Chemistry Research Journal, 2017, 2(4):191-197

Available online www.chemrj.org

Research Article

ISSN: 2455-8990
CODEN(USA): CRJHA5

A preliminary infrared study of the cellulose of some world stamps

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

[1]Department of Chemistry, Faculty of Sciences, University of Chile. Las Palmeras 3425, Santiago 7800003, Chile.
[2]Chilean Philatelic Society,Almirante Simpson 75, Providencia, Santiago7500867, Chile

Abstract The infrared spectrum of seven heavily damaged stamps was measured to analyze the cellulose, fillers and sizing elements composing them. In five of them kaolinite was detected as a filler. In one of them Prussian blue was detected as a component of a greenish-blue paper. An attempt to classify them employing a decision tree led to the conclusion that more data from other experimental analysis (XRF) is needed to achieve this goal.

Keywords Philately, infrared spectrum, cellulose, archeology, postage stamps, telegraph stamps, decision tree

Introduction

Technically, postage stamps are gummed, printed paper documents that have been issued by governments since 1840 as prepayment for a mail delivery service to be rendered by an official governmental agency. Stamps are affixed to envelopes, mailing cylinders, packets, boxes or any other mail item. At the beginning, stamps were commonly made from paper designed specifically for them, and were printed in sheets, rolls or small booklets. Paper has as its chief component, a "carpet" of cellulose fibers. Fillers are added to the pulp to fill the pores of the paper. Also, sizing is added to make the fibers water resistant. Fillers can be glues made from animal products, starches from rice or wheat, resins or gums, or minerals such as calcium carbonate, titanium dioxide or kaolin.

Today, collecting topical postage stamps and associated items such as envelopes, postmarks, and first day covers is a very popular hobby. Collectors of postage stamps are called philatelists. On the other hand, and like other collectibles, "***stamps are frequently considered a comparatively safe investment in times of financial turmoil, and one that potentially hedges better against changes in the aggregate price level***" [1].Stamps and definite postal cancellations are issued to commemorate certain events and to inform and educate the public. Due to their worldwide circulation, stamps can be fast, powerful and effective messengers of what the State considers of enough importance for being represented in such a way.

Some stamps have been printed in large quantities (several millions) and are easily available for the collector. Nevertheless a rule states that "*the quantity of a given stamp remains constant or diminishes*" (the diminishing process is due to natural disasters, wars, human mistakes, etc.). Stamps that could be common today may become precious objects with the passing of time. In the future archeological excavations some portions of stamps can be found and in some cases with no possibility of identification. Then, if we consider stamps as being future objects of archeological interest, all the information we may accumulate about them could be useful in due time. Many people manipulate stamps in a careless way, sometimes damaging them beyond all possibility of restoration or reparation. This generates a large quantity of objects that can be studied by destructive means without philatelic ethical concerns. Usually, stamps have been analyzed with several non-invasive techniques [2-13].

As we said before one of the basic components of stamps is cellulose. Given that there is good information about the infrared (IR) spectra of cellulose and its derivatives, fillers and sizing components, we decided to undertake a preliminary IR study of several damaged stamps to see if the data obtained is of enough interest to start the creation of a database. This paper reports the results of this study.

Experimental

Seven stamps were randomly selected from a large set of heavily damaged ones. Fig. 1 shows reference photos (numbered S1 to S7 from left to right and from top to bottom).

Figure 1: Reference photos of the selected stamps

S1is from the time of German hyperinflation (1923).S2 is from Colombia (*circa* 1888-96, telegraph use, blue paper). S3 is from Portugal (1930).S4 is from Honduras (1865, greenish paper).S5 is from Mexico (1934, airmail use). S6 is from Uruguay (1910). S7 is from Saargebiet (Germany, 1923).The stamps were immersed in deionized water (DW) for 6 hours to remove possible remains of the gum, dirtiness and/or hinges. After, they were rinsed abundantly with DW and placed on an inert surface for atmospheric drying. The procedure was repeated three times. The samples were obtained by cutting the external border of the stamps avoiding cancellation marks.

