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Ascertaining the degradation state of ceramic tiles: A preliminary non-destructive step in view of conservation treatments

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ABSTRACT

Conserving the cultural heritage is a general concern and the use of non-destructive techniques to characterize ancient materials is important. Serious deterioration effects in environmentally exposed ancient glazed ceramic tiles arise from the development of micro-organisms (algae/fungi) within the pore system. Subsequent biodegradation processes are particularly harmful once the decorated glaze is damaged by exfoliation/detachment.
Three case studies will be addressed: Portuguese polychrome decorated tiles from the interior of two churches (16th–17th century) and from the outdoor of a Palace (18th century). Small tile fragments were directly irradiated in a wavelength-dispersive X-ray fluorescence spectrometer for glaze chemical characterization and subsequently irradiated in a powder diffractometer to assess the phase constitution of both glaze and ceramic body.
Cleaning and conserving these ancient cultural artifacts involve a decontamination process applying innovative non-destructive techniques. The present work is intended as a contribution to diagnose the actual degradation state of ancient tiles in view of future decontamination actions using gamma radiation.

1. Introduction

Glazed ceramic tiles ("azulejos" in Portuguese) deserve particular attention due to their wide application in important public buildings like churches or palaces for esthetic purposes. Attractive tiles placed inside and/or outside the edifice — most of them built some hundred years ago — constitute an important patrimony within cultural heritage that is important to preserve.

Ancient panels exposed to environmental conditions are liable to the development of various pathologies that could give rise to tile degradation: in outside panels the degradation is mainly due to the action of the sun, rain, air currents and humidity while inside the buildings, liquid water and vapor ascending through the porous system of the ceramic body may give rise to a network of fissures ("craquelé") and to glaze detachment, formation/efflorescence of salts or even development of micro-organisms (algae/fungi) that are particularly harmful on decorated glazes (Figueiredo et al., 2009).

When undertaking a restoration procedure, the choice of products and techniques for consolidation is critical for the restored tile durability. Although polymeric materials (e.g. Paraloid B-72) have nowadays a wide use in ceramic tiles conservation, the effect of the consolidation treatment on water absorption properties still requires further study (Vaz et al., 2008). The impregnation efficiency attained with different methods of consolidant application was recently approached through the visualization of the glazed tile inner structure by applying neutron tomography (Prudêncio et al., 2012).

The occurrence of stains in the glaze surface of ceramic tiles due to the presence of micro-organisms requires a quite different approach. Dark tarnishing on 19th century polychrome tile glazes was ascribed to the simultaneous presence of Cyanophyta and Bacillariophyta algae (Oliveira et al., 2001) but other micro-organisms (algae/fungi) may give rise to green stains, particularly in blue-and-white glazes from the 16th to the 18th century (Figueiredo, 2003; Silva et al., 2011).

Recently, new methodologies for decontamination based on the use of gamma radiation were successfully applied to art objects made of wood and paper (Rizzo et al., 2009; Severiano et al., 2010) and the need for a careful study of materials composition, prior to the treatment, was claimed.

The present work aims at characterizing in detail the degradation state of decorated tiles – produced in the 16th–18th century. Their glazes are lead-rich calco–sodic silica glasses, with tin oxide as opacifier (Figueiredo et al., 2002) – and their characterisation can be considered as a preliminary non-destructive step in view of conservation treatments using gamma radiation. Accordingly, non-destructive techniques based on X-ray characterization methodologies were applied by directly irradiating small tile fragments: diffraction (XRD) to identify the constituting

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crystalline phases of the glaze and the ceramic body, plus fluorescence spectrometry (XRF) to assess the glaze elemental constitution.

2. Materials

Portuguese polychrome decorated tiles from the interior of two Churches and from the outdoor of a Palace were studied (Fig. 1).

The Church of *Madre de Deus* (MD) in Lisbon belongs to a convent built in the 16th century. Rehabilitation works took place in the 19th century and polychrome tiles dated from the 16th century were removed from the convent's cloisters, corridors and refectory to cover the walls of the lower choir of the new church. This church was classified a National Monument in 1910 and today the ancient convent building hosts the National Tile Museum, considered one of the most important museums for its unique collection of tiles.

The Church of *Nossa Senhora dos Aflitos* (NSA) in Elvas (southern Portugal), was originally a place of Templar's worship that was destroyed in the 16th century. The new church was built just after, keeping the original octagonal dome shape. The interior decoration with yellow, blue and white glazed tiles reaching the cupola dates from the 17th century (Carvalho, 2008). This church (rehabilitated in the last century) is also known as *Nossa Senhora da Consolação* and is considered a National Monument since 1910.

