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A preliminary FTIR-ATR and XRF analyses of the cellulose of four postcards from the Reichskommissariat Ostland and the German occupations of Pleskau (Russia) and Latvia

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Abstract FTIR-ATR and XRF techniques have been employed to carry out a preliminary characterization of the cellulose of four postcards issued during the Third Reich war in the East. Two postcards were printed in Berlin while the other two corresponded to communist Russian postcards with German overprints. The XRF results show that only the paper of the German postcards contains potassium. The four postcards present Fe and Cu that could oxidize cellulose. The possible presence of cotton is suggested but not proved.

Keywords Postcards, Raman, FTIR-ATR, XRF, cellulose, Third Reich, Reichskommissariat Ostland, Latvia, German occupation of Russia, German occupation of Latvia, Russia, philately, infrared spectroscopy, Pleskau, X-Ray fluorescence

Introduction

After the Third Reich armies invaded the Soviet Union, the necessity of a civilian organization of the occupied territories was obvious. The 17 July 1941 decree of Adolf Hitler created the Reichskommissariat Ostland (RKO). It included Estonia, Latvia, Lithuania, the northeastern part of Poland (Vilnius) and the west part of the Belarusian SSR (Byelo-Russian SSR or White Ruthenia, see Fig. 1). Each of the former states had a General kommissar assigned to it.Riga was selected as the civilian administration center with the Schleswig-Holstein's Oberpräsident and National Socialist Gauleiter, Hinrich Lohse, as the first Reichskommissar. The whole apparatus was theoretically subordinate to the Ministry of the Occupied Eastern Territories under Alfred Rosenberg, the chief National Socialist ideologist of Baltic German origin.

The postage stamps and other philatelic material of the first days of the German invasion and of what will be the future Reichskommissariat Ostland are well described and studied [1-6]. One of the authors (J.S. G.-J.) is a collector of philatelic material of the RKO and adjacent areas. From the scientific point of view and for more than one year, we have been interested in studying the composition of cellulose in postage stamps and books using infrared, Raman, XRF and SEM/EDX techniques [7-13]. As far as we know, no philatelic material of RKO and adjacent areas has been studied with similar scientific methods.

Figure 1: The Reichskommissariat Ostland

In this paper we present the results of an infrared and X-Ray fluorescence (XRF) analysis of the paper of four postcards. The first is a German postal stationery card with a ‘Hitler head’ violet stamp overprinted ‘OSTLAND’ in black, with a face value of 6 Pfennig and catalogued as P1 (Figure 1, left, S1, issued 11.1941). The second is a German postal stationery card with a ‘Hitler head’ green stamp overprinted ‘OSTLAND’ in black, with a face value of 5 Pfennig and catalogued as P2 (Figure 2, right, S2, issued 03.07.1943). P2 was intended for local use only. The actual color of the paper of both postcards seems to be white, very slightly darkened by time. These postcards were printed by German Reichsdruckerei Berlin and both were made of ordinary postcard carton. The third one is a Soviet postcard with the communist symbol covered by a set of horizontal black lines and with the 20 kopecks stamp with ‘peasant woman’ overprinted with ‘LATVIJA/1941./1. VII’ in black (Figure 3, left, S3). Considering that the Latvian postal services were placed under the control of the Generalpostkmommisar Ostland only the 1 October 1941 [2], we may consider this postcard as being an early occupation postal piece. The fourth postcard is a Soviet postcard with a 10 kopeck printed stamp overprinted with ‘Pleskau / 20 kop’ and a Pskov City Post Office CTO (Figure 3, right, S4). The Commandant of Pleskau, incapable to get a stock of stamps for the town, issued both German and Soviet stamps with the overprint ‘PLESKAU’. When the Reichspost head office in Berlin discovered that German stamps had been unlawfully overprinted, the issue was withdrawn, but a number had already gone through the post. All Pleskau stamps became invalid when German "OSTLAND" stamps were issued in May 1942. The reader may find the city of Pleskau in Fig. 1. Our efforts for finding an exact description of the color of the paper of the Russian postcards with the help of specialized color guides [14, 15] were not successful. We can describe the actual color of the postcards as 'slightly brown' or 'pale brown'.

