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MICRO-INFRARED AND RAMAN SPECTROSCOPY APPLIED FOR STUDYING ANCIENT EARTH PIGMENTS

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Abstract: *Micro-infrared and Raman spectroscopy are non-destructive, local methods providing valuable information about the type of material (organic or inorganic), atomic groups, phase impurities, isomorphic substitution, inhomogeneity, i.e. carries information on both chemical composition and structural characteristics. Raman spectroscopy is based on the inelastic Raman scattering of monochromatic light in the visible, near-infrared or ultraviolet range. Fourier transform infrared spectroscopy examines the direct absorption of light at frequencies corresponding to the vibrational energy of atomic group. Due to the different selection rules for Raman scattering and infrared absorption, the two methods are complementary. The use of both methods for the study of ancient pigments gives good results in the identification of colouring substances, in the study of mixtures, as well as in alteration products. Various examples of Raman and infrared spectra of black, red, purple, yellow pigments from archaeological samples are presented. The advantages and disadvantages of the two methods for the identification of various ancient pigments with natural origin are summarized.*

Key words: *Infrared microscopy, Raman spectroscopy, ancient pigments, archeology*

INTRODUCTION

Vibrational spectroscopy methods (Raman and infrared) are non-destructive and widely applicable in areas such as restoration and archeology for pigment identification (Clark, R. 2002). Raman spectroscopy is based on the inelastic scattering of monochromatic light in the visible, near-infrared or ultraviolet range during the interaction with the vibrations of the atoms that make up the structure of substances, i.e. carries information on both chemical composition and structural characteristics. The use of Raman spectroscopy allows the identification of pigments and dyes „in situ” in manuscripts, paintings, ceramics, textiles and plasters without destroying the integrity of the fragment. A disadvantage of the method is that some materials have a strong fluorescence that interferes with the useful signal and worsen the signal-to-noise ratio.

Raman spectroscopy has a better spatial resolution than infrared spectroscopy when using a microscope.

Fourier transform infrared spectroscopy (FTIR) examines the direct absorption of light by atomic vibrations in the corresponding energy range. Micro-Infrared spectroscopy (μ -FTIR) in reflectance or attenuated total reflection (ATR) mode has the advantage of not destroying the sample, but has the disadvantage of a weaker signal compared to the standard transmission method in potassium bromide tablets. The best approach is to analyze the same area of an object's surface with both methods in the 1-5 μm size region for Raman spectroscopy and in the 20-100 μm size region for micro-infrared spectroscopy.

EXPERIMENTAL

Hyperion 2000 infrared microscope with the ability to operate in transmission, reflection and attenuated total reflection (ATR-Ge crystal) modes of micro-spectroscopy, connected with Tensor 37 spectrometer (Bruker). Spectra were collected from area of 50x50 micrometers with 4 cm^{-1} spectral resolutions after averaging 128 scans in the 600-4000 cm^{-1} spectral range.

HR LabRam (Horiba) spectrometer (600 grooves/mm grating) coupled with an Olympus BH2 optical microscope. Spectra were measured with a 50x magnification objective, spectral

resolution $\pm 2 \text{ cm}^{-1}$ in the spectral range $100\text{-}4000 \text{ cm}^{-1}$. The 632.8 nm line of He-Ne laser was used for sample excitation. The spectrum acquisition time has been changed, and the power of the laser excitation radiation has been reduced by using filters to below 1 mW . The Origin 9.0 software package was used to plot and process the spectra. Samples studied were fragments from several tombs near villages Maglizh, Dolno Lukovo, Bulgaria and from the regions of Stara Zagora and Haskovo, Bulgaria which are well described and studied from an archaeological point of view and have been researched within funded projects (Nechrizov et al., 2017).

RESULTS AND DISCUSSION

Red color

The surface of the sample from Dolno Lukovo (Ivailovgrad area) (Fig. 1a) is covered by a secondary white, dense layer of calcite, which interferes the measurements. After mechanical removal of the plaques, only the surface pigmented red layer (2) was examined. In the surface pigmented layer, the predominant phase responsible for the red color is hematite (Fe_2O_3), which is evidenced by the peaks at 228 , 295 , 413 , and 612 cm^{-1} . The peak at 1320 cm^{-1} is characteristic of hematite. Calcite (CaCO_3) (peaks at 1087 , 713 cm^{-1}) is almost always present.