The Palace at *Quinta de Santo António* (QSA) *da Bela Vista*, in Pragal (surroundings of Lisbon) was built in the 18th century. An outdoor tile panel with a polychrome frame representing our Lady surrounded by Saint Joachim and Saint Anne, placed near a well at the entrance of the palace courtyard, was selected for study.

By visual inspection, NSA tiles have a well preserved white ceramic body. No fissures or detachments were noticed on the glaze and small tile fragments of yellow and blue glaze were directly irradiated in the area assigned in Fig. 1. Conversely, MD fragments collected near the church floor revealed expansion of the red ceramic body giving rise to detachment of the green glaze. QSA polychrome tiles also show glaze detachment in some areas but the ceramics are compact and well conserved.

3. Experimental

A Philips PW 1500 powder diffractometer with Bragg–Brentano geometry equipped with a large-anode copper tube and a graphite crystal monochromator was used to check the eventual development of new phase(s) as a result of degradation processes of the glaze and to identify the crystalline components of the ceramic body. For that purposes, the small tile fragments were directly irradiated in a non-destructive, despite slightly invasive way.

A comparative chemical characterization of the glazes was performed using an automated Philips PW 1400 wavelength dispersive X-ray fluorescence spectrometer (XRF-WDS) with X-41 software, equipped with a rhodium tube. Fixed-time countings (5×10 s) were carried out over the diagnostic lines of relevant elements using a LiF200 analyzing crystal. The $K\alpha$ line of representative chromophore elements (Sb, Mn, Fe, Co, Cu) and of glaze components (K, Ca, Zn) was used to carry out the countings, along with the Sn $L\beta$ line and Pb $L\alpha$ line (Table 1). Due to the superposition of this line to As $K\alpha$ line, the $K\beta$ line of arsenic and the $L\gamma$ line of lead were also measured to correctly ascertain the presence of each one of these elements.

4. Results and conclusions

X-ray diffraction patterns of glazes collected from the interior of 16th–17th churches are illustrated in Fig. 2. As expected, an amorphous contribution due to the vitreous silica-rich component is observed. The identified crystalline phase in MD green and NSA blue glazes is cassiterite (SnO_2) — the opacifier currently used in the manufacture of 16th–17th Portuguese tile glazes — while bindheimite

