ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

A Characterization Of Cellulose In Seven Books Using Raman Spectroscopy In The 800-1800 cm^{-1} Range.

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ABSTRACT

Raman spectroscopy was employed to study the non-printed area of a page of seven books printed in the 18th and 19th centuries. We employed the Vancouver Raman Algorithm to deal with the strong fluorescence background, obtaining spectra only in the 800 – 1800 cm^{-1} range. Two samples contain lignin, suggesting the presence of wood fibers. One sample (year 1799) contains only cellulose and gelatin. Two samples contain rosin. There are several Raman bands that we could not ascribe. Based on the results we propose a way to prepare the samples that could guarantee that the infrared and Raman spectra can be compared with confidence.

Keywords: Paper composition, cellulose, lignin, Raman spectroscopy, gelatin, rosin, carbonate, sulfate, alum, Vancouver Raman algorithm.

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INTRODUCTION

In the document entitled '*Physical and Chemical Properties of Book Papers'* we find a clear and short presentation of papermaking from 1507 until 1949[1]. From this text we took the ensuing information. At the beginning of papermaking in Europe, white rags were employed as raw materials. Gelatin size was used for the first time around 1337. The first type of gelatin was produced from animals[1, 2]. The use of alum (potassium aluminum sulfate, $KAl(SO_4)_2{\cdot}12H_2O$) with gelatin is mentioned during the 16th century. It was reported that alum was found in 12 of the 45 books tested from the 16th century[1]. Calcium and magnesium carbonates also appear because of the use of hard water and/or milk. The increasing demand of paper produced a shortage of rags but the bleaching of colored rags with chlorine and the search for new fibers (cotton, linen, straw and wood) alleviate the problem. For the group of 18th century books it was found that 85% contained alum and 22% contained carbonate. Prof. Rosenband gives the following depiction of what someone observing paper making in 18th century France could see: '*He would have seen women sorting rags, water-powered mallets macerating old linen, vatmen "promenading" newly minted sheets, couchers transferring the fresh paper onto dampened felts, men tugging at the bar of the great press, the layman separating still-moist sheets from the felts, women hanging the paper to dry, a sizerman stirring his cauldron of finish, more women inspecting the freshly sized paper for flaws, a teller counting quires, the loftsman wrapping reams, and swarms of children performing odd jobs. It was as if an assortment of guilds—for the tasks of papermaking were that distinct and specialized—had been yoked together under one roof'*[3]. At the end of the 18th century the Fourdrinier machine, designed for producing paper, paperboard, and other fiberboards, is invented in France by Louis Robert[4]. During the 19th century the alum-rosin (in the form of an aluminum rosinate) sizing began to replace gelatin sizing (around 1805)[1]. The use of wood as a source of paper fibers began during the 1840s. In the books analyzed by Barrows, wood fibers began to appear about the middle of the 19th century. The invention of the stone groundwood procedure for newspapers in 1845, the soda-pulping process in 1866, the bisulfite method in 1875, and the Kraft process in 1882 allowed the paper production to grow to substantial levels and making possible the use of wood as a raw material *par excellence*. By the end of 19th century, wood fibers were present in a very high percentage of the papers tested. At the beginning, the fibers were not purified and they contained approximately equal amounts of cellulose (a polysaccharide consisting of a linear chain of several hundred to many thousands of β(1→4) linked D-glucose units) and non cellulose materials, mostly lignin (a polymeric material consisting of the cross-linked component of coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol). At the beginning of the 20th century alum was substituted with aluminum sulfate ($Al_2(SO4)_3$), the so-called 'papermaker's alum'. Today, almost all printing paper is made from wood-derived fibers, mainly from bleached Kraft pulp (composed mostly of cellulose and hemicelluloses) or from mechanical pulps (lignin-containing fibers). Among fillers used in papermaking we may mention alum, barium sulfate, calcium carbonate, calcium sulfate, calcium sulfite, clay, gypsum, kaolin, titanium dioxide, white lead, wax and zinc oxide.

Recently, we presented the results of a preliminary infrared (IR), SEM and XRF analysis of the non-printed area of the paper of seven books of the 18th and 19th centuries[5]. 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 probably because of the transformation of this anion into CO_2. One IR sulfate band appears in all the samples, suggesting the presence of alum. We suggested also that some IR bands could be ascribed to proline and that neither colophony nor lignin seemed to be present. With the aim of complementing the above mentioned results, we present here the characterization of cellulose of the paper of the same books employed in our previous study using Raman spectroscopy. The use of Raman spectroscopy in historical and archeological studies is well documented[6-17]. This article is a part of a more extended effort to describe the composition of paper from old books and especially from postage stamps[18-22].

EXPERIMENTAL

We employed the same samples of our previous study, named S1 to S7. It is necessary to mention that the samples were the same but that Raman measurements were done in different areas of the remaining of the samples because previously some parts of them were used (and destroyed) for IR analysis. More precisely, Raman measurements were carried out in the same paper area where XRF analysis was done. Therefore, if the paper is not homogeneous, some differences between the different results are to be expected. Raman spectra were recorded on a Raman Renishaw InVia Reflex apparatus, equipped with 532, 633 and 785 nm laser lines for

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excitation, a Leica microscope and an electrically cooled charge-coupled device detector. The instrument was calibrated using the 520 cm^{-1} line of a Si wafer and a 50x objective. Its resolution was set to 4 cm^{-1} and 1-5 scans of 10-50 s each were averaged. Spectra were recorded in the 800-1800 cm^{-1} region. The power of the laser 785 nm was set between 10 to 100 mW. Spectral scanning conditions were chosen to avoid sample degradation and photodecomposition. Data was collected and plotted using the GRAMS software. The 785 nm laser line was employed for obtaining the spectra. In two cases more than one spectrum was recorded at different places of the sample.

It is well known that the major obstacle in obtaining reasonably good Raman spectra is the strong fluorescence background. To circumvent this problem we have applied the Vancouver Raman Algorithm to the original spectra.

RESULTS AND DISCUSSION

Before presenting the results it is important to stress their main limitation. The Vancouver Raman Algorithm (VCR) produces results only for the 800-1800 cm^{-1} range. Therefore, we do not expect to provide clear information about some inorganic chemicals that could be present in the samples. We are working in a possible way to circumvent this problem. For band assignments we have searched the literature for Raman spectra of the chemical species we are interested in: kaolinite[23, 24], alum[25-27], $MgCO_3$ and $CaCO_3$[28-32], gelatin[33], lignin[34-37], cellulose and its components[8, 36, 38, 39], hemicellulose[40] (a smaller branched carbohydrate which can be made of different monosaccharides[41], hemicellulose found in hardwood trees is predominantly xylan with some glucomannan), colophon (rosin)[26, 33, 42] and sulfate[43, 44]. Also, some compilations of Raman data were used[33, 45-47]. Some chemicals that could be present in the paper have no signals or very weak ones inside this interval. This is the case of, for example, barium sulfate (1087vw, 1105vw, 1142w and 1168vw), gypsum (1009vs, 1136m) and magnesium carbonate (1122w). An exception is calcium carbonate (1087vs). On the other hand, it is known that there are regions of the spectra of wood where cellulose and hemicelluloses do not contribute and where only features of lignin are observed. For example, in the 1600 cm^{-1} region aromatic ring, C=C and C=O stretching are observed. Unhappily, the samples studied in the present work contain other chemicals that also present bands in that region, suggesting that some of the assignments are necessarily subjective in some cases. For this reason we marked some suggestions with (?). Figures 1 to 10 show the Raman spectrum of samples S1-S7 after treatment of the original spectra with the VRA.

