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Investigations on Empire series postage stamps of Ottomans (printed 1880–1890) by vibrational spectroscopic and energy dispersive X-ray fluorescence techniques

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ABSTRACT

In this study Empire series of stamps, the first postage stamps of Ottomans (printed in 1880–1890) after the Ottoman Empire became a member of Universal Postal Union, have been analyzed for the first time, non-destructively, using Fourier-transform infrared (FTIR), Raman and energy dispersive X-ray fluorescence (EDXRF) spectrometry methods Lead chromate, Prussian blue, vermillion, calcium carbonate, gypsum, cellulose, and oil were identified. The merging of data coming from vibrational spectroscopy and EDXRF techniques has allowed the characterization of the pigments used on the surface of each stamp and dispersed between the paper fibers. Additionally, the paper of the stamps was also analyzed.

1. Introduction

The first known postage stamps were issued in the Ottoman Empire in 1863 [1]. After becoming a member of Universal Postal Union founded in 1875, Ottomans issued a new set of stamps known as the Empire series, which was first done in September 1876 [1]. The Empire series stamps bore the name of the country and the values in western characters as well as Arabic. The design consists of a crescent, with ends pointing upward. For this reason they are also known as "Crescent Stamps". The text writing in Arabic letters "post of the Ottoman Empire" (Posta-i Devleti Osmaniye) is surrounded by this upturned crescent (see Fig. 1). Below the crescent there is a label written as "EMP:OTTOMAN", which means Ottoman Empire, and below the label the denomination in western numerals and letters is present. The stamps were typographed in two colors, and the color combinations used were often striking (pink and black; lilac and blue; orange and light blue; blue and grey, etc.), as seen in Fig. 1. The postage stamps are considered a cultural heritage, due to their historical and social value. They constitute a sort of artwork which could be very rare and precious. Many chemical pigments and dyes are used as colorant for the colored inks. Mineral-based or inorganic pigments and dyes, particularly those containing heavy metals, were widely used in past, but due to their toxic effect, environmental concerns have reduced the application of heavy metal containing pigments at the present time. X-ray fluorescence (XRF) analysis is a powerful tool for investigations of elemental and mineral constituents of the pigments and dyes [2–4]. Furthermore, Raman spectroscopy and infrared spectroscopy technique in attenuated total reflection (ATR) mode allow rapid, sensitive, and non-destructive approach for identification of pigments, papers, and adhesives [3–8]. In this work we report the first detailed spectroscopic study of Ottoman postage stamps; nine stamps of the Ottoman Empire series (printed in 1880–1890) have been analyzed non-destructively, using Fourier-transform infrared (FTIR), Raman, and energy dispersive X-ray fluorescence (EDXRF) spectrometry methods. The aim of the present study was to determine the characteristics of the Ottoman Empire series stamps on the basis of the pigments and paper used. To the best of our knowledge, such a complete and thorough examination on Ottoman stamps has not been reported yet.

2. Experimental

2.1. Materials

The stamps analyzed were dated between 1880 and 1890. The photographs of the investigated stamps are shown in Fig. 1. Their Scott catalog numbers [9], colors, and issued dates are given in Table 1. The stamps O-8 and O-9 were the Crescent Stamps that

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Fig. 1. The photographs of the investigated stamps.

were specifically printed for Eastern Rumelia. Eastern Rumelia was an autonomous unit within the Ottoman Empire that began using Turkish stamps with various overprints in 1880. After 1881 the stamps were issued by the Ottoman Empire for Eastern Rumelia using the design elements from the existing Ottoman postage stamps, but they differed from them by having the Greek inscription Ανατ◯λική Ρωμυλία (*Anatolian (i.e. Eastern) Rumelia*) above the "Emp. Ottoman" and with French and Bulgarian inscriptions of the name in small letters along the left and right sides [10].

2.2. EDXRF analysis

EDXRF spectra of the stamps were recorded non-destructively on a SPECTRO iQ-II model spectrometer. The stamps were analyzed for 300 s using an air-cooled low power Pd end window X-ray tube (25–50 kV) combined with highly oriented pyrolytic graphite (HOPG) crystal for monochromatization and polarization of the primary tube spectrum. The orientation of HOPG crystal enables to focus Pd L_α line onto sample. A silicon drift detector (SDD) was used to collect the fluorescence radiation from the sample. The resolution of the SDD was better than 175 eV (for Mn K_α at an input count rate of 10,000 cps). During the measurement, the excitation area was flushed with helium gas.

2.3. FTIR spectral analysis

The infrared analysis of the samples was carried out using attenuated total reflectance (ATR) technique. The ATR-FTIR spectra were recorded on a Bruker Tensor FTIR spectrometer using a diamond ATR sampling unit. The data were collected over a spectral range of 4000–400 cm^{-1}, and 200 scans were collected with a resolution of 1 cm^{-1}. The same pressure was applied to all samples, to ensure good optical contact between the sample and the ATR crystal. The area, sampled by the ATR attachment, was about 2 mm-squared. The depth of penetration of the IR beam to the sample varies with wavelength and for different materials; however, using a diamond ATR window, it can be estimated that the medium depth of penetration is approximately 2 μm.