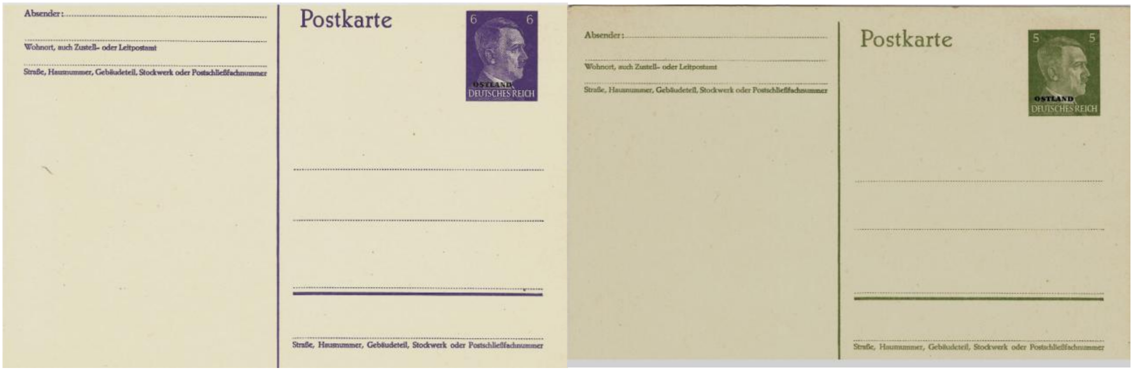

Figure 2: Postcards from Reichskommissariat Ostland. Samples S1 (left) and S2 (right).

Figure 3: Postcards from the German occupations of Latvia (sample S3, left) and Pleskau (sample S4, right)

Experimental

Methods

For infrared analysis, a small sample was taken from the left or right inferior corner of each postcard (left side for the ones in Fig. 2, right side for the ones in Fig. 3). Later, the postcards were signed by the main author (J.S. G.-J.). Infrared spectra were recorded on a Perkin-Elmer FTIR Spectrum Two coupled to a UATR unit. The sample was directly positioned over the diamond, pressed up to 30% of the total supported pressure and scanned in the range of 4000–500 cm^{-1} with a resolution of 1 cm^{-1}.

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 did not use 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. XRF measurements were carried out on the unprinted area of the postcards.

Results and Discussion

Before presenting and discussing the results we must comment of the following important point. In our previous IR studies we used the KBr technique to prepare the sample. One of the steps of this procedure consists in crushing the paper sample before mixing it with the KBr. In this way even the interior layers of the paper will be exposed. In the present study the whole sample is simply pressed without any previous process. Therefore, the resulting spectrum is likely to reflect only the composition of the paper surface. It is known that FTIR-ATR is not the best method to analyze fiber. If this is the case; these spectra should serve mainly as a preliminary identification of some characteristics of the sample. For this reason we shall assign here only those bands that correspond with theoretical frequencies from a large cellulose model calculated with Density Functional Theory (Gómez-Jeria, unpublished). Figure 4 shows the infrared spectrum of sample S1.

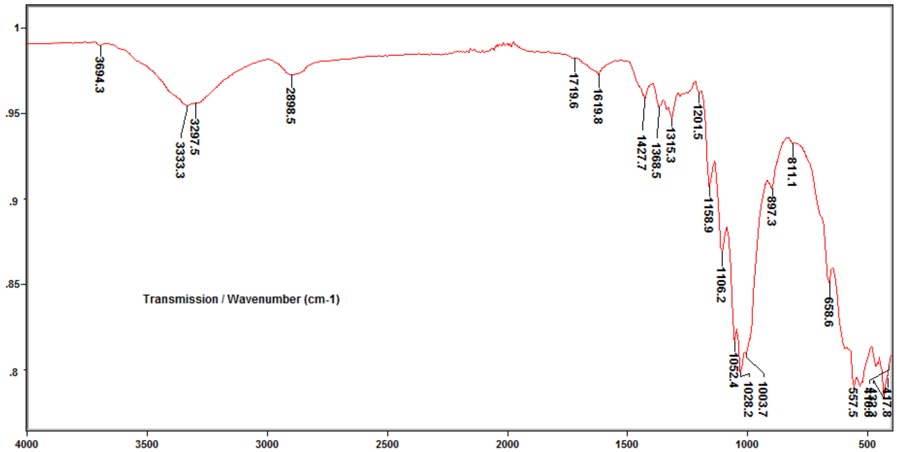

Figure 4: Infrared spectrum of sample S1

Figure 5 shows the XRF results for sample S1.

