A multi-technique study for the spectroscopic characterization of the ceramics from Santa Maria do Castelo church (Torres Novas, Portugal)

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ABSTRACT

An excavation in a 14th c. church at Torres Novas, named Santa Maria do Castelo, provided some green glazed ceramic sherds, archaeologically dated from 14th c. to the 16th c. The town of Torres Novas is located at the center of Portugal, about 100 km north of Lisbon. The obtained results evidence three types of pastes of the pottery: type 1 with Quartz, Illite, Muscovite and Microcline as the main constituents, type 2 with Quartz, Calcite and Gehlenite; and finally type 3 with Quartz, Calcite and Diopside being the major components. Type 1 pastes are related to clay sources of Pliocene origin, and all this pottery was most probably made in Portuguese kilns. However, types 2 and 3 spectroscopic trends are remarkably different, indicating that those ceramics were produced in Seville.

All the studied ceramics are lead glazed, and green glazed. In one of the samples from the Seville kiln, Ceresite was the main pigment used to obtain the greenish colouration. In what regards the origin of all samples produced with Pliocene clays, the 16th c. ones were most likely produced in the Santo António da Charneca or Mata da Machada kilns, both located in the south shore of the Tagus river, region of Lisbon. In what regards the green glazed jug rim (14th c.) and the jug spout (15th c.) they could also have been produced in the two mentioned kilns south of Lisbon city, but another interesting hypothesis - due to richness of the decoration - is the production in Lisbon workshops, with the use of Pliocene clays imported by Lisbon potters, now documented both in Lisbon archaeological findings and also in documental sources.

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1. Introduction

Archaeological excavations made in 2004 and 2011 in the remains of the Medieval church of Santa Maria do Castelo (Torres Novas), at the centre of Portugal, and about 100 km north of Lisbon, provided many different finds. Among those there are some green glazed pottery sherds, dated from the 14th century (the time when the church was built) and others from the 15th–16th centuries.

Among the older objects there is a jar rim fragment with a tall neck, decorated with vertical lines printed with a roller (sample SMC1, Fig. 1). This type of decoration technique was largely used in the Saintonge productions (Southwest of France) and in some Flanders pottery workshops during the Middle Ages.

This archaeological site also provided sherds of tiles with Hispano-Moresque decoration (Vieira Ferreira et al., 2014), imported from Seville at the beginning of the 16th c., where the tin glazed technique was already in use. It is well known that Hispano-Moresque tiles were widely spread in Portugal at the end of the 15th c., and especially during the 16th c., due to a significant importation from Seville (Triana kilns) under the Portuguese King Manuel the 1st (Vieira Ferreira et al., 2014). Many of these tiles covered the walls of the royal Palace of Sintra and others were used in the decoration of many churches and monasteries spread all over the country.

No medieval kilns are known in the area of Torres Novas, but other kilns producing tin glaze or lead glaze wares are well known in the region of Lisbon, and were located either in the city of Lisbon or in the south shore of the Tagus river at Santo António da Charneca (SAC) and Mata da Machada (MM), both active from the end of the 15th century to the mid-16th century (Torres, 1990; Carmona and Santos, 2005; Barros et al., 2012; Gaspar and Gomes, 2012; Mangucci, 1996; Vieira Ferreira et al., 2015b).

The sherds from this excavation site were studied with the use of non-invasive spectroscopies, namely by correlating information obtained with different techniques: Ground State Diffuse Reflectance absorption (GSDR), micro-Raman and X-Ray Fluorescence emission (XRF), X-Ray Diffraction (XRD) experiments were also performed. This multidisciplinary approach to the archaeometric study of Portuguese
Micro-Raman is probably the most powerful non-destructive method to characterize archaeological artefacts, namely glazed ceramics and coloured glasses, and has been extensively used to investigate ancient ceramic art objects (de Waal, 2004, 2009; Colomban, 2003, 2005, 2006, 2008, 2010, 2012). Micro-Raman can be used to obtain information regarding the crystalline or glassy structures, which are built from covalent bonds between the SiO4 tetrahedra in different modes. The ratio of the stretching (i.e. −1000 cm−1) and bending (−500 cm−1) Raman envelopes, measured as the band area ratio \(I_p = \frac{A_{500}}{A_{1000}}\), where \(I_p\) is the polymerization index proposed by Colomban (2003, 2005, 2006, 2008, 2012) can be correlated to the temperature of the kiln, glaze composition and different fluxing agents. Also the correlation of the polymerization index \(I_p\) with the Si stretching maximum \(\nu_{\text{max}}\) may provide information regarding the glaze composition (Kirmizi et al., 2010; Colomban et al., 2010).