The IR spectra were recorded with a Perkin Elmer Systems 2000 spectrophotometer. For the samples the standard technique of disk pressing in KBr was employed. Briefly, 0.5-1.0milligrams of sample and 80-100 mg of IR grade KBrwere used. The mixture was submitted to a pressure of 15 t /cm^2 for 30 seconds to form a 13 mm diameter disk.

Results

Figures 2 to 5 shows photos of the backside of stamps after the treatment with deionized water (200x magnification). The blue color is an effect of the equipment employed.

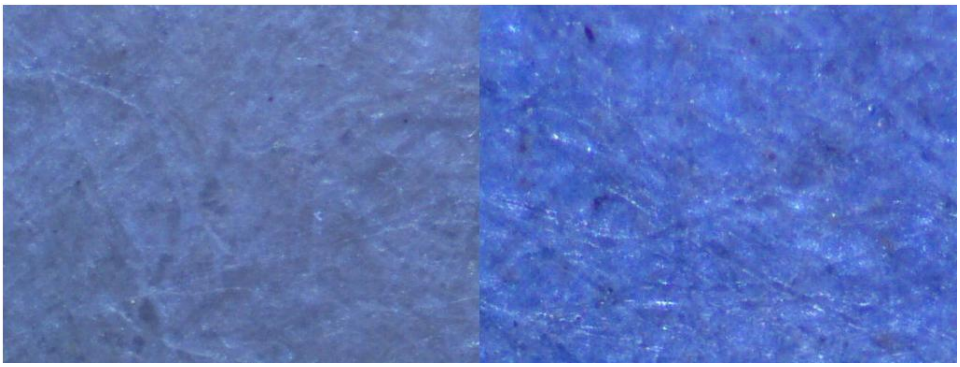

Figure 2: 200X magnification of the backside of S1 (left) and S2 (right)

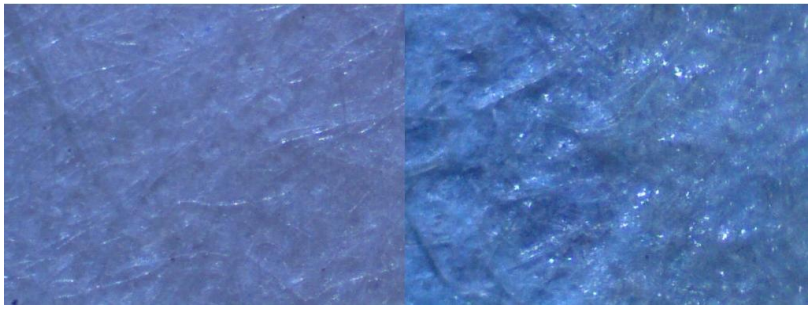

Figure 3: 200X magnification of the backside of S3 (left) and S4 (right)

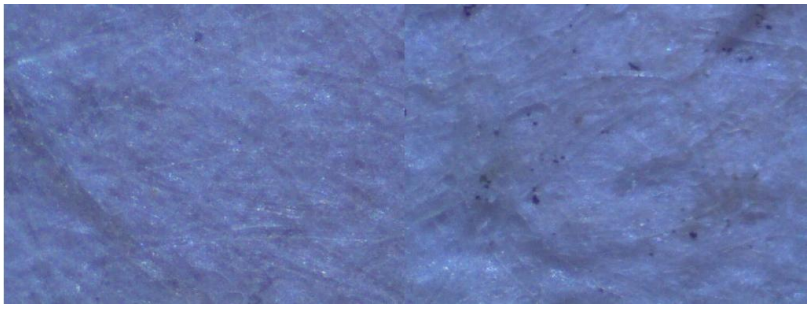

Figure 4: 200X magnification of the backside of S5 (left) and S6 (right)

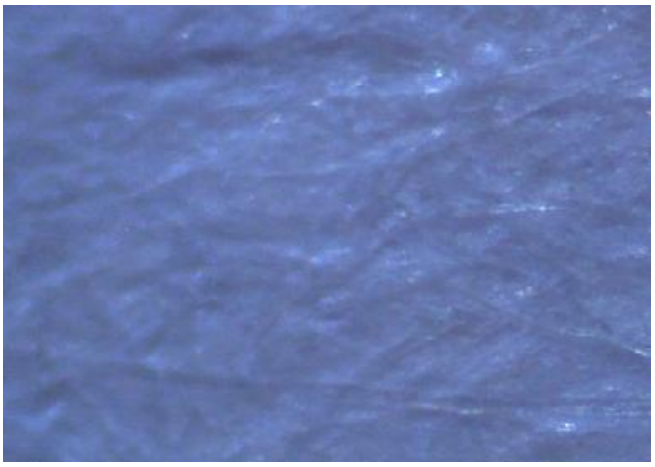

Figure 5: 200X magnification of the backside of S7 (left)

Figures 6 to 12 show the IR spectrum of stamps 1-7.

