Spectroscopic pigment identification in ornamentation tiles (XIII - XV ac) from Aveh, Qom and Masshad in Iran

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Abstract—In this work, Raman spectroscopy and complementary techniques are used to identify and compare pigment components in the ornamentation tiles excavated in the archaeological sites of Aveh, Qom, and Masshad in Iran, which are dated for XIII–XVc. The results concerning different blue pigments used for the production of tiles found in sites distanced by ca 100 km indicate the usage of Fe oxide based ochre and red pigments in mixtures and confirm an advanced luster technique with Pb-rich oxides and traces of corroded Ag.

Raman spectroscopy (RS) in combination with complementary techniques represents a well proven tool in the research on historical objects and materials aimed at answering questions regarding the identification, provenance and manufacturing technologies of the past. The above approach is used in the present work to investigate the chemical composition of the blue, brown and white pigmented areas of the ornamentation tiles recently excavated in archaeological sites in Iran. The pigment compositions of the tile samples from Aveh are analyzed and compared to the sample compositions from the archaeological sites in Mashhad and Qom in order to clarify the questions regarding pigment components and production technology. The results are an important element of the study on the provenance of the tiles. All the excavation sites are localized ca 100 km apart from each other and date back to the Medieval Period (XIII–XV AC). It is worth mentioning that Aveh has been once a vital place on the trade route from Soltaniyeh (former capital of Mongol Ilkhanate) to Saveh, Qom, Kashan, Ispahan and Shiraz up to the coast of the Persian Gulf.

The surface examination of the samples was performed with the use of optical (OM), SMZ 800 (Nikon) and electron scanning (SEM) microscopes, and the elemental composition was analysed by means of energy dispersive (SEM/EDX) and Raman (RS) spectroscopic measurements. For the SEM analysis an EVO MA10 (Zeiss) instrument equipped with an EDAX spectrometer and a secondary electron detector (spatial resolution ~ 2.0nm) operated at 20.0kV was applied and the other parameters (excitation current, magnification) were adapted depending on the analysed sample. The Raman spectra were acquired by means of a μ-Raman apparatus InVia (Renishaw) equipped with two lasers providing excitation at 785nm and 514nm. The confocal microscope with objectives 20, 50 and 100× assured the spectral footprint of the sample surface down to $5\times5\mu m^2$. For dispersion of the backscattered signal, the grating of 1200 groves/mm was used and detection was provided by a CCD array detector. Spectra were acquired over a range of $100\div3200 cm^{-1}$ at a resolution of $2 cm^{-1}$. For each sample several spectra were accumulated and averaged and identification was performed with the use of the reference data from digital Raman libraries.

The presence of coloured ornamentation of the tiles which has been already observed on site even with the naked eye becomes more impressive when the decoration details are considered by means of OM. The inspection of the tile surface as well as the cross sections confirm the presence of three major pigments – blue, brown and white - see Fig. 1. The blue and white pigments appear to be a mixture with silica, which is also the main component of the body matrix.

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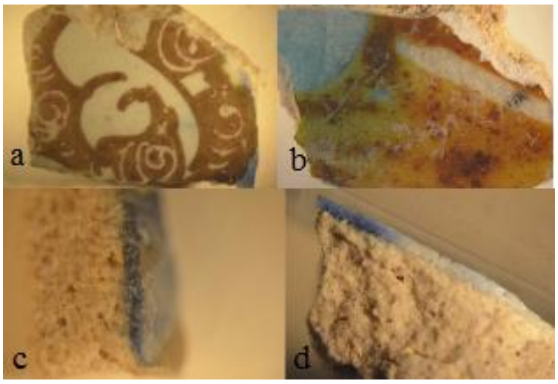

Fig. 1. Optical microscope images of the tile fragments from Aveh (a) and Mashhad (b), and cross sections of the samples (c,d).

When observed at higher magnification, the paint (pigment) layers show no uniformity in structure resulting most probably from firing, i.e. high temperature applied during the tile production - see Fig. 2.

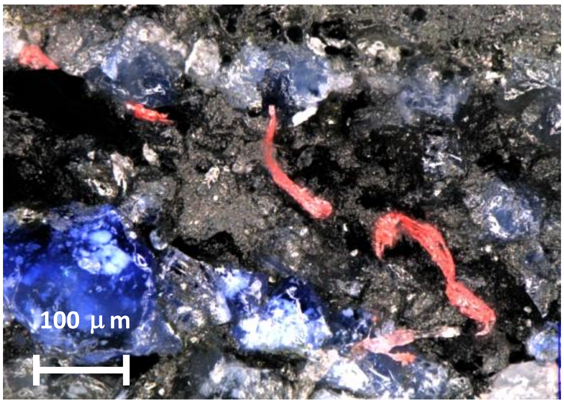

Fig. 2. OM image of the sample #1 from Aveh showing silica glaze and pigment layers (blue, reddish-brown and white); the black area corresponds to the resin matrix embedding the sample.

