

Research Journal of Pharmaceutical, Biological and Chemical Sciences

A preliminary infrared, SEM and XRF analysis of the paper of seven books of the 18th and 19th centuries.

Juan S Gómez-Jeria^{1*}, Ernesto Clavijo¹, Sebastián Gutiérrez², and Juan Carlos Machuca-Otarola³.

¹Department of Chemistry, Faculty of Sciences, University of Chile. Las Palmeras 3425, Santiago 7800003, Chile.

²Instituto de Alta Investigación, Laboratorio de Análisis e Investigaciones Arqueométricas, Universidad de Tarapacá, Antofagasta 1520, Arica, Chile.

³Biblioteca Central, Facultad de Ciencias, Universidad de Chile. Las Palmeras 3425, Santiago 7800003, Chile.

ABSTRACT

Infrared, scanning electron microscopy and X-ray fluorescence studies were performed on a set of seven paper samples taken from books printed at different places between 1799 and 1873. A large number of contaminants were detected (Si, P, Pb, Ti, Mn, Fe, Ni, Cu, Sr, As and Zn). The probable origin of most of them was the El Teniente (mine)/ Caletones (smelter) copper complex located at the south of Santiago de Chile. In all samples Al, Ca, K and S were found by SEM and XRF. No IR bands for carbonate were present in any of the samples. This is probably due to the transformation of this anion into CO₂. One sulfate band appears in all the samples, suggesting the presence of alum. This study shows the necessity of carrying out large scale quantum chemical simulations of the IR and Raman spectra of several cellulose and lignin models and also on cellulose interacting with rosin, alum, etc. We feel that this is the only way to clarify some points of the IR spectra.

Keywords: Cellulose, XRF, SEM, IR, book conservation, rosin, alum, gelatin, calcium carbonate

**Corresponding author*

INTRODUCTION

Our original research is centered on the analysis of the paper, gums, inks and cancellations of postage stamps [1-3]. In a previous paper we analyzed the components of the paper of a 1588 Spanish book, finding Ca, Al, K and S; and possibly gelatin [4]. Also we found that the paper was contaminated with numerous metallic elements (at least with Mn, Fe, Ni, Cu, Zn, Pb, P, V, Cr, Si, Na and Cl). At that moment we have not a clear idea of what was the source of contamination.

William James Barrow, who introduced the field of conservation to paper deacidification through alkalization, carried out a very interesting analysis of the physical and chemical properties of book papers dating from 1507 to 1949 [5]. In this technical document rosin, alum and groundwood content are mentioned as agents that can be detrimental to the permanence and durability of paper. We described alum in a previous paper [4]. The groundwood process does not remove lignin from the pulp. This causes the paper to yellow, become brittle and deteriorate. Rosin (also called colophony or Greek pitch) is used as an internal sizing. Barrow mentions that '*alum, and to a lesser degree, rosin, have an acid reaction that weakens paper fibers*' [5]. To these agents we must add calcium carbonate, present in hard waters and milk in the case of old papers and deliberately added to modern papers. This mildly alkaline chemical can counteract any acid that paper may originally contain or later acquire from its environment [5]. Finally we must consider gelatin (the first use of gelatin size in Europe occurs in year 1337). '*Animal gelatin size (the first type of gelatin size) was produced from horns, hooves and hides of animals and was applied to the formed paper sheet by soaking it in a hot solution of the gelatin*' [5].

At the beginning of the 19th century the demand for the cheapest possible printing paper increased enormously. This produced several technological changes in paper making [5]. Gelatin sizing was replaced by alum-rosin sizing (in the final form of an aluminum rosinate). It is mentioned that '*the sized paper tends to become somewhat brittle with age, probably due to the oxidation of the rosin by air*' [5]. The progressive disappearance of the use of calcium carbonate seriously affected the permanence and durability of the papers because of increasing acidity [5, 6]. The reader may find other reasons for the low quality of many 19th century papers in Barrow's work [5].

In this paper we present the preliminary results of IR, XRF and SEM studies of seven books dated between 1799 and 1879, were printed in different places.

METHODS

Small paper samples were taken from the following books kept in a small cellar of the Central Library of the Faculty of Sciences of the University of Chile [7-13]:

1. Cooke, *The new chemistry*, 1879, London. The book's leaves are white but slightly yellowish.
2. Balbis, *Flore Lyonnaise*, 1827, Lyon. The book's leaves are white, brittle, with many large brown spots.
3. Ferguson, *Lectures on Select Subjects in Mechanics, Hydrostatics, etc.,... and Dialling*, 1823, Edimburgh. The book's leaves are white, slightly yellowish, with small and large brown spots.
4. Vázquez, *Tratado Elemental de Química Orgánica etc.*, 1877, Santiago de Chile. The book's pages are white, yellowish with brown spots in some places.
5. Bails, B. *Principios de matemática de la Real Academia de San Fernando*, 1799, Madrid. The book's pages are white but very slightly yellowed.
6. Fischer, *Physique mécanique*, 1806, Paris. The book's pages are yellowish with abundant brown spots of different sizes.
7. Darwin, *L'origine des espèces au moyen de la sélection naturelle, ou La lutte pour l'existence dans la nature*, 1873, Paris. The book's pages are white.

It is interesting to note that only the pages of book number seven are still white. Paper is an active material: in almost all cases it is not neutral, and as a hygroscopic system it interacts constantly with all the components of the surrounding air, drying when the environment changes, etc. Several paper browning or yellowing or discoloration processes in certain areas have been described but we shall not study them in this paper [14-19]

Each sample was divided into smaller samples for the different studies. The selected areas for extraction did not contain any printed text. Samples were numbered according to the above book numbering: S1 refers to book 1, etc.

The IR spectra were recorded with a Perkin Elmer Systems 2000 spectrophotometer. The standard technique of disk pressing in KBr was employed [20]. Briefly, 0.5-1.0 milligrams of sample and 80-100 mg of IR grade KBr were used. The mixture was subjected to a pressure of 15 t /cm² for 30 seconds to form a 13 mm diameter disk.

XRF spectra were recorded with an XRF Bruker Tracer III-SD portable device with a detector fitted with a 10 mm² XFlash® SDD, Peltier-cooled and equipped with an X-ray tube Rh target; maximum voltage 40 kV. The specifications for this particular study were 40 kV, 37.8 μA, and an acquisition time of 200 seconds. We also used a vacuum pump. Data were collected and plotted using Tracer software S1PXRF 3.8.3. All results obtained are semi-quantitative, normalized as areas for each element. Normalization was performed using the following formula: $N=A/\Sigma A$, where N= Net Normalized, A= Net and ΣA = Sum of Net.

The SEM analysis was done with a JCM-6000 NeoScope Benchtop apparatus. An electron beam with variable energy of 5, 10 or 15 keV was used to scan the sample under a vacuum of 10⁻² Pa. The analyzed area varied in the range of about 22 mm² (magnification 22x) down to 12 μm² (magnification 30000x).

RESULTS

Infrared spectra

Figures 1 to 14 show the infrared spectrum of each sample.

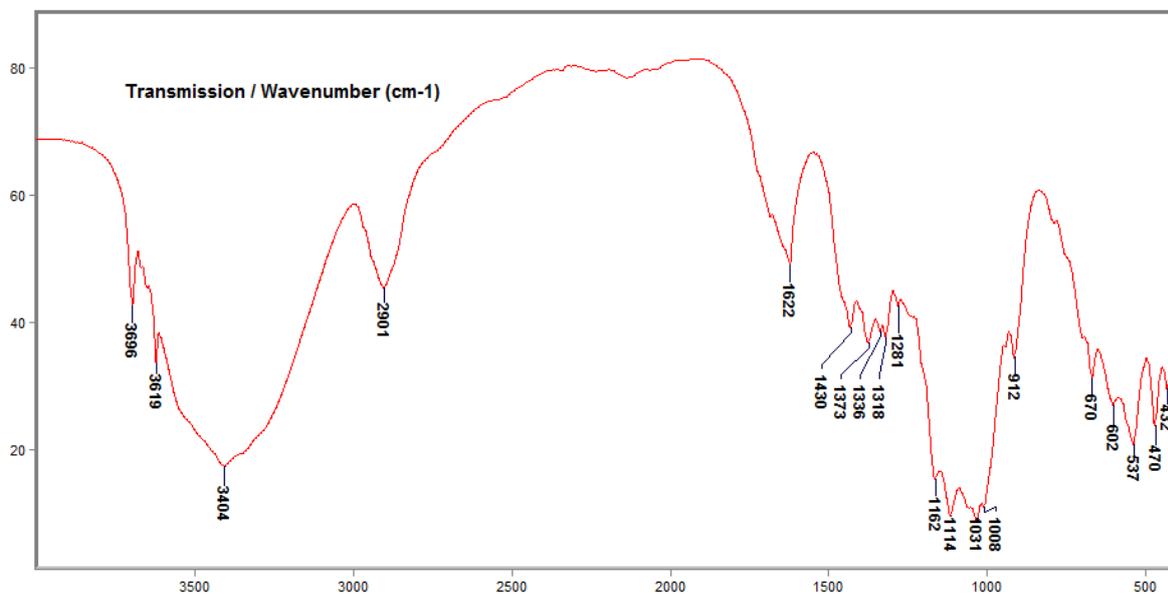


Figure 1: IR spectrum of S1.