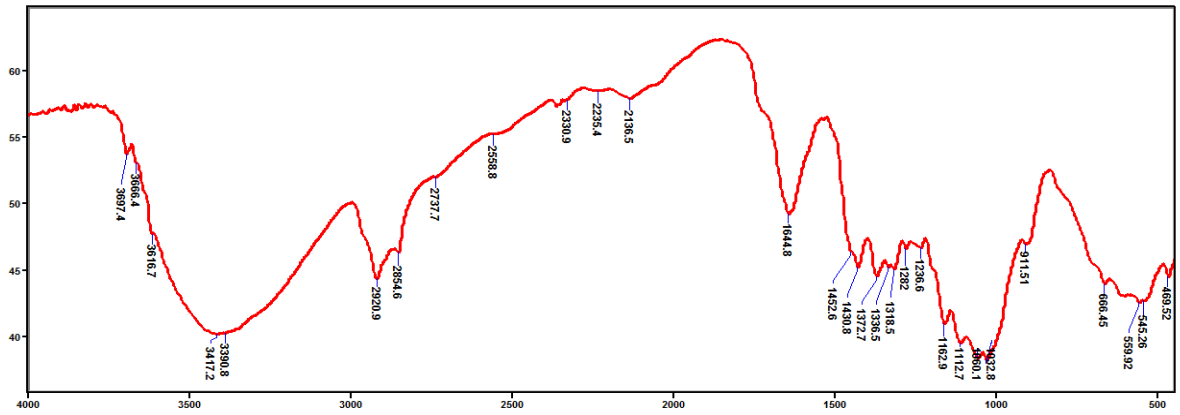

Figure 6: IR spectrum of S1 (X axis shows the wavenumber in cm^{-1} and the y axis the transmission. This is valid for all figures below)

