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Raman characterization of the paper of a 1588 Spanish book

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Abstract We employed Raman spectroscopy for the analysis of three samples of paper from the book entitled *Treated of the True and False Prophecy* printed in Segovia, Spain, during 1588. Fluorescence allowed studying only the 400-1600 cm^{-1} region for the moment. We were able to confirm the presence of gelatin and proline. Sulfate ion seems to be also present. The most important finding is a sharp band at about 735-736 cm^{-1} that is tentatively ascribed to the presence of adenine, perhaps from denaturalized DNA.

Keywords Raman spectroscopy, cellulose, paper analysis, gelatin, collagen, proline, adenine

Introduction

Recently, we have focused our interest in the analysis of the composition of postage stamps papers [1-4]. The interesting results obtained prompted us to analyze the components of papers from books printed in 1588 and during 17^{th} and 18^{th} centuries [5, 6]. The experimental tools used were infrared spectroscopy (IR), scanning electron microscopy and X-ray fluorescence. On the other hand, Raman spectroscopy is a useful tool for the study of papers, inks, fillers, pigments, etc [7-22]. Molecules that cannot be detected with IR can be easily detected with Raman spectroscopy. Only recently we have gained access to the Raman technique. Here, we present the first results of the application of this technique to the analysis of three samples of paper from the book entitled *Treated of the True and False Prophecy* printed in Segovia, Spain, during 1588 [6, 23].

Experimental

We employed three samples (named S1, S2 and S2) extracted from the same pages used our previous study. Raman spectra were recorded on a Raman Renishaw In Via Reflex apparatus, equipped with 532, 633, and 785 nm laser lines for 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 10-50s each were averaged. Spectra were recorded in the 400-4000 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 program WIRE 3.4, GRAMS 9.0 and Origin. The 785 nm laser line was employed for obtaining the spectra.

Results

Figures 1-3 show, respectively, the original Raman spectra of S1-S3. They were not employed for the analysis and are presented to show the extent of the effect of fluorescence [24].

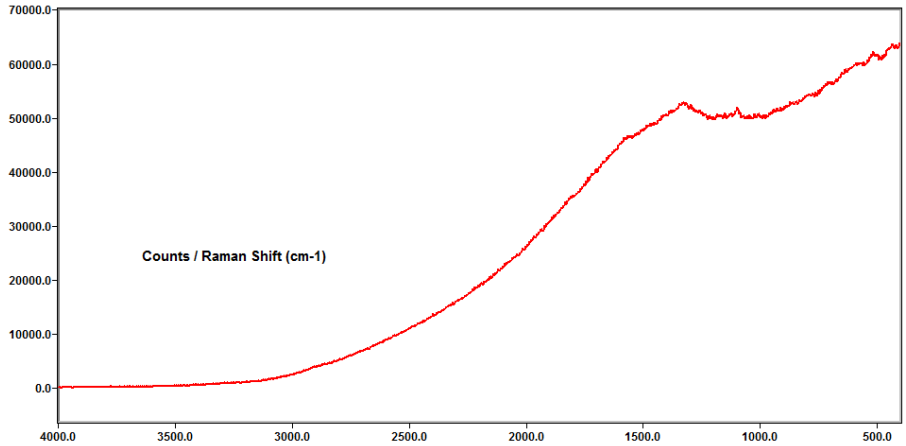

Figure 1: Raman spectrum of sample 1 (S1)

