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Elemental and spectroscopic characterization of plasters from Fatih Mosque-Istanbul (Turkey) by combined micro-Raman, FTIR and EDXRF techniques

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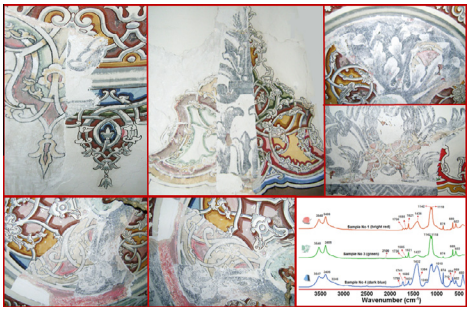
HIGHLIGHTS

- Wall paintings of an Ottoman mosque were analyzed by means of micro-Raman, FTIR and EDXRF.
- Identification of pigments and plasters of wall-paintings was obtained.
- Plaster mortars belong to mixed lime–gypsum mortar group.

GRAPHICAL ABSTRACT



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ABSTRACT

The characterization of the plasters and coloring agents of the wall paintings of Fatih Mosque have been performed using combined micro-Raman, FTIR and EDXRF techniques. The investigations show that the plaster used on the walls has mixed gypsum–lime binders. Cinnabar {HgS}, lead red {Pb_3O_4} and hematite {α-Fe_2O_3} were identified in the red surfaces. Blue color is attributed to ultramarine blue {$Na_{8-10}Al_6Si_6O_{24}S_{2-4}$}. Green color is assigned to mixtures of green earth, copper phthalocyanine {$Cu(C_{32}Cl_{16}N_8)$} and brochantite {$CuSO_4{\cdot}3Cu(OH)_2$}. Strontium yellow {$SrCrO_4$} and zinc white {ZnO} were also used to ensure the color tone. The results provide a basis for future restoration of wall paints.

Introduction

The Fatih Mosque is an Ottoman Empire Mosque located in the Fatih district of Istanbul-Turkey [1,2]. It was firstly built between 1463 and 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 [1–3]. 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. Previously two restorations (in the last quarter of nineteen century and the second half of 20th century) had been carried out to the Mosque.

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Mortars and plasters, containing lime binder, have been used in ancient times and even after the discovery of cement [4–6]. Vibrational spectroscopy, combined with X-ray Fluorescence (XRF) analysis, is a powerful tool for investigations of elemental and mineral constituents of the plasters, mortars and pigments [5–9]. 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 toward the selection and employment of the most appropriate conservation and restoration procedures, as well as the repair materials. The aim of this study is to investigate the chemical composition of plasters used in the wall paintings of the Ottoman mosque as well as the coloring agents used for surface decoration. The photographs of the wall paints, Fatih Mosque and the investigated samples are given in Fig. 1.

Experimental

Samples

The plaster samples which were decorated by red, green and blue colored paints were taken in August 2008, from two corner domes (KK1 and KK2) of Fatih Mosque during the restoration process [10] carried out in between 2008–2011. The photographs of the paint samples are given in Fig. 1.

EDXRF spectrometry

Energy Dispersive X-ray Fluorescence (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 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.

FTIR spectroscopy

The Fourier transform infrared (FTIR) spectra were recorded on a Bruker Tensor FTIR spectrometer, by preparing KBr discs. About 1 mg of the sample was ground finely with 100 mg of anhydrous potassium bromide (KBr) 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).

Raman spectroscopy

Micro-Raman spectra were recorded by a Jasco NRS 3100 micro Raman spectrometer (1200 lines/mm and high sensitivity cooled CCD) equipped with a 785 nm diode laser. Rayleigh scattering was rejected by an edge filter. The spectrometer was calibrated with the silicon phonon mode at 520 cm^{-1}. A 20× microscope objective (Olympus) was used to focus the laser and collect Raman scattering on the sample. Spectral resolution was 2.93 cm^{-1}.The laser power during signal acquisition was 25 mW, the exposure time was 1 s and 300 spectra were accumulated.

Spectral manipulations such as baseline adjustment, smoothing, obtaining the second derivative and band fitting procedures, were performed using GRAMS/AI 7.02 (Thermo Electron Corporation) software package. Band fitting was done using Gaussian function and fitting was undertaken 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 Raman spectrum was used as a guide. The second derivatives of the spectra were obtained by using Savitzky–Golay function (two polynomial degrees, 13 points).

Results and discussion

Plasters

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

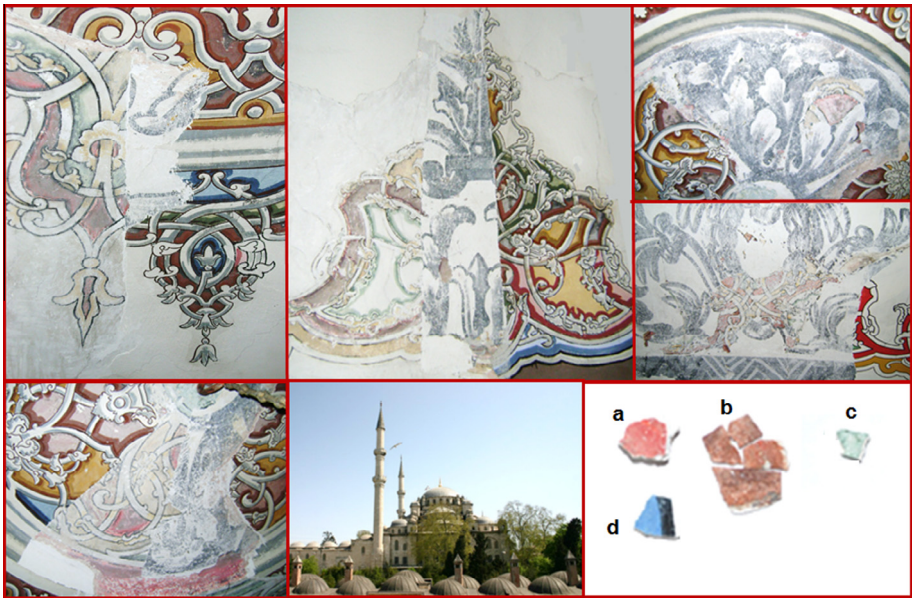

Fig. 1. The photographs the wall paints, Fatih Mosque and investigated samples; Sample 1 (a), sample 2 (b), sample 3 (c) and sample 4 (d).