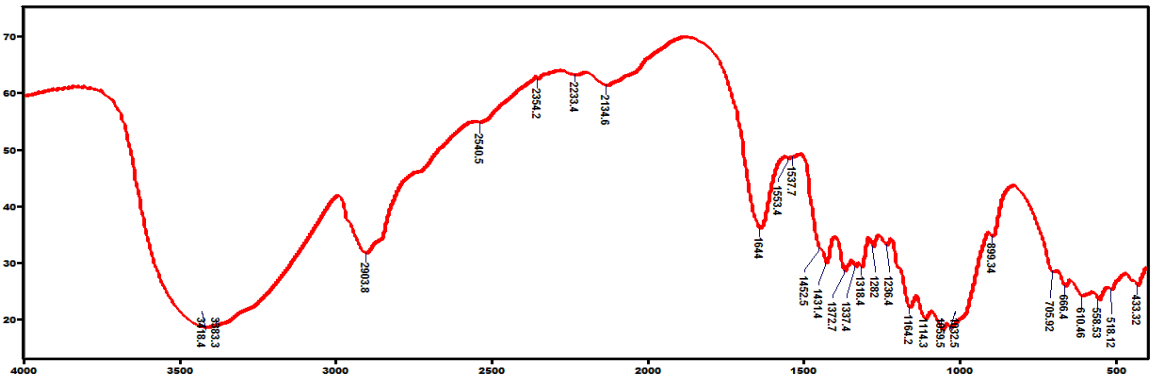

Figure 7: IR spectrum of S2

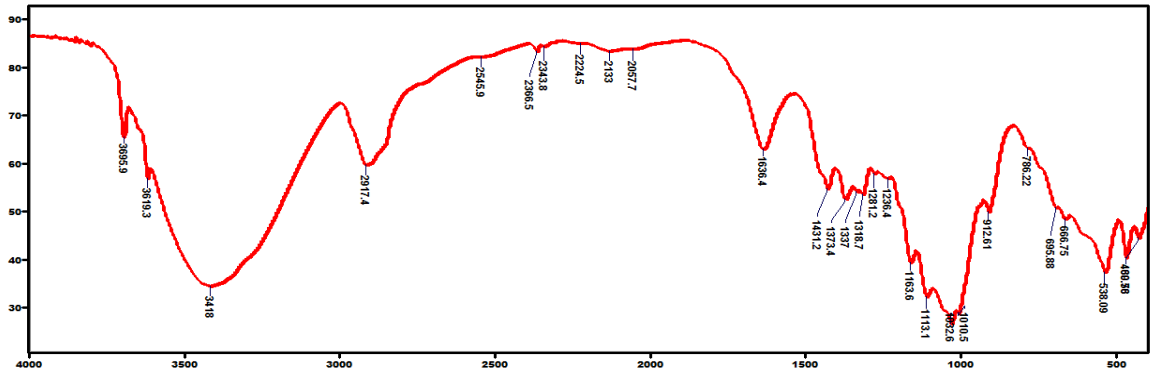

Figure 8: IR spectrum of S3

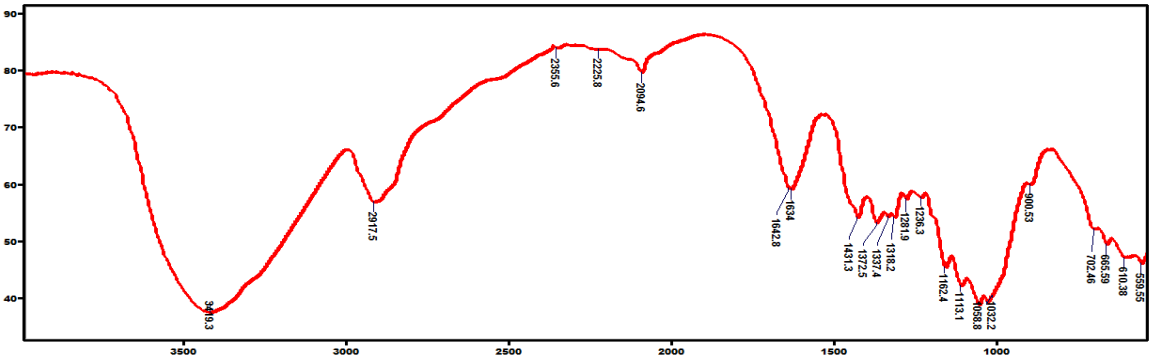

Figure 9: IR spectrum of S

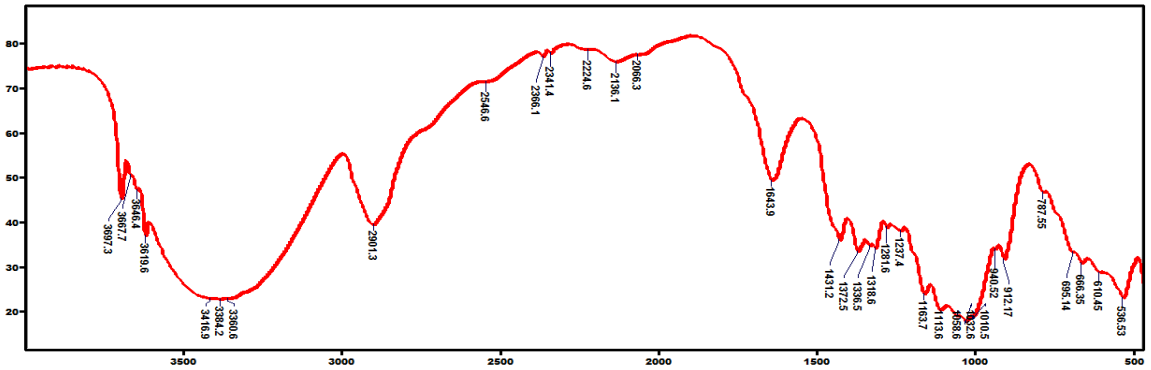

Figure 10: IR spectrum of S5

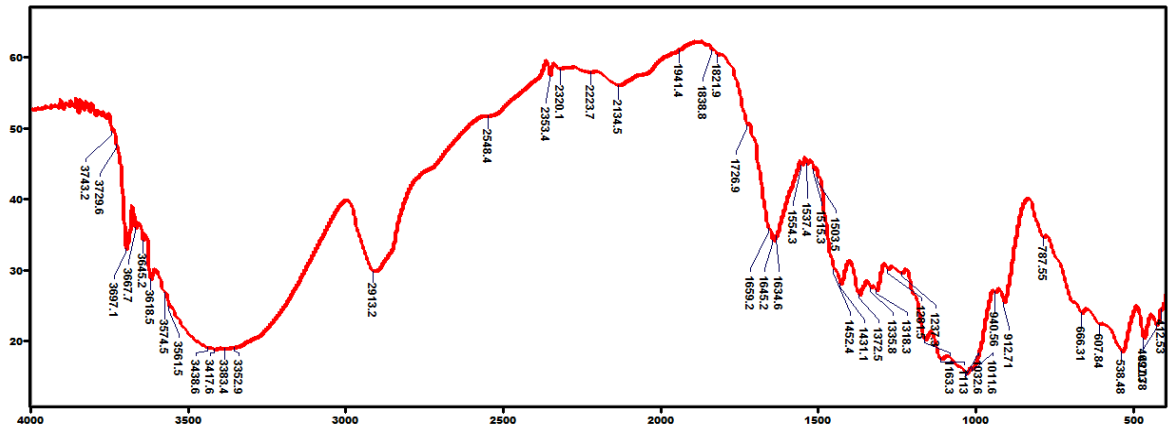

Figure 11: IR spectrum of S6

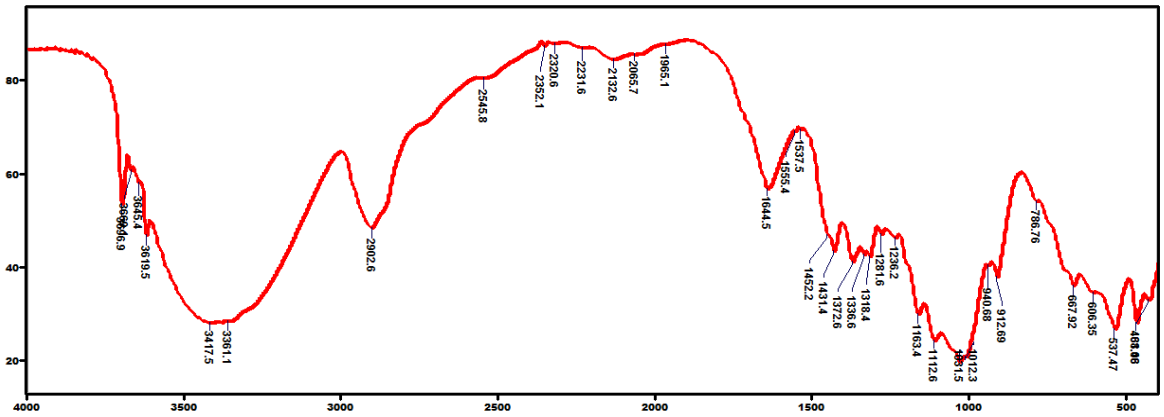

Figure 12: IR spectrum of S7

Discussion

No stamp responded to 254 nm and 365 nm UV lights. The 200x magnification shows the cellulose fibers (Figs. 2-5). No regular pattern is observed. Unhappily, we cannot be sure if this is the original cellulose structure or the result of the previous treatment with DW. Some stamps had hinge remains and they were so dirty that their washing was unavoidable. The same problem appeared in the front side. Also, we must mention that all stamps were without the original gum, implying that there were washed by their anterior proprietaries with unknown liquids (probably distilled or drinking water). Perhaps this part of our study can be improved by using mint, never hinged stamps and carrying out the microscopic study on the non-printed frontal side. Note that some samples show black and/or white incrustations. These can be ascribed to crystals of the filler(s), and/or sizing agent(s), and/or color crystals, and/or to a bad external manipulation along time allowing some external agents to fix over the fibers.

