the stamps, with a 1 cm diameter, energy of 40 keV, a current flux of 38.7 µA and 200 s of exposition.The SEM analysis was performed with a JCM-6000 NeoScope Benchtop equipment. An electron beam with variable energy of 5, 10 or 15 keV is used to scanning the sample under a vacuum of 10^{-2} Pa. The analyzed area can be varied in the range of about 22 mm^2 (magnification 22x) up to 12 µm^2 (magnification 30000x).

RESULTS AND DISCUSSION

Figures 2-4 show the IR spectrum of samples 1-3 respectively.

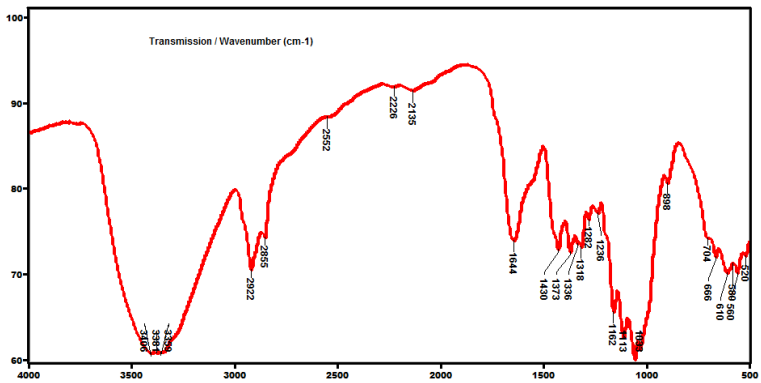

Figure 2: IR spectrum of Sample 1.

ISSN: 0975-8585

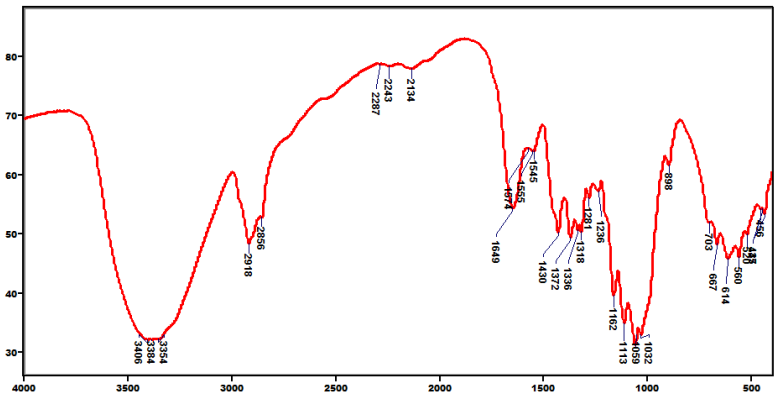

Figure 3: IR spectrum of Sample 2.

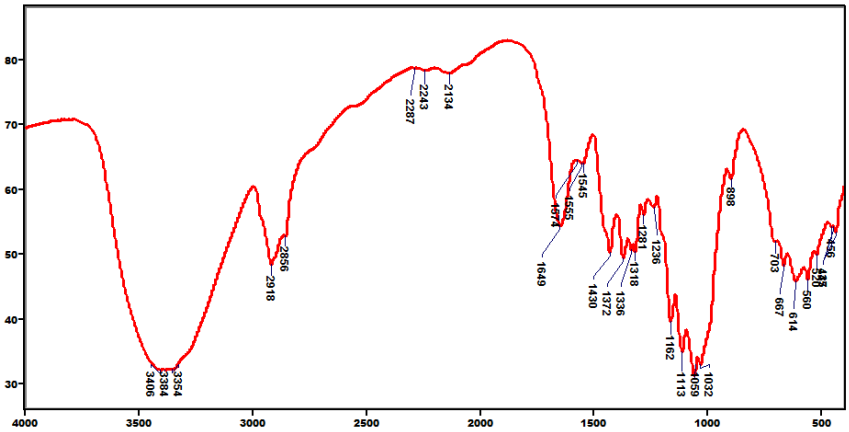

Figure 4: IR spectrum of Sample 3.