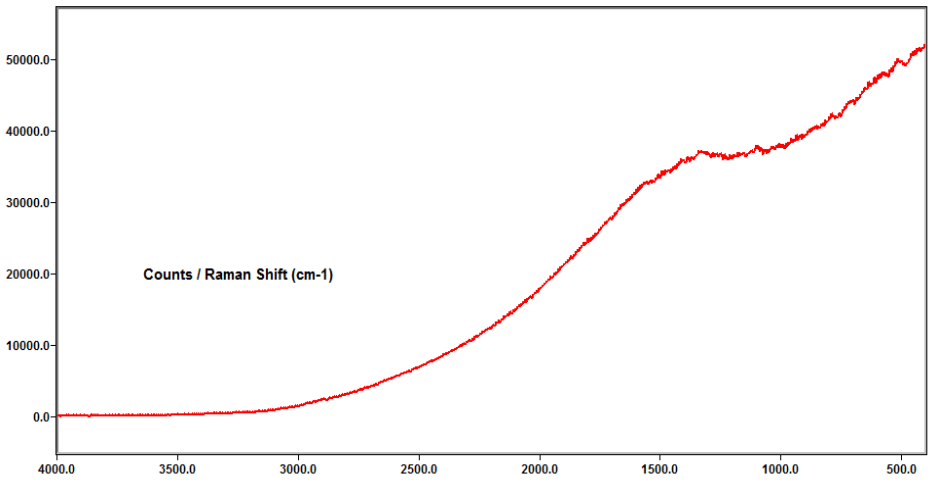

Figure 2: Raman spectrum of sample 1 (S2)

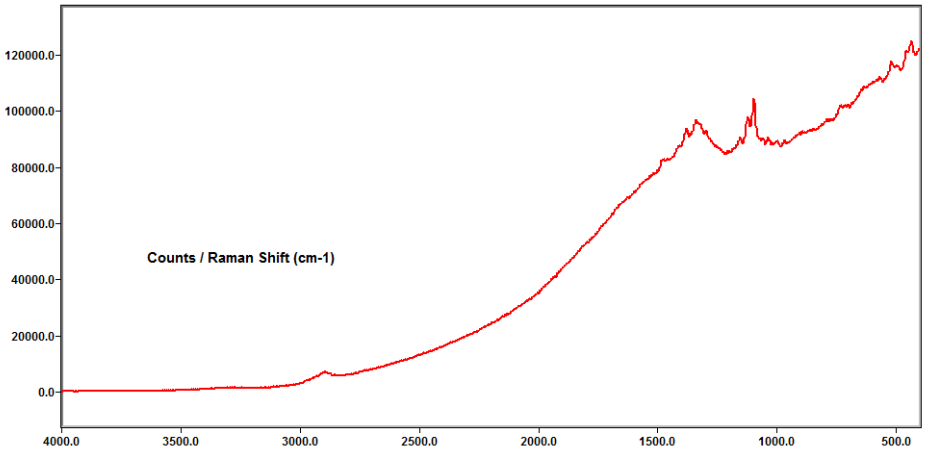

Figure 3: Raman spectrum of sample 1 (S3)

To carry out the analysis we have selected the 400-1600 cm^{-1} region. Figures 4 to 6 show the corresponding Raman spectra of the three samples.

