



Methodological problems in the analysis of the Raman spectra of the paper of some postage stamps from Crete

Juan S. Gómez-Jeria^{1*}, Camilo Segura¹, José J. Cárcamo-Vega²

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

²Museo Arqueológico San Miguel de Azapa – UTA. Camino Azapa, Km 12.5, Arica, 1001236, Chile

Abstract A Raman spectroscopy study has been carried out with 633 and 768 nm laser lines to characterize three Cretan postage stamps. The first corresponds was issued by the Russian Empire Administration area and the other two belong to the 1905 Revolutionary Issues. The resulting Raman spectra are not of enough quality allowing a direct interpretation. Possible corrections to these spectra are, for example, the removal of the background fluorescence, the baseline correction and/or smooth. These tools are available in several spectroscopy software packages. The central question is the reliability of the spectra obtained after one or more corrections are applied. In order to begin creating a common procedure to treat all samples we ascribed only those bands that coincide with the cellulose calculated Raman frequencies. The first results suggest that it is necessary to carry out more studies with a significant number of samples before proposing a common treatment for all Raman spectra of postage stamps presenting fluorescence.

Keywords Cretan Postage stamps, Raman spectroscopy, cellulose, Crete, fluorescence, Vancouver Raman algorithm, baseline correction, smooth

Introduction

Crete was once the center of the magnificent and exquisite Minoan civilization (c. 2700–1420 BP). After the devastation provoked by the Thera eruption, Mycenaeans from the continent took over Knossos, the ancient capital.



Figure 1: Map of Crete by Baldwin & Cradock, 1829

They were later replaced by the Dorians. City-states were formed and they began an endless series of wars among them. Much later it was part of the Crete & Cyrenaica Roman province (69 BP), a province within the eastern half of the Roman Empire, the piratical Emirate of Crete (820), part of the Byzantine Empire (961) and a colony of Venice (1205). The Ottomans conquered Crete in 1669. Crete Christians revolved incessantly against Ottoman rule. On a Sunday, the 1st of December, 1913 the Greek flag was raised on top of the fortress of Firka, signaling the union of Crete with Greece (Fig. 1).

The philatelic history of Crete is composed by several periods. During the first one, Ottoman postage stamps were used (until 1899). The second period begins in 1898 when Crete acquired autonomy under Ottoman suzerainty, but was garrisoned by an international military force from British Empire, French Empire, Kingdom of Italy and Russian Empire. The first stamps of Crete were issued on 1 March 1900. In September 1908, the stamps of the earlier issues were overprinted "ΕΛΛΑΣ" after the deputies unilaterally declared the union with Greece. On their side the Austro-Hungarian, Russian, French and British Empires, together with the Kingdom of Italy, operated post offices on the territory of Crete with their own stamps. From 1913 Greek stamps have been used on the island. The remaining Cretan stamps were overprinted and issued in Greece in 1923. During a short interval (1944-45) the Third Reich troops employed Feldpost stamps overprinted "Inselpost" to transport their mail.

As far as we know, no scientific studies have been carried out on Crete stamps. Our previous studies employed infrared and SEM tools [1-4]. Here we present the results of Raman spectroscopic analyses of three Crete stamps. This was the original goal of this study. Nevertheless, as stamps' paper is prone to fluorescence giving poor-quality Raman spectra we have considered as the main goal the test of different laser lines and the analysis of the results of some mathematical treatments of the spectra. This study will not provide a final answer to these questions but it could help to pave a way to obtain credible information. The other problem is related to the very small surface were the laser points. This, coupled with the inhomogeneity of the paper (and possibly of the ink or inks), makes the task more difficult.

Materials and Methods

We selected three stamps for analysis. The first one was issued by the Russian Administration and corresponds to member of a lithographed set with a Poseidon's trident design and two stars in the frame around the trident (sample S1, Sc. 39) (Fig. 2).



