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TILE PATHOLOGIES: GREEN STAINS IN BLUE-AND-WHITE GLAZES FROM AN 18TH CENTURY TILE PANEL FIGURING LISBON *

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Introduction

Glazed ceramic tiles ("azulejos" in Portuguese, from the original Arab designation "al-zulayj") deserve particular attention due to a wide application in the cultural heritage of the Mediterranean area.

Ancient tile panels exposed to different environmental conditions are liable to the development of micro-organisms that play a major role in tile pathologies and degradation. This is the case of a large 18th century panel of blue-and-white tiles exposed at the National Tile Museum (MNAz) figuring Lisbon before the earthquake of 1755 [1] where green stains and pinkish areas are nowadays perceptible in the glaze of many tiles.

The present work reports recent studies focused on the diagnosis of the green tarnishing of the glaze as a preliminary step towards future tile conservation actions using neutron beams and gamma radiation.

Fig. 1 – General view of *Vista de Lisboa* at the *Museu Nacional do Azulejo* (MNAz) and a magnified partial image of the tile panel, both taken in 2010.

Brief History of *Vista de Lisboa*

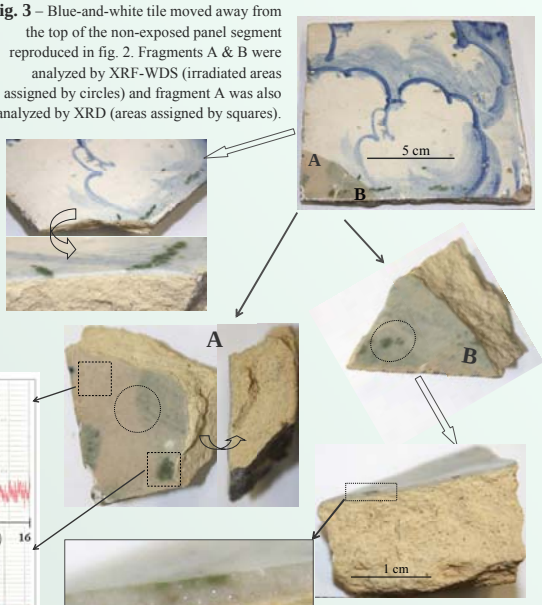
For stylistic reasons attributed to Gabriel del Barco - a Spanish painter and tile decorator - the panel named *Grande Panorama de Lisboa* or just *Vista de Lisboa* (fig. 1), is one of the most remarkable Portuguese tile panels, both for the rarity of its iconography and its huge dimensions (~23m x 1m and more than 1200 tiles with 14x14cm). The original length of the panel is yet unknown and the frame - very common in Portuguese tile panels from in the same period - was lost. The iconography of the panel (churches, convents, palaces, public buildings, bridges, fountains, etc.) represents Lisbon's Architecture viewed along the Tagus river border in the first half of the 18th century, before the reconstruction that followed the severe 1755 earthquake. The panel was transferred to the National Tile Museum in 1960 and fixed to a mobile wooden support applying a hot gluing process and in the eighties, it was re-mounted with silicone glue on a *Plexiglas* sheet. In 1990, the advanced degradation state of such an impressive Art piece lead to a consolidation treatment using *Paraloid* B-72 [2] with the aim of stabilizing the whole panel. Some tiles from the extreme segments of the panel were then stored apart.

Studied Materials

A tile displaying green stains was retired from the top of the non-exposed panel segment stored in the depository of MNAz (fig. 2). Small fragments collected from this tile (fig. 3) and observed under a stereomicroscope clearly showed stains were located at the surface of the glaze without attaining the underlying ceramic body (fig. 5).

Fig. 2 – Segment of the original panel *Vista de Lisboa* at present stored in the depository of the National Tile Museum.

Fig. 3 – Blue-and-white tile moved away from the top of the non-exposed panel segment reproduced in fig. 2. Fragments A & B were analyzed by XRF-WDS (irradiated areas assigned by circles) and fragment A was also analyzed by XRD (areas assigned by squares).



Experimental

Tile fragments were studied using non-destructive techniques by direct irradiation of the glaze.

X-ray diffraction (XRD) was applied to check the eventual development of new phases in green areas due to glaze degradation using a Bragg-Brentano X-ray diffractometer equipped with a large-anode copper tube and a graphite crystal monochromator.