Figures 5-7 display the XRF results.

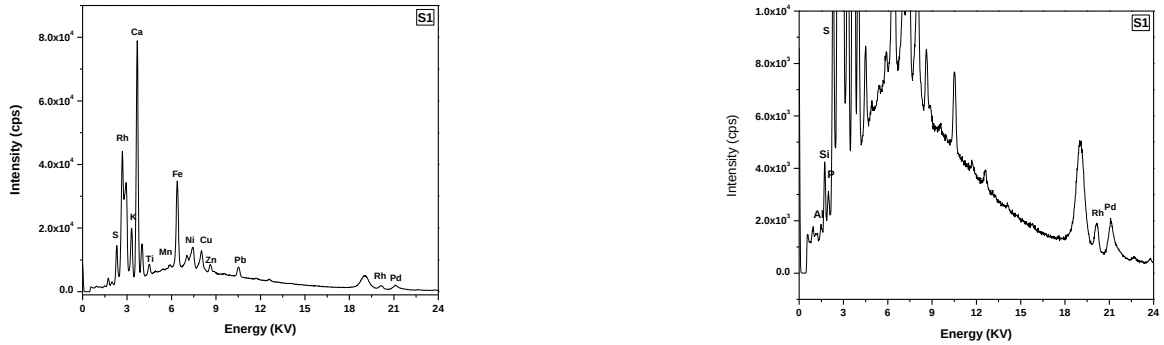

Figure 5: XRF results for S1 (Cr is not shown).

ISSN: 0975-8585

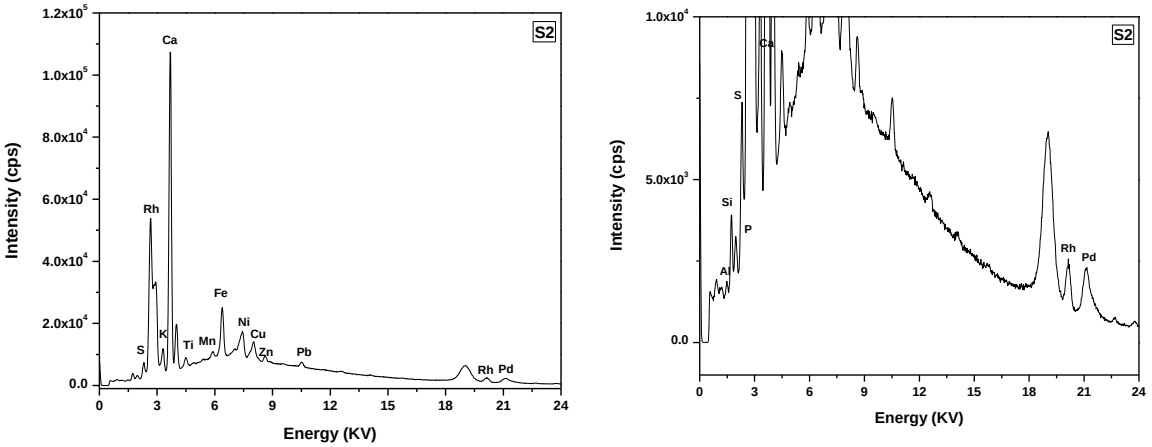

Figure 6: XRF results for S2.