X-ray fluorescence (XRF) was used here due to the availability of portable instruments, although it only allows the determination of elemental compositions for elements heavier than sodium. It is also a very important tool for determining chemical compositions (Simsek et al., 2014). X-ray fluorescence (XRF) was used here due to the availability of portable instruments, although it only allows the determination of elemental compositions for elements heavier than sodium. It is also a very important tool for determining chemical compositions (Simsek et al., 2014).

The main objectives of this study are the mineralogical and spectroscopic characterization of the pastes, glazes and pigments of the archaeological material found at Santa Maria do Castelo. Glazes will be analysed, aiming to distinguish the different productions of the ceramic body, by using a diffraction pattern database (Vieira Ferreira et al., 2014).

Micro-Raman spectroscopy, ground-state diffuse reflectance set-up, X-ray fluorescence spectrometry, and X-ray diffraction techniques used in this work are described below.

2.1. Spectroscopic tools under use

2.1.1. Micro-Raman spectrometry set-up

Micro-Raman measurements were carried out in a back-scattering micro-configuration, with two instruments: i) a homemade apparatus with a Cobolt solid state laser, continuum wave, model Samba, 300 mW, 532 nm as the excitation source, coupled to an Olympus microscope, model BX-FM, equipped with 10×, 50× or 100× Olympus LWD objectives. The laser beam was focused on a diameter of about 25 and 1.5–2 μm respectively. The Raman probe was coupled to an Andor monochromator (Shamrock 163 with a 100 μm entrance slit), and a Newton DU 971P-BV camera from Andor was used as the detector for the Raman signals, working at −60 °C (Vieira Ferreira et al., 2013a, 2014, 2015a). ii) A LabRam HR Evolution, from Horiba - Jobin Yvon, was also used in some cases for more detailed spectral information, with a 532 nm excitation source. The light was focused with a 50× LWD or a 100× objective and the laser power on the sample was approximately 10 mW. Spectra were acquired using 10s of signal collection time and 5 accumulations. Two gratings were used, 600 or 1200 groves per mm, depending on the spectral resolution needed, 120 cm−1 to 3600 cm−1 or 100 cm−1 to 1760 cm−1, respectively. The spectral resolution of the Raman spectrometers was −4 cm−1 when using the 600 groves’ grating, and −2 cm−1 when using the 1200 groves’ grating. All Raman spectra were recorded at least 5 times for each
sample in different locations, and all spectra presented in this paper are representative (Vieira Ferreira, 2013a, 2014, 2015a).

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

2.1.2. Ground state diffuse reflectance spectra (GSDR)

Ground-state absorption studies were performed using a homemade diffuse reflectance laser flash photolysis setup, with a 250 W W-Hal lamp as monitoring lamp, triggering the system in the normal way but without the laser fire (Vieira Ferreira and Ferreira Machado, 2007). In this way the lamp profile was recorded for all samples under study and also for two standards: the barium sulfate powder and a Spectralon disk. A fixed monochromator - coupled to an ICCD with time gate capabilities - was used for detecting the reflectance signals (Vieira Ferreira and Ferreira Machado, 2007). The reflectance, R, from each sample was obtained in the UV–Vis-NIR spectral regions, and the remission function, F(R), was calculated by 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 (Vieira Ferreira and Ferreira Machado, 2007) and the references quoted therein.

2.1.3. X-ray fluorescence experiments

The chemical composition of ceramic glazes and pastes was also accurately determined by X-ray fluorescence with the use of a Niton XL3T GOLDO spectrometer from Thermo Scientific with an X-ray generator of 50 kV/200 μA, equipped with a CCD for image location (3 mm spot diameter) and storage (Vieira Ferreira et al., 2013a, 2014, 2015a).

2.1.4. X-ray diffraction experiments

The identification of the ceramic body powder crystalline phases was carried out with an X-Ray diffractometer at CERENA (Pananalytical XPERT PRO model) by using CuKα radiation. The measurement parameters used were: 2θ (5–65°); step size 2θ = 0.033° and a scan step time of 80 s with generator settings of 35 mA and 40 kV. The analysis was performed with the program High Score Plus by using the PDF4 data base.