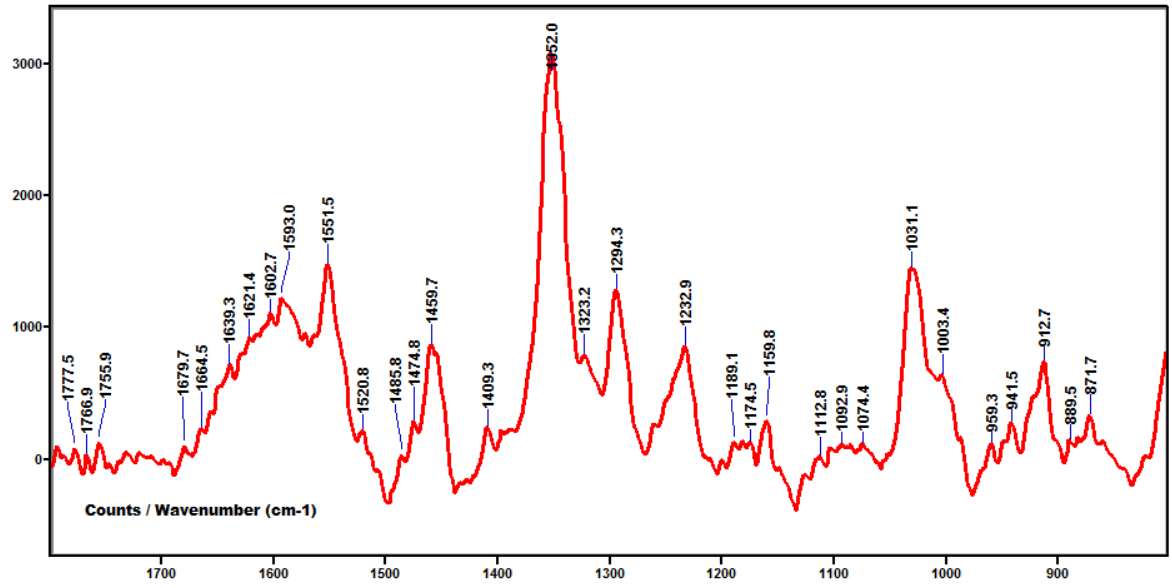

Figure 1. Raman spectrum of sample S1 (J.P. Cooke. The new chemistry. Revised edition. C. Kegan & Co., London, 1879).

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Table 1 shows the tentative assignments of some bands of the Raman spectrum of sample S1.

Table 1. Tentative assignments of some bands of the Raman spectrum of sample S1.

Band (cm^{-1})	Chemical(s)		Band (cm^{-1})	Chemical(s)
889.5	MC cellulose		1294.3	Cellulose
912.7	Cellulose		1352.0	Cellulose
941.5	Cellulose		1409.3	Cellulose, CO_3 (?)
1003.4	Cellulose		1459.7	Cellulose
1074.4	Cellulose, CO_3 (?)		1474.8	Cellulose
1092.9	MC cellulose, CO_3 (?)		1485.8	Cellulose
1112.8	SO_4 (?), Cellulose		1593.0	Lignin
1159.8	SO_4 (?)		1602.7	Lignin
1174.9	Cellulose		1621.4	Lignin
1189.1	Lignin		1664.5	Lignin
1232.9	Cellulose		1755.9	CO_3 (?)

We can see that we are in the presence of wood cellulose containing lignin and perhaps microcrystalline cellulose. XRF and SEM results for this sample showed the presence of Al, S, K and Ca. We have suggested here possible bands for sulfate and carbonate dianions but note that there could be a superimposition with some cellulose bands. Several bands are ascribed to lignin, suggesting that this paper was made from by wood cellulose. Note that this sample is from year 1879 when wood fibers began to be massively employed. Gelatin seems to be absent.

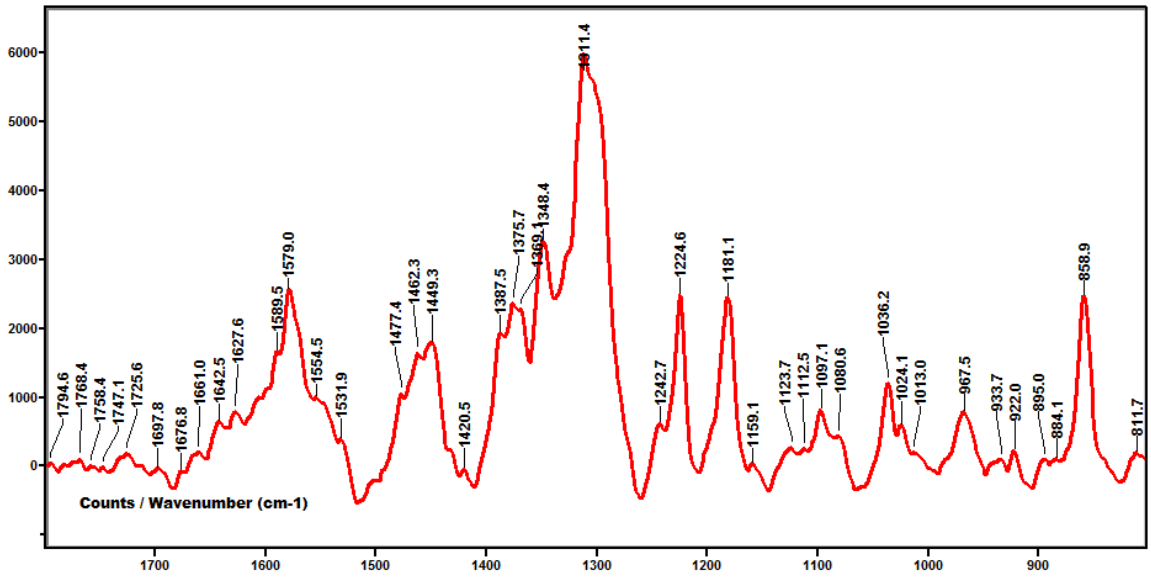

Figure 2. Raman spectrum of sample S2 (G.B. Balbis. *Flore Lyonnaise*, *Tome Premier*. *Deuxieme Partie*, Lyon, 1827).

Table 2 shows the tentative assignments of some bands of the Raman spectrum of sample S2.