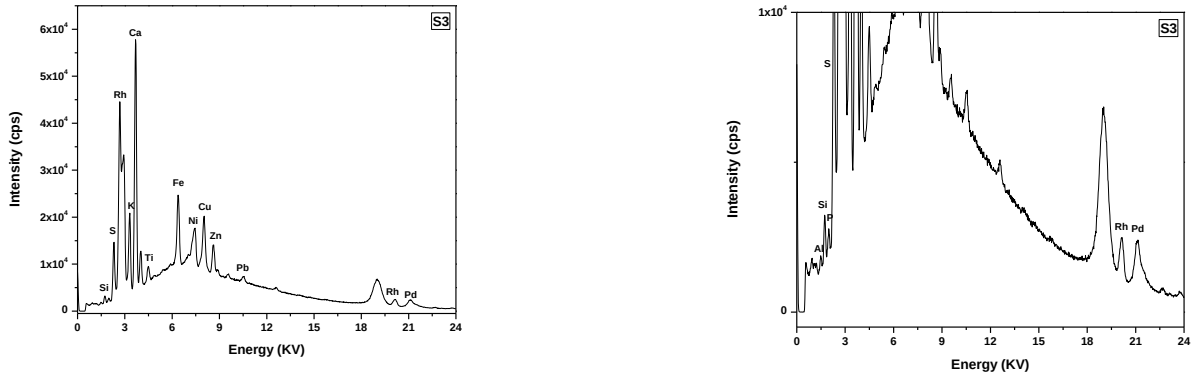

Figure 7: XRF results for S3 (V is not shown).

Figures 8-10 showthe SEM results.

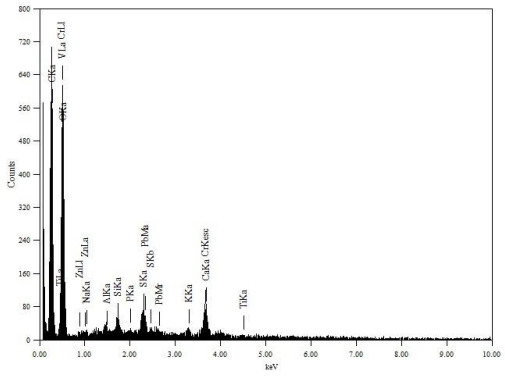

Figure 8: SEM results for S1.

ISSN: 0975-8585

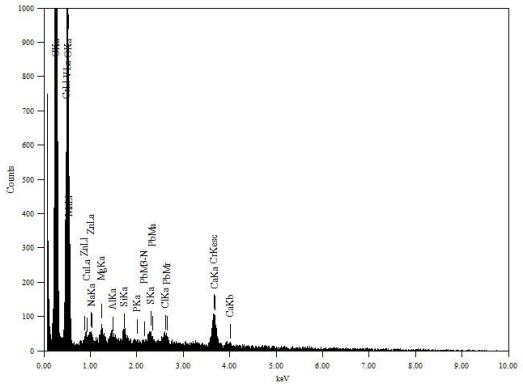

Figure 9: SEM results for S2.

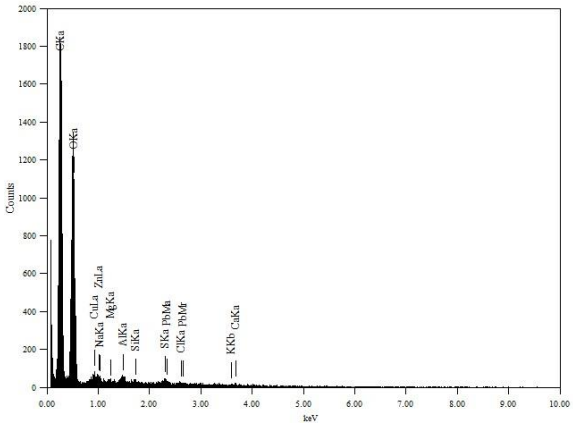

Figure 10: SEM results for S3.

Figures 11-13 show microphotographs of the three samples.

