ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

An Infrared and SEM study of the Margins Of Some Estonian Postage Stamps.

Juan S Gómez-Jeria[1, 2]*, Ernesto Clavijo[1], and Sebastián Gutiérrez[3]*.

[1]Department of Chemistry, Faculty of Sciences, University of Chile. Las Palmeras 3425, Santiago 7800003, Chile
[2] Chilean Philatelic Society,Almirante Simpson 075, Providencia, Santiago, Chile
[3]Instituto de Alta Investigación, Laboratorio de Análisis e Investigaciones Arqueométricas, Universidad de Tarapacá, Antofagasta 1520, Arica, Chile.

ABSTRACT

Infrared spectroscopy and scanning electron microscopy (SEM) studies were performed on the margins of a set of eighteen Estonian postage stamps dated between 1918 and 1924. SEM results showed the presence of Al, Si and Zn in the samples in different combinations.Two stamps contain kaolin and one ZnO. We could not find a clear relationship between the structure of the IR spectrum and the assumed geographical origin of the papers, but the need to accumulate a large set of results to use statistical methods is clear.
Keywords: Cellulose, postage stamps, infrared spectra, archeology, archeophilately, SEM, Estonia, scanning electron microscopy, philately.

Corresponding author

ISSN: 0975-8585

INTRODUCTION

Estonia (Eesti) is one of the three Baltic states together with Latvia (Latvija) and Lithuania (Lietuva). Its territory has been inhabited for at least 11,000 years. Ancient Estonians were among the last Europeans believing in what is called paganism (a pejorative term used by the followers of any one of the Abrahamic religions), and were christianized during a crusade in the 13th century [1-4]. After centuries ofDanish, German, Russian and Swedish rule, Estonians gained independence from the Russian Empire on February 24,1918,later secured through a War of Independence [5]. In 1920 a peace treaty was signed with Bolshevik Russia. After a period of liberal bourgeois democratic government from 1918 to 1934, Prime Minister Konstantin Pats established his authoritarian rule[6, 7]. In 1939, the Soviet Union forced Estonia to accept Soviet military bases, during June 1940 Soviet troops entered Estonia and in August of the same year Estonia was incorporated into the Soviet Union. About 10,000 people were deported from Estonia during 14-17 June 1941, including almost 7,000 women, children and elderly people. The extent of this genocide is indicated by the fact that more than 25% of all the people deported in June 1941 were minors (less than 16 years old). In June 1941, German troops entered Estonia and expelled the Bolsheviks (during the year 2004, veterans of the 20th Estonian Waffen SS division paraded through Tallin, attended a church service, lay flowers at a war memorial and attended a celebratory concert). Many Estonians fought together with the Germans in what was called the Crusade against Bolshevism [8]. During 1944 Estonia was re-annexed by the Soviet Union and tens of thousands of Estonians were killed or deported to Siberia and Central Asia [9]. For example, on March 25, 1949, a massive deportation occurred when over 20,000 people (near 2.5% of the 1945 Estonian population), were apprehended in a few days and dispatched to remote areas of Siberia. These deportations have been declared crimes against humanity by the European Parliament and the European Court of Human Rights. Anti-Soviet resistance lasted until the mid-1950s. The Soviet Union began arussification process, with hundreds of thousands of Russians being induced to settle in Estonia [10]. In the midst of the disintegration of the Soviet regime, and during the coup attempt in Moscow, Estonia declared the restoration of its independence on August 20, 1991. The Estonian Postal Administration considers the date of appointment of Hindrek Rikand as Director of the Tallinn Post and Telegraph Office as its organizational founding day. Postage stamp use began in independent Estonia when the two first stamps were issued on November 24, 1918.

In our first research on postage stamps, the infrared (IR) spectrum of some world stamps was recorded to study the cellulose [11]. In another study, we employed IR spectroscopy and scanning electron microscopy (SEM) to study the margins (the area without printed colors) of a set of German postage stamps dated 1923 [12]. In this paper we have used IR spectroscopy and SEM techniques to study the margins of a set of Estonian postage stamps. The main goal was to obtain information about cellulose and fillers/sizers. A long-range and secondary objective is to try to accumulate IR data about the different kinds of papers used in Europe for stamp printing during the 19thcentury and the first quarter of the 20th.

MATERIALS AND METHODS

Eighteen Estonian stamps were selected from a larger set of stamps with medium to severe physical damage. Figure 1 shows good quality exemplars for the sake of clarity (from J.S. G.-J's collection).

Figure 1: Estonian postage stamps. From left to right and top to bottom: S1, S2, S3,..,S18.

A specialized catalogue was consulted to guarantee that no interesting varieties existed within the set [13, 14]. The first two stamps, S1 and S2, were issued in November 1918, having the nominal values of 5 (four printings) and 15 kopecks (five printings). A flower design was printed on both (1 and 2 in Fig. 1).White, smooth paper of fairly good quality of Finnish origin was used. Occasionally the paper absorbs the gum and adopts a yellowish look. The colors have frequently faded throughout the years. In the case of the 5 kopeks stamp, it is reported that the following paper varieties exist: rose-greyish white paper, rose-lilac rose paper (printed on the back of cinema tickets) and black-greenish blue paper (printed on the back of cinema tickets). For the case of the 15 kopeks stamp, black-cigarette paper, black-greenish blue paper and blue-lilac rose (cinema tickets) are reported.S3 corresponds to aviolet or black hand stamped overprint '*Eesti Post*' on Russian stamps of Arms type in provisionally issued at Tallin.As these stamps are relatively expensive and forgeries of the overprint abound, we used the original Russian stamp (stamp 3).Stamps S4 and S5 have a numeral design printed. For the 5 pennistamp we find three printings with different paper thickness. There were two printings of the 10 penni stamp which shows little variation in paper thickness but a 0.07-0.08 mm thick paper exists. Stamp S6 (15 p, 6 in Fig. 1) has a Sun design printed on a white, very thin (cigarette) paper. Some exemplars exist printed on patched paper. Stamps S7 and S8have a seagull printed on them and with face values of 35 and 70 penni respectively. There were several printings of the 35 penni stamp. Smooth white paper was used but exemplars printed on silk paper, thinner paper and paperboard are known. In the case of the 70 penni stamp, thin (cigarette) paper was used. The thickness can vary slightly. In the later printings the paper may be bluish. Stamp S9 has a Viking ship printed on it and a face value of 5 marka. Two printings exist. For the first one, white paper was employed. It has a harder surface and a different degree of silkiness. In the case of the second one a soft, porous and dirty grey paper was used. Stamp S10 (Fig. 1) has the Viking ship printed on it, but a face value of 25 marka. The same paper that was used for the second printing of stamp 9 was used here. Stamps S11 to S14 bear a panorama of Tallinn. The face values analyzed here are 25 penni (stamp S12), 35 penni (stamp S13), 1 mark (stamp S14) and 2 marka (stamp S15).For the 25, 35 and 1 mark penni stamps, white and very thin (cigarette paper) and thicker papers were used. In the case of the 2marka stamp, white and very thin, thicker and thicker greyish papers were used. Stamp S15, showing a weaver, has ½ mark as face value. They were printed on Ligat paper (a 0.06-0.07 mm semi-transparent paper with smooth surface). Stamps S16 and S17 were issued to benefit the invalids of the War of Independence against Bolshevism. They were printed on soft and porous paper, dirty grey in color. Stamp S18 was a charity issued to benefit the Estonian Red Cross. A stiff white paper with a vertical or horizontal mesh pattern of thin and short lines was used. All stamps but 3, 4 and 5 were imperforate. Table 1 provides some extra data, such us the paper thickness without gum, color and probable origin of the paper.

Table 1: Data about Estonian stamps studied here

S	Facial value	Scott	Date	Color, paper thickness without gum (mm), paper origin.
S1	5k	1	1918	Pale red, imperforate, 0.04, paper of Finnish origin, four printings.
S2	15k	2	1918	Bright blue, imperforate, 0.05, paper of Finnish origin, five printings.
S3	3k	23	1919-05-07	Red, 0.04, stamp of Russian Empire.
S4	5p	29	1919-05-15	Orange, 0.05, three printings.
S5	10p	30	1919-10-08	Green, 0.05, two printings.
S6	15p	31	1919-09-17	Rose, 0.03, also printed on patched paper.
S7	35p	32	1919-07-04	Blue, 0.04, a few stamps are known to have been printed on Räpina paper.
S8	70p	33	1920-02-13	Dull violet, 0.02.
S9	5Mk	35	1919-09-01	Yellow & black, 0.06, paper from the factory in Räpina.
S10	25Mk	37	1920-09-09	Ultramarine & black brown, 0.05, paper from the factory in Räpina.
S11	25p	39	1920-24	Green, 0.02.
S12	35p	41	1921	Rose, 0.02
S13	1Mk	43	1920-24	Vermilion, 0.02
S14	2Mk	44	1920-24	Blue, 0.02
S15	½ Mk	65	1923	Orange, 0.04, papers from Latvia and Germany.
S16	35p+10p	B1	1920	Red & olive green, 0.05, paper from the factory in

				Räpina.
S17	70p+15p	B2	1920	Deep blue & brown, 0.05, paper from the factory in Räpina.
S18	2½ (3½)Mk	B5	1921	Orange brown & carmine, 0.04, paper is probably a product of the Latvian Ligat Mills.

The samples were washed carefully with deionized water to remove gum, other soluble material, and dust. IR and SEM studies were carried out in the same way and with the same equipment used in our study of hyperinflation German stamps. We refer the reader to this paper [12].

RESULTS AND DISCUSSION

Appendices A and B show, respectively, the IR spectra and the SEM results of the samples. The SEM results are summarized in Table 2.

Table 2: SEM results

Element(s)	Samples	
Al	S1, S2, S4-S9, S11-S18	Al_2O_3?
Al, Si, Zn	S3	Kaolinite, ZnO
Al, Si	S10	Kaolinite

We have suggested that unaccompanied Al possibly corresponds to Al_2O_3. The appearance of the couple Si-Al is credited to kaolinite. The presence of zinc in sample S9 could correspond to "zinc white" (ZnO).SEM results for samples S1, S2, S4-S9 and S11-S18 show only aluminum. We have suggested that under the action of time, moisture and other environmental factors it is possible that some amounts of Al_2O_3 formed hydrates [15-18].Therefore, and as in our previous work, we searched for bands that could suggest the presence of $Al(OH)_x$. The results are shown in Table 3.

