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Scientific face of the artwork: Investigation of the pigments and plasters of the wall paints of some ottoman mosques by FTIR and EDXRF techniques

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Abstract

The characterization of the pigments and plasters of the wall paints of some Ottoman Mosques have been performed using combined Energy Dispersive X-Ray Fluorescence (EDXRF) and Fourier Transform Infrared (FTIR) spectrometry (both in reflection and transmission modes) techniques. The colored wall paints were obtained from Fatih Mosques of Istanbul-Turkey and Pristina-Kosovo, and Suleymaniye Mosque of Istanbul-Turkey, during the restoration periods of the mosques. The investigations show that the plaster used on the walls has mixed gypsum-lime binders. The pigments identified in wall paints are: cinnabar (HgS), lead red (Pb_3O_4) and hematite (α-Fe_2O_3) in red colors, ultramarine blue ($Na_{8-10}Al_6Si_6O_{24}S_{2-4}$) as blue and green earth as green colors. The results provide a basis for future restoration of the wall paints.

Keywords: Pigments, Plasters, FTIR spectroscopy, EDXRF.

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1. Introduction

The Fatih Mosque is an Ottoman Empire Mosque located in the Fatih district of Istanbul-Turkey (Demir & Teyyime, 1991, Gunuc & Ozcan, 2007). It was firstly built between 1463-1471 years by famous Ottoman architect of 15th Century, "Sinaüddin Yusuf bin Abdullah" by the order of Ottoman Sultan, Sultan Mehmed the Conqueror, who captured Constantinople in 1453. The Fatih mosque was the first monumental project in the Ottoman imperial architectural tradition in Istanbul (Gunuc & Ozcan, 2007). The original mosque was damaged in the 1509-, 1557- and 1754- earthquakes and after all had been repaired. Unfortunately, it was completely destroyed by the earthquake on 22 May 1766. The current mosque was reconstructed between 1767 and 1771 years by the architect "Mimar Mehmet Tahir" by the order of Ottoman Sultan Mustafa the Third.

Fatih Mosque of Pristina-Kosovo was built in 15th AC and restored in 18th AC. The Suleymaniye Mosque was built by the famous Ottoman architect Mimar Sinan by the order of Ottoman Sultan, Suleyman the Magnificent. The construction work began in 1550 and finished in 1558.

Mortars and plasters, containing lime binder, have been used in ancient times and even after the discovery of cement (Anderson *et al*., 2014, Duran *et al.* 2010). Fourier Transform Infrared (FTIR) spectroscopy, combined with Energy Dispersive X-Ray Fluorescence (EDXRF) analysis, is a powerful tool for investigations of elemental and mineral constituents of the plasters, mortars and pigments (Anastasiou *et al*., 2006, Duran *et al*., 2010, Gulzar *et al*., 2013, Corti *et al*., 2013, Sing *et al*., 2014). The identification of mortars and plasters used for cultural heritage materials are crucial for the deep understanding of the raw materials, as well as for protection purposes as it could contribute significantly towards the selection and employment of the most appropriate conservation and restoration procedures, as well as the repair materials. The information about the chemical composition of the plaster used in the wall paints is of great interest. The restoration to be carried out to the mosque should often use similar materials with the original one both in composition and properties.

The aim of this study is to investigate the chemical composition of plasters used in the wall paints of the Ottoman mosque as well as the colouring agents used for surface decorations.

2. Experimental

The photographs of some wall paintings are shown in figure 1.

Figure 1. Some photographs of wall painting of Fatih Mosque-Istanbul.

2.1. Energy Dispersive X-Ray Fluorescence (EDXRF) Spectrometry

EDXRF spectra of the plasters were recorded on a spectro iQ-II model spectrometer. The samples were analyzed for 300 s using an air cooled low power palladium (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 Lα 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 Kα at an input count rate of 10,000 cps). During the measurement, the excitation area was flushed with helium gas.

2.2. Fourier Transform Infrared (FTIR) Spectrometry

The Fourier transform infrared spectroscopic analysis of the samples were carried out by using both transmittance and reflectance techniques. The FTIR transmittance spectra were recorded on a Bruker Tensor FTIR spectrometer, by preparing potassium bromide (KBr) discs. About 1mg of the sample was ground finely with 100 mg of anhydrous potassium bromide and the powder mixture was then pressed in a mechanical die press to form a translucent pellet. 100 sample and 20 background spectra were accumulated (1 cm^{-1} resolution). The FTIR-Diffuse Reflection (DRIFT) spectra of the samples were recorded on a Bruker alpha FTIR spectrometer. 100 sample and 20 background spectra were accumulated (4 cm^{-1} resolution). Spectral manipulations such as baseline adjustment and smoothing were performed using GRAMS/AI 7.02 (Thermo Electron Corporation) software package.