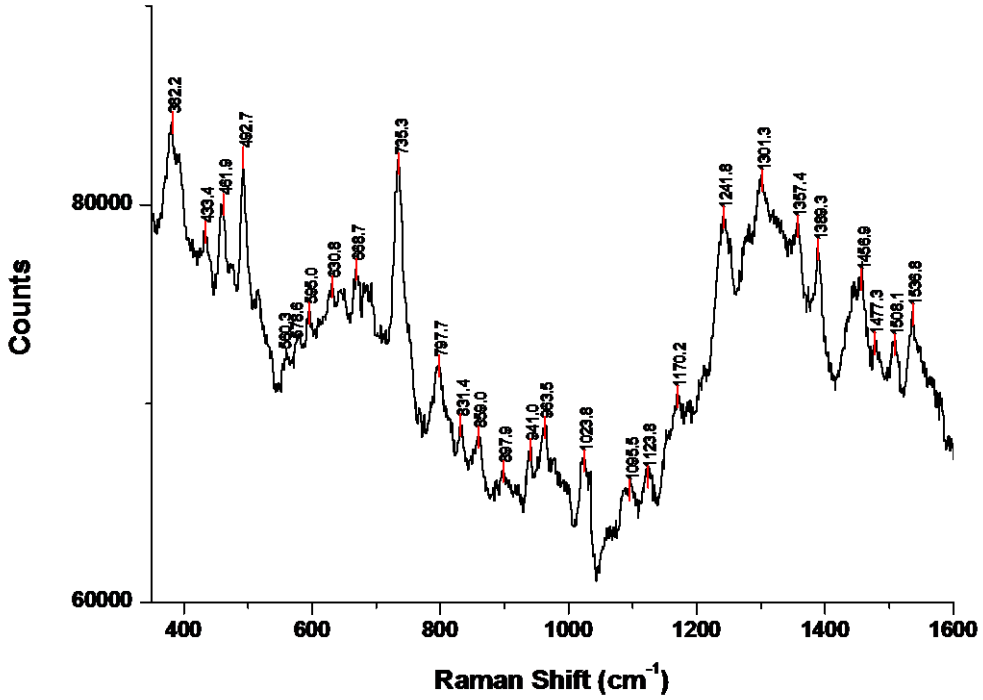

Figure 4: Raman spectrum of sample S1 in the 400-1600 cm^{-1} region

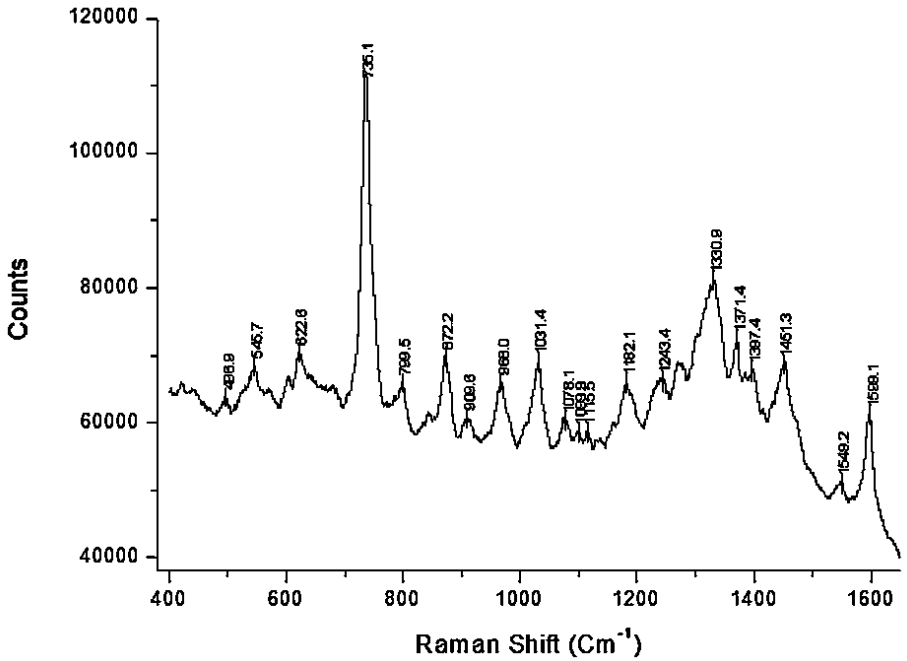

Figure 5: Raman spectrum of sample S2 in the 400-1600 cm^{-1} region

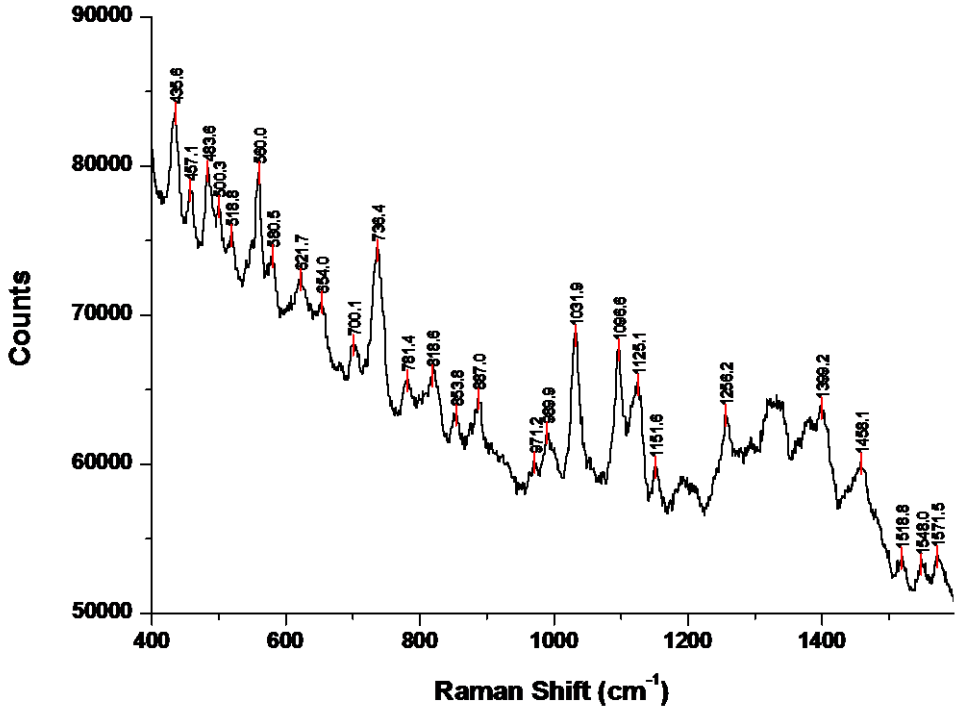

Figure 6: Raman spectrum of sample S3 in the 400-1600 cm^{-1} region

Figures 7 to 9 show a comparison of each couple of spectra.

