PIGMENT IDENTIFICATION IN HELLENISTIC CERAMICS FROM THE TUZ GÖLÜ REGION OF CENTRAL ANATOLIA BY CONFOCAL RAMAN SPECTROSCOPY

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The chemical nature of the black and red pigments of four samples of Hellenistic ceramics from the Salt Lake (Tuz Golu) region of Central Anatolia has been identified by Confocal Raman Spectroscopy. The black and red pigments are found to be magnetite (Fe3O4) and hematite (α-Fe_2O3). Raman spectrum of alumina (Al_2O_3) was also taken on white coloured glazes.

INTRODUCTION

The object of the present work is the identification by Raman spectroscopy of the chemical nature of the black and red pigment employed in the manufacture of some Hellenistic ceramics in the Salt Lake region of Central Anatolia. Studies on the identification of pigments in archaeological ceramics by Raman spectroscopy have increased recently [1,2,3,4]. The identification of pigments is important for understanding the technology and use of raw materials in the production of ceramics.

Raman spectroscopy is leading the way in many novel applications, providing far more detail and contrast than is possible through more traditional techniques [5]. This technique provides high level of spatial and depth resolution, requires little or no sample preparation, robust to temperature changes, not suffer from water absorption effects, directly proportional to the concentration of the particular species and not require sophisticated data analysis protocols and detailed algorithms.

Raman technique focuses a laser beam down to a small volume (1 μm^3 in air), backscattered light is collected by the same objective and focused onto the photodetector. The optical resolution (OR) is given by OR = 0,56 λ / NA for x-y; OR = 0,89 λ / $(NA)^2$ for z. NA - numerical aperture of the objective lens, λ - the light wavelength.

Confocal Raman spectroscopy measures intensity Raman lines as a function of spatial position and a two or three dimensional image of the chemical composition of the sample. The Raman spectrum is unique to each material and can therefore be treated as a 'fingerprint', thereby allowing characterisation of that material [6]. The Raman spectrum collected have to be compared with those obtained previously from reference materials. Published databases of spectra are now available in the literature [7,8].

EXPERIMENTAL

The custom-built confocal Raman spectroscopy was used for measurements (Figure 1). The experiments were performed with an inverted microscope Swift M100 equipped with a semiapochromat objective Leica PL FLUOTAR 100× /0.75. The sample was mounted on a three-dimensional piezotranslator TRITOR 102 (Piezosystem Jena). The band pass fitler (AHF Analysentechnik) was used for suppressed plazma lines of the HeNe laser (632.8 nm).

The same objective lens was performed for focusing of the laser and collimation of scattered light. The dichroic beam splitter was used for separating the excitation and the detection light paths. The collimated signal light was sent through a notch fitler (Kaiser Optical Systems) for suppressing the Rayleigh line and focused through a pinhole (80 μm) into a single monochromator (Acton Research SpectraPro-500i) equipped with a grating of 300 grooves per mm. CCD camera (Princeton Instruments, 1340×100 pixels, a liquid-nitrogen-cooled) at the exit focal plane of the monochromator was used for detecting the signal. The laser light was linearly polarized. Its power was adjusted to a few milliwatts at the location of the sample. The integration time of the spectra was 1 s.

Samples description

An archaeological survey was conducted in the south part of the Salt Lake of Central Anatolia and sites yield ceramics from the Neolithic to Byzantine periods was discovered [9]. During the survey painted Hellenistic sherds were found in number of sites namely Ikizce, Mezgitli, Bozyer, Dokuzlu and Kötücük. Seven sherds from these sites have been selected for pigment identification and only four of them have better results (Figure 2). All the spectra have been mainly compared with the database of known minerals edited by the Chemistry Department of University College of London, and by M. Bouchard and D. C. Smith.