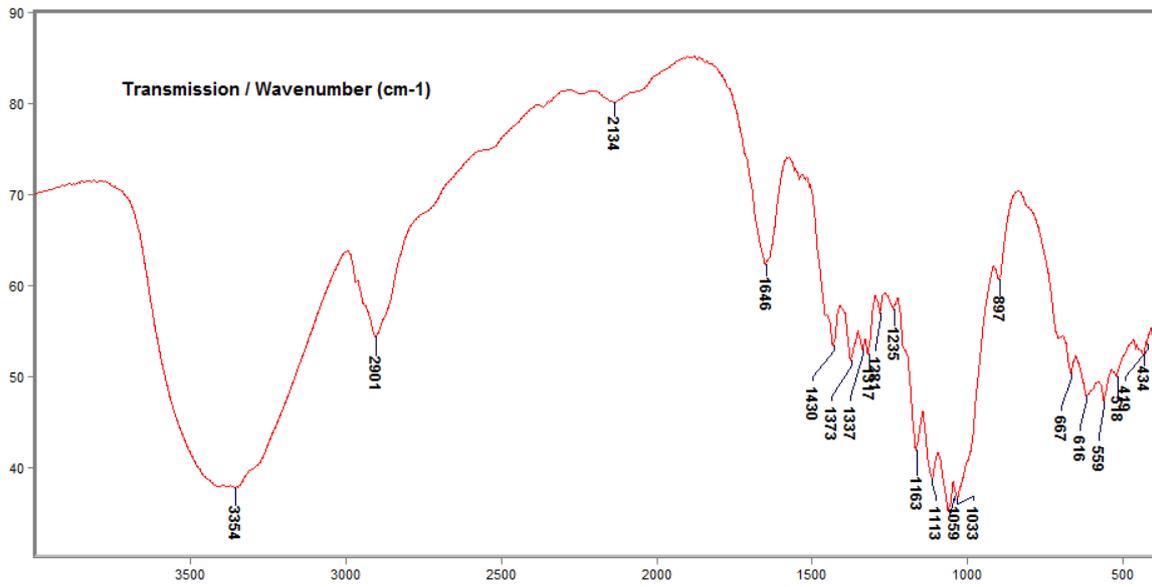


Figure 2: IR spectrum of S2

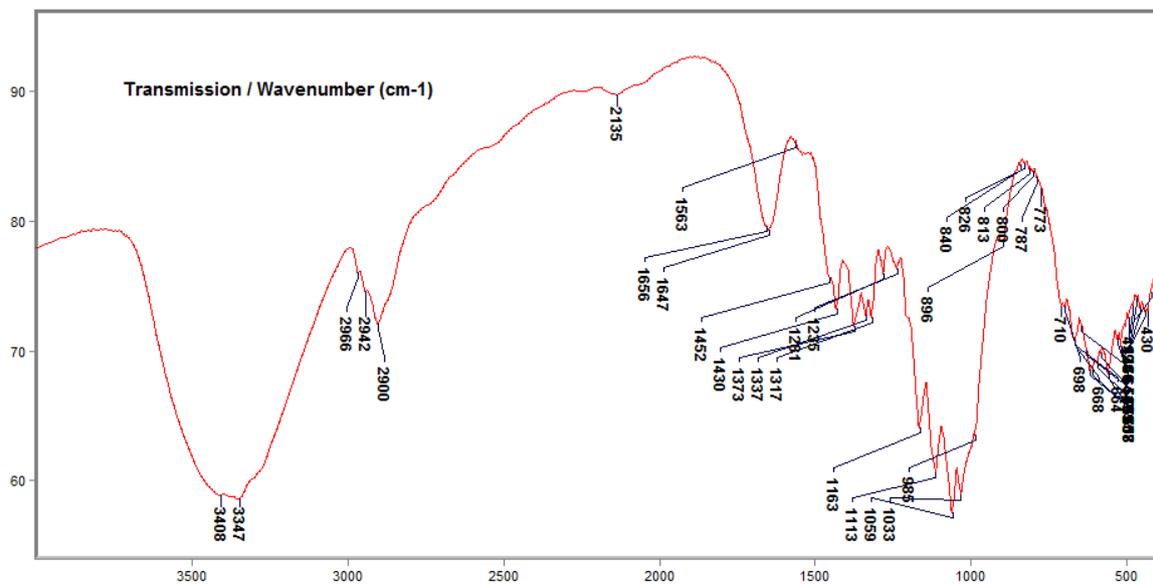


Figure 3: IR spectrum of S3.

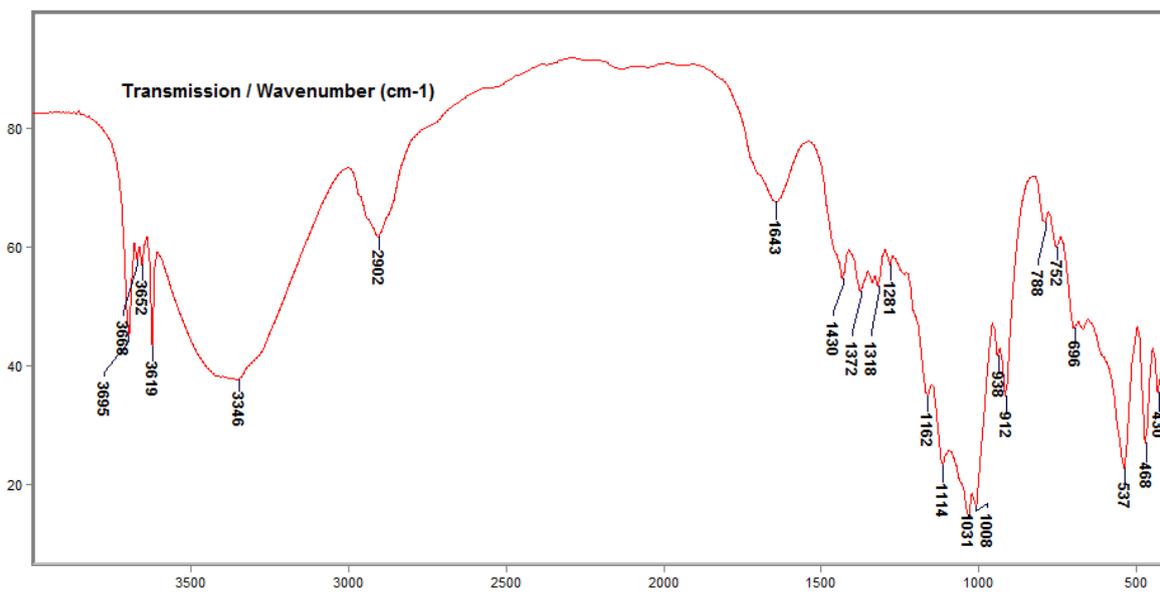


Figure 4: IR spectrum of S4.

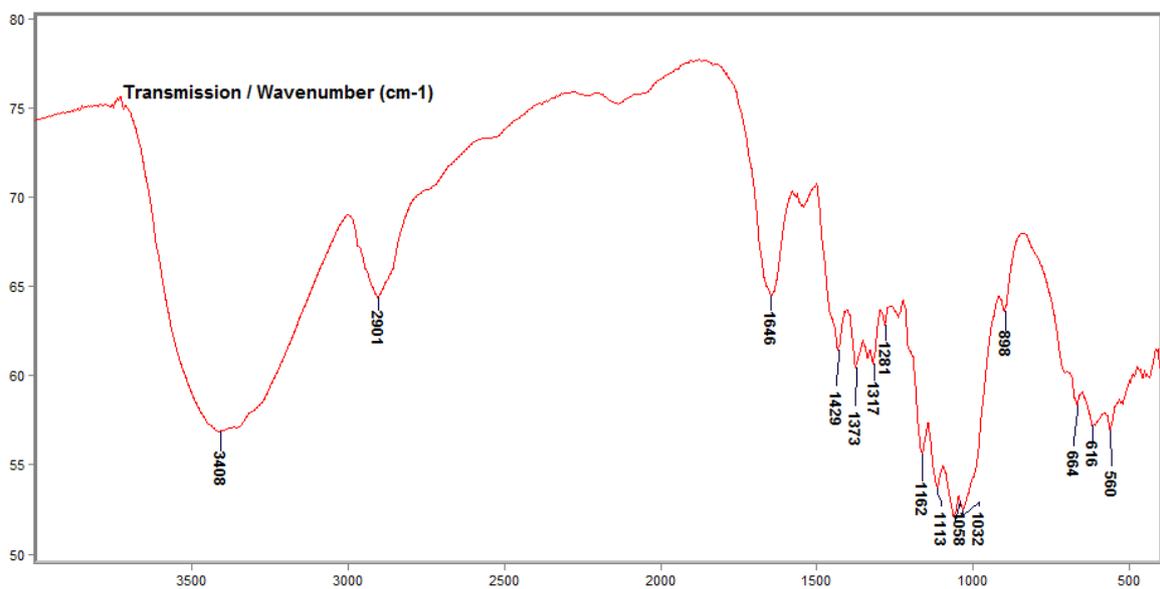


Figure 5: IR spectrum of S5.