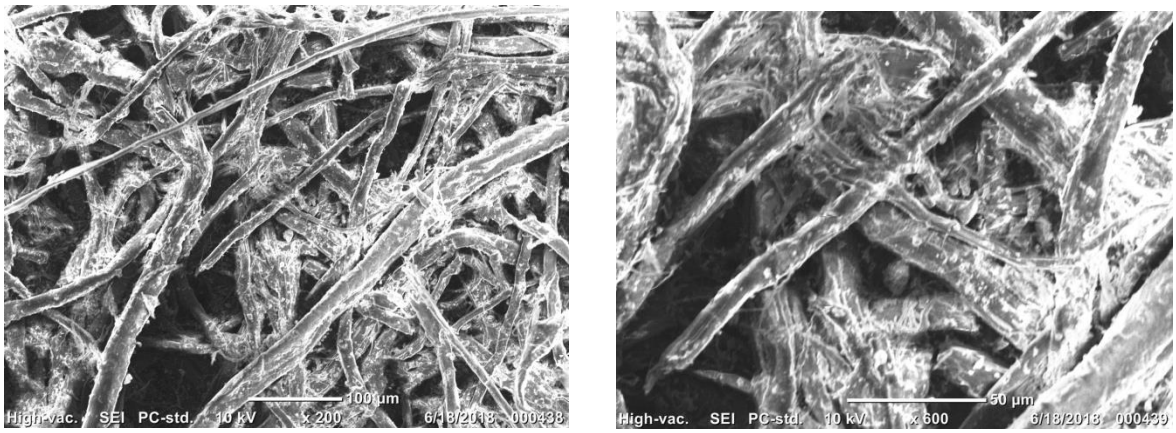

Figure 11: Microphotographs of sample S1.

ISSN: 0975-8585

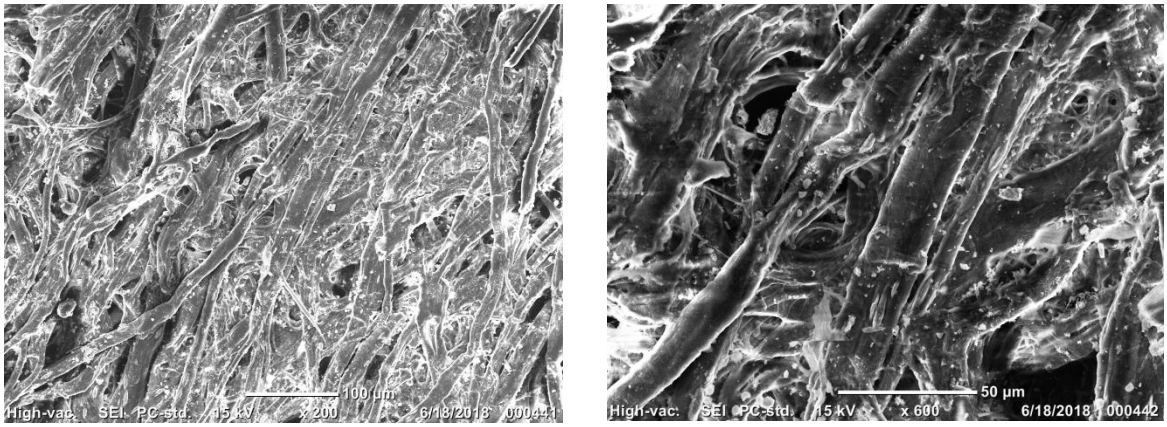

Figure 12: Microphotographs of sample S2.