The first and the second analyzed samples are rim sherds of incurving rim bowls that are well known in Hellenistic times [10,11,12]. The first analyzed sample has metallic white glaze on its both sides, which is characteristic feature for the late 3rd century and the early 2nd century BC vessels [13]. In this sample black glazed paint was applied on lustrous red slipped surface. The second analyzed sample is a gray monochrome ware. S. Omura who made a surface survey in Central Anatolia suggested that grey monochrome wares can be dated to the Hellenistic and Roman periods, later than Kaman Kalehöyük Iron Age layer IIa [14]. The third and the forth analyzed samples are body sherds of bowls. The fourth analyzed sample has bi-coloured, black and red mottled, surface. The bi-coloured effect on this sherd may have been explained by temperature and atmospheric conditions in the kiln.

There are still gaps in our knowledge of the Hellenistic period of Central Anatolia. Our survey area is geographically in the Phrygian region, and on the basis of latest excavations at Gordion [15], our analysed samples can be dated between 330-150 cal. BC.

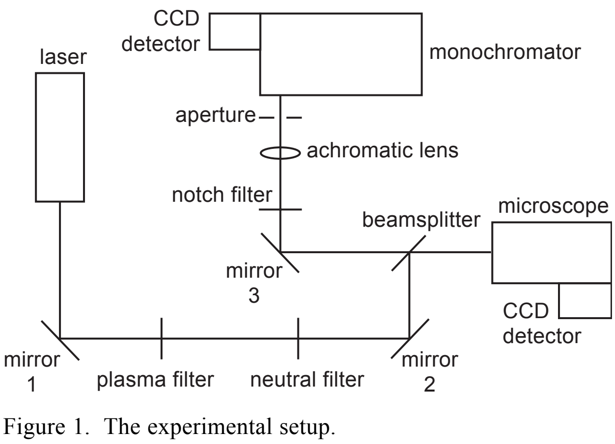

Figure 1. The experimental setup.

RESULTS AND DISCUSSION

The black pigments in all analysed samples are magnetite (Fe_3O_4). The result indicates the presence of iron oxide in the paint samples [16]. In Figure 3, a spectrum obtained from the black pigment is shown. In the first sample, three lines centred at 300 cm^{-1}, 500 cm^{-1} and 670 cm^{-1}. Our spectrums match the black surface of some Greek ceramic analysed by Perez and Esteve-Tebar [2]. In other samples, the principal feature of magnetite Raman line at 672 cm^{-1} is evident (Figure 4).

The spectrum recorded from the red paint is hematite (α-Fe_2O_3). It can be noted that there is a good correspondence between our spectrum and the one from the UCL database corresponding to hematite: the lines at 290 cm^{-1}, 408 cm^{-1}, 490 cm^{-1}, 604 cm^{-1} correspond well (Figure 5). The first peak is not visible, because the notch filter tends to cut off this wavelength region. The band at 1302 cm^{-1} can also be observed. This peak is more probably interpreted as 2 LO phonon scattering [17]. In addition, a minor contribution of magnetite is also present here, as indicated by the band at 661 cm^{-1}. According to Bouchard and Smith [8], the band at 660/661 cm^{-1} exists in the spectra of hematite because of partial transformation into magnetite under the laser beam.

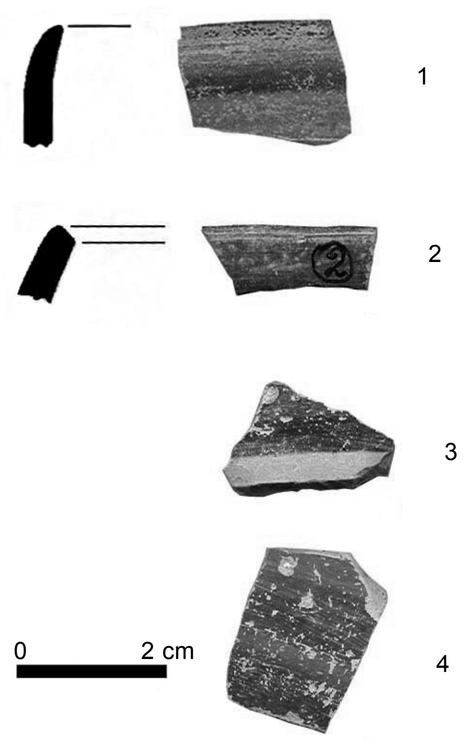

Figure 2. Analyzed samples.