The results of an elemental EDX analysis (sample Aveh #1) refer to the superficial surface layer (depth < 1μm) with visible brown and blue colored regions (Fig. 2), with their spectra shown in Fig. 3. In addition to Si and O (silica in a glaze and paint admixture), the presence of elements Na, Mg, Al and Ca in both paints can be concluded from the overlapping bands, while a larger content of Cl, K, and Ca is revealed by the blue band in comparison to brown. Most of the light elements can originate from oxides used in glaze, however, Na, Ca and K can be observed in the surface contamination, too [1].

Interestingly, the EDX data of the other sample (Aveh #2, glaze) show an exclusively metallic content dominated by Pb (~ 50 %), considerable amounts of Sn and Cu, and smaller ones of Zn, As, Ni, Co, Sb and Fe - see Fig. 4.

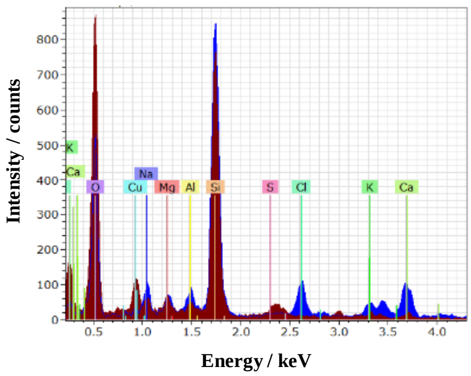

Fig. 3. EDX spectrum for the Aveh tile (Aveh #1) obtained for the blue and brown pigment components observed in Fig. 2; traces of Cu present in the brown areas indicate the luster wire technique applied.

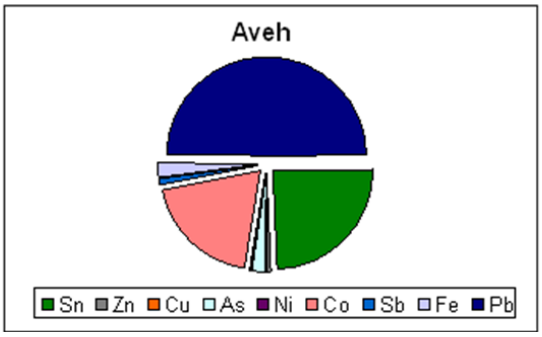

Fig. 4 Diagram of the EDX results showing elemental content (wt) obtained for the sample Aveh #2; measurement inaccuracy <10%.

Raman spectra of the blue pigmentation clearly indicate different chemical compositions depending on the archaeological site. In the sample (sM1) the dominant compound corresponds to *lazurite* $[(Na,Ca)_8(SO_4,S,Cl)_2(AlSiO_4)_6]$ and bands ascribed to silica are observed, too (Fig. 5a). In one of the samples from Aveh (p4), the peak at 667 cm^{-1} and the surrounding bands indicate a compound of Co and Sn oxides known as *cerulean blue* ($CoO \cdot nSnO_2$), in a mixture with silicates (Fig. 5b) accompanied by an extensive matrix with carbonates and aluminosilicates of Na, K, Ca and Mg, which is in agreement with the EDX analysis [2-4]. In another sample of blue (s2292), the Raman band at 464cm^{-1} indicates the presence of smalt - Fig. 5c. To explain the differences in color saturation and depth in the samples of brown pigmented areas, the pigment compositions deduced from the Raman spectra in Figs. 6 and 7 should be considered. Two of the samples (1321 and sA297M) show the presence of mixed iron ores of magnetite (brown), hematite (red) and goethite (yellowish-brown) with the latter one being a major component (up to 70%) of mineral yellow ochre (Fe_2O_3-H_2O) often mixed with lepidocrocite (gamma-FeO-OH), clay and silica sand (Fig. 6a,b).