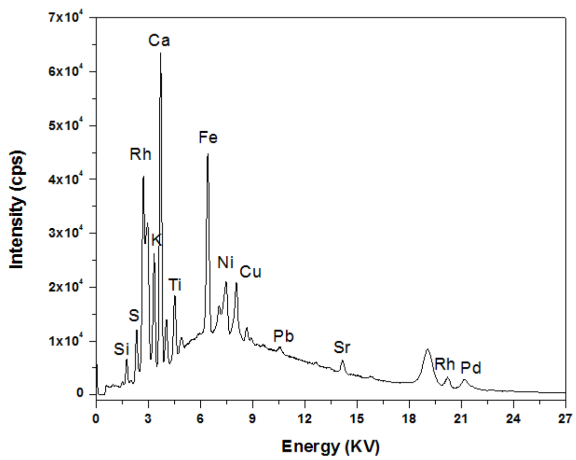

Figure 5: XRF spectrum of sample S1

The presence of calcium, apart from the fact that it is a component of the paper, can be ascribed to $CaCO_3$ and/or to $CaSO_4$. Iron is present in the basic paper and perhaps its presence is modifying the color of the postcards. The presence of copper is another source of concern. Sulfur can be associated with calcium as said before. Let us remember that metal ions such as Al(III), Cu(II), Fe(II) and Fe(III) are usually found in paper and are potent catalysts for hydrolysis and oxidation. Transition metals, particularly Fe and Cu, can play a significant role in cellulose oxidation if their concentrations are quite high. Table 1 shows the peaks of the IR spectrum of S1.

Table 1: Peaks of the IR spectrum of S1.

S. No.	Bands (cm^{-1})	Cellulose Theor. (cm^{-1})
1	432.9	432.4
2	465.5	465.4
3	530.5	n.a.
4	557.6	558.2
5	664.2	663.5

6	809.8	n.a.
7	898.1	897.5
8	1003.6	n.a.
9	1028.5	1029.4 (?)
10	1052.5	n.a.
11	1105.2	1107.2
12	1159.5	n.a
13	1280.6	1282.1 (?)
14	1315.2	1313.9, 1317.8 (?)
15	1368.4	1368.5
16	1427.8	1428.7 (?)
17	1508.4	n.a.
17	1718.6	n.a
19	2896.9	CH (?), cotton (?)
20	3333.9	Cotton (?)
21	3696.6	3689.4 (OH str.)

We can see that the bands of cellulose show only one short peak at 3696.6 cm^{-1} that could correspond to an OH stretching band. Our calculations of the IR spectrum of cellulose (Gómez-Jeria, unpublished) shows more frequencies corresponding to hydroxyl groups. The first idea to explain this fact is that almost all hydroxyl groups are below the paper's surface and that they are not 'seen' during the experimental measurement. We are designing an experiment that should restrict the possible explanations. Figure 6 shows the infrared spectrum of sample S2. Bands at 2896,8 and 3333.9 are tentatively ascribed to cotton[16], but it will be the subject of future studies.

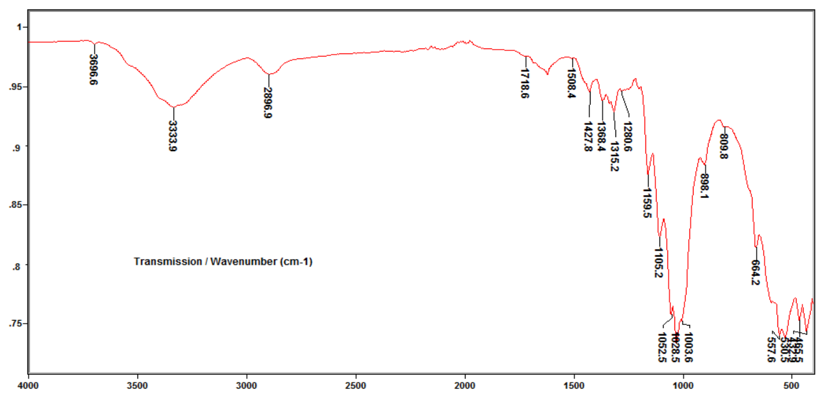

Figure 6: Infrared spectrum of sample S2

Figure 7 shows the XRF results for sample S2.