Cellulose has not absorption bands in the 2000-2600 cm^{-1} region[14]. The stretching vibrations of the CH_2 groups give a band in the 2800-3000 cm-1 region, which is observed in Figs. 6-12. The 3000-3800 cm^{-1} corresponds to the OH region[14].In the seven samples the band at 1645 cm^{-1} corresponds unequivocally to rosin (Greek pitch or colophony), a solid form of resin that was used for paper sizing [15].

Kaolinite was used as filler in S1, S3 and S5-S7. The bands around 3667 and 3619 cm^{-1} show its presence. The band at 3690 cm^{-1} is ascribed to the Si-OH stretching mode (or maybe to the Al-OH stretching mode) [16]. The kaolinite OH stretching modes show four bands at 3697, 3669, 35664 and 3620 cm^{-1}.Valli et al. relate the absence of one peak in the spectrum to the position of the filler into the cellulose fibers[8]. Some pure kaolinite reported bands are 3693s, 3655sh, 3620, 1115s, 1090s, 1032s, 1006s, 939, 914s, 792, 753, 696 642, 600sh, 536s, 470s and 429 cm^{-1} (white powdery aggregate from Margaritas mine, Pena Blanca uranium distr., W. of Chihuahua, Mexico)[17].

Interestingly S2 and S4, which have blue and greenish paper respectively, have not bands around 3667 and 3619 cm^{-1}, indicating the absence of kaolinite. This perfectly coincides with the fact that at the time when S2 and S4 were

printed, kaolinite was not used as filler. The band at 2095 cm^{-1} in the IR spectrum of S4 (greenish paper) clearly shows that Prussian blue is present in the paper[17]. We could not find the compound giving the greenish component to the color. In S2 (blue paper), Prussian blue is not present and we could not find the causative agent of this color.The 950-1200 cm^{-1} region of the cellulose spectrum displays broad diffuse absorption[14]. Kaolinite also shows several bands in this region [17]. Therefore the interpretations of the bands in this region are somewhat difficult. S1, S2 and S5-S7 display a band around 2135-2137 cm^{-1}. Cellulose derivatives containing C≡C and C≡N bonds display sharp bands at 2150-2250 cm^{-1}[14]. Despite that the bands are outside this range, we tentatively suggest that they could correspond to these bonds.

Figure 13 shows the decision tree built with the abovementioned main information.

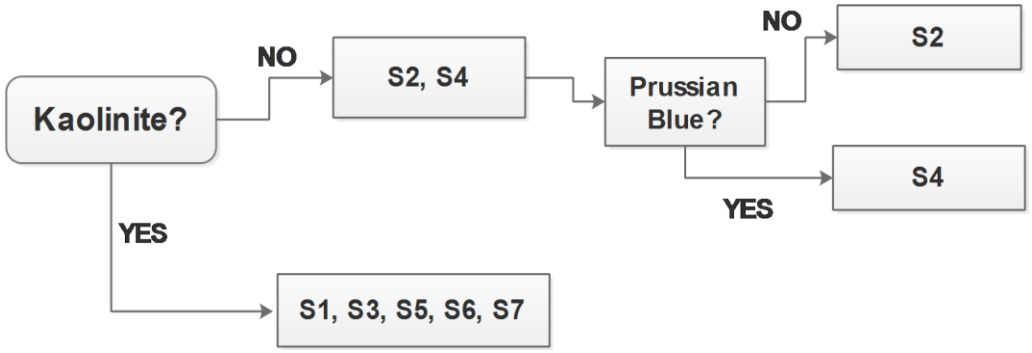

Figure 13: Decision tree for the classification of S1-S7

It is clear from Fig. 13 that there are not important adequate elements in the IR spectra to discriminate between S1, S3 and S5-S7 at this stage of the research. Nevertheless, in the case of S1 we may observe that the bands around 2900 cm^{-1} are better defined, fact that could be an indication of the presence of hemicellulose [18, 19].On the other hand, a comparison of the seven IR spectra shows that there are enough interesting differences among them to expand this study to more stamps. However, the data presented here should be supplemented with IR results of the printed parts and, if possible, with X-ray fluorescence studies.

