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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

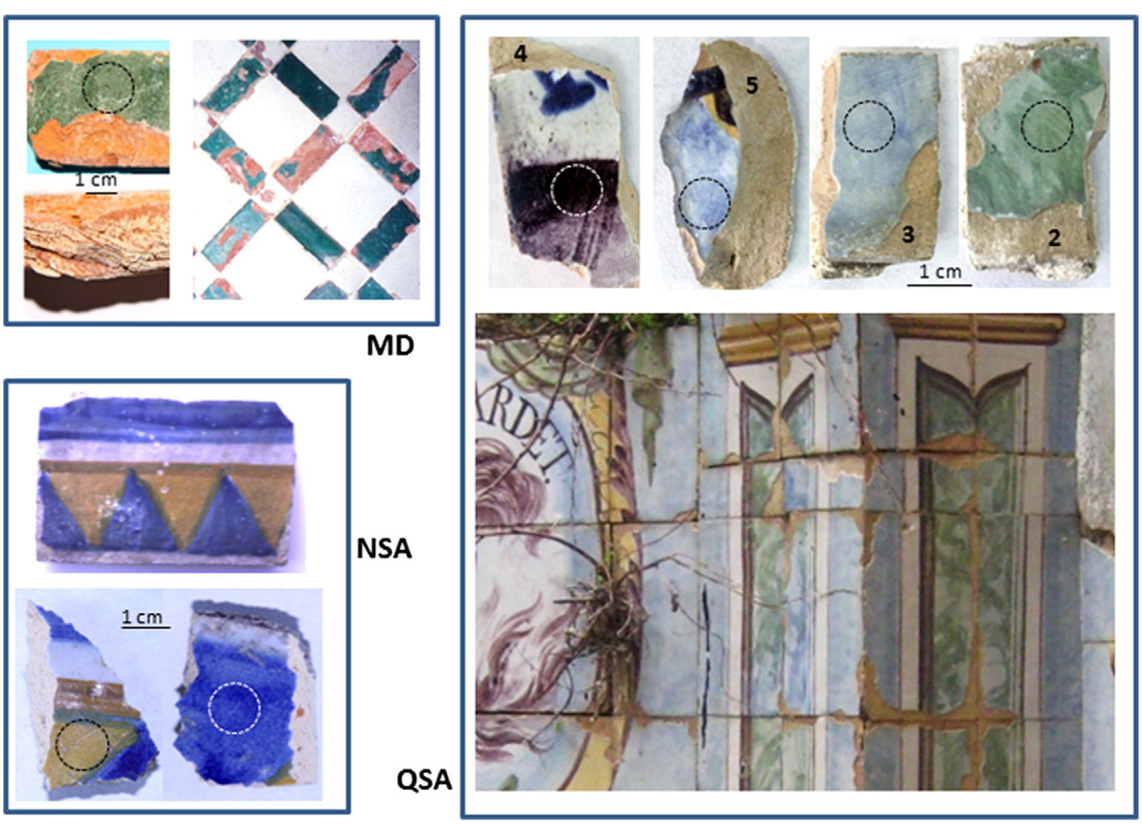

Fig. 1. Studied glazed tile fragments: MD — *Madre de Deus* Church (16th century, from the interior); NSA — *Nossa Senhora dos Aflitos* Church (17th century, interior); QSA — *Quinta de Santo António da Bela Vista* (18th century, exterior). A circle assigns the area irradiated in laboratorial assays.