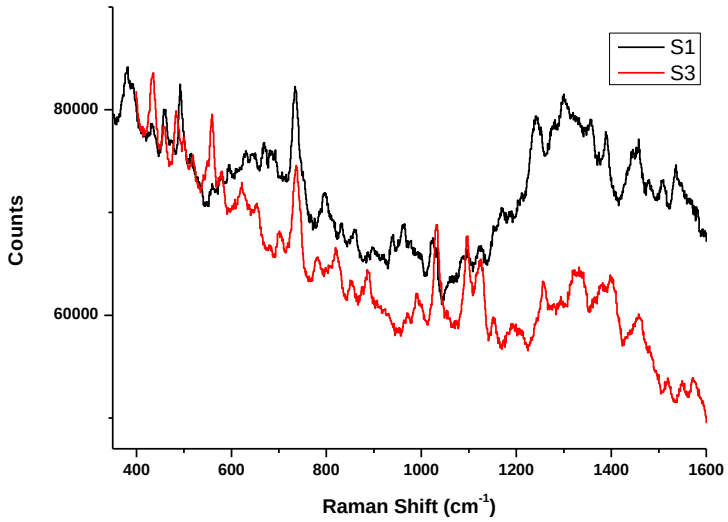

Figure 7: Raman spectra of samples S1 and S3 in the 400-1600 cm^{-1} region

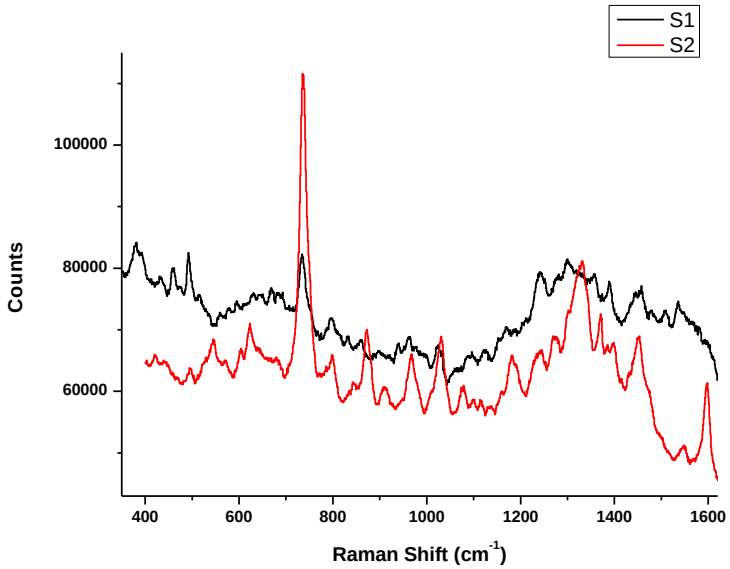

Figure 8: Raman spectra of samples S1 and S2 in the 400-1600 cm^{-1} region

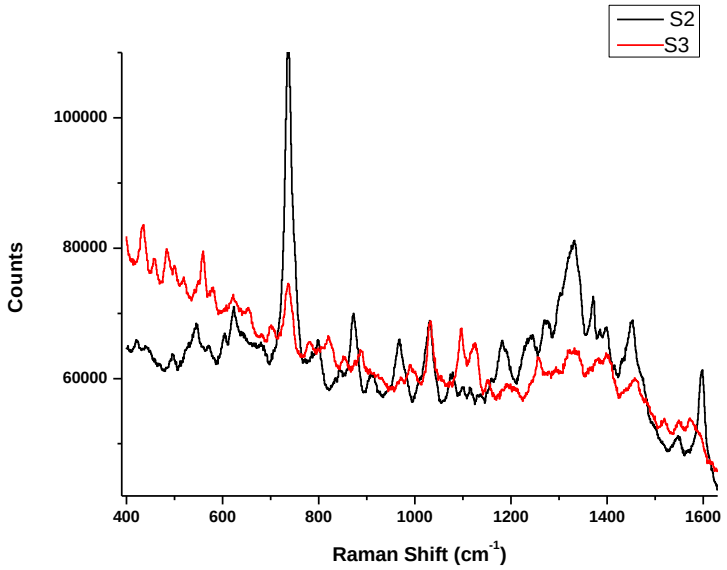

Figure 9: Raman spectra of samples S2 and S3 in the 400-1600 cm^{-1} region

Discussion

The analysis of Figs. 7-9 shows some differences in the spectra of the samples. This is due to the fact that the paper used for printing was not homogeneous [25-27]. The main purpose of this work is the characterization of cellulose and other possible components of the paper. We avoided commenting on the microscopic origin of the many bands because we are working on quantum chemical analyses of some cellulose models to get a better insight. We present in Tables 1 to 3 the Raman bands assigned to cellulose in the three samples [28-31].

Table 1: Proposed Raman bands for cellulose in S1

Sample S1		Literature	
Band (cm^{-1})	**Intensity**	**Band (cm^{-1})**	**Reference(s)**
382.2	s	380, 381	[29, 31]
433.4	w	436, 437	[29-31]