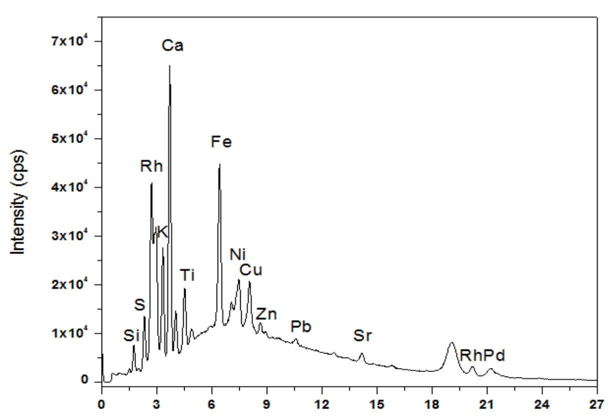

Figure 7: XRF spectrum of sample S2

We can see that the XRF spectrum of S2 is quite similar to the XRF spectrum of S1. This is because both postcards were fabricated at the same place but not at the same time. Table 2 shows the peaks of the IR spectrum of sample S2.

Table 2: Peaks of the IR spectrum of S2

S. No.	Bands (cm^{-1})	Cellulose Theor. (cm^{-1})
1	410.6	412.9
2	417.8	416.6
3	432.3	432.4
4	557.5	558.2
5	658.6	658.3
6	811.1	n.a.
7	897.3	897.5
8	1003.7	n.a.
9	1028.2	1029.4 (?)
10	1052.4	n.a.
11	1106.2	1107.2
12	1158.9	n.a.
13	1201.5	n.a.
14	1315.3	1313.9 (?)
15	1368.5	1368.5
16	1427.7	1428.7
17	1619.8	n.a.
18	1719.6	n.a.
19	2898.5	Cotton (?)
20	3297.5	n.a.
21	3333.3	Cotton (?)
22	3694.3	3689.4 (?)

Table 2 shows a series of peaks in a region of the spectrum that do not correspond to cellulose (about 1550-2900 cm^{-1}). As we said before, we shall wait for a new series of different IR measurements to try to ascribe these bands. Figure 8 shows the infrared spectrum of sample S3.

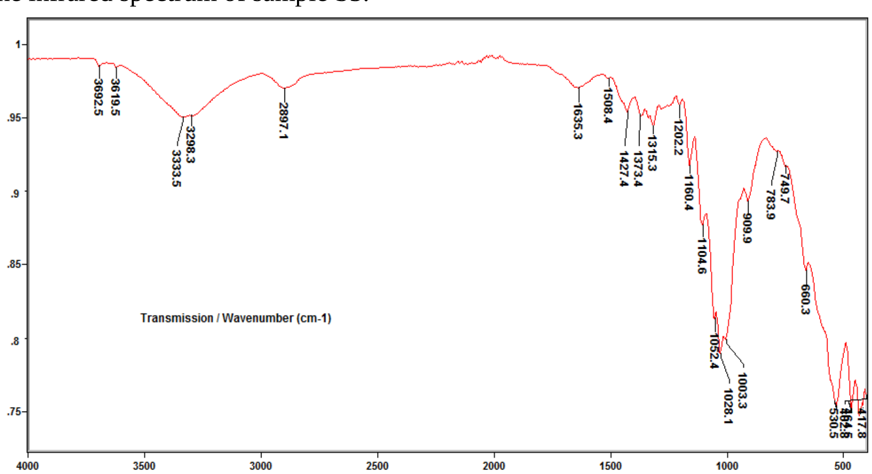

Figure 8: Infrared of sample S3

Figure 9 shows the XRF results for sample S2.

