Fourier transform infrared (FTIR) and Energy Dispersive X-Ray Fluorescence (EDXRF) investigations of Ottoman Empire postage stamps printed in 1865-1913

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Postage stamps are cultural heritage that shows the historical, economical and political development of a country and society.

The first known hand stamps issued in the Ottoman Empire date from 1840, and the and the first postage stamps in 1863.

The first Ottoman Empire adhesive postage stamps were Tughra stamps. These first stamps showed the tughra (the sultan's signature) of the current sultan, Abdulaziz, over a crescent in which **The Sublime Ottoman Empire** (Devleti Aliye Osmaniye) was written. The rest of the stamp was filled with a baroque decoration

The Tughra stamps were followed by Duloz series of stamps, which were printed between 1865-1882. Since these stamps were prepared by the French artist Duloz, were known as the "Duloz" series

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Following the Duloz series stamps, **Crescent Stamps of Ottoman Empire** were first issued in September 1876, after being a member of **Universal Postal Union.** Unlike the previous Duloz series postage stamps, **Crescent stamps bears the name of the country and Western characters and values.**

From 1901 through 1913, the Ottoman Empire issued a number of stamps with similar designs including the Tughra of the reigning monarch and had a distinct Turkish appearance.

Tughra Duloz Crescent

The Crescent 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 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 Figure). 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 Figure.

The postage stamps are considered as cultural heritage, due to their historical and social value [1]. 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. Energy Dispersive X-ray fluorescence (EDXRF) analysis is a powerful tool for investigations of elemental and mineral constituents of the pigments and dyes [2-4]. Furthermore, Fourier transform infrared (FTIR) technique in attenuated total reflection (ATR) mode allow rapid sensitive and non-destructive approach for identification of pigments, papers and adhesives [3-8].

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In this study, Ottoman Empire postage stamps, printed in 1865-1913, have been analyzed for the first time, non-destructively using Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) and Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometry methods. The merging of data coming from ATR-FTIR and EDXRF techniques has allowed the characterization of the pigments used on the surface of each stamp and dispersed between the paper fibers

Fig 1. Investigated stamps and their dates of issue.

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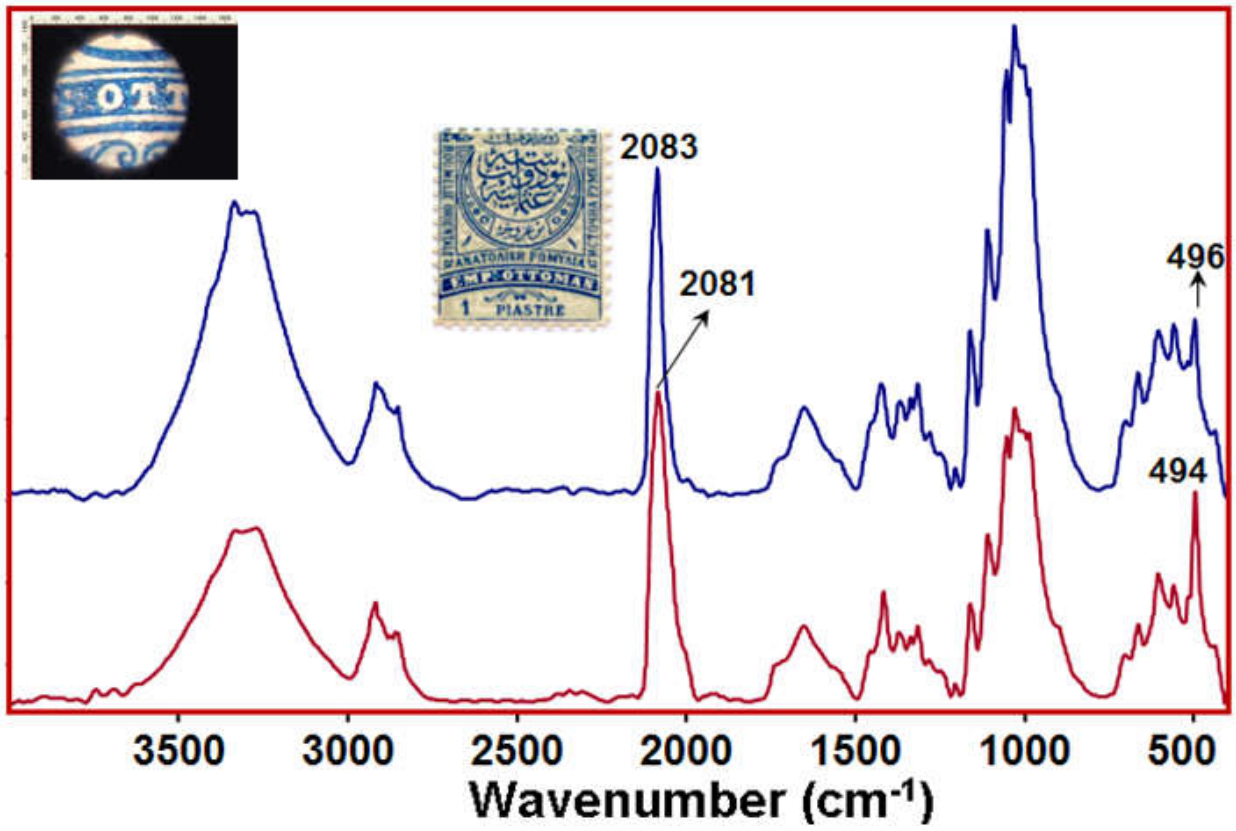

The stacked FT-IR (ATR and Drift) spectra of a blue stamp, are shown in the figure.