2.4. Raman spectral analysis

The Raman spectra of the stamps were recorded using two dispersive Raman spectrometers; a Jasco NRS-3100 micro-Raman spectrometer (1800 lines/mm grating and high sensitivity cooled CCD) equipped with 785 nm line of the diode laser excitation source found to be useful for low wavenumber region (500–50 cm^{-1}) whereas a Bruker BRAVO Raman portable spectrometer was found to be useful for the entire spectral range (3200–300 cm^{-1}). Although in the case of Jasco NRS-3100 micro-Raman spectrometer several spectra were collected on different areas of the color shades of the stamps with 2.9 cm^{-1} resolution, due to high fluorescence background we could only obtain certain bands, particularly at low wavenumber region. On the other hand, the Bruker BRAVO Raman spectrometer uses SSE^{TM} (Sequentially Shifted Excitation) patented fluorescence mitigation and has the Duo LASER^{TM} excitation (1100 and 700 nm lines of diode lasers) that enables to measure Raman spectra of fluorescent materials. We were able to record fluorescence-free Raman spectra of the samples over a spectral range of 3200–300 cm^{-1} at 10 cm^{-1} resolution.

The GRAMS/AI 7.02 (Thermo Electron Corporation) software package was used to perform a comprehensive processing (baseline and smoothing corrections, derivative and band fitting procedures), visualization and reporting. For IR and Raman spectra band fitting was done using Gaussian + Lorentzian functions, until reproducible and converged results were obtained with squared correlations better than $r^2 \sim 0.9999$. The second derivative profile gives valuable information about the position of the bands and band widths. Thus for the band fitting procedure (to locate the position of the peaks), the second derivative of the absorption

Table 1
List of the investigated Ottoman Empire series of stamps.

Sample number	Color	Issued Year	Denomination	Scott No
O-1	Black on pink	1880	20 paras	61
O-2	Dark green on beige	1884	10 paras	67
O-3	dirty yellow on olive	1884	1 piastre	90
O-4	Dark pink on light pink	1884	20 paras	68
O-5	Lilac on light blue	1888	2 piastres	84
O–6	Orange on light blue	1886	2 piastres	75
O–7	Dark blue on grey	1890	1 piastre	89
O–8	Dark blue on grey	1885	1 piastre	38B
O–9	Dark pink on light pink	1885	20 paras	32

40 Paras = 1 Piastre (in 1863) (http://www.efilateli.com/pullarimiz.tr.php)

spectrum was used as a guide. The second derivatives of the spectra were obtained by using Savitzky-Golay function (two polynomial degrees, 17 points).

3. Results and discussion

The results from IR, Raman and EDXRF analyses of different colors on the nine stamps are summarized in Table 2.

3.1. The paper used in the printing of postage stamps

FTIR and Raman spectroscopy were used for the characterization of the paper of the stamps, as well as for identifying type of fillers employed. The 1770–750 cm^{-1} region of the ATR-FTIR spectra of the frontface of the stamps O-2, O-6 and O-8 are shown in Fig. 2. Although the infrared light in ATR-FTIR penetrates a small amount into the sample, if the depth of penetration in ATR-FTIR is greater than the thickness of the ink, information on both the paper and ink will be present in an ATR-FTIR spectrum. In all the IR spectra there is a large contribution from the paper on which the stamps were printed. The ATR-IR spectra of the frontface of the stamps displayed characteristic cellulose bands; 1741 cm^{-1} ($\nu C{=}O$); 1425 cm^{-1} (δCH_2 + calcite); 1368 cm^{-1} (δCH); 1336 cm^{-1} (δCOH); 1315 cm^{-1} (δHCC); 1202 cm^{-1} (νCO); 1161 cm^{-1} ($\nu_a COC$); 1106 cm^{-1} (ring asymmetric stretch); 1052 cm^{-1} (νCO); 1029 cm^{-1} (νCO); 998 and 982 cm^{-1} (CO and ring stretching modes) [11–13]. Some contribution of calcite ($CaCO_3$; νCO_3) to 1425 cm^{-1} band of cellulose cannot be excluded [14]. Presence of a small amount of calcite is confirmed by the presence of a weak band at 876 cm^{-1} in ATR-FTIR spectra of all investigated stamps. Kaolin is common filler used in the paper of stamps [5,8]. Imperio et al. [5] investigated Italian postage stamps in a course of time and showed that kaolin was used as filler till 1915 and after 1915 it has been used as coating. Presence of kaolin as a filler or coating can be differentiated by ATR-FTIR spectra [5]: If kaolin acts as a coating layer above the front of mail stamp, its characteristic OH stretching vibrations around 3700–3600 cm^{-1} are more intense than when it acts as a filler [5,15]. In our case the presence of a weak band around 3697–3693 cm^{-1} due to Si-OH stretching mode indicates that kaolin has been used as filler, not acting as a coating layer. We also observed characteristic kaolin bands at 473 and 433 cm^{-1} [14]. Fig. S1 (in the Supplementary data file) shows the FTIR spectra of the 2800–2700 cm^{-1} region of O-2, O-3 and O-5 stamps and the 730–410 cm^{-1} region of the green colored part of O-2 stamp. Kaolin bands are clearly seen at 3697–3693, 473, and 433 cm^{-1}.

