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Portuguese tin-glazed earthenware from the 16th century: A spectroscopic characterization of pigments, glazes and pastes

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ABSTRACT

Sherds representative of the Portuguese faience production of the early-16th century from the "Mata da Machada" kiln and from an archaeological excavation on a small urban site in the city of Aveiro (from late 15th to early 16th century) were studied with the use of non-invasive spectroscopies, namely: ground state diffuse reflectance absorption (GSDR), micro-Raman, Fourier-transform infrared (FT-IR) and proton induced X-ray (PIXE). These results were compared with the ones obtained for two Spanish productions, from Valencia and Seville, both from same period (late 15th century and 16th century), since it is well know that Portugal imported significant quantities of those goods from Spain at that time.

The obtained results evidence a clear similarity in the micro-Raman spectrum in the glaze and clays of Portuguese pottery produced at "Mata da Machada" and sherds found at the mediaeval house of Homem Cristo Filho (HCF) street at Aveiro.

The blue pigment in the sample from the household of Aveiro is a cobalt oxide that exists in the silicate glassy matrix in small amounts, which did not allow the formation of detectable cobalt silicate microcrystals. White glaze from Mata da Machada and Aveiro evidence tin oxide micro-Raman signatures superimposed on the bending and stretching bands of SiO_2.

All these are quite different from the Spanish products under study (Seville and Valencia), pointing to an earlier production of tin glaze earthenware in Portugal than the mid 16th century, as commonly assumed.

1. Introduction

The Portuguese were the first Europeans to send merchant vessels regularly to China, bringing back, since the first half of the 16th century porcelains and other goods highly appreciated in Western Countries. Copies of those porcelains started to be produced in Lisbon, but in the form of faience, trying to imitate Chinese patterns [1]. There is now archaeological evidence that such production started in Lisbon at least in the middle of the 16th century ([2] and references therein).

Glazed earthenware, however, was a much older production in the country, namely at "Mata da Machada" [3] and Santo António da Charneca from about 1480 to 1530 [4], both South of Lisbon, and also in Lisbon at Santos o Velho at least from 1561 onwards [5].

In this study our first goal is the spectroscopic characterization of pigments, glazes and pastes of the 16th century Portuguese Faience, which still remains to be done. A comparison with Spanish production of Valencia and Seville was also performed. Micro-Raman spectroscopy was used as our main tool for such characterization ([6] and references therein). Ground state diffuse reflectance spectra (GSDR), with the use of the Kubelka–Munk treatment for colour evaluation were also obtained as well as FT-IR spectra for the pigment, glaze and paste characterization [6,7].

Micro-Raman spectrometry has been extensively used to investigate ancient ceramic art objects [8–14]. It is probably the most powerful non-destructive method to characterize archaeological artefacts, namely glazed ceramics and coloured glasses. It can be used to obtain information regarding the crystalline or glassy structures, which are built from covalent bonds between the SiO_4 tetrahedra in different modes. The ratio of the stretching (i.e. $\sim 1000\ cm^{-1}$) and bending ($\sim 500\ cm^{-1}$) Raman envelopes, measured as the band area ratio ($I_p = A_{500}/A_{1000}$), where I_p is the index

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of polymerization proposed by Colomban [10–13] could be correlated to the temperature of the kiln, glaze composition and different fluxing agents.

The particle-induced X-ray emission (PIXE) was used to provide elemental characterization for the majority of the samples under study in this work. PIXE has high sensitivity down to trace elements and has been extensively used in applications to cultural heritage due to its non-destructive character [15,16]. X-ray fluorescence (XRF) was also used here in a few cases due to the availability of portable instruments, although it only allows the determination of the elemental compositions for elements heavier than sodium, it is also a very important tool for determinations of chemical composition [17].

The aim of this study is the characterization of some sherds representative of the Portuguese faience production of the late 15th and early 16th century, through different (non-destructive) spectroscopic methodologies. The results have been compared with the ones obtained for Spanish productions of the same period, aiming to point out evaluable differences.

A comparison of the spectroscopic data obtained from sherds from Mata da Machada [3] and several other from an archaeological excavation on a small urban site in the city of Aveiro (late 15th century and 16th century) [18] was performed. Also sherds of imported pottery from Valencia and Seville were studied, since it is well know that Portugal imported significant quantities of those goods from Spain at that time [19,20].

These two Portuguese archaeological sites were chosen due to its importance concerning early 16th century tin glaze ware productions. Mata da Machada, located in the south bench of the Tagus River, thus close to Lisbon is, at the moment, the oldest known kiln to produce tin glazed ware ceramics in Portugal. It closed around 1530s, possibly due to the growth of the Lisbon industry, although most of its production was in fact coarse wares. In this sense, these should in fact be the first tin glaze ware experiments in the country.