3. Results and discussion

3.1. EDXRF results

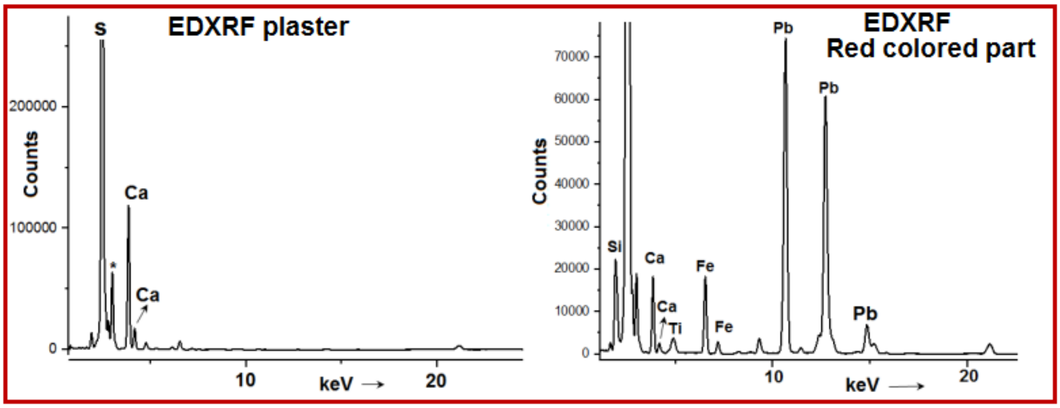

Figure 2. (a) The EDXRF spectra of uncolored and (b) red colored parts of the plaster of Fatih mosque-Kosovo. The marked (*) peaks are due to the equipment not concerning with the sample.

The EDXRF spectra of the uncolored plaster together with its red colored part, obtained Fatih Mosque of Pristina-Kosovo, are shown in figure 2. The uncolored part of the sample contains abundant sulphur (S) and calcium (Ca), indicating that mortar is mainly made of lime ($CaCO_3$) and gypsum ($CaSO_4.2H_2O$). This result is also confirmed by FTIR spectroscopy. The red colored part of the plaster contained abundant lead (Pb), indicated that the red pigment was mainly lead red (Pb_3O_4). Presence of moderate amount of iron (Fe) implies sample contains also red earth (hematite; α-Fe_2O_3). Some elemental concentrations of colored plasters of Ottoman Mosques are given in Table 1. The high amount of Hg and S in the reddish brown samples from Fatih Mosque-Istanbul and Suleymaniye Mosque implies the use of cinnabar (HgS) (Pessenha et al., 2010).

Table 1. Some elemental concentrations (mg/kg unless where indicated) of the colored plasters of Ottoman mosques

	Fatih Mosque-Istanbul			Fatih Mosque-Kosovo		Suleymaniye Mosque	
Element/Color	Green	Dark blue	Reddish brown	Green	red	Blue-gray	Reddish brown
K %	0.4	0.2	0.3	0.2	-	0.1	0.1
Ca %	38	26	32	44	34	26	20
Fe %	3.8	0.05	0.25	4.4	1.2	0.2	0.4
S	2.0	3.1	1100	2.1	3.0	2.1	660
Cr	295	10	7	74	8	14	Nd
Zn	840	7	9	Nd	Nd	Nd	Nd
Hg	Nd	Nd	7000	Nd	nd	42	4200
Pb	Nd	Nd	Nd	300	48800	2200	nd

Nd= not dedected

3.2. FTIR results

FTIR spectroscopy is a useful characterization method for mortars. It allows classifying the samples as lime binder or as mixed mortars (carbonate or carbonate + sulfate) according to the identifying bands of carbonate (*ca*. 1400 cm^{-1}) or sulfate (1150 - 1100 cm^{-1}) vibrational bands (Gadsden, 1975).

The FTIR spectrum of the blue colored part of the wall painting of Fatih Mosque-Istanbul is shown in Fig. 3. The bond stretching (1432 cm^{-1}) and angle bending (873 cm^{-1} and 713 cm^{-1}) vibrational bands of calcium carbonate were identified in all investigated samples. On the other hand the vibration frequencies of the antisymmetric bond stretching (1142 and 1117 cm^{-1}) and antisymmetric angle bending (669 and 603 cm^{-1}) vibrations of sulphate ion together with 3547, 3406 (OH stretching) and 1685, 1621 cm^{-1} (H_2O bending) vibrations of water molecule, are indicative of the presence of gypsum ($CaSO_4.2H_2O$) (Gadsden, 1975) in all the samples. In addition the FTIR spectrum of the blue colored part of the wall painting of Fatih Mosque-Istanbul shows all characteristic bands of ultramarine blue pigment ($Na_{8-10}Al_6Si_6O_{24}S_{2-4}$). The observed band at 1011 cm^{-1} is assigned to the (Si-O-Si) antisymmetric stretching mode, whereas the band at 451 cm^{-1} is related to the (O-Si-O) deformation mode of the pigment (Silva *et al.,* 2006) (see Fig 3). The calcite (713 cm^{-1}) and gypsum (669 and 603 cm^{-1}) (Gadsden, 1975) bands are also observed.

