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Raman and X-ray fluorescence spectroscopy analysis of decorative ceramic tiles manufactured by Niculoso Pisano from the church of Flores de Ávila (Ávila, Spain)

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***Abstract* – This paper shows the results obtained in the chemical and dynamic vibrational characterization of a set of decorative tiles from the Capilla de los Reyes of the church of Nuestra Señora del Castillo at Flores de Ávila (Ávila, Spain). This tilework, dating from 1526, contains extraordinary pieces produced by the famous Renaissance ceramicist and painter named Francisco Niculoso "El Pisano". However, this relevant tilework has been relocated and rearranged along history. The last arrangement of the tiles was quite arbitrary, potentially mixing the work of "El Pisano" with other tile sets. The main objective of this work is the identification of the types of pigments used in the different shades of color, relating them with other works of the same author.**

I. INTRODUCTION

Francisco Niculoso, called "El Pisano", a famous tile master established in Seville (Spain) at the end of the 15th century, is the best known ceramicist, if not almost the only one, in Spain at the time. He was born in Pisa (Italy) and there he learned the majolica technique: a ceramic decoration technique that use several metallic products (Sb, Co, Cu, Fe, Mn) on glaze with an alkalized lead-siliceous glaze (K-Ca±Na) mattified (opacified) with SnO_2 (at low concentrations). A virtuous ceramist, he stood out for applying the pictorial technique to majolica pottery, especially perspective, and was also responsible for the introduction of grotesques such as decorative element.

From the extensive catalog of this author, two works stand out: the altarpiece of the Visitation that Niculoso made for the oratory of Queen Isabel the Catholic, in the Real Alcázar of Seville (1504), and the altarpiece of Our Lady of Tentudía, in the monastery of the same dedication, in Segura de León (Badajoz) (1518).[1] Moreover, one of his last known works is the tilework of the former "Capilla de los Reyes" (currently known as "Capilla de San Zoilo") of the church of "Nuestra Señora del Castillo" at Flores de Avila (1526), the subject of this work (Figure 1).

However, this tilework have suffered alterations along history. According to Gomez-Moreno,[2] in 1901 the tiles were placed as the flooring of another chapel. When repositioned in the current chapel, seven panels have been formed that have nothing to do with the original distribution or with the volumes on which the tiles were originally placed. As can be seen in Figure 2, the placement of the tiles has been arbitrary. Only some motifs that were easily recognizable have been recovered, but the rest of the tiles have been placed with no other objective than to cover the maximum possible surface regardless of the type of tile used. In addition, a significan number of tiles were found stored in boxes.

a)

b)

c)

Fig. 1. (a) Location of Flores de Avila (Spain). (b) Picture of the church of Flores de Avila. (c) Scheme of the church indicating the "Capilla de los Reyes".

The main part of the tilework can be attributed without doubt to Francisco Niculoso "El Pisano", taking into account the perfect outline of the figures, the iconographic repertoire and the palette of colors used, together with the cartouches that, distributed around the plinth, reproduce inscriptions such as "NICVLOSO" or "PISANO" (see Figure 2). Nevertheless, the lost of the original arrangement and context of the tilework allows the potential mixing of tiles from the original set designed by "El Pisano" with other sets, difficulting the appreciation and valorization of this tilework. The detailed physico-chemical characterization of the tiles could provide valuable information about the manufacture of the tiles, revealing characteristic features of the work of "El Pisano", which could help indentifying and preserving the original tilework. Scarce previous works can be found in the literature with this aim, highlighting the work of Gomez-Moron et al. [1] which provided the first analytical data about the work of "El Pisano", showing that the combination of Raman spectroscopy and X-ray fluorescence is suitable for this aim.

Fig. 2. Example of the arbitrary arrangement of the tiles (one of them includes the inscription "PISANO").

Herein, a representative set of tiles from the tilework of the church of Flores de Avila have been studied by Raman spectroscopy and X-ray fluorescence, looking forward to identify the characteristic features of the tiles produced by Francisco Niculoso "El Pisano".

II. MATERIALS AND METHODS

A. Samples

A representative selection of 6 well-preserved tiles from the tilework of the church of Flores the Avila has been chosen for this work (Figure 3). The selection was performed to ensure the study of the diverse colours present on the tilework, as well as several of the main tile sets/motifs.

Fig. 3. Tiles analyzed in this work.