The FT-IR spectra display the characteristic C≡N stretching band 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 1800-1900 years due to the limited selection of blue pigments available for printing inks, Prussian blue pigment was used in most of the blue stamps. The 494-496 cm^{-1} IR band is assigned to bending vibration of cyanide group, δ(Fe-C≡N).

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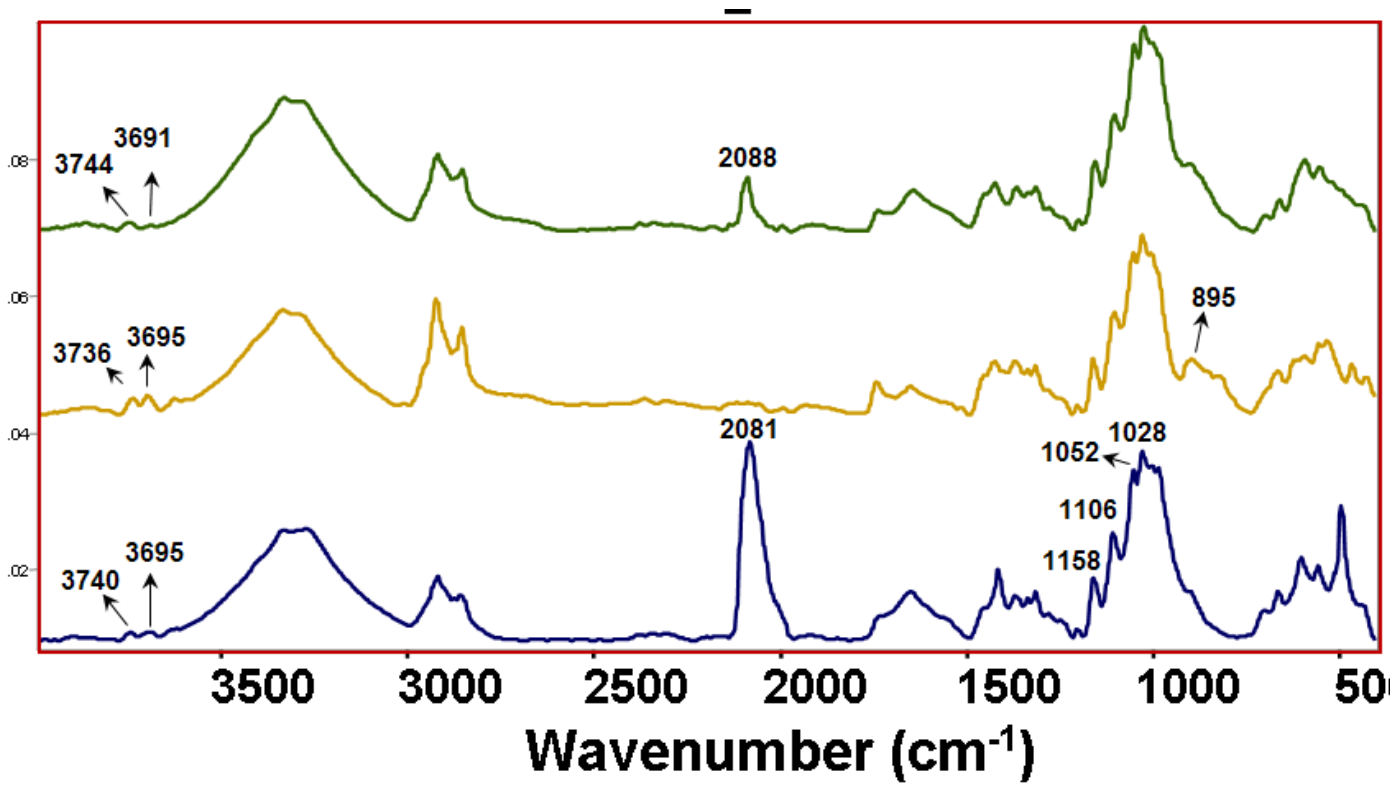

Kaolin is common filler used in the paper of stamps [5, 8]. Imperio *et al*. [5] investigated Italian postage stamps in a course of time and showed that kaolin was used as filler till 1915 and after 1915 it has been used as coating.

Presence of kaolin as a filler or coating can be differentiated by ATR-FTIR spectra; 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.

In our case the presence of a weak band around 3695-3691 cm^{-1} due to Si-OH stretching mode indicates that kaolin has been used as filler, not acting as a coating layer.

