Journal of Cultural Heritage 66 (2024) 593–601

Contents lists available at ScienceDirect

Journal of Cultural Heritage

journal homepage: www.elsevier.com/locate/culher

VSI: TECHNART 2023 selected papers

The colour palette of 16th-18th century azulejos: A multi-analytical non-invasive study

Mario Bandiera[a], Umberto Veronesi[a], Marta Manso[a,b], Andreia Ruivo[a,c], Márcia Vilarigues[a,c], Lurdes Esteves[d], Alexandre Pais[d], Susana Coentro[a,c,*]

[a] VICARTE, Research Unit Glass and Ceramics for the Arts, FCT-NOVA, Campus de Caparica, 2829-516 Caparica, Portugal
[b] LIBPhys - Laboratory for Instrumentation, Biomedical Engineering and Radiation Physics, FCT-NOVA, Campus de Caparica, 2829-516 Caparica, Portugal
[c] Departamento de Conservação e Restauro, FCT-NOVA, Campus de Caparica, 2829-516 Caparica, Portugal
[d] Museu Nacional do Azulejo, Rua da Madre de Deus, 4, 1900-312 Lisboa, Portugal

ARTICLE INFO

Article history:
Received 10 November 2023
Accepted 17 January 2024
Available online 5 February 2024

Keywords:
Azulejo
Maiolica
Naples yellow
Cobalt
Tiles

ABSTRACT

This work provides an overview of the pigments used by Portuguese *azulejo* painters through the study of 34 glazed tiles belonging to the National *Azulejo* Museum in Lisbon, Portugal. The tiles are dated from the late 16th century to the early 19th century, with most samples attributed to the 17th and 18th centuries. Building on a previous study where the chemical composition of the 17th-century colour palette was characterised [1], we used a non-invasive methodology to further identify compositional differences among groups of colours spanning a wider timeframe. Blue, white, yellow, orange, purple, green and brown decorations were analysed by EDXRF to obtain qualitative and (in some samples) quantitative information on their chemical composition. µ-Raman spectroscopy was used to identify the main colouring agents. Finally, colorimetric measurements of the different hues of each colour were performed to address the relation between colour and chemical composition. Our results show that greens could be obtained through a copper-based pigment or by mixing lead-antimonate with cobalt-blue pigment. Although cobalt is the colouring agent of all blue decorations, compositional differences suggest the use of different types of raw materials or the addition of specific reagents to modify the hue. On the other hand, yellow hues ranging from lemon yellow to orange were manufactured by adding zinc, tin, or iron oxide to a lead antimonate base. Finally, a manganese ore was used to make the purple pigment. Overall, we noted that while the basic pigments remained the same, the colour palette was progressively widened during the 18th century. This was done by using more pure pigments (*i.e.*, with less iron), by changing the ratio in pigment mixtures (*i.e.*, blue and yellow), or by overlapping colour layers for artistic effects. Finally, the results of the chemical and colorimetric analyses are always influenced by the concentration of the pigment in the glaze, its thickness and the overlapping of pigments used by *azulejo* painters to expand the shades available for the final artistic composition.

Introduction

The *azulejo* (Portuguese glazed tile) heritage is one of the most recognisable traits of Portuguese architecture and has been so for more than five centuries since the first maiolica tile panels were made in the country in the second half of 16th century. The *maiolica* technique, which involves painting the colours over an opaque white lead-tin glaze substrate, was perfected in Italy during the 15th century [1]. It then spread to Spain and the Flanders, and from there, it arrived in Portugal thanks to the activity of Flemish artists operating in the country [2]. In the 17th century, the chromatic palette of Portuguese tile makers reached a peak: colours comprised blue, various shades of yellow and orange, different types of green, purple, brown and a very dark, almost-black colour used for contours [3,4]. The onset of the so-called “blue-and-white period” towards the end of the century gave rise to some of the most remarkable *azulejo* works, completely covering church interiors and restricting the decoration to cobalt blue over a white background. Then, during the 18th century, the other colours were progressively reintroduced [5].

---

[*] Corresponding author.
E-mail address: scoentro@fct.unl.pt (S. Coentro).

https://doi.org/10.1016/j.culher.2024.01.011
1296-2074/

Despite the enormous importance of *azulejos* in Portugal, the scientific studies that investigate their colour technology are still relatively few and mostly focused only on blue and yellow [3,4,6–15]. Coupled with the complete lack of primary sources, this means that our knowledge of how artists decorated the tiles in a more practical sense, what techniques they employed, and which pigment recipes they selected is still rather limited. We know that colours were obtained through 3d transition metal oxides (copper green, manganese purple, cobalt blue) or with previously synthesised pigments (lead antimonate yellow), and we also know that pigments could either be used singularly or mixed (*e.g.*, lead antimonate + iron for oranges) [3]. In this sense, Portuguese technology presents important similarities with other *maiolica* traditions of which we know much more and that represent an invaluable source of information about the materials and techniques used in the 16th and 17th centuries [1,16,17]. However, the available data seems to suggest relevant local peculiarities in Portuguese technology, such as the mixing of lead antimonate yellow and cobalt blue to obtain olive green decorations, practically unparalleled elsewhere [3]. Furthermore, previous scientific studies have focused mainly on the 17th century [3,4,11] and, more recently, on the 16th century [12,13,15], leaving the 18th-century palette, and the changes it may have suffered after the blue-and-white period, mostly unexplored.

Research aim

Against this backdrop, the present work aims to identify pigments, their variants and mixtures used to decorate Portuguese tiles before the industrial period. An assemblage of *azulejo*s from the National *Azulejo* Museum (MNAz), in Lisbon, spanning from the late 16th to the early 19th centuries was selected to chart chronological changes in the palette and address their relation with coeval European productions. The results are intended as a first step towards better understanding the technological traits of Portuguese *azulejo* manufacturers. A multi-analytical, non-invasive approach was chosen, which establishes a procedure that future studies can replicate with tiles and panels from other collections where sampling is not an option.

Materials and methods

Samples

A group of 34 glazed tiles from the National *Azulejo* Museum was studied (*Fig. S1*). These are dated between the late 16th and the early 19th centuries and show decorations made with different colours. Two Dutch tiles were included for comparison purposes (MNAz 18D and 19D). The list of the tiles, their approximate date and colour palette are detailed in Table 1.

Analytical techniques

A multi-analytical approach was used to chemically characterise the pigments responsible for the observed colours. Analyses were performed, whenever possible, avoiding the areas where two or more colours were overlaid. The white glaze was also analysed for comparison purposes. The analytical methodology was developed to be non-invasive (no samples were collected) and non-destructive (the tiles were not damaged during the analysis) [18,19]. All analyses were performed on the surface of the tiles.

µ-EDXRF was used first for qualitative chemical analysis, followed by EDXRF quantitative analyses and µ-Raman on selected tiles. Colorimetry was used to obtain the colour coordinates that allow for comparison with future analyses and to address a possible correlation between the colour shade and the chemical composition of the pigments.

µ-Raman microscopy

Raman microscopy was carried out using a Labram 300 Jobin Yvon spectrometer, equipped with a He–Ne laser of 17 mW power operating at 632.8 nm. Spectra were recorded as an extended scan. The system was calibrated using a silicon standard. The laser beam was focused either with a 50 × or a 100 × Olympus objective lens and discrete pigment crystals were targeted. The laser power at the surface of the samples was controlled with neutral density filters (optical densities 0.3 and 0.6). Raman data analysis was performed using LabSpec 5 software. All spectra are presented as acquired without any baseline correction or other treatment.

