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A Qualitative Infrared and Scanning Electron Microscopy Study of the Margins of Fourteen World Postage Stamps.

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ABSTRACT

Fourteen heavily damaged postage stamps were chosen for an infrared and scanning electron microscopy (SEM) characterization of their non-printed margins. The results show the presence of kaolinite used as filler in all but two samples. These last two contain aluminum (with an Al-OH moiety). One stamp seems to contain barium in the form of sulfate. One stamp contains lead in an unknown chemical compound. All these results were incorporated into a database for future analysis. Quantum chemical calculations of diverse large models of cellulose seem absolutely necessary for the IR band assignments.

Keywords: Philately, infrared spectroscopy, cellulose, archeology, postage stamps, scanning electron microscopy, kaolinite

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INTRODUCTION

Postage stamps, when they become useless from all points of view, constitute a group of objects that can still be studied scientifically using sometimes destructive means without anyphilatelic ethical concerns. Stamps have been analyzed with several non-invasive techniques [1-12]. In our laboratories we initially began to analyze only the margin (the non-printed area) of postage stamps [13-15] and continued with the analysis of the paper of some books [16, 17]. Recently one of us (J.S. G.-J.) obtained a small set of stamps that were in a state of such deterioration that it rendered them useless as a collecting items. In all of them the colored ink(s) were almost gone, some lackedpart of the paper parts and others were folded or had holes. Instead of disposing of them we decided to give them a last use. Therefore, and continuing with our line of research, we here present the results of an infrared (IR) and scanning electron microscopy (SEM)study of their margins. The results will contribute to a growing database of IR results.

EXPERIMENTAL

Figs. 1-3 show, respectively, reference photos of samplesS1-S5, S6-S10 and S11-S14. Table 1 presents some information about them.

Figure 1: Samples S1-S5.

Figure 2: Samples S6-S10.

Figure 3: Samples S11-S14.

Table 1: Information about the samples

Sample	Country	Year	Scott	Original color
S1	Brazil	1893	111	Rose
S2	Western Australia	1890-93	62	Carmine rose
S3	Czechoslovakia	1918-19	4	Bluish green
S4	São Tomé e Príncipe Islands - Portugal	1869-75	2 (II)	Yellow
S5	Inhambane – Mozambique - Portugal	1903	15	Gray
S6	Yugoslavia – Slovenia	1919	3L2	Green
S7	Mozambique – Portugal	1886	62	Violet
S8	Spain	1882	252a	Reddish orange
S9	Austria	1890-96	54	Rose
S10	Portuguese Congo	1898-1903	14	Yellow
S11	Angola – Portugal	1893-94	25	Yellow
S12	Spain	1879	249	Bright rose
S13	Philippines – Spain	1880-88	86	Bright rose
S14	Cuba – Spain	1871	52	Gray green

All the samples are postage stamps. Sample S1is a stamp from Brazil and displays the head of a Liberty effigy symbolizing freedom. Sample S2 is a stamp from Western Australia (WA), a state occupying the entire western third of Australia and one of the six colonies that united on January 1, 1900 to form the Commonwealth of Australia. It depicts a swan (the black swan is the official state emblem of WA). Sample S3 is a stamp from Czechoslovakia. It depicts Prague Castle with the sun symbolically rising behind it symbolizing the birth of the new state. Unhappily, the sun does not actually rise behind the castle. Sample S4 is a stamp from St. Thomas & Prince Islands, a Portuguese colony until 1975. It depicts the Portuguese Crown. Sample S5 is a stamp from Inhambane, a district of Portuguese Mozambique. It depicts a portrait of King Carlos “The Martyr” (he was assassinated in 1908). S6 is a stamp from Slovenia, then a federal state of the new Kingdom of Yugoslavia. It depicts an allegorical representation of "breaking the chains of bondage". These provisional stamps exist in many shades. S7 is a stamp used in Mozambique (also called Portuguese East Africa). It depicts King Carlos. S8 is a stamp from the Kingdom of Spain depicting King Alfonso XII. S9 is a stamp from the Austro-Hungarian Empire and depicts Emperor Franz Josef I. S10 is a stamp from Portuguese Congo depicting King Carlos. S11 is a stamp from the Portuguese colony of Angola and depicts King Carlos. S12 is a stamp from Spain and depicts King Alfonso XII. S13 is a stamp from the Spanish colony of the Philippines. It depicts King Alfonso XII. S14 is a stamp from the Spanish colony of Cuba. It depicts a symbolic representation of “*España*”.

The stamps were washed in deionized water (DW) for 6 hours to remove possible remains of the gum, dirt and/or hinges. Next, they were rinsed abundantly with DW and placed on an inert surface to dry. The process was repeated three times.IR and SEM studies were performed on the clean margins of samples that were obtained by cutting the outer edge of the stamps avoiding cancellation marks. As in our previous work, the IR spectra were recorded with a Perkin Elmer Systems 2000 spectrophotometer. The standard technique of disk pressing in KBr was employed for the samples. Briefly, 0.5-1.0milligrams of sample and 80-100 mg of IR grade KBr were used. The mixture was submitted to a pressure of 15 t /cm^2 for 30 seconds to form a 13 mm diameter disk. The SEM analysis was performed with a JCM-6000 NeoScope Bench top apparatus. An electron beam with variable energy of 5, 10 or 15 keV was used to scan the sample under a vacuum of 10^{-2} Pa. The analyzed area can be varied in the range from about 22 mm^2 (magnification 22x) down to 12 µm^2 (magnification 30000x). The reflected backscattered electrons were collected with a detector yielding the morphology picture (SEM). In the “mapping” mode the distribution of the elements within the sample is presented.

RESULTS

SEM results

Figures 4 to YY show the SEM results.

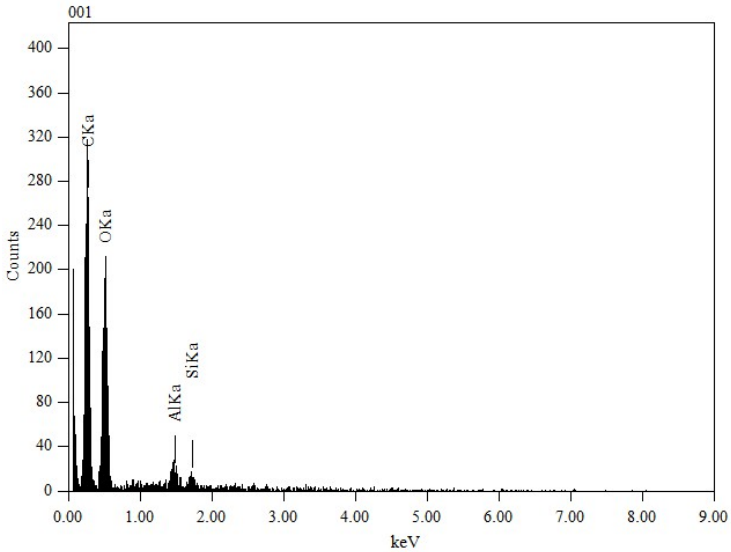

Figure 4: SEM results for S1.