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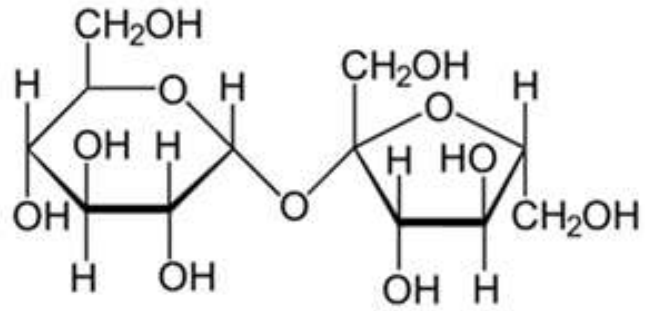

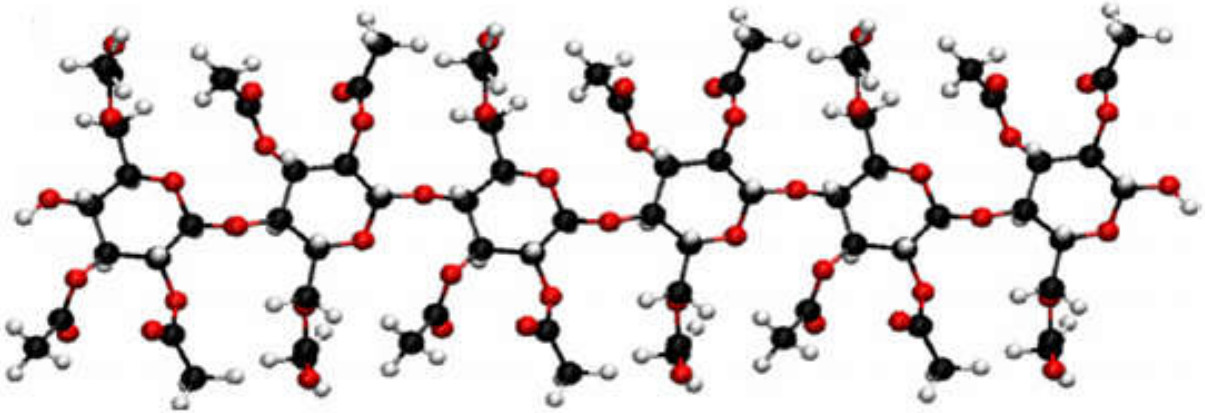

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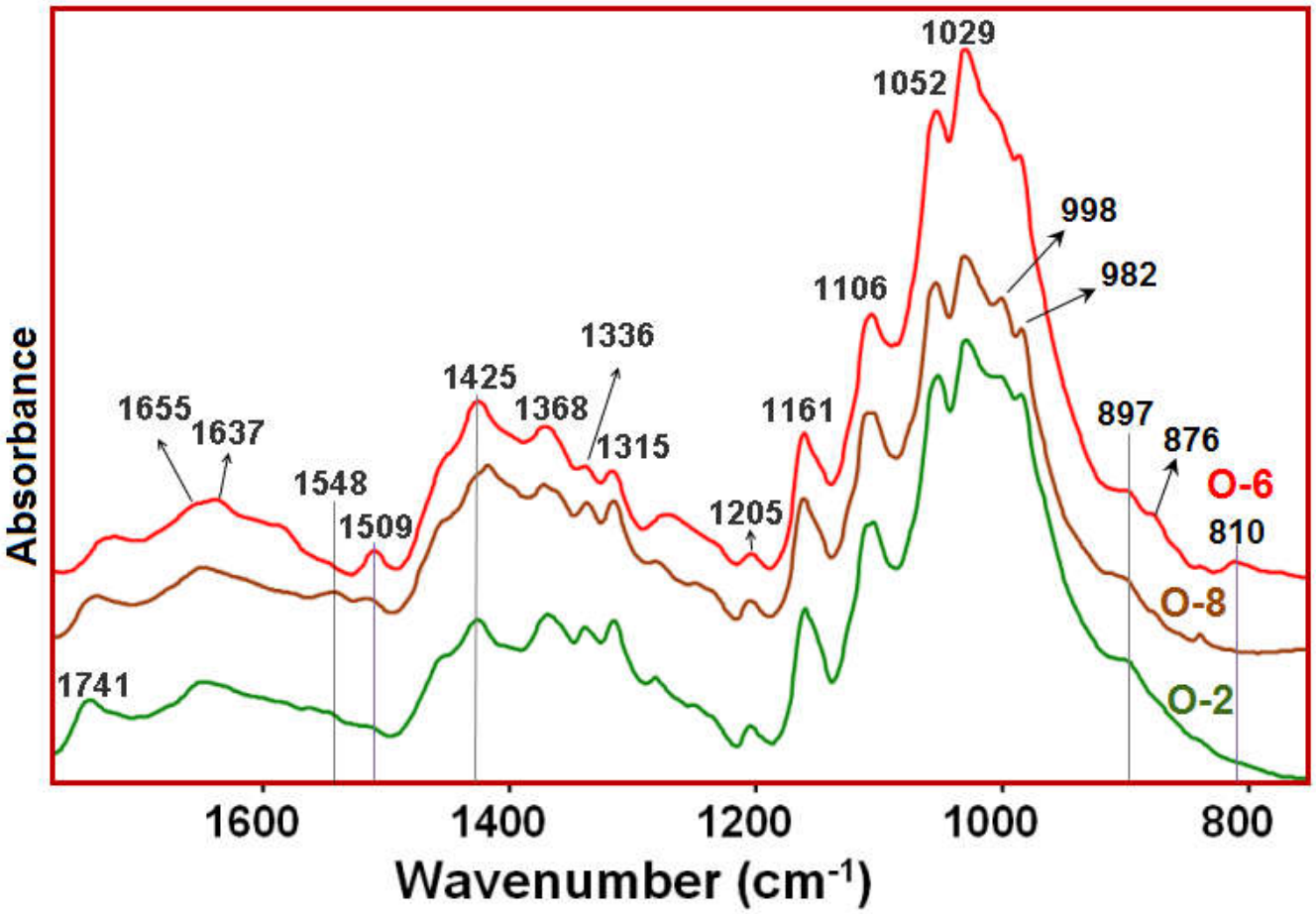
FTIR spectroscopy were used for the characterization of the paper of the stamps, as well as for identifying type of fillers employed. The 1770-750 cm^{-1} region of the ATR- FTIR spectra of the frontface of the three stamps are shown Although the infrared light in ATR-FTIR penetrates a small amount into 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.