Figure 2: Postage stamp from the Russian Empire Administration in Crete (sample S1)

Its facial value is of 2 metallik and its color rose. This stamp has a violet control mark, in the form of a double eagle. All of these stamps have been extensively forged. The second and third stamps are shown in Fig.3 and are known as the 1905 Revolutionary Issues (samples S2 and S3). Both stamps have a cancellation 'Theriso' (Θέρισο in Greek), the name of the village that was the center of the revolutionary activity.





Figure 3: Revolutionary Issues. Samples S2 (left) and S3 (right)

Figure 4 shows another two examples of these postage stamps for their better appreciation.



Figure 4: Other examples of the Revolutionary Issues (they are not the samples)

Because the Cretan post service was not working in the revolutionary territory, they printed their own stamps. The first ones were issued between August 30 and September 1 1905 and were very primitive hand-stamped. 5400 exemplars of each value were printed by D. Kokinokos. The facial value of the stamps is 20 lepta and 1 drachma. The circular motif in the center represents Nike, the Goddess of Victory. It seems that the inks of these two stamps are slowly fading. Some catalogues do not include these stamps because they feel that they were printed only for collectors and dealers. They have been extensively forged. It is thought that forgeries account by about 75% of stamps on sale.

Experimental

The stamps were used without any previous treatment. Raman spectra were obtained with two equipments. The first is a Raman Renishaw InVia apparatus, equipped with a 785 nm laser line 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 $50\times$ objective. The resolution was set to 4 cm^{-1} , and 1–20 scans of 10–30 s each were averaged; spectra were recorded in the $200\text{--}3500\text{ cm}^{-1}$ region to observe the Raman spectra. The power of laser was set between 0.001 and 5 %. The spectral scanning conditions were chosen to avoid sample degradation and photodecomposition. The selected power of the laser was 200 mW. The spectra were taken by J.J. C-V. The second one is a Witec alpha-300 RA apparatus with a 633 nm laser line and equipped with a CCD camera, a $50\times$ objective and a 300 grooves/mm grating. The spectra were taken by C.S. Figure 5 shows the three typical places selected for obtaining Raman spectra of sample S1.





Figure 5: Places selected for obtaining Raman spectra of S1

1 refers to the white margin (S1-1), 2 to the red area (S1-2) and 3 to the violet area (S1-3). Figures 6 and 7 show the points selected for obtaining Raman spectra in samples S2 and S3.



Figure 6: Points selected for measurement in sample S2

Point 1 corresponds to white paper (S2-1), point 2 to the red frame (S2-2), point 3 to the blue circle (S2-3) and point 4 to the cancellation on the white paper (S2-4, see also Fig. 4).



Figure 7: Points selected for measurement in sample S3

Point 1 corresponds to white paper (S3-1), point 2 to the blue frame (S2-2), point 3 to the red/rose circle (S3-3) and point 4 to the cancellation on the white paper (S3-4, see also Fig. 4).

Results

All samples showed a strong fluorescence. Figure 8 shows as an example the original Raman spectrum of sample 1 taken with the 785 laser line. We can see that it is almost impossible to provide even one band assignment.