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Table 2. Tentative assignments of some bands of the Raman spectrum of sample S2.

Band (cm^{-1})	Chemical(s)		Band (cm^{-1})	Chemical(s)
858.9	Gelatin		1387.5	Cellulose
895.0	Cellulose		1420.5	Cellulose, gelatin (?)
922.0	Gelatin (?)		1449.3	Cellulose, CO_3 (?), gelatin (?)
933.7	Gelatin		1462.3	Cellulose
967.5	Cellulose		1477.4	Cellulose, CO_3 (?)
1013.0	SO_4 (?)		1531.9	H_2O (?)
1024.1	--		1554.5	Gelatin
1036.2	Cellulose		1579.0	--
1080.6	Cellulose		1589.5	Rosin ?
1097.1	Cellulose, CO_3 (?)		1627.6	Rosin?
1112.5	Cellulose		1642.5	--
1123.7	Cellulose, gelatin (?)		1661.0	ν(C=O) (?), ν(C=C) *cis*, gelatin
1159.1	Gelatin, SO_4 (?)		1676.8	H_2O (?)
1181.1	Gelatin		1697.8	--
1224.6	Cellulose		1725.6	--
1242.7	Gelatin		1747.1	ν(C=O),CO_3 (?)
1311.4	Cellulose (?)		1758.4	--
1348.4	Gelatin		1768.4	CO_3 (?)
1369.1	Cellulose		1794.6	
1375.7	Cellulose, gelatin (?)			

Table 2 shows that, besides cellulose, gelatin and a carbonate ($CaCO_3$) seem to be present in this sample. The book is from 1827 and no lignin appears to exist in the sample. Perhaps rosin and/or an inorganic sulfate may exist but the evidence is uncertain.

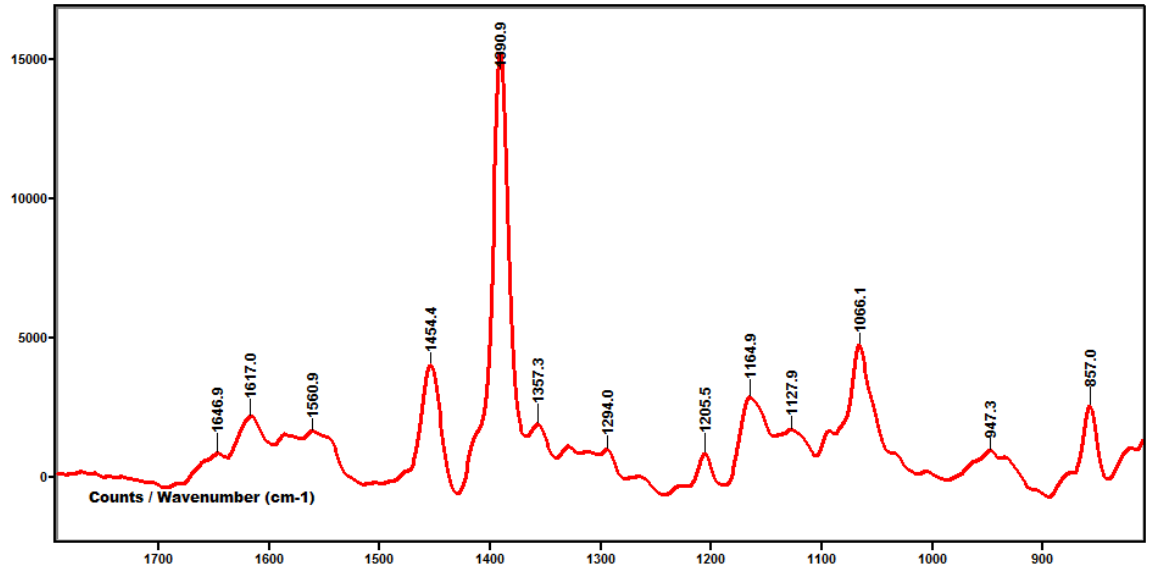

Figure 3. Raman spectrum of sample S3-A (J.F.R.S. Ferguson. Lectures on Select Subjects in Mechanics, Hydrostatics, etc.,.. and Dialling, Vol. 1, Edinburgh, 1823).

Table 3 shows the tentative assignments of some bands of the Raman spectrum of sample S3-A. Samples S3-A, S3-B and S3-C are from different places of the same sample.

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Table 3. Tentative assignments of some bands of the Raman spectrum of sample S3-A.

Band (cm^{-1})	Chemical(s)
857.0	Gelatin
947.3	--
1066.1	Cellulose
1127.9	Cellulose, gelatin (?)
1164.9	Cellulose, gelatin (?)
1205.5	Cellulose, gelatin (?)
1294.0	Cellulose
1357.3	Cellulose (?)
1390.9	Cellulose
1454.4	Cellulose, gelatin (?)
1560.9	--
1617.0	C=C aromatic
1646.9	--

Sample S3-A seems to contain cellulose and gelatin. Compare below with samples S3-B and S3-C.

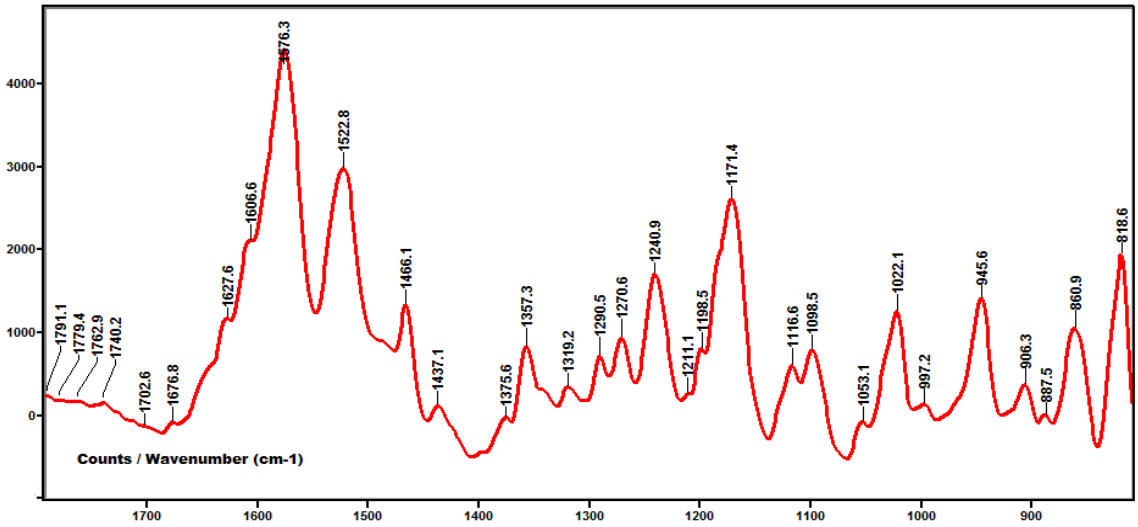

Figure 4. Raman spectrum of sample S3-B.