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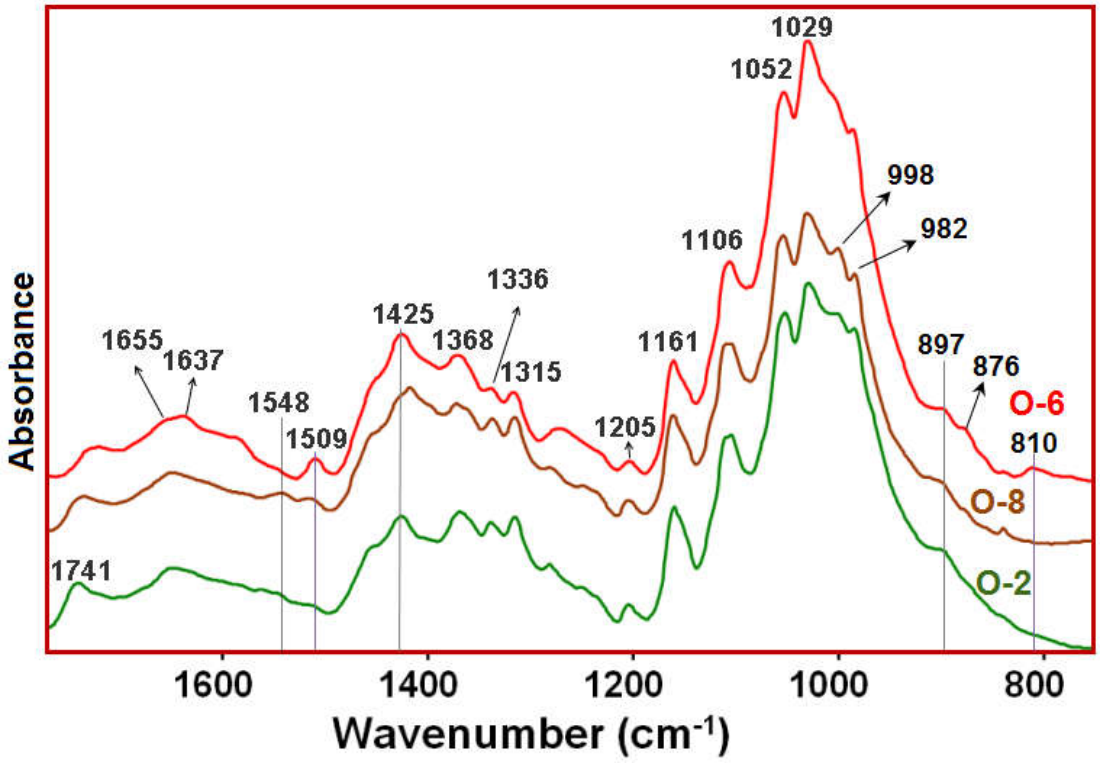
In all the IR spectra there is a large contribution from the paper on which the stamps were printed. The ATR-IR spectra of the frontface of the stamps displayed characteristic cellulose bands; 1741 cm^{-1} (νC=O); 1425 cm^{-1} (δCH_2+ calcite); 1368 cm^{-1} (δCH); 1336 cm^{-1}(δCOH); 1315 cm^{-1} (δHCC); 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 *ca.* 985 cm^{-1} (CO and ring modes). Some contribution of calcite ($CaCO_3$; νCO_3) to 1425 cm^{-1} band of cellulose cannot be excluded .