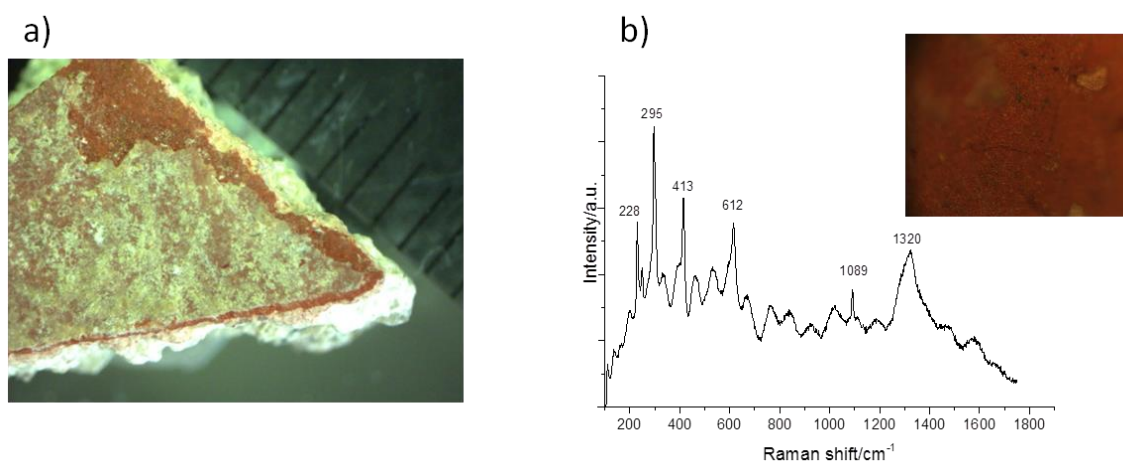


Fig. 1 a) Fragment from tomb near Dolno Lukovo, Ivaylovgrad- chamber; b) Raman spectrum of red colored area. Raman spectra were measured on a fragment pigmented in red and black from tomb Maglizh (Kazanlak district) (Fig.2 and Fig.3). The bright red color (Fig.2) was achieved by the mercury sulphide - cinnabar (HgS), which gives intense Raman peaks at 253 (ν_1), 285 and 344 cm^{-1} (Frost et al., 2002). This phase cannot be identified by micro-infrared spectroscopy, as the active infrared modes are beyond the spectral range of the method ($600\text{-}4000 \text{ cm}^{-1}$). There are no deposits or mineral occurrences of mercuric sulphides nearby in the region, suggesting a more distant source of the pigment.

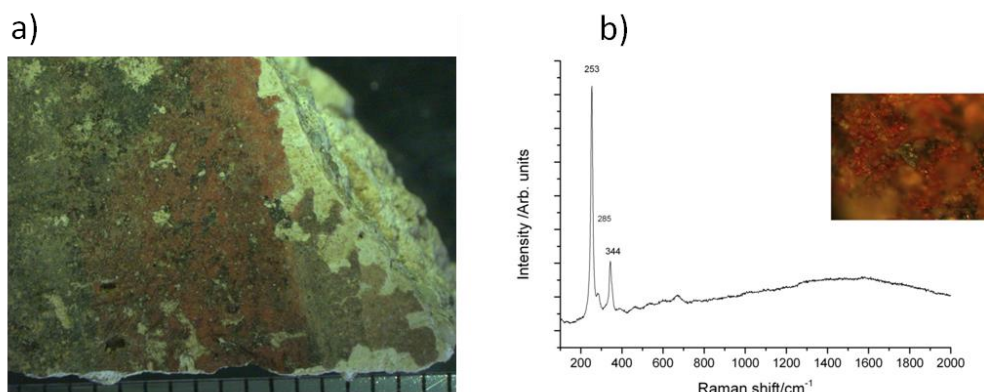


Fig. 2 a) Fragment from tomb Maglizh (Kazanlak); b) Raman spectrum of red colored area

Black color

The black color was achieved by using charcoal as a pigment, as seen in the Raman spectrum on Fig 3b. Two broad and overlapping peaks with maximum intensity at approximately 1580 cm^{-1} (G band) and 1340 cm^{-1} (D band) observed, are characteristic for carbon black materials.

