

THE YELLOW PIGMENT IN PORTUGUESE 17TH CENTURY AZULEJOS

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Main scientific topic: Raman microscopy, X-ray Microanalysis

Introduction

The Naples Yellow pigment (lead antimonite) and its variants ((Pb-Sb-Sn and/or Pb-Sb-Zn triple oxides) have been the subject of several studies in the last decade [1-3].

This study focuses on the chemical characterization of the yellow pigment used by Portuguese historic glazed tile makers in the 17th century, using non-destructive techniques. Special attention was given to understanding of the production techniques at the time, namely the pigment synthesis and its posterior modifications occurred during the firing of the glaze.

Experimental

A set of 17th century tile fragments was used to study the yellow pigment. The analytical techniques used were Raman microscopy with mapping, energy dispersive X-ray fluorescence (μ -EDXRF qualitative analysis), scanning electron microscopy with X-ray microanalysis (SEM-EDS), X-ray diffraction and optical microscopy. Reproductions of yellow painted tiles were produced according to the various traditional recipes [4] and analysed in order to validate the results of the chemical composition of the yellow pigment.

Results

Raman analysis of the yellow pigment indicate the presence of a modified pyrochlore structure, typical for the Pb-Sb-Sn and Pb-Sb-Zn triple yellows, with a single or double very strong band at ca. 120-140 cm^{-1} and a strong band at ca. 508-511 cm^{-1} (Fig. 1). Some variations in the most intense bands occur not only in different samples but also in the same sample. This variation will be followed by Raman mapping.

μ -EDXRF spectra revealed very intense peaks of Zn, while Sn was inexistent or difficult to detect. Also, Sb and Pb were identified, confirming the use of a type of Naples yellow. Most yellows also contain Si and K, which could indicate the addition of a glaze frit to the pigment before firing.

The question on whether the glaze frit was added to the pigment before or during the final firing will be discussed with resort to reproductions.

Conclusions

An uncommon Pb-Sb-Zn triple oxide was extensively used by Portuguese 17th century tile makers and its synthesis was discussed with the results provided by all the techniques with special emphasis to Raman mappings and XRD. The presence of Si, K and Sn may be explained by adding a glaze frit to the pigment to improve its behaviour during firing and also to achieve a better final result.

Acknowledgments

Samples were provided by the National Tile Museum, in Lisbon.

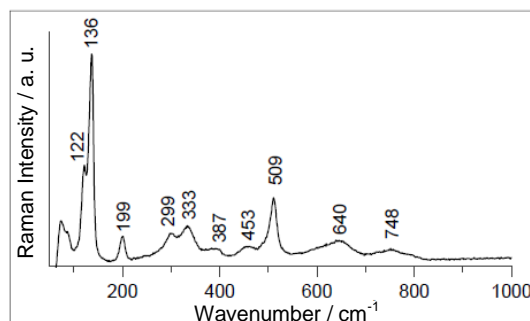


Figure 1: Typical Raman spectrum of the yellow pigment

References

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