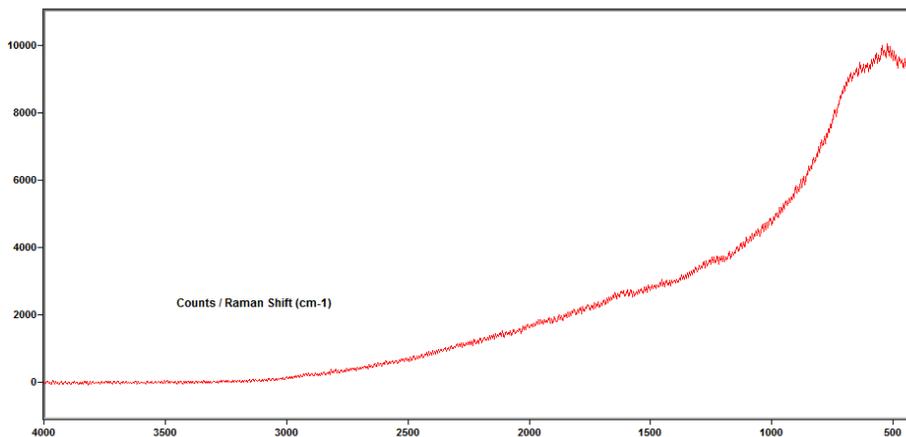


Figure 8: Raman spectrum of sample S1 taken with the 785 nm laser line

For this reason it was necessary to subject all the spectra to some mathematical treatments. The first step involved the use of the Vancouver Raman Algorithm for fluorescence background removal [5]. This was done for the 400 – 1800 cm^{-1} region (see below). We also employed Spectragryph 1.2 (<https://www. effemm2.de/spectragryph/>) software for advanced baseline correction and smoothing. We noticed that with smoothing some bands disappear or their partially fuse. The questions of ‘how much’ smoothing we should apply and whether that smoothing procedure should be exactly the same for all samples analyzed or should be a standard for any paper study of stamps or similar objects cannot be answered yet. Hopefully these results will contribute to a future response. The calculated Raman frequencies of a large model of cellulose show a very low intensity in the range up to 1534 cm^{-1} (Gómez-Jeria, unpublished, DFT, B3LYP/6-31g(d,p) calculations with full geometry optimization). Between this value and near 2933 cm^{-1} cellulose shows no Raman frequencies. As these methodologies have never been tested on postage stamps, our primary interest is to see if we can relate the structure of the final spectra with the calculated frequencies of cellulose or with other possible components. We expect that, if the mathematical procedures employed are the correct ones, a large percentage of the experimental peaks will coincide with cellulose calculated frequencies. The procedure was carried out for the 400-1534 cm^{-1} range. This should indicate that we are in the correct way. Here we report only the results for the non-printed areas of the stamps (‘white paper’ in Figs. 5-7, point 1 in all samples). Figures 9 and 10 show, respectively, the Raman spectra of point 1 (white margin) of sample S1.



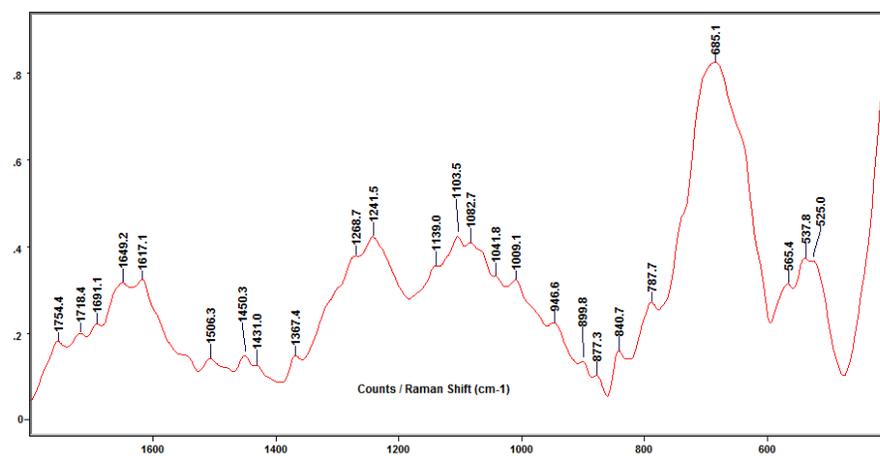


Figure 9: Raman spectrum of point S1-1 (768 nm laser line)