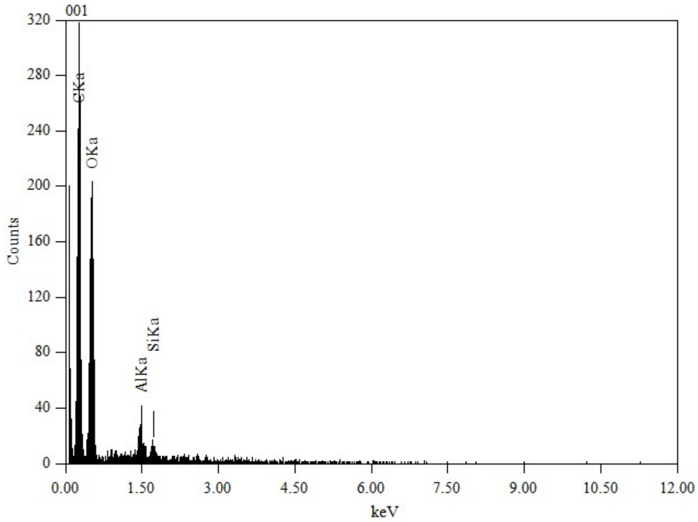

Figure 5: SEM results for S2.

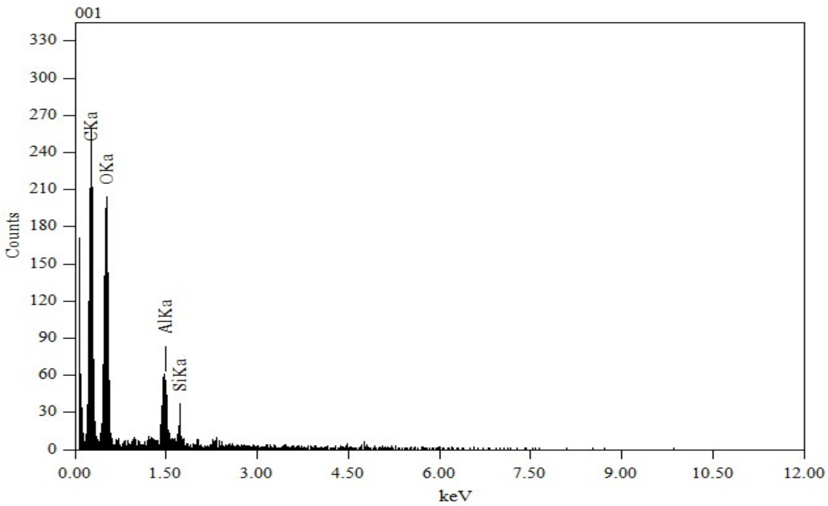

Figure 6: SEM results for S3.

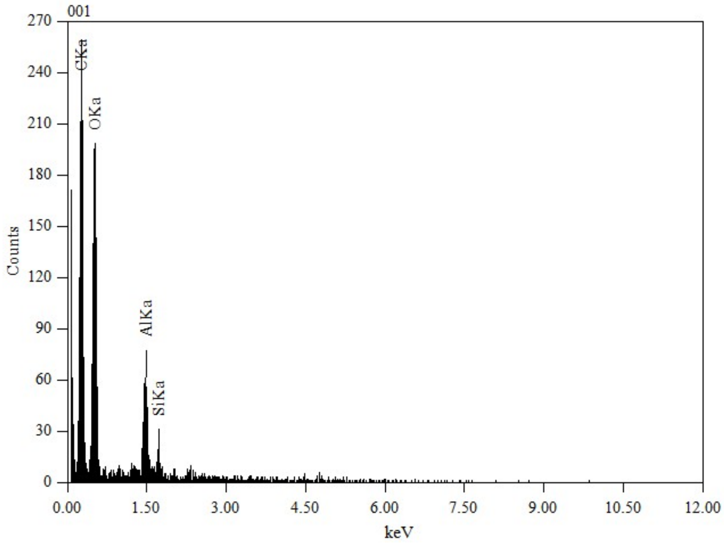

Figure 7: SEM results for S4.

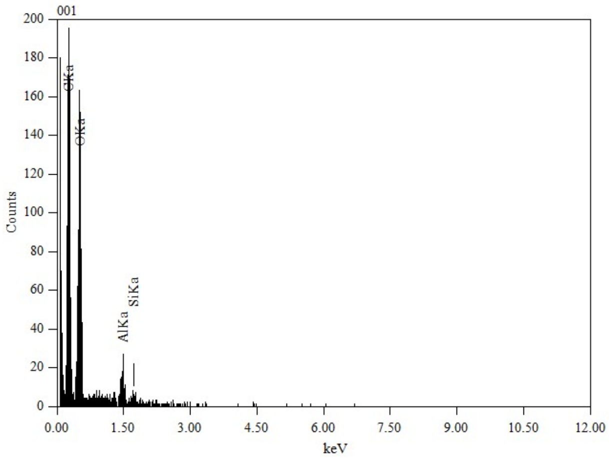

Figure 8: SEM results for S5.

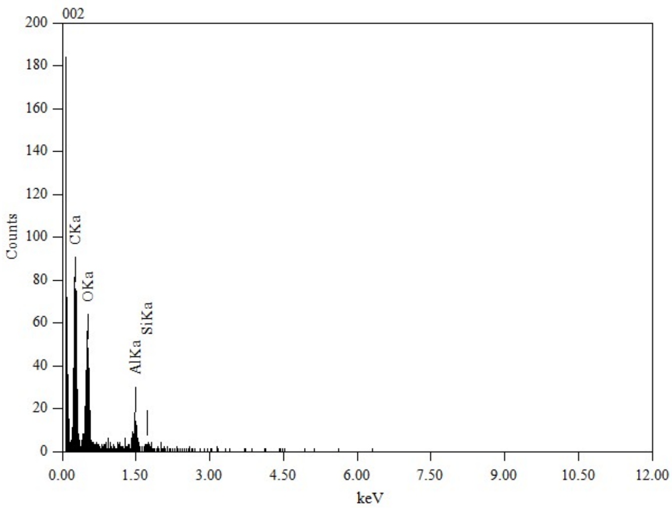

Figure 9: SEM results for S6.