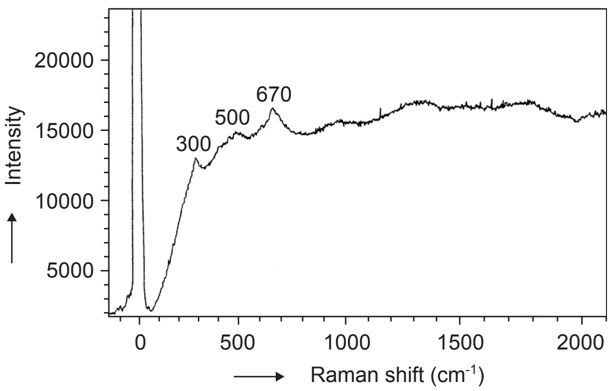

Figure 3. Raman spectrum of magnetite recorded from the sample 1.

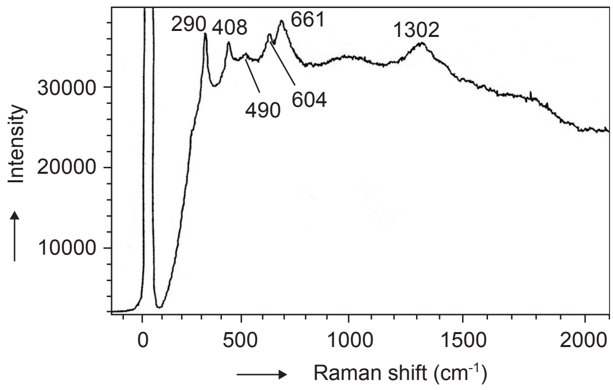

Figure 5. Raman spectrum from hematite recorded from the sample 4.

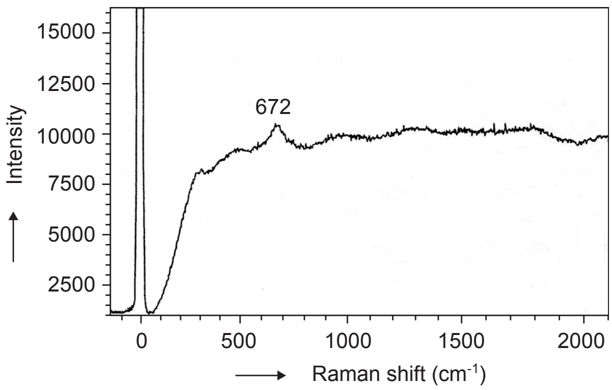

Figure 4. Raman spectrum of magnetite recorded from the samples 2 and 3.

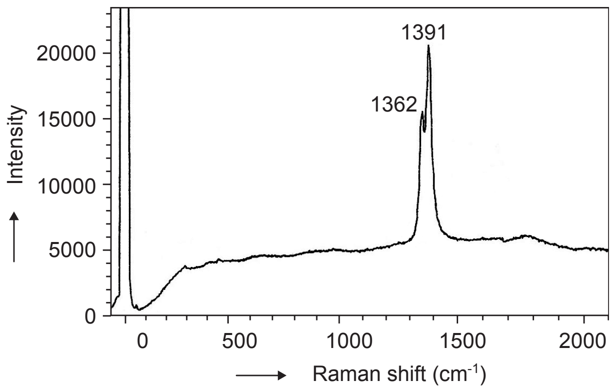

Figure 6. Raman spectrum recorded from the white glaze.