The characteristic lignin bands (1603, 1508, 810 cm^{-1}) [16] were only detected in the ATR-FTIR spectra of O-6 (see Fig. 2 and Fig. 3).

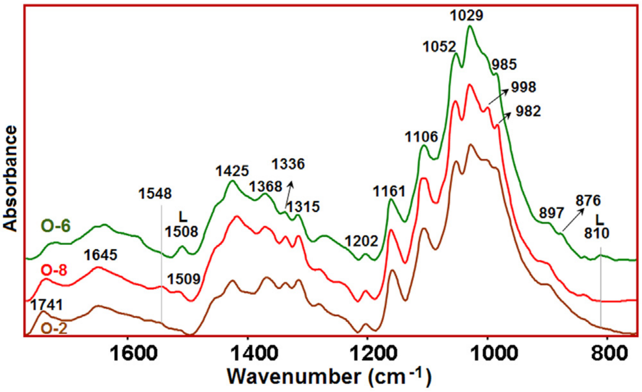

Fig. 2. The 1770-750 cm^{-1} region of the ATR- FTIR spectra of the light blue (top), grey (middle) and beige colored parts of the samples O-6, O-8 and O-2, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

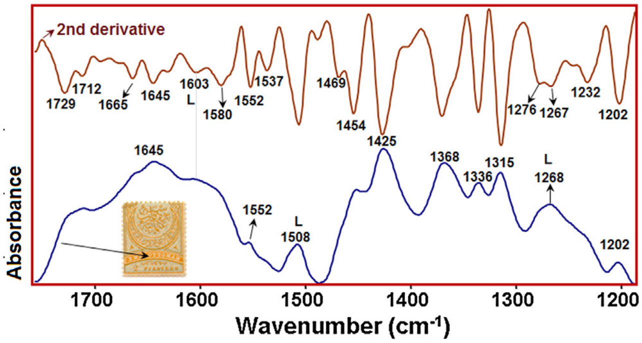

Fig. 3. The 1760-1185 cm^{-1} region of the ATR-FTIR spectrum of the light blue colored part of the stamp O-6 (bottom) and its second derivative profile (top). L = lignin. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The 1760–1185 cm^{-1} region of the ATR-FTIR spectrum of sample O-6 is given in Fig. 3 together with its second derivative profile and the lignin bands indicated. Stamps O-2 and O-8 might contain smaller amount of lignin than O-6, since only *ca.* 1509 cm^{-1} marker band was detected at very weak intensity (see Fig. 2). We did not observe any evidence of lignin in other stamps. The absence or presence of lignin is relevant to the knowledge of the raw material used in the manufacture of paper [17,18]. Paper without lignin is made from semi-chemical or chemical mixtures from which lignin is removed by specific chemical agents [17]. Lignin was probably

Table 2
Sample numbers analyzed, their featured IR and Raman bands and EDXRF results.

No	IR bands (cm^{-1})	Raman bands (cm^{-1})	EDXRF results
O-1	Black: 2124, 2085, 2060, 2000 (Prussian blue with decomposition by products).	Pink: 343, 284, 253 (vermillion) + 1007 (gypsum). Black: 2153, 2090, 532 (Prussian blue) + 672 (magnetite) + 620 (MnO_2).	Al, Si, **S**, **K**, **Ca**, **Mn**, **Fe**, Cu, **Hg**.
O-2	Green: 2085, 594 (Prussian blue) + 854, 819 (chrome yellow).	Green: 2154, 2090 (Prussian blue) + 841, 378, 357, 335 (chrome yellow).	Al, Si, **K**, Ca, Ti, **Cr**, **Fe**, **Pb**.
O-3	Yellow: 850, 830, 813 (chrome yellow). White: 874 (calcite).	Yellow: 841, 403, 376, 359, 336 (chrome yellow).	Al, Si, K, **Ca**, **Cr**, **Pb**.
O-4	White: 666, 602 (gypsum).	Red: 344, 284, 254 (vermillion).White: 1007 (gypsum).	Mg, Al, Si, **S**, K, **Ca**, **Hg**.
O-5	Lilac and blue: 2083 (Prussian blue).	Lilac: 343, 284, 253 (vermillion) + 2156, 2095 (Prussian blue).	Mg, Al, Si, **S**, **K**, Ca, **Fe**, **Hg**.
O-6	Orange: 851, 813 (chrome yellow) + 872 (calcite). Blue: 2090 (Prussian blue).	Orange: 343, 283, 253 (vermillion), 376, 360 (chrome yellow). Blue: 2154, 2090 (Prussian blue).	Al, Si, **S**, **K**, Ca, Ti, **Cr**, **Fe**, Cu, Sr, **Pb**, **Hg**.
O-7	Blue: 2081, 494 (Prussian blue).	Blue: 2154, 2090 (Prussian blue).	Mg, Al, Si, **K**, Ca, **Fe**.
O-8	Blue: 2083, 496 (Prussian blue).	Blue: 2153, 2124, 2090 (Prussian blue).	Mg, Al, Si, **K**, Ca, **Fe**.
O-9	White: 669, 602 (gypsum).	Red: 344, 284, 254 (vermillion). White: 1007 (gypsum).	Mg, Al, Si, **S**, K, **Ca**, **Hg**.