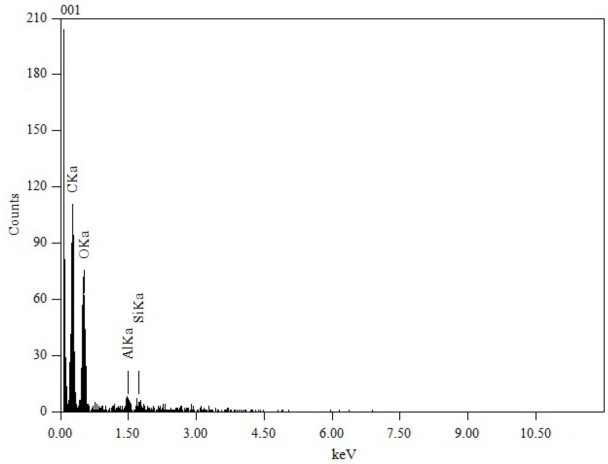

Figure 10: SEM results for S7.

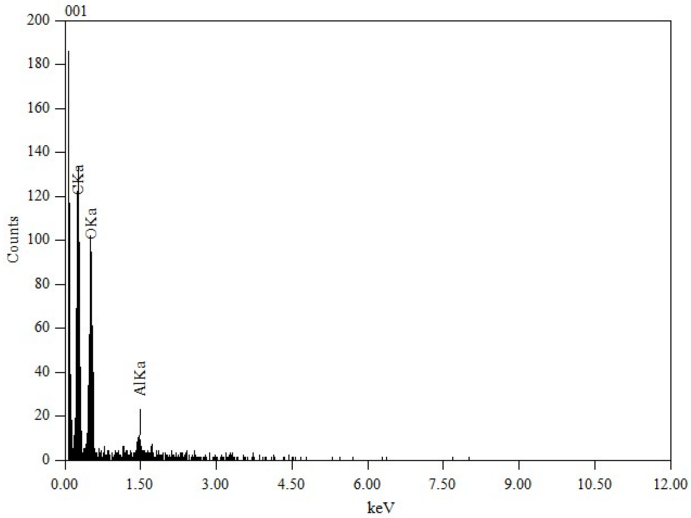

Figure 11: SEM results for S8.

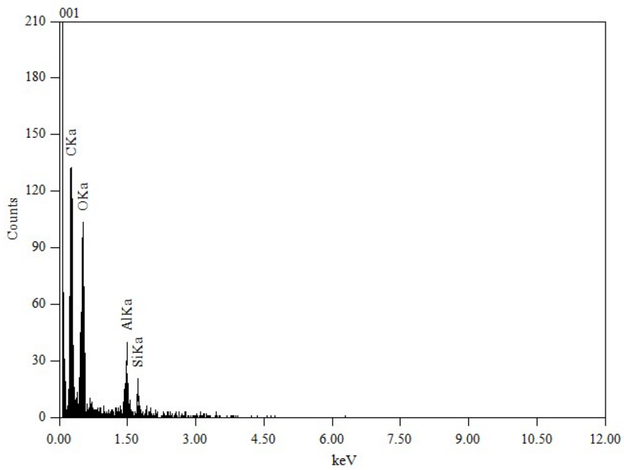

Figure 12: SEM results for S9.

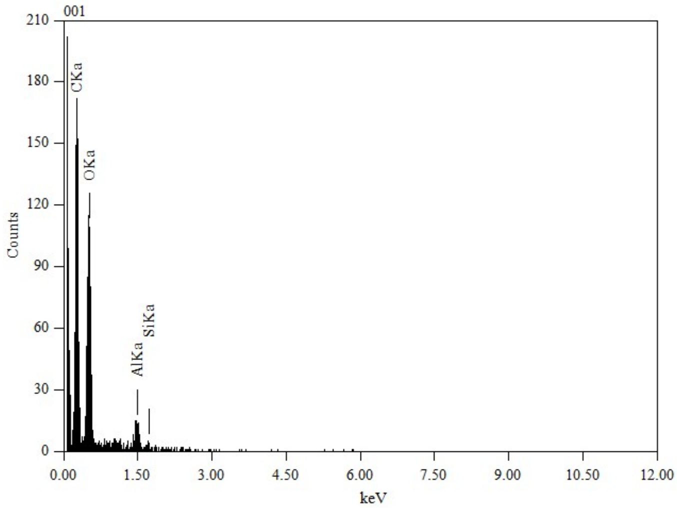

Figure 13: SEM results for S10.

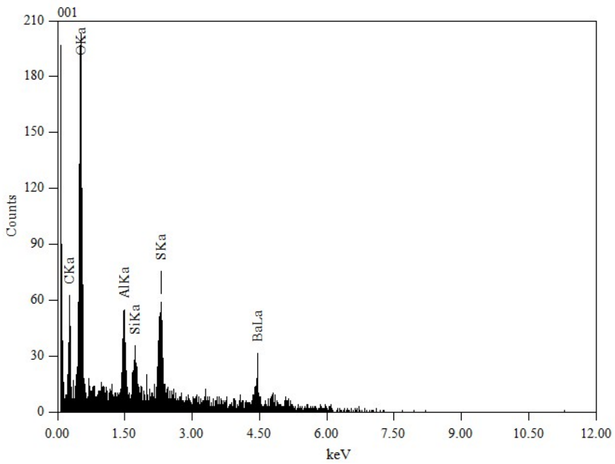

Figure 14: SEM results for S11.

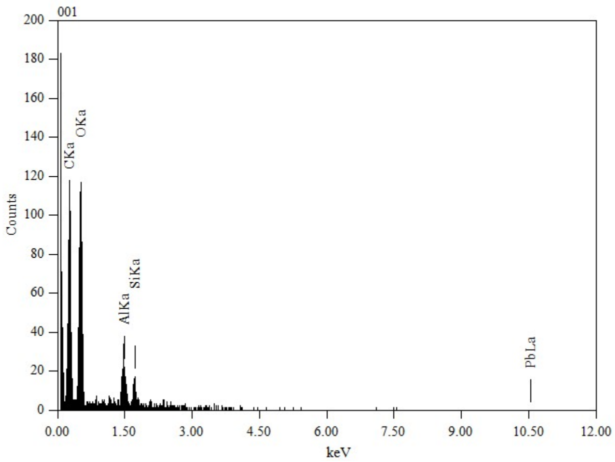

Figure 15: SEM results for S12.