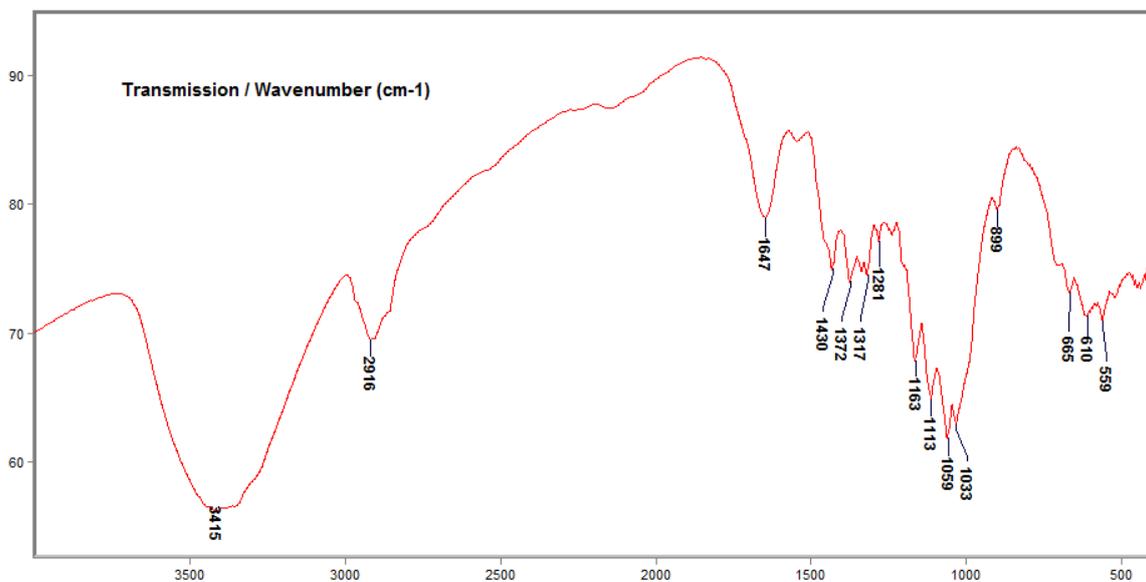


Figure 6: IR spectrum of S6.

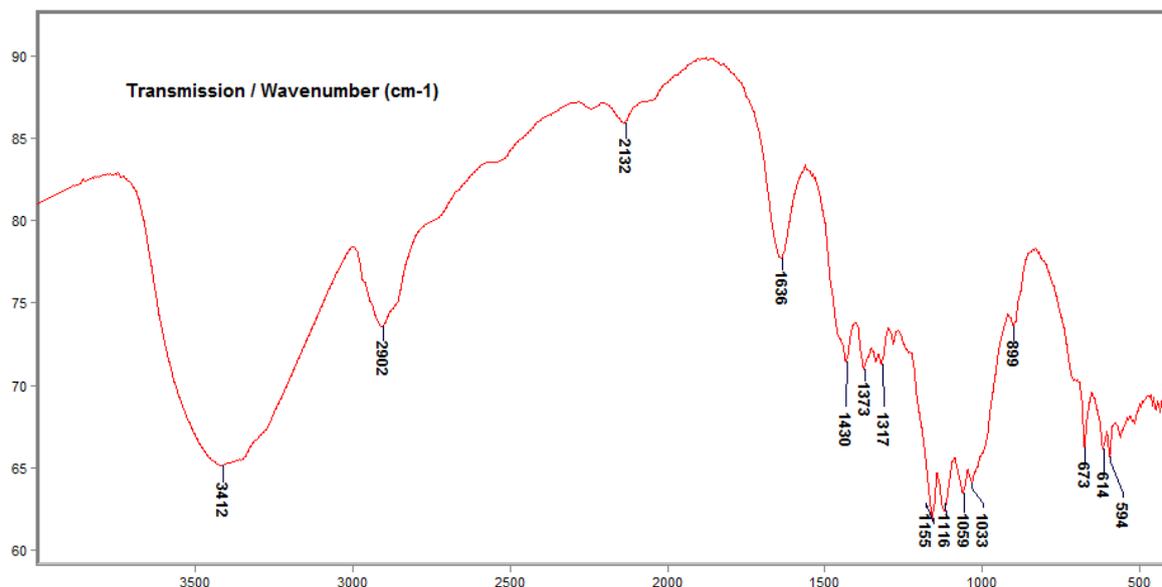


Figure 7: IR spectrum of S7.

XRF results: Figures 8-14 show the XRF results.

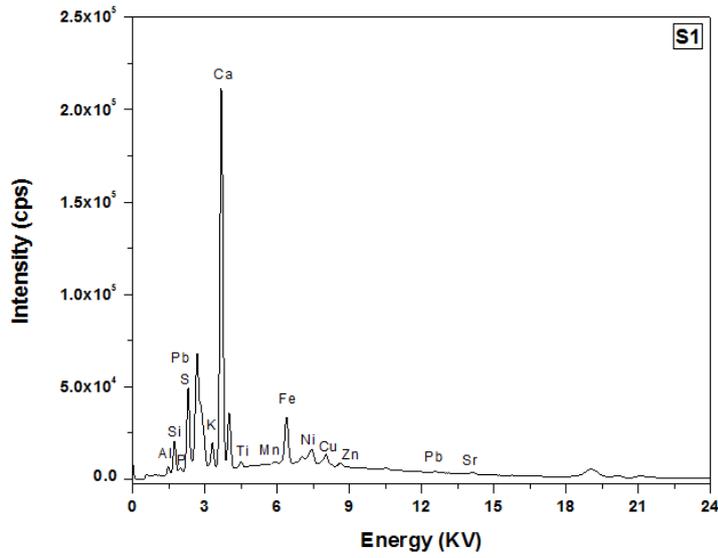


Figure 8: XRF results for S1.

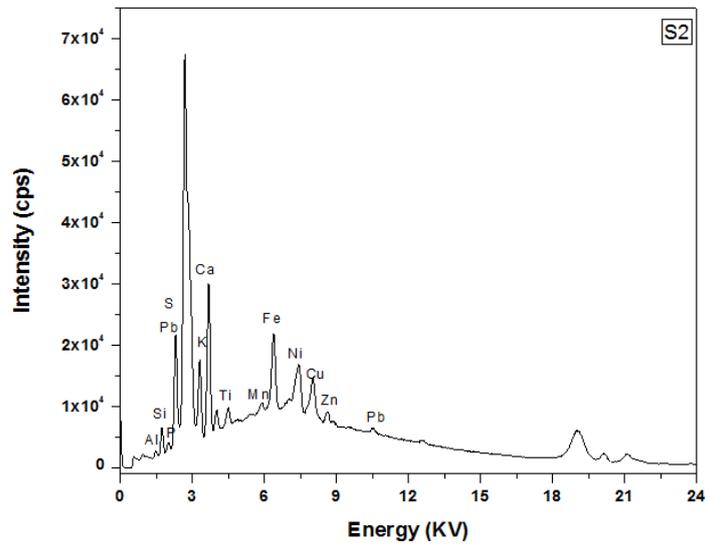


Figure 9: XRF results for S2.

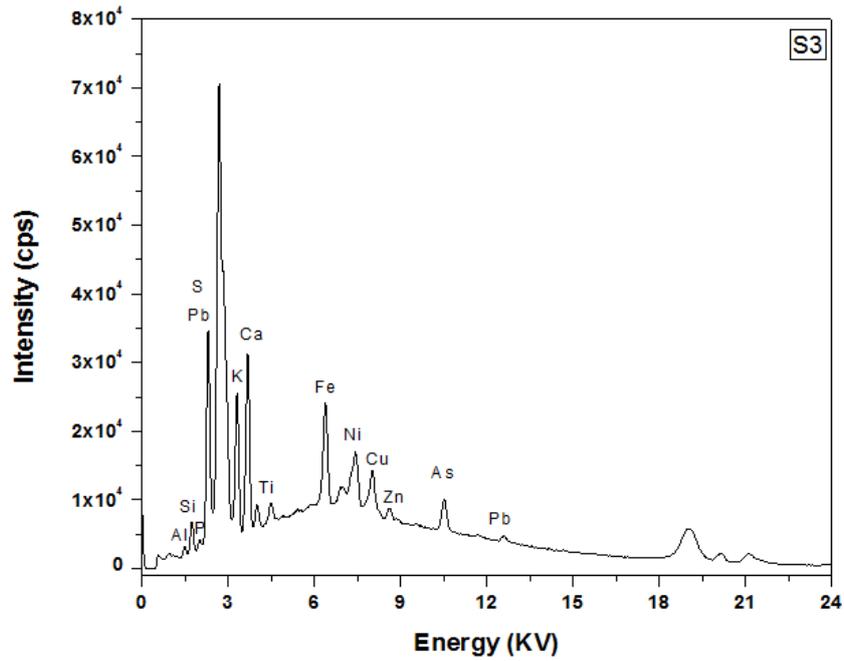


Figure 10: XRF results for S3.