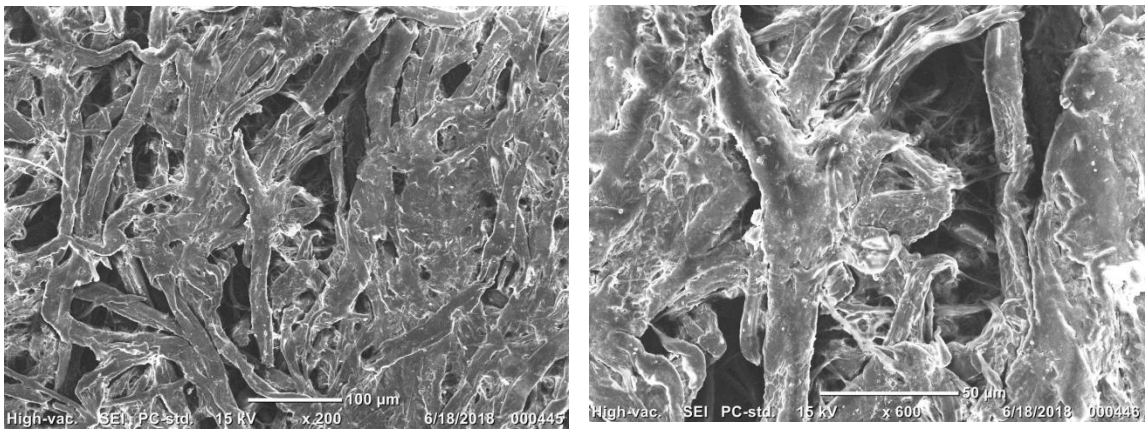

Figure 13: Microphotographs of sample S3.

DISCUSSION

Before beginning our analysis it is necessary to provide some historical facts about papermaking at that time and place. The works of the Barrow Research Laboratory and of Hunter are a prolific source of information[6, 7]. Mr. Arsenio Sánchez, from the Restoration Workshop of the Spain National Library thinks that, '*by appearance, the paper appears to be made of linen, glued with gelatin and rock alum. It is the usual in the sixteenth century*' (e-mail to J.S.G.-J.). By rock alum we understand potassium aluminum sulfate, $KAl(SO_4)_2{\cdot}12H_2O$. Barrow Research Laboratory reported that in the tests alum was found in twelve of the forty-five test books from the 16th century [7]. Also calcium carbonate should be existent because this compound is present in the hard water used in making papers. Now, if the paper was made from rags fermented in milk, we have another source of calcium [7]. Regarding animal gelatin, it was first used as an external surface sizing for paper in 1337 till the mid-nineteenth century [6]. Gelatin was applied to finished paper either alone or in combination with alum. Alum was added to gelatin size to control the viscosity of gelatin at different temperatures and concentrations, to prevent the growth of molds and bacteria, and to reduce the absorption of inks into the gelatin and paper substrate [7]. The earliest use of alum in combination with gelatin is believed to have occurred during the 1500's [7]. Barrett and Mosier stated that despite the variation in gelatin molecule lengths, the amino acid composition of all gelatins is distinguished by its relatively high content of 4-hydroxyproline, an amino acid found in large amounts in no other animal protein. Approximately one out of every eleven amino acids in gelatin is hydroxyproline [8].

Therefore, and in a first approach, we should search at least for calcium carbonate, potassium aluminum sulfate and hydroxyproline. Table 1 shows a summary of the XRF results and Table 2 of the SEM results. We marked in bold those elements detected by both methods.

ISSN: 0975-8585

Table 1: Elements shown by XRF analysis.

Sample	Elements
S1	**S**, **K**, **Ca**, **Ti**, Mn, Fe, Ni, Cu, Zn,**Pb**, **Al**, **P**, **V**, **Cr**.
S2	**S**, K, **Ca**, Ti,**Mn**, Fe, Ni, **Cu**, **Zn**, **Pb**, **Al**, P, V, Cr.
S3	**Si**, **S**, **K**, **Ca**, Ti, Fe, Ni, **Cu**, **Zn**, Pb, **Al**, P.

Table 2: Elements shown by SEM analysis.

Sample	Elements
S1	**Ti**, **V**, **Cr**, Zn, Na, Si, **P**, **S**, **Pb**, **K**, **Ca**, **Al**.
S2	**Mn**, V, Cr, **Zn**, Na, **Cu**, Mg, **Al**, Si, P, **Pb**, **S**,Cl, **Ca**.
S3	**Zn**, Na, **Cu**, Mg, **Al**, **Si**, **S**, Cl, **K**, **Ca**.