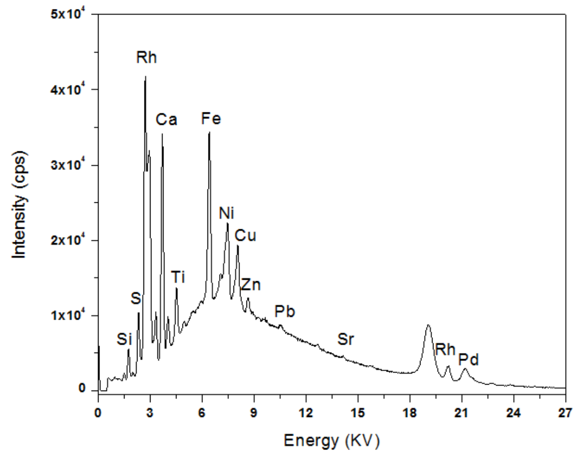

Figure 9: XRF spectrum of sample S3

This postcard and the next one were fabricated in the Communist Russia. Interestingly the XRF spectrum differs from the ones of the German postcards in that it has not potassium. This could be of help at the moment of the analysis of the IR bands that were not ascribed here. Table 3 shows the peaks of the IR spectrum of sample S3.

Table 3: Peaks of the IR spectrum of S3.

S. No.	**Bands (cm^{-1})**	**Cellulose Theor. (cm^{-1})**
1	417.8	416.6
2	464.5	465.4
3	530.5	n.a.
4	660.3	661.4
5	746.4	747.9 (?)
6	783.9	n.a.
7	909.9	907.1 (?)
8	1003.3	n.a.
9	1028.1	1029.4
10	1052.4	n.a.
11	1104.6	1103.4
12	1160.4	1162.9
13	1315.3	1314
14	1369.1	1368.5
15	1427.4	n.a.
16	1508.4	n.a.
17	1635.3	n.a.
18	2897.1	Cotton (?)
19	3298.3	n.a.
20	3333.5	Cotton (?)
21	3619.5	n.a.
22	3692.5	3689.4 (?)

We can see that the bands of Table 3 are very similar to the ones of the previous tables. Figure 10 shows the infrared spectrum of sample S4.

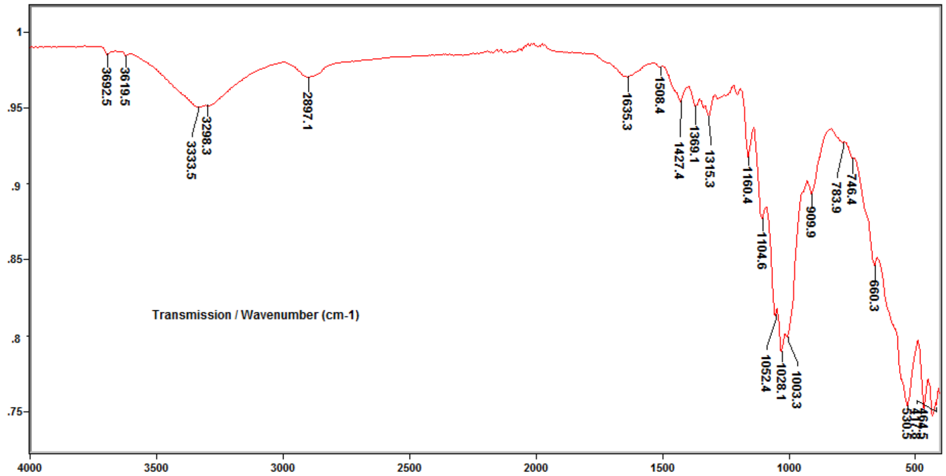

Figure 10: Infrared spectrum of sample S4

Figure 11 shows the XRF results for sample S4.

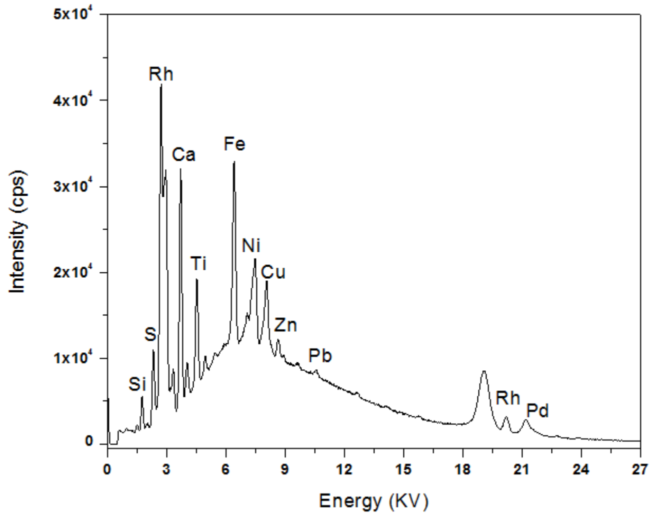

Figure 11: XRF spectrum of sample S4

Zinc could be associated with zinc white (ZnO) and lead with white lead ($2PbCO_3{\cdot}Pb(OH)_2$). Sulfur is probable associated with calcium as sulfate or carbonate. Table 4 shows the peaks of the IR spectrum of sample S3.