Table 4 shows the tentative assignments of some bands of the Raman spectrum of sample S3-B.

Table 4. Tentative assignments of some bands of the Raman spectrum of sample S3-B.

Band (cm^{-1})	Chemical(s)		Band (cm^{-1})	Chemical(s)
818.6	Gelatin (?)		1319.2	Cellulose
860.9	Gelatin (?)		1357.3	Cellulose
887.5	MC cellulose (?)		1375.6	Cellulose, resin (?)
906.3	Cellulose (?)		1437.1	Cellulose (?)
945.6	Cellulose (?)		1466.1	Cellulose, rosin (?)
997.2	Cellulose		1522.8	--
1022.1	Gelatin (?)		1576.3	--
1053.1	Cellulose, rosin (?)		1606.6	--
1098.5	Cellulose		1627.6	Rosin

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1116.6	Cellulose (?)		1676.8	H_2O
1171.4	Cellulose		1702.6	--
1198.5	Rosin		1740.2	--
1211.1	--		1762.9	--
1240.9	Gelatin (?)		1779.4	--
1270.6	Gelatin (?)		1791.1	--
1290.5	Cellulose			

We can notice that the Raman spectrum of this sample is different than sample S3-A spectrum. Here we observe cellulose and gelatin but also rosin that seems to be absent in sample S3-A. Note that we were not able to ascribe the several bands existing in the 1522 – 1791 cm^{-1}.

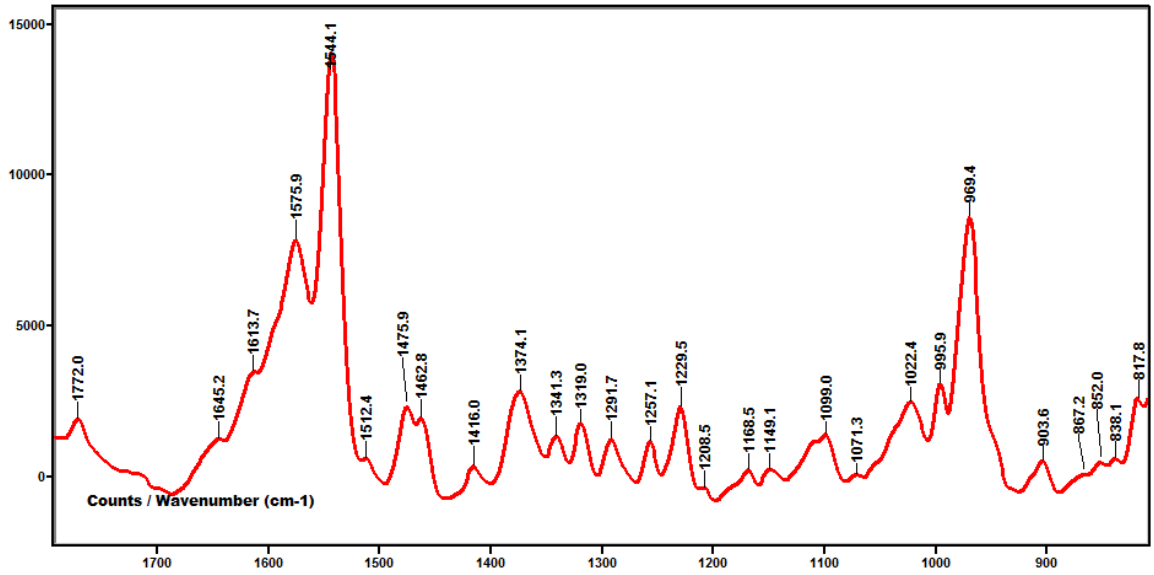

Figure 5. Raman spectrum of sample S3-C.

Table 5 shows the tentative assignments of some bands of the Raman spectrum of sample S3-C.

Table 5. Tentative assignments of some bands of the Raman spectrum of sample S3-C.

Band (cm^{-1})	Chemical(s)		Band (cm^{-1})	Chemical(s)
817.8	Gelatin		1257.1	Cellulose (?), gelatin
838.1	--		1291.7	Cellulose
852.0	Gelatin		1319.0	Cellulose (?), gelatin
867.2	--		1341.3	Cellulose, HC (?), gelatin
903.6	Cellulose (?)		1374.1	Cellulose, HC (?), gelatin
969.4	Cellulose, HC (?), rosin (?)		1416.0	Cellulose, gelatin
995.9	Cellulose, gelatin		1462.8	Cellulose
1022.4	--		1475.9	Cellulose (?)
1071.3	Cellulose, gelatin		1512.4	--
1099.0	Cellulose, gelatin		1544.1	--
1149.1	Cellulose		1575.9	--
1168.5	Gelatin (?)		1613.7	Arom. (C=C), rosin (?)
1208.5	Gelatin (?)		1645.2	(C=C), rosin (?)
1229.5	Cellulose (?)		1772.0	--

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Sample S3-C contains cellulose and gelatin (like sample S3-A) and also rosin (like sample S3-B). If the band assignments are correct, then we may suggest that the paper was not homogeneous regarding the distribution of the chemicals added to cellulose. In any case, we have still some samples and we intend to carry out other studies to clarify this point.

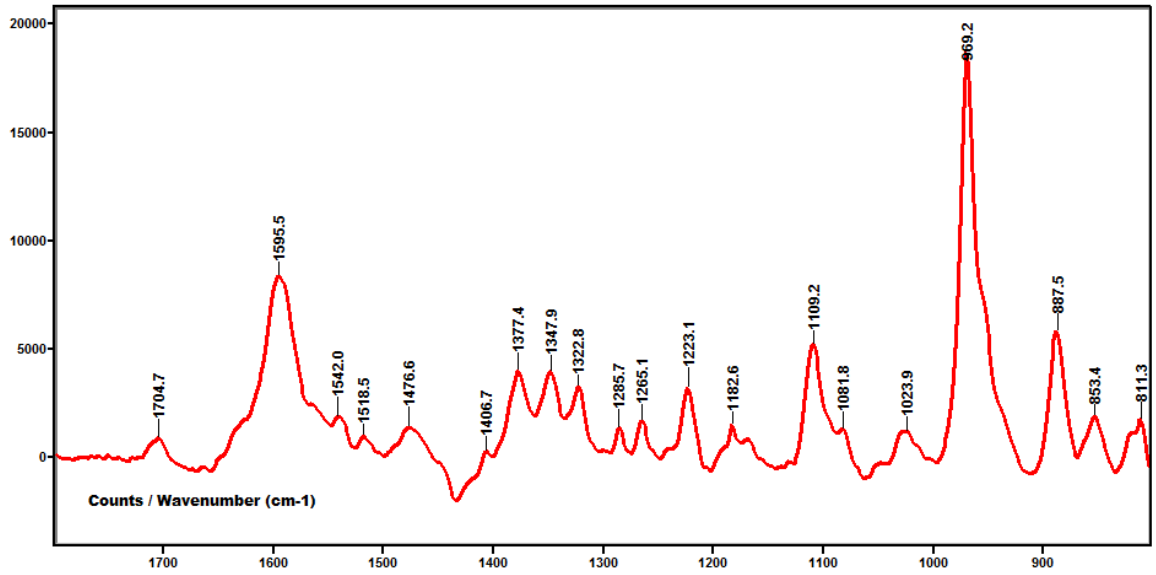

Figure 6. Raman spectrum of sample S4 (A. Vázquez. Tratado Elemental de Química Orgánica etc. Segunda edición. Tomo II. Librería de Servat. Santiago de Chile, 1877).