Micro-EDXRF (energy dispersive X-ray fluorescence)

Qualitative analysis by µ-EDXRF was performed at the DCR-FCT-NOVA using a Bruker ArtTAX 800 spectrometer (Intax GmbH) equipped with a molybdenum (Mo) anode and a Si(Li) Xflash® detector capable of detecting elements with $Z \geq 14$. The experimental parameters used were 40 kV and 600 µA for 360 s, under a Helium gas flux.

Energy dispersive X-ray fluorescence spectrometry

EDXRF analyses were carried out using a Bruker Tornado M4 spectrometer. The instrument is equipped with an Rh anode X-ray tube and an SDD detector. The X-ray tube uses a polycapillary lens accounting for a spot size down 25 µm at the sample. Considering the inhomogeneity of the samples, it was decided to proceed with 2D area scans of 2 × 2 mm, with a step size of 20 µm and a time per step of 20 ms. The X-ray tube operated at 50 kV and 300 µA for 180 s. Spectra acquisition was run under 20 mbar pressure. Quantitative results were obtained through the analysis of 3 areas per sample and the data was treated using the Bruker M-Quant software considering the oxides present in the tiles.

The results of the quantitative analysis of the white glaze (*Table S1*) and colours (*Table S2*) are available as supplementary files.

Colorimetry

Colorimetric measurements were performed with a Lovibond® TR520 handheld spectrophotometer with an optical geometry of 8 ° viewing angle, diffused illumination, and a measurement aperture of 4 mm. Colour coordinates were calculated using CIE Illuminant D65 and are presented under the CIE L*a*b* system. All measurements are available in the supplementary file *Table S3*.

Results and discussion

White glaze

The chemical characterisation of the white glaze was performed to address its influence on the results obtained for the colours. It also contributes to distinguishing different productions based on the glaze recipe. The results from the quantitative analysis obtained by EDXRF are presented in *Table S1*.

The white glaze in Portuguese tiles shows a characteristic tin glaze composition where SiO_2 (62–75 wt.%) and PbO (10–22 wt.%) are the main components, followed by Al_2O_3 (3.5–6.6 wt.%) and SnO_2 (2.0–7.7 wt.%).

The measured PbO/SiO_2 ratio falls between 0.2 and 0.4 for the majority of the white glazes, which is in accordance with the literature on 17th and 18th Portuguese tiles [20]. Three samples (MNAz 12, 13, and 27) are exceptions, with a PbO/SiO_2 ratio of 0.1, although no other apparent characteristics would suggest a common production.

Two samples (MNAz 30 and 31) exhibit a very similar composition and stand out for their higher PbO (21.6 and 21.2 wt.%) and SnO_2 (7.7 and 7.5 wt.%) contents (Fig. 1). These tiles, dated around

Table 1
List of samples with chronology and colour palette.

Sample	Approx. chronology										Colours							Outlines	
		1600		1650		1700		1750		1800	Blue	Purple / Brown	Turquoise green	Olive green	Yellow	Orange	Light brown	Dark brown	Blue
MNAz 01	▨										x	x			x	x		x	
MNAz 02	▨										x	x	x		x				x
MNAz 03	▨	▨									x				x	x			x
MNAz 04		▨	▨								x			x	x	x			x
MNAz 05		▨	▨								x				x	x			x
MNAz 06		▨	▨								x				x	x			x
MNAz 07		▨	▨								x	x			x			x	
MNAz 08			▨								x			x	x	x			x
MNAz 09			▨								x			x	x	x			x
MNAz 10			▨								x			x	x	x			x
MNAz 11			▨								x				x	x			x
MNAz 12				▨							x	x			x		x	x	
MNAz 13				▨							x	x						x	
MNAz 14				▨								x	x		x			x	
MNAz 15				▨							x	x						x	
MNAz 16				▨							x	x	x		x			x	
MNAz 17				▨								x	x		x			x	
MNAz 18D						▨	▨				x								x
MNAz 19D						▨	▨					x						x	
MNAz 20								▨			x	x		x	x		x	x	x
MNAz 21								▨			x								x
MNAz 22								▨			x	x		x	x			x	
MNAz 23								▨	▨		x	x						x	x
MNAz 24								▨	▨			x			x			x	
MNAz 25									▨			x		x	x		x	x	
MNAz 26									▨			x		x	x			x	
MNAz 27									▨			x		x	x			x	
MNAz 28									▨		x	x		x	x			x	
MNAz 29									▨		x			x					
MNAz 30									▨	▨	x	x		x	x			x	
MNAz 31									▨	▨	x	x			x			x	x
MNAz 32									▨	▨	x	x		x	x			x	x
MNAz 33										▨	x	x		x	x			x	
MNAz 34										▨	x	x		x	x			x	

the turn of the 19th century, possibly belong to the same workshop. Sample MNAz 15 also stands out for its higher PbO content (21.1 wt.%), although its SnO_2 content is the lowest one measured (2.0 wt.%).

The results obtained for the two Dutch tiles (MNAz 18D and 19D) suggest a different tin glaze recipe with higher PbO and SnO_2 contents (18–19 wt.% and 10 wt.%, respectively), and lower Al_2O_3 (2 wt.%) and TiO_2 (< 0.1 wt.%) contents than the Portuguese samples. Manganese contents are also higher (0.11 and 0.12 wt.%). This composition is compatible with Dutch tin glaze tiles from the last quarter of the 17th century [21].

Blue

The blue colour comes from cobalt in all samples. Cobalt was identified by μ-EDXRF along with iron (Fe), nickel (Ni), and arsenic (As), as expected for the chronological timeframe of the tiles [3,6,22,23]. These elements, however, show different peak intensi-

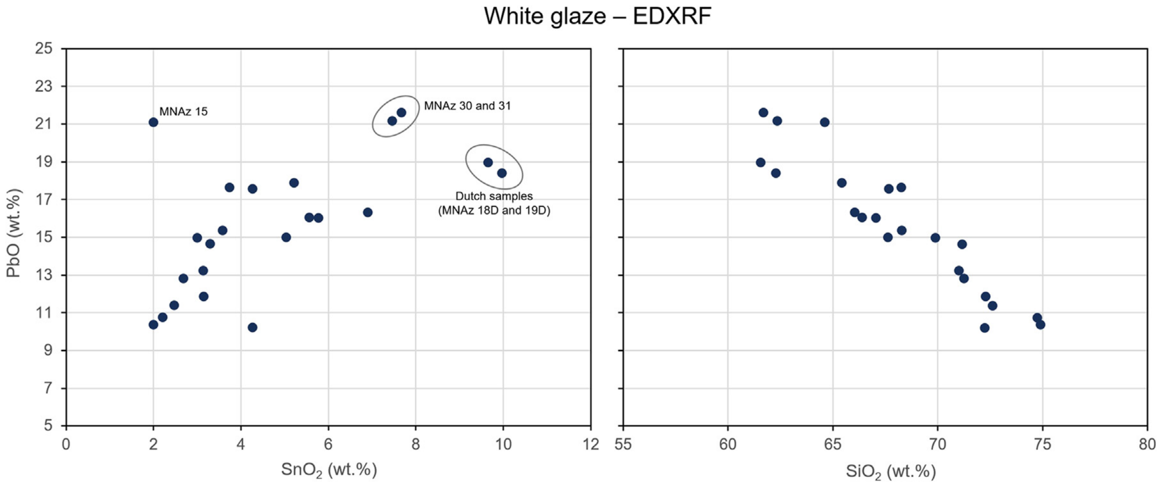


Fig. 1. Plot of SnO_2 vs. PbO and SiO_2 vs. PbO, in wt.%, obtained by EDXRF.

ties in the µ-EDXRF spectra, and can be divided into three groups of tiles:

- a group with Co as the most intense peak, suggesting the use of a purer pigment (MNAz 02, 03, 05, 08, 21, 29, and 32);
- a group with Fe stronger than Co (MNAz 04, 06, 09, 10, 11, 18D, 28, 31, and 34), which includes a sub-group exhibiting strong peaks of Zn (MNAz 04, 06, 09, 10, and 11);
- and a third composition, richer in Ni, identified in samples MNAz 15, 23, 30, and 32.