461.1	m	458, 459, 460, 462	[28, 29, 31]
492.7	s	493, 496	[29, 30]
578.6	w	577	[29]
897.9	w	896	[29]
1097.5	w	1096, 1097	[29-31]
1123.8	w	1117, 1118, 1120, 1122	[28-31]
1456.9	m	1454, 1455, 1456	[28, 31]
1477.3	w	1475, 1477,1478, 1479	[30, 31]

Table 2: Proposed Raman bands for cellulose in S2

Sample S2		Literature	
Band (cm^{-1})	**Intensity**	**Band (cm^{-1})**	**References**
496.9	w	493, 496	[29, 30]
545.7	w	542	[30]
909.6	w	910, 913	[28, 31]
969	m	968, 969, 971, 972	[28-31]
1031.4	m	1034, 1035	[28, 31]
1099	w	1095, 1096, 1097	[29-31]
1115.5	w	1117, 1118	[31]
1330.9	s	1335, 1337, 1338	[28-30]
1371.4	m	1377, 1378, 1379	[28, 29, 31]
1451.3	m	1454, 1455, 1456, 1459	[28, 29, 31]

Table 3: Proposed Raman bands for cellulose in S3

Sample S3		Literature	
Band (cm^{-1})	**Intensity**	**Band (cm^{-1})**	**References**
435.1	s	436, 437, 438	[28, 29, 31]
457.1	m	458, 459, 460	[29-31]
518.5	w	519, 520	[29-31]
580.5	w	577	[29]
971.2	w	968, 969	[29, 31]
1031.9	vs	1034, 1035, 1037, 1038	[28, 30, 31]
1096.6	s	1095, 1096, 1097	[29-31]
1125.1	s	1120, 1122	[29]
1151.6	w	1151, 1153	[30, 31]
1458.1	m	1455, 1456	[28, 31]