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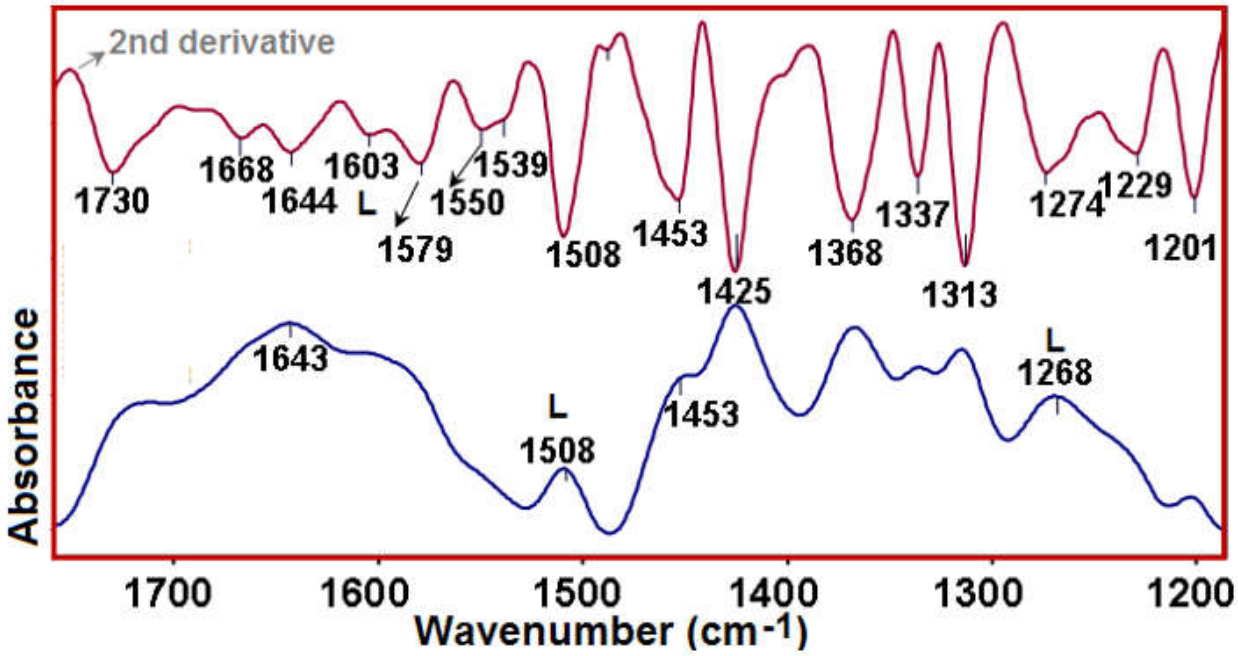

Presence of lignin in only in a small quantity in three stamps was detected. The absence of lignin in all of the other stamps implies that lignin has been removed by chemical processes but left in some of the stamps' paper as an impurity.

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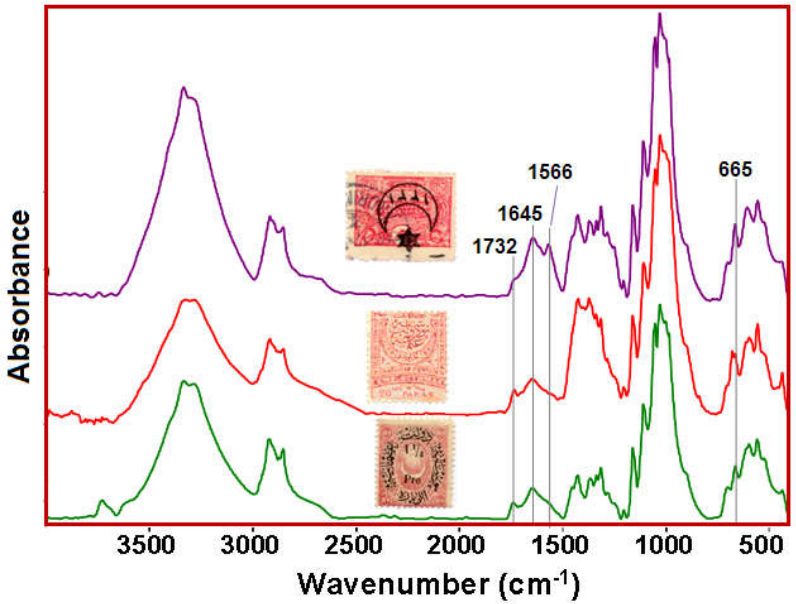
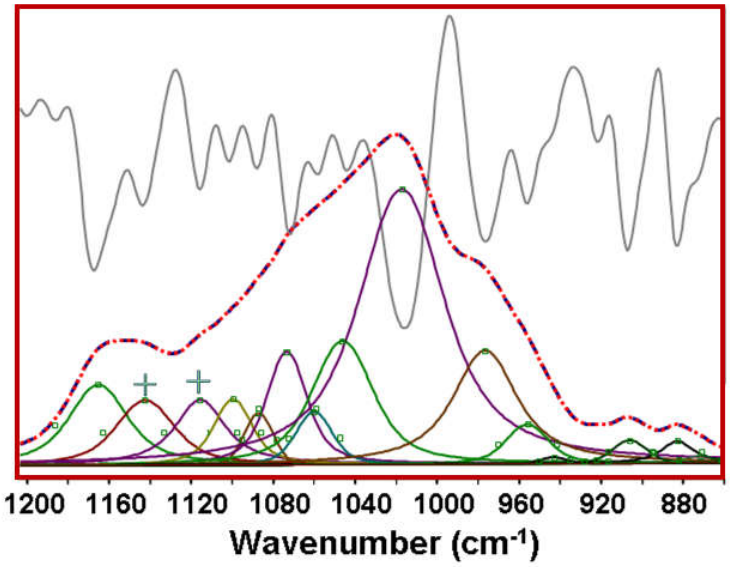
Vermilion is red mercuric sulfide

Vermillion; red mercury sulfide



Pink and lilac colorations

The ATR-IR spectra of the pink areas of the three stamps did not indicate any particular red pigment showing that an organic nature of red pigment was not used. On the other hand EDXRF spectra indicated presence of HgS (vermillion). The gypsum bands were identified at 1146 and 1116 cm-1 under cellulose absorptions by band component analysis of IR spectra.



