SPECTROSCOPY OF CLAY GODS

PIGMENTS ON TERACOTTA FIGURINES OF THE HELLENISTIC PERIOD FROM PIRAEUS: NON-DESTRUCTIVE CHEMICAL ANALYSIS WITH XRF AND RAMAN SPECTROSCOPY

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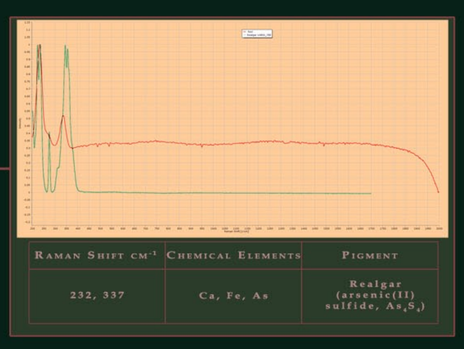
INTRODUCTION

This is a preliminary investigation on pigments' identification, carried out for the purposes of my Master's thesis. Ten fragmentary terracotta Hellenistic figurines from the metro excavations in Piraeus were examined, chosen for the preservation of their pigments, the range of colours, and the pattering of colours. Due to the burial environment, which often do not favour their preservation, the pigments are preserved in traces.

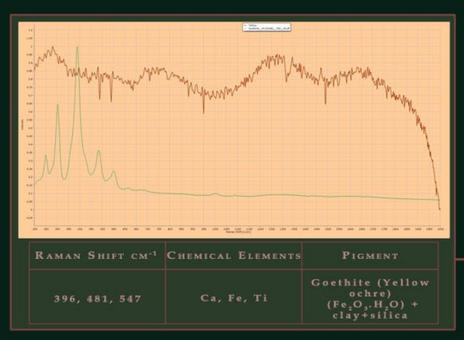
The figurines with registration numbers Π0049-50, Π0052, Π0055, Π 0059, Π0081, Π0043 and ΡΠ0081 were found in the square of Ag. Konstantinos. The figurines numbered Π0224, Π0205, and Π0088 came from the southern part of Deligianni Square (towards Gortynias Street) and the figurine Π0004 came to light in a section of Pavlos Bakoyannis Square.

The analysis took place in the storeroom of the Ephorate of Pireaus, where they are kept, using non-destructive, spectroscopic, portable XRF and Raman devices. Measurements were performed on every painted spot of the figurines and also on the unpainted interiors to ensure that the results register pigment and not a clay spectrum.

Π0052 (1:1)
EROS

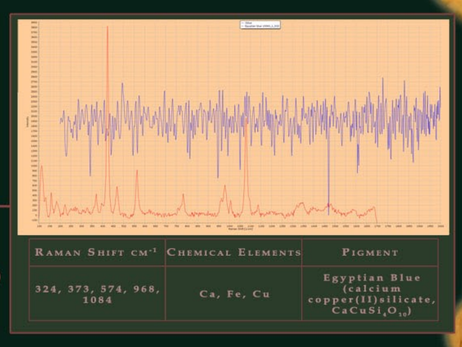


Raman Shift cm^{-1}	Chemical Elements	Pigment
232, 337	Ca, Fe, As	Realgar (arsenic(II) sulfide, As_4S_4)

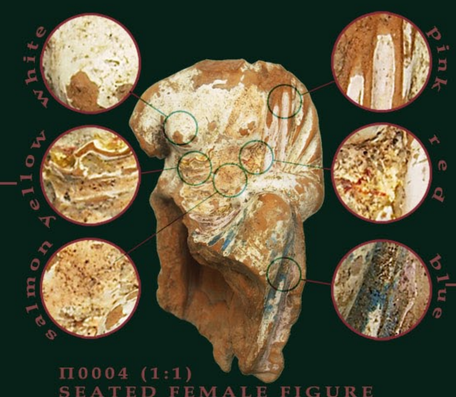


Raman Shift cm^{-1}	Chemical Elements	Pigment
396, 481, 547	Ca, Fe, Ti	Goethite (Yellow ochre) ($Fe_2O_3.H_2O$) + clay+silica

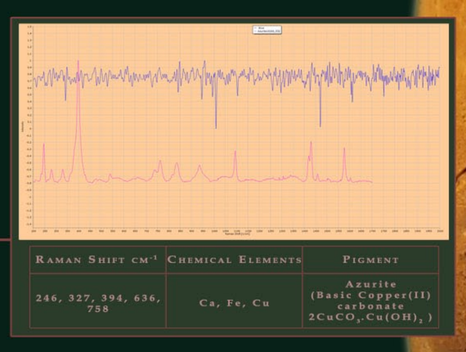
Π0205 (1:1)
MOURNING FEMALE FIGURE(?)



Raman Shift cm^{-1}	Chemical Elements	Pigment
324, 373, 574, 968, 1084	Ca, Fe, Cu	Egyptian Blue (calcium copper(II)silicate, $CaCuSi_4O_{10}$)



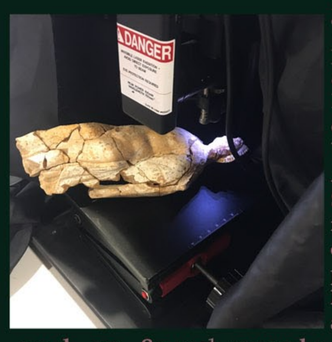
Π0004 (1:1)
SEATED FEMALE FIGURE



Raman Shift cm^{-1}	Chemical Elements	Pigment
246, 327, 394, 636, 758	Ca, Fe, Cu	Azurite (Basic Copper(II) carbonate $2CuCO_3.Cu(OH)_2$)

METHODS

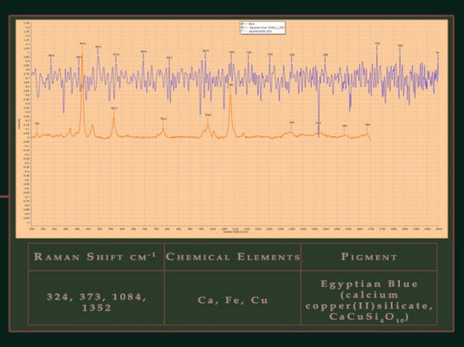
To detect the chemical elements in percentages (%) and in traces (ppm), a Skyray portable XRF, EDX Pocket III P730 was used, which provides an elemental detection from S(16) to U(92) and a 40kV/50μA X-ray tube of Ag/W anode.