In the case of XRD measurements only about 10 mg of powder sample were used to perform an experiment.

2.2. Studied materials

Fig. 1 shows the representative samples selected for this work, SMC1 to SMC7. All samples except SMC2 are green glazed. SMC2 is whitish/greenish, and apparently non-glazed. All sherds have dimensions of about 4–5 cm except in case SMC2 where the dimension is about 2 cm × 3 cm. SMC1 is a jar rim fragment with a tall neck, decorated with vertical lines printed with a roller, and SMC3, another pitcher spout fragment seems to present similar fabrics and glaze. SMC4 a third rim fragment, also from a jar, and SMC2 is a fragment from a bottle’s body decorated with horizontal cannelures. SMC5 and SMC7 are basin rims and SMC6 is a fragment from a plate. The choice of the earthenware sherds SMC1 to SMC7 was based on the fact that they were found in secure and well dated archaeological contexts (samples SMC1 and SMC3 are from the 14th c., samples SMC2 and SMC4 from the 15th c., and samples SMC5 to SMC7 from the 16th c.). Sherds were recovered from the church archaeological site or from the surrounding waste areas and dated based on archaeological stratigraphy.

2.3. Characterization studies

GSDR. Micro-Raman and XRF are non-invasive spectroscopies and were applied directly onto the glaze or the paste of the sherd. In the XRD case, about 10 mg of the ceramic’s body were needed for the pastes’ study. Those small amounts of powder were removed from the sherds and used for the XRD determinations, i.e. the pastes’ mineralogical characterization, by drilling the sherds’ edge with a 1 mm tungsten carbide drill, coupled to a small electric drill.

The LabRaman equipment has accurate confocal capabilities, enabling in depth studies from the surface to about 200 μm deep, but the penetration depth doesn’t go over 50–70 μm in most cases, depending on the coloured glaze under study. For XRF the estimated penetration depth is about 60 μm for Pb glazes. For the GSDR studies all the glaze depth was analysed due to the use of a powerful W-Hal lamp (250 W).

3. Results and discussion

3.1. XRD studies

Fig. 2 shows the XRD experimental patterns for pastes of Santa Maria do Castelo ceramics SMC1 to SMC7. The XRD peaks were assigned to: Quartz (Q, SiO2, main peaks at 2θ = 21.0, 26.7, 36.7, 46.0, 50.2, 60.0), Gehlenite (G, Ca2Al(AlSi)O7, main peaks at 2θ = 24.3, 29.3, 31.4, 37.2, 44.5, 52.2, 61.3), Diopside (D, CaMgSi2O6, main peaks at 2θ = 29.9, 30.5, 31.0, 35.1, 35.7), Anorthite (An, CaAl2Si2O8, main peaks a 2θ = 22, 28), Calcite (C, CaCO3, main peaks at 2θ = 29.4, 47.5), Muscovite (M, KAl2(Si3Al)O10(OH)2, with main XRD peaks at 2θ = 8.8, 17.8, 26.7, 45.3), Microcline (Mic, KAlSi3O8, main peak at 2θ = 27.3), Analcime (Anl, NaAlSi4O10·H2O, main peaks at 2θ = 15.9, 26.3) and Illite (I, main peaks at 2θ = 8.8, 19.7, 27, 35). All these assignments were made by using the high XRF peak fitting from panalytical and PDF4

Fig. 2. Representative XRD patterns for pastes from Santa Maria do Castelo samples: i) SMC1, jug side, 14th c.; ii) SMC2, jug sherd, Islamic, 15th c.; iii) SMC3, jug spout, 14th c.; iv) SMC4, jug side, 15th c.; v) SMC5 sherd from a basin, 16th c.; the XRD peaks are assigned to: Quartz (Q), Gehlenite (G), Diopside (D), Anorthite (An), Calcite (C), Analcime (Anl), Illite (I), Muscovite (M) and Microcline (Mic).
From a mineralogical standpoint the main features to point out are the following: the pastes from the sherds SMC1, SMC3 and SMC5 to 7 are quite similar and most probably they were made with the use of raw materials from the same clay source. Similar XRD patterns were observed for a quartz from Alhos Vedros church and small ceramic sherds from Santo António da Charneca (SAC) and Mata da Machada (MM) (Vieira Ferreira et al., 2014, 2015b). The dominating mineral is Quartz, although small amounts of Microcline of and Illite could also be detected, as curves i), ii) and v) from Fig. 2 show. Illite is decomposed at 600 °C into amorphous phases (meta-kaolinite, etc.). Thus Illite Bragg peaks may occur due to soil contamination.