We can see that many elements of a given sample are detected by both, XRF and SEM analysis. We cannot expect having a perfect match because of the way these analyses are performed. Anyway we may state that at least Mn, Fe, Ni, Cu, Zn, Pb, P, V, Cr, Si, Na, Cl seem to be contaminants. It is probable that many of them arrive by air[9]. The small differences between the samples could be because of a different direct exposition to air or any other contamination source. We are not in position to provide even an approximate date for sample S3 but it is interesting to notice that its contamination is very similar to S1 and S2, suggesting that most contaminants arrived after the book binding.

XRF and SEM analyses show that calcium is present in all samples. Interestingly, IR results (Figs. 2-4) show that no bands ascribed to the carbonate moiety appear (1083, 854.5, 713 and 700 cm^{-1})[10, 11].This carbonate disappearance is probably due to the reaction [12]:

$$CaCO_3 + 2H_3O^+ \rightarrow Ca^{+2} + CO_2 + 3H_2O$$

Regarding the presence of existence of potassium aluminum sulfate, XRF results show the presence of K, Al and S (Figs. 5-7 and Table 1). Figures 14 to 16 show, respectively, the SEM results for the distribution of these elements within the samples.

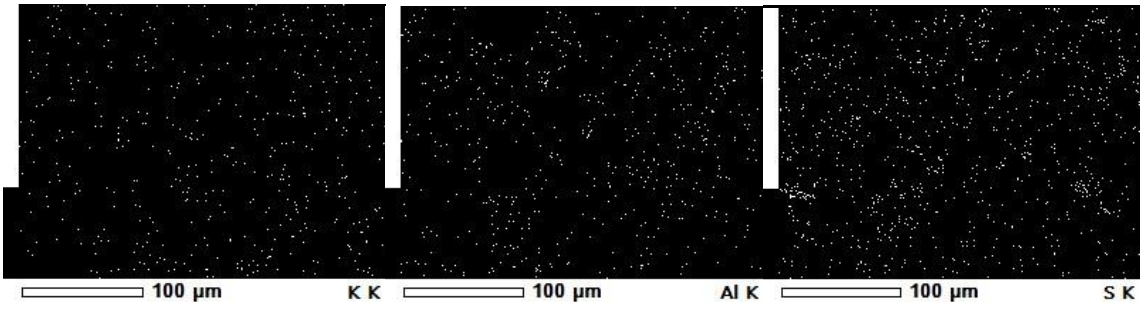

Figure 14: From left to right: distribution of K, Al and S in sample S1 (SEM).

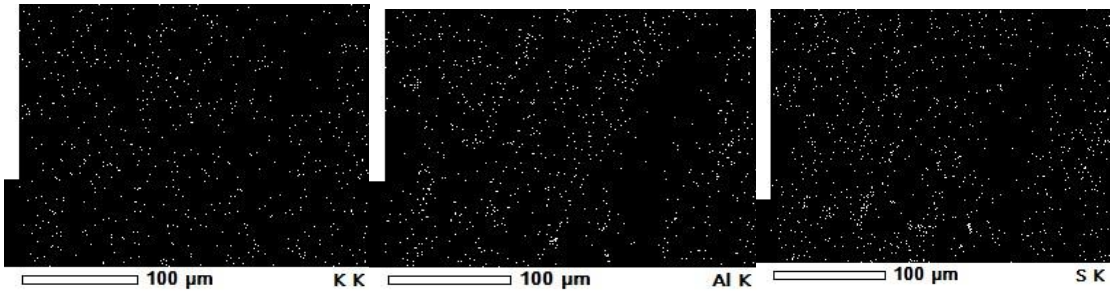

Figure 15: From left to right: distribution of K, Al and S in sample S2 (SEM).

