Combined spectroscopic approach for the characterization of pigments used in prehistoric pottery from the region of Western Bulgaria

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Introduction

This work presents the results from spectroscopic analyses of red and brown pigments used for decoration of Early-Neolithic pottery. A total of 22 fragments of ceramic vessels from two archaeological sites – the settlement of Bukhovo and Galabnik, Western Bulgaria have been analyzed. For determining the elemental and mineral composition of the pigments two complementary analytical techniques are applied – Laser Induced Breakdown Spectroscopy (LIBS) and Fourier Transformed Infrared spectroscopy in Attenuated Total Reflectance mode (ATR-FTIR). The LIBS analysis provides information on elemental composition of pigments and based on the detected elements a semi-quantitative analysis was performed. A statistical method Principal Component Analysis (PCA) was applied on the obtained semi quantitative data in order to classify the objects and to cluster the sherds with similar elemental composition of the decorations. To complement the results from LIBS measurement and identify the minerals in pigments, an ATR-FTIR was applied. Based on the results from LIBS and FTIR analysis assumptions about production technology and the raw materials used for manufacture of painted motifs can be made. Referring to these assumptions a hypothesis about possible trade relations or connections between the people inhabiting the territory of Balkan peninsula during the Early-Neolithic can be drawn.

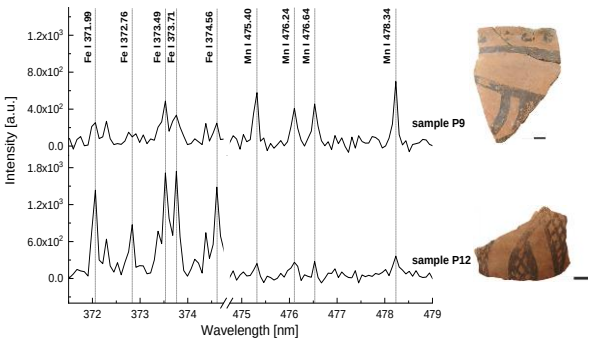
Experimental setup and parameters of LIBS analyses

Portative system LIBSCAN25+ (Applied Photonics Ltd) consisting of:
six spectrometers which cover the spectral range of 200 – 750 nm (three are for UV-VIS and three for VIS-NI regions).
Q-switched Nd:YAG laser (wavelength - 1064 nm; pulse duration – 10 ns; laser pulse energy 8 mJ).
A focusing lens with focal length of 90 mm.
Delay of signal registration 1 μs after the laser pulse.

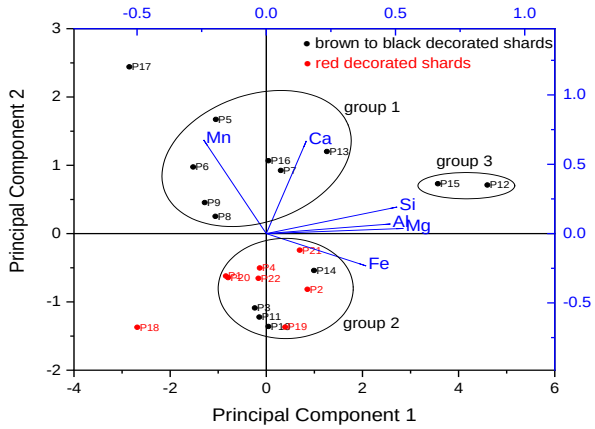
Results from LIBS analyses

Element	Wavelength [nm]
Si	250.69 I, 251.61 I, 252.41 I, 252.85 I, 288.16 I
Ca	315.89 II, 317.93 II, 393.36 II, 396.85 II, 457.85 I, 458.14 I, 458.59 I, 487.82 I, 671.77 I
Fe	271.90 I, 275.01 I, 297.31 I, 302.06 I, 344.10 I, 356.54 I, 357.01 I 358.12 I, 374.55 I, 427.17 I, 489.07 I, 495.76 I
Al	308.22 I, 309.27 I, 394.40 I, 396.15 I
Mn	353.21 I, 354.78 I, 403.08 I, 403.31 I, 403.45 I, 475.40 I, 476.24 I 476.64 I, 478.34 I, 482.35
Mg	279.55 II, 280.27 II, 285.21 I, 382.93 I, 383.23 I
Ti	323.45 II, 328.77 II, 334.19 II, 334.90 II, 336.12 II, 337.28 II, 338.38 II, 498.17 I, 499.10 I
Na	589.00 I, 589.59 I
K	766.49 I, 769.90 I
Li	610.36 I, 670.78 I
Sr	407.77 II, 421.55 II, 460.73 I
Ba	455.40 II, 493.41 II, 553.55 I
Cu	327.40 I, 324.75 I