Examining the position, width, and intensity ratio of these bands can provide information to the type of carbonaceous material and its origin (Tomasini et al., 2012). The G band is due to the stretching vibrations of carbon atoms (sp^2), while the D band is a disordered band originating in structural defects. These characteristic peaks are observed only in the Raman spectra, and are not active in the infrared spectra. The absence of a peak around 960 cm^{-1} characteristic of the phosphate stretching mode of hydroxyapatite indicates that the charcoals are of plant origin.

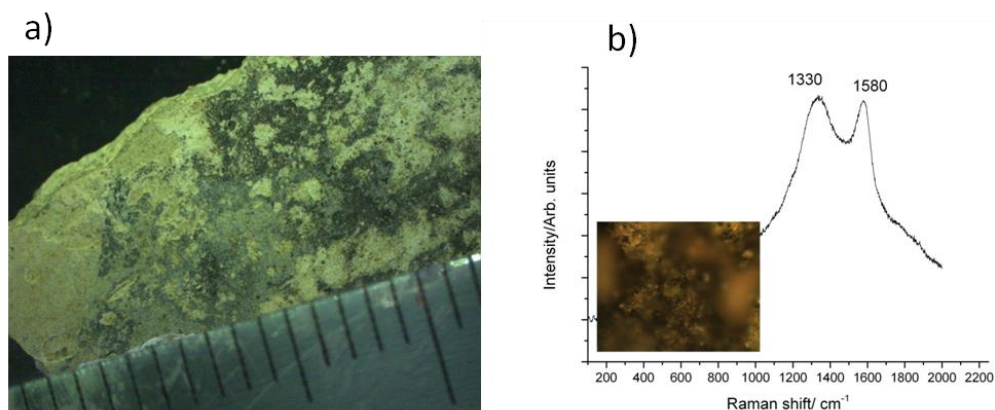


Fig. 3 a) Fragment from tomb Maglzh (Kazanlak); b) Raman spectrum of black colored area

The dark red (purple) color is due to mixing the red plaster with a larger amount of black pigment. Analysis of the black mineral grains proves that the material used to produce the 'purple' shade is charcoal. The Raman spectra (Fig. 4b) show the characteristic peaks for disordered carbon at 1330 (D disordered line) and 1580 (G graphitic line) cm^{-1} together with peaks of hematite.

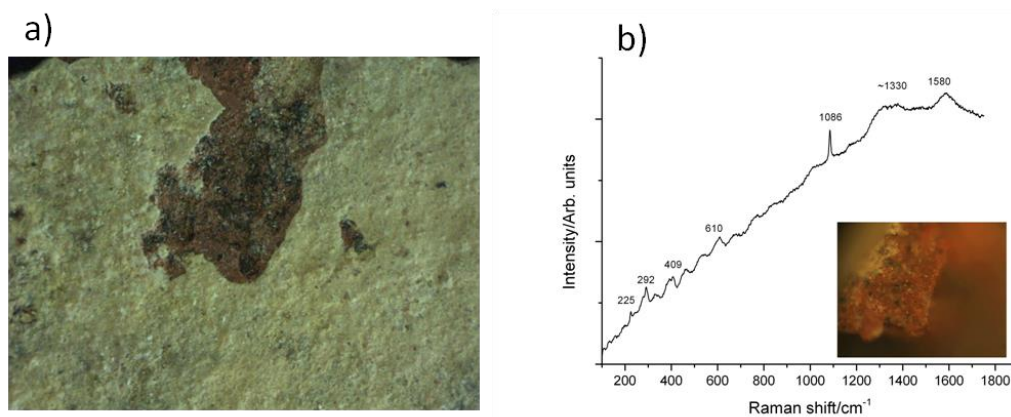


Fig. 4 a) Fragment from tomb Maglzh (Kazanlak); b) Raman spectrum of dark red (purple) color area

Yellow color

The yellow pigment used most often to decorate Thracian tombs is goethite ($\alpha\text{-FeOOH}$) (Fig.5). This mineral is formed by the weathering of other iron-rich minerals. The infrared spectrum taken from the yellow colored fragment from tomb near Dolno Lukovo reveals absorption peaks at 667 , 792 , 886 and 3090 cm^{-1} of goethite. The red line in Fig. 5a is the reference goethite spectrum (R050.1) taken from the RRUFF spectral database (Lafuente et al., 2012).