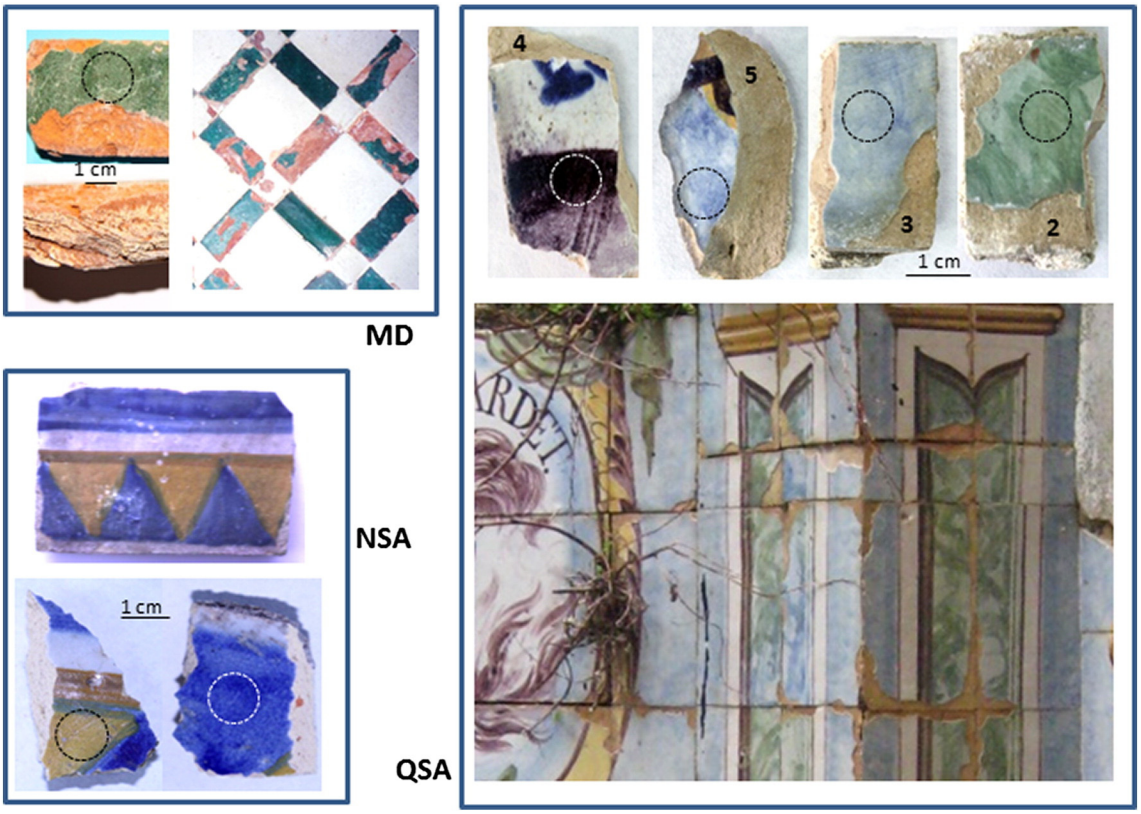

Fig. 1. Studied glazed tile fragments: MD — *Madre de Deus* Church (16th century, from the interior); NSA — *Nossa Senhora dos Aflitos* Church (17th century, interior); QSA — *Quinta de Santo António da Bela Vista* (18th century, exterior). A circle assigns the area irradiated in laboratorial assays.

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Table 1
XRF-WDS chemical data: average of five measurements.

Element	Sample (°2θ)	Green (MD)	Yellow (NSA)	Blue (NSA)	Green (QSA 2)	Bluish (QSA 3)	Violet (QSA 4)	Blue (QSA 5)
K *Kα*	136.8	11,120	56,020	187,933	108,856	68,219	162,424	94,142
Background	134.0	374	548	1109	1043	587	1203	804
Sb *Lα*	117.5	639	30943	3526	16,862	1344	4725	3766
Sn *Lβ*	114.4	1234	3469	2352	19,011	19,053	26,904	26,006
Ca *Kα*	113.1	17,690	26,299	48,335	88,359	38,529	48,545	81,229
Background	71.00	426	328	569	1171	473	835	652
Mn *Kα*	62.97	1229	1202	2403	2642	1369	136,312	3008
Fe *Kα*	57.52	34,345	66,112	105,667	80,091	27,220	33,992	30,859
Co *Kα*	52.80	1355	2451	32,702	13,185	5881	5290	9199
Background	50.00	1307	1176	1306	1707	865	1469	1208
Cu *Kα*	45.03	43,780	2904	5375	6170	3945	7579	4775
Zn *Kα*	41.80	4361	21,079	37,798	4660	1998	3219	3016
As *Kα* + Pb *Lα*	34.00	216,602	129,738	394,215	818,885	407,668	689,250	548,989
As *Kβ*	30.45	2446	2327	7034	5740	2424	5585	3798
Pb *Lγ*	24.07	19,243	14,670	33,446	56,610	29,046	52,456	41,471
Background	21.50	1868	1809	1605	1449	808	1452	1154

($Pb_2Sb_2O_7$) is the dominant phase in NSA yellow glaze, in accordance with the common use of the synthetic pigment "Naples yellow" to paint the glaze and subsequently firing it at a lower temperature (Coentro et al., 2012). Despite the expansion of the ceramic body and partial detachment of the green glaze in MD sample, no additional crystalline phases were detected — namely, cristobalite, the low temperature form of silica that denotes the aging of old glazes, a degradation process that starts with the partial de-vitrification of the siliceous glassy matrix (Figueiredo et al., 2009).

Cassiterite is also well expressed in the XRD patterns collected from the environmentally exposed 18th century tile glazes of *Quinta de Santo António* (Fig. 3). Additionally, α-quartz (SiO_2) was assigned in the violet (QSA 4) and in the blue (QSA 5) glazes, denoting the devitrification of the siliceous coating, as assigned in contemporary glazes (e.g. Pereira et al., 2009). An extra line in the XRD pattern of QSA 4 violet glaze could possibly result from the Mn silicate braunite (B? in Fig. 3), stemming from the violet pigment. The environmental exposure has led to the formation of calcite ($CaCO_3$), well represented in the surface of the green (QSA 2) and blue (QSA 5) glazes, in accordance with the comparative high contents of calcium assigned in these glazes (Table 1).