Table 3: IR bands possibly associated with Al $(OH)_x$.

Sample	Bands (cm^{-1})		Sample	Bands (cm^{-1})
S1	3806, 3693		S10	3804, 3694
S2	3787, 3695		S11	3806, 3692
S3	3807, 3694		S12	3809
S4	3806, 3693		S13	3806, 3693
S5	3806, 3693		S14	3808, 3692
S6	3805, 3692		S15	3806, 3693
S7	3806,3693		S16	3806, 3693
S8	3806, 3693		S17	3811?, 3695
S9	3806, 3692		S18	3815?, 3697

The bands at about 3694 cm^{-1} are attributed to alumina interacting with water to stretching vibrations of surface hydroxyl groups that are not hydrogen-bonded. In kaolinite, the bands at about 3690 cm^{-1} are attributed also to hydroxyl stretching bands. Bands at 3795 and 3787 cm^{-1} are attributed to OH stretching frequencies. If all the previous reasoning is correct, as long as no SEM results are available, we can use the IR results to differentiate between kaolinite and alumina using the other IR bands of the former [19-21]. Also, SEM results show no relationship allowing classification of the different papers following their presumed geographical origin (Table 1).In the case of ZnO, isolated and hydrogen-bonded surface hydroxyls present bands at about 3670, 3620, 3555 and 3440 cm^{-1}. Sample S3 shows bands at 3677, 3620, 3568 and 3449 cm^{--1}, evidencing the presence of hydrated ZnO [18, 22].

It is interesting to mention at this point that stamp S3, from the Russian Empire and probably not printed in Estonian territory, is the only one having ZnO.Also, kaolinite is found in stamp S10, with paper coming from the factory in Räpina. But stamps S9, S16 and S17 with paper presumably coming also from Räpina and issued at a date close to S10 (specially S9), do not have kaolinite. Reasonable hypotheses are that the paper of S10 either comes from a different paper stock in Räpina or that the paper has another geographical source. We think that the latter hypothesis is more plausible. In summary, Table 2 strongly suggests that samples S3 and S10 form two groups separate from the rest of the samples.

Now, the next step consists in the analysis of specific regions of the IR spectrum to see if we may form groups associated with specific bands. The bands in the 2800-3000 cm^{-1} have been attributed to the absorption of CH groups and should appear in all samples. Table 4 shows these bands.

Table 4: IR bands in the 2800-3000 cm^{-1} region

Sample	Bands (cm^{-1})		Sample	Bands (cm^{-1})
S1	2902, 2915		S10	2903, 2917
S2	2857, 2901		S11	2899
S3	2900, 2967		S12	2899
S4	2898		S13	2898
S5	2910		S14	2903
S6	2900		S15	2855, 2923, 2962
S7	2898, 2940		S16	2902
S8	2902		S17	2902, 2968
S9	2900		S18	2915, 2965

Because of their nature, the bands in Table 4 are not useful to identify specific kinds of paper. Nevertheless, there are some subtle differences that deserve to be analyzed. Cellulose itself does not have absorption bands in the 2000-2600 cm^{-1} region. Therefore, bands in this region, even if they are not assigned, could possibly serve to make some qualitative comments. Table 5 shows them.

Table 5: IR bands in the 2000-2600 cm^{-1} region

Sample	Bands (cm^{-1})
S1	**2139**, *2228*, *2241*, *2257*, **2342**, **2363**, 2542, 2563
S2	**2138**, *2230*, *2243*, **2367**
S3	2070,**2138**, *2241*, *2255*, 2279, **2344**, **2363**, 2541
S4	2053,**2137**, *2240*, **2344**, **2368**, 2543
S5	**2139**, *2256*, **2343**, **2367**, 2560
S6	**2139**, *2241*, *2256*, **2342**, **2362**
S7	**2139**, *2250*, **2343**, 2545
S8	**2138**, *2222*, *2233*, *2256*, **2342**, **2362**, 2538, 2562
S9	**2137**, *2258*, **2343**, **2364**, 2544
S10	**2139**, *2256*, **2340**, **2361**, 2539
S11	2055, **2138**, *2241*, **2344**, **2364**, 2544
S12	**2137**, *2239*, 2256, **2342**, **3262**, 2545
S13	**2138**, *2242*, *2257*, **2343**, **2362**, 2539
S14	**2139**, *2231*, *2256*, **2341**, **2362**, 2539, 2561
S15	**2139**, *2241*, *2264*, **2342 (wm)**, **2362 (wm)**
S16	2068, **2137**, *2242*, 2299, 2333, **2345**, **2372**
S17	**2142**, *2253*, **2348**, **2358**
S18	**2139**, *2242*, **2333**, **2360**

All these bands are weak. Many of the bands in the 2150-2250 cm^{-1} region are attributed to C≡N and C≡C bonds (in italics in Table 5). But we can see that there are other bands in this region. All samples have a band below 2150 cm^{-1} (2137-2142 cm^{-1}, in bold in Table 5). Also, sixteen samples have bands around 2342 and 2360 cm^{-1}, one sample has a band only at 2367 cm^{-1} and another sample at 2343 cm^{-1}. Moreover, twelve samples have bands at 2540 and 2560 cm^{-1}. We are not in a position to ascribe them for the moment. Table 6 shows the bands in the 1500-2000 cm^{-1} region.

ISSN: 0975-8585

Table 6: IR bands in the 1500-2000 cm^{-1} region

Sample	Bands (cm^{-1})
S1	1511, 1528, 1545, 1563, 1650, 1719, 1813, 1831, 1849, 1872, 1880, 1911
S2	1513, 1535, 1549, 1566, 1647
S3	1527, 1548, 1629, 1638, 1657, 1719, 1774, 1794, 1802, 1814, 1832, 1848, 1872, 1899, 1912
S4	1509, 1526, 1545, 1562, 1628, 1639, 1654, 1685, 1702, 1720, 1736, 1751, 1774, 1795, 1801, 1813, 1832, 1848, 1872, 1897, 1911, 1926
S5	1510, 1526, 1544, 1562, 1628, 1639, 1564, 1702, 1720, 1736, 1774, 1795, 1801, 1814, 1832, 1848, 1872, 1912
S6	1513, 1533, 1549, 1562, 1641, 1651, 1833, 1849, 1873
S7	1512, 1528, 1548, 1640, 1721, 1775, 1802, 1814, 1833, 1849, 1880, 1913
S8	1512, 1528, 1547, 1563, 1641, 1654, 1832, 1849, 1872, 1912
S9	1510, 1548, 1640, 1652, 1721, 1831, 1848, 1872, 1912
S10	1505, 1512, 1553, 1609, 1634, 1644, 1659, 1713, 1727, 1836, 1862
S11	1526, 1545, 1562, 1639, 1652, 1719, 1735, 1774, 1794, 1812, 1832, 1848, 1872, 1897, 1911, 1935
S12	1512, 1528, 1551, 1642, 1833, 1849
S13	1526, 1545, 1562, 1639, 1720, 1735, 1774, 1794, 1801, 1813, 1832, 1849, 1872, 1898, 1912, 1935
S14	1528, 1550, 1642, 1705, 1722, 1834, 1850, 1862
S15	1527, 1545, 1628, 1639, 1654, 1702, 1720, 1774, 1801, 1813, 1832, 1848, 1859, 1872, 1912
S16	1510, 1546, 1641, 1721, 1847, 1873, 1912
S17	1511, 1550, 1641, 1708, 1724, 1837, 1850, 1863
S18	1513, 1529, 1552, 1644, 1724, 1819, 1838, 1863

There are some known bands. For example, the band about 1642 cm^{-1} is ascribed to C=C stretching. The one at 1650 cm^{-1} belongs to water and is important to check the degree of drying of the cellulose. Until now it has not been possible to find a way to group the stamps following the supposed geographical origin of the papers employed to print them, but if the data obtained here are added to past and future results, there will be a moment in which statistical methodologies will be applied searching for qualitative or quantitative correlations.

The authors think that an effort on the part of philatelists (do not confuse with stamp collectors!) is necessary in the following sense. Many dealers and stamp collectors simply destroy stamps that been damaged. These stamps are the ones we need to save because they can be used, first to determine the exact geographical origin of the paper, and later be employed as material for destructive studies. In this way a database with the correlation between IR spectrum and geographical origin of stamp papers can be built.

In summary, we have provided IR and SEM results for a set of Estonian postage stamps. SEM results allow two stamps to be separated from the rest, but we could not find a method to order the remaining stamps according to the assumed geographical origin of the paper.

ACKNOWLEDGEMENTS

One of us (J.S.G.-J.) gratefully acknowledges Mr. Martín Urrutia-Muñoz, Vice President of the Chilean Philatelic Society, for his generous donation of Estonian postage stamps. The files with the IR spectra presented in all our papers are available on request for joint research.

APPENDIX A: Infrared spectra of samples S1-S18.

