Tin-glazed ceramics production and trade in Italy and Spain through multi-technique archaeometric investigation

Diletta Paghi
Department of Earth Sciences, University of Firenze, Via G. La Pira 4, 50121 Firenze
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INTRODUCTION

Tin-glazed ceramic is a significant legacy of medieval and Renaissance society, reflecting the societal and cultural values and illustrating changes in art, fashion, and the economy. This type of ceramic was highly valued in Europe and quickly became one of the most traded goods in the Mediterranean region. Over the past few decades, several Italian production centres have been the subject of archaeometric research (see, for example, Tite, 2009, and references therein). These studies have offered a broad overview of the types of ceramics, their production methods, and raw materials used in Italy. Nevertheless, our understanding of how production methods developed, how materials and technological knowledge were exchanged among various centres in the western Mediterranean, and the unique local characteristics remains limited. In this framework, the present study employs a multi-technique archaeometric approach to strengthen our understanding of the cultural and commercial exchanges that contributed to the origins and development of tin glazing techniques in key production centres in Italy (Pisa and Montelupo Fiorentino) and Spain (Catalonia and Valencia), and to provide reliable reference data for the non-invasive characterisation of glazed pottery directly within museum environments.

Scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS) was used to analyse the stratigraphy, microstructure, and chemical composition of the ceramic bodies, glazes, and colours, while thermal ionisation mass spectrometry (TIMS) was employed to determine the lead isotopic signature, providing insights into the origin and commercial dynamics of lead. A comprehensive reference database of European and circum-Mediterranean lead ore deposits mined between the 13th and 18th centuries CE was also compiled for this study to establish the source of the lead. This metal is a crucial raw material used as flux in tin glaze production and is usually available locally in many manufacturing regions. However, previous studies have provided evidence of long-distance trade routes (Mason et al., 1992; Habicht-Mauche et al., 2000; Wolf et al., 2003; Klesner et al., 2021), and the author's master's thesis (Paghi, 2021; Paghi et al., 2024), which examined a limited set of tin-glazed ceramics from Montelupo Fiorentino, indicated an inconsistency with the local lead deposits of Tuscany, suggesting foreign sources and emphasising the need for a more in-depth investigation into the history of lead supply and trade over the centuries.

Finally, hyperspectral imaging (HSI) analysis was conducted on the glazes and colours of tin-glazed ceramics produced in Montelupo Fiorentino (14th–18th century), resulting in a dataset intended to serve as a reference for in situ analysis of glazed pottery colours in museums. Hyperspectral spectroscopy in the visible and near-infrared range (400–1000 nm) is already well-established for analysing colours in paintings, textiles, and manuscripts (see, for example, Maybury et al., 2018; Picollo et al., 2020; De La Codre et al., 2021; Claisse et al., 2023; Cucci et al., 2023). Nevertheless, glazed ceramics are more complex to analyse due to their uneven and highly reflective surfaces. Consequently, few studies have focused on them, and a specific reference dataset is still lacking.

METHODS

Forty-six sherds from the production centres of Pisa (13th century to 15th century), Catalonia and Valencia (14th century), and Montelupo Fiorentino (late 14th to 18th century) were examined using scanning electron microscopy (SEM-EDS) and lead isotopes analysis (Fig. 1). SEM-EDS analysis of the Pisa and Montelupo samples was conducted at the *Centro di Servizi di Microscopia Elettronica e Microanalisi* (MEMA-UNIFI) using a Zeiss EVO MA15 instrument, equipped with a Si-Li spectrometer and Oxford Aztec software, while samples from Catalonia and Valencia were examined at the Centre de Recerca en Nanoenginyeria (CNRE) of the Universitat Politècnica de Catalunya using a Zeiss Neon 40 instrument with an Ultim EDS detector and Oxford Aztec software. Both instruments were operated under the same conditions: an accelerating voltage of 20 kV, a beam current of 20 nA, a working distance of 7.5–8.5

mm, and a measurement duration of 120 seconds. The lead isotope composition of the samples was analysed using the ThermoFinnigan® Scientific Triton-Plus at the Radiogenic Isotope Laboratory of the University of Florence. Instrumental mass bias was corrected using replicate analyses of the NIST SRM 981 standard. External precision (reproducibility) and accuracy were monitored through repeated measurements of the international rock standard AGV-1, whose ratios $^{208}Pb/^{204}Pb$ = 38.559 ± 28; $^{207}Pb/^{204}Pb$ = 15.657 ± 19; $^{206}Pb/^{204}Pb$ = 18.946 ± 1 (2SE, n = 4), were substantially in agreement with those of the literature (Thirlwall, 2000; Baker et al., 2004; Weis et al., 2006).