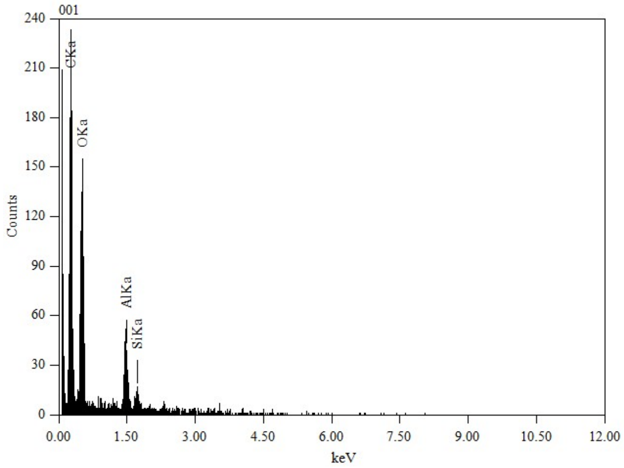

Figure 16: SEM results for S13.

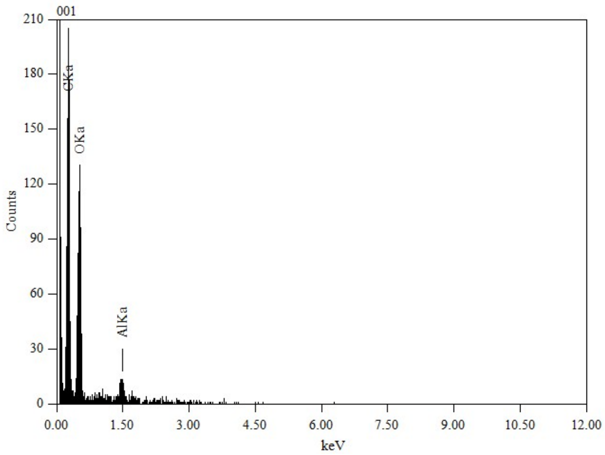

Figure 17: SEM results for S14.

Infrared results

Figures 18 to 31 show the IR spectra of S1-S14.

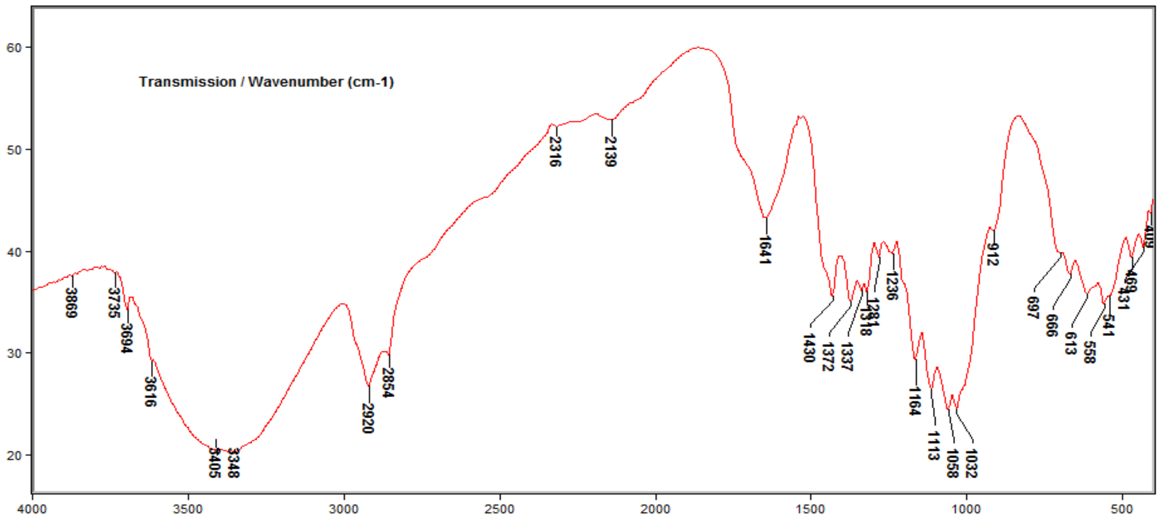

Figure 18: IR spectrum of S1.

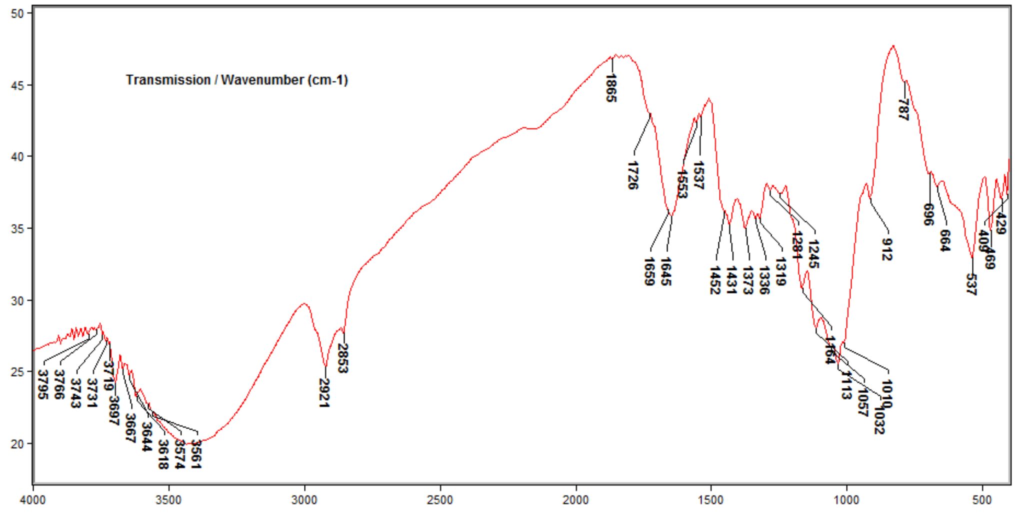

Figure 19: IR spectrum of S2.