Certainly the clays used in these ceramics had the same origin, i.e. the Pliocene raw materials that exist in that region, south of the Tagus river and close to Lisbon city (Vieira Ferreira et al., 2014, 2015b; Zbyszewski, 1963; Lepierre, 1899; Carvalho, 1921). All the ceramic pastes from Santo António da Charneca and most from Mata da Machada exhibit the same mineralogical pattern, and only differences in the iron oxide content were observed, the more iron oxide the darker the raw material (Vieira Ferreira et al., 2014, 2015b).

The use of Pliocene clays (rich in Quartz, Kaolinite, Illite, Muscovite and Microcline) to produce the ceramics’ pastes is a very specific and original feature. In previous published work (Vieira Ferreira et al., 2013b, 2015b) coeval ceramics from Triana (Seville), Valencia and others were studied. The diffractogram obtained for these ones, resemble the Miocene clays from the Lisbon clay sources (Vieira Ferreira et al., 2015b), however with specific differences in the calcium carbonate content and also Andradite absence.

These results are in clear contrast with SMC2 and SMC4 sherds, both using different raw materials in the ceramic productions. As one can see, the XRD patterns for the sherd’s ii) and iv) evidence a high amount of Calcite (main peaks at 2θ = 29.4, 47.5) which did not exist in the ceramics with Pliocene clay materials (Vieira Ferreira et al., 2014, 2015b). Sample SMC4 exhibits Quartz, Diopside (or Augite, which XRD peaks are almost identical to those of Diopside), and Anorthite as the main mineral constituents. In sample SMC2, the rim jug sherd, Gahlenite is more relevant than Diopside.

These diffractograms present some similarity with the Lisbon XRD patterns described in a previous paper (Vieira Ferreira et al., 2015b), although with a remarkable difference: no CaCO3 exists in the Lisbon pottery from this period or exist only in very small amounts; also the relative amounts of Diopside and Gahlenite are different. Andradite is common in Lisbon pastes but not in the Seville productions. Therefore we conclude that different clays (raw materials) were used in SMC2 and SMC4 for the ceramic productions, and that these ceramics were not produced in the Lisbon workshops. In fact, a comparison with the pastes of 16th c. tiles produced in Seville, recently reported by our group (Vieira Ferreira et al., 2014), shows that the pastes of SMC2 and SMC4 are Seville productions. The two diffractograms for the two Seville tiles are presented in Figs. S1 and S2 for comparison. For Seville tile patterns references (Betts and Weinstein, 2010; Meco, 1989; Pleguezuelo, 1996) are indicated.

3.2. XRF studies

XRF is a sensitive, non-destructive elemental analysis technique using a sub-millimetre or millimetre scale respectively, which allows for a quantification of elements between magnesium and uranium which may exist in the samples under study from major to trace levels. All the analyses both on pastes and glazes were performed, at least, in three spots of about 3 mm in diameter of the sherd, but in most cases five spots for each sample. In the cases where the pastes’ analysis was performed in a powdered sample, at least three essays were also done (Vieira Ferreira et al., 2014, 2015b; Simsek, 2014). Apart the internal calibration, the equipment was calibrated with standards IRRM-BCR-126A – Lead Crystal Glass, and BAM-S005B – Multi-element Glass for XRF Analysis.

Table 1 presents the chemical composition of the ceramic pastes for the samples under study, obtained by XRF analysis, expressed as weight % of the indicated oxides (or recalculated to 100 wt.% as sum of the different oxides). Representative XRF spectra are depicted in Fig. 3, obtained with an acquisition time of 360 s for each spectrum.

The elemental compositions of the ceramic bodies as well as the spectra allow us to considered two main groups of samples: samples SMC1 and SMC3 present a similar overall composition. Both pastes present a SiO2 content of ~75 wt.% and Al2O3 ~ 17 wt.% (amount of SiO2 + Al2O3 ~ 90 wt.%). The calcium oxide content is very small (less than 1 wt.%) in samples SMC 1 and SMC 3. By opposite, the Fe2O3 content varies between 3 and 4%. For samples SMC5, SMC6 and SMC7 the SiO2 and the Al2O3 contents together are also about 90 wt.% with almost no calcium oxide (0.6–0.7 wt.%). The iron oxide content does not exceed 3.5 wt.%. Very similar ceramic bodies' composition patterns were already observed by us in previous studies (Vieira Ferreira et al., 2014, 2015b).