Finally, hyperspectral imaging analysis was conducted on the glaze and colours of fifty sherds from Montelupo Fiorentino (end of the 14th–18th century) using two devices developed by SPECIM (Finland) that operate over a wavelength range from 400 to 1000 nm:

Figure 1 *Tin-glazed ceramic sherds investigated in this study.*

i) The ultraportable IQ push-broom Vis-NIR hyperspectral camera (referred to as SPECIM IQ) measures 207 × 91 × 126 mm and weighs 1.3 kg. The spectral resolution is 7 nm, and the acquisition step is 3.5 nm; each pixel measures 17.58 µm × 17.58 µm. The acquired image has a resolution of 512 × 512 pixels. It was captured at a distance of 20 cm, using two halogen lamps positioned at 45° and 60 cm from the sample, with an illumination of 2200 lx. The analysis employed an integration time of 32 ms. Calibration was performed using a white Spectralon® standard.

ii) The Vis-NIR hyperspectral camera (referred to as SPECIM HS-XX-V10E), equipped with an HS-XX-V10E CCD detector, provides a spectral resolution of 2.8 nm (FWHM). The spectral sampling interval is 0.7 nm, with a pixel size of 8 x 8 µm. The exposure time is 30 ms, and the focal length is 23 mm. The camera system is mounted horizontally on a 1.30 m translation rail and controlled remotely using the IDAQ spectral software. The rail features two halogen lamps, each positioned at 45° and 60 cm from the sample, which move synchronously with the camera during data collection to ensure consistent illumination across the scan. Analyses were performed at a working distance of 50 cm under 2200 lx. Sample data were collected sequentially, line by line. A calibrated diffuse reflectance target (Spectralon, Labsphere, USA) was used for spectral calibration.

Data processing was performed using Spectronon and ENVI 5.0 + IDL software. Both tools enable the creation of RGB images by selecting three wavelengths (R = 650 nm; G = 540 nm; B = 450 nm). Similarly, an infrared false-colour (IRFC) image can be generated by replacing the red band with an infrared band and choosing two additional visible bands (R = 900 nm, G = 650 nm, B = 540 nm). To minimise noise, the Savitzky-Golay smoothing filter with a window size of 13 points was applied. Spectral Angle Mapper (SAM) classification was used to analyse the spatial distribution of colouring materials within each sample (Cucci et al., 2020; Galluzzi et al., 2024). This method evaluates the spectral similarity between each pixel and a reference spectrum, known as an endmember, which is selected by manually identifying the purest pixels. After extracting the endmembers, the SAM mapping visualised their distribution across the image. All endmember spectra were normalised and expressed as relative absorbance log(1/R). To create the reference dataset, spectra were extracted from a 5 x 5 pixel area. For each sample, spectra obtained from three different areas of the same colour were compared. These colour spectra were analysed, and a representative spectrum was ultimately chosen for each spectrally uniform coloured area.

RESULTS AND DISCUSSION

The results are divided into three sections, each discussing different aspects. The first section explores and compares the early tin-glazed production in the manufacturing centres of Pisa, Catalonia, and Valencia. The second section presents the data collected from Montelupo Fiorentino samples and compares them with those from Pisa. The final section discusses the HSI images and spectra gathered for the colours in the Montelupo sherds.

Comparison of Pisa and Catalonia-Valencia (13th–15th century CE) and potential sources of lead

The ceramic bodies from the three analysed productions exhibit distinct matrix colours that reflect differences in inclusions and chemical composition. Pisa samples have a non-calcareous and ferric ceramic body with a characteristic red hue and contain high concentrations of SiO_2, Na_2O, and MgO, mainly due to abundant quartz and feldspars. Barcelona ceramics exhibit a calcareous matrix with approximately 16 wt.% CaO, along with a high Fe_2O_3 content and lower levels of Na_2O and MgO. Additionally, Barcelona artisans intentionally incorporate ground ceramic fragments (grogs) into the matrix, a feature typical of this type of production. Finally, the Valencia samples are characterised by a calcareous ceramic body rich in CaO (about 20 wt.%) with a yellowish-pink colour.