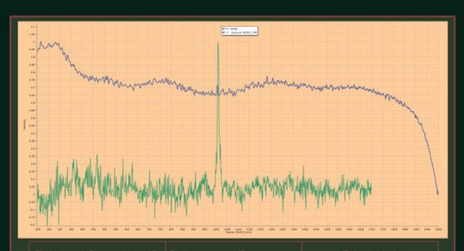
Supplementary to XRF measurements, so as to identify the chemical composition of each pigment, a portable Rock Hound Delta Nu Raman Spectrometer, equipped with a near infrared 785nm laser source and an 8cm^{-1} resolution, was used. Raman spectra were received in the wavelength of 200cm^{-1} to 2000cm^{-1}. To ensure the correct Raman shift measurement and operation, calibration tests were conducted.

SpectraGryph software was used to analyze the spectra and then, the identification of those chemical compositions was achieved through cross-referencing them to the international pigment databases, Clark, Checker and Rruff.

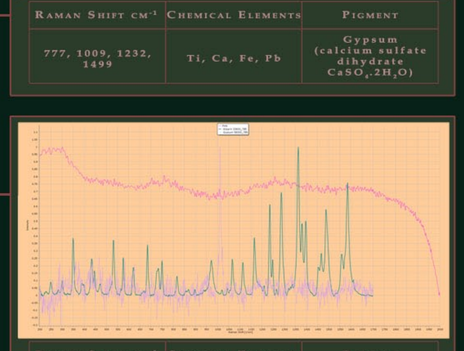
Π0088 (1:1)
SATYR



Raman Shift cm^{-1}	Chemical Elements	Pigment
324, 373, 1084, 1352	Ca, Fe, Cu	Egyptian Blue (calcium copper(II)silicate, $CaCuSi_4O_{10}$)



Raman Shift cm^{-1}	Chemical Elements	Pigment
777, 1009, 1232, 1499	Ti, Ca, Fe, Pb	Gypsum (calcium sulfate dihydrate $CaSO_4.2H_2O$)



Raman Shift cm^{-1}	Chemical Elements	Pigment
302, 536, 1303, 1499, 1580, 1009	—	Alizarin ($C_{14}H_8O_4$)

Π0081 AND Π0093 (1:2)

RESULTS AND DISCUSSION

For this work the identified colours were black, white, red, pink, yellow, salmon, brown, blue, and light blue. They were analyzed as follows:

1) Black colour identified as Carbon black based on the absence of other characteristic elements, which would identify it as another pigment.
2) White colour was used mostly as a substrate and is identified as gypsum. In only one case the analysis shows the mixture of calcite with white lead.
3) Red colour, applied to represent the lips (Π0052), is identified as realgar from its characteristic Raman peaks and the presence of Arsenic (As). However, it has to be further investigated because there is a strong possibility that the pigment refers to cinnabar and not to realgar. Repeated XRF measurements are necessary.
4) Pink colour, visible on three of the figurines, was identified as madder since the Raman spectra revealed vibrations of alizarin. Madder seems to be the main pigment of a mixture for salmon colour as well.
5) Yellow is identified as iron oxide, namely goethite.
6) Brown colour is likely a mixture of different iron oxides, ochres, and calcite.
7) Blues are copper-based pigments. In two out of three cases, it is identified as Egyptian blue, and in the third, which visibly is a lighter blue colour, as azurite.

Though the results are predominantly in accordance with the relevant literature, they have to be considered preliminary. The limited time for performing these measurements, the heterogeneity of the samples, the preservation state of the pigments, the presence of organic compounds, and the inefficiency of the XRF apparatus used, which could not detect mercury (Hg), demonstrate the need for further investigation with repetitious measurements as well as applying alternative analytical methods.

Π0055
WINGED
MALE
FIGURE

REFERENCES

1) Mau A. Laura & Farrell E., A pigment analysis of Greek Hellenistic Tanagra figurines, Harvard University Art museums Bulletin, Vol.1, No 3, Greek terracottas of the Hellenistic world : The Coroplast's Art , 1993, pp 55-62
2) Fostiridou A. et al, Identification of pigments in Hellenistic and Roman funeral figurines, Archaeometry 58, 2016, pp 453-464
3) Elslande E., Lecomte S., Le Hô A.S., Micro-Raman, spectroscopy (MRS) and surface-enhanced Raman scattering (SERS) on organic colourants in archaeological pigments, Journal of Raman Spectroscopy, 2008
4) Brecoulaki H., "Precious Colours" in ancient Greek polychromy and painting: material aspects and symbolic values., Presses Universitaires de France, Revue archeologique, 2014 no57, p. 3-35
5) Bell M. I., et al, Raman spectroscopic library of natural and synthetic pigments (pre-~1850 AD), Spectrochimica Acta Part A 53 , 1997
6) Caggiani M.C., Cosentino A., Mangone A., Pigments Checker version 3.0, a handy set for conservation scientists: A free online Raman spectra database., Microchemical Journal, 2016, pp.123-132

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