

**OLD AND MODERN PIGMENTS IDENTIFICATION FROM A 14<sup>th</sup> CENTURY SCULPTURE BY MICRO-RAMAN.** M.L. Franquelo<sup>1</sup>, A. Duran<sup>1</sup>, D. Arquillo<sup>2</sup> and J.L. Perez Rodriguez<sup>1</sup>, <sup>1</sup>Materials Science Institute of Seville, Americo Vespucio 49, 41092 Seville, Spain [jlperez@icmse.csic.es](mailto:jlperez@icmse.csic.es) <sup>2</sup>Fine Arts Faculty of Seville, University of Seville, Laraña 3, 41003 Seville, Spain

**Introduction:** Pigments identification in polychromed sculptures is very important for understanding the history of the works of art and the resolution of problems related to its conservation, restoration treatments and author attribution. Portable systems (XRF, Raman, XRD) only provide information from the external layers of the artifact, so in polychromies with a high number of layers, it is necessary to use other experimental techniques. The full identification of the pigments within the artworks requires collecting samples with all the layers, from the varnish to the support. If a sample contains all the layers, it will provide wide information about the way in which the polychromy and the repaint/restoration treatments were carried out. Micro-Raman spectroscopy can be used for the identification of pigments within the cross-sections containing all the layers of the polychromy [1-3]. The purpose of this work is to full characterize the different layers of cross-sections performed on samples from a 14<sup>th</sup> century polychromed sculpture that had suffered subsequent restoration treatments by using micro-Raman spectroscopy. Also a chromatic study was carried out.

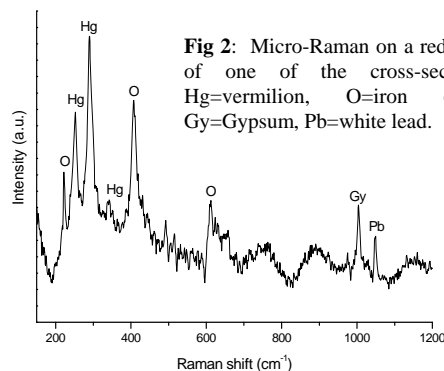


**Fig 1:** Santa Ana triplex sculpture

**Experimental:** A triplex polychromed sculpture of Santa Ana, the Virgin and the Child, dating from the Spanish Gothic period, has been studied. The dispersive integrated Horiba Jobin-Yvon LabRam HR 800 system was employed for recording the Raman spectra. The experiments were performed directly on the cross-sections performed from sculpture samples. Two external visible diode lasers are available in this apparatus: at 532.1 nm (green) and at 784.6 nm (red). An optical microscope is coupled confocally to the Raman spectrometer. The chromatic characterization was performed *in situ* using a portable spectrometer Dr. Lange Neurtek model LMC3/DIAM5.

**Results:** Five red layers were found together with the preparation layer in one of the cross-sections. The Raman spectra of the internal layers showed characteristic bands of vermilion (bands at 251, 289 and 343 cm<sup>-1</sup>). The presence of red lead was also detected (bands at 118, 147, 221, 307, 386 and 546 cm<sup>-1</sup>). The amount of red lead is higher than vermilion. The external red layer showed the characteristic bands

of vermilion and also those of red ochre: iron oxides mixture with clay minerals (bands at 221, 289, 406 cm<sup>-1</sup>). Also gypsum (1004 cm<sup>-1</sup>) and lead white (1049 cm<sup>-1</sup>) were detected.



**Fig 2:** Micro-Raman on a red layer of one of the cross-sections: Hg=vermilion, O=iron oxide, Gy=Gypsum, Pb=white lead.

Titanium oxide (bands at 141, 447 and 609 cm<sup>-1</sup>) was detected in the external layers of white colour. The shoulder that appear at 438 cm<sup>-1</sup> could be attributed to zinc white. Zinc was found by XRF (using a portable system) in most areas of the external part of the sculpture. Two blue color layers have been found in one of the stratigraphies, the internal layer is constituted by lazurite (bands at 258, 549, 810 and 1098 cm<sup>-1</sup>); this pigment accompanied by titanium oxide appeared in the external layer. Other old and modern pigments have been identified using this technique.

Chromatic characterization of the different zones of the sculpture showed heterogeneous values of L\*, a\*, b\*, according with the different colors visually observed. The composition was also confirmed by other techniques such as chemical analysis (SEM-EDX), micro-X ray diffraction and IR spectroscopy.

**Conclusions:** The micro-Raman spectroscopy study of cross-sections from a sculpture from 14<sup>th</sup> century has shown the presence of old pigments such as vermilion, lazurite, lead white, red lead, red ochre or red lac in the internal layers and zinc white, titanium oxide, litopon, ultramar blue as modern pigments in the external layers attributed to subsequent restoration/repaint treatments.

**References:** [1] Clark R.J.H. (2007) *J. Mol. Struct.*, 834-836, 74-80. [2] Franquelo M.L., Duran A., Herrera L.K., Jimenez de Haro M.C., Perez-Rodriguez J.L. (2009) *J. Mol. Struct.*, 924-926, 404-412. [3] Duran A., Jimenez de Haro M.C., Perez-Rodriguez J.L., Franquelo M.L., Herrera L.K., Justo A. (2010) *Archaeometry*, 52, 286-307.