Table 1. The symmetry and frequency of the Raman and infrared active modes of different mineral phases

Mineral	Formula	Color	Raman peaks Position (cm ⁻¹)	Active mode	Infrared peaks Position (cm ⁻¹)	Active mode
Hematite	α -Fe ₂ O ₃	Red Orange Dark red	226 293 410 500 610 ~1315 vs	A _{1g} Fe-O str. E _g Fe-O bend. E _g A _{1g} E _g	660	E _u Fe-O bend
Cinnabar	HgS	Red	146 252 289 345	A _{1g} E E	Below 400 cm ⁻¹	
Goethite	α -FeOOH	Yellow	384	ν_1 Fe-O	410 610 800 900 3100	ν_3 Fe-OH stretching Fe-O stretching OH deformation OH deformation OH stretching
Calcite	CaCO ₃	White	1087- 1090	ν_1 CO ₃	1085	ν_1 CO ₃
					1432	ν_3 CO ₃
			879	ν_2 CO ₃ out plane	876	ν_2 CO ₃ out plane
			715	ν_4 CO ₃ in plane	712	ν_4 CO ₃ inplane
			1750	$\nu_1+\nu_4$; $2\nu_2$	1795 2512 2873	$\nu_1+\nu_4$; $2\nu_2$ $2\nu_2+\nu_4$ $2\nu_3$
280 153	T (Ca, CO ₃)					

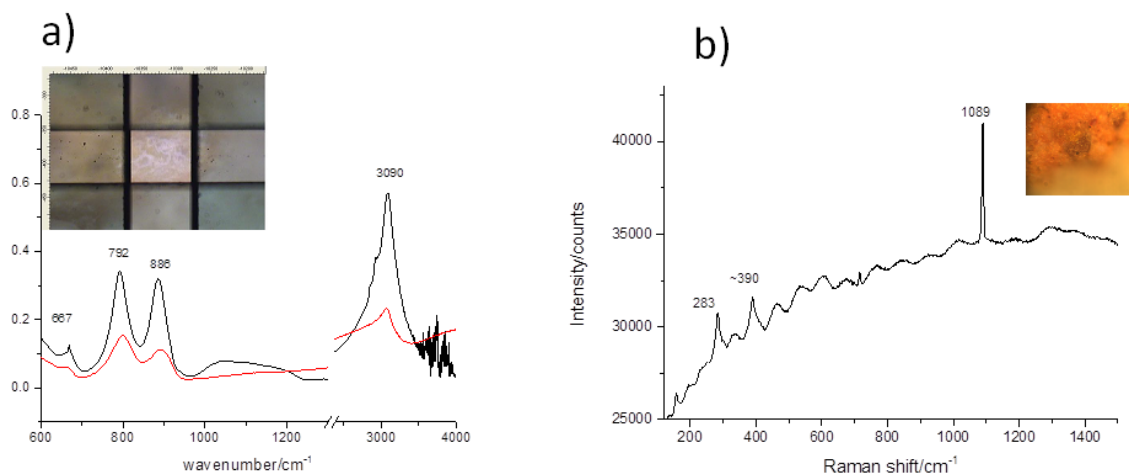


Fig. 5 a) Micro infrared spectrum of yellow colored fragment from tomb near Dolno Lukovo, Ivaylovgrad; b) Raman spectrum of orange colored area (Dolno Lukovo)

When goethite is mixed with hematite, secondary orange colors are obtained as it is shown on Fig.5b. The frequency and symmetry of the Raman and infrared active modes are summarized in Table 1.

CONCLUSIONS

The powder FT-IR spectra of the investigated bulk materials reveal a predominance of calcite or gypsum in the plaster. The pigments used are better identified by local methods measuring micrometer-sized areas. High levels of fluorescence, which is a drawback of Raman spectroscopy, can be partially overcome by varying the power of the excitation radiation and the acquisition time. A disadvantage of micro-infrared microscopy is the weaker signal and limited spectral range when measuring in micro-ATR or reflectance mode. Analyzing the same area of an object's surface with both methods is recommended because it provides complementary information.

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