Iron is always identified in the white glaze and, therefore, its quantification on blue decorations usually reflects both its content in the cobalt blue pigment and the white glaze beneath it. In the tiles with the Zn-containing blue, the white glaze also exhibits elevated peaks of the same element. Therefore, the only compositional difference that can be securely separated is the Ni-rich one of samples MNAz 15, 23, 30, and 32.

EDXRF quantitative analyses (*Table S2*) showed a concentration of cobalt oxide (CoO) varying from 0.16 wt% to 2.20 wt.% in most samples, except in two where it was considerably higher (4.34 wt.% in MNAz 01 and 6.56 wt% in MNAz 03). The concentration of Co reflects the amount of pigment used in a specific-coloured area.

Beyond the previously mentioned Fe-Co-Ni-As association identified by µ-EDXRF, also bismuth (Bi) was detected by EDXRF in most blue glazes. The presence of a Co-Fe-Ni-As(-Bi) association suggests the use of a cobalt-based pigment from the Erzgebirge region in Germany [22,24]. Here, since (at least) the beginning of the 15th century, silver, copper, and lead were extracted, and an unrefined cobalt-bearing slag was obtained and exported to the rest of Europe. Usually, chloanthite ($(Ni,Co)As_3$) and safflorite ($(Co,Fe)As_2$) are mentioned as the main ores used to make this blue pigment, also known as *zaffre* [25]. There is documented evidence of Portuguese trade of *zaffre* from Germany, dating from the beginning of the 16th century [6]. Other possible sources of the pigment could be considered, such as a well-documented site of cobalt production in Teruel, Spain, although there is no known evidence of the use of Spanish cobalt in Portuguese tiles in the 17th and 18th centuries [26].

The blue pigment of the Dutch sample (MNAz 18 D) does not stand out from the Portuguese ones, which is consistent with both regions using the same cobalt source. Furthermore, the purchase and commercialisation of different qualities of German zaffre by the Dutch potters is well documented [27].

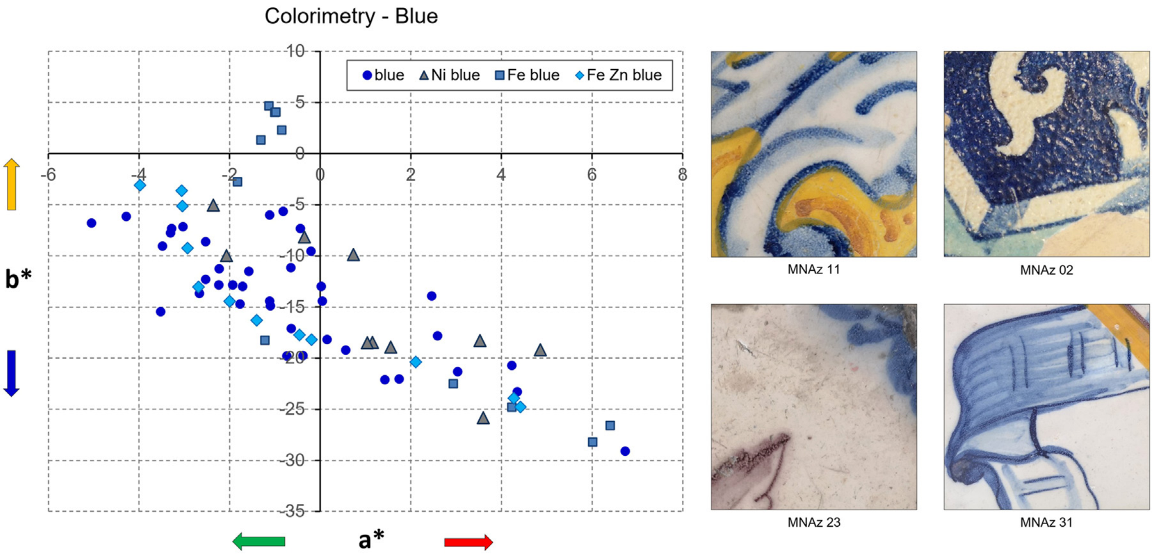
Differences in the chemical composition of the cobalt source would have influenced the final shade observed in the tiles, as previously argued for Ni-rich cobalt blue decorations, which exhibit a greyer shade [3,6]. However, as Fig. 2 illustrates, the results obtained with colorimetric analysis do not show a correlation between the chemical composition and the colour coordinates measured on our samples. Instead, differences in the blue shade seem more dependent on the pigment concentration, with a less concentrated pigment meaning higher transparency and the subsequent higher influence of the white glaze underneath.

Because the cobalt pigment is generally dissolved in the glaze matrix, its identification with µ-Raman spectroscopy is problematic. However, spectra from two tiles (MNAz 08 and MNAz 21) show bands consistent with spinel (AB_2O_4) and olivine (M_2SiO_4) structures simultaneously (Fig. 3). According to the literature, the bands at 478–480 cm^{-1} and 698–700 cm^{-1} may be assigned either to a cobalt ferrite ($CoFe_2O_4$) or a nickel ferrite ($NiFe_2O_4$), whereas the doublet at 817–819 cm^{-1} and 842–846 cm^{-1} is characteristic of Co-Ni-olivines [28–30]. Both structures have been previously identified by µ-Raman in cobalt pigment particles in glazed tiles [3,31] and they suggest an incomplete transformation of the pigment during the firing of the glaze.

Purple / brown

EDXRF data shows that manganese is responsible for the purple decorations and the dark brown outlines of the tiles analysed, with concentrations varying between 1.4 wt% and 14.5 wt% MnO in the first and 7–44 wt.% MnO in the latter (*Table S2*). Either a manganese ore or manganese-rich compound was therefore employed as a pigment. Manganese ores are commonly found in Portugal and it is likely that local sources were used to obtain this pigment [32]. In a glassy matrix such as that of glass and glazes, manganese may occur as Mn^{3+}, producing a purple colour [33]. Relatively high iron and barium peaks were also detected in most of the samples, particularly when manganese is higher, suggesting that these three elements are associated with the raw material used to obtain the pigment. This is consistent with previous studies characterising manganese pigment in *azulejos* [3,11,13,34,35].

Considering the quantification analysis, a small group of samples stand out for their higher MnO/Fe_2O_3 ratio, suggesting the use of a purer pigment with less iron in its composition. These are a 16th-century sample (MNAz 01), three late 18th to early 19th-century samples (MNAz 26, 30, and 31), and a Dutch tile (MNAz 19D). Colorimetric measurements have higher a* values, although no obvious distinction is visible (Fig. 4).



MNAz 11

MNAz 02

MNAz 23

MNAz 31

Fig. 2. Plot of a* vs. b* coordinates obtained for blue decorations (CIE L*a*b*). Blue: MNAz 01–03, 05, 07, 08, 12, 13, 16, 20–22, 29, 30, 33. Ni blue: MNAz 15, 23, 32. Fe blue: MNAz 18D, 28, 31, 34. Fe-Zn blue: MNAz 04, 06, 09–11.