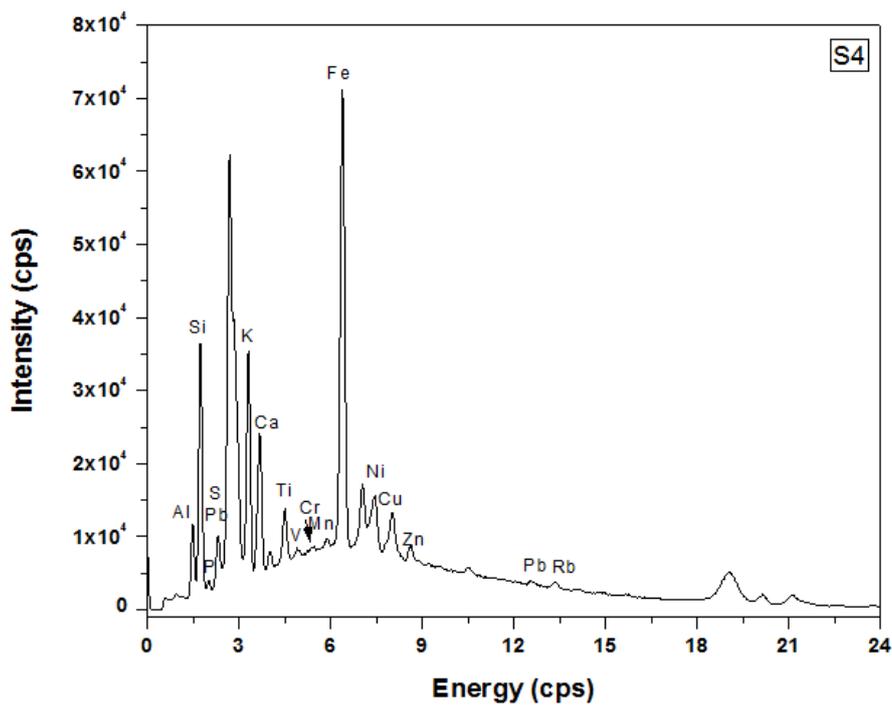


Figure 11: XRF results for S4.

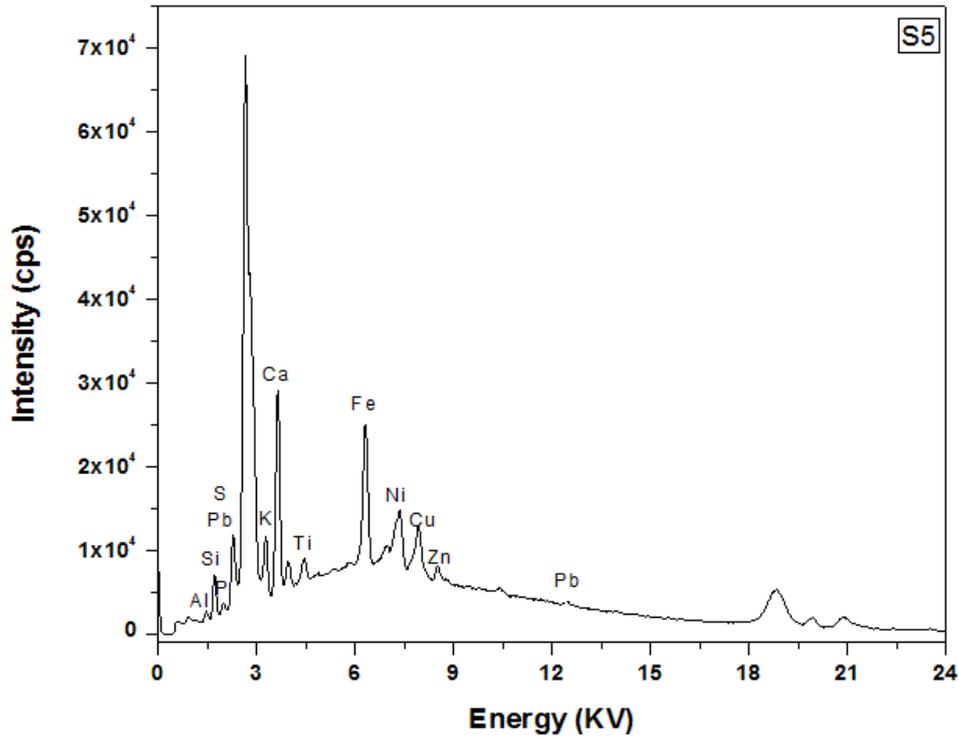


Figure 12: XRF results for S5.

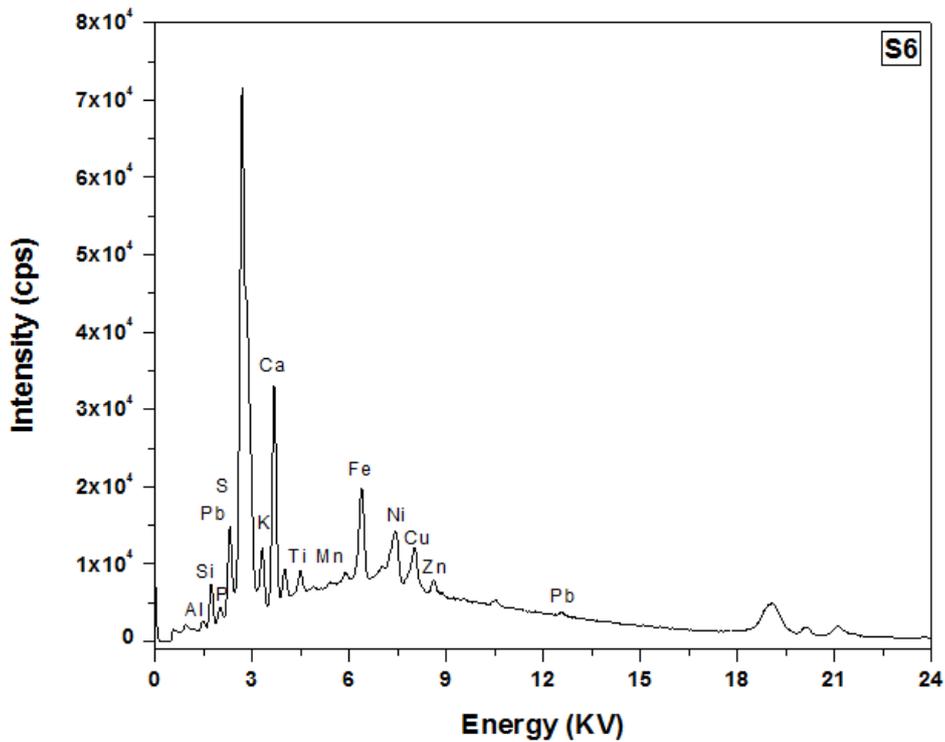


Figure 13: XRF results for S6.

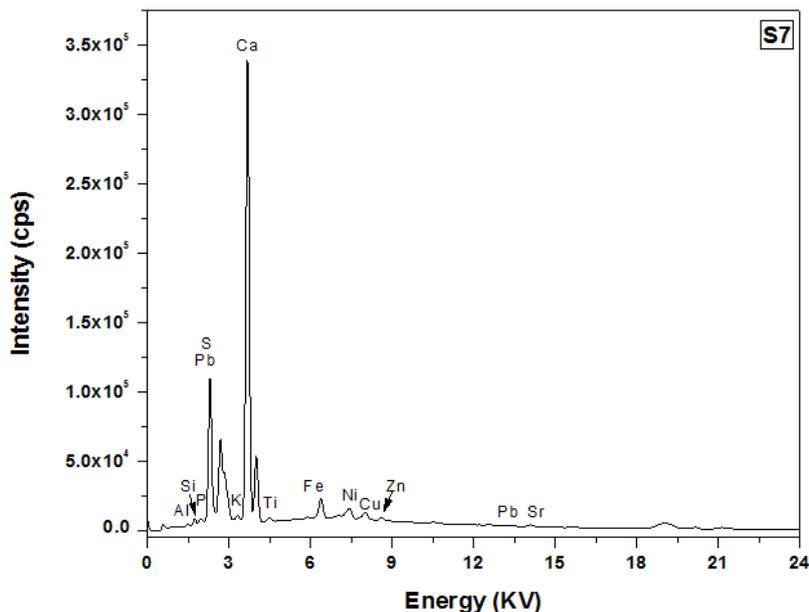


Figure 14: XRF results for S7.

Tables 1 and 2 show a summary of XRF results.

Table 1: Normalized net areas of the elements detected by portable XRF

Sample	Al	Si	P	S	K	Ca	Ti	V	Cr
S1	0.0111	0.0321	0.0112	0.0795	0.0361	0.3661	0.0216	n.d.	n.d.
S2	0.0090	0.0193	0.0140	0.0676	0.0599	0.1012	0.0411	n.d.	n.d.
S3	0.0087	0.0176	0.0122	0.0882	0.0713	0.0889	0.0343	n.d.	n.d.
S4	0.0248	0.0770	0.0102	0.0251	0.0861	0.0637	0.0407	0.0283	0.0304
S5	0.0109	0.0261	0.0163	0.0489	0.0498	0.1142	0.0463	n.d.	n.d.
S6	0.0097	0.0241	0.0167	0.0518	0.0469	0.1205	0.0421	n.d.	n.d.
S7	0.0056	0.0111	0.0117	0.1343	0.0169	0.4430	0.0156	n.d.	n.d.

Table 2: Normalized net areas of the elements detected by portable XRF

Sample	Fe	Ni	Cu	Zn	As	Pb	Sr	Rb	Mn
S1	0.0739	0.0407	0.0350	0.0249	n.d.	0.0889	0.0123	n.d.	0.0243
S2	0.0940	0.0785	0.0708	0.0477	n.d.	0.0925	n.d.	n.d.	0.0499
S3	0.0854	0.0657	0.0574	0.0388	0.0445	0.0445	0.0159	n.d.	0.0382
S4	0.2038	0.0547	0.0485	0.0339	n.d.	0.0435	n.d.	0.0172	0.0348
S5	0.1102	0.0716	0.0675	0.0498	n.d.	0.0737	n.d.	n.d.	n.d.
S6	0.0934	0.0734	0.0645	0.0447	n.d.	0.0762	n.d.	n.d.	0.0464
S7	0.0401	0.0304	0.0260	0.0192	n.d.	0.1345	0.0098	n.d.	n.d.