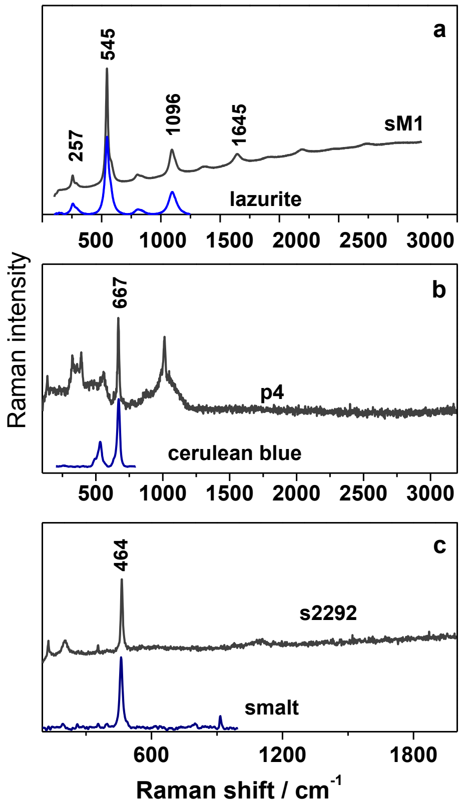

Fig. 5. Raman spectra of the blue pigment samples from Massad (a) and Aveh (b,c) and the reference spectra of lazurite, cerulean blue, and smalt from [5].

The pigment mars red – hematite (Fe_2O_3) can be identified by the presence of bands ascribed to deforming and stretching oscillations of Fe-O and Fe=O [6,7].

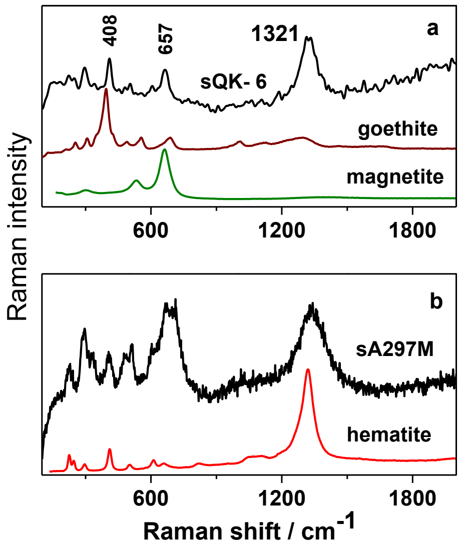

Fig. 6. Stack-plotted Raman spectra of brown (a) and red pigments (b), and reference spectra of goethite, magnetite, (brown and yellow ochres) and hematite (mars-red) taken from [5].

The band of carbonate group at 1085cm^{-1} (calcite, $CaCO_3$) is clearly observed for the white colored areas (sample sM1, Masshad - not shown), while it is not evidenced in the spectra of the light brown areas. This indicates that admixture of calcite was not applied in measurable amounts in the above case, in contrary to blue pigments. The spectra of red pigment particles (cf. Fig. 2) show strong Raman bands at 221, 292 and 408cm^{-1} and a weaker one at 613cm^{-1}, which coincides with the reference data of the mineral mars orange (Fe_2O_3) [6,7] - Fig. 7.

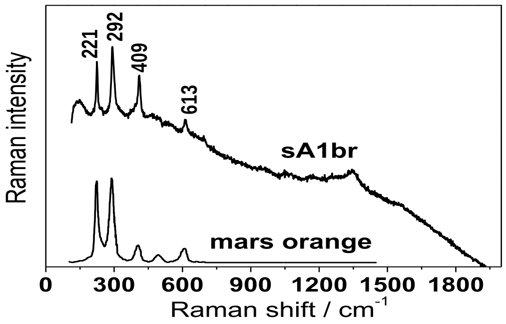

Fig. 7. Raman spectrum of the brown pigment and the reference spectrum of mars orange from [5].

In summary, the blue colored samples from Masshad show predominant use of lazurite, whereas those from Aveh indicate cerulean blue or smalt as the main component. In all measured samples, Cu is present as a trace element only and $CaCO_3$ is responsible for the white color. Brown pigments are mixtures of iron ores. The glaze samples indicate the use of a luster technique with the application of a Pb-rich oxide glaze matrix. The bronze pigmentation, which is observed only in the luster layer, shows traces of Ag, which is most probably degraded due to long-term corrosion. This could also be the reason for the decomposition of Fe and Sn oxide-based pigment compounds.

The results of the present research broaden our knowledge on the pigment chemical composition of coloured tiles in medieval Iran. Moreover, this contributes to correct reconstruction and maintenance of destructed and eroded historical objects in Iran, representing an invaluable part of the world’s cultural heritage.

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