ISSN: 0975-8585

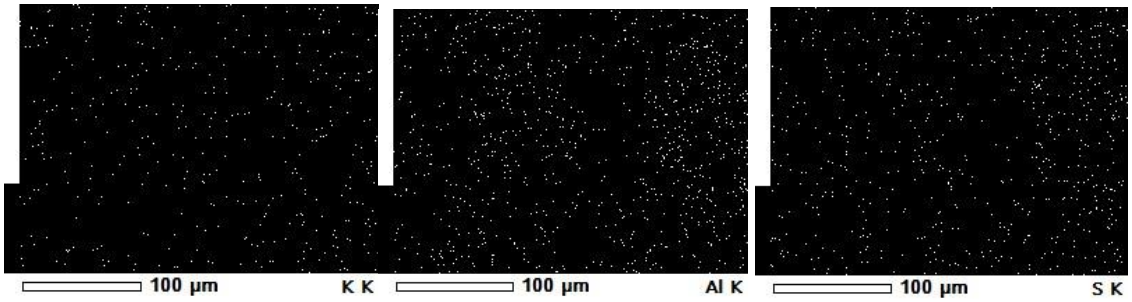

Figure 16: From left to right: distribution of K, Al and S in sample S3 (SEM).

We think that these suggest the presence of alum in the samples. Nevertheless, the reader must consider the following fact. Ross reported the infrared spectra for potassium alum as 981, 465, 1200, 1105, 618 and 600 cm^{-1} [13, 14], and most of these peaks do not appear in the IR spectrum. More work to clarify definitively this point is being done.

Regarding gelatin, we searched for IR bands of proline [15, 16]. We tentatively suggest that in the case of sample S1, bands at 898.5, 1033.0, 1162.4, 1318.5, 1336.5, 1373.0 and 2922.1 cm^{-1} can be ascribed to proline. S2 and S2 have similar bands. Amide I band in polyproline II has a peak at 1653-1645 cm^{-1} [15]. S1 has a band at 1644 cm^{-1} and S2 and S3 a band at that 1649 cm^{-1} that could correspond to an amide band. Therefore there is a first set of data suggesting the possible presence of gelatin.

IR bands of cellulose were collected from a book and some papers [17-20]. Valli et al. mention cellulose signals at 1158, 1106, 1055, 1030 (all C-O stretching), 1647 and 1546 cm^{-1} (primary and secondary amide bands from protein glue) [18]. Brittain mentioned bands at 1025 and 3330 cm^{-1}[20]. Ferrer and Vila quote bands at 1158, 1111, 1061, 1036 and 3346 cm^{-1}[19]. We investigated only for these bands. Table 5 shows our findings.

Table 3: Proposed cellulose IR bands.

Sample	Possible cellulose bands (cm^{-1})
S1	1033.0, 1059.2, 1113.4, 1162.4, 1644.2.
S2	1032.7, 1059.3, 1113.5, 1162.9, 1545.4, 1649.2.
S3	1032.4, 1059.5, 1113.3, 1162.7, 1649.5.

Note that for example, in sample S1 bands at 1033.0 and 1162.4 of Table 5 are also mentioned as possible bands for proline. We need therefore to develop an approach, if it exists, to clarify these assignments.

The main conclusion of this study is that IR, SEM and XRF combined can provide enough data to obtain a good idea of the composition of paper. In this precise case, the presence of a large number of contaminant agents was detected. Also, there is sufficient data to confirm the presence of gelatin, calcium and alum used for sizing. The actual molecular status of calcium, potassium and aluminum is to be determined in the future. Detailed IR, SEM and XRF results are available on request only for conjoint research.

REFERENCES

[1] Gómez-Jeria, J. S.; Clavijo, E.; Gutiérrez, S. An Infrared and SEM study of the Margins Of Some Estonian Postage Stamps. Research Journal of Pharmaceutical, Biological and Chemical Sciences **2018,** 9, 1258-1279.