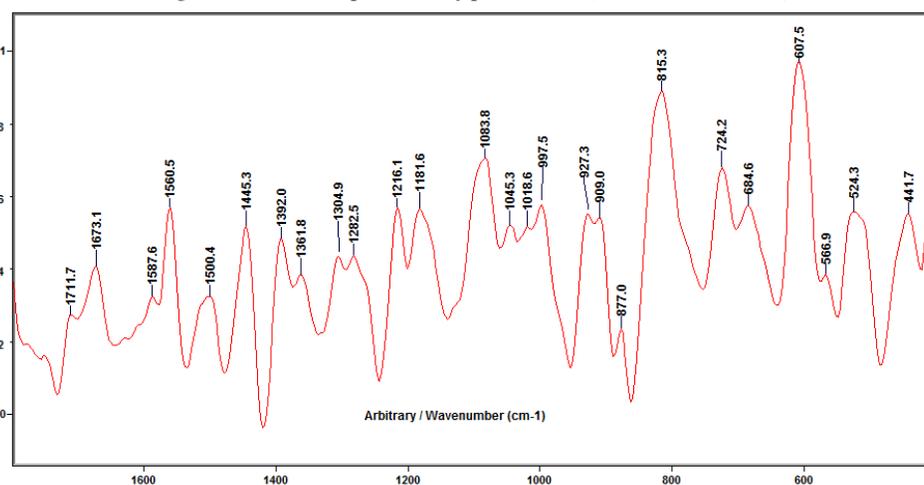


Figure 10: Raman spectrum of point S1-1 (633 nm laser line)

Table 1 lists the peaks of Figs. 9 and 10 and theoretical Raman frequencies.

Table 1: Peaks of Figs. 9 and 10 and theoretical Raman frequencies (cm^{-1})

Peak (785 nm.)	Peak (633 nm.)	Theor. Freq.	Peak (785 nm.)	Peak (633 nm.)	Theor. Freq.
---	441.7	443.42	---	1181.6	1181.8
525	524.3	n.a.	---	1216.1	1215.9
537.8	---	538.7	1241.5	---	n.a.
565.4	566.9	562.8	1268.7	---	n.a.
685.1	684.6	686.5	---	1282.5	1282.1
---	724.2	725.6	---	1304.9	1305.3
787.7	---	786	---	1361.8	1361.9
---	815.3	n.a.	1367.4	---	n.a.
840.7	---	n.a.	---	1392	1392.5
877.3	877	n.a.	1431	---	1432.2
899.8	---	898	---	1445.3	n.a.
---	909	907.2	1450.3	---	1450.7
---	927.3	927.8	---	1500.4	n.a.

946.6	---	945.5	1506.3	---	1505.7
---	997.5	996			
1009.1	---	n.a.			
---	1018.6	n.a.			
---	1045.3	1044.7			
1041.8	---	1041.2			
1082.7	1083.8	1082.5 1083.5			
1103.5	---	1103.4			
1139	---	1138.9	n=20, 50%	n=21, 71%	

We can see that for the 785 nm laser line, 50% of the peaks could be ascribed to cellulose's theoretical frequencies. Half of the peaks were not assigned. In the case of the 663 nm laser line, 71% of the peaks could be ascribed to cellulose's theoretical frequencies. Figure 11 shows the Raman spectra of point 1 (white margin) of sample S2.