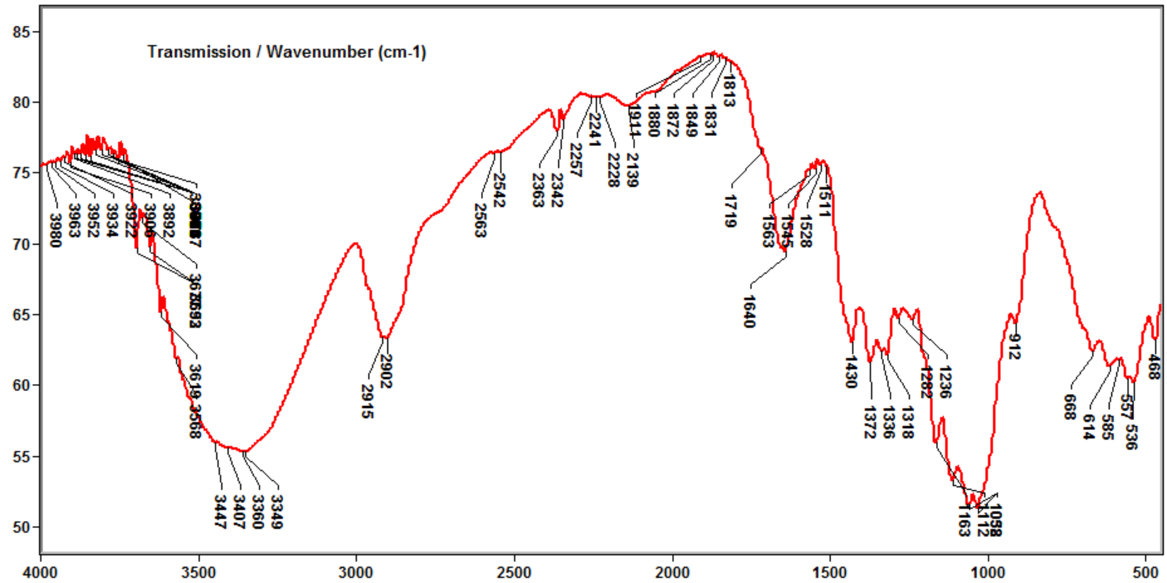

Figure A1: IR spectrum of sample S1

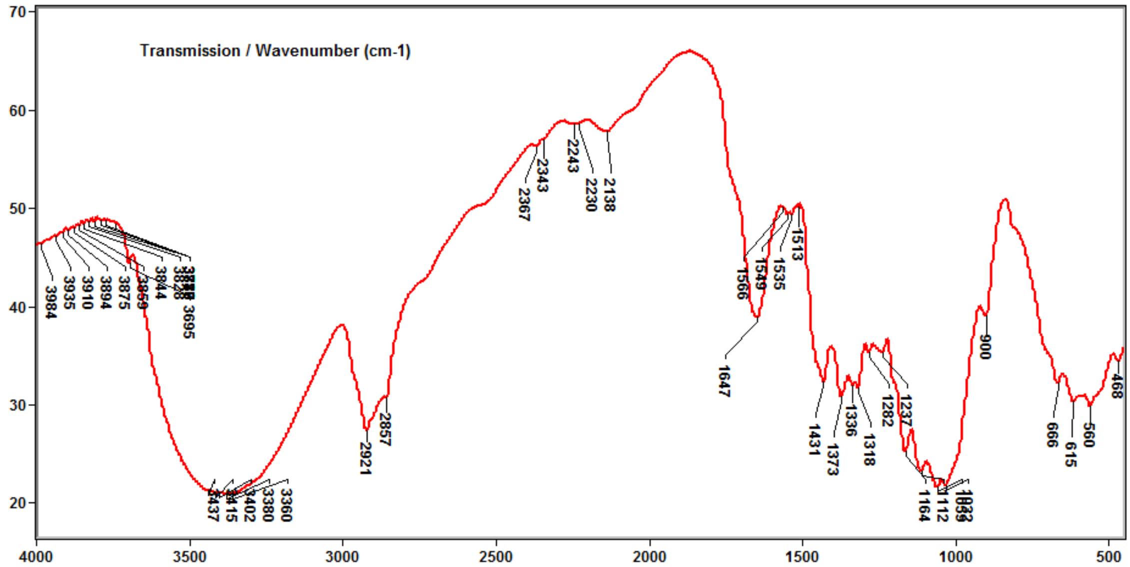

Figure A2: IR spectrum of sample S2

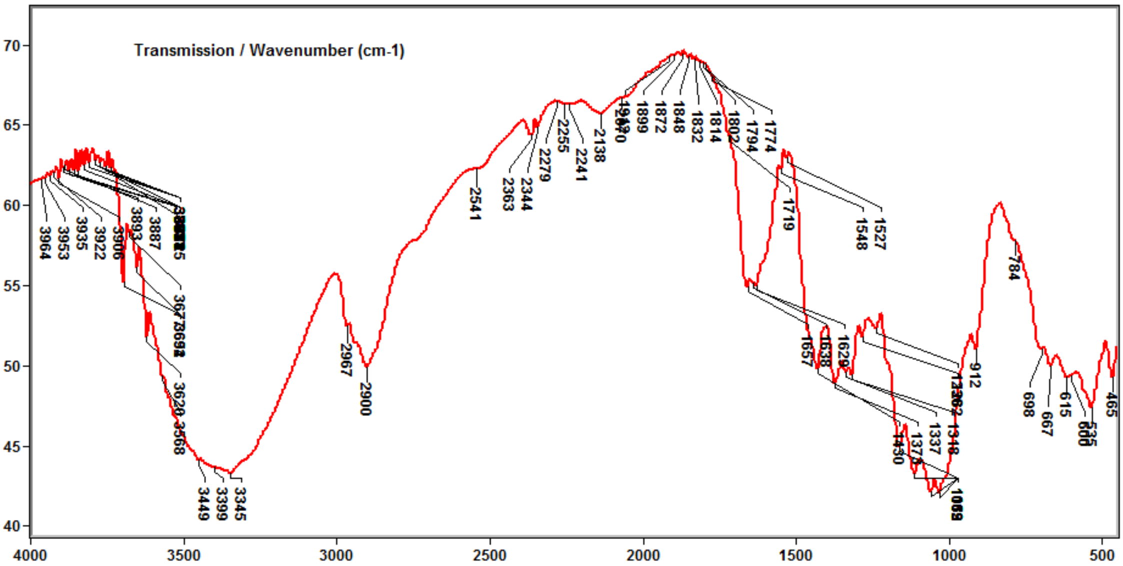

Figure A3: IR spectrum of sample S3

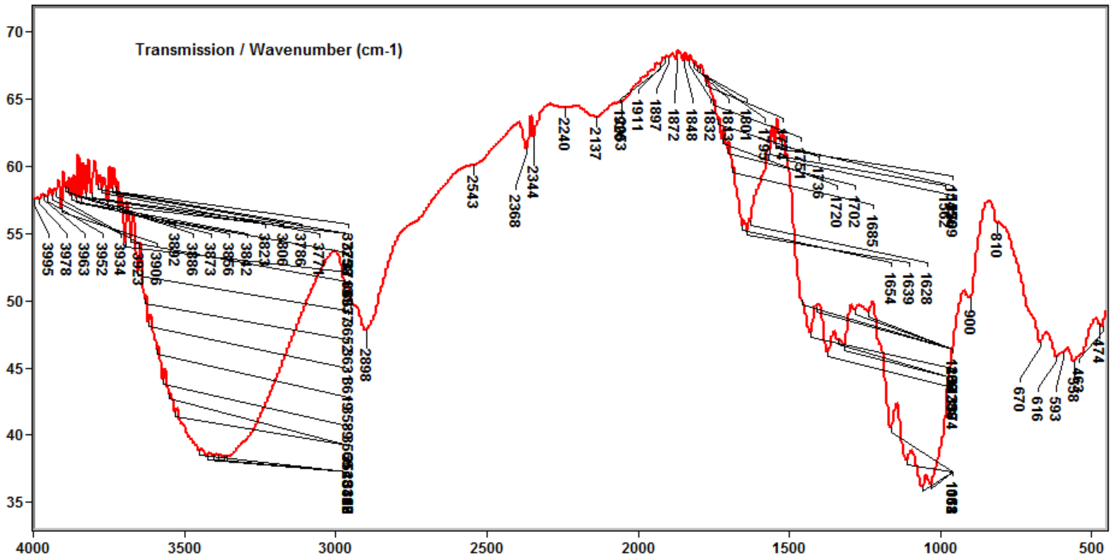

Figure A4: IR spectrum of sample S4

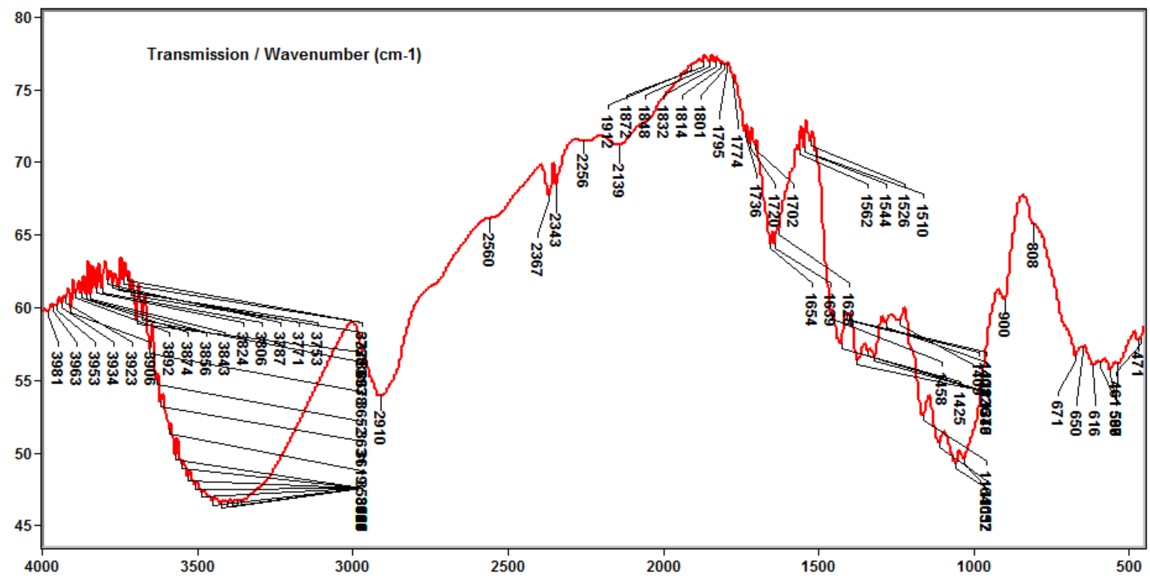

Figure A5: IR spectrum of sample S5.

