

RAMAN SPECTROSCOPY ANALYSIS OF A PLAYING CARD FROM THE XVIII CENTURY. A. C. Prieto¹, M. Avella^{1,2}, O. Martínez¹, J. Jiménez¹, J.L. Alonso³, I. Sánchez⁴, R. Martín⁴ and M. Barrera⁴, ¹GdS Optron-lab, Parque Científico UVA, Edificio de I+D, Campus “Miguel Delibes”, Paseo de Belén, 11, E-47011 Valladolid, Spain (prieto@fmc.uva.es). ²Unidad de Microscopía Avanzada. Parque Científico UVA, Edificio de I+D, Campus “Miguel Delibes”, Paseo de Belén, 11, E-47011 Valladolid, Spain. ³Servicio de Restauración de la Diputación Foral de Alava, Urarte 4, E-01010 Vitoria-Gasteiz, Spain. ⁴Centro de Conservación y Restauración de Bienes Culturales. Junta de Castilla y León. Carretera 2. E- 47130 Simancas, Valladolid, Spain.

Introduction: We present herein the characterization, by means of three complementary experimental techniques (light microscopy-LM, scanning electron microscopy equipped with energy dispersive X-Ray spectroscopy-SEM-EDX and micro-Raman spectroscopy- μ Raman), of a card belonging to a deck of the Spanish pattern, made in Perú at the time of *Virreinato de Peru* (XVIII century): The objective is to obtain detailed information of the pictoric palette used for the decoration of the cards, where two basic colors, red and green, are seen. Small samples from both colored regions have been analysed.

Experiment: The material selected for the study is a piece of civil goldsmiths, a card (number five, swords) of a traditional deck which has been restored in the Servicio de Restauración de la Diputación Foral de Alava and analysed in the Centro de Conservación y Restauración de Bienes Culturales de la Junta de Castilla y León. In particular, the study concerns to a piece made of Silver alloyed with a small amount of Copper, whose typology corresponds to the colonial culture of that period (XVIII century).

A first inspection of the samples (stratigraphies) was performed by LM, using a petrographic microscope LEICA DMLP, with transmitted and epi-illumination. Elemental analysis was performed by using an environmental SEM (ESEM), model FEI Quanta 200FEG, equipped with EDX, Genesis XM2i from EDAX. μ Raman analysis was performed using a LABRAN HR 800 UV (Horiba Jobin-Yvon). The Raman spectra were collected in backscattering configuration, using a x100 magnification objective and a HeNe laser ($\lambda=632.8$ nm) for excitation. The nominal power onto the sample was 100 kWcm^{-2} . The spectral resolution is better than 1 cm^{-1} using a diffraction grating of 1200 lines/mm.

Results and Discussion: The analysis of the samples using LM –white light illumination – shows three pictoric layers in a stratigraphic disposition, for both samples from red and green regions. That from the green area shows a non homogeneous distribution of micro-crystals in the three stratigraphic layers. The EDX analysis of the green samples show the presence of Cu salts as the main pigment. An EDX profile along the three layers, with a step size of $0.08 \mu\text{m}$, shows the presence of Cu in the two lower layers. The upper

layer shows high Fe/low Cu concentrations. The EDX analysis of the samples from red areas show the presence of cinnabar (HgS) as the main pigment. The lower (glue) layer present high contents on Si, O, Al, C and K, with Mg and Fe traces. (The composition of the glue layer of both green and red areas is similar). The upper layer, which is a re-painting layer, has high contents of C, Al, Si, O and Fe, with some traces of K, Ca, S and Hg, coming from the intermediate layer (first painting layer). Such composition suggests the presence of silicoaluminates of clay type used as dispersion vehicles, and crystals containing some Fe pigment as a chromophore.

The Raman spectra for the green areas show, for the upper layer, broad and not well defined bands, together with a sharp peak at 2154 cm^{-1} – with a shoulder at 2128 cm^{-1} –, as well as a band with intermediate intensity at 2092 cm^{-1} , ascribable to the $\text{Fe}^{+3}\text{-C}\equiv\text{N-Fe}^{+3}$ bonding. Intense bands are also observed at 271 and 527 cm^{-1} , ascribable to the Prussian blue pigment, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, as well as two intense bands at 1368 and 1399 cm^{-1} , due the Cr^{3+} fluorescence; Cr^{3+} appears as an impurity associated to the Al_2O_3 used during the polishing of the sample. The two lower layers in the green areas show bands associated to the verdigris pigment, corresponding to the copper acetate with different hydration levels. The Raman spectra for the red areas show peaks at 254 and 344 cm^{-1} – with a shoulder at 354 cm^{-1} –, together with a small band at 285 cm^{-1} , ascribable to the A_1 , E_{LO} and E_{TO} modes of HgS (Vermilion), respectively. The upper layer shows the intense bands of the Vermilion and Prussian blue pigments. The lower layer shows a fluorescence band centered at $\sim 682 \text{ nm}$. Broad and not well defined bands superposed to this band could be ascribable to colophony (rosin) used as a glue.

Conclusions: The complementary use of Raman spectroscopy together with high resolution analytical techniques allows to reveal the pigments used for the decoration and the further manipulation history of cards belonging to the historic and archeological heritage.