The use of gelatin in the manufacture of paper was important, since it gives rigidity and consolidation to paper[32]. Gelatin is a substance that is obtained when the collagen present in cartilage, bones and connective tissue is dissolved in water and subjected to a cooking process (i.e., gelatin is the thermal denaturation product of collagen). At the end of the process, a gel is produced which, in its pure state, is insipid, odorless and colorless. Glycine is found at almost every third residue and proline constitutes about 17% of collagen. Based on bibliography, we show in Table 4 the proposed Raman bands assigned to gelatin and collagen in the three samples[33, 34].

Table 4: Proposed Raman bands assigned to gelatin and collagen.

Raman band (cm^{-1})			**Raman Literature**	
S1	**S2**	**S3**		
-----	**622.6**	**621.7**	622	Collagen
		818.6	818-821	Collagen and gelatin
859			856	Collagen
		887	890	Collagen and gelatin
941			942	Gelatin
963.5			966	Collagen
	969	971.2	969	Gelatin
	1031.4	1031.9	1037	Collagen and gelatin
1123.8		1125.1	1128	collagen and gelatin
	1182.1		1182	gelatin
1241.8	1243.4		1248	collagen and gelatin
1389.3			1389	gelatin
	1397.4	1399.2	1399	gelatin
	1451.3		1451	collagen and gelatin

Also, when comparing our results with the proline bands reported by Zhu et al. we can identify the following bands: 560.3, 1097.5, 1171.2 and 1241.8 cm^{-1} for S1; 909.6, 1031.4, 1243.4 cm^{-1} for S2 and 781.5, 818.6 and 989.9 cm^{-1} for S3.

The three samples show a strong sharp band around 735-736 cm^{-1} (see Figs. 4-6). Several assignments of this band have been proposed for the 730 cm^{-1} line the in SERS spectra of bacteria [35]. In this case, Ivleva et al. assign this band to adenine-related compounds. In our case the presence of this adenine band and the absence of bands of other nucleobases suggest that we are in presence of denaturized DNA coming from gelatin, but more analysis of the data and more experimental results on other paper samples of the same book seems to be needed for the sake of clarity. A new analysis of the data using software to deal with fluorescence is underway. Finally the sulfate ion seems to be present as shown in Table 5.

Table 5: Raman bands that could correspond to sulfate ion

Sample	Raman band (cm^{-1})	
S1	941	
	963.5	sulfate
	1023.8	
	1097.5	cellulose
S2	969	
	1031.4	cellulose
	1078.1	sulfate
S3	1099	cellulose
	971.2	cellulose
	989.9	sulfate
	1031.9	cellulose
	1096.6	

We can see in the Table that because of the complex constitution of the samples some sulfate bands can overlap with cellulose ones: this could be the case of bands at 969-971, 1031 and 1097-99 cm^{-1}.

In summary, using Raman spectroscopy and analyzing the 400-1600 cm^{-1} region we were able to obtain new information about the components of paper samples of a Spanish book printed in 1588. The presence of gelatin and proline is confirmed. The sulfate ion seems to be present also. The most important finding is a sharp band at about 735-736 cm^{-1} that is tentatively ascribed to the presence of adenine, perhaps from denaturalized DNA.