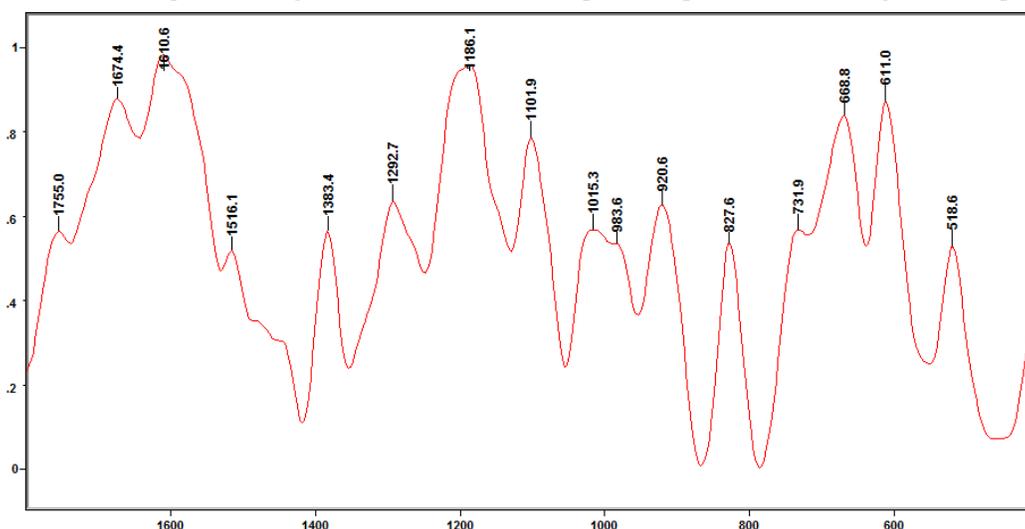


Figure 11: Raman spectrum of point S2-1 (633 nm laser line)

Table 2 lists the peaks of Fig. 11 and theoretical Raman frequencies.

Table 2: Peaks of Fig. 11 and theoretical Raman frequencies (cm^{-1})

S. No.	Peak (633 nm.)	Theor. Freq.	S. No.	Peak (633 nm.)	Theor. Freq.
1	518.6	518	9	1101.9	1100.1, 1103.4
2	611.0	611.3	10	1186.1	n.a.
3	668.8	n.a.	11	1292.7	1292.1
4	731.9	730.4	12	1383.4	1382.7
5	827.6	825.6 (?)	13	1516.1	1515.8
6	920.6	919.5			
7	983.6	n.a.			
8	1015.3	n.a.			
			n=13, 69.2%		

We can see that 69.2 % of the peaks coincide with the calculated frequencies of cellulose.

Figure 12 shows the Raman spectra of point 1 (white margin) of sample S3.



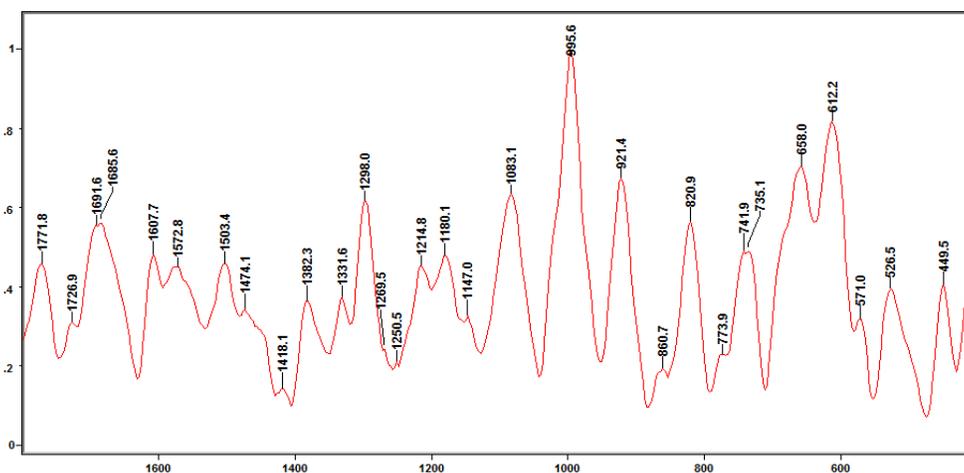


Figure 12: Raman spectrum of point S3-1 (633 nm laser line)

Table 3 lists the peaks of Fig. 12 and theoretical Raman frequencies.

Table 3: Peaks of Fig. 12 and theoretical Raman frequencies (cm^{-1})

S. No.	Peak (633 nm.)	Theor. Freq.	S. No.	Peak (633 nm.)	Theor. Freq.
1	449.5	447.5 (?)	13	1083.1	1083.5
2	526.5	526.6	14	1147.0	1147.0
3	571.0	569.8 (?)	15	1180.1	1181.9 (?)
4	612.2	611.3	16	1214.8	1215.9
5	658.0	658.2	17	1250.5	1250.6
6	735.1	n.a.	18	1269.5	1269.9
7	741.9	741.4	19	1298.0	1297.4
8	773.9	n.a.	20	1331.6	1331.5
9	820.9	n.a.	21	1382.3	1382.7
10	860.7	n.a.	22	1418.1	1416.8 (?)
11	921.4	922.4	23	1474.1	1474
12	995.6	995.9	24	1503.4	1501.7 (?)