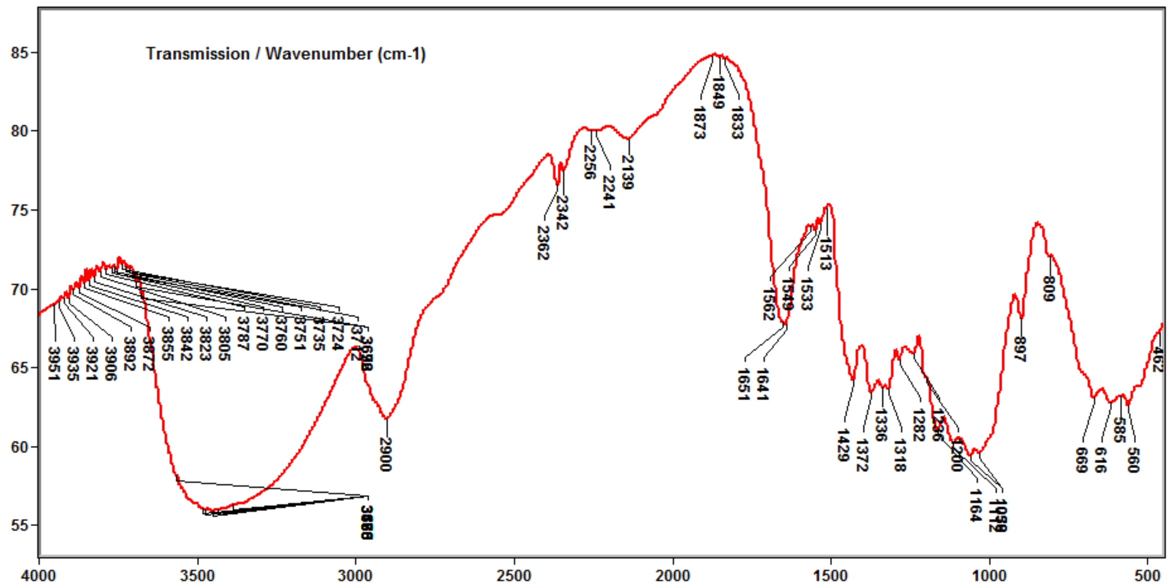

Figure A6: IR spectrum of sample S6

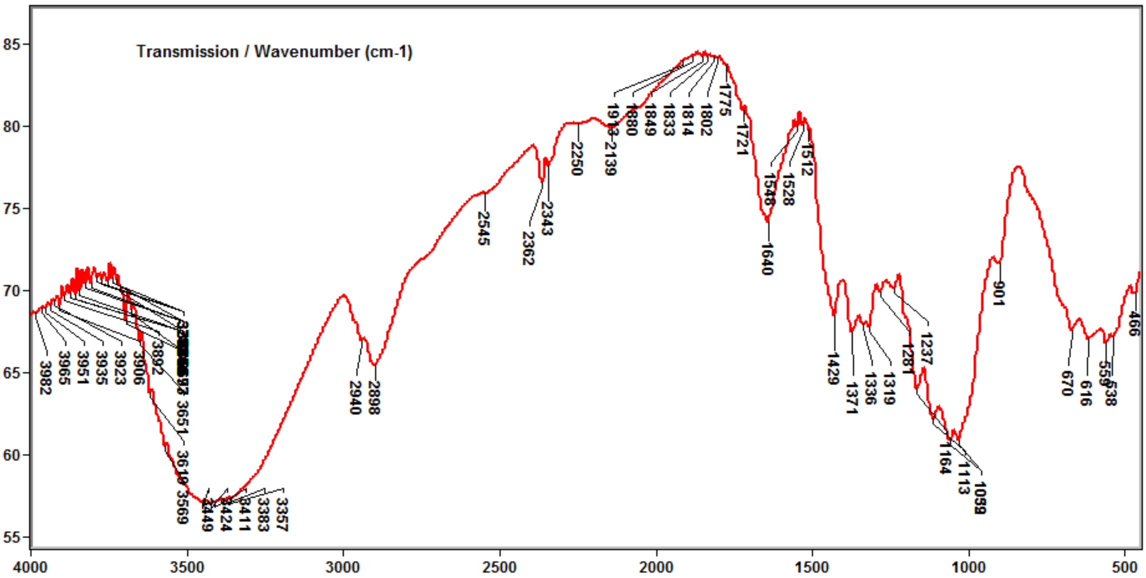

Figure A7: IR spectrum of sample S7

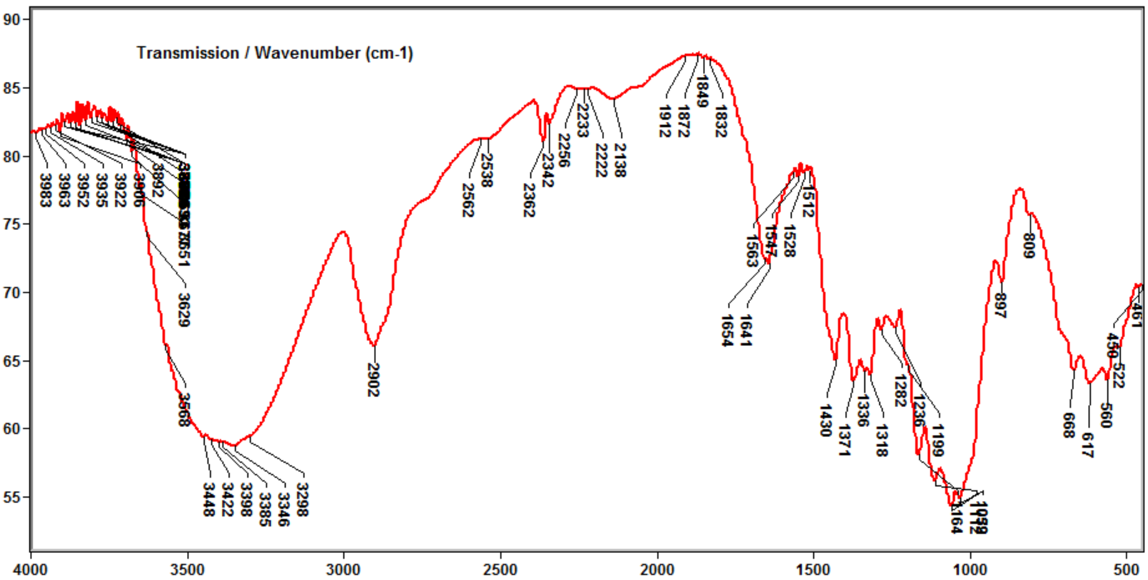

Figure A8: IR spectrum of sample S8

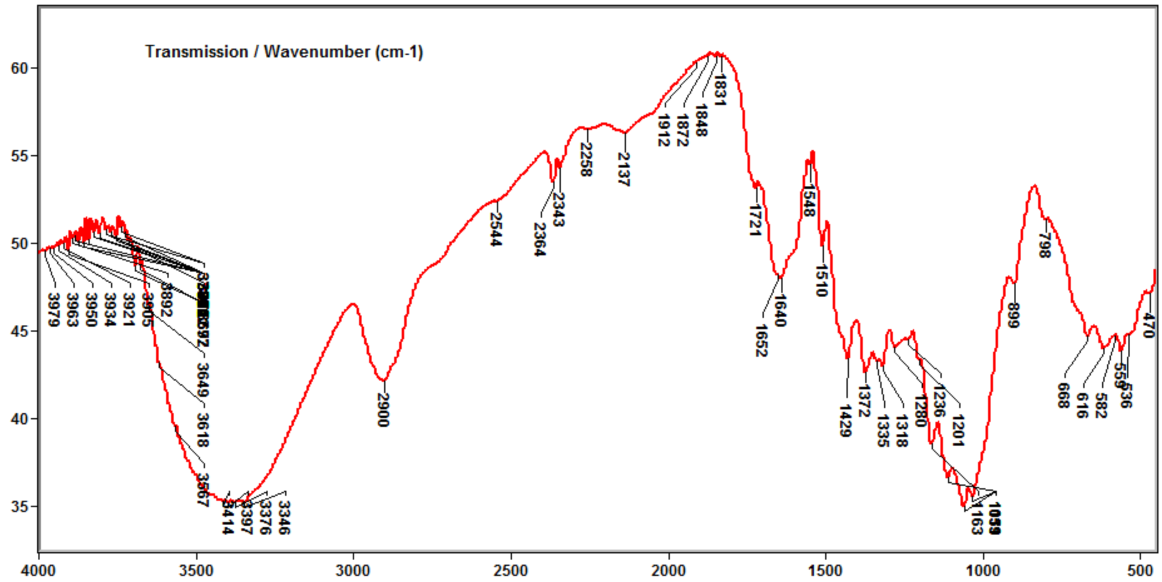

Figure A9: IR spectrum of sample S9

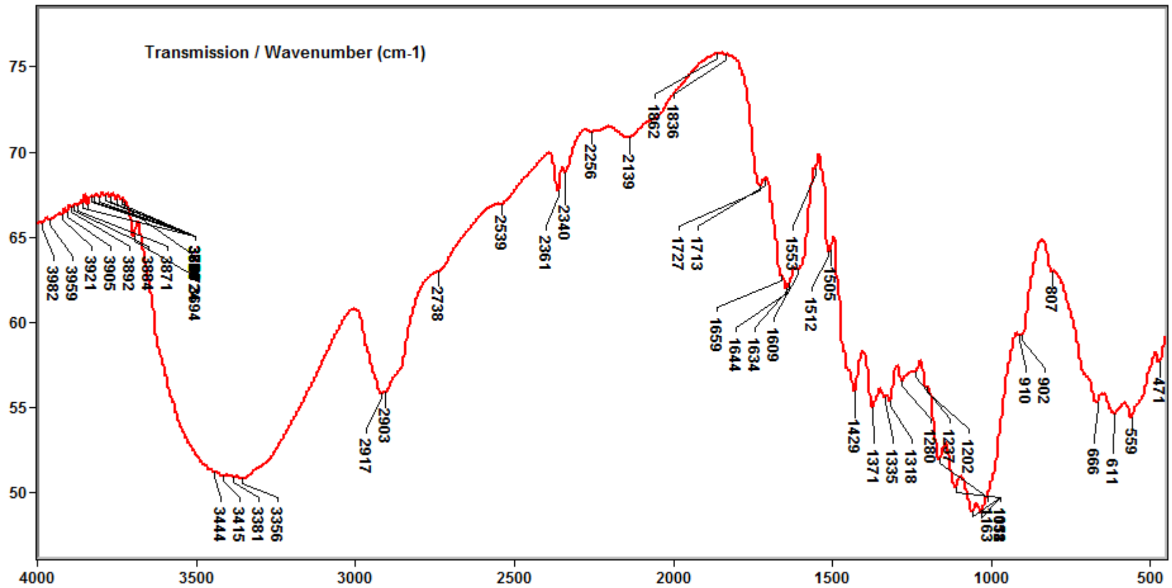

Figure A10: IR spectrum of sample S10

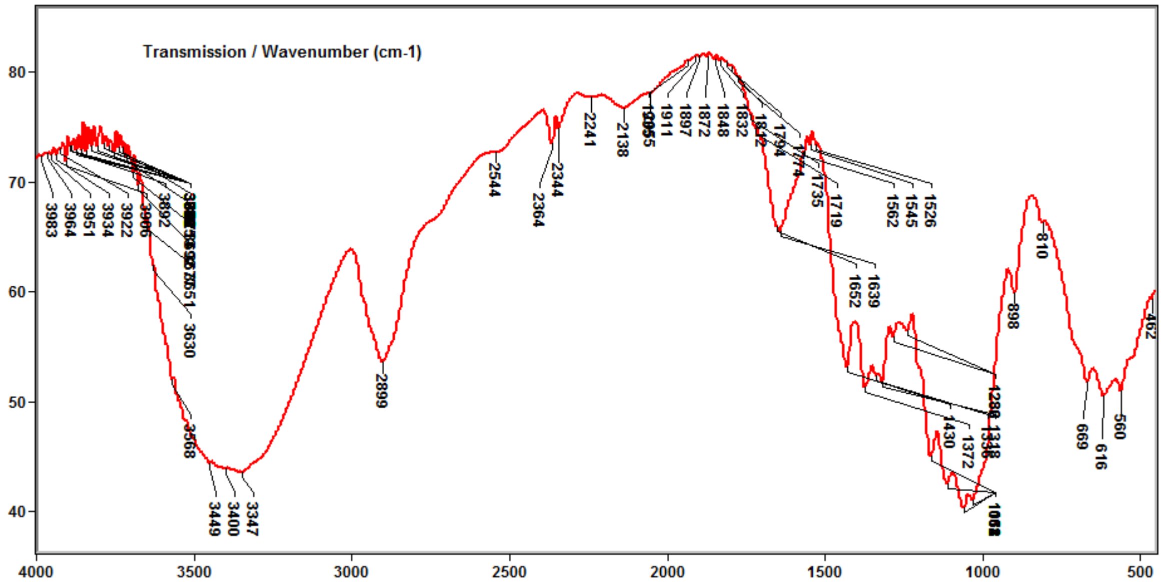