[2] Gómez-Jeria, J. S.; Clavijo, E.; Cárcamo-Vega, J. J.; Guitérrez, S. An infrared and SEM study of the margins of some German hyperinflation postage stamps. Research Journal of Pharmaceutical, Biological and Chemical Sciences **2018,** 9, 870-892.

[3] Gómez-Jeria, J. S.; Clavijo, E. A preliminary infrared study of the cellulose of some world stamps. Chemistry Research Journal **2017,** 2, 191-197.

[4] Hidalgo Brinquis, M. d. C. In La fabricación del papel en España e Hispanoamérica en el siglo XVII, Actas del X Congreso de Historia del Papel en España, Madrid, 2013; Madrid, 2013; pp 207-223.
[5] Hidalgo Brinquis, M. d. C. Técnicas medievales en la elaboración del libro: aportaciones hispanas a la fabricación del pergamino y del papel y a los sistemas de encuadernación. Anuario de Estudios Medievales **2011,** 41, 755-773.
[6] Hunter, D. Papermaking : the history and technique of an ancient craft. Dover Publications: New York, 1978; p xxiv, 611, xxxvii p.
[7] Barrow, W. J. Permanence/Durability of the Book-VII. Physical and Chemical Properties of Book Papers, 1507 - 1949.; W.J. Barrow Research Laboratory, Richmond, Virginia, 1974.
[8] Barrett, T.; Mosier, C. The Role of Gelatin in Paper Permanence. Journal of the American Institute for Conservation **1995,** 34, 173-186.
[9] Harrison, R. M.; Hester, R. E.; Querol, X. Airborne Particulate Matter: Sources, Atmospheric Processes and Health. Royal Society of Chemistry: 2016.
[10] Andersen, F. A.; Brecevic, L. Infrared spectra of amorphous and crystalline calcium carbonate. Acta Chem. Scand **1991,** 45, 1018-1024.
[11] Chukanov, N. V. IR Spectra of Minerals and Reference Samples Data. In Infrared spectra of mineral species: Extended library, Chukanov, N. V., Ed. Springer Netherlands: Dordrecht, 2014; pp 21-1701.
[12] Priest, D. J. Permanence and Alkaline—Neutral Papermaking. In Historic Textile and Paper Materials II, American Chemical Society: 1989; Vol. 410, pp 2-12.
[13] Farmer, V. C. The Infrared spectra of minerals. Mineralogical Society: London, 1974; p x, 539 p.
[14] Locke Ashley, J.; Martens Wayde, N.; Frost Ray, L. Natural halotrichites—an EDX and Raman spectroscopic study. Journal of Raman Spectroscopy **2007,** 38, 1429-1435.
[15] Doyle Barbara, B.; Bendit, E. G.; Blout Elkan, R. Infrared spectroscopy of collagen and collagen-like polypeptides. Biopolymers **1975,** 14, 937-957.
[16] Herlinger, A. W.; Long, T. V. Laser-Raman and infrared spectra of amino acids and their metal complexes. III. Proline and bisprolinato complexes. Journal of the American Chemical Society **1970,** 92, 6481-6486.
[17] Zhbankov, R. G. Infrared spectra of cellulose and its derivatives. Springer: New York, 1966.
[18] Imperio, E.; Giancane, G.; Valli, L. Spectral Database for Postage Stamps by Means of FT-IR Spectroscopy. Analytical Chemistry **2013,** 85, 7085-7093.
[19] Ferrer, N.; Vila, A. Fourier transform infrared spectroscopy applied to ink characterization of one-penny postage stamps printed 1841–1880. Analytica Chimica Acta **2006,** 555, 161-166.
[20] Brittain, H. G. Attenuated Total Reflection Fourier Transform Infrared (ATR FT-IR) Spectroscopy as a Forensic Method to Determine the Composition of Inks Used to Print the United States One-cent Blue Benjamin Franklin Postage Stamps of the 19th Century. Applied Spectroscopy **2016,** 70, 128-136.