Table 4: Peaks of the IR spectrum of S3

S. No.	Bands (cm^{-1})	Cellulose Theor. (cm^{-1})
1	402.8	401.8
2	417.8	416.6
3	464.5	465.1
4	530.5	n.a.
5	660.3	661.4
6	749.7	n.a.
7	783.9	n.a.
8	909.9	907.1 (?)
9	1003.3	n.a.
10	1028.1	1029.4

11	1052.4	n.a.
12	1104.6	1103.4
13	1160.4	n.a.
14	1202.2	n.a.
15	1315.3	1313.9 (?)
16	1373.4	1372.6
17	1427.4	1428.9 (?)
18	1508.4	n.a.
19	1635.3	n.a.
20	2897.1	Cotton (?)
21	3298.3	n.a.
22	3333.5	Cotton (?)
23	3619.5	n.a.
24	3692.5	3689.4 (?)

This is the sample having more bands (24 against 22 and 21). In general, the four Tables present a quite similar list of bands.

In summary we have employed FTIR-ATR and XRF techniques for a preliminary characterization of four Third Reich postcards, two printed in Germany and two communist ones with German overprints. XRF results show that the four postcards contain the same elements but that the German ones contain also potassium. It is possible that the existence of iron and copper plays a main role in the future formation of foxing spots in these postcards. Regarding FTIR-ATR results we were able to assign several bands to cellulose but, considering that the FTIR-ATR technique is not the best way to analyze fiber, we have postponed the analysis of the other bands. This, because we shall prepare two or three samples in very different ways to analyze the similarity of the resulting FTIR-ATR spectra.

References

[1]. Hurt, V.; Ojaste, E. *Estonia. Philately & Postal History Handbook & Catalogue*. Göteborgs Grafiska Grupp AB: Göteborg, Sweden, 1986.

[2]. v. Hofmann, H. *Latvia; Handbook of Philately and Postal History. Latvia before and as part of the "Generalpostkommissariat Ostland" (in German and English).* Harry v. Hofmann Verlag: Hamburg, 2001; p 448.

[3]. Jankauskas, A. *Special Lithuanian Postage Stamp Catalogue (1918-2012)*. Antanas Jankauskas: vILNIUS, 2012.

[4]. Michel. *MICHEL Deutschland-Spezial. Band 1*. Schwaneberger: Unterschleißheim, 2016.

[5]. Fischer, A.; Walocha, J. *Katalog Polskich Znaków Pocztowych. Tom 2.* Katowice, 2016.

[6]. Lyapin, V. A. *The catalogue of the postage stamps of Russia 1856-1991*. Lyapin, V.A: Moscow, 2009.

[7]. Gómez-Jeria, J. S.; Gutiérrez, S.; Surco-Luque, J. C.; Olivos-Núñez, G. Raman characterization of the paper of a 1588 Spanish book. *Chemistry Research Journal* 2018, 3, 135-144.

[8]. 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.

[9]. 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.

[10]. 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.

[11]. 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.

[12]. 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.

[13]. Gómez-Jeria, J. S.; Clavijo, E. A preliminary infrared study of the cellulose of some world stamps. *Chemistry Research Journal* 2017, 2, 191-197.

[14]. Michel. *Michel-Farbenführer : [inklusive Lochschablone]*. Schwaneberger Verlag: Unterschleissheim, 2011.

[15]. Rogondino, M.; Rogondino, P. *Process Color Manual: 24,000 CMYK Combinations for Design, Prepress, and Printing*. Chronicle Books: San Francisco, USA, 2000.

[16]. Vahur, S.; Teearu, A.; Peets, P.; Joosu, L.; Leito, I. ATR-FT-IR spectral collection of conservation materials in the extended region of 4000-80 cm–1. *Analytical and Bioanalytical Chemistry* 2016, 408, 3373-3379.