Figure A11: IR spectrum of sample S11

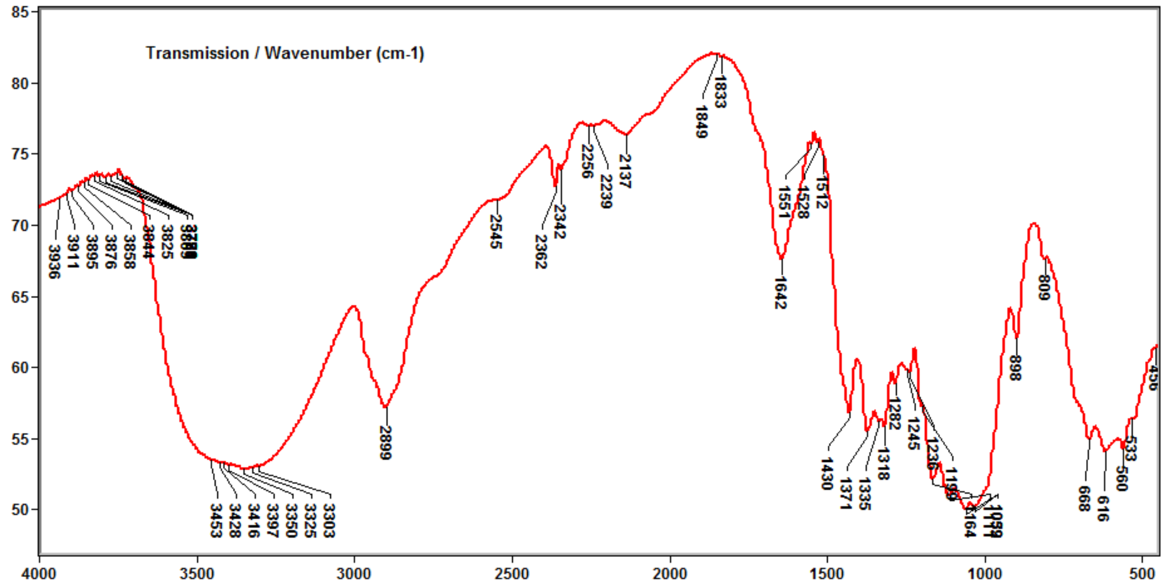

Figure A12: IR spectrum of sample S12

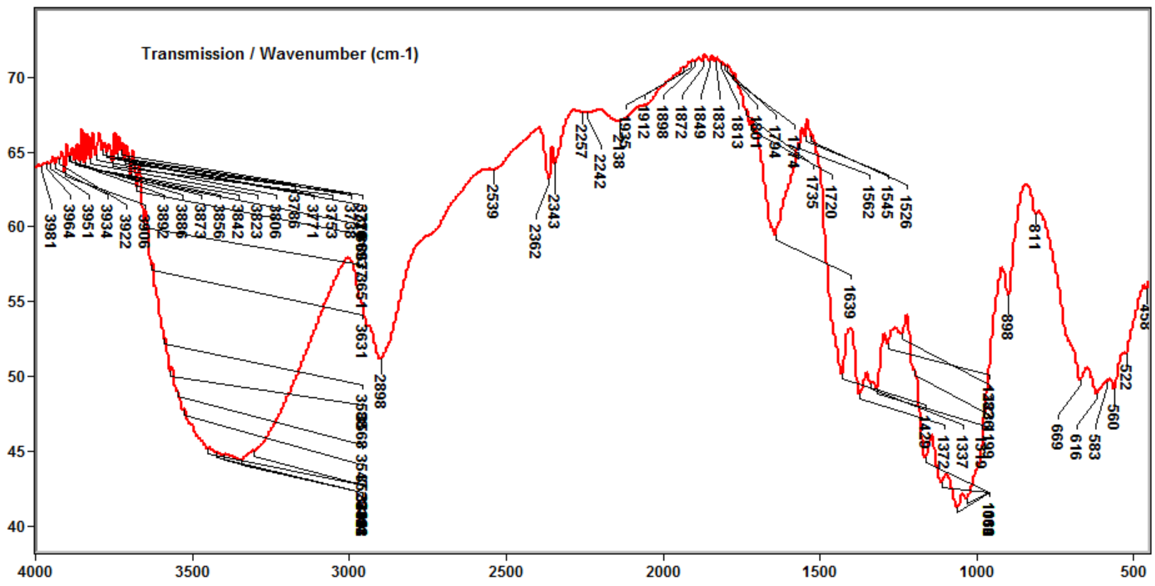

Figure A13: IR spectrum of sample S13

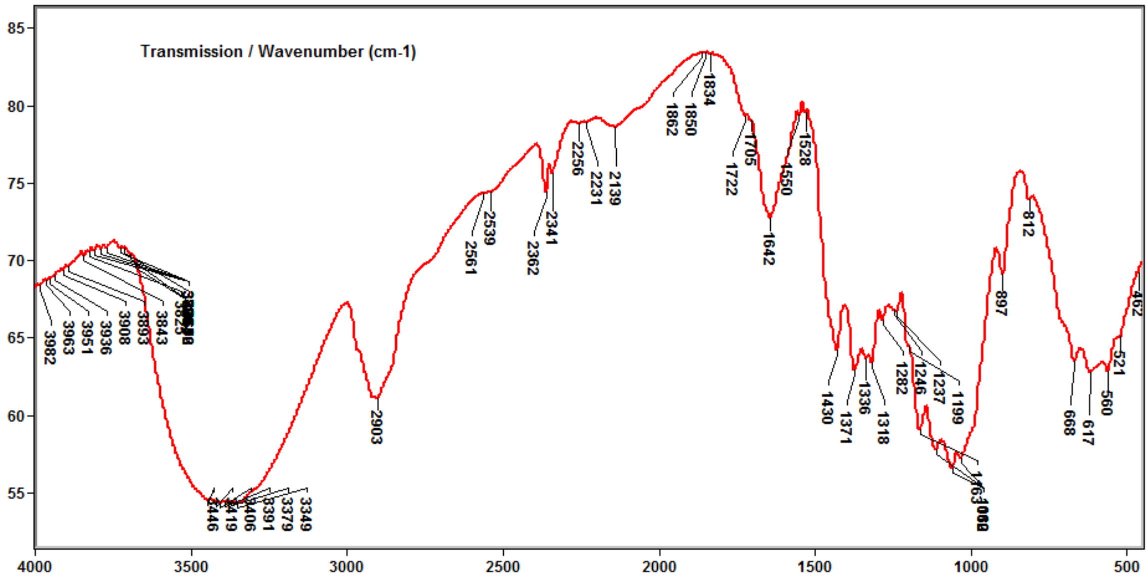

Figure A14: IR spectrum of sample S14

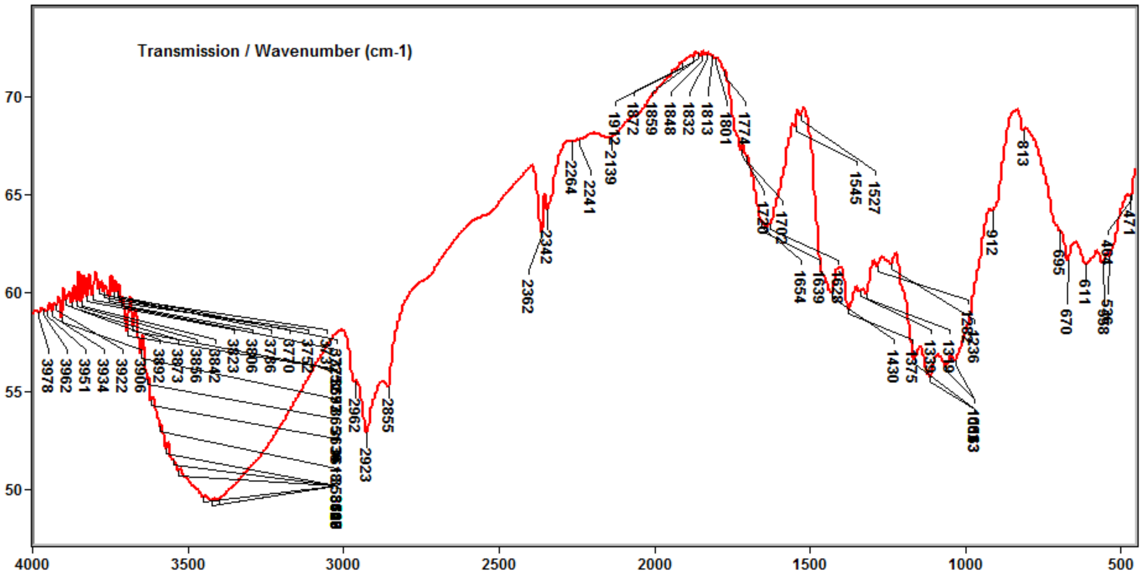

Figure A15: IR spectrum of sample S15

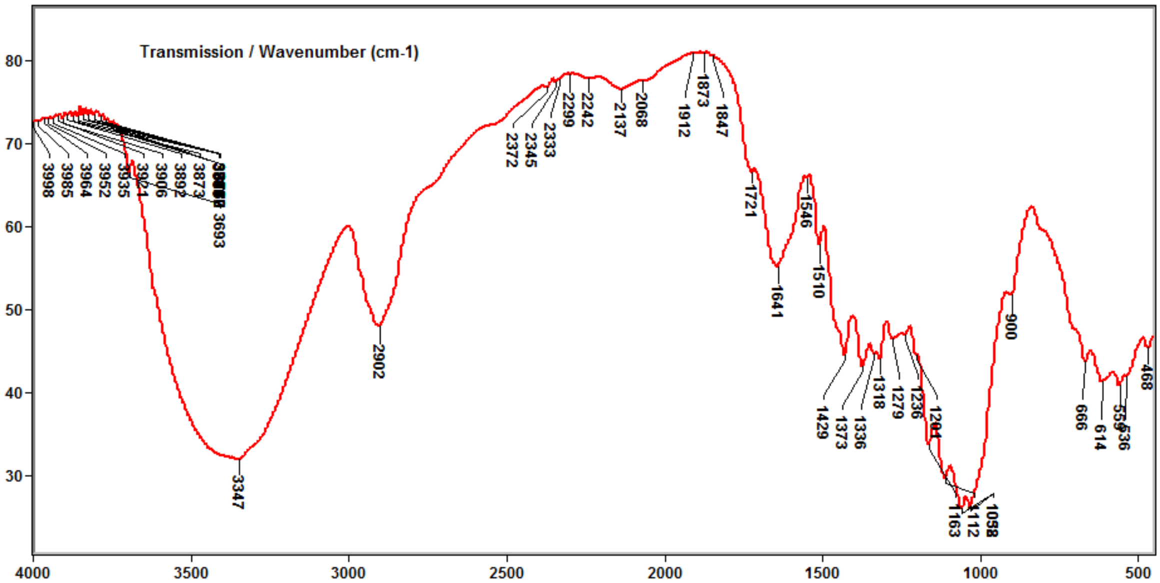

Figure A16: IR spectrum of sample S16