References

1. J. S. Gómez-Jeria, E. Clavijo, and S. Gutiérrez, "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 *vol. In press*.
2. J. S. Gómez-Jeria, E. Clavijo, and S. Gutiérrez, "An Infrared and SEM study of the Margins Of Some Estonian Postage Stamps", *Research Journal of Pharmaceutical, Biological and Chemical Sciences*, 2018 *vol. 9*, no. 3, pp. 1258-1279.
3. J. S. Gómez-Jeria, E. Clavijo, J. J. Cárcamo-Vega, and S. Guitérrez, "An infrared and SEM study of the margins of some German hyperinflation postage stamps", *Research Journal of Pharmaceutical, Biological and Chemical Sciences*, 2018 *vol. 9*, no. 2, pp. 870-892.
4. J. S. Gómez-Jeria, and E. Clavijo, "A preliminary infrared study of the cellulose of some world stamps", *Chemistry Research Journal*, 2017 *vol. 2*, no. 4, pp. 191-197.
5. J. S. Gómez-Jeria, E. Clavijo, S. Gutiérrez, and J. C. Machuca-Otarola, "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 *vol. 9*, no. 5, pp. 700-719.
6. J. S. Gómez-Jeria, E. Clavijo, and S. Gutiérrez, "An infrared, SEM and XRF study of the paper of a 1588 Spanish book.", *Research Journal of Pharmaceutical, Biological and Chemical Sciences*, 2018 *vol. 9*, no. 4, pp. 1581-1590.
7. R. Simonetti, P. Oliveri, A. Henry, L. Duponchel, and S. Lanteri, "Has your ancient stamp been regummed with synthetic glue? A FT-NIR and FT-Raman study", *Talanta*, 2016 *vol. 149*, no. Supplement C, pp. 250-256.
8. E. Imperio, G. Giancane, and L. Valli, "Spectral characterization of postage stamp printing inks by means of Raman spectroscopy", *Analyst*, 2015 *vol. 140*, no. 5, pp. 1702-1710.
9. V. Librando, Z. Minniti, and S. Lorusso, "Ancient and modern paper characterization by FTIR and Micro-Raman spectroscopy", *Conservation science in cultural heritage*, 2011 *vol. 11*, no. 1, pp. 249-268.

10. C. Daher, C. Paris, A.-S. Le Hô, L. Bellot-Gurlet, and J.-P. Échard, "A joint use of Raman and infrared spectroscopies for the identification of natural organic media used in ancient varnishes", *Journal of Raman Spectroscopy*, 2010 *vol. 41*, no. 11, pp. 1494-1499.
11. D. de Waal, "Micro-Raman and portable Raman spectroscopic investigation of blue pigments in selected Delft plates (17–20th Century)", *Journal of Raman Spectroscopy*, 2009 *vol. 40*, no. 12, pp. 2162-2170.
12. R. Garcia Moreno, D. Strivay, and B. Gilbert, "Maya blue–green pigments found in Calakmul, Mexico: a study by Raman and UV-visible spectroscopy", *Journal of Raman Spectroscopy*, 2008 *vol. 39*, no. 8, pp. 1050-1056.
13. K. Castro, Á. Benito, I. Martínez-Arkarazo, N. Etxebarria, and J. M. Madariaga, "Scientific examination of classic Spanish stamps with colour error, a non-invasive micro-Raman and micro-XRF approach: The King Alfonso XIII (1889–1901 "Pelón") 15 cents definitive issue", *Journal of Cultural Heritage*, 2008 *vol. 9*, no. 2, pp. 189-195.
14. M. A. Legodi, and D. de Waal, "Raman spectroscopic study of ancient South African domestic clay pottery", *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2007 *vol. 66*, no. 1, pp. 135-142.
15. A. S. Lee, P. J. Mahon, and D. C. Creagh, "Raman analysis of iron gall inks on parchment", *Vib Spectrosc*, 2006 *vol. 41*.
16. J. Ambers, "Raman analysis of pigments from the Egyptian Old Kingdom", *Journal of Raman Spectroscopy*, 2004 *vol. 35*, no. 8-9, pp. 768-773.
17. T. D. Chaplin, R. J. H. Clark, and D. R. Beech, "Comparison of genuine (1851–1852 AD) and forged or reproduction Hawaiian Missionary stamps using Raman microscopy", *Journal of Raman Spectroscopy*, 2002 *vol. 33*, no. 6, pp. 424-428.
18. S. Pagès-Camagna, S. Colinart, and C. Coupry, "Fabrication processes of archaeological Egyptian blue and green pigments enlightened by Raman microscopy and scanning electron microscopy", *Journal of Raman Spectroscopy*, 1999 *vol. 30*, no. 4, pp. 313-317.
19. N. Gobeltz, A. Demortier, J. P. Lelieur, and C. Duhayon, "Correlation between EPR, Raman and colorimetric characteristics of the blue ultramarine pigments", *Journal of the Chemical Society, Faraday Transactions*, 1998 *vol. 94*, no. 5, pp. 677-681.
20. R. J. H. Clark, L. Curri, G. S. Henshaw, and C. Laganara, "Characterization of Brown–Black and Blue Pigments in Glazed Pottery Fragments from Castel Fiorentino (Foggia, Italy) by Raman Microscopy, X-Ray Powder Diffractometry and X-Ray Photoelectron Spectroscopy", *Journal of Raman Spectroscopy*, 1997 *vol. 28*, no. 2-3, pp. 105-109.
21. S. P. Best, J. H. C. Robin, A. M. D. Marcus, C. A. Porter, and R. Withnall, "Identification by Raman Microscopy and Visible Reflectance Spectroscopy of Pigments on an Icelandic Manuscript", *Studies in Conservation*, 1995 *vol. 40*, no. 1, pp. 31-40.
22. B. W. Singer, D. J. Gardiner, and J. P. Derow, "Analysis of white and blue pigments from watercolors by Raman microscopy", *The Paper Conservator*, 1993 *vol. 17*, no. 1, pp. 13-19.
23. J. de Orozco y Covarrubias, and P. Pope Sixto V, *Tratado de la verdadera y falsa prophecia. Summi Pontificis Sixti V bulla contra Astrologiae judiciariae artem exercentes et quaecumque alia divinationum genera, librosque legentes vel tenentes*, Iuan de la Cuesta, Segouia, 1588.
24. M. Pelletier, "Quantitative analysis using Raman spectrometry", *Applied Spectroscopy*, 2003 *vol. 57*, no. 1, pp. 20A-42A.
25. D. Hunter, *Papermaking: the history and technique of an ancient craft*, Dover Publications, New York, 1978.
26. M. d. C. Hidalgo Brinquis, "La fabricación del papel en España e Hispanoamérica en el siglo XVII," *Actas del X Congreso de Historia del Papel en España*, pp. 207-223, Madrid, 2013.