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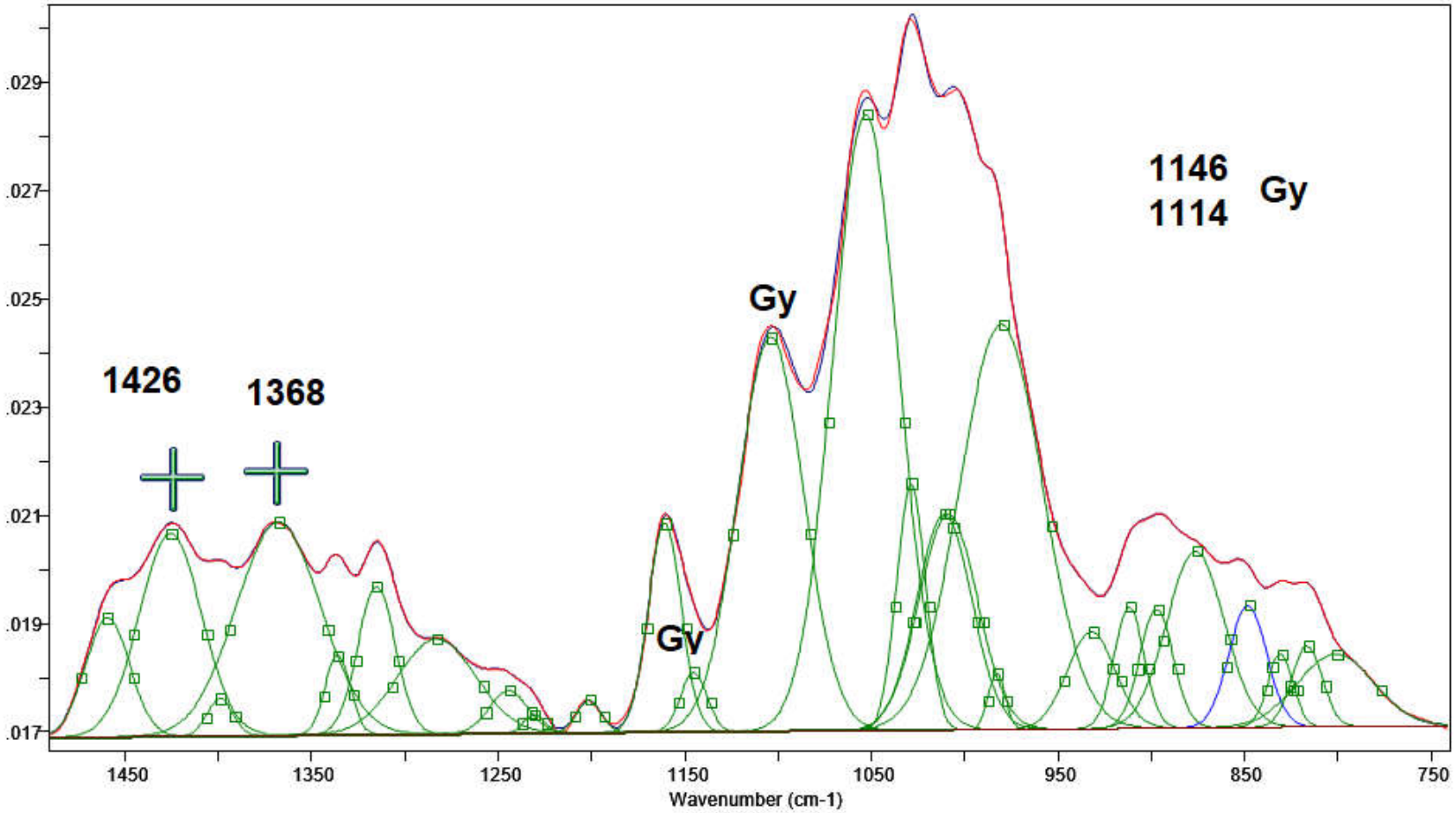
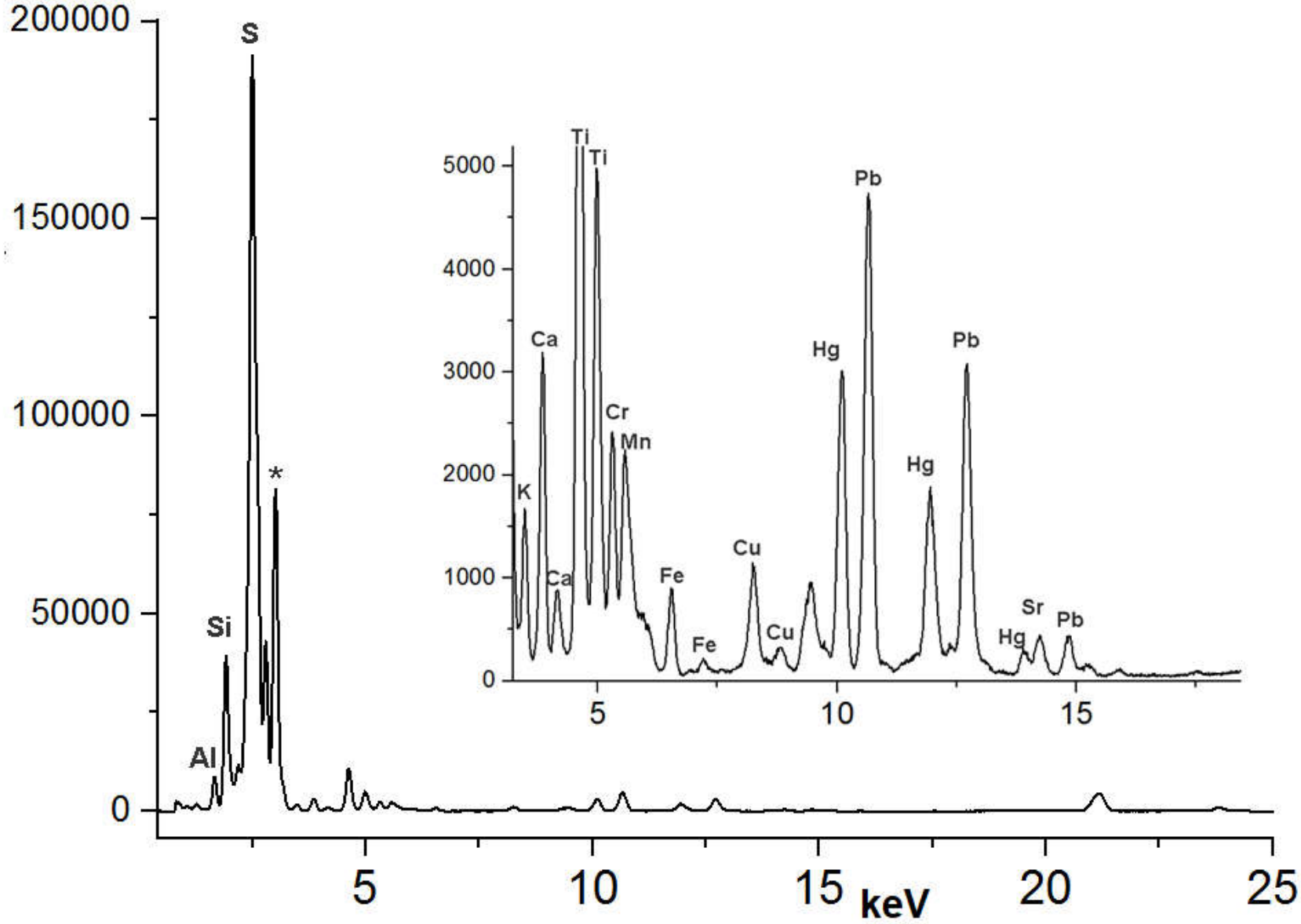