SEM results:

Figures 15-21 show the SEM results.

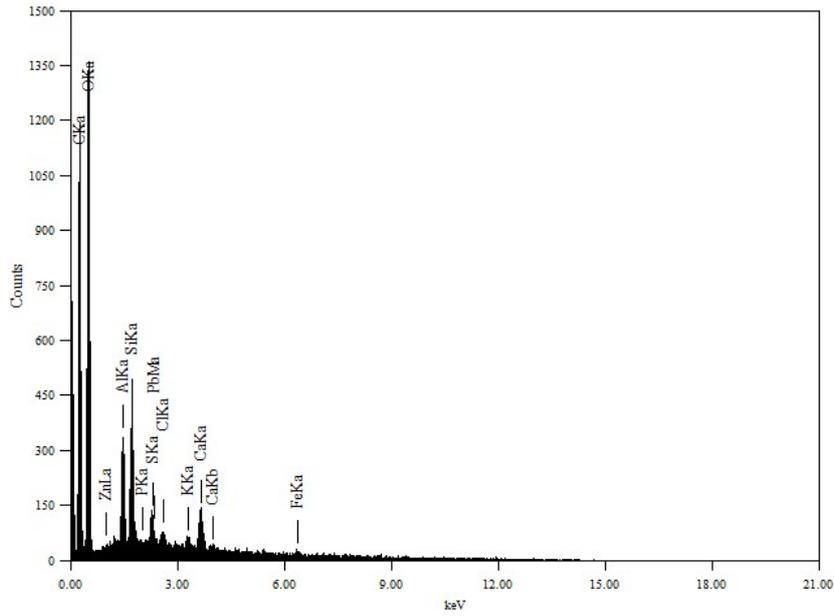


Figure 15: SEM results for S1.

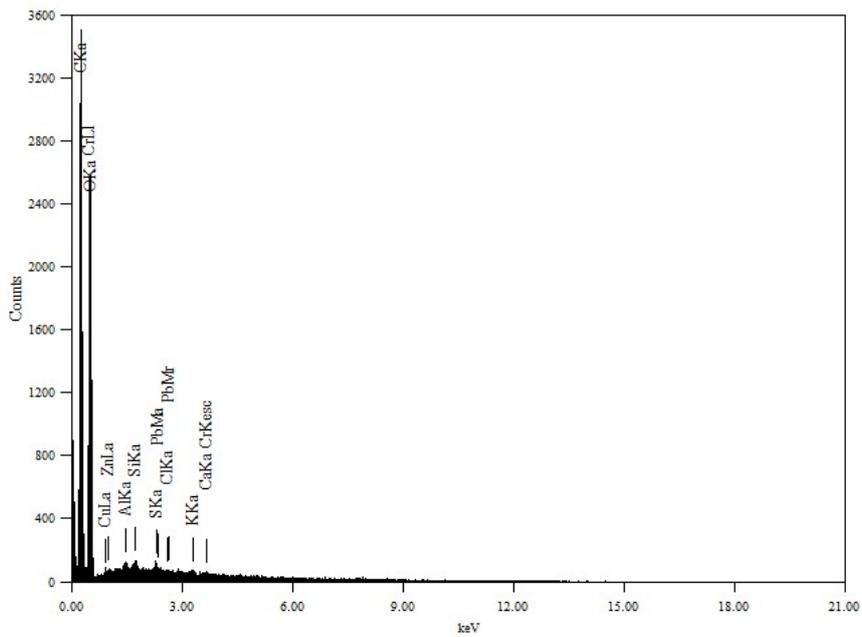


Figure 16: SEM results for S2.

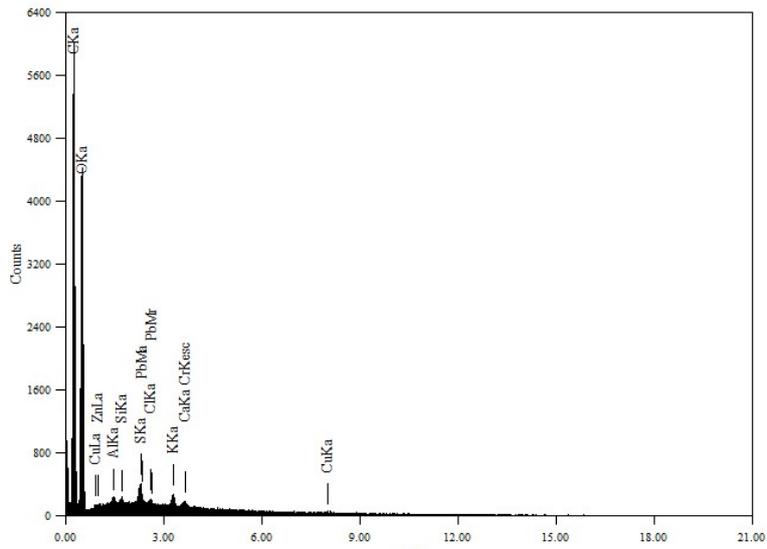


Figure 17: SEM results for S3.

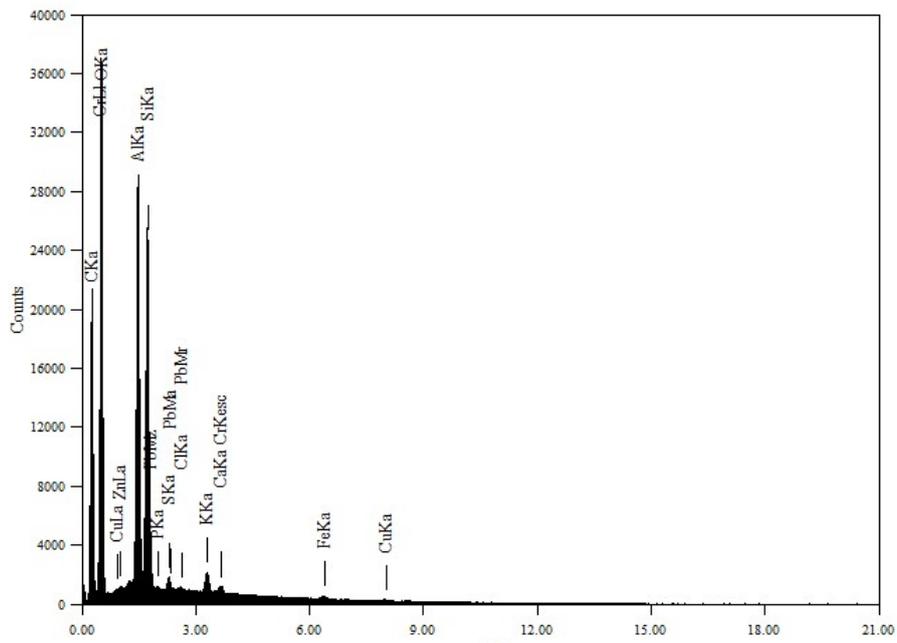


Figure 18: SEM results for S4.

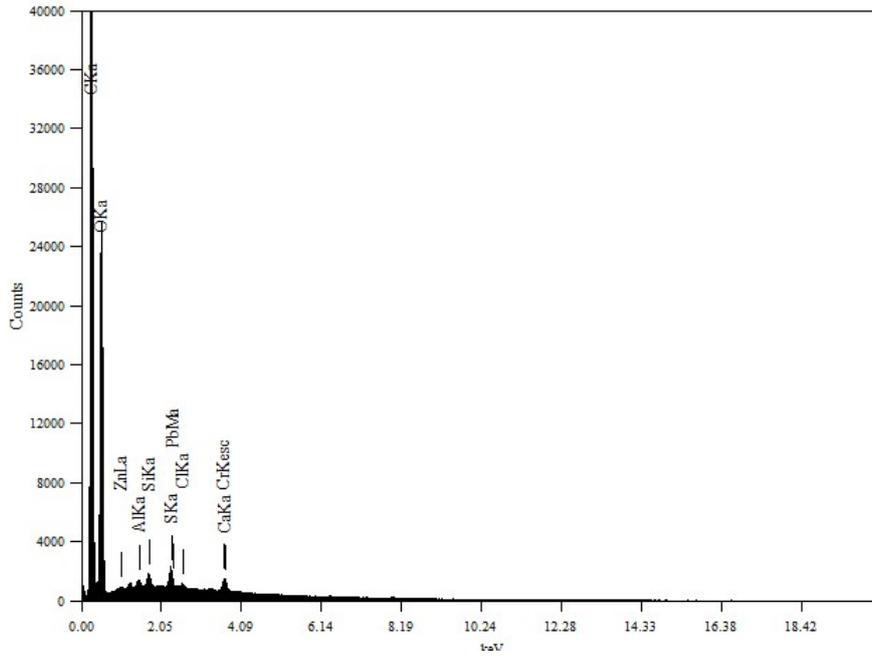


Figure 19: SEM results for S5.