References

1. E. Dimson, and C. Spaenjers, "Ex post: The investment performance of collectible stamps," *Journal of Financial Economics*, 2011 *vol. 100*, no. 2, pp. 443-458.
2. L. Burgio, and R. J. H. Clark, "Library of FT-Raman spectra of pigments, minerals, pigment media and varnishes, and supplement to existing library of Raman spectra of pigments with visible excitation," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2001 *vol. 57*, no. 7, pp. 1491-1521.
3. 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.
4. 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.
5. T. D. Chaplin, A. Jurado-Lopez, R. J. Clark, and D. R. Beech, "Identification by Raman microscopy of pigments on early postage stamps: distinction between original 1847 and 1858-1862, forged and reproduction postage stamps of Mauritius," *Journal of Raman Spectroscopy*, 2004 *vol. 35*, no. 7, pp. 600-604.
6. N. Ferrer, and A. Vila, "Fourier transform infrared spectroscopy applied to ink characterization of one-penny postage stamps printed 1841–1880," *Analytica Chimica Acta*, 2006 *vol. 555*, no. 1, pp. 161-166.
7. T. E. Gill, "Analysis of Postage Stamps by Proton-Induced X-Ray Emission Spectrometry," *Smithson. Contrib. Hist. Technol*, 2013 *vol. 57*, pp. 83-90.

8. E. Imperio, G. Giancane, and L. Valli, "Spectral Database for Postage Stamps by Means of FT-IR Spectroscopy," *Analytical Chemistry*, 2013 *vol. 85*, no. 15, pp. 7085-7093.
9. I. Jelovica Badovinac, N. Orlić, C. Lofrumento, J. Dobrinić, and M. Orlić, "Spectral analysis of postage stamps and banknotes from the region of Rijeka in Croatia," *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 2010 *vol. 619*, no. 1, pp. 487-490.
10. E.-M. Johanson, S. A. E. Johanson, K. G. Malmqvist, and I. M. B. Wiman, "The feasibility of the pixe technique in the analysis of stamps and art objects," *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 1986 *vol. 14*, no. 1, pp. 45-49.
11. J. J. Melendez-Perez, D. N. Correa, V. V. Hernandes, D. R. de Morais, R. B. de Oliveira, W. de Souza, J. M. Santos, and M. N. Eberlin, "Forensic Application of X-ray Fluorescence Spectroscopy for the Discrimination of Authentic and Counterfeit Revenue Stamps," *Applied Spectroscopy*, 2016 *vol. 70*, no. 11, pp. 1910-1915.
12. M. Poslusny, and K. E. Daugherty, "Nondestructive Adhesive Analysis on Stamps by Fourier Transform Infrared Spectroscopy," *Applied Spectroscopy*, 1988 *vol. 42*, no. 8, pp. 1466-1469.
13. N. V. Schwab, J. A. Da-Col, P. Meyer, M. I. M. S. Bueno, and m. N. Eberlin, "Energy Dispersive X-Ray Fluorescence Profile of Some Brazilian Postage Stamps," *Journal of the Brazilian Chemical Society*, 2016 *vol. 27*, no. 7, pp. 1305-1310.
14. R. G. Zhbankov, *Infrared spectra of cellulose and its derivatives*, Springer, New York, 1966.
15. H. G. Brittain, "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 *vol. 70*, no. 1, pp. 128-136.
16. B. J. Saikia, and G. Parthasarathy, "Fourier Transform Infrared Spectroscopic Characterization of Kaolinite from Assam and Meghalaya, Northeastern India," *J. Mod. Phys.*, 2010 *vol. 1*, no. 4, pp. 206-210.
17. N. V. Chukanov, *Infrared spectra of mineral species: extended library*, Springer, Dordrecht, 2014.
18. V. Daniels, "The Discolouration of Paper on Ageing," *The Paper Conservator*, 1988 *vol. 12*, no. 1, pp. 93-100.
19. M. Fan, D. i. Da, and B. Huang, "Fourier Transform Infrared Spectroscopy for Natural Fibres," in *Fourier Transform - Materials Analysis*, S. Salih Ed., pp. 45-68, InTech Europe, Rijeka, Croatia, 2012.