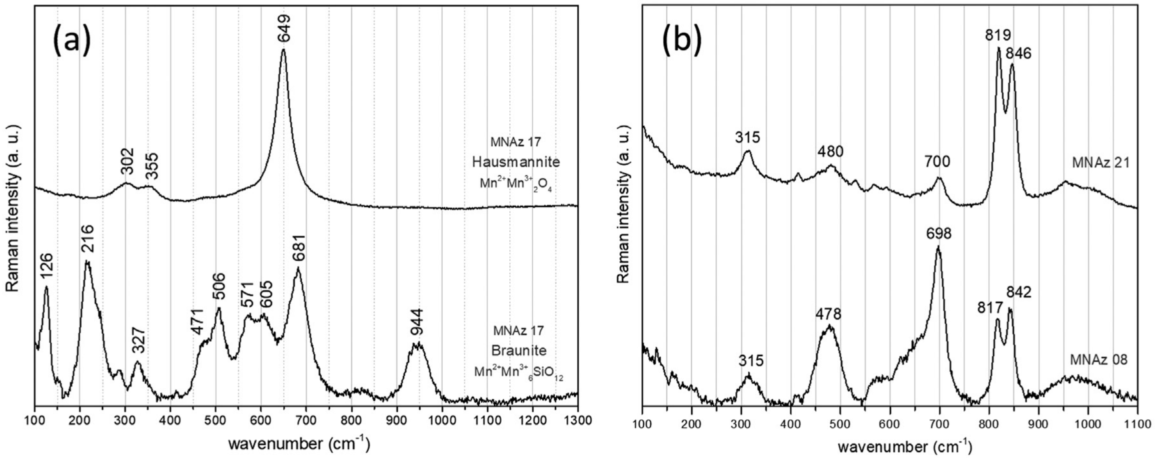


Fig. 3. µ-Raman spectra of: (a) hausmannite and braunite in the purple decoration of MNAz 17; (b) Ni-Co olivine (doublet at 817–819 cm^{-1} and 842–846 cm^{-1}) and Co-Ni ferrite (bands at 478–480 cm^{-1} and 698–700 cm^{-1}) in blue decorations of MNAz 08 and MNAz 21.

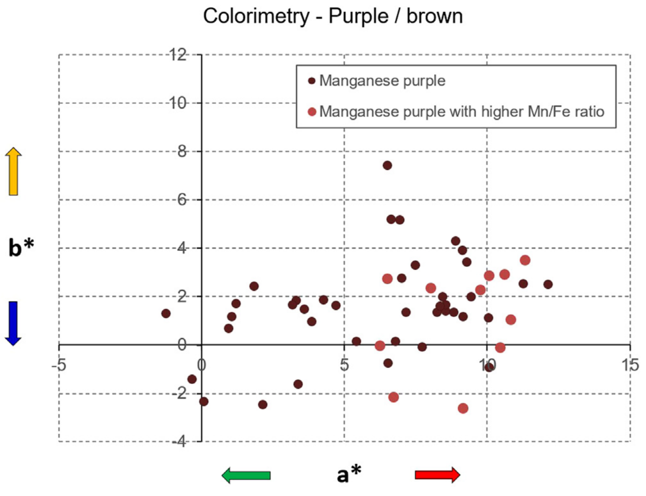


Fig. 4. Plot of a* vs. b* coordinates obtained for purple/brown decorations (CIE L*a*b*). Manganese purple: MNAz 19, 26, 30, 31. Manganese purple with higher Mn/Fe ratio: MNAz 01–03, 12–15, 17, 20, 22- 25, 27, 28, 33, 34.

Raman data (Fig. 3) allowed the identification of braunite ($(Mn^{2+},Mn^{3+})_6O_8SiO_4$) and hausmannite ($Mn^{2+}Mn^{3+}{}_2O_4$), both manganese compounds that can result from firing pyrolusite (MnO_2), a common manganese ore [31,36].

Yellow

The presence of Sb in every XRF analysis (*Table S2*) and the characteristic pyrochlore ($Pb_2Sb_2O_7$) spectrum identified by µ-Raman (Fig. 5) indicate that yellow colours are obtained with the lead antimonate pigment Naples yellow.

Most yellows analysed (samples MNAz 04–06, and 14) appear to be a modified version of the pigment characterised by the addition of zinc, as shown by a strong Zn peak in µ-EDXRF spectra, which is absent in the corresponding white glaze (Fig. 6). The tiles MNAz 09, 10 and 11, however, also exhibit an intense Zn peak in the white glaze, as well as in the blue and green decorations.

When looking at the quantification results in *Table S2*, a group of tiles shows a ZnO content between 1.2 and 4.7 wt.% (samples MNAz 01, 03, 08, and 12). In the others zinc is below 0.15 wt.% and, therefore, it is likely not something intentionally added. All samples where Zn is clearly added to the pigment recipe are restricted

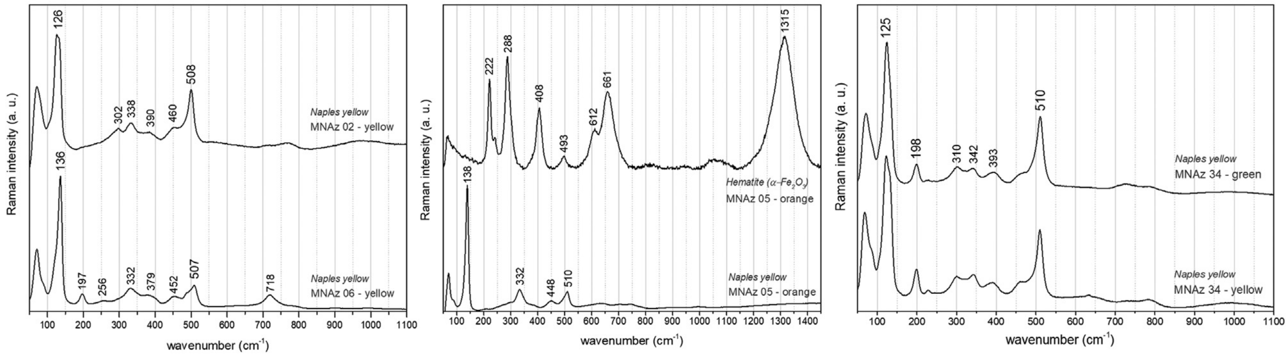


Fig. 5. μ-Raman spectra of the Naples Yellow pigment in tiles MNAz 02 (yellow), MNAz 05 (orange) MNAz 06 (yellow), and MNAz 34 (yellow and green), and μ-Raman spectrum of hematite in MNAz 05 (orange).