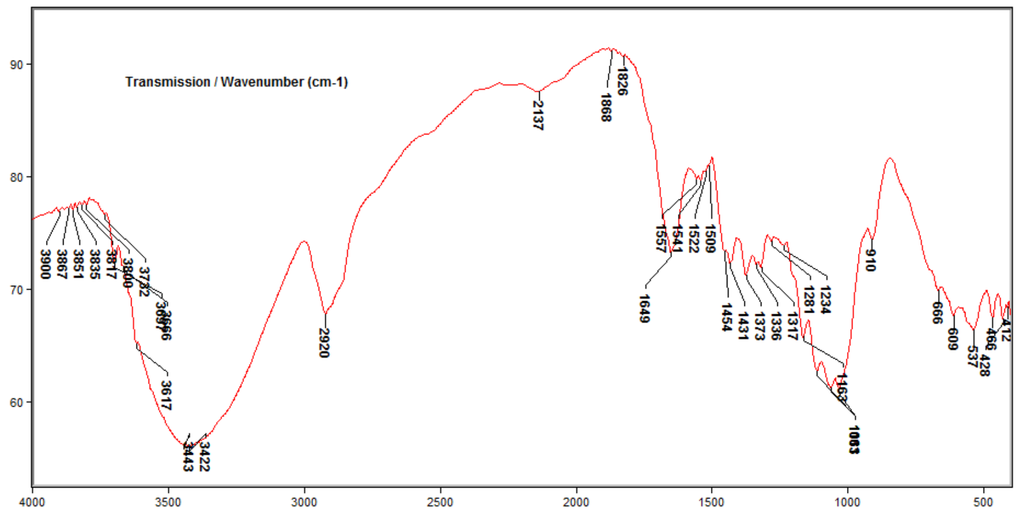

Figure 20: IR spectrum of S3.

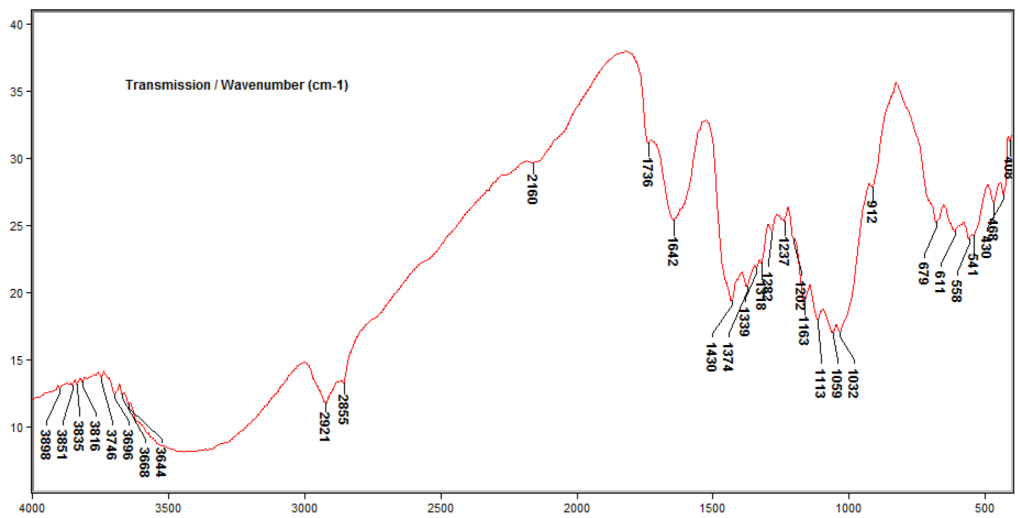

Figure 21: IR spectrum of S4.

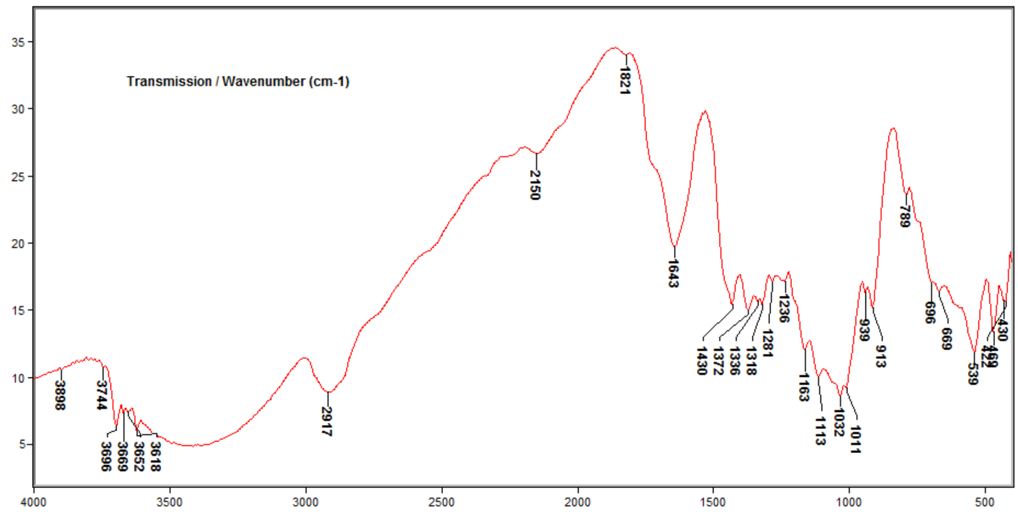

Figure 22: IR spectrum of S5.