Gy = Gypsum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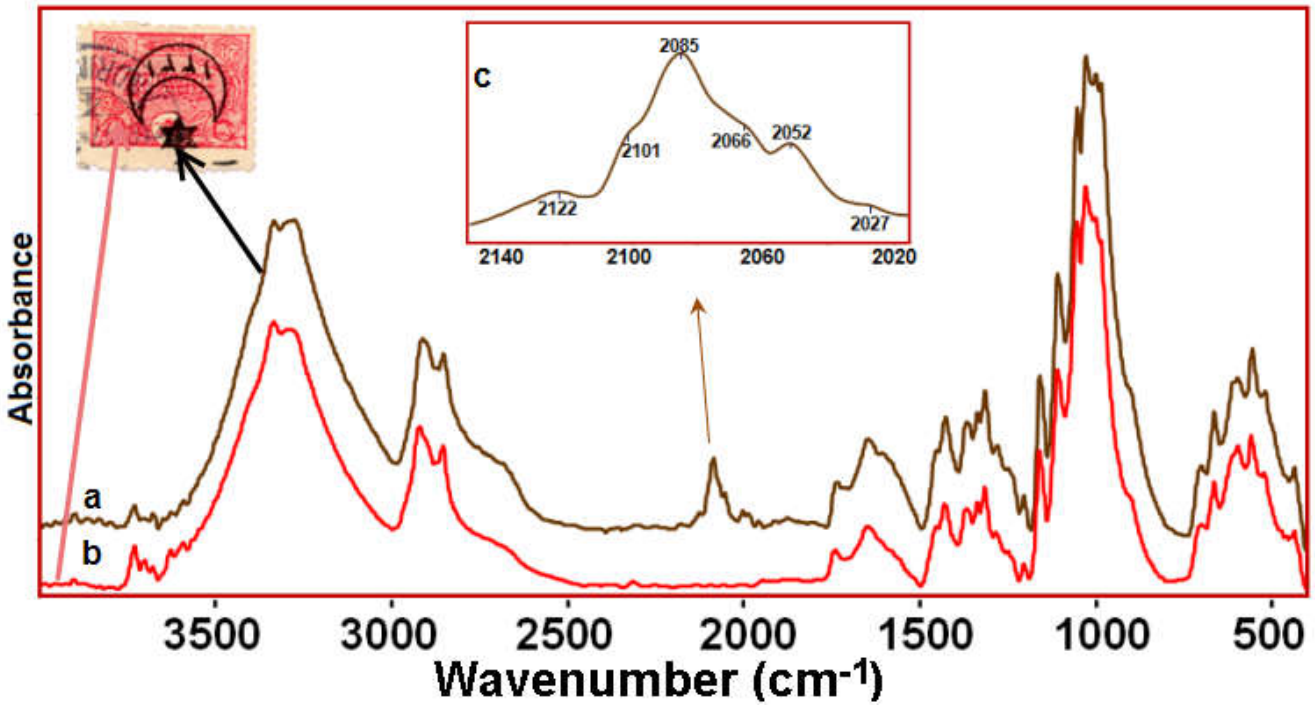
Black pigments

The Figure shows the ATR-IR spectrum of the black area of stamp in comparison with its pink colored part.