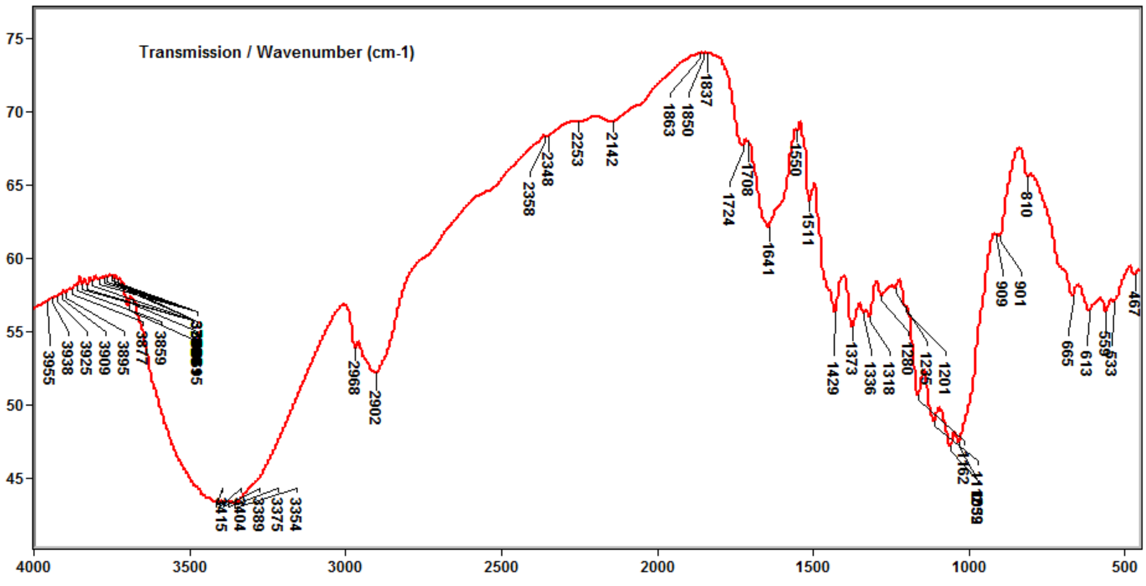

Figure A17: IR spectrum of sample S17

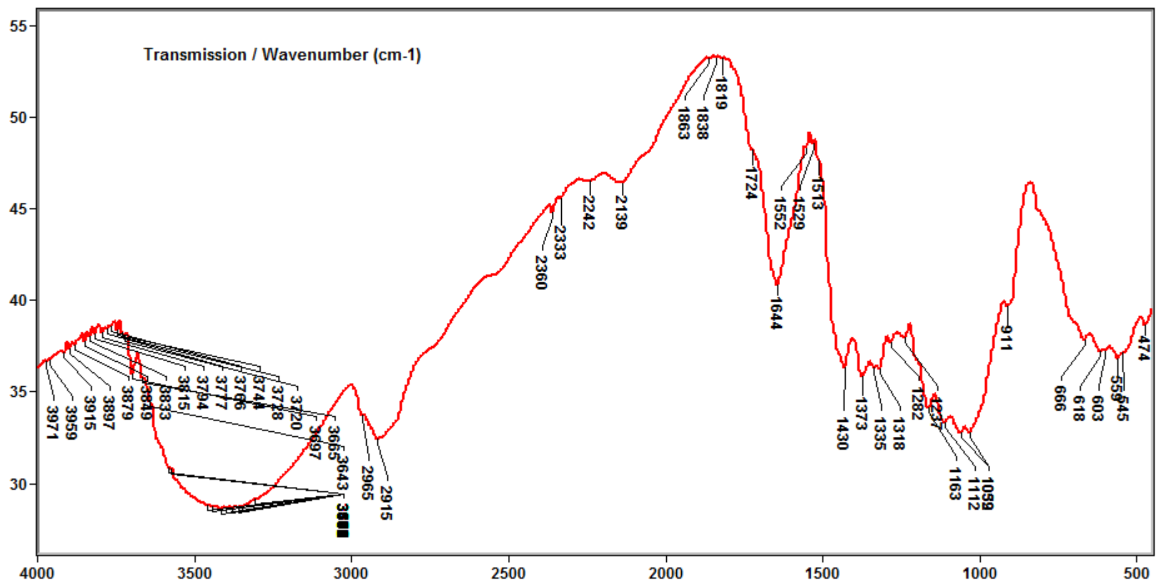

Figure A18: IR spectrum of sample S18

Appendix B. SEM results for samples S1-S18.

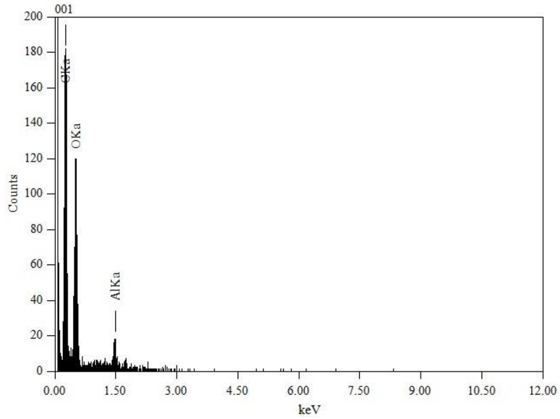

Figure B1: SEM results for S1.

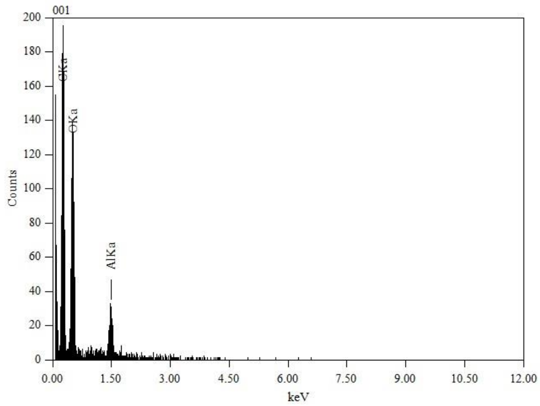

Figure B2: SEM results for S2.

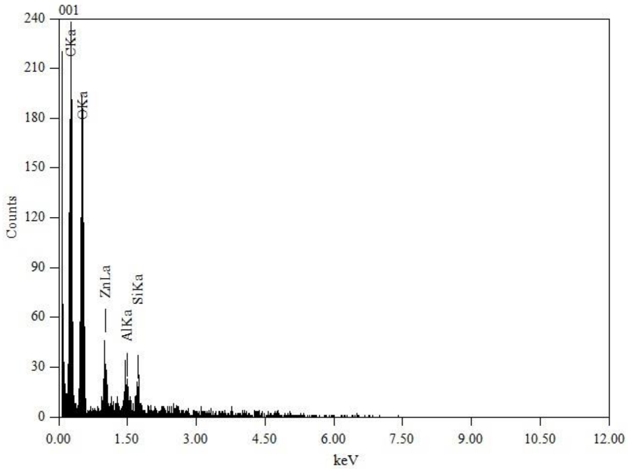

Figure B3: SEM results for S3.