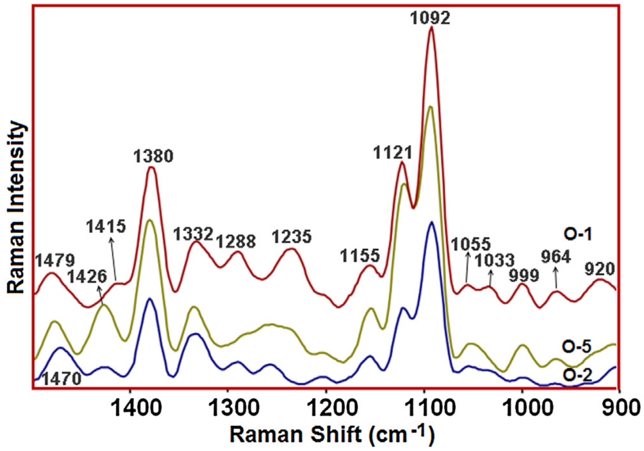

Fig. 4. The 1500-900 cm^{-1} region of the Raman spectra of the frontface of the stamps O-1 (top), O-2 (bottom) and O-5 (middle). Spectra were recorded by the Bruker BRAVO portable dispersive Raman spectrometer.

removed from most of the paper support but a small amount of lignin impurity was left in the papers of stamps O-2, O-6 and O-8.

The 1500–900 cm^{-1} region of the Raman spectra of the frontface of the stamps O-1, O-2 and O-5 are given in Fig. 4. The 1479-1470, 1426-1415, 1380 and 1332 cm^{-1} (δCH_2), 1288 (CH_2 twisting), 1235 (COH out-of-plane bending), 1155 (νCC), 1121 (νCOC), 1092 (νCOC), 1055 and 1033 (νCO), 999 and 964 (ρCH_2) bands of cellulose were revealed [19,20].

The IR spectra of the stamps also displayed the characteristic secondary amide bands *ca.* 1655-1637cm^{-1} (amide I) and 1548cm^{-1} (amide II), attributable to protein glue sited between the fibers. The increase of intensities of the 998 and 982 cm^{-1} bands in the fingerprint region of O-2, O-3, O-8 and O-9 samples suggests presence of starch [21].

3.2. Blue pigment

The stacked FT-IR and Raman spectra of the two blue stamps, O-7 and O-8, with denomination of 1 piastere issued in 1890 and 1884 are given in Fig. 5a and b, respectively. The FT-IR spectra display the characteristic C≡N stretching band, ν(C≡N), at around 2080 cm^{-1}. The iron(III) hexacyanoferrate(II) ($Fe_4\{Fe(CN)_6\}_3$), commonly known as Prussian blue, is the earliest modern synthetic pigment. In the 1800–1900 period, due to the limited selection of blue pigments available for printing inks, Prussian blue pigment was used in most of the blue stamps [6,7,22]. The 496–494 cm^{-1} IR band is assigned to bending vibration of cyanide group, δ(Fe—C≡N) [23]. Raman analysis confirms the presence of Prussian blue. The two strong Raman bands at 2153 and 2090 cm^{-1} and a weak band at 2013 cm^{-1} are attributed to stretching vibrations of cyanide group [6,8,24], ν(C≡N) (see Fig. 5b). The vibrational analysis confirms presence of such a pigment in the light blue coloration parts of O-5 and O-6 stamps (see Fig. 6A) and in the green coloration part of O-2 (see Section 3.5). As seen in Table 2, the EDXRF results are in agreement with the vibrational spectroscopic findings.

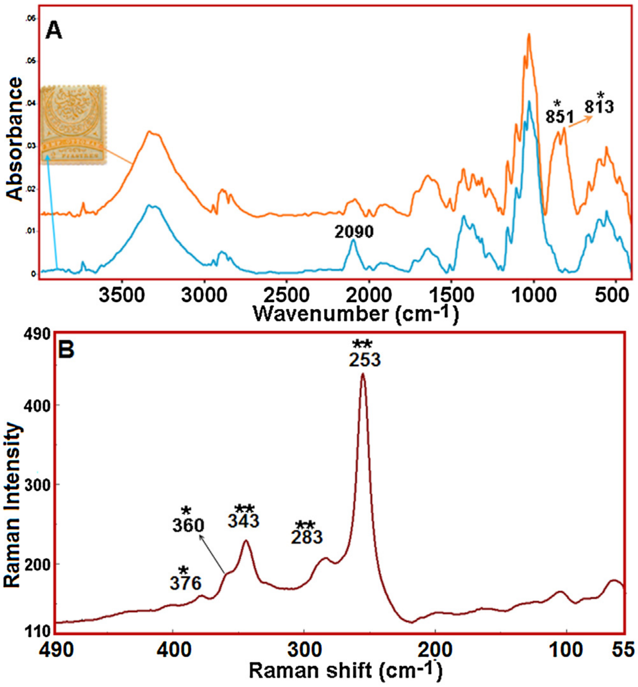

Fig. 6. ATR-FTIR spectra of the orange (top) and blue (bottom) parts (A) and micro Raman spectra of the orange part (B) of stamp O-6 with domination of 2 piasteres, issued in 1886. Micro Raman spectrum was recorded by the Jasco NRS-3100 micro-Raman spectrometer (785 nm laser). *Lead chromate (PbCrO4) and **vermillion (HgS) bands. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.3. Orange coloration