We can see that the coincidence between the peaks and the theoretical frequencies is 62.5% or 83% if we include the doubtful ones.

Discussion

Before discussing the experimental results and the results derived from them we would like to comment on the authenticity of the samples. As we have mentioned before, the industry of stamp forgery appeared around 1860. Forgers such as Jean de Sperati, Louis-Henri Mercier and François Fournier forged high-value stamps and some forgeries are very expensive today. Some people collect only forgeries. But today, with the advances in computing, software and printing a new wave of forgeries has flooded the market. Today is not necessary to forge an expensive stamp but produce large quantities of moderately cheap ones and sell them through bidding sites in Internet. Technology used to detect forgeries has advanced also but there is still a lack of reliable scientific information about postage stamps. Most forgers concentrate specifically on replicating the overprints of expensive stamps (think, for example, in the overprinted German postage stamps used in the Eastern territories and in the Balkans during WW II), and many of them are of enough quality even for deceiving the expert. As the composition of printing inks is very different from the pre-1945 ones, tools like Raman spectroscopy are necessary to differentiate them.

In the cases analyzed here it seems at first sight that the relatively high percentage of coincidences between the cellulose theoretical frequencies and the experimental Raman peaks allow us to employ these spectra for future studies. The question is that we cannot do this until we are able to define a unique procedure to treat the experimental spectra for *all* cases, present and future. The Vancouver Raman Algorithm places a limit in the range



to be analyzed (between 400 and 2000 cm^{-1}). Moreover, employing other software, such as Spectragryph, allow more mathematical treatments. A pictorial example follows. Figure 13 shows the spectrum of point 1 of sample S3 after the use of VRA.

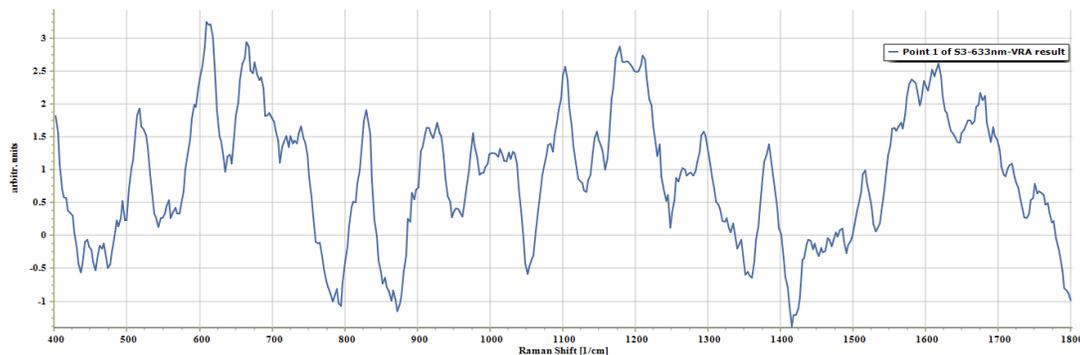


Figure 13: Raman spectrum of point 1 of sample S3 after application of VRA

Now, we will modify this spectrum to eliminate negative 'arbitrary units' through 'baselining'. The result is shown in figure 14.