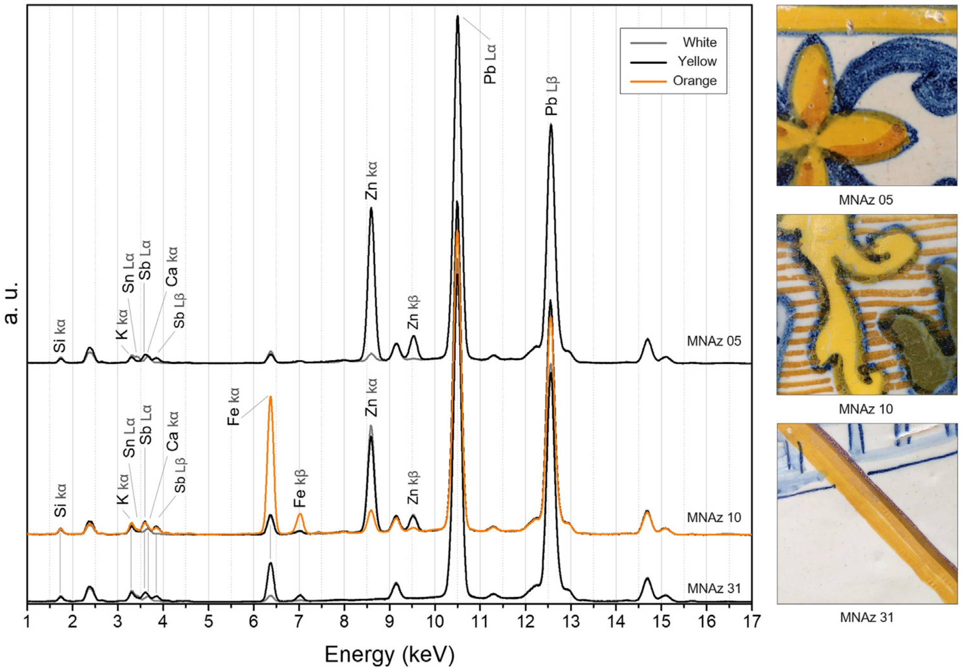


Fig. 6. μ-EDXRF spectra of yellow and orange decorations.

to the 16th and 17th centuries, suggesting that its use might have been abandoned in the 18th century.

Since the identification in 1998 of a Pb-Sb-Sn Naples Yellow variant by Roy and Berrie, the use of this modified version of lead antimonate yellow has been confirmed by several studies in different types of artworks [37–40]. On the other hand, the identification of the Pb-Sb-Zn variant is not nearly as common, with most cases coming from Spanish and Portuguese tiles of the 16th and 17th centuries [3,34,41], as well as in a few Italian maiolica pieces [38,40,42]. More recently, a number of experimental replications carried out by Veronesi et al. (2023) [43] have shown that the identification of the Pb-Sb-Sn ternary pigment variant in lead-tin glazes is extremely problematic, due to the high level of glaze-pigment interaction. Thus, the presence of tin in all yellows analysed here does not necessarily imply that the painter used a Sn-modified Naples yellow pigment. Furthermore, tin was quantified between 2.2 wt.% and 8.6 wt.% (see *Table S2*), but it appears to be higher in samples where the white glaze too shows higher values. The thickness of the pigment layer, its composition, and its reaction with the underlying lead-tin glaze, are all factors affecting the final quantification results of surface analysis.

Lead antimonate was identified by μ-Raman through the characteristics bands of its pyrochlore structure ($Pb_2Sb_2O_7$). These are the bands between 120 and 140 cm^{-1} assigned to the Pb–O stretching mode; the bands in the 200–400 cm^{-1} range associated both to Pb-O and Sb-O modes; and the strong band at 506–516cm^{-1}, corresponding to the Sb–O stretching mode of the SbO_6 octahedra (Fig. 5). The spectra of dark to orange yellows are characterised by signs of a modified pyrochlore structure. These originates a shift of the band at 124–126 cm^{-1} towards values above 130 cm^{-1}, the collapse of the band at around 510 cm^{-1}, and the appearance of a shoulder at around 450 cm^{-1} [38,39].

The plot in Fig. 7 shows the colour coordinates measured in the yellows and oranges. The yellows with Zn are sensibly darker, exhibiting mostly higher a* and b* values. Orange stands out for even higher a* values, closer to red. Zinc seems to influence the yellow colour towards an orange shade, as has been demonstrated by Veronesi et al. [43].

Orange

μ-EDXRF results of the orange decorations show that the spectra are very similar to those of the yellows discussed above, confirming that this colour orange was also achieved by using Naples yellow as a base (Fig. 6). But unlike yellows, oranges show a very intense iron peak, a clear indication that the pigment is in-

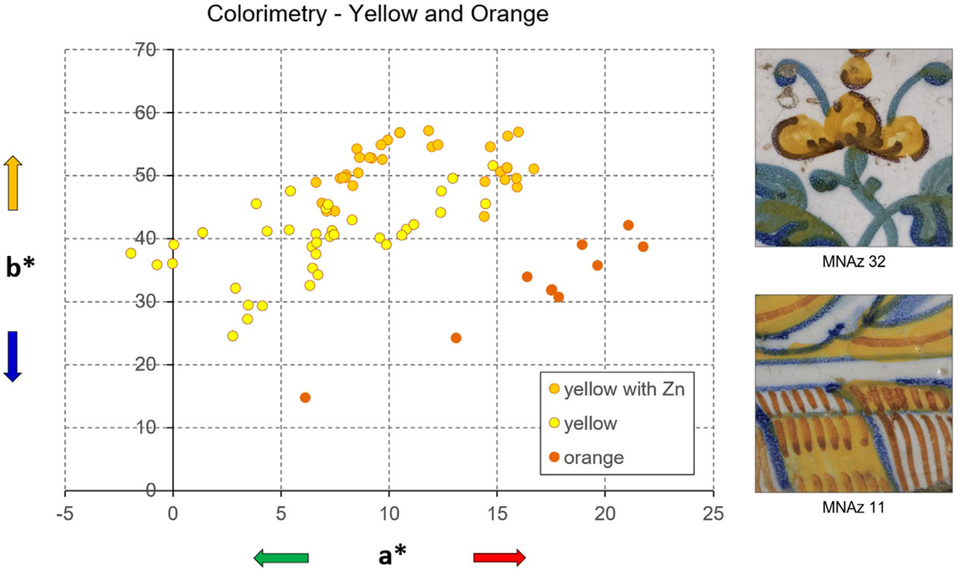


Fig. 7. Plot of a* vs. b* coordinates obtained for yellow and orange decorations (CIE L*a*b*). Yellow with Zn: MNAz 01, 03–07, 09–12, 14. Yellow: MNAz 02, 16, 17, 22, 24, 27, 28, 30–34. Orange: MNAz 05, 06, 09, 11.

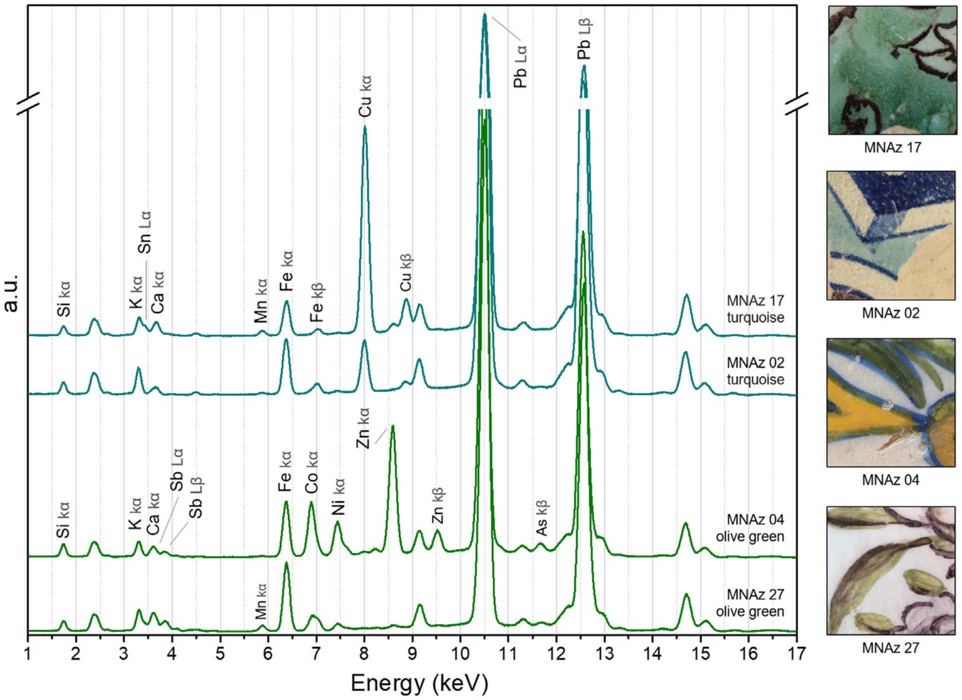


Fig. 8. μ-EDXRF spectra of green decorations.