The ATR-FTIR and Raman spectra of stamp O-6 with domination of 2 piasteres, issued in 1886 is given in Fig. 6. ATR-IR spectrum of the orange part of the stamp displays two intense bands at 851 and 813 cm^{-1} which can be attributed to lead chromate [7,25–27].

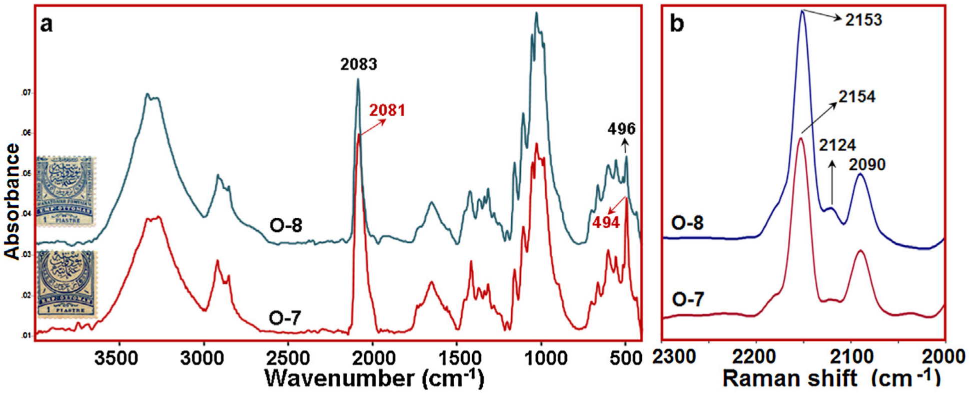

Fig. 5. The ATR-IR (a) and Raman spectra (b) of the blue coloration parts of the stamps O-7 (bottom) and O-8 (top). The Raman spectra were recorded by the Bruker BRAVO spectrometer. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

These strong bands were not observed in the ATR-IR spectrum of the blue coloration part of the stamp. The micro Raman spectrum of the orange part of the stamp displays mercury sulfide pigment (HgS) known as vermillion (or cinnabar) [28], with bands at 343, 283, and 253 cm^{-1} due to the trigonal mercury sulfide structure, and chrome yellow pigment (lead chromate) with bands at 376 and 360 cm^{-1} due to ν_2 bending mode of chromate moiety (Fig. 6B) [24,28]. Thus the vibrational results revealed that the orange color was due to a mixture of chrome yellow (lead chromate) and vermillion.

The EDXRF spectrum of stamp O-6 confirmed the presence of vermillion (Hg and S peaks) and chrome yellow (Cr and Pb peaks) pigments (see Fig. 7). The Fe peak is associated with Prussian blue, as the light blue part of the stamp this pigment was used. Titanium white (TiO_2) and calcite ($CaCO_3$) were probably used for lighting the color. The presence of Cu and Sr would be related to the manufacturing process of the paper. The presence of K, Si and Al would be related to the presence of filler (kaolin) in the paper.

3.4. Yellow pigment

The Raman spectrum of yellow stamp O-3 with denomination of 2 piasteres issued in 1884 is given in Fig. 8. The Raman spectrum revealed that the yellow pigment is chrome yellow [28]. The 1185–750 cm^{-1} region of the ATR-FTIR spectrum of stamp O-3 and the 972–800 cm^{-1} region of the second derivative profile is given in Fig. S2. The chrome yellow pigment is revealed by 850, 830 and 813 cm^{-1} peaks in the second derivative profile. The 874 cm^{-1} peak indicates the presence of calcite. Probably calcite was used for lighting the color. EDXRF results confirmed the vibrational spectroscopic findings; the EDXRF spectrum of stamp O-3 shows the presence of lead, chromium and calcium as the main elements.

