NATURAL EARTH PIGMENTS FROM ROMAN AND ARABIC WALL PAINTINGS REVEALED BY SPECTROSCOPIC TECHNIQUES.

I. Garofano[1], A. Duran[1], J.L. Perez-Rodriguez[1] and M.D. Robador[2]
[1]Materials Science Institute of Seville, Americo Vespucio 49, 41092 Seville, Spain adrian@icmse.csic.es [2]Technical Architecture Faculty, University of Seville, Reina Mercedes 4, 41002 Seville, Spain

Introduction: Natural earths and minerals have been used as pigments since prehistoric times. They have been found in works of art everywhere and in any historical period due to their availability, high colouring capacity and stability [1]. The main aims of this work are the identification and comparative study of the pigments used in Roman and Arabic wall paintings by only using spectroscopic methods. In this form, a multi-analytical approach including micro-Raman, FT-Infrared and UV-visible, accomplished by chromatic studies, provided complete information on the compositions of the paintings, which can be regarded as a powerful tool for conservators, restorers, art historians and archaeologists.

Experimental: Fragments from Roman wall paintings of Reales Alcazares Palace in Seville (1st century B.C.) and Pompeii Houses (2nd century B.C.) were studied. In addition, we studied some Arabic wall painting fragments (11th century A.D.), also collected from Reales Alcazares Palace. The dispersive integrated Horiba Jobin-Yvon LabRam HR 800 system was employed for recording the Raman spectra directly on the fragments. Lasers emitting at 532.1 nm (green) and at 784.6 nm (red) were used. An optical microscope was coupled confocally to the Raman spectrometer. FTIR spectra were collected using a Jasco FT-IR-6200 FV spectrometer (DTGS detector). KBr was mixed with powder samples for performing these experiments. UV-Vis spectra (Cary 100, Varian) were recorded in the diffuse reflectance mode. Powder samples were mixed with $BaSO_4$ that does not absorb in the UV-Vis range. The chromatic characterization was determined over the fragments using a Dr Lange Neurtek model LMC3/DIAM 5 portable spectrometer that produces normalized D65 light.

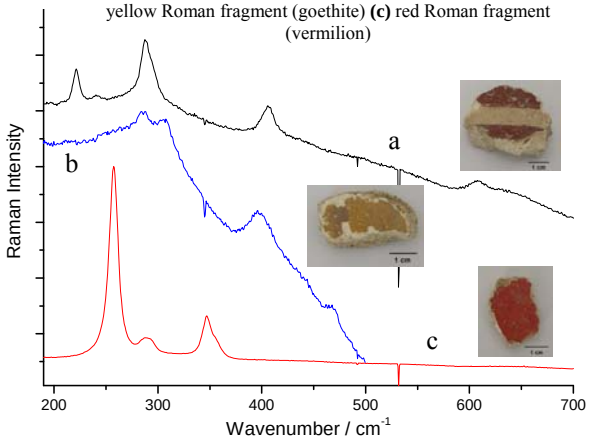

Fig 1: Raman spectra of: **(a)** red Arabic fragment (hematite) **(b)** yellow Roman fragment (goethite) **(c)** red Roman fragment (vermilion)

Results: Raman spectroscopy allowed the indistinguishable identification of the majority of the pigments found in the paintings: hematite (bands at 227, 245, 294, 300, 409, 610 cm^{-1}), goethite (287, 303, 397, 469 cm^{-1}), vermilion (257, 290, 347 cm^{-1}), carbon black (1325, 1592 cm^{-1}), Egyptian blue (431, 1085 cm^{-1}), calcite (277, 710, 1083 cm^{-1}).

We used infrared spectroscopy to distinguish the presence of ochre colours (clays mixed with hematite or goethite) by the detection of bands associated to clays (hydroxyl ions: 3695, 3648, 3617, 3352, 3418, 3185 cm^{-1}, and aluminosilicates: 1032 cm^{-1}). Green earth was also identified by FTIR due to the detection of absorption bands assigned to celadonite (3601, 3556, 3531, 1106, 1075, 961, 799, 683 cm^{-1}) and glauconite (3615, 3531, 979, 962 cm^{-1}). However, poor Raman spectra were obtained for the green colour fragments. FTIR band-shoulder at 1025 cm^{-1}, observed in the black fragment, could be attributed to the presence of phosphate groups (ivory black).

Red ochre, yellow ochre, vermilion, green earth, carbon black, ivory black, Egyptian blue and calcite were the compounds detected in the Roman wall paintings, while hematite and calcite were observed in the Arabic ones (the ornamentation palette of all Islamic buildings is dichromatic, usually red and white).

UV-Vis and chromatic studies agree with the results found with the other experimental techniques. λ_{dom} (dominant wavelengths) are in the adequate zone within the visible region (400-800 nm) in all the cases, and CIE L*a*b* parameters match with those from pigments described in the literature. These latter studies permitted to identify slight variations of hue attributed to mixtures of pigments, such as in the case of blue and green fragments.

Conclusions: The combined application of the above mentioned spectroscopy methods allowed a full characterization of the pigments employed by Romans and Arabs in the wall paintings studied. Natural earths and minerals were the pigments mainly employed by both civilizations although some differences were found. The identification could help in tracing the possible routes of pigments origin and diffusion. The present work is one of the first articles devoted to the study of both Roman and Arabic wall paintings by using exclusively spectroscopic methods.

References: [1] Genestar C., Pons C. (2005) *Anal. Bioanal. Chem.* 382, 269-274.