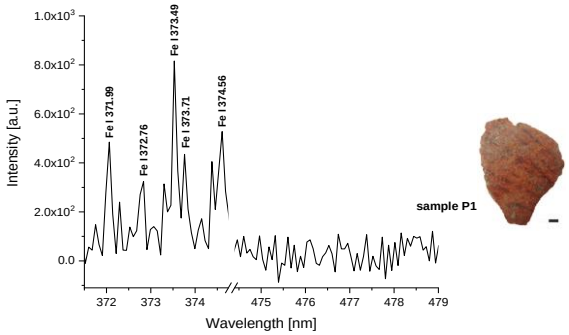
Wavelengths of spectral lines by which the elements are detected.



Illustrative spectra of two of the brown decorated samples, one of which falls into group 1 (P9) and the other falls into group 2 (P12) on the PCA graph. The spectra demonstrate the increased amount of manganese in sample P9 and the increased amount of iron in sample P12.



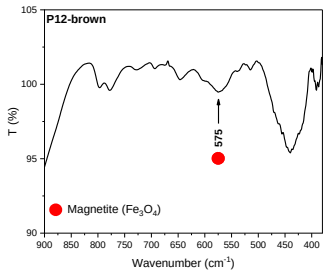
PCA is used to classify the samples in different groups on the basis of their compositional similarities and differences.

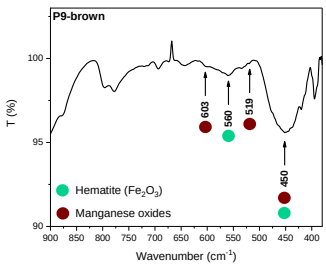


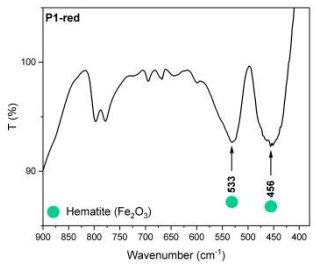
Illustrative spectrum of red decorated sample P1which falls into group 2 on the PCA graph.

Experimental setup and parameters of ATR-FTIR

FTIR in attenuated total reflection (ATR) mode using a Perkin Elmer Spectrum Two spectrometer equipped with a PIKE GladiATR accessory (monolithic diamond ATR crystal, Pike Technologies). The spectra were obtained in the mid-infrared region 4000–400 cm^{-1} by averaging 32 interferograms with a resolution of 4 cm^{-1}.







Conclusions

In this study a total of 22 prehistoric ceramics were analyzed to identify the mineral pigment used for decoration. The results of LIBS analysis show the presence of the elements typical for ceramics. Semi-quantitative estimation of these elements was performed and based on these results a PCA analysis was carried out to classify the shards into different groups according to the content of the main elements. Thus it was found that an iron-bearing mineral had been applied to produce the red decorations. For obtaining brown paint manganese-bearing mineral had been used in part of the samples while in other part iron-bearing mineral had been used. On the basis of these results It is suggested that for acquiring brown coloration of the decorative motifs two different techniques have been used: 1) by burning iron-based pigment in reducing conditions (iron reducing technique); 2) by applying manganese-based pigment which gives dark-brown color independently of firing conditions. To validate and complement the results from LIBS measurement and to identify the minerals in pigments, all samples were analyzed with FTIR. The results of FTIR analyses show presence of hematite in all of the red paints and in some of the brown paints and magnetite in the other brown decorated shards. Also manganese oxides are detected in some brown decorated samples.

Acknowledgements

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