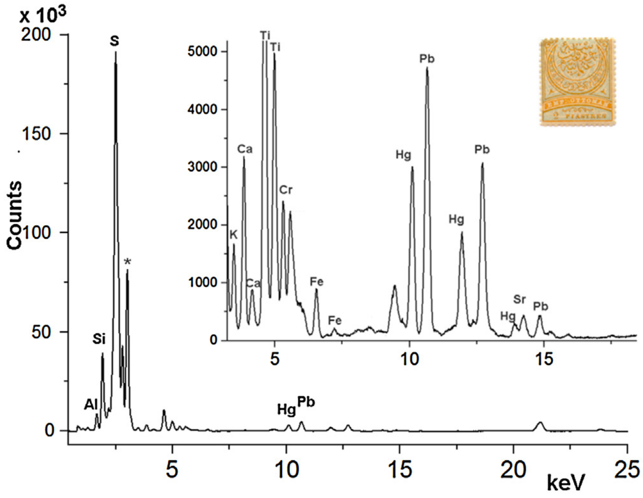

Fig. 7. The 1–25 keV region of the EDXRF spectrum of stamp O-6. The enlarged 3.2-18 keV region is given in the upper frame. The peak marked with asterisk (*) is due to the equipment (not related to the sample).

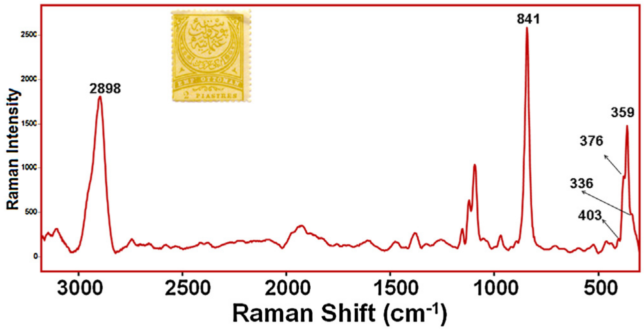

Fig. 8. The Raman spectrum of yellow stamp O-3 with denomination of 2 piasteres issued in 1884. The Raman spectrum was recorded by the Bruker BRAVO spectrometer. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.5. Green coloration

The EDXRF analysis of the green coloration of stamp O-2 revealed the presence of iron, chromium and lead, possible due to Prussian blue ($Fe_4[Fe(CN)_6]_3$) and chrome yellow. As seen in Fig. 9, the Raman spectra of the green pigment in the stamp O-2 revealed a mixture of Prussian blue (2154 and 2090 cm^{-1}) and chrome yellow (841, 378, 357, and 335 cm^{-1}).

3.6. Pink and lilac colorations

The ATR-IR spectra of the pink areas of the stamps O-1, O-4 and O-9 (Fig. 10) did not indicate any particular red pigment showing that an organic nature of red pigment was not used. On the other hand micro Raman spectra revealed presence of vermillion (255, 283, 344 cm^{-1}) (Fig. 11a). The gypsum bands were identified under cellulose absorptions by band component analysis of IR and Raman spectra. Fig. 11 b shows a band component analysis of the 1165–980 cm^{-1} region of the Raman spectrum. Gypsum band was

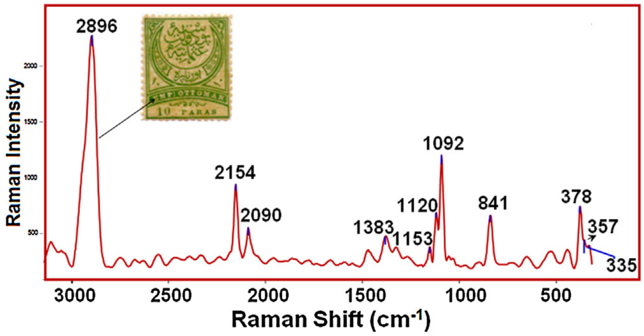

Fig. 9. The Raman spectrum of the green part of the stamp O-2 with denomination of 10 paras issued in 1884. The Raman spectrum was recorded by the Bruker BRAVO spectrometer. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

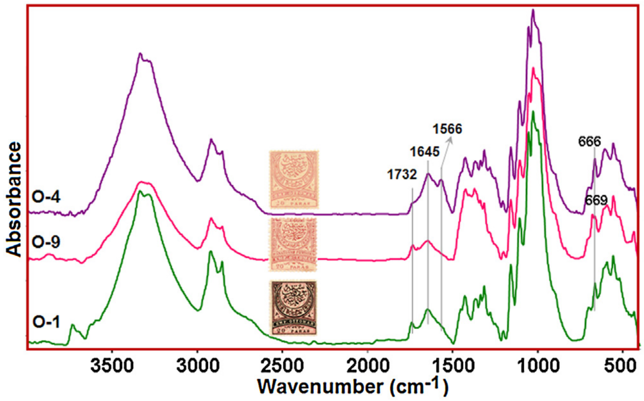

Fig. 10. ATR-FTIR spectra of the pink part of the stamps O-4 (top), O-9 (middle) and O-1 (bottom). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