Two lines between 1360 and 1390 cm^{-1} can also observed when focusing on thin white layered glaze of some samples, and it fits the alumina (Al_2O_3) spectrum (Figure 6).

CONCLUSION

Raman Spectroscopy is now established as an effective tool in pigment identification of archaeological ceramics. The chemical nature of black and red pigments of some Hellenistic sherds from the Tuz Gölü region has identified. The black pigment is found to be magnetite (Fe_3O_4). Raman spectrum of hematite (α-Fe_2O_3) was also taken on the red paint. It also contains a minor and variable amount of magnetite because of the particular firing conditions and/or the characteristics of the mixture of the iron oxides employed. Either different raw materials were used to produce the ceramic colouring or a single component was used to coat the ceramics and different sintering temperatures and kiln atmospheres used to achieve the final colour. Raman spectrum of alumina (Al_2O_3) was also taken on white coloured glazes.

References

1. Smith D. G., Clark R. J. H.: Journal of Archaeological Science *8*, 1145, (2004).
2. Perez J.M., Esteve-Tebar R.: Archaeometry 46, 607 (2004).
3. Zoppi A., Lofromento C., Castellucci E. M., Migliorini M. G.: Annali di Chimica *95*, 239, (2005).
4. Angeli L., Arias C., Cristoforetti G., Fabbri C., Legnaioli S., Palleschi V., Radi G., Salvetti A, Tognoni E.: *Laser Chemistry 2006*, Article ID 61607, (2006).
5. Kador L., Schittkowski T., Bauer M., Fan Y.: Applied Optics *40*, 4965 (2001).
6. Chaplin T. D., Clark R. J. H.: In Focus *3*, 88 (2006).
7. Burgio, L., Clark, R. J. H.: Spectrochimica Acta, Part *A 57*, 1491 (2001).
8. Bouchard M., Smith D. C.: Spectrochimica Acta, Part A 59, 2247 (2003).
9. Erdogu, B., Fazlioglu I.: Anatolia Antiqua XIV, *189* (2006).
10. Edwards R.: *Corinthian Hellenistic Pottery*, Corinth VII, p.225, Princeton 1975.
11. Crowfoot J. M., Crowfoot G. M., Kenyon K.: *The Objects From Samaria, Pottery Hellenistic and Later*, Samaria-Sebaste 3 Chap. IX, p.248-249, fig. 49:12, London 1957.
12. Coldstream J. N., Eiring L. J., Forster G.: *Knossos Pottery Handbook Greek and Roman*, p.98-99, 3.3 h, The British School at Athens 7, London 2001.

13. Rotroff S. I.: Hesperia *51*, 163 (1982).
14. Omura S.: Araştirma Sonuçlari Toplantisi *18*, 86 (2001).
15. Ed. Kealbofer L.: *The Archaeology of Midas and The Phrygians*, Recent Work at Gordion, p.27, Table 2, Philadelphia 2005.
16. de Faria D. L. A., Silva, V., de Oliveira M. T.: J. Raman Spectrosc. *28*, 873 (1997).
17. Massey M. J., Baier R., Merlin R., Weber W. H.: Phys. Rev. *B41*, 7822 (1990).

IDENTIFIKACE PIGMENTU V HELÉNISTICKÉ KERAMICE Z OBLASTI TUZ GÖLÜ VE STŘEDNÍ ANATOLII POMOCÍ RAMANOVY KONFOKÁLNÍ SPEKTROSKOPIE

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Chemická povaha černých a červených pigmentů čtyř vzorků helénistické keramiky z oblasti Solného jezera (Tuz Golu) ve střední Anatolii byla identifikována pomocí Ramanovy konfokální spektroskopie. Černé a červené pigmenty jsou na základě analýzy z magnetitu (Fe_3O_4) a hematitu (α-Fe_2O_3). Ramanovo spektrum oxidu hlinitého (Al_2O_3) bylo rovněž měřeno na bíle zbarvených glazurách.