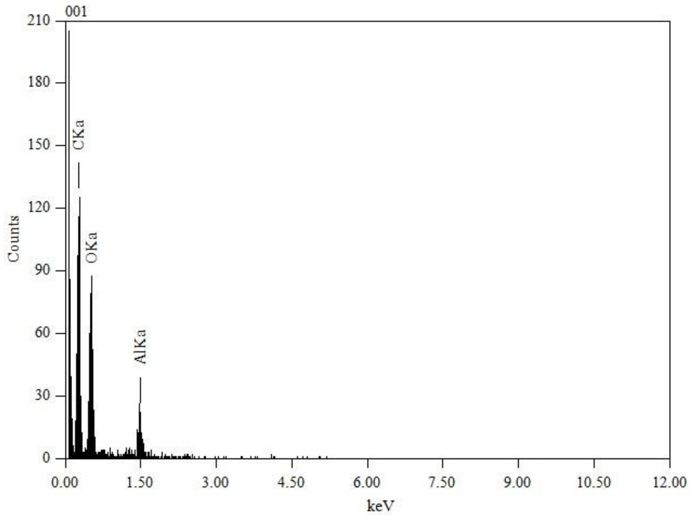

Figure B4: SEM results for S4.

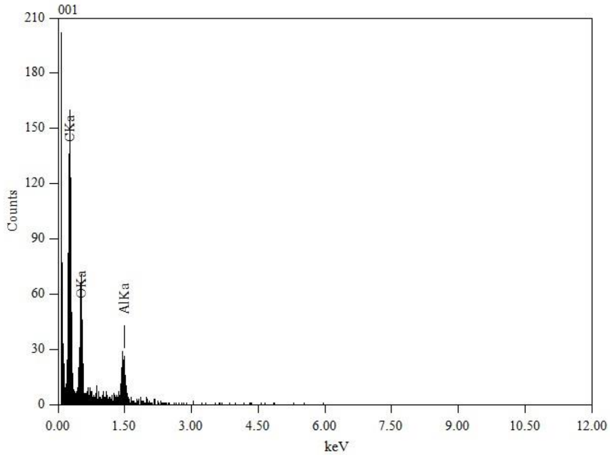

Figure B5: SEM results for S5.

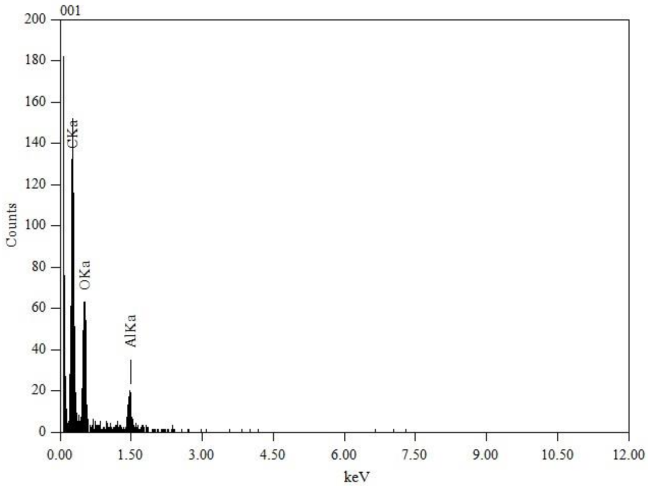

Figure B6: SEM results for S6.

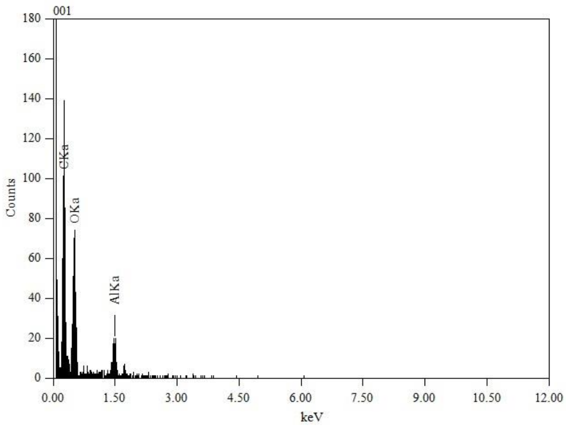

Figure B7: SEM results for S7.

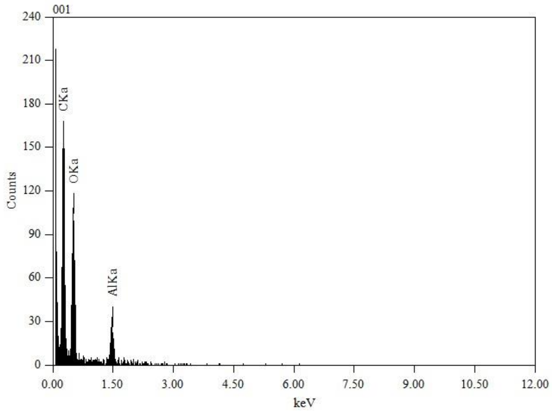

Figure B8: SEM results for S8.

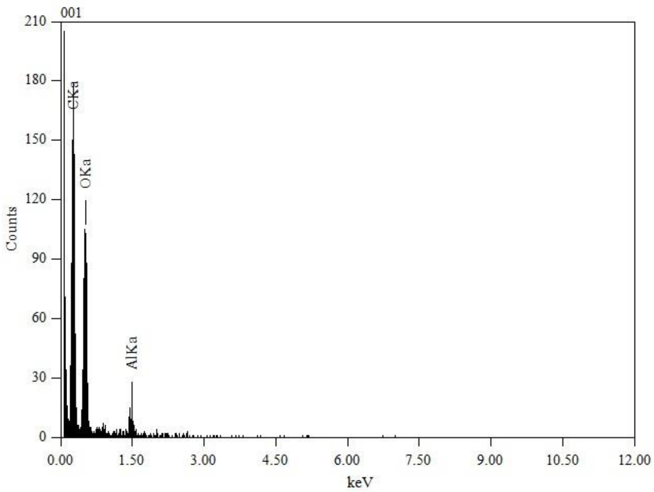

Figure B9: SEM results for S9.

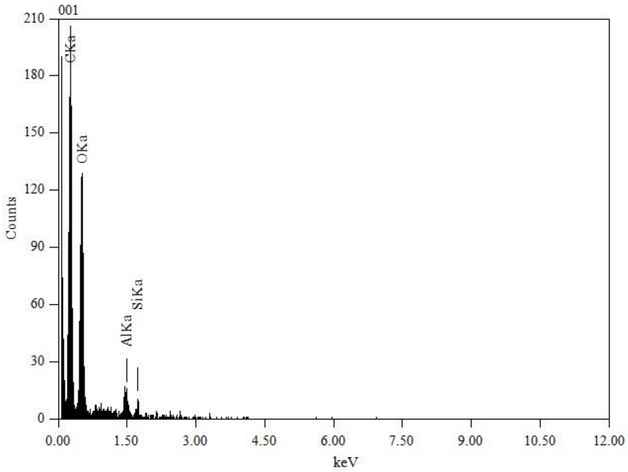

Figure B10: SEM results for S10.

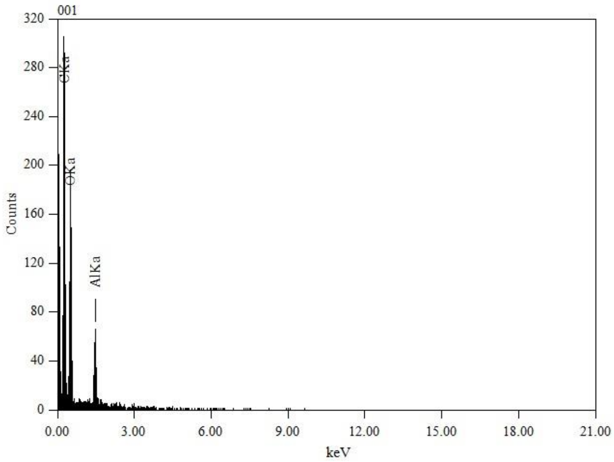

Figure B11: SEM results for S11.

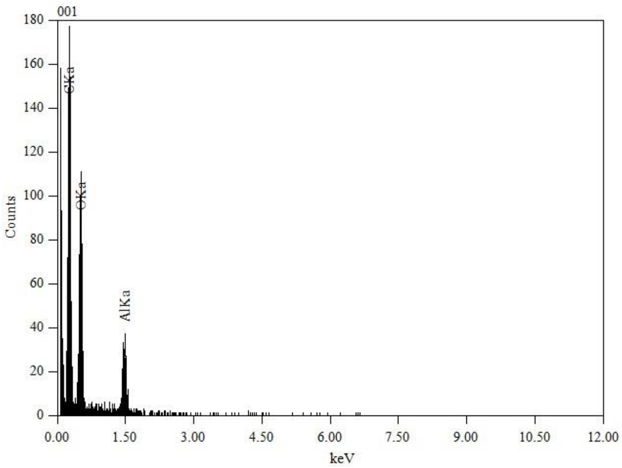

Figure B12: SEM results for S12.

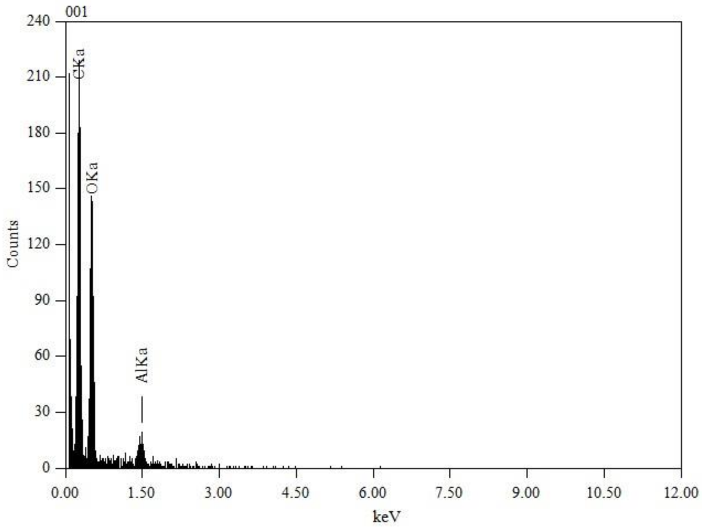

Figure B13: SEM results for S13.