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 2066 cm^{-1} is related with Prussian blue.

In past many cyanide based inks were used; Prussian yellow, Prussian red, Prussian blue, Chinese blue, Prussian green and Prussian brown [9]

Presence of many C≡N stretching bands indicates presence of different oxidation states of iron.

Additiona magnetite (Fe_3O_4) (672 cm^{-1}) MnO_2 (620 cm^{-1}) were identified. EDXRF results also confirmed presence of Mn in addition to Ca, K, S, Fe and Hg. 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 MnO2, Fe3O4 and cyanide based pigments

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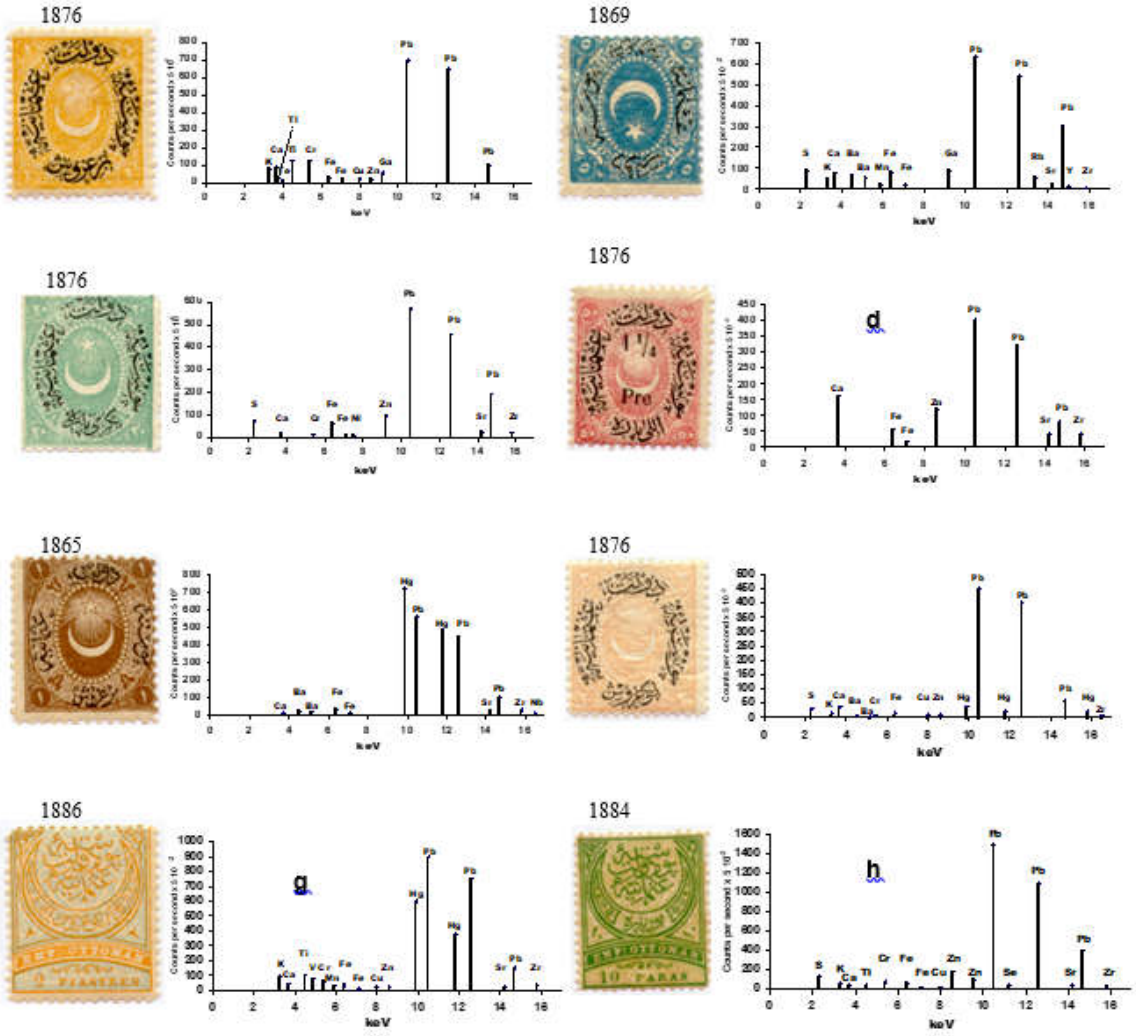
OTTOMAN EMPIRE STAMPS EDXRF



In the EDXRF spectra Pb was found in all stamps. This is due to the use of Pb molds in the printing system. Additionally in some of them lead red were used as red pigment.

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CONCLUSION

Through the combined use of vibrational spectroscopy and EDXRF analysis, the composition of inks used to print Ottoman stamps printed 1865-1913 has been established. The results have shown that the main colors (blue, orange, yellow, green pink and black) on the 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 spectroscopy and in all cases the paper was identified as cellulose. Presence of lignin in only in a small quantity in three stamps 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.

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