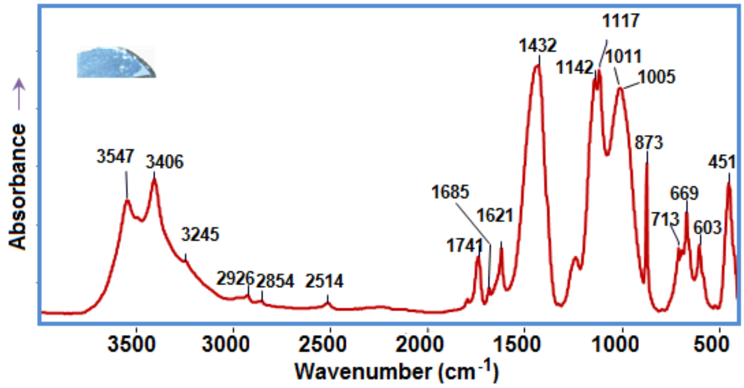

Figure 3. FTIR spectrum of blue coloured plaster of Fatih Mosque-Istanbul.

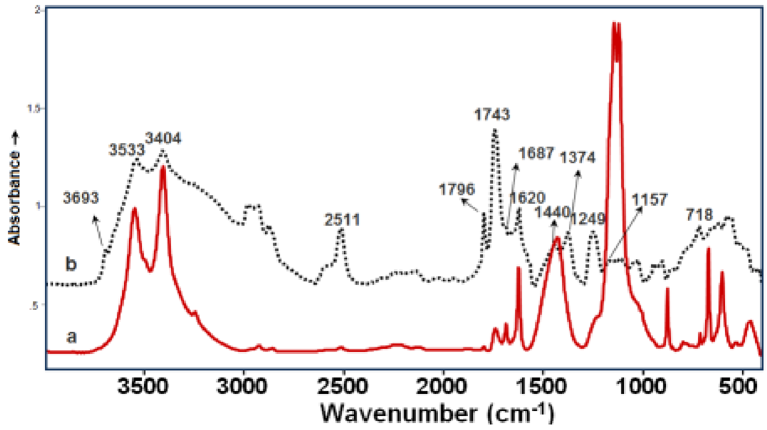

Figure 4. FTIR spectra of red coloured plaster of Fatih Mosque Kosovo, obtained (a) KBr and (b) DRIFT techniques.

The diffuse reflectance (FTIR-DRIFT) spectra of the samples were also recorded and compared with corresponding transmittance (KBr) spectra. Fig. 4 shows FTIR spectra of red colored plaster of Fatih Mosque-Kosovo, obtained according to the two different techniques. We observed some differences in the band shapes and wavenumbers due to the difference in recording techniques as seen in Fig 4. Even though the same samples are used for both transmission and DRIFT experiments, IR-DRIFT and IR-transmittance spectra may not be identical because the different penetration depth together with the effect of specular reflection in DRIFT measurements plays role in this alteration (Beasley *et al.,* 2014). DRIFT spectrum can be adversely affected by particle size differences and incident IR wavelengths. Comparison of the two spectra indicates that amount of calcite and organic constituents are higher in surface spectrum (DRIFT) (see Fig 4). It was also known that in some mortars and plasters, used in ancient times until the discovery of cement, contained egg whites as an additive (Boke *et al.*, 2006). The band appearing near 1743 cm^{-1} is evidence for the presence of ester carbonyl groups (C=O carbonyl stretching), and the bands near 1157 and 1249 cm^{-1} are spectral features attributed to cholesterol ester groups involved in oxidized molecules of cholesterol (Cheilakou *et al.*, 2014). The latter could also be assigned to vibrations of phosphate groups of phospholipids and/or DNA due to the presence of egg white (Cheilakou *et al.*, 2014).

4. Conclusion

Combined EDXRF and FT-IR spectral investigations are found to be very informative in shedding light on the characterization of the inorganic and organic compounds of the plasters and coloring agents of the wall paints of Ottoman Mosques. Based on the analysis results it was found that plaster mortars belong to mixed lime-gypsum mortar group. Presence of egg white was also detected by FTIR. Cinnabar, lead red, hematite, green earth and ultramarine blue were used as coloring agents. The results provide a basis for future restoration.

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