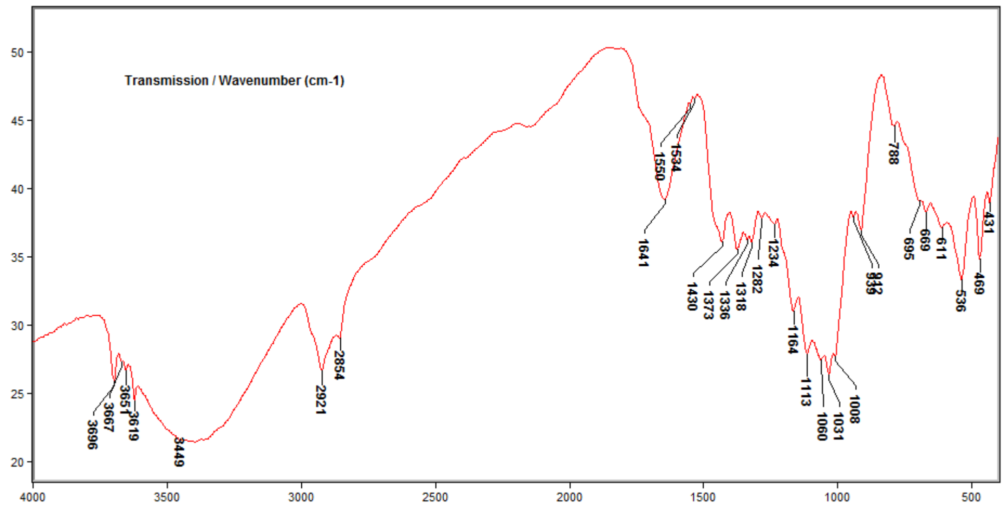

Figure 23: IR spectrum of S6

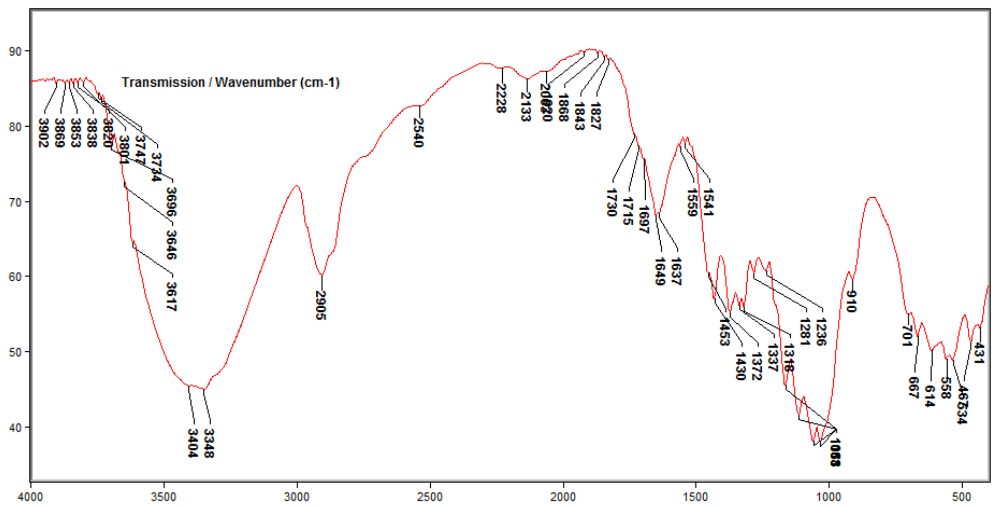

Figure 24: IR spectrum of S7.

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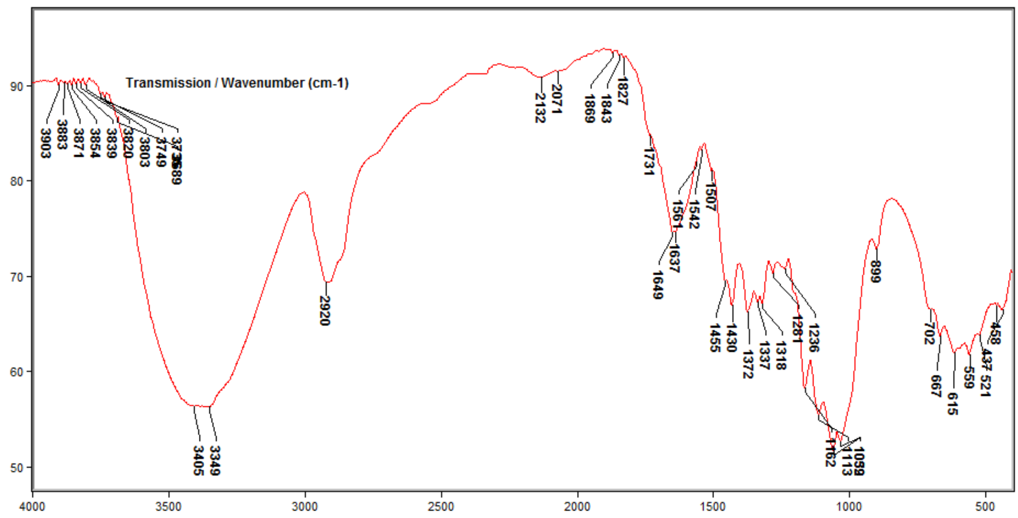

Figure 25: IR spectrum of S8

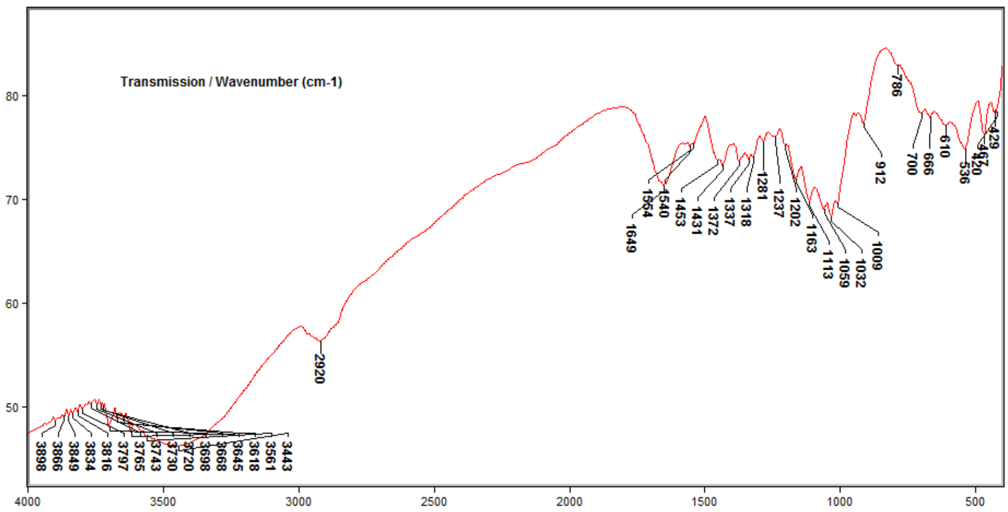

Figure 26: IR spectrum of S9.

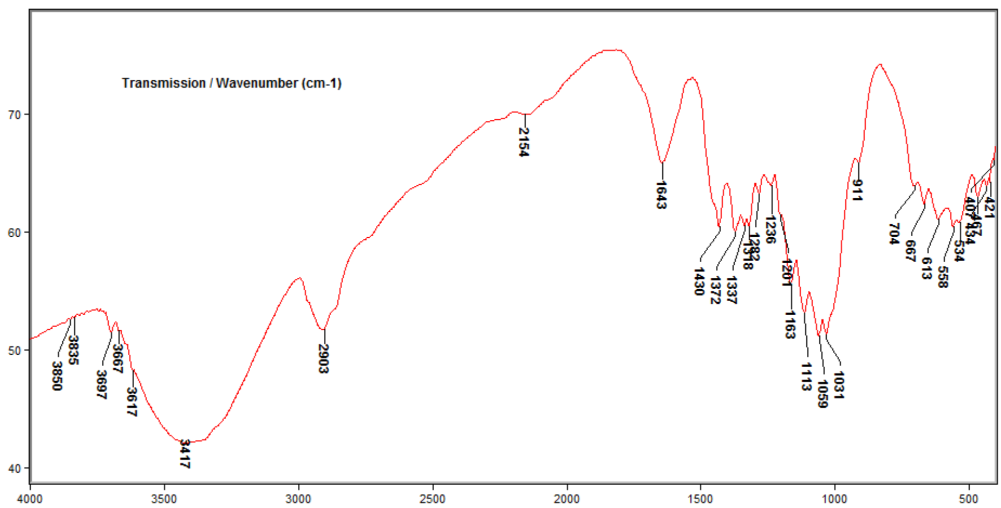

Figure 27: IR spectrum of S10.