B. *Experimental techniques*

The selected samples have been characterized by Raman Spectroscopy and X-ray Fluorescence spectroscopy. On the one hand, Raman measurements were carried out with a modular BWTEK Raman Spectrometer with a BWTEK CleanLaze 450 mW and 785 nm laser. On the other hand, X-ray fluorescence was performed with a Bruker ELIO non-contact micro-XRF scanning spectrometer with a microfocusing X-ray rhodium tube (10-50 kV, 5-200 A, 4 W) and a 50 mm² SDD detector with CUBE technology.

A total of 180 measurement points were selected on the tiles: 27 on blue, 20 green, 15 yellow, 9 brown and 4 black colors, in addition to 34 analyzes on the glazed enamel (white) and another 71 points on the base ceramic paste. The study by Raman spectroscopy has presented significant experimental difficulties, essentially due to the photoluminescence induced over 1000 cm^{-1} in the material studied by the equipment's laser source, for which reason only the range between 100-1000 cm^{-1} has been considered.

In addition to these measurements, elemental compositional maps of the tiles were obtained by X-ray fluorescence for each tile, evidencing the presence of diverse elementes related to the employed pigments.

a)

b)

c)

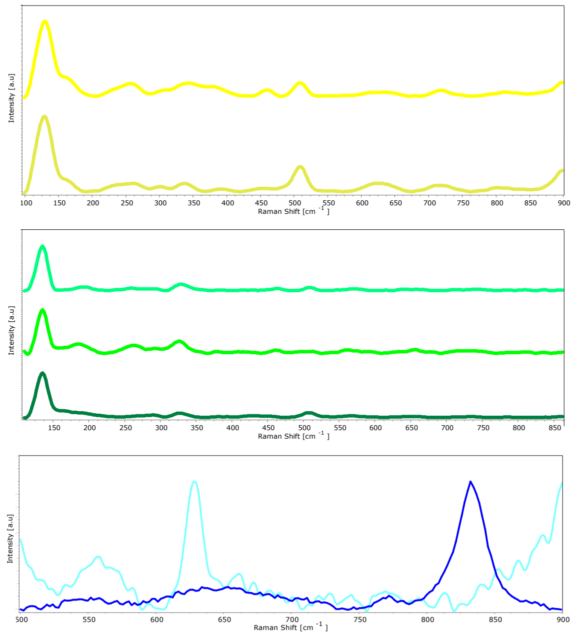

Figure 3. Representative Raman spectra of (a) yellow, (b) green, and (c) blue regions.

III. RESULTS AND DISCUSSION

The study of the base pastes, both on the back of the tiles and the flaked parts from the fronts, presents homogeneous composition that indicates a single fabric mainly constituted by clays (kaolinite-illite-montmorillonite), K-feldspar, carbonates, quartz, products of thermal transformation of clays, and occasionally gypsum. This composition is consistent with other studies carried out on the ceramics of this author that indicate that the base pastes were made up of cordobian kaolinitic clays and siliceous sands of the lower terrace of the Guadalquivir river that would contribute the rest of minerals.[1]

Francisco Niculoso worked five pure colors in addition to white, which would be the base glaze (frits, glazes). Despite the limitedness of the basic color palette, the mixture of pigments and their dilution generates a important chromatic diversity that is rare in the ceramic field at that moment. The frits (white) are made up of an plumbosiliceous alkalized (K-Ca ±Na) glaze and opacified through SnO_2.

Yellow shades have been clearly identified as being due to the presence of lead-antimony oxides (130-135, 330, and 507 cm^{-1}), a pigment better known as "Naples Yellow" (Figure 3.a).[3]

This author uses classic formulas based on Cu as a chromophore element for green tones (Figure 4), although always in low proportions. In addition, small amounts of Naples Yellow type pigments are detected (130-135, 330, and 507 cm^{-1}) (Figure 3.b).[3] The use of yellow pigments, such as Naples Yellow, in combination with blue matrices has been previously reported as a common procedure for obtaining green tones in this type of materials.[4]

Blue shades can be divided into two families: deep blue tone and the other with a lighter indigo blue coloration. Tiles with intense blue present Co as the main chromophore element (Figure 4), although in amounts normally less than 1%. The addition of Co minerals as a blue pigment (sulfoarsenides, arsenides, and previously roasted arsenates, which volatilizes As) is a characteristic of this author's tiles.[1] In fact, the analysis by Raman spectroscopy of deep blue shades shows the presence of small cobalt arsenate contents (about 820 cm^{-1}) (Figure 3.c). On the other hand, pale blue shades present lower amounts of Co and higher amounts of Sn, related to the presence of cassiterite (SnO_2, 634 cm^{-1}) (Figure 3.c) which could have been used to reduce the blue hue.[5]