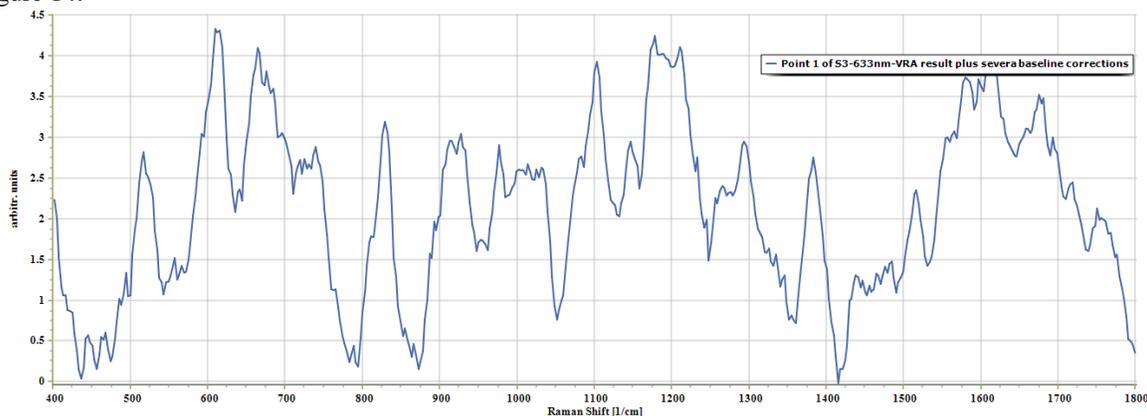


Figure 14: Baselining of the spectrum of Fig. 13

No changes are observed. Now we shall try to eliminate the minor peaks through smoothing methods. An example of this procedure is shown in Fig. 15.

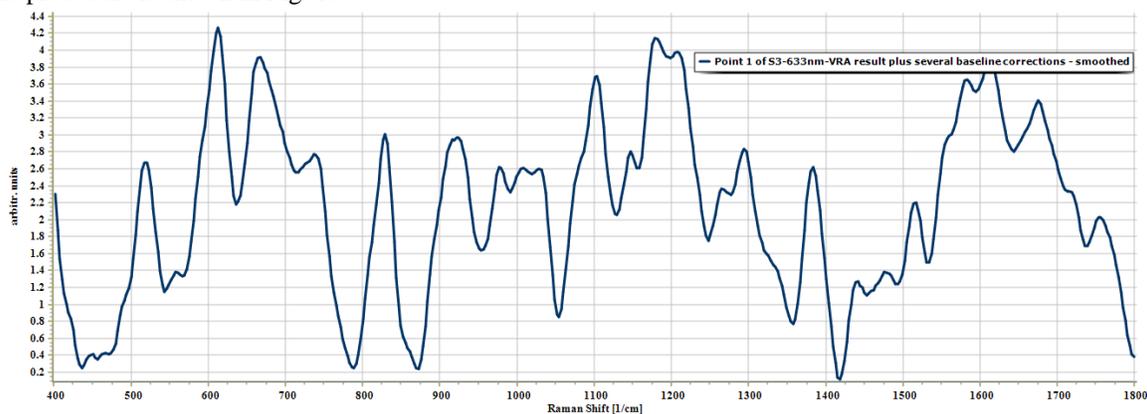


Figure 14: Example of smoothing of the spectrum of Fig. 13

It is easy to see that the spectrum is notoriously different and that some peaks have disappeared. The question to answer is at this level of analysis. Is there a smoothing procedure that will be useful for *all* postage stamps Raman spectra in case we need it? We think that this search must begin with postage stamps that present fluorescence but



we know all about them: kind(s) of cellulose, chemicals used as fillers and/or coaters if they exist and the chemical formulae of the color or colors appearing on it. In this way, and thorough an iterative process, we should be able to propose an answer to the abovementioned question.

References

- [1]. 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.
- [2]. 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.
- [3]. Gómez-Jeria, J. S.; Clavijo, E.; Cárcamo-Vega, J. J.; Gutiérrez, 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.
- [4]. Gómez-Jeria, J. S.; Clavijo, E. A preliminary infrared study of the cellulose of some world stamps. *Chemistry Research Journal* 2017, 2, 191-197.
- [5]. Zhao, J.; Lui, H.; McLean, D. I.; Zeng, H. Automated Autofluorescence Background Subtraction Algorithm for Biomedical Raman Spectroscopy. *Applied Spectroscopy* 2007, 61, 1225-1232.