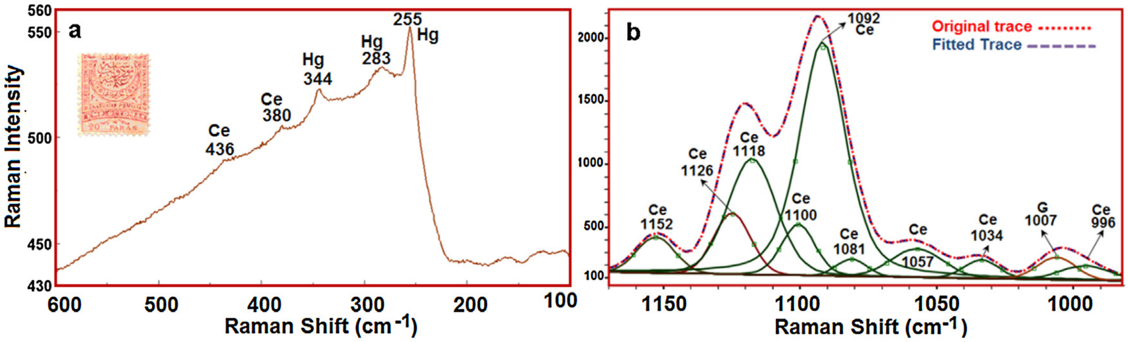

Fig. 11. The Raman spectra of stamp O-9. (a) The 600–100 cm^{-1} region, recorded by the Jasco NRS–3100 micro Raman; (b) the 1160–980 cm^{-1} region, recorded by the Bruker BRAVO spectrometers. Notations used: Ce = Cellulose; G = Gypsum; Hg = HgS bands.

revealed at 1007 cm^{-1} [28]. As for the pink coloration, a mixture of vermillion red and gypsum white was used.

Mixtures of vermillion and Prussian blue have been observed in the micro Raman and ATR-FTIR spectra of lilac color part of stamp O-5.

3.7. Black pigments

Fig. 12 shows the ATR-IR spectrum of the black area of stamp O-1 in comparison with its pink colored part (Fig. 12a) and micro Raman spectrum of the black colored point (Fig. 12B). The ATR-FTIR spectrum implies that the black colored ink was cyanide (—C≡N) based. The peak at 2085 cm^{-1} with the shoulder around 2060 cm^{-1} is related with Prussian blue. In the past many cyanide based inks were used: Prussian yellow, Prussian red, Prussian blue, Chinese blue, Prussian green, and Prussian brown [29]. Presence of many C≡N stretching bands indicates the presence of different oxidation states of iron. In the micro-Raman spectrum recorded on the black area, the presence of magnetite (Fe_3O_4) (672 cm^{-1}) and MnO_2 (620 cm^{-1}) were identified [30]. EDXRF results also confirmed the presence of Mn in addition to Ca, K, S, Fe and Hg (see Table 2). Since we could only record the EDXRF spectrum of the stamp as a whole, pink and black pigments were detected together. The results indicate that black ink was made of a mixture of MnO_2, Fe_3O_4 and cyanide based pigments.

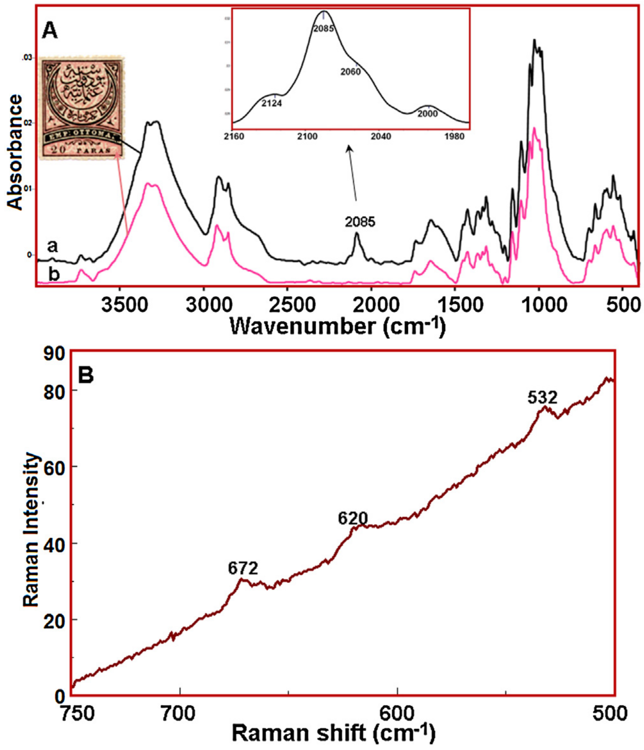

Fig. 12. (A) The ATR-IR spectra of the black (a) and pink (b) areas, and the enlarged 2160–1965 cm^{-1} region of black area of stamp O-1(c). (B) Micro Raman spectrum of the black colored point of stamp O-1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Conclusions

Through the combined use of vibrational spectroscopy and EDXRF analysis, the composition of inks used to print nine Empire series of stamps of Ottomans printed in the 1880–1890 period has been established. The results have shown that the main colors (blue, orange, yellow, green, pink, and black) on the nine stamps were all prepared from inorganic pigments, including chrome yellow, Prussian blue, vermillion, magnetite, and MnO_2. Gypsum and/or calcite were used for lighting the color or to produce a whole different hue. All pigments are consistent with the period of time in which the stamps were printed. Paper support was also analyzed by ATR-FTIR and Raman spectroscopy and in all cases the paper was identified as cellulose. Presence of lignin in only in a small quantity in three stamps (O-2, O-6 and O-8) was detected. The absence of lignin in all of the other stamps implies that lignin has been removed by chemical processes but left in some of the stamps' paper as an impurity. Good correlations were observed comparing vibrational spectroscopy with EDXRF results.

