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The Colors and Techniques of 17th Century Portuguese *Azulejos*: A Multi-Analytical Study

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Azulejos (ceramic glazed tiles) are the most important form of classical decorative art in Portugal. They have been decorating interior and exterior walls of public and private buildings such as churches, palaces, and even gardens for over 400 years. In the 17th century, Portuguese *azulejo* manufacture was already well established and widespread. The tiles were produced by the majolica technique and had a relatively rich palette which included blue, green, yellow, orange and a set of tones ranging from purple to dark brown.

Only a few scientific studies concerning the chemical characterization of Portuguese glazed tiles have been published [1-5]. This work focuses on the identification of the pigments and pigment mixtures and also on the morphology of color in the lead-tin glaze. A multi-analytical approach was used, with preference for the non-destructive techniques such as energy-dispersive X-ray fluorescence (μ-EDXRF), Raman microscopy and optical microscopy. In selected samples, polished cross-sections were prepared for observation in scanning electron microscope with microanalysis (SEM-EDS), which was used both for the chemical and the morphological studies. A set of 28 17th century *azulejo* fragments was analyzed, all with white lead-tin glazes. Two types of colors were identified: "simple" colors composed of only one pigment; and "mixed" colors obtained from the mixing of two pigments. Simple colors are the blue, emerald-green, yellow and purple. Mixed colors are shades of orange (yellow pigment and iron oxide), olive-green (yellow and blue pigments) and the brown/purple shades (manganese purple and iron oxide). Portuguese tile painters used, therefore, a limited number of basic pigments to achieve a wide palette and a remarkable overall decorative outcome.

Blue was identified, as expected, as a cobalt oxide pigment. μ-EDXRF analysis identified a Fe-Co-Ni-As association, which could indicate a likely German source of the cobalt pigment [6]. In one sample it was possible to identify cobalt and nickel olivines, by μ-Raman. Emerald-green is obtained from copper oxide and purple from manganese oxide. Conjugating μ-EDXRF, SEM-EDS and μ-Raman results, the yellow pigment was identified as a Pb-Sb-Zn ternary oxide, a modified form of Naples Yellow (lead antimonite) pigment. μ-Raman spectra show a pyrochlore-type structure, similar to the Pb-Sb-Sn triple yellow that has been the subject to several scientific papers in the last decade [7-9]. However, despite the presence of Sn, μ-EDXRF spectra show very intense peaks of Zn, only surpassed by the lead peaks. In order to correctly identify the yellow pigment used by Portuguese tile painters, reproductions are now being made to try and recover the pigment recipe. Hematite was identified by μ-Raman in the orange shades (mixed with the yellow pigment) and in the brown/purple colors (mixed with manganese oxide), indicating that it was added to obtain darker tones. Also the manganese source was disclosed in the analysis of some samples, by μ-Raman, as being braunite, a manganese silicate.
SEM-EDS analysis was an essential tool for this study. In backscattering mode, the glaze was clearly distinct from the clay body due to its high lead content. Many crystalline inclusions and gas bubbles were observed, showing a very heterogeneous glaze. Also, very small SnO-rich

crystals were identified by EDS analysis and are consistent with cassiterite identified by μ-Raman. Observation and X-ray mapping of the polished sections has shown that the yellow pigment does not dissolve into the glaze like the copper, manganese and cobalt oxides do, not even when mixed with them. Instead, it remains insoluble at the surface of the glaze (Fig. 1) where the pigment particles are easily observed and identified with X-ray mapping.

This study is a first step towards the knowledge of the 17th century Portuguese *azulejo* manufacturing technology. Hopefully, a broader study will help establishing both geographical provenance and chronology, offering valuable information to art conservators and art historians alike [10].

[1] M. O. Figueiredo et al., *Appl. Phys. A*, 83 (2006) 209
[2] J. P. Veiga and M. O. Figueiredo, *X-Ray Spectrom.*, 37 (2008) 458
[3] J. P. Veiga and M. O. Figueiredo, *Appl. Phys. A*, 92 (2008) 229
[4] M. O. Figueiredo et al., Nucl. Instrum. Meth. B, 238 (2005) 134
[5] M. Pereira et al., *J. Nano Res.*, 8 (2009) 79
[6] A. Zucchiatti et al., *Archaeometry*, 48, 1 (2006) 131
[7] C. Sandalinas et al., *J. Raman Spectrosc.*, 37 (2006) 1146
[8] F. Rosi e tal., *J. Raman Spectrosc.,* 40 (2009) 107
[9] F. Rosi e tal., *J. Raman Spectrosc.*, (2010) (in press)
[10] This work had the support of the National Tile Museum, in Lisbon, Portugal, which provided the samples.

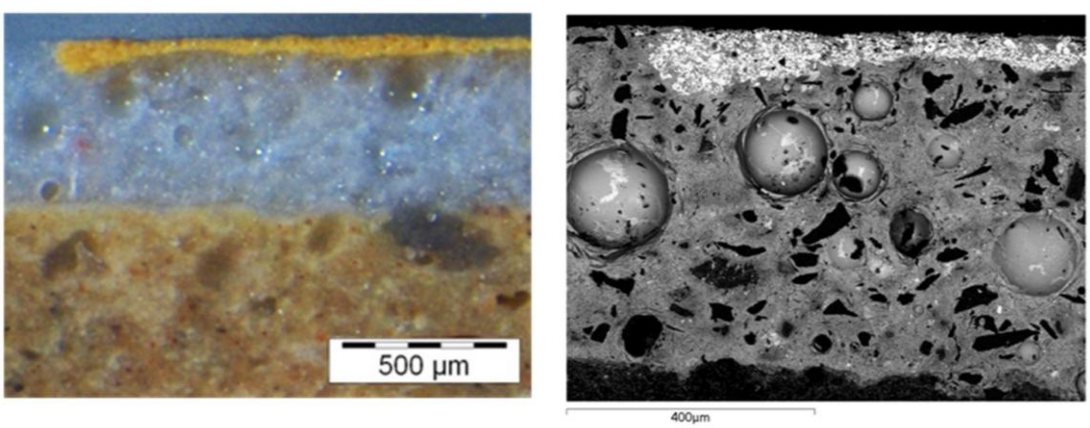

Fig. 1 – Cross-section of a tile showing the yellow pigment forming a layer on the surface of the glaze. On the right, the BSE image of the same sample.

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