The chemical characterization of white and blue areas of the glaze was performed with a Philips PW 1400 wavelength dispersive X-ray fluorescence spectrometer (XRF-WDS) equipped with a rhodium tube and a LiF_{200} analysing crystal. Fixed-time counting was carried out over the $K\alpha$ diagnostic peak of the relevant elements (Table 1). Due to the superposition of Pb $L\alpha$ line to As $K\alpha$ line, the $K\beta$ peak of arsenic and the $L\gamma$ peak of lead were also measured to ascertain the presence of both elements.

Fig. 4 – X-ray diffraction patterns obtained for irradiated areas in fragment A: (a) white glaze; (b) green stain. The relative intensities of assigned diffraction peaks are indicated.

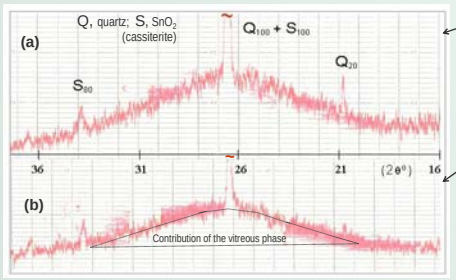


Table 1 – Chemical data obtained by XRF-WDS. Areas irradiated in the fragments are assigned in Fig. 3

Counts-per-second / Element	2θ°	Frag. A White & blue glaze	Frag. B Green stains on glaze
Background	*134.00*	*984*	*585*
K $K\beta$	118.15	13 926	5 870
Sn $L\beta$	114.40	7 906	3 520
Ca $K\alpha$	113.10	23 391	15 516
Ti $K\alpha$	86.14	1 626	824
Background	*84.00*	*286*	*191*
	71.00	*626*	*411*
Cr $K\alpha$	69.36	700	680
Mn $K\alpha$	62.97	1 463	1 299
Fe $K\alpha$	57.52	32 098	39 761
Co $K\alpha$	52.80	2 455	2 957
Mn / Co		0.8	0.5
Fe / Co		29.4	23.4
Co / Cu		0.2	0.7
Co / Ni		1.4	1.6
Background	*50.00*	*1 410*	*1 314*
Ni $K\alpha$	48.67	2 168	2 370
Cu $K\alpha$	45.03	6 107	3 594
Zn $K\alpha$	41.80	6 282	5 047
As $K\alpha$+Pb $L\alpha$	34.00	447 793	167 327
As $K\beta$	30.45	3 120	2 477
Pb $L\gamma$	24.07	38 167	16 863
Pb $L\gamma$ / As $K\beta$		27.1	30.5
Background	*21.50*	*1 775*	*1 989*

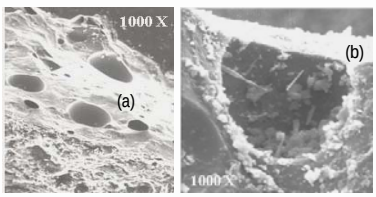


Fig. 6 – SEM micro-graphs showing vacuoles inside (a) and at the surface (b) of the glaze from an 18th cent. blue-&-white tile [3]

Final Comments

It is foreseen to apply electron microscopy and even other destructive techniques to characterize the micro-organisms (*algae* colonies?) responsible for the green staining of the glaze in the 18th century tile panel *Vista de Lisboa*. On the other hand, the means to overcome the smoky effect noticed in the glaze following the irradiation with X-rays in the laboratory (fig. 3) is also under study.

Results and Conclusions

XRD patterns (fig. 4) collected from the blue-and-white glaze and from green stained areas are identical: beyond the diffuse contribution due to the *vitreous component*, the crystalline phases observed are *cassiterite* - the *opacifier* currently used to manufacture tile glazes in the 18th century - and *quartz*.

Likewise, no mayor chemical changes could be detected by XRF-WDS due to the presence of green stains (Table 1), particularly in what concerns the *chromophore elements* - copper, cobalt, plus nickel and iron, which ratios are highlighted in blue - and the *main vitrifying glaze component* - lead, which ratio towards arsenic is also shown. These ratios do not vary significantly from white-and-blue glaze (fragment A) and green stains (fragment B) – irradiated areas assigned in fig. 3.

It is therefore concluded that the bulk constitution of the blue-and-white glaze has not been affected by the green staining which is just a superficial effect (see fig. 5). Indeed, spherical vacuoles are common in ancient glazes (fig. 6), frequently hosting newly formed degradation materials and micro-organisms when at the surface.

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