Table 6 shows the tentative assignments of some bands of the Raman spectrum of sample S4.

Table 6. Tentative assignments of some bands of the Raman spectrum of sample S4.

Band (cm^{-1})	Chemical(s)		Band (cm^{-1})	Chemical(s)
811.3	--		1285.7	--
853.4	Gelatin		1322.8	Cellulose (?)
887.5	MC cellulose		1347.9	--
969.2	Cellulose		1377.4	Cellulose
1023.9	--		1406.7	Cellulose
1081.8	Cellulose		1476.6	Cellulose
1109.2	Cellulose (?)		1518.5	--
1182.6	v(CC) ring breathing (?)		1542.0	--
1223.1	Cellulose		1595.5	--
1265.1	Cellulose		1704.7	--

Sample S4 seems to contain cellulose and perhaps gelatin. No lignin bands are present. This book was printed in 1877 in the city of Santiago de Chile but we have not information about the geographical origin of this paper.

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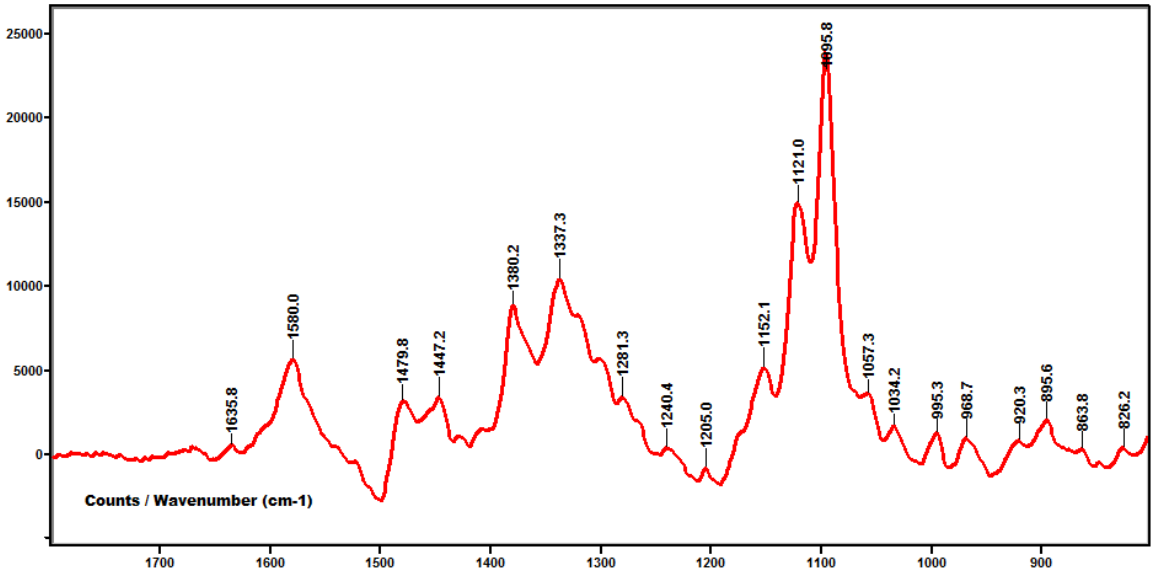

Figure 7. Raman spectrum of sample S5 (B. Bails. Principios de matemática de la Real Academia de San Fernando. Tomo III. Tercera Edición. Imprenta de la viua de D. Joaquin Ibarra. Madrid, 1799).

Table 7 shows the tentative assignments of the Raman spectrum of Fig. 7.

Table 7. Tentative assignments of some bands of the Raman spectrum of sample S5.

Band (cm^{-1})	Chemical(s)		Band (cm^{-1})	Chemical(s)
863.8	Gelatin		1121.0	Cellulose, gelatin
895.6	Cellulose		1152.1	Cellulose
920.3	Gelatin (?)		1240.4	Cellulose, gelatin (?)
968.7	Gelatin		1337.3	Cellulose, gelatin
995.3	Cellulose		1380.2	Cellulose
1034.2	Cellulose		1479.8	Cellulose
1057.3	Cellulose		1580.0	Cellulose
1095.8	Cellulose		1635.8	Gelatin

Sample S4 is from a book printed in 1799 in Madrid. Its spectrum is simple, like the one of the S4 sample: only cellulose and gelatin, as expected from a book of this year and place.

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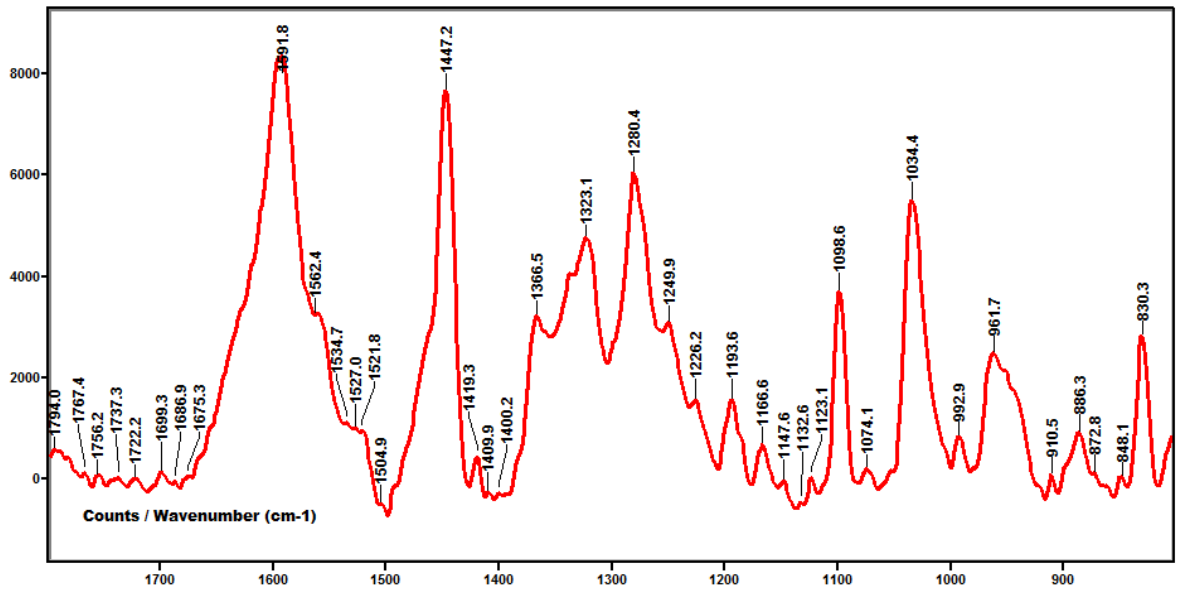

Figure 8. Raman spectrum of sample S6-A (E.G. Fischer. Physique mécanique. Chez Bernard. Paris, 1806).