deed a mixture of lead antimonate yellow and iron oxide. This result is confirmed by the identification of both Naples yellow and hematite by μ-Raman in the orange areas (Fig. 5) and agrees with the previously published literature on Portuguese azulejos [3,4,13,34,35,44].

When it was possible to analyse both orange and yellow from the same tile (MNAz 06, MNAz 10, and MNAz 11), it was noted that the former has a very weak Zn peak, contrasting with the high Zn present in the latter (Fig. 6). This suggests that, while both colours are made from a lead antimonate base, different recipes are used, the most relevant difference being the absence of zinc in orange pigments indicating the use of a simple Naples yellow.

Green

The green colour displays visibly distinct shades among the tiles: turquoise green (MNAz 02, 14, 16, and 17) and olive green (MNAz 04, 08–10, 20, 22, 25–30, and 32–34). The latter was identified as a mixture of yellow and blue pigments, whereas the first was obtained with copper oxide dissolved in the glaze.

The characteristic elements of yellow (Sb and sometimes Zn) and blue (Co) pigments were identified with μ-EDXRF in all olive greens (Fig. 8). μ-Raman spectra too are consistent with a lead antimonate pigment (Fig. 5). Both qualitative and quantitative EDXRF analyses also showed that, when zinc is present in higher amounts, the same is true for the yellow decoration of the same tiles. There-

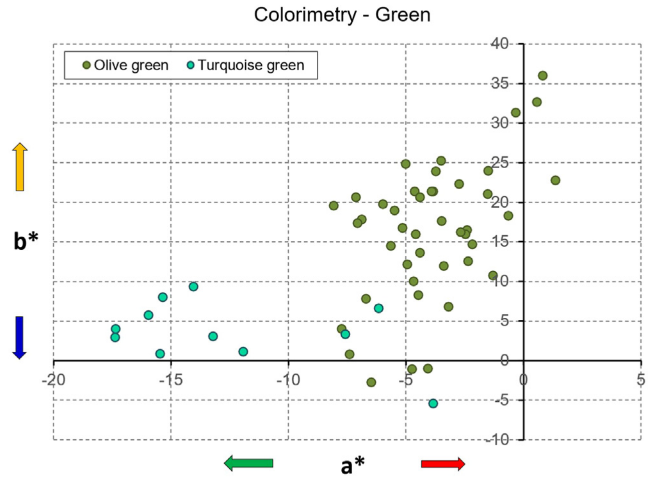


Fig. 9. Plot of a* vs. b* coordinates obtained for green decorations (CIE L*a*b*). Olive green: MNAz 04, 08–10, 20, 22, 25–30, 32–24. Turquoise green: MNAz 02, 14, 16, 17.

fore, contrary to what seems to happen in oranges where Zn was not part of the recipe, olive green decorations are obtained by mixing cobalt blue with the very same pigment used for the yellow.

Mixing yellow with cobalt blue rather than copper green seems to have been the most common choice among Portuguese tile painters to obtain olive green. Perhaps this is because copper tends to spread more in the glaze and the final result is therefore more difficult to control. However, copper is by far the most commonly used green pigment in contemporary maiolica/faience productions, either alone [41,45,46] or mixed with Naples yellow [46]. Both solutions are described in Cipriano Piccolpasso's 16th-century treatise on *maiolica*, where the mixture of cobalt blue and yellow identified here is not mentioned [16]. Equally, the latter is practically non-existent in contemporary European productions, although it has been identified in an 18th-century Italian *maiolica* plate [45] and on early 19th-century French faience [47].

Colorimetric results in Fig. 9 reveal two groups mostly consistent with the two chemical compositions: turquoise green with lower a* and b* values than olive green. Samples MNAz 28 and 32 are exceptions because, despite being a mixture of yellow and blue pigments, show measurements with lower b* coordinates than the other olive greens. Both samples are dated from the 18th-19th centuries and reveal that a wider palette of green hues was used at this time than in the 17th century.

Conclusions

During the two-and-a-half centuries of *azulejo* production studied in this work, tile painters appear to have used the same base pigments, namely cobalt blue, copper green, manganese purple/brown, and Naples yellow. These were mixed among themselves or with other compounds such as zinc or iron oxides to extend the colour palette. Adding to this, painters also took artistic liberties in overlapping colour layers, using very diluted pigments as background for decorations or very concentrated ones for shadows and outlines. Therefore, the results of the chemical and colorimetric analyses are always influenced by the concentration of the pigment in the glaze, its layer thickness and the overlapping of colours.

Cobalt blue exhibits a Fe-Co-Ni-As chemical association throughout the timeframe of this study, consistent with the literature mentioning the cobalt mines in Saxony as the likely source of this pigment. While different shades of cobalt blue are visible, a deeper study is necessary to address a correlation between the measured colour coordinates and the chemical composition. Manganese purple also displays a consistent chemical composition in most tiles, except in those where a purer pigment with less iron was used, suggesting a change in the late 18th century, when other manganese compounds became available to *azulejo* painters. Copper green, although one of the most important colourants in ceramics, seems to have been less used in Portugal and mainly restricted to turquoise decorations, while olive greens were obtained by adding cobalt blue to a lead antimonate yellow base (Naples yellow). Lead antimonate was also the base pigment for yellow and orange decorations. Our study reveals a predominance of a zinc-modified Naples yellow in the 17th century, which was replaced by its unmodified, binary Pb-Sb form in the 18th century. Both were mixed with cobalt blue to obtain an olive green colour, although the latter exhibited a higher variety of shades in the 18th and early 19th centuries than in the 17th century. Finally, orange seems to have been obtained by adding iron oxide (identified as hematite) to an unmodified Naples yellow base. Using a non-invasive methodology, the authors were able to increase the knowledge on the colour palette of *azulejos* up to the early 19th century. These results will serve as an important basis for comparison with future and ongoing studies on other *azulejo* collections.

Funding

Funding has been provided by the Fundacão para a Ciência e a Tecnologia (FCT). This work is the result of the projects "ChromAz: the Chromatic Journey of the Portuguese Azulejo" (https://doi.org/10.54499/PTDC/HAR-HIS/1899/2020), White Glazes (https://doi.org/10.54499/CEECIND/00882/2017/CP1462/CT0020), and LumiGLAD (https://doi.org/10.54499/2020.00252.CEECIND/CP1586/CT0002). The work was carried out at the VICARTE Research Unit (https://doi.org/10.54499/UIDB/00729/2020 and https://doi.org/10.54499/UIDP/00729/2020), the Associated Laboratory for Green Chemistry – Clean Technologies and Processes (LA/P/0008/2020) and LIBPhys-UNL Research Unit (https://doi.org/10.54499/UIDB/04559/2020 and https://doi.org/10.54499/UIDP/04559/2020).