The analysis of the rest of the shades (browns, beiges, blacks) have not yielded conclusive results by Raman spectroscopy. However, in some cases their analysis by XRF provided some hints about the employed chromophores. The brown tones suggest a classic formula based on Mn as a chromophore element, which was probably achieved by adding Fe-Mn oxides (Figure 5), the higher the Fe and Mn contents the darker the color. The dark tones (blacks) do not provide conclusive information and seem to derive, in our case, from “burnt” blues due to excessive roasting.

a)
b)
c)

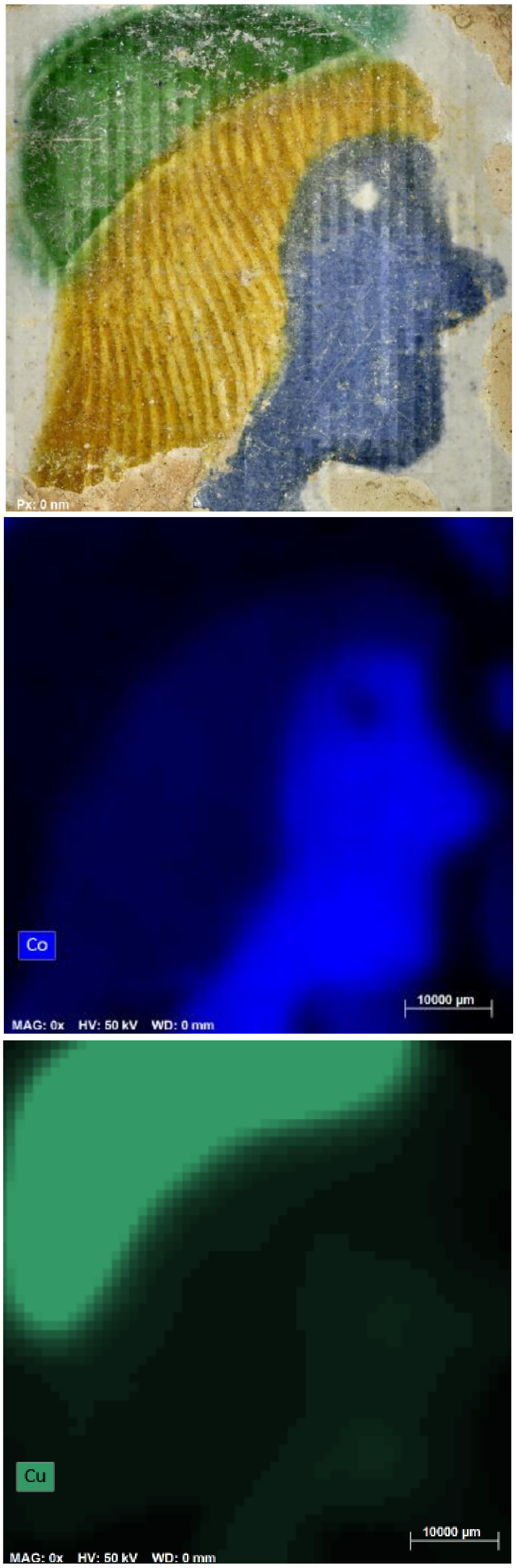

Figure 4. (a) Picture of one of the studied tiles and elemental compositional maps showing the distribution of (b) Co and (c) Cu related to blue and green hues, respectively.