Table 8 shows the tentative assignments of the Raman spectrum of Fig. 8.

Table 8. Tentative assignments of some bands of the Raman spectrum of sample S6-A.

Band (cm^{-1})	Chemical(s)		Band (cm^{-1})	Chemical(s)
830.3	Cellulose (?)		1366.5	Rosin
848.1	--		1400.2	--
872.8	--		1409.9	Cellulose
886.3	MC cellulose		1419.3	Cellulose (?)
910.5	Cellulose		1447.2	Cellulose, CO_3
961.7	--		1504.9	--
992.9	Cellulose (?)		1521.8	--
1034.4	Cellulose		1527.0	--
1074.1	Cellulose, rosin		1534.7	--
1098.6	Cellulose, CO_3		1562.4	Rosin
1123.1	Cellulose		1591.8	--
1132.6	SO_4 (?)		1675.3	H_2O (?)
1147.6	Cellulose		1686.9	--
1166.6	--		1699.3	--
1193.6	--		1722.2	--
1226.2	Rosin		1737.3	--
1249.9	Cellulose		1756.2	--
1280.4	Cellulose (?)		1767.4	CO_3 (?)
1323.1	--		1794.0	

Sample S6-A seems to contain cellulose, rosin and perhaps an inorganic carbonate and/or sulfate. The case of rosin is interesting because it could be the oldest cases of its use.

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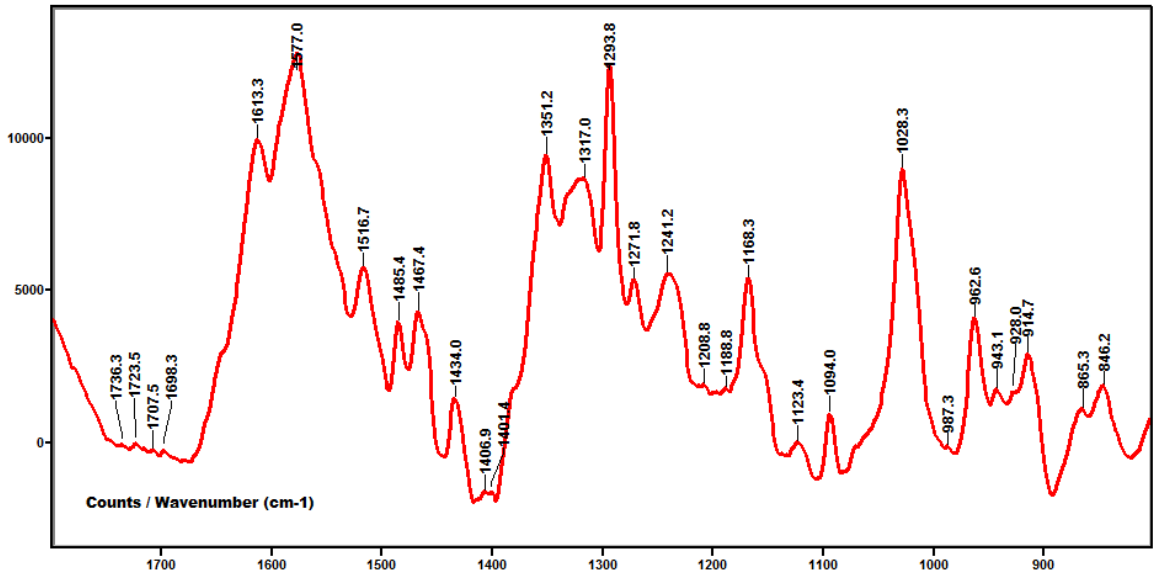

Figure 9. Raman spectrum of sample S6-B.

Table 9 shows the tentative assignments of the Raman spectrum of Fig. 9.

Table 9. Tentative assignments of some bands of the Raman spectrum of sample S6-B.

Band (cm^{-1})	Chemical(s)		Band (cm^{-1})	Chemical(s)
846.2	--		1293.8	Cellulose
865.3	--		1317.0	Cellulose
914.7	Cellulose		1351.2	Cellulose
928.0	--		1401.4	Cellulose (?)
943.1	Cellulose		1406.9	Cellulose
962.6	--		1434.0	Cellulose
987.3	--		1467.4	Cellulose
1028.3	--		1485.4	--
1094.0	Cellulose		1516.7	--
1123.4	Cellulose		1577.0	Cellulose (?)
1168.3	--		1613.3	Arom. ν(C=C) (?)
1188.8	--		1698.3	--
1208.8	Cellulose (?)		1707.5	ν(C=O) (?)
1241.2	--		1723.5	--
1271.8	Cellulose (?)		1736.3	--

We can see that this sample contains cellulose as expected but also several bands that could not ascribe such as in the case of sample S6-A. Interestingly, rosin does not appear here. As we have still samples we shall carry out new analysis (see below for a general comment).

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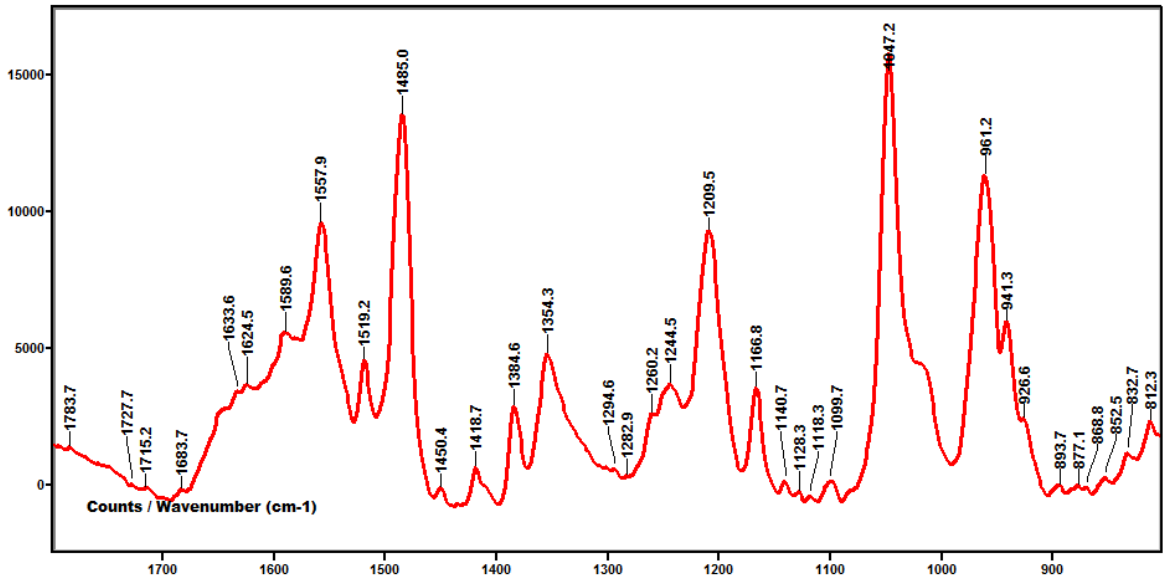

Figure 10. Raman spectrum of sample 7 (C. Darwin, J.J. Moulinié (Ed.). L'origine des espèces au moyen de la sélection naturelle, ou La lutte pour l'existence dans la nature. C. Reinwald. Paris, 1873).