Acknowledgements

The authors would like to express their gratitude to Dr Graça Silva from the National Azulejo Museum for the help with the selection of samples for this study. They are also grateful to the anonymous reviewers whose suggestions contributed to an improved final version of this work.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.culher.2024.01.011.

References

[1] M.S. Tite, The production technology of Italian maiolica: a reassessment, J. Archaeol. Sci. 36 (2009) 2065–2080, doi:10.1016/j.jas.2009.07.006.
[2] A. Pais, M.da C. Reis, J. Campelo, J.M. Mimoso, M.Â. Silva, The beginning of the production of majolica azulejos in Portugal - João and Filipe de Góis in 16th century Lisbon, in: J.M. Mimoso, A.N. Pais, J. Delgado Rodrigues, S.R.M. Pereira (Eds.), Orig. Majolica Azulejos Prod. Port, 1st ed., LNEC - Laboratório Nacional de Engenharia Civil, Lisbon, 2019, pp. 1–24.
[3] S. Coentro, J.M. Mimoso, A.M. Lima, A.S. Silva, A.N. Pais, V.S.F. Muralha, Multi-analytical identification of pigments and pigment mixtures used in 17th century Portuguese azulejos, J. Eur. Ceram. Soc. 32 (2012) 37–48, doi:10.1016/j.jeurceramsoc.2011.07.021.
[4] M. Pereira, T. de Lacerda-Arôso, M.J.M. Gomes, A. Mata, L.C. Alves, P. Colomban, Ancient Portuguese ceramic wall tiles ("azulejos"): characterization of the glaze and ceramic pigments, J. Nano Res. 8 (2009) 79–88, doi:10.4028/www.scientific.net/JNanoR.8.79.
[5] M.L.M.L.E Brito, Estudo Do Fabrico e da Degradação de Azulejos Portugueses Históricos, Estudo do Fabrico e da Degradação de Azulejos Portugueses Históricos, Universidade de Évora, 2016.

[6] M. Fares, J.M. Mimoso, A. Pais, I.M. Martins, S.X. Coentro, S.R.M. Pereira, V.S.F. Muralha, Azulejo blues – an analytical study of the blue colours in Portuguese azulejos, (2012). doi:10.13140/2.1.2871.2647.

[7] S. Almeida, Caracterização Material e Conservação e Restauro De Um Painel De Azulejos Do Séc, XVII do Ecomuseu do Seixal, Portugal, Dissertação para obtenção do Grau de Mestre em Conservação e Restauro - Especialização em Cerâmica e Vidro, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa, 2011.

[8] J. Coroado, C. Gomes, Physical and chemical characterisation of ceramic wall tiles, dated to the 17th century, from the "Convento de Cristo, in: Tomar, Portugal, Trab. Arqueol. 42 Underst. People Their Pottery Proc. 7th Eur. Meet. Anc. Ceram. EMAC03, 2003, pp. 33–39.

[9] A. Guilherme, Spectroscopic Techniques for Characterizing Portuguese Glazed Ceramics: A Contribution to the Study of Ancient Faiences of Coimbra, Faculdade de Ciências da Universidade de Lisboa, 2013 PhD Thesis - Physics.

[10] A. Guilherme, G. Buzanich, M. Radtke, U. Reinholz, J. Coroado, J.M.F. Dos Santos, M.L. Carvalho, Synchrotron micro-XRF with Compound Refractive Lenses (CRLs) for tracing key elements on Portuguese glazed ceramics, J. Anal. At. Spectrom. 27 (2012) 966, doi:10.1039/c2ja30030c.

[11] A. Guilherme, J. Coroado, J.M.F. dos Santos, L. Lühl, T. Wolff, B. Kanngießer, M.L. Carvalho, X-ray fluorescence (conventional and 3D) and scanning electron microscopy for the investigation of Portuguese polychrome glazed ceramics: advances in the knowledge of the manufacturing techniques, Spectrochim. Acta Part B At. Spectrosc. 66 (2011) 297–307, doi:10.1016/j.sab.2011.02.007.

[12] J.M. Mimoso, S.R.M. Pereira, A.N. Pais, M.A. Antunes, A.M. Cardoso, M. de L. Esteves, A. Candeias, A technical comparison of three renaissance azulejo panels from the workshops of Lisbon, in: Stud. Herit. Glazed Ceram. No 1, LNEC, Lisboa, 2019, pp. 113–132.

[13] J.M. Mimoso, A.N. Pais, M. Ferreira, M. de L. Esteves, S.R.M. Pereira, M.A. Antunes, R. Valona, A.M. Cardoso, A. Candeias, Instrumental study of the 16th century azulejo panel decorating a public fountain in Alcácer do Sal - Portugal, in: Stud. Herit. Glazed Ceram. No 2, LNEC, Lisboa, 2019, pp. 19–34.

[14] A.N. Pais, J.M. Mimoso, Pe.R. Rosmaninho, L. Esteves, S.R.M. Pereira, M.A. Antunes, A.M. Cardoso, J. Mirão, Study of a finding of 16th century azulejo panels at the Cathedral of Setúbal in Portugal, in: Stud. Herit. Glazed Ceram. No 2, LNEC, Lisboa, 2019, pp. 1–18.

[15] A. Pais, M.J. Sequeira, M. de J. Monge, M. de L. Esteves, I. Castanheira, A. Valongo, C. Manso, V. Filipe, A.M. Cardoso, J.M. Mimoso, 16th century azulejos - what lies beneath the ground of Lisbon? in: GlazeArt 2018 - Int. Conf. Glazed Ceram. Cult. Herit., LNEC - Laboratório Nacional de Engenharia Civil, Lisbon, 2018, pp. 298–312.

[16] C. Piccolpasso, The Three Books of the Potter's art : a Facsimile of the Manuscript in the Victoria and Albert Museum, Scholar Press, LondonLondon, 1980.

[17] C. Viti, I. Borgia, B. Brunetti, A. Sgamellotti, M. Mellini, Microtexture and microchemistry of glaze and pigments in Italian Renaissance pottery from Gubbio and Deruta, J. Cult. Herit. 4 (2003) 199–210, doi:10.1016/S1296-2074(03)00046-3.

[18] T. Calligaro, J.-C. Dran, J. SalomonK. Janssens, R. Van Grieken (Eds.), Ion beam microanalysis, Non-Destr. Micro Anal. Cult. Herit. Mater. (2004) 227–276.

[19] D. Barceló, Series Editor's Preface, in: K. Janssens, R.Van Grieken (Eds.), Non-Destr. Micro Anal. Cult. Herit. Mater., Elsevier, The Netherlands, 2004 pp. xxv–xxvi.

[20] S.R.M. Pereira, G. Conte, L. Esteves, A.N. Pais, J.M. Mimoso, Evolution of azulejo glaze technology in Portugal from the 16th to the onset of the 19th century, J. Eur. Ceram. Soc. 43 (2023) 3804–3815, doi:10.1016/j.jeurceramsoc.2023.01.038.

[21] K. van Lookeren Campagne, Understanding Dutch tin-Glazed Tiles (1600-1750) Through the Interpretation of texts, Analysis and Recipe Reconstruction, University of Amsterdam, 2022 PhD Thesis.

[22] B. Gratuze, I. Soulier, M. Blet-Lemarquand, L. Vallauri, De l'origine du cobalt : du verre à la céramique, ArchéoSciences Rev. Archéom. 20 (1996) 77–94, doi:10.3406/arsci.1996.939.