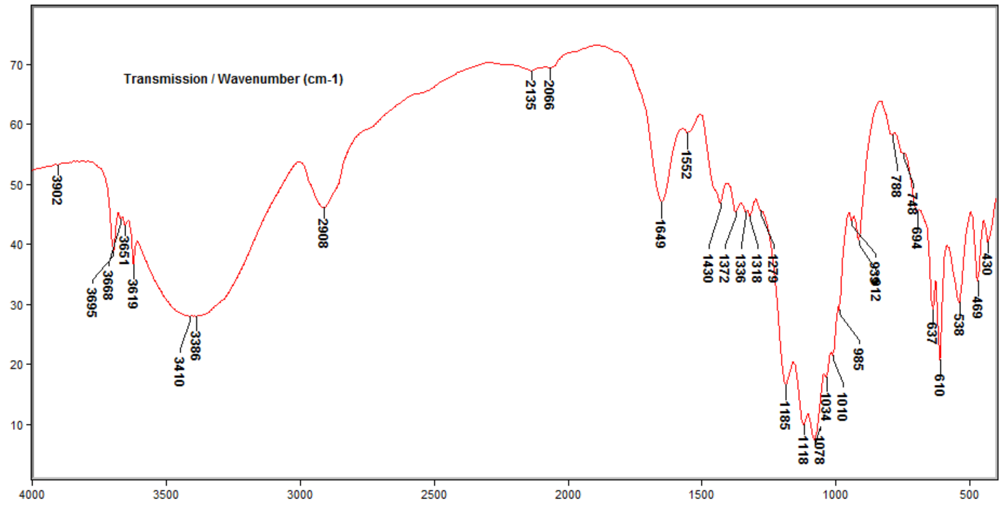

Figure 28: IR spectrum of S11.

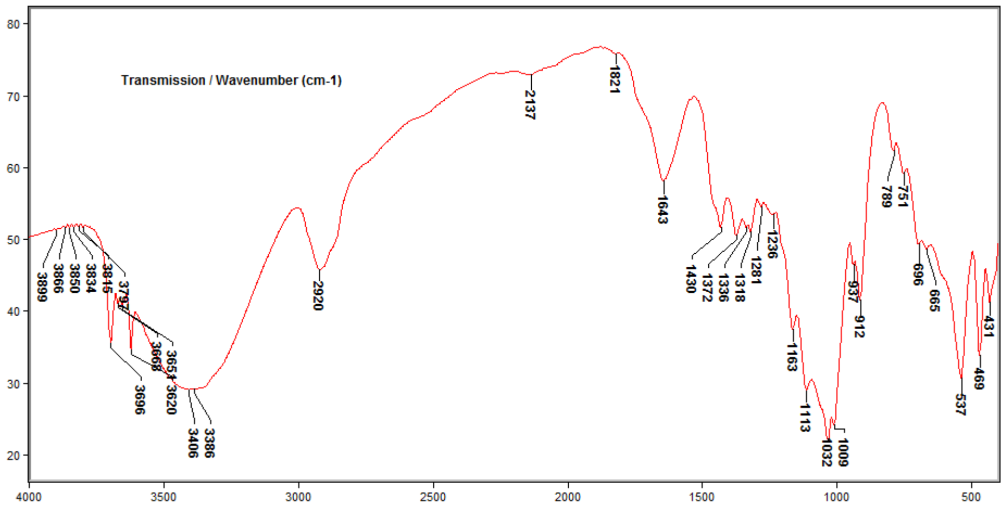

Figure 29: IR spectrum of S12.

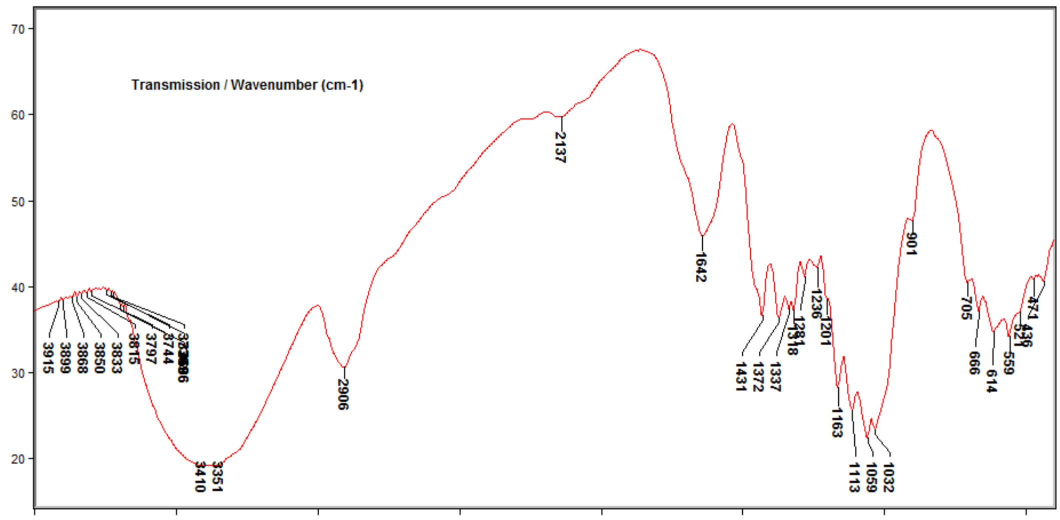

Figure 30: IR spectrum of S13.

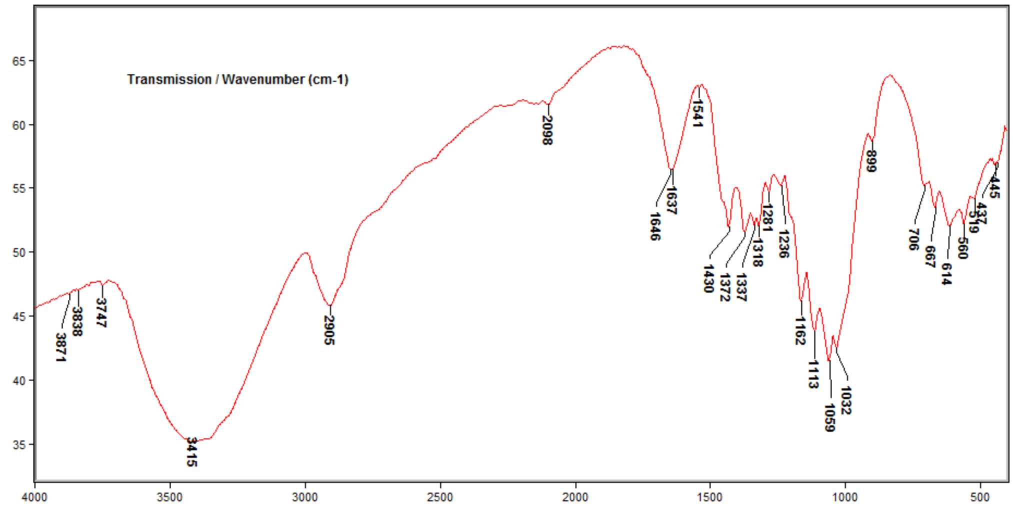

Figure 31: IR spectrum of S14.