Samples SMC2 and SMC4 are part of a second group which presents a SiO2 content below 50 wt.% and very high calcium oxide content, lying in a range 27–34 wt.% These samples showed the lowest SiO2 content (with an amount of SiO2 + Al2O3 of about 60 wt%) and the highest calcium oxide content of all samples in this study.

In what regards the coloured glaze phases, their chemical composition is presented in Table 2 for samples under study.

Apart from sample SMC2, which presents a very low PbO content (below 1 wt.%), we observed that the major components of the glazes are SiO2 and PbO resulting in ca 70–80% of the overall glaze’s composition as is the case of lead based glasses. However, the silica content is quite different. In samples SMC5 and SMC6, the silica content is below 30 wt.% and the PbO/SiO2 ratio is the highest (PbO/SiO2 ~ 2.0–2.4). In SMC1 and SMC3 the silica content is below 40 wt.% and the PbO/SiO2 ratio ~ 1.2–1.6. Samples SMC2 and SMC4 present the highest silica content (~45–56 wt.% SiO2) and a Pb/SiO2 ratio smaller than 1.0. A common observation for all samples is that almost no SnO2 was detected in all the glazes under study (very low amounts 0.02–0.1 wt.%).

Another important observation, depicted in Table 2, is that copper seems to be responsible for the green pigment in all studied samples. Apart from the SMC2 sample, the copper oxide content lays in the range 3–5 wt.%, and no chromium was detected. This statement is in agreement with the ground sate absorption spectra of the glazes, as we will show later in this paper.

<table>
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<th>Element</th>
<th>SMC1</th>
<th>SMC2</th>
<th>SMC3</th>
<th>SMC4</th>
<th>SMC5</th>
<th>SMC6</th>
<th>SMC7</th>
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3.3. Raman microspectroscopic studies

Micro-Raman spectroscopy is a very useful technique not only in the identification of pigments and analysis of the glazes at the sherds’ surface but also for the analysis of pastes. These information are of particular importance when correlated with the XRD diffractograms. The paste (Fig. 4ii)) is essentially the same as the SMC1 paste (Fig. 4i)). This shows again the use of the same clays in both pastes (Fig. 4ii)), This shows again the use of the same clays in both ceramics under study and are shown in Fig. 4i) to x).

Raman spectra of SMC1 green glaze (jug spout, 14th c.) is shown in Fig. 4i) and exhibits clear signatures of Quartz (peaking at 202, 352, 463 cm$^{-1}$), and also of Anatasie at 145, 393, 512 and 634 cm$^{-1}$). These bands are superimposed in the bending band of the silica glaze, and the stretching band is much larger, peaking at 959 cm$^{-1}$, a common value for lead based glazes (Colomban, 2003, 2005, 2006, 2008, 2012). The ratio of the SiO$_2$ stretching and bending Raman envelopes gave an $I_b$ value of about 0.4, and from this value we can estimate the kiln’s temperature to be ~750 °C, as proposed by Colomban. The absence of Rutile is in accordance with the estimated temperature of the kiln, since only for temperatures above 900 °C, does Anatasie start to be transformed into Rutile (Simsek et al., 2014).

Another aspect to be mentioned is the absence of tin oxide (SnO$_2$, peaking at 475, 633 and 775 cm$^{-1}$) usually used as a whitening agent in the white and green glazes of the Santo António da Charneca tiles, and in the white faience of Mata da Machada, also produced with the use of Pliocene clay materials.

For the body (Fig. 4ii)) this sherd reveals the same crystalline materials, Quartz and Anatasie, however the stretching and the bending bands of the glaze are absent, as expected. In some sherds of this pottery obtained from Pliocene clay sources, small amounts of the clays of the initial raw material, Kaolinite, Illite and Muscovite may remain as the XRD data showed, but they rarely can be observed by Raman spectrometry (Vieira Ferreira et al., 2014).

The ceramics were normally fired twice: the first one to go from the initial raw materials to the biscuit and the second are to produce the coloured glaze. Since we are dealing with very simple ceramics, with one colour only, no further firing was needed in these cases.