Acknowledgement

We thank Mr. Taha Yuce, Product manager of Bruker (Turkey), for recording the Raman spectra of the samples using a Bruker BRAVO spectrometer.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.vibspec.2016.12.012.

References

[1] https://en.wikipedia.org/wiki/Postage_stamps_and_postal_history_of_Turkey.
[2] M. Mantler, M. Schreiner, X-ray Spectrom. 29 (2000) 3–17.
[3] S. Pessanha, M.L. Carvalho, M.I. CabaçS. Valadas, J.-L. Bruneel, M. Besnard, M.I. Ribeiro, J. Raman Spectrosc. 41 (2010) 1510–1516.
[4] I. Nastova, O. Grupce, B. Minceva-Sukarova, M. Kostadinovska, M. Ozcatal, Vib. Spectrosc. 78 (2015) 39–48.
[5] E. Imperio, G. Giancane, L. Valli, Spectrosc.-Eur. 26 (2014) 9–12.
[6] E. Imperio, G. Giancane, L. Valli, Analyst 140 (2015) 1702–1710.

[7] N. Ferrer, A. Vila, Anal. Chim. Acta 555 (2006) 161–166.
[8] A. Vila, N. Ferrer, J.F. Garcia, Anal. Chim. Acta 588 (2007) 96–107.
[9] Scott numbers are from: Complete list of Empire issues with all major catalog numbers, http://yanstan.com/ottoman/3/3. htm; http://www.sariucak.com/ottoman/187684.html.
[10] https://en.wikipedia.org/wiki/Postage_stamps_and_postal_history_of_Eastern_Rumelia.
[11] K. Kavkler, Z. Smit, D. Jezersek, D. Eichert, A. Demsar, Polym. Degrad. Stab. 96 (2011) 1081–1086.
[12] N. Abidi, L. Cabrales, C.H. Haigler, Carbohydr. Polym. 100 (2014) 9–16.
[13] K. Kavkler, N. Gunde-Cimerman, P. Zalar, A. Demsar, Polym. Degrad. Stab. 96 (2011) 574–580.
[14] J.A. Gadsden, Infrared Spectra of Minerals and Related Inorganic Compounds, Butterworth & Co Publishers, London, 1975.
[15] E. Imperio, G. Giancane, L. Valli, Anal. Chem. 85 (2013) 7085–7093.
[16] C. Ferrer, FTIR Technique Used to Study Acidic Paper Manuscripts Dating from the Thirteenth to the Sixteenth Century from the Archive of the Crown of Aragón, The Book and Paper Group Annual 26, 2007, pp. 21–25.
[17] S. Manente, A. Micheluz, R. Ganzerla, G. Ravagnan, A. Gambaro, Int. Biodeterior. Biodegrad. 74 (2012) 99–108.
[18] L. Hajji, A. Boukir, J. Assouik, H. Lakhiari, A. Kerbal, P. Doumenq, G. Mille, M.L. De Calvalho, Spectrochim. Acta A 136 (2015) 1038–1046.
[19] H.G.M. Edwards, D.W. Farwell, D. Webster, Spectrochim. Acta A 53 (1997) 2383–2392.
[20] K. Kavkler, A. Demsar, Spectrochim. Acta A 78 (2011) 740–746.
[21] V. Librando, Z. Minniti, S. Lorusso, Conserv. Sci. Cult. Heritage 11 (2011) 249–268.
[22] W.-H. Zhou, Q. Gan, J.-X. Ji, N. Yao, J.-G. Wang, Z. Zhou, X.-K. Qi, J.-L. Shi, J. Raman Spectrosc. 47 (2016) 316–320.
[23] S. Vahur, A. Teearu, I. Leito, Spectrochim. Acta A 27 (2010) 1061–1072.
[24] T.D. Chaplin, A. Jurado-Lopez, R.J.H. Clark, D.R. Beech, J. Raman Spectrosc. 35 (2004) 600–604.
[25] F.A. Miller, C.H. Wilkins, Anal. Chem. 24 (1952) 1253–1294.
[26] R. Newman, J. Am Inst. Conserv. (JAIC) 19 (1979) 42–62.
[27] L. Monico, G. Van der Snickt, K. Janssens, W. De Nolf, C. Miliani, J. Verbeeck, H. Tian, H.Y. Tan, J. Dik, M. Radepont, M. Cotte, Anal. Chem. 83 (2011) 1214–1223.
[28] L. Burgio, R.J.H. Clark, Spectrochim. Acta A 57 (2001) 1491–1521.
[29] T. Lera J. Giaccai N. Little, A Scientific Analysis of the First Issues of Chile 1853–1862, London Printing Smithsonian Contributions to history and technology, No 57 2013 19–33 https://repository.si.edu/bitstream/handle/10088/21394/03.Lera.etal.SCHT57_Lera_web_FINAL.pdf?sequence=1&isAllowed=y.
[30] J.D. Smith, R.J.H. Clark, J. Archaeol Sci. 31 (2004) 1137–1160.