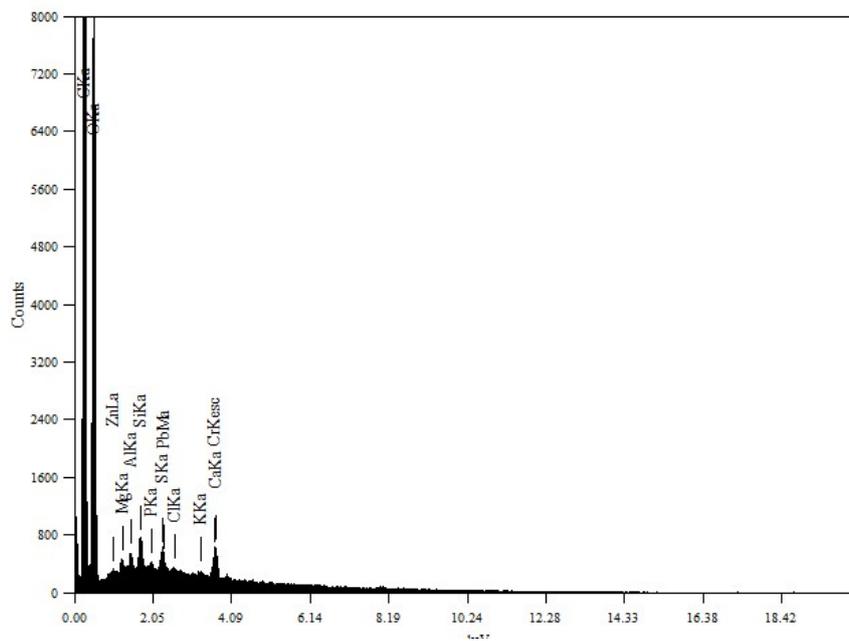


Figure 20: SEM results for S6.

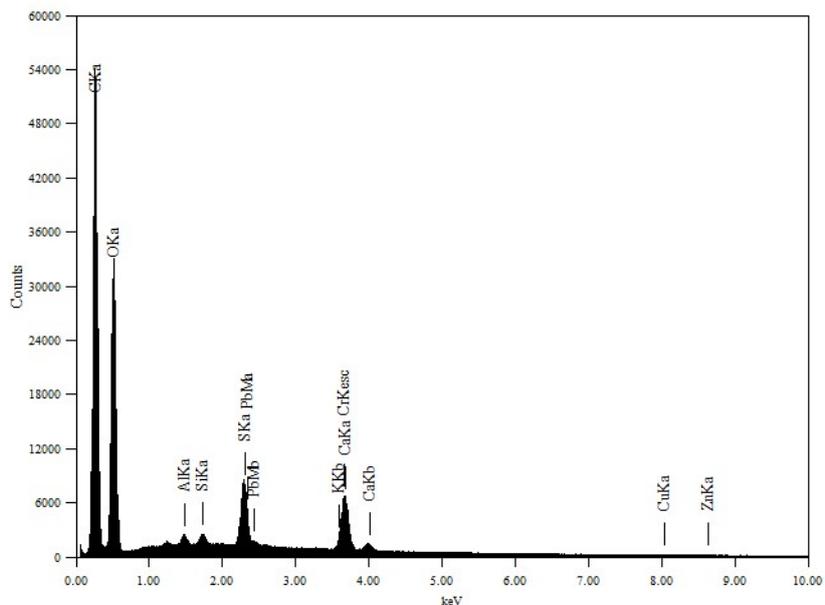


Figure 21: SEM results for S7.

DISCUSSION

Table 3 shows the elements detected by XRF.

Table 3: XRF results

Sample	Elements
S1	Al, Si, P, S, Pb, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Sr.
S2	Al, Si, P, S, Pb, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn.
S3	Al, Si, P, S, Pb, K, Ca, Ti, Fe, Ni, Cu, Zn, As.
S4	Al, Si, P, S, Pb, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Rb.
S5	Al, Si, P, S, Pb, K, Ca, Ti, Fe, Ni, Cu, Zn.
S6	Al, Si, P, S, Pb, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn.
S7	Al, Si, P, S, Pb, K, Ca, Ti, Fe, Ni, Cu, Zn, Sr.

For the moment we shall group the elements in two sets. The first one contains the following elements:

$$S_1 = \{Al, S, K, Ca\}$$

The reason is that they are, besides cellulose, expected paper components. In the second set we place:

$$S_2 = \{Si, P, Pb, Ti, Mn, Fe, Ni, Cu, Sr, As, Zn\}$$

and consider all them as being contaminants. Table 4 shows the elements detected by SEM.

Table 4: Elements detected by SEM

Sample	Elements
S1	Zn, Al, Si, P, S, Pb, Cl, K, Ca, Fe.
S2	Cu, Zn, Al, Si, Pb, S, Cl, K, Ca, Cr.

S3	Cu, <u>Zn</u> , <u>Al</u> , Si, <u>S</u> , Pb, Cl, <u>K</u> , <u>Ca</u> , Cr.
S4	Cu, <u>Zn</u> , <u>Al</u> , Si, Pb, P, <u>S</u> , Cl, <u>K</u> , Cr, <u>Ca</u> , Fe.
S5	<u>Zn</u> , <u>Al</u> , Si, <u>S</u> , Pb, Cl, <u>Ca</u> , Cr, <u>K</u> .
S6	<u>Zn</u> , Mg, <u>Al</u> , Si, P, <u>S</u> , Pb, Cl, <u>K</u> , <u>Ca</u> , Cr.
S7	<u>Al</u> , Si, <u>S</u> , Pb, <u>K</u> , <u>Ca</u> , Cr, Cu, <u>Zn</u> .

We can see from Table 4 that all the elements of set S_1 are present in the seven samples. In the case of set S_2 , it must be enlarged with Cl, Cr and Mg, as follows:

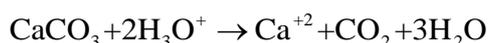
$$S_2 = \{Si, P, Pb, Ti, Mn, Fe, Ni, Cu, Sr, As, Cl, Cr, Mg\}$$

Given the nature and number of the contaminants it seems necessary to look for their possible source(s). The first fact to note is that the seven samples have almost all the contaminants except As and Sr. The possible sources of contamination are, theoretically, the place where the books were kept for a long time and/or aerial deposition. As we did not quantify the contaminants, the ensuing discussion is only qualitative.

Snow sampling in the Cerro Colorado area (36 km NE of central Santiago, Chile, about 2800 m above sea level) by Pinilla Gil et al. showed the presence of As, Pb, Cd, Mn, Co, Ba, Cu, Zn, Mo, Ni, V, Cr and Sb [21]. These authors assert that their *results are in support of a significant impact of emission sources from Santiago de Chile in the area, but the data can also reflect the impact of mining-smelting activities* [21]. The higher Cu levels could be due to the open cut copper mining operation at Los Bronces. Also, particulate matter transport from the El Teniente (mine)/Caletones (smelter) copper complex (95 km SW of Santiago), could explain the enhanced levels of some elements in the Cerro Colorado snow [21]. Note that for Santiago, south to south-westerly wind prevails through the year and that, as Romo-Kröger and Llona pointed out [22], *'the alignment of the Coya river, El Extravio stream and the Maipo river forms a canyon that funnels air masses from Caletones to the Santiago basin'*. In another study with samples taken in places close to El Teniente mine (and also close to the Caletones smelter) it was shown that El Teniente copper mine was an important source of pollution [22]. A very clear relationship between the distance to El Teniente and the aerosol content of heavy metals (Cu, Zn and As) and sulfur was found. Another study with samples collected at about 13 km from the Caletones smelter during a strike period showed that S, Cu, Zn and As came from the copper smelter and Si, K, Ca and Fe have their main origin in the soil [23]. Finally, an analysis of a sample prepared with helmet filter material from the crushing plant area located at Lo Aguirre copper mine, located 30 km west of Santiago [23] found Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Kr, Rb and Zr. We think that all these results explain our findings presented here.

Given that new smelting technologies have been installed in the El Teniente mine and measures to reduce emissions were and are applied [24], it seems necessary to update analyses of the aerial contaminants arriving in Santiago mainly from the south. We think that an analysis of the paper of books arriving at different dates and kept in the same library could give a preliminary idea about how the concentration of pollutants has varied over time.

Now we face the problem of knowing if the members of set S_1 (Al, S, K, Ca) are really in the paper because they were introduced during the manufacture procedure and/or are airborne contaminants. If they were introduced during the fabrication, we can expect to find CaCO_3 and/or $\text{KAl}(\text{SO}_4)_2$ and/or $\text{Al}_2(\text{SO}_4)_3$ [25, 26]. Note that calcium carbonate may disappear as follows:



The presence of sulfate is established by IR bands around 990, 1113, 1089, 620 and 552 cm^{-1} [27]. Only the band around 1113 cm^{-1} is present in all samples. No carbonate bands appear in any of the seven samples [28]. Regarding aluminum, we cited in an earlier paper the suggestion that aluminum oxides and hydroxides absorb at least a monolayer of water when exposed to moisture and that the top layer of oxide ions is converted to hydroxyl ions [29]. Chamberlain pointed out that the scheme where the charge on the metal complex is decreased sequentially as protons are released is quite simple, [30] but it is useful in the absence of excess of gelatin and/or carbonate anion. Therefore, we must search for AlO-H groups. Absorption bands at 3698, 3737 and 3795 cm^{-1} corresponding to "isolated" hydroxyl groups were proposed, and three

AlO-H stretching frequencies at 3787.0, 3752.4 and 3738.7 cm^{-1} have been suggested [31]. Also bands for Al-O stretching (921.5, 886.7 and 810.4 cm^{-1}) and weak O-H bending absorptions at 655.0 and 576.7 cm^{-1} have been proposed. Only sample S1 shows a band around 3696 cm^{-1} . Figures 29 to 35 show the SEM results for Al, Ca, K and S in all samples.