In what regards the green glaze we could not observe it’s signature in all the SMC samples under study here. XRF indicates the presence of a copper mineral as being responsible for the green colour. Cu$^{2+}$ ions are dissolved in the glaze matrix, producing the green colour of the glaze, in spite of non-being detected by micro-Raman. The use of micro FT-IR spectroscopy also failed in the tentative identification of the initial used copper pigment. Moreover this assignment could be made with the use of the ground state absorption spectra presented later in Fig. 5.

In the Islamic sherd SMC2, the whitish/greenish cover (Fig. 4iii)) exhibits a very clear Raman signature from lead carbonate. Cerussite (C$_4$PbCO$_3$, peaking at 148, 175, 213, 681, 838, 1054, 1376 and 1478 cm$^{-1}$). The very light green colour of this glaze is certainly associated with presence of this mineral, certainly formed by reaction of the sample’s calcium carbonate with the lead oxide added for the glaze formation. The paste (Fig. 4iv)) shows the presence of Anatasie, Calcite (Ca, CaCO$_3$, peaking at 273, 710 and 1086 cm$^{-1}$, and a clear signature of Carbon Black (CB, –1325 and –1580 cm$^{-1}$). Gehlenite signature, which XRD diffractogram presented before proved to exist in this paste, could hardly be identified in this paste, its main Raman peaks being located at 230, 308, 620, 662, 911 and 955 cm$^{-1}$.

Sample SMC3 paste (Fig. 4vi)) is essentially the same as the SMC1 paste (Fig. 4ii)). This shows again the use of the same clays in both pastes, could hardly be identified in this paste, its main Raman peaks being located at 230, 308, 620, 662, 911 and 955 cm$^{-1}$.

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Another aspect to be mentioned is the absence of tin oxide (SnO$_2$, –1325 and –1580 cm$^{-1}$). Gehlenite signature, which XRD diffractogram presented before proved to exist in this paste, could hardly be identified in this paste, its main Raman peaks being located at 230, 308, 620, 662, 911 and 955 cm$^{-1}$.

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ceramics. In what regards the glaze (Fig. 4v)) the main difference in this case is due to the existence of Carbon Black in larger amounts. The temperature of the kiln also seems to be lower than in case SMC1, curve i).

Raman spectrum of the paste of SMC4 sample, the top edge of the green jug, is shown in Fig. 4viii) and is quite similar to the paste of sample SMC2, revealing a high content of Quartz and Calcite. Anatase and Carbon Black also exist, although in reduced amounts. Diopside Raman signature, peaking at 318, 359, 390, 664 and 1011 cm$^{-1}$ exists in this paste, as revealed by XRD, however it is almost absent as compared to the Quartz and Calcite Raman signatures.

This sherd’s green glaze (curve vii) is similar to the previous green glazes of SMC1 and SMC3, although with no Anatase peaks superimposed, and no Carbon Black. The polymerization index is very small for SMC3, $I_p = 0.15$, pointing to the use of the kiln’s lowest temperature in all samples under study (T ~ 650°–700 °C).

Finally, only one Raman curve is presented in Fig. 4 for the green glaze (curve ix) and another for the paste (curve x) of sample SMC5. The Raman spectra obtained for samples 5, 6 and 7 were the same within experimental error. These samples were stratigraphically dated as 16th c. samples and indeed they were clearly produced with the same Pliocene raw material from the Santo António da Charneca and Mata da Machada raw materials. They are only lead glazed, i.e., no tin oxide was used as it was common for the courseware productions of those two kilns. Only tiles and better quality pottery productions...
revealed the use of the faience technique in these two 15th/16th c. kilns, situated south of Lisbon.

One should also stress here the similarity between these 16th c. productions (samples SMC5, 6 and 7) and the 14th c. (sample SMC1) and 15th c. productions (sample SMC3). There are no reported kilns in the Lisbon city area or in the South of Lisbon area dated 14th c. The discovery of sample SMC1 in the Torres Novas excavation may point to the existence of a kiln dated 14th c. in the region of Mata da Machada and to Santo António da Charneca kilns, or at least to a kiln in another area using the same raw materials characteristic of those two kilns, i.e. the Pliocene kaolinitic sands. A very interesting possibility is that samples SMC1 and SMC3 were produced in Lisbon workshops, since it is now well documented that some workshops from Lisbon imported those Pliocene raw materials from the South shore of the Tagus river (Alho et al., 2015).