27. M. d. C. Hidalgo Brinquis, "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 *vol. 41*, no. 2, pp. 755-773.
28. J. Cael, K. Gardner, J. Koenig, and J. Blackwell, "Infrared and Raman spectroscopy of carbohydrates. Paper V. Normal coordinate analysis of cellulose I", *The Journal of Chemical Physics*, 1975 *vol. 62*, no. 3, pp. 1145-1153.
29. J. De Gelder, K. De Gussem, P. Vandenabeele, and L. Moens, "Reference database of Raman spectra of biological molecules", *Journal of Raman Spectroscopy*, 2007 *vol. 38*, no. 9, pp. 1133-1147.
30. H. Edwards, D. Farwell, and A. Williams, "FT-Raman spectrum of cotton: a polymeric biomolecular analysis", *Spectrochimica Acta Part A: Molecular Spectroscopy*, 1994 *vol. 50*, no. 4, pp. 807-811.
31. J. H. Wiley, and R. H. Atalla, "Band assignments in the Raman spectra of celluloses", *Carbohydrate Research*, 1987 *vol. 160*, pp. 113-129.
32. T. Barrett, and C. Mosier, "The role of gelatin in paper permanence", *Journal of the American Institute for Conservation*, 1995 *vol. 34*, no. 3, pp. 173-186.
33. G. Zhu, X. Zhu, Q. Fan, and X. Wan, "Raman spectra of amino acids and their aqueous solutions", *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2011 *vol. 78*, no. 3, pp. 1187-1195.
34. B. G. Frushour, and J. L. Koenig, "Raman scattering of collagen, gelatin, and elastin", *Biopolymers: Original Research on Biomolecules*, 1975 *vol. 14*, no. 2, pp. 379-391.
35. P. Kubryk, R. Niessner, and N. P. Ivleva, "The origin of the band at around 730 cm^{-1} in the SERS spectra of bacteria: a stable isotope approach", *Analyst*, 2016 *vol. 141*, no. 10, pp. 2874-2878.