a)
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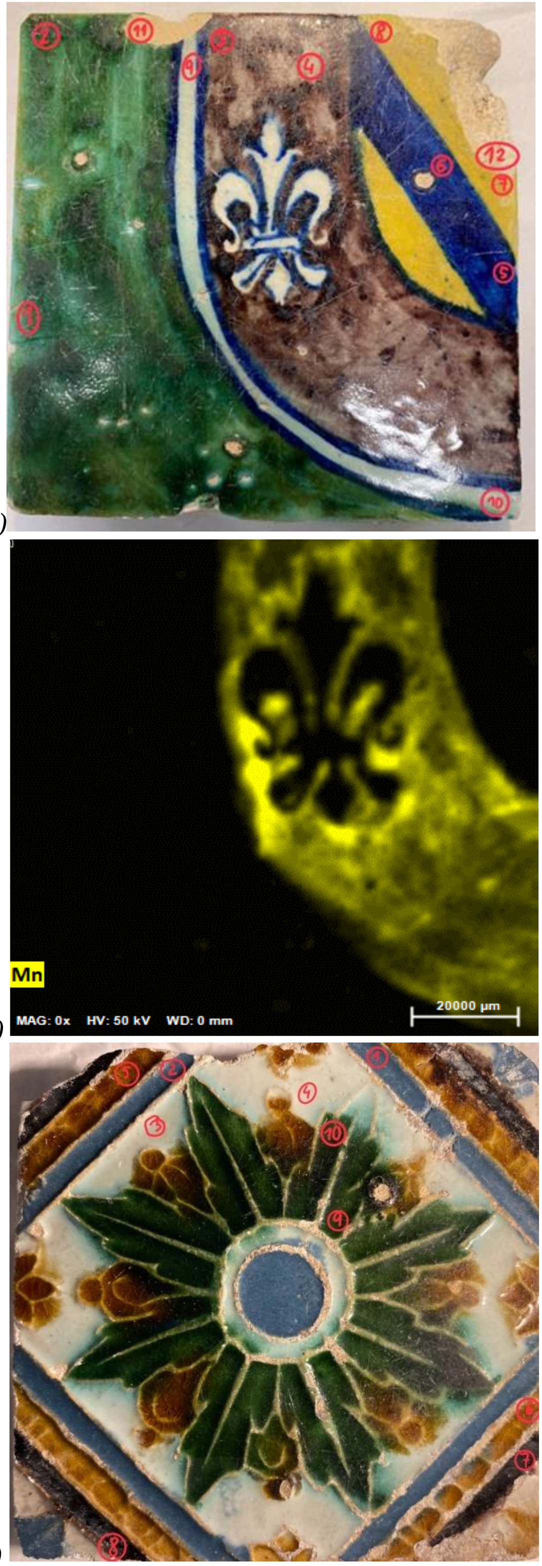


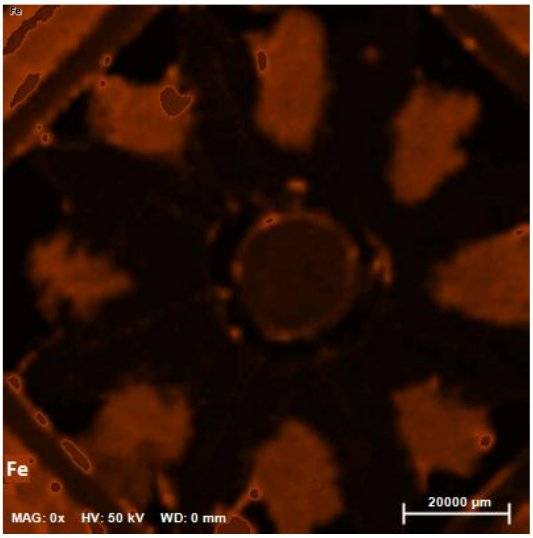
d) 

Figure 5. (a) Picture of one of the studied tiles and (b) elemental compositional map showing the distribution of Mn. (c) Picture of another of the studied tiles and (d) elemental compositional map showing the distribution of Fe.

IV. CONCLUSIONS

The data obtained are consistent with those published by other authors on the work of Nicoloso Pisano and allow us to confirm the authorship of the studied tiles.

The pastes used are typical of the Andalusian school with bases made at moderate firing on the siliceous sands of the lower terrace of the Guadalquivir river. Coating frits (white enamel) are the characteristics of the majolica ceramics of this period with a Si-Pb glaze alkalized (K-Ca±Na) and opacified with low concentrations of SnO_2. The results of the pigments are coherent with the work of this author, with a predominance of the use of "Naples Yellow" for the yellow tones, the use of green colors based on copper combined with "Naples Yellow", blue tones obtained with minerals from Co as a chromophore element and the incorporation of cassiterite to obtain light shades, and brown tones obtained by adding Mn (and Fe).

The results obtained in this small selection of samples make it possible to identify common patterns compatible with Pisano's production, and which will serve as starting data for a more extensive study of the complete decorative set of the chapel.

V. ACKNOWLEDGEMENTS

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