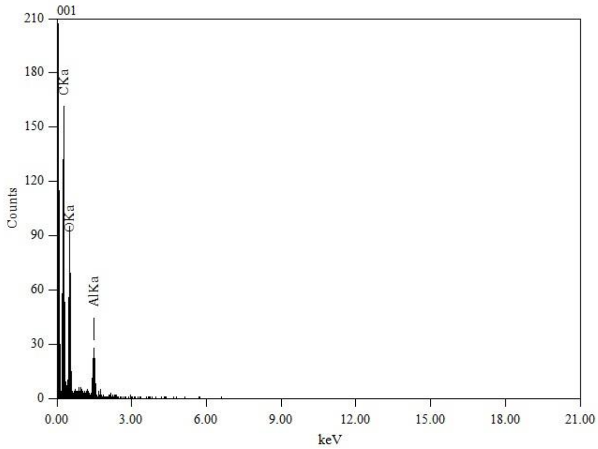

Figure B14: SEM results for S14.

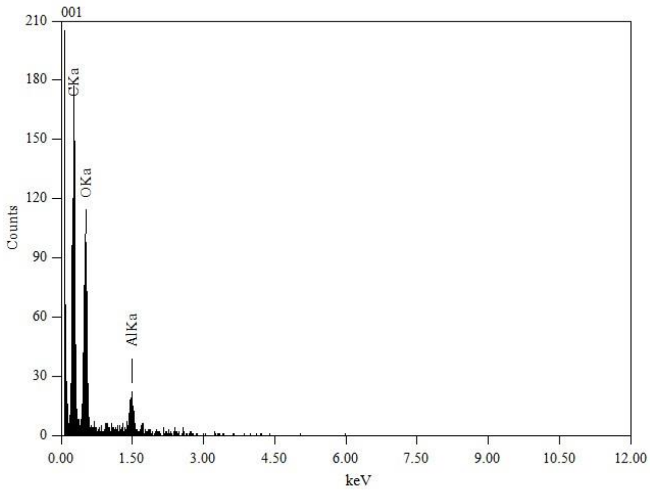

Figure B15: SEM results for S15.

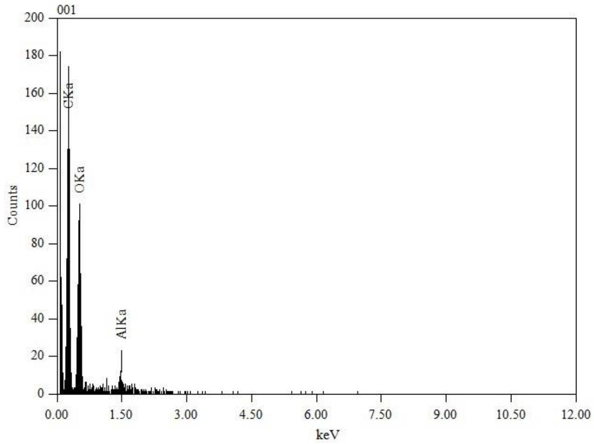

Figure B16: SEM results for S16.

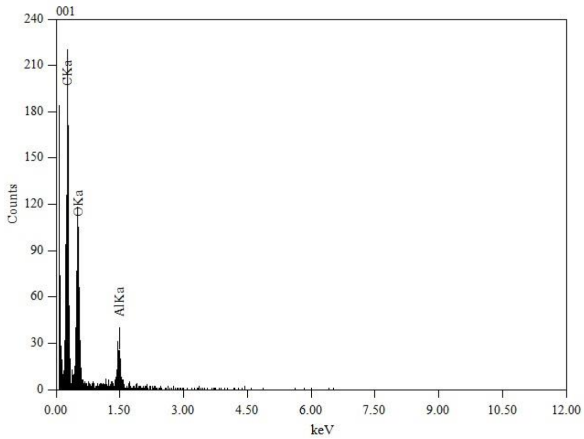

Figure B17: SEM results for S17.

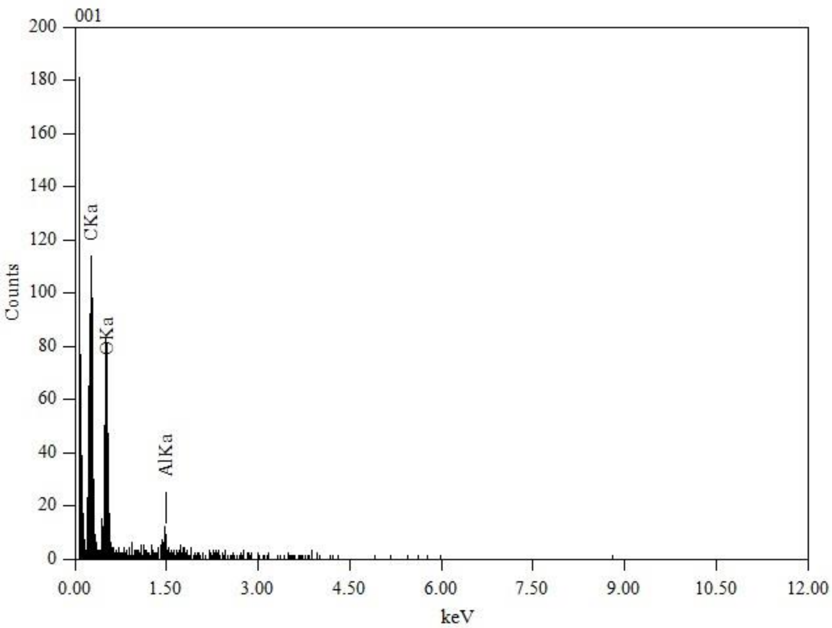

Figure B18: SEM results for S18.

REFERENCES

[1] Christiansen, E. *The northern crusades: the Baltic and the Catholic frontier, 1100-1525*. University of Minnesota Press: Minneapolis, 1980; p xv, 273 p., 4 leaves of plates.

[2] Kasekamp, A. *A history of the Baltic states*. Palgrave Macmillan: Basingstoke, 2010.

[3] North, M.; Kronenberg (Tr.), K. *The Baltic: a history*. Harvard Universoty Press: Cambridge, MA, 2015.

ISSN: 0975-8585

[4] Turnbull, S. R.; Dennis, P. *Crusader castles of the Teutonic Knights. 2. The stone castles of Latvia and Estonia 1185-1560*. Osprey: Oxford, 2004.

[5] Smith, G. *The Baltic States: the national self-determination of Estonia, Latvia, and Lithuania*. St. Martin's Press: New York, 1994; p xii, 214 p.

[6] Felder (Ed.), B. M.; Weindling (Ed.), P. *Baltic eugenics: bio-politics, race and nation in interwar Estonia, Latvia and Lithuania 1918-1940*. Editions Rodopi B.V.: Netherlands, 2013.

[7] Kasekamp, A. *The radical right in interwar Estonia*. Macmillan: Basingstoke, 2000.

[8] Michaelis, R. *Esten in der Waffen-SS: die 20. Waffen-Grenadier-Division der SS (estnische Nr. 1)*. Michaelis: Berlin, 2000.

[9] Baxter, I. *Battle in the Baltics, 1944-45: the fighting for Latvia, Lithuania and Estonia: a photographic history*. Helion & Co.: Solihull, 2009; p vii, 110 p.

[10] Vetik, R.; Helemäe, J. *The Russian second generation in Tallinn and Kohtla-Järve: the TIES study in Estonia*. Amsterdam University Press: Amsterdam, 2011; p 242 p.

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

[12] Gómez-Jeria, J.-S.; Clavijo, E.; Cárcamo-Vega, J.; Gutierrez, 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] Hurt, V.; Ojaste, E. *Estonia. Philately & Postal History Handbook & Catalogue*. Göteborgs Grafiska Grupp AB: Göteborg, Sweden, 1986.

[14] Houseman, D. E. *Scott Classic Specialized Catalogue of Stamps & Covers: Stamps & Covers of the World Including U.S. 1840-1940 (British Commonwealth to 1952)*. Scott Publishing Company: Sidney, OH, 2017.

[15] Peri, J. B.; Hannan, R. B. Surface hydroxyl groups on γ-alumina. *The Journal of Physical Chemistry* **1960,** 64, 1526-1530.

[16] Kloprogge, J. T.; Ruan, H.; Frost, R. L. Near-infrared spectroscopic study of basic aluminum sulfate and nitrate. *Journal of materials science* **2001,** 36, 603-607.

[17] Wang, X.; Andrews, L. Infrared Spectroscopic Observation of the Group 13 Metal Hydroxides, M(OH)1,2,3 (M =Al, Ga, In, and Tl) and HAl(OH)2. *The Journal of Physical Chemistry A* **2007,** 111, 1860-1868.

[18] Tombácz, E. pH-dependent surface charging of metal oxides. *Periodica Polytechnica Chemical Engineering* **2009,** 53, 77-86.

[19] Olejnik, S.; Aylmore, L. A. G.; Posner, A. M.; Quirk, J. P. Infrared spectra of kaolin mineral-dimethyl sulfoxide complexes. *The Journal of Physical Chemistry* **1968,** 72, 241-249.

[20] Balan, E.; Saitta, A. M.; Mauri, F.; Calas, G. First-principles modeling of the infrared spectrum of kaolinite. *American Mineralogist* **2001,** 86, 1321-1330.

[21] Saikia, B. J.; Parthasarathy, G. Fourier Transform Infrared Spectroscopic Characterization of Kaolinite from Assam and Meghalaya, Northeastern India. *Journal of Modern Physics* **2010,** 1, 206-210.

[22] Atherton, K.; Newbold, G.; Hockey, J. A. Infra-red spectroscopic studies of zinc oxide surfaces. *Discussions of the Faraday Society* **1971,** 52, 33-43.