As for Rua Homem de Cristo Filho, located inside the mediaeval city walls, the excavation identified a house and all the evidence of domestic daily activities, in a city trading with different parts of the world based mostly in salt industry, among other commodities [18]. The sherds analyzed in this paper were found inside a well, sealed by a mid-16th century deposit, therefore, and dated from the beginning of that century. This chronology was also supported by all the other material culture elements also found inside the well, such as other pottery types. Initially and only based on macroscopical observations, the sherds were believed to be Spanish, since nothing indicated that the Mata da Machada would produce enough be able to supply northern territories.

The choice of both these sites as providers of sherds is related to the fact that both of them were still operational in early 16th century and both provided a not so well known commodity at this time, Portuguese tin glaze ware.

The obtained results evidence a clear similarity in the micro-Raman spectrum in the white glaze and clays of Portuguese pottery produced at “Mata da Machada” [3] and the sherds found at the mediaeval house of Aveiro [18]. All these are quite different from the Spanish products under study, pointing to an earlier production of tin glaze earthenware in Portugal than the mid-16th century, as commonly assumed.

2. Experimental

2.1. Samples under study

Fig. 1 shows five representative samples selected in this work, the sherds’ dimensions are about 7 cm (a) is from Mata da Machada, Portugal; (b), and (c) Homem Cristo Filho street, Aveiro; (d) 16th century Valencia lustreware, from an excavation in Évora; (e) 16th century, blue on white Seville productions, recovered in Triana.

The choice of the faience sherds was based on the fact that they were found in secure and well dated archaeological contexts: Mata da Machada, 15th to 16th century [3], south of Lisbon production; Aveiro, 15th to 16th century [18]; Évora in a 16th century context and in the potter’s area in Triana Seville. The chronological determination was based not only in style but most importantly in stratigraphical layers. The experimental results are presented only for five sherds, but they were obtained for many other samples (faiences and tiles found in specific archaeological contexts). The selected sherds are considered to be representative of Portuguese and Spanish production, as dated.

2.2. Spectroscopic tools under use

2.2.1. Ground state diffuse reflectance absorption spectra (GSDR)

Ground-state absorption studies were performed using a home-made diffuse reflectance laser flash photolysis setup, with a powerful 450 W xenon lamp as monitoring lamp, by triggering the system in the normal way but without the laser fire [7], and in this way recording the lamp profile for all samples under study and also for two standards, barium sulfate powder and a Spectralon disc. This procedure has the advantage of excluding the sample luminescence (if it exists) because of the use of the analyzing fixed monochromator which is coupled to the ICCD which has time gate capabilities [7]. The reflectance, R, from each sample was obtained in the UV–vis–NIR spectral regions and the remission function, F(R), was calculated using the Kubelka–Munk equation for optically thick samples. The remission function is $F(R) = (1 - R)^2/2R$. Details regarding the data treatment can be found in [7,21] and references quoted therein.

2.2.2. Raman microspectrometry set-up

Raman spectra were obtained in a back-scattering micro-configuration, with two instruments: (i) a home made apparatus with a Cobolt Samba CW DPSSL, 300 mW, 532 nm as the excitation source, coupled to a SuperHead 532 from Horiba Jobin Yvon equipped with a 50× Edmund (or 100× Olympus) LWD objectives. The Raman probe was coupled to a HeadWall Photonics spectrograph (Raman Explorer 532 with a 100 μm entrance slit) and a Newton DU 971P-BV camera from Andor was used as detector for the Raman signals, working at −60 °C. The spectral resolution of this Raman spectrometer was ∼2 cm^{-1}; (ii) a mobile HE532 Horiba Jobin Yvon (France), equipped with a matrix CCD detector cooled by Peltier effect at 200 K associated with Laser Quantum Ventus (UK) YAG laser lined at 532 nm, with a maximum power of 300 mW. The measuring 532 SuperHead from Horiba Jobin Yvon head equipped with a ×100 Long Working Distance Olympus microscope objective is movable and the light (incident and scattered) is transmitted by optical fibres. The spectral resolution is ∼4 cm^{-1}. All Raman spectra were recorded at least 5 times for each sherd in different locations, and all spectra presented in this paper were representative.

Data acquisition was performed with the Andor software and data processing, namely the base line correction, when needed, was done with the LabSpec software from JY.

2.2.3. FT-IR spectroscopy

Infrared spectra were measured on a Varian 7000 FT-IR spectrometer in ATR mode (Golden-Gate, Diamond from Specac) or transmittance mode by the use of KBr pellets. Spectra were recorded at 1.0 cm^{-1} resolution, in the range 4000–400 cm^{-1} as a ratio of 72 single-beam scans of the sample to the same number of background scans from air. Baseline corrections were introduced