The mineralogical characterization of the whitish ceramic body from NSA samples agrees with the data obtained in a previous study focused on neutron tomography (Prudêncio et al., 2012). According

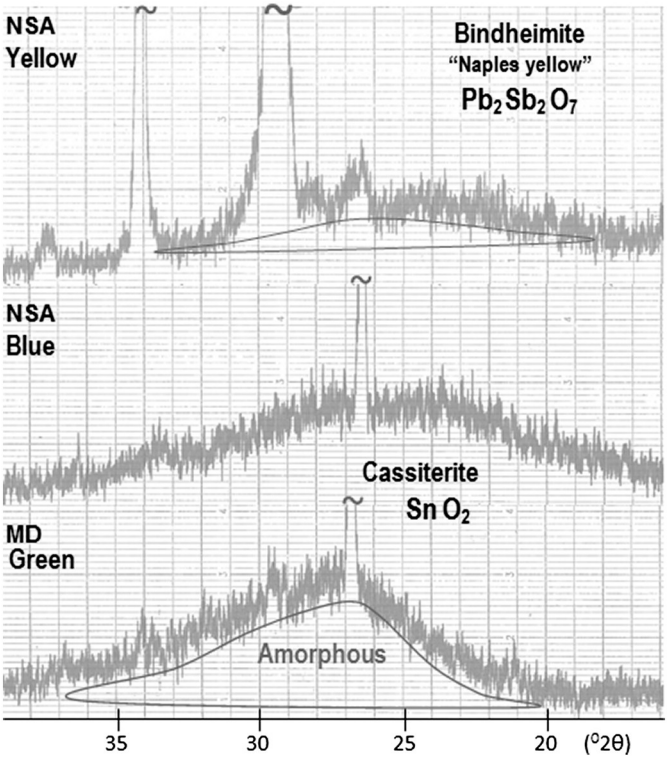

Fig. 2. X-ray diffraction (XRD) patterns (Cu *Kα* radiation) collected from glaze fragments: MD — *Madre de Deus* Church (16th century); NSA — *Nossa Senhora dos Aflitos* Church (17th century).

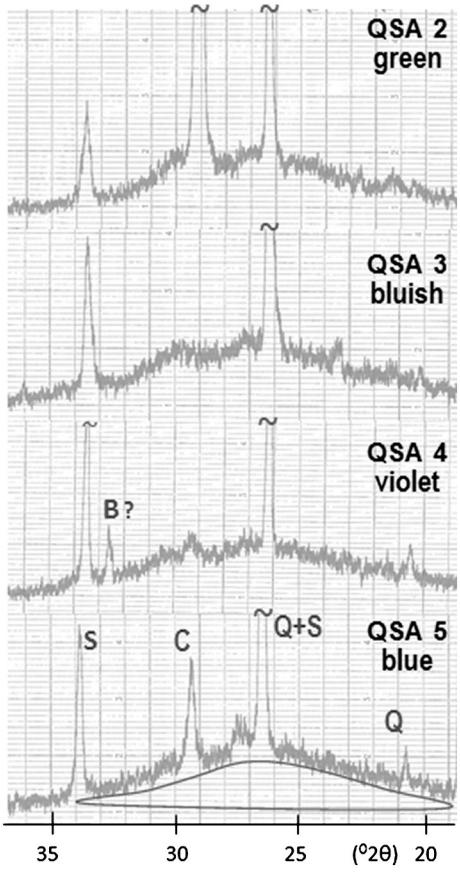

Fig. 3. XRD patterns collected from 18th century glaze fragments (QSA — *Quinta de Santo António*). The contribution of an amorphous phase is assigned; identified crystalline phases: S, cassiterite (SnO_2); Q, quartz (SiO_2); C, calcite ($CaCO_3$); B?, braunite ($3Mn_2O_3 \cdot MnSiO_3$).

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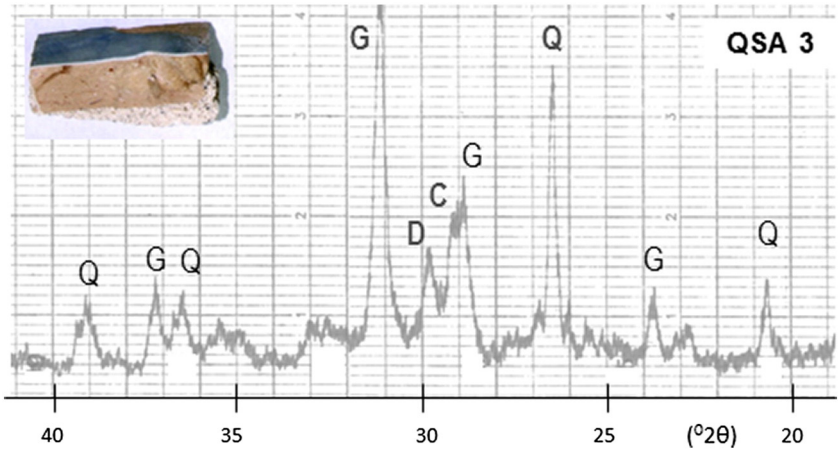