[23] P. Colomban, B. Kırmızı, G. Simsek Franci, Cobalt and associated impurities in blue (and green) glass, glaze and enamel: relationships between raw materials, processing, composition, phases and international trade, Minerals 11 (2021) 633, doi:10.3390/min11060633.

[24] Z. Zlámalová Cílová, M. Gelnar, S. Randáková, Smalt production in the Ore Mountains: characterization of samples related to the production of blue pigment in Bohemia, Archaeometry 62 (2020) 1202–1215, doi:10.1111/arcm.12584.

[25] M. Fares, The Blue in Portuguese Historical Azulejos, University of Bologna, 2012 MSc Thesis.

[26] C. Roldán, J. Coll, J. Ferrero, EDXRF analysis of blue pigments used in Valencian ceramics from the 14th century to modern times, J. Cult. Herit. 7 (2006) 134–138, doi:10.1016/j.culher.2006.02.003.

[27] J.M. Mimoso, Origin, early history and technology of the blue pigment in azulejos, in: Proc. Int. Conf. Glazed Ceram. Archit. Herit., LNEC - Laboratório Nacional de Engenharia Civil, Lisbon, 2015, pp. 357–375.

[28] R.B. Kamble, V. Varade, K.P. Ramesh, V. Prasad, Domain size correlated magnetic properties and electrical impedance of size dependent nickel ferrite nanoparticles, AIP Adv. 5 (2015) 017119, doi:10.1063/1.4906101.

[29] P. Chandramohan, M.P. Srinivasan, S. Velmurugan, S.V. Narasimhan, Cation distribution and particle size effect on Raman spectrum of CoFe2O4, J. Solid State Chem. 184 (2011) 89–96, doi:10.1016/j.jssc.2010.10.019.

[30] T. Mouri, M. Enami, Raman spectroscopic study of olivine-group minerals, J. Mineral. Petrol. Sci. 103 (2008) 100–104, doi:10.2465/jmps.071015.

[31] S. Coentro, R.C. da Silva, C. Relvas, T. Ferreira, J. Mirão, A. Pleguezuelo, R. Trindade, V.S.F. Muralha, Mineralogical characterization of hispano-moresque glazes: a μ-Raman and scanning electron microscopy with X-ray energy dispersive spectrometry (SEM-EDS) study, Microsc. Microanal. 24 (2018) 300–309, doi:10.1017/S1431927618000338.

[32] R. Salema de Carvalho, A Pintura Do Azulejo Em Portugal [1675-1725]. Autorias e biografias - um novo paradigma., Doutoramento em História - Ramo De História da Arte, Faculdade de Letras da Univseridade de Lisboa, 2012.

[33] J.M.F. Navarro, El Vidrio, Editorial, CSIC, Madrid, 2003.

[34] E. Figueiredo, L. Esteves, A.N. Pais, M. Vilarigues, S. Coentro, As cores na azulejaria portuguesa: uma revisão, Conserv. Património (2023), doi:10.14568/cp27252.

[35] M.L. Coutinho, J.P. Veiga, L.C. Alves, J. Mirão, L. Dias, A.M. Lima, V.S. Muralha, M.F. Macedo, Characterization of the glaze and in-glaze pigments of the nineteenth-century relief tiles from the Pena National Palace, Sintra, Portugal, Appl. Phys. A 122 (2016) 696, doi:10.1007/s00339-016-0214-5.

[36] J. Molera, J. Coll, A. Labrador, T. Pradell, Manganese brown decorations in 10th to 18th century Spanish tin glazed ceramics, Appl. Clay Sci. 82 (2013) 86–90, doi:10.1016/j.clay.2013.05.018.

[37] J. Dik, E. Hermens, R. Peschar, H. Schenk, Early production recipes for lead antimonate yellow in Italian art*, Archaeometry 47 (2005) 593–607, doi:10.1111/j.1475-4754.2005.00221.x.

[38] F. Rosi, V. Manuali, T. Grygar, P. Bezdicka, B.G. Brunetti, A. Sgamellotti, L. Burgio, C. Seccaroni, C. Miliani, Raman scattering features of lead pyroantimonate compounds: implication for the non-invasive identification of yellow pigments on ancient ceramics. Part II. In situ characterisation of Renaissance plates by portable micro-Raman and XRF studies, J. Raman Spectrosc. 42 (2011) 407–414, doi:10.1002/jrs.2699.

[39] F. Rosi, V. Manuali, C. Miliani, B.G. Brunetti, A. Sgamellotti, T. Grygar, D. Hradil, Raman scattering features of lead pyroantimonate compounds. Part I: XRD and Raman characterization of $\mathrm{Pb}_2\mathrm{Sb}_2\mathrm{O}_7$ doped with tin and zinc: Raman scattering features of lead pyroantimonate compounds, J. Raman Spectrosc. 40 (2009) 107–111, doi:10.1002/jrs.2092.

[40] L. Cartechini, F. Rosi, C. Miliani, F. D'Acapito, B.G. Brunetti, A. Sgamellotti, Modified Naples yellow in Renaissance majolica: study of Pb–Sb–Zn and Pb–Sb–Fe ternary pyroantimonates by X-ray absorption spectroscopy, J. Anal. At. Spectrom. 26 (2011) 2500, doi:10.1039/c1ja10190k.

[41] A.G. Gómez Morón, Á.J. Polvorinos del Río, J. Castaing, A. Pleguezuelo, Ceramics by Niculoso Pisano and quantitative analysis of glazes using portable XRF, Ph. Investig. (2016) 1–23.

[42] E. Buzzegoli, R. Cardaropoli, D. Kunzelman, P. Moioli, L. Montalbano, M. Piccolo, C. Seccaroni, Valerio Mariani Da Pesaro, IL Trattato "Della Miniatura": Primi Raffronti Con Le Analisi E Le Opere, OPD Restauro (2000) 248–206.

[43] U. Veronesi, M. Bandiera, M. Manso, A. Ruivo, M. Vilarigues, S. Coentro, Naples yellow: Experimental re-working of historical recipes and the influence of the glazing process in the in situ analysis of historical artwork, Bol. Soc. Esp. Cerámica Vidr. 62 (6) (2023) 558–570, doi:10.1016/j.bsecv.2023.01.006.

[44] S.A.B. Lins, M. Manso, P.A.B. Lins, A. Brunetti, A. Sodo, G.E. Gigante, A. Fabbri, P. Branchini, L. Tortora, S. Ridolfi, Modular MA-XRF scanner development in the multi-analytical characterisation of a 17th century azulejo from Portugal, Sensors 21 (2021) 1913, doi:10.3390/s21051913.

[45] C. Meucci, L. Carratoni, Identification of the majolica polychromatic decoration by IRFC methodology, J. Archaeol. Sci. Rep. 8 (2016) 224–234, doi:10.1016/j.jasrep.2016.06.027.

[46] G. Padeletti, G.M. Ingo, A. Bouquillon, S. Pages-Camagna, M. Aucouturier, S. Roehrs, P. Fermo, First-time observation of Mastro Giorgio masterpieces by means of non-destructive techniques, Appl. Phys. A 83 (2006) 475–483, doi:10.1007/s00339-006-3549-5.

[47] M. Maggetti, Ch. Neururer, J. Rosen, Antimonate opaque glaze colours from the faience manufacture of le bois d'épense (19th century, northeastern France)*, Archaeometry 51 (2009) 791–807, doi:10.1111/j.1475-4754.2008.00442.x.