Table 10 shows the tentative assignments of the Raman spectrum of Fig. 10.

Table 10. Tentative assignments of some bands of the Raman spectrum of sample S7.

Band (cm^{-1})	Chemical(s)		Band (cm^{-1})	Chemical(s)
812.3	--		1260.2	Cellulose
832.7	--		1282.9	Cellulose (?)
852.5	--		1294.6	Cellulose
868.8	--		1354.3	Cellulose
877.1	Crystalline cellulose		1384.6	Cellulose
893.7	Cellulose		1418.7	Cellulose (?)
926.6	Lignin (?)		1450.4	Cellulose
941.3	Cellulose		1485.0	--
961.2	--		1519.2	--
1047.2	Cellulose		1557.9	--
1099.7	Cellulose		1589.6	--
1118.3	Cellulose (?)		1624.5	Lignin (?)
1128.3	Cellulose		1633.6	--
1140.7	Lignin (?)		1683.7	--
1166.8	--		1715.2	v(C=O) (?)
1209.5	--		1727.7	--
1244.5	Cellulose		1783.7	--

Sample S7 contains cellulose and lignin. There are several bands that we could not ascribe. Table 11 shows the main results besides cellulose.

Table 11. Summary of the main results, excluding cellulose.

Sample	Year	Chemicals
S1	1879	Lignin, carbonate and sulfate
S2	1827	Gelatin
S3-A	1823	Gelatin
S3-B	1823	Gelatin, rosin
S3-C	1823	Gelatin, rosin
S4	1877	?
S5	1799	Gelatin
S6-A	1806	Rosin, inorganic carbonate
S6-B	1806	?
S7	1873	Lignin

The oldest book analyzed here was printed in 1799 (sample S5). The paper contains cellulose and gelatin, a normal mixture for this epoch. Sample S2 (book printed in 1827) also has only gelatin, suggesting that some mills still used the same recipe for papermaking. We can see that lignin appears in books printed in years 1879 (sample S1) and 1873 (sample S7). This indicates that almost all the paper was manufactured from wood cellulose (at least in Europe). The carbonate is probably from $CaCO_3$. It is not clear for the moment what the origin of the sulfate dianion is. In the case of the book printed in1877 (sample S4) gelatin presence must be confirmed because we ascribed only one band to it. The question of the difference between samples S6-A and S6-B is difficult to answer. It would be easy to suggest that the paper was not homogeneous but another possibility is that sample S6-B was simply a contaminant. A third possibility is that the laser pointed to areas with different constitution. Samples S3-A, S3-B and S3-C have gelatin but only two of them have rosin. At the light of this and other analysis we made, the following procedure is suggested for paper analysis. One or more microphotographs of the sample (possibly 100x or more) should be taken to get a good idea of the fiber distribution and orientation and the presence or not of microparticles of chemicals (for example micro particles of Prussian blue) on the fibers. The sample must be ground and homogenized dry. We think that the homogenization is fundamental here. A quantity may be used for the KBr pellet and another can be flattened and used in the Raman study. In this way IR and Raman spectra can be compared. Spectra of the original samples should be taken for comparison.

REFERENCES

[1] Barrow, W. Physical and Chemical Properties of Book Papers, 1507-1949. Permanence/Durability of the Book, VII. In WJ Barrow Research Laboratory, Inc.: Richmond, VA, 1974.

[2] Gómez-Jeria, J. S.; Gutierrez, S.; Surco-Luque, J. C.; Olivos-Núñez, G. Raman characterization of the paper of a 1588 Spanish book. *Chemistry Research Journal* 2018, In press.

[3] Rosenband, L. N. *Papermaking in Eighteenth-Century France: Management, Labor, and Revolution at the Montgolfier Mill, 1761-1805*. The Johns Hopkins University Press: London, 2000.

[4] Clapperton, R. H. *The Paper-making Machine: Its Invention, Evolution, and Development*. Pergamon Press: Oxford, 1967.

[5] Gómez-Jeria, J. S.; Clavijo, E.; Gutiérrez, S.; Machuca-Otarola, J. C. A preliminary infrared, SEM and XRF analysis of the paper of seven books of the 18th and 19th centuries. *Research Journal of Pharmaceutical, Biological and Chemical Sciences* 2018, 9, 700-719.

[6] Imperio, E.; Giancane, G.; Valli, L. Spectral characterization of postage stamp printing inks by means of Raman spectroscopy. *Analyst* 2015, 140, 1702-1710.

[7] Librando, V.; Minniti, Z.; Lorusso, S. Ancient and modern paper characterization by FTIR and Micro-Raman spectroscopy. *Conservation science in cultural heritage* 2011, 11, 249-268.

[8] Kavkler, K.; Demšar, A. Examination of cellulose textile fibres in historical objects by micro-Raman spectroscopy. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 2011, 78, 740-746.

[9] Garcia Moreno, R.; Strivay, D.; Gilbert, B. Maya blue–green pigments found in Calakmul, Mexico: a study by Raman and UV-visible spectroscopy. *Journal of Raman Spectroscopy* 2008, 39, 1050-1056.