Fig. 4. XRD pattern collected from the ceramic body of a QSA tile sample. Assigned phases by decreasing representativity: G, gehlenite ($CaAl_2SiO_7$); Q, quartz (SiO_2); D, diopside ($CaMgSi_2O_6$); C, calcite ($CaCO_3$).

to this study, the main constituting phases of the red ceramics from MD sample are quartz and phyllosilicates thus indicating a lower firing temperature and explaining the expansion nowadays visible in the ceramics (Fig. 1). The XRD patterns obtained in the present study for the ceramic body of QSA samples are similar to each other and the constituting phases are gehlenite ($CaAl_2SiO_7$) — the dominant phase — quartz (SiO_2), diopside ($CaMgSi_2O_6$) and minor calcite ($CaCO_3$) as illustrated by the XRD pattern obtained for QSA 3 sample (Fig. 4).

The chemical characterization of the glazes was performed by XRF-WDS as previously mentioned. It is apparent from the values listed in Table 1 that tin is less concentrated in the 16th–17th century glazes comparatively to the glazes manufactured latter on.

In order to ascertain the origin of chromophore elements, comparative ratios of fixed-time countings calculated for significant elements after subtracting the background were calculated taking tin as reference (Table 2); from the listed ratios, it is likely that zinc and lead were less used as glass-formers in glaze manufacture along the 18th century. Dominant chromophore elements are assigned in bold: Mn for the violet 18th century glaze QSA 4 and Sb plus Fe for the yellow NSA 17th century glaze. It becomes clear from the ratios listed in this table that the green pigments of studied glazes differ according to the period of manufacture; Fe and Cu are the chromophore ions for the single colored, uniform MD 16th century glaze, while iron alone is the main pigmenting agent for the 18th century glaze QSA 2.

Concerning the blue colored tile glazes, samples QSA 3 & 5 owe their coloring to iron whose ions provide a great variety of greenish to bluish colorings (Figueiredo et al., 2010). Conversely, the blue color of NSA glaze is most probably due to a different pigment once *As* and *Pb* contents are higher, conforming to an imported arsenic-rich Persian cobalt-based pigment (Garner, 1956).

Table 2
Counting ratios calculated from XRF-WDS data.

	Green (MD)	Yellow (NSA)	Blue (NSA)	Green (QSA 2)	Bluish (QSA 3)	Violet (QSA 4)	Blue (QSA 5)
Ratio	16th century		17th century	18th century			
Mn/Sn	0.9	0.3	1.5	0.1	<0.1	5.3	0.1
Sb/Sn	0.3	10.4	1.9	0.9	<0.1	0.1	0.1
Fe/Sn	38.4	22.2	84.0	4.4	1.4	1.3	1.3
Co/Sn	0.1	0.4	25.3	0.6	0.3	0.1	0.3
Cu/Sn	49.4	0.6	3.3	0.2	0.2	0.2	0.1
Zn/Sn	3.6	6.8	29.4	0.2	0.1	0.1	0.1
As/Sn	0.7	0.2	4.4	0.2	0.1	0.2	0.1
Pb/Sn	20.2	4.4	25.6	3.1	1.5	2.0	1.6

5. Final comments

The assessment of the degradation state from the studied 17th century ceramic tiles (azulejos) indicates that the tile decoration of the Church of *Nossa Senhora dos Aflitos* is well preserved in what concerns both the ceramics and the glaze. The tile pathology assigned in *Madre de Deus* Church (16th century) results mainly from the expansion of the low quality ceramics, occasionally giving rise to glaze detachment. Conversely, the study of 18th century polychrome tiles of *Quinta de Santo António* showed that the ceramic body is in a good state of conservation, while glaze deterioration was noticed as expected from a long exposure to the environment in an outdoor decorative panel. As a whole, the application of non-destructive analytical assays using X-rays (XRD and XRF-WDS) and directly irradiating small tile fragments proved to be very suitable for evaluating the degradation state of ancient tiles with great cultural value. In fact the present study has demonstrated the capability of the technique to identify serious degradation effects. In the case of MD tiles, degradation was so extensive that any restoration would be impossible. However, in other cases, like in QSA tiles, acted as a guide for the design of future preservation interventions. Furthermore, when the development of microorganisms is noticed (Silva et al., 2013) the present results will eventually contribute to the design of the implementation of non-destructive decontamination actions, based on gamma radiation.

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