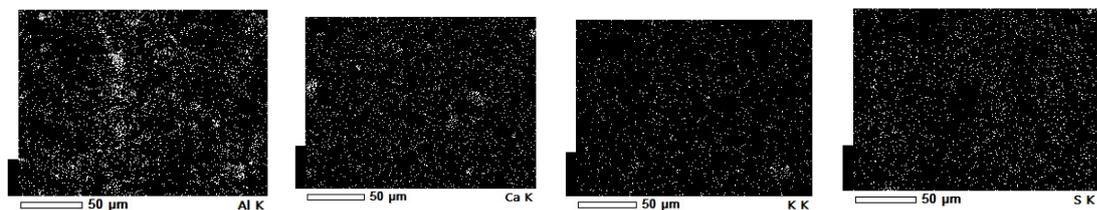


Figure 22: SEM results for Al, Ca, K and S in sample S1.

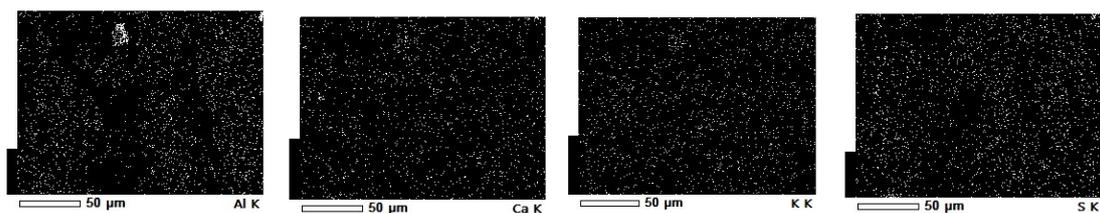


Figure 23: SEM results for Al, Ca, K and S in sample S2.

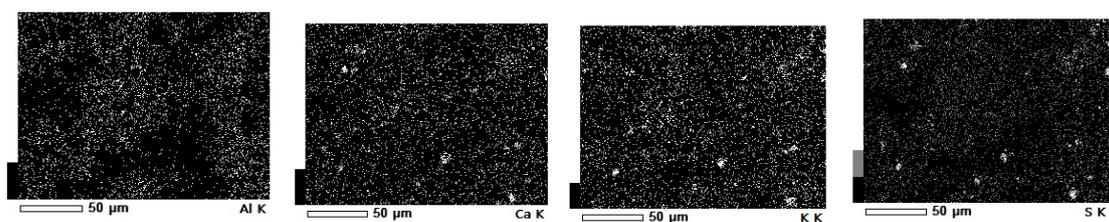


Figure 24: SEM results for Al, Ca, K and S in sample S3.

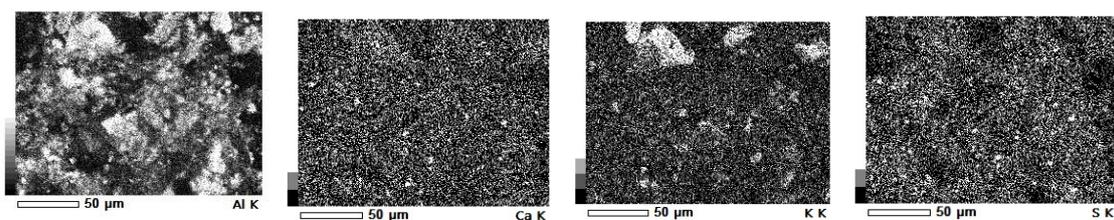


Figure 25: SEM results for Al, Ca, K and S in sample S4.

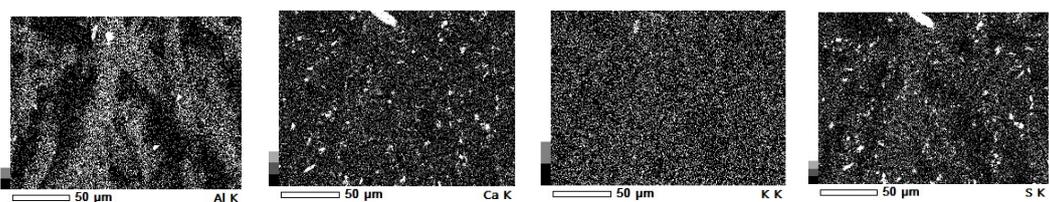


Figure 26: SEM results for Al, Ca, K and S in sample S5.

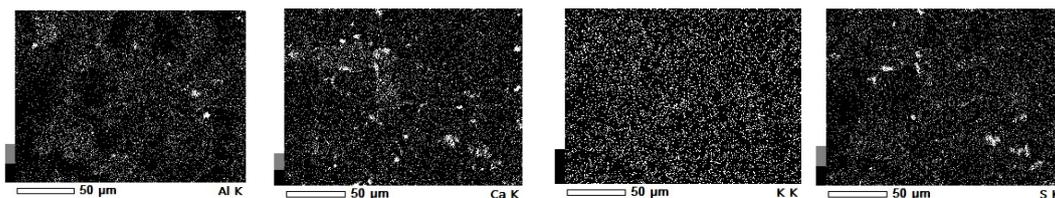


Figure 27: SEM results for Al, Ca, K and S in sample S6.

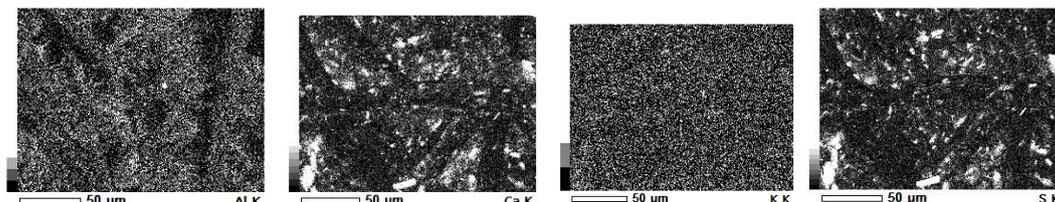


Figure 28: SEM results for Al, Ca, K and S in sample S7.

As before[4], we looked for the following IR bands of cellulose collected from a book and some papers [32-35]: 1158, 1106, 1055, 1030 (all C-O stretching), 1647 and 1546 cm^{-1} (primary and secondary amide bands from protein glue) [33], 1025 and 3330 cm^{-1} [35], 1158, 1111, 1061, 1036 and 3346 cm^{-1} [34]. We only looked for these bands. Table 5 shows our findings.

Table 5: Proposed cellulose IR bands.

Sample	Possible cellulose bands (cm^{-1})
S1	1031.9, 1162.8
S2	1033.0, 1163.6, 1647.0
S3	1033.0, 1163.9, 1647.4
S4	1032.0, 1162.8, 1643.7
S5	1032.4, 1162.8, 1646.7
S6	1033.6, 1163.1, 1647.6
S7	1033.9, 1155.9, 1636.0 (?)

We can see in the Table that in sample S1 the band at about 1645 cm^{-1} does not exist. Moreover, the band at 1645 cm^{-1} also corresponds to the H-O-H bending mode of liquid water and serves as a measure of the dryness of a paper. 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 to clarify these assignments. No colophony seems to be present in the samples [36]. A noticeable presence of lignin can be also discarded [37]. It seems that calcium and alum are present in all the samples. This fact could explain the relatively good state of the paper of these books (the damage has been produced by bad handling and storage and by humidity). The exception seems to be book 2 (printed in 1827) with somewhat brittle corners in some pages. As a tentative hypothesis we suggest that in this case this cracking effect is being produced by light.

We can see in the Table that in sample S1 the band at about 1645 cm^{-1} does not exist. Moreover, the band at 1645 cm^{-1} also corresponds to the H-O-H bending mode of liquid water and serves as a measure of the dryness of a paper. Regarding gelatin, we searched for IR bands of proline [38, 39]. We cautiously suggest that bands at 898.5 (S2, S3, S5-S7), 1318.5 (S1-S7), 1336.5 (S1-S3) and 1373.0 (S1-S7) cm^{-1} could be ascribed to proline. 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. No colophony seems to be present in the samples [36]. A noticeable presence of lignin can be also discarded [37].

We find that the IR analysis is highly unsatisfactory because of the lack of detailed information about more complex systems. Therefore we are undertaking a large scale theoretical study of several models of

cellulose and of several chemicals interacting with cellulose (rosin, Al cations, proline, etc.) to accumulate a large amount of data about IR and Raman spectra. Brückle's text shows some basic models to start from [25].

To end this paper we show in Figures 29-31 microphotographs of the paper samples.

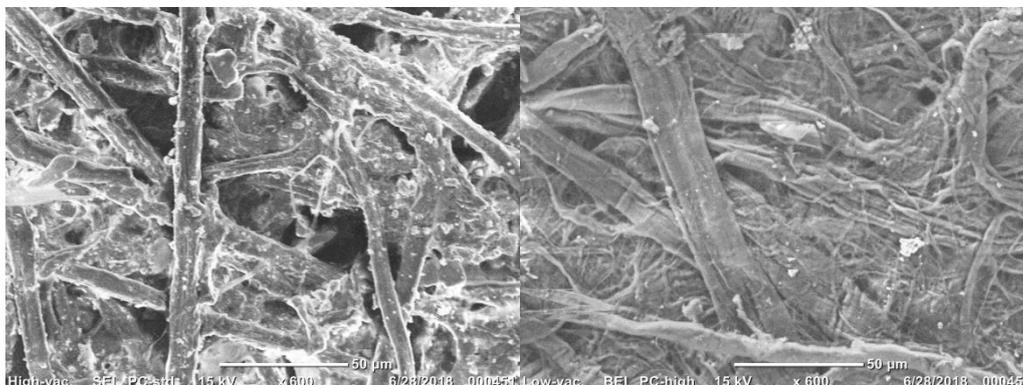


Figure 29: From left to right: microphotographs of samples S1 and S2.