DISCUSSION

We began by verifying the presence of kaolinite used as filler. Using only the SEM results we assumed that the presence of the Al/Si couple was an almost sure indicator of kaolinite presence. This suggested that samples S1-S7 and S9-S13 could contain kaolinite. Table 2shows the SEM results grouped by elements found on the samples.

Table 2: SEM results

Element(s)	Sample(s)	Suggestion
Al, Si	S1-S7, S9, S10, S13	Kaolinite
Al	S8 (Spain, 1882), S14 (Cuba, Spain, 1871)	Al_2O_3 or $Al(OH)_3$
Al, Si, S, Ba	S11 (Angola, Portugal, 1893-94)	Kaolinite, $BaSO_4$ (?)
Al, Si, Pb	S12 (Spain, 1879)	Kaolinite, ($2PbCO_3 \cdot Pb(OH)_2$)

The assignments for kaolinite were made accordingly to our previous work [13-15].

Table 3: IR bands suggesting the possible presence of kaolinite

Sample	IR band(s) (cm^{-1})
S1	3516.5, 3694.7, 912.51, 1032.3, 1113.5
S2	3618.5, 3667.9, 3697.6, 537.0, 912.6, 1032.5, 1114.0
S3	3617.7, 3666.8, 3697.2, 537.8, 1031.8, 1113.01
S4	3616.3, 3668.4, 3696.7, 912.9, 1032.5, 1113.7
S5	3618.9, 3652.4, 3669.5, 3696.3, 913.2, 1032.6, 1113.9
S6	3619.4, 3667.9, 3996.8, 536.5, 1008.7, 1031.6, 1113.3
S7	3617.6, 3696.6, 534.6, 1032.0, 1113.5
S9	3618.4, 3668.8, 3698.3, 536.7, 912.5, 1032.5, 1113.9
S10	3617.4, 3667.5, 3697.6, 911.2, 1031.9, 1113.9
S11	3620.0, 3668.4, 3695.4, 912.7, 1034.4, 1118.8 (?)
S12	3620.2, 3669.0, 3696.2, 537.7, 912.6, 1032.5, 1113.6
S13	3696.7, 1032.7, 1113.5

Three samples contained only Al (S8 and S14). It is probably aluminum oxide that was used as filler [18]. Employing the same reasoning used in our work on German and Estonian postage stamps, we searched for IR bands associated with Al-OH.

Table 4: Some bands possibly associated with Al(OH)x.

Sample	Bands (cm^{-1})
S8	3735.5, 3749.3(?), 3689.6
S14	3733.9, 3799.6

What seems to be interesting is the fact that the papers of two Spanish stamps, dated 1871 and 1882 do not contain kaolinite. One is from the metropolitan territory and the other from Cuba, then a Spanish colony. We suggest that the original chemical was Al_2O_3 employed as filler, but this question is still open. Anyway, the paper used to print them seems to have been prepared differently or to have come from different sources. Lead white ($2PbCO_3 \cdot Pb(OH)_2$), suggested in Table 2 for S12, is discarded due to the absence of the corresponding IR bands (3534, 2916, 2849, 1729, 1541, 1397, 1364, 1045, 891, 853, 833, 762, 691 and 678 cm^{-1}, http://lisa.chem.ut.ee/IR_spectra/paint/pigments/lead-white/).The absence of IR bands related to Pb-O-H bending and Pb-O stretching excludes lead oxides or hydroxides [19]. In the case of sample S11 the presence of the sulfate ion is attested by the presence of the following IR bands [20, 21]:1649.3, 1185.3, 985.4, 637.3 and 610.5 cm^{-1}.

The assignment of cellulose bands was done as before. We searched for the IR bands around1158, 1106, 1055, 1030 (all C-O stretching), 1647 and 1546 cm^{-1} (primary and secondary amide bands from protein glue), 1025 and 3330 cm^{-1}, 1158, 1111, 1061, 1036 and 3346 cm^{-1} [5, 7, 22, 23]. Table 5 shows the results.

Table 5: Possible IR bands of cellulose

Sample	IR band(s) (cm^{-1})
S1	1032.3, 1058.7, 1113.5, 1641.2 (?), 3348.3
S2	1032.5, 1057.5, 1114, 1645.7
S3	1031.8, 1061.3, 1113, 1649.7
S4	1032.5, 1059.4 (?), 1117.7, 1642.5 (?)
S5	1032.6, 1113.9, 1643.3, 3298.8
S6	1031.6, 1060.5, 1113.3, 1550.8 (?), 1641.5 (?), 3349.1
S7	1032, 1058.7, 1113.5, 1541.3 (?), 1649.4, 3348.6
S8	1032.6, 1059.4, 1113.1, 1162.8 (?), 1649.3, 3349.5
S9	1032.5, 1059.3, 1113.9, 1163.5 (?), 1649.5, 3443.2
S10	1031.9, 1059.4, 1113.9, 1163.7 (?), 1643.4
S11	1034.4, 1118.8 (?), 1649.3
S12	1032.5, 1113.6, 1163.4 (?), 1643.5
S13	1032.7, 1059.5, 1113.5, 1163.5 (?), 1642.4 (?), 3351.2 (?)
S14	1032.6, 1059.7, 1113.7, 1162.7 (?), 1541.1 (?), 1646.3,

The results of Table 5 are similar to previous studies. Theoretical calculations of the IR spectra of different large cellulose molecular models are needed for future assignments of the bands.

In summary, by employing infrared and scanning electron microscopy techniques we have characterized the non-printed area of fourteen world stamps. Twelve of them contained kaolinite. One seems to contain barium sulfate. Two Spanish postage stamps contain aluminum including possibly Al-OH bonds. One stamp contains lead in the form of an unknown chemical compound.

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