3.4. Ground state diffuse reflectance spectroscopy studies

The ground state diffuse reflectance absorption spectra could be obtained from the reflectance curves, and also with the use of the Kubelka Munk function $F(R) = (1 - R)^2 / 2R$, for pastes and coloured glazes of the 14th c. to 16th c. ceramics gathered at SMC excavation at Torres Novas. Those results are presented in Fig. 5, SMC1 to SMCS (for samples SM6 and 7 the results are similar to SM5).

The ground state diffuse reflectance absorption spectra for the ceramics’ pastes for the Pliocene clays, SMC1, 3 and 5–7, exhibit a maxima peaking at about 350 nm with tails in the visible region of the absorption spectra, as Fig. 5 shows (curves 1 are for the pastes). These data are in agreement with similar ones published by our group for the 16th c. ceramic productions in the region of Lisbon (Vieira Ferreira et al., 2014, 2015b). For the Seville pastes (SMC2 and SMC4) the maxima for these curves are not too different and spread from about 320 nm to about 350 nm, also with long tails in the visible region of the absorption.

For all samples, except SMC2, the green glaze curves (dark green) exhibit two maxima at about 400 nm and 750 nm, while for the light green glazes the UV region presents smaller absorptions. This immediately excludes the use of chromium oxide pigments which exhibit absorption peaks at 455 nm and 636 nm, characteristic of Cr$^{3+}$ ions (Vieira Ferreira et al., 2014), and is also in agreement with the XRF data presented in Table 2, where the amount of chromium oxide detected is negligible. For all dark green glazes the amount of copper oxide revealed by XRF is significant, pointing to the presence Cu$^{2+}$ ions as the origin of the green colour. The source of this green pigment is, most probably, basic copper carbonate (Taylor and Doody, 2014), and the absorption spectra presented for the dark green glazes are compatible with this assignment (Vieira Ferreira et al., 2014).

The light green glaze from sample SMC2 differs from the other light and dark glazes, most likely due to the presence of the lead carbonate, and exhibits strong absorption in the UV (max. at about 330 nm), while the visible absorption at about 750 nm is much more moderate.

4. Conclusions

Archaeometric studies were recovered from the excavation of Santa Maria do Castelo 14th c. church at Torres Novas. The obtained results were compared with those obtained from 16th c. Portuguese ceramics, either tiles and pottery sherds from Santo António da Charneca’s kiln or sherds from Mata da Machada’s kiln (Vieira Ferreira et al., 2014, 2015b) or even with tiles of Spanish provenance, namely from the Triana kilns of Seville (Vieira Ferreira et al., 2014; Betts and Weinstein, 2010). The latter tiles (Hispano-Moresque) were found in this excavation at Santa Maria do Castelo church and were imported in the beginning of the 16th c. from Seville in large quantities, and are commonly found in Portuguese territory.

By the use of the mineralogical composition for the pastes obtained from the XRD diffractograms, and also from the spectroscopic characterization presented here for pastes and green glazes, we conclude that five of the seven sherds studied here were produced with the use of Pliocene clays (south of Lisbon clay sources) and could have been produced either in the Santo António da Charneca or in the Mata da Machada kilns (end-15th to mid-16th c.). However, since the Lisbon workshops also used clay materials from the south bench of the Tagus river (Vieira Ferreira et al., 2015b), Lisbon workshops are very good candidates for the production of SMC1 and SMCS samples. The two final sherds, the bottle sherd SMC2 and the jug rim SMCS are Seville productions. All sherds are lead glazes and no tin oxide was used in their fabrication.

Taking into account the polymerization index, we determined $I_p = 0.4$ for the green jug rim from the 14th c., and slightly smaller $I_p$ for the other green lead glazes $I_p = 0.15$. In the former case we estimate a 750 °C kiln temperature and in the latter lead glazes of about 650 °C–700 °C.

The archaeometric analysis in this paper indicates that most objects are in fact Portuguese, despite formally similar to North European productions, chemically resembling to productions of the Tagus river south bench. These belong to the same production area of the three SMC5 to SMCS fragments, although these are later productions. The bottle fragment reveals a Seville origin and easily associated to the well-known trade of tiles and pottery from that Spanish city during the Middle and Early Modern Ages.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jasrep.2016.02.013.

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