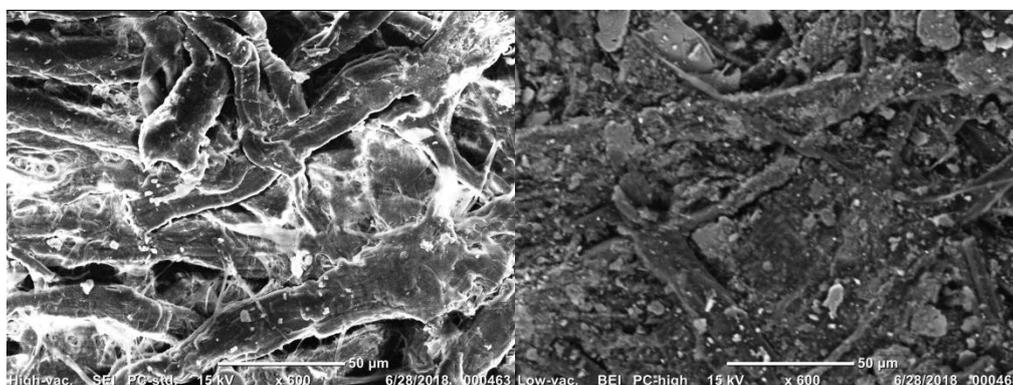


Figure 30: From left to right: microphotographs of samples S3 and S4.

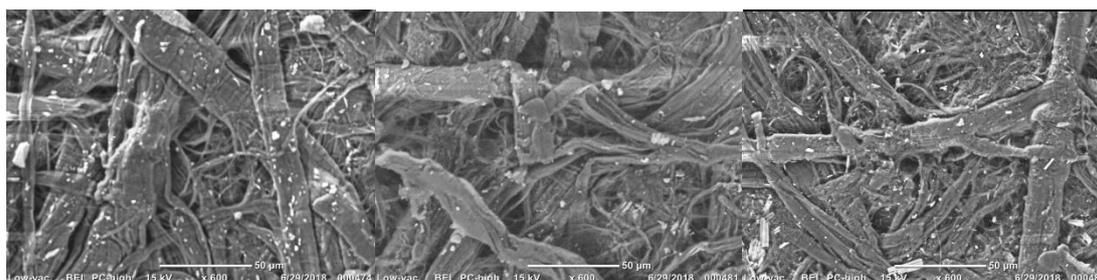


Figure 31: From left to right: microphotographs of samples S5, S6 and S7.

Full IR, XRF and/or SEM results are available on a basis of joint investigation.

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] Gómez-Jeria, J. S.; Clavijo, E.; Gutiérrez, S. An infrared, SEM and XRF study of the paper of a 1588 Spanish book. *Research Journal of Pharmaceutical, Biological and Chemical Sciences* **2018**, 9, 1581-1590.
- [5] 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.
- [6] Baty, J.; Minter, W.; Lee, S. In *The role of electrophilic metal ions aluminum (III) and magnesium (II) in paper degradation and deacidification*, American Institute for the Conservation of Historic and Artistic Works. 38th Annual Meeting. Milwaukee, WI, 2010; 2010.
- [7] Cooke, J. P. *The new chemistry*. Rev. ed.; C. Kegan & Co.: London, 1879; p xvii p., 1 l.
- [8] Balbis, G. B. *Flore lyonnaise. Tome Premier. Deuxieme Partie*. C. Coque: 1827.
- [9] Ferguson, J. F. R. S. *Lectures on Select Subjects in Mechanics, Hydrostatics, Hydraulics, Pneumatics, Optics, Geography, Astronomy and Dialling. Vol. I*. Third edition with Plates. ed.; Sitrling & Slade, and Bell & Bradford: Edinburgh, 1823.
- [10] Vázquez, A. *Tratado Elemental de Química Orgánica etc. Segunda edición. Tomo II*. Librería de Servat: Santiago, 1877.
- [11] Bails, B. *Principios de matemática de la Real Academia de San Fernando. Tomo III. Tercera Edición*. Imprenta de la viua de D. Joaquin Ibarra: Madrid, 1799.
- [12] Fischer, E. G. *Physique mécanique*. Chez Bernard: Paris, 1806.
- [13] Darwin, C.; Moulinié (Ed.), J. J. *L'origine des espèces au moyen de la sélection naturelle, ou La lutte pour l'existence dans la nature*. C. Reinwald: Paris, 1873.
- [14] Zotti, M.; Ferroni, A.; Calvini, P. Microfungal biodeterioration of historic paper: Preliminary FTIR and microbiological analyses. *International Biodeterioration & Biodegradation* **2008**, 62, 186-194.
- [15] Nol, L.; Henis, Y.; Kenneth, R. G. Biological factors of foxing in postage stamp paper. *International Biodeterioration & Biodegradation* **2001**, 48, 98-104.
- [16] Ligterink, F. J.; Porck, H. J.; Smit, W. J. T. Foxing stains and discolouration of leaf margins and paper surrounding printing ink: Elements of a complex phenomenon in books. *The Paper Conservator* **1991**, 15, 45-52.
- [17] Hutchins, J. K. Water-stained Cellulosics: A Literature Review. *Journal of the American Institute for Conservation* **1983**, 22, 57-61.
- [18] Daniels, V. Discoloration of Paper Induced by Pigments Containing Zinc. In *Restaurator*, 1990; Vol. 11, pp 236-243.
- [19] Stephens, C. H.; Barrett, T.; Whitmore, P. M.; Wade, J. A.; Mazurek, J.; Schilling, M. Composition and Condition of Naturally Aged Papers. *Journal of the American Institute for Conservation* **2008**, 47, 201-215.
- [20] Gómez-Jeria, J.-S.; Clavijo, E.; Cárcamo-Vega, J.; Gutierrez, 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.
- [21] Cereceda-Balic, F.; Palomo-Marín, M. R.; Bernalte, E.; Vidal, V.; Christie, J.; Fadic, X.; Guevara, J. L.; Miro, C.; Pinilla Gil, E. Impact of Santiago de Chile urban atmospheric pollution on anthropogenic trace elements enrichment in snow precipitation at Cerro Colorado, Central Andes. *Atmospheric Environment* **2012**, 47, 51-57.
- [22] Romo-Kröger, C. M.; Lloná, F. A case of atmospheric contamination at the slopes of the Los Andes mountain range. *Atmospheric Environment. Part A. General Topics* **1993**, 27, 401-404.
- [23] Romo-Kroger, C. M.; Morales, R.; Llonad, F.; Auriold, P.; Wolleter, G. E. Risks of Airborne Particulate Exposure in a Copper Mine in Chile. *Industrial Health* **1989**, 27, 95-99.
- [24] von Gunten, L.; Grosjean, M.; Eggenberger, U.; Grob, P.; Urrutia, R.; Morales, A. Pollution and eutrophication history AD 1800–2005 as recorded in sediments from five lakes in Central Chile. *Global and Planetary Change* **2009**, 68, 198-208.
- [25] Brückle, I. The role of alum in historical papermaking. *Abbey Newsletter* **1993**, 17, 1-13.
- [26] Hubbe, M. A.; Gill, R. A. Fillers for papermaking: A review of their properties, usage practices, and their mechanistic role. *BioResources* **2016**, 11, 2886-2963.
- [27] Klopogge, J. T.; Ruan, H.; Frost, R. L. Near-infrared spectroscopic study of basic aluminum sulfate and nitrate. *Journal of materials science* **2001**, 36, 603-607.
- [28] 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.

- [29] Tombácz, E. pH-dependent surface charging of metal oxides. *Periodica Polytechnica Chemical Engineering* **2009**, 53, 77-86.
- [30] Chamberlain, D. Anion mediation of aluminium-catalysed degradation of paper. *Polymer Degradation and Stability* **2007**, 92, 1417-1420.
- [31] Wang, X.; Andrews, L. Infrared Spectroscopic Observation of the Group 13 Metal Hydroxides, $M(OH)_{1,2,3}$ ($M = Al, Ga, In, \text{ and } Tl$) and $Al(OH)_2$. *The Journal of Physical Chemistry A* **2007**, 111, 1860-1868.
- [32] Zhbakov, R. G. *Infrared spectra of cellulose and its derivatives*. Springer: New York, 1966.
- [33] Imperio, E.; Giancane, G.; Valli, L. Spectral Database for Postage Stamps by Means of FT-IR Spectroscopy. *Analytical Chemistry* **2013**, 85, 7085-7093.
- [34] 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.
- [35] 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.
- [36] Rao, Z.; Dong, K.; Yang, X.; Lin, J.; Cui, X.; Zhou, R.; Deng, Q. Natural amber, copal resin and colophony investigated by UV-VIS, infrared and Raman spectrum. *Science China Physics, Mechanics and Astronomy* **2013**, 56, 1598-1602.
- [37] Boeriu, C. G.; Bravo, D.; Gosselink, R. J. A.; van Dam, J. E. G. Characterisation of structure-dependent functional properties of lignin with infrared spectroscopy. *Industrial Crops and Products* **2004**, 20, 205-218.
- [38] Doyle Barbara, B.; Bendit, E. G.; Blout Elkan, R. Infrared spectroscopy of collagen and collagen-like polypeptides. *Biopolymers* **1975**, 14, 937-957.
- [39] 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.