[10] Legodi, M. A.; de Waal, D. Raman spectroscopic study of ancient South African domestic clay pottery. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 2007, 66, 135-142.
[11] Clark, R. J. H. Raman microscopy as a structural and analytical tool in the fields of art and archaeology. *Journal of Molecular Structure* 2007, 834, 74-80.
[12] Rosi, F.; Miliani, C.; Borgia, I.; Brunetti, B.; Sgamellotti, A. Identification of nineteenth century blue and green pigments by in situ x-ray fluorescence and micro-Raman spectroscopy. *Journal of Raman Spectroscopy* 2004, 35, 610-615.
[13] Hayez, V.; Denoël, S.; Genadry, Z.; Gilbert, B. Identification of pigments on a 16th century Persian manuscript by micro-Raman spectroscopy. *Journal of Raman Spectroscopy* 2004, 35, 781-785.
[14] Ambers, J. Raman analysis of pigments from the Egyptian Old Kingdom. *Journal of Raman Spectroscopy* 2004, 35, 768-773.
[15] Chaplin, T. D.; Clark, R. J. H.; Beech, D. R. Comparison of genuine (1851–1852 AD) and forged or reproduction Hawaiian Missionary stamps using Raman microscopy. *Journal of Raman Spectroscopy* 2002, 33, 424-428.
[16] Pagès-Camagna, S.; Colinart, S.; Coupry, C. Fabrication processes of archaeological Egyptian blue and green pigments enlightened by Raman microscopy and scanning electron microscopy. *Journal of Raman Spectroscopy* 1999, 30, 313-317.
[17] Best, S. P.; Robin, J. H. C.; Marcus, A. M. D.; Porter, C. A.; Withnall, R. Identification by Raman Microscopy and Visible Reflectance Spectroscopy of Pigments on an Icelandic Manuscript. *Studies in Conservation* 1995, 40, 31-40.
[18] Gómez-Jeria, J. S.; Clavijo, E.; Gutiérrez, S. A qualitative Infrared and Scanning Electron Microscopy study of the margins of fourteen world postage stamps. *Research Journal of Pharmaceutical, Biological and Chemical Sciences* 2018, 9, 1719-1733.
[19] 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.
[20] 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.
[21] 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.
[22] Gómez-Jeria, J. S.; Clavijo, E. A preliminary infrared study of the cellulose of some world stamps. *Chemistry Research Journal* 2017, 2, 191-197.
[23] Frost, R. L. Fourier transform Raman spectroscopy of kaolinite, dickite and halloysite. *Clays and Clay Minerals* 1995, 43, 191-195.
[24] Clifford, T. Raman spectroscopic study of kaolinite in aqueous suspension. *Clays Clay Miner* 1985, 33, 483-489.
[25] Barashkov, M.; Komyak, A.; Shashkov, S. Vibrational spectra and structure of potassium alum $KAl(SO_4)_2 \cdot 12[(H_2O)_x(D_2O)_{1-x}$. *Journal of Applied Spectroscopy* 2004, 71, 328-333.
[26] Gess, J. The sizing of paper with rosin and alum at acid pHs. In *Paper Chemistry*, Springer: 1996; pp 120-139.
[27] Brückle, I. The role of alum in historical papermaking. *Abbey Newsletter* 1993, 17, 1-13.
[28] Wang, D.; Hamm, L. M.; Bodnar, R. J.; Dove, P. M. Raman spectroscopic characterization of the magnesium content in amorphous calcium carbonates. *Journal of Raman Spectroscopy* 2012, 43, 543-548.
[29] Gunasekaran, S.; Anbalagan, G.; Pandi, S. Raman and infrared spectra of carbonates of calcite structure. *Journal of Raman Spectroscopy* 2006, 37, 892-899.
[30] Edwards, H. G.; Villar, S. E. J.; Jehlicka, J.; Munshi, T. FT–Raman spectroscopic study of calcium-rich and magnesium-rich carbonate minerals. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 2005, 61, 2273-2280.
[31] Behrens, G.; Kuhn, L. T.; Ubic, R.; Heuer, A. H. Raman spectra of vateritic calcium carbonate. *Spectroscopy letters* 1995, 28, 983-995.
[32] Tlili, M.; Amor, M. B.; Gabrielli, C.; Joiret, S.; Maurin, G.; Rousseau, P. Characterization of CaCO3 hydrates by micro-Raman spectroscopy. *Journal of Raman Spectroscopy* 2002, 33, 10-16.

[33] Vandenabeele, P.; Wehling, B.; Moens, L.; Edwards, H.; De Reu, M.; Van Hooydonk, G. Analysis with micro-Raman spectroscopy of natural organic binding media and varnishes used in art. *Analytica Chimica Acta* 2000, 407, 261-274.

[34] Larsen, K. L.; Barsberg, S. Theoretical and Raman Spectroscopic Studies of Phenolic Lignin Model Monomers. *The Journal of Physical Chemistry B* 2010, 114, 8009-8021.

[35] Agarwal, U. P.; Reiner, R. S.; Pandey, A. K.; Ralph, S. A.; Hirth, K. C.; Atalla, R. H. In *Raman spectra of lignin model compounds*, 59th Appita Annual Conference and Exhibition: Incorporating the 13th ISWFPC (International Symposium on Wood, Fibre and Pulping Chemistry), Auckland, New Zealand, 2005; Auckland, New Zealand, 2005; pp 1-8.

[36] Agarwal, U. P.; Ralph, S. A. FT-Raman Spectroscopy of Wood: Identifying Contributions of Lignin and Carbohydrate Polymers in the Spectrum of Black Spruce (Picea Mariana). *Applied Spectroscopy* 1997, 51, 1648-1655.

[37] Brody, R. H.; Edwards, H. G.; Pollard, A. M. Fourier transform-Raman spectroscopic study of natural resins of archaeological interest. *Biopolymers: Original Research on Biomolecules* 2002, 67, 129-141.

[38] Cael, J. J.; Gardner, K. H.; Koenig, J. L.; Blackwell, J. Infrared and Raman spectroscopy of carbohydrates. Paper V. Normal coordinate analysis of cellulose I. *The Journal of Chemical Physics* 1975, 62, 1145-1153.

[39] Wiley, J. H.; Atalla, R. H. Band assignments in the Raman spectra of celluloses. *Carbohydrate Research* 1987, 160, 113-129.

[40] Schulz, H.; Baranska, M. Identification and quantification of valuable plant substances by IR and Raman spectroscopy. *Vibrational Spectroscopy* 2007, 43, 13-25.

[41] Scheller, H. V.; Ulvskov, P. Hemicelluloses. *Annual Review of Plant Biology* 2010, 61, 263-289.

[42] 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.

[43] Liu, Y.; Wang, A.; Freemen, J. In *Raman, MIR, and NIR spectroscopic study of calcium sulfates: gypsum, bassanite, and anhydrite*, Lunar and Planetary Science Conference, Washington University, 2009; Washington University, 2009.

[44] Berger, J. Infrared and Raman spectra of $CuSO_4 \bullet 5H_2O$; $CuSO_4 \bullet 5D_2O$ and $CuSeO_4 \bullet 5H2O$. *Journal of Raman Spectroscopy* 1976, 5, 103-114.

[45] Jehlička, J.; Edwards, H. G. M.; Vítek, P. Assessment of Raman spectroscopy as a tool for the non-destructive identification of organic minerals and biomolecules for Mars studies. *Planetary and Space Science* 2009, 57, 606-613.

[46] De Veij, M.; Vandenabeele, P.; De Beer, T.; Remon, J. P.; Moens, L. Reference database of Raman spectra of pharmaceutical excipients. *Journal of Raman Spectroscopy* 2009, 40, 297-307.

[47] De Gelder, J.; De Gussem, K.; Vandenabeele, P.; Moens, L. Reference database of Raman spectra of biological molecules. *Journal of Raman Spectroscopy* 2007, 38, 1133-1147.