Regarding the glaze microstructure, the three examined productions display similar glaze-layer thicknesses. The reaction layer between the glaze and the ceramic body is less than 20 µm thick, indicating a double-firing process in which the ceramic body is fired first, followed by glaze application, as reported by Molera et al. (2001). Quartz and K-feldspar crystals are either rare or absent. The Pisa samples also contain Ca-Mg pyroxenes, possibly linked to the use of dolomitic sand in glaze preparation. Opacification occurs through the dispersion of cassiterite (SnO_2) crystals within the glaze. These crystals appear as large clusters (15–50 µm) evenly distributed throughout the glaze in the samples from Pisa and Barcelona, while Valencia glazes show SnO_2 as smaller crystals (2–10 µm) distributed more heterogeneously within the glaze. This variation in SnO_2 crystal length and distribution likely reflects the different production techniques used by Valencian artisans to create tin glazes. The glazes are of the high-lead type (Tite, 2009) and exhibit similar concentrations of SiO_2, PbO, Al_2O_3, and CaO, indicating the use of comparable recipes. The SnO_2 content in Pisa and Barcelona samples is similar, ranging from 8.9 to 17.4 wt.%, while glazes from Valencia generally have lower SnO_2 levels. The main difference among the three productions lies in their MgO and alkali contents. The white glazes from Catalonia and Valencia have a high alkali amount (ranging from 2.5 to 6.4 wt.%), whereas Pisa samples contain more MgO (0.8–1.4 wt.%), reflecting the use of sand containing dolomite.

Regarding the colours, green and brown show similar chemical compositions in their main chromophores: CuO content ranges from 1.0 to 2.4 wt.% and MnO from 1.0 to 6.0 wt.%. These compositions align with findings from other studies on these products (Peix Virsedo, 2022). Instead, the technique for applying the colours varies. In Pisa, artisans employed the overglaze technique, applying colour to the unfired white glaze and firing it together (Pradell & Molera, 2020). In contrast, Barcelona utilised underglaze decoration, which leads to the formation of a reaction layer between the ceramic body and glaze during firing, characterised by crystalline phases such as braunite, bustamite, hausmannite, kentrolite, and bixbite. In Valencia production, green and brown colours are evenly distributed across the glaze. In only one sample, the presence of bustamite crystals in the brown indicates underglaze application. These different decorative methods show that, although knowledge of glaze and colour recipes and production techniques may have been shared among the production centres of Pisa, Barcelona, and Valencia, the decorative technique appears to be connected to local traditions and practices.

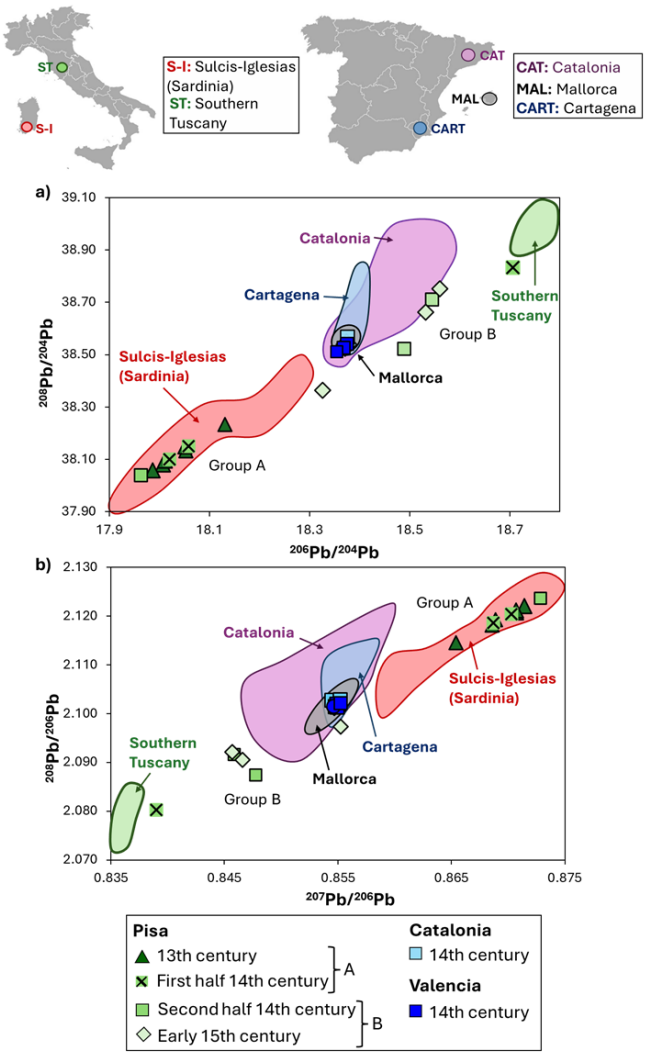

Figure 2 Lead isotope composition of the investigated samples from Pisa, Catalonia and Valencia compared with the Italian and Spanish Pb ore deposits: **a)** $^{206}Pb/^{204}Pb$ versus $^{208}Pb/^{204}Pb$; **b)** $^{207}Pb/^{206}Pb$ versus $^{208}Pb/^{206}Pb$.

Lead isotope analysis enables us to hypothesise potential sources of lead across the three investigated production centres. Pb isotope signatures of Pisa samples significantly differ from those of the Spanish samples, indicating the use of distinct lead ore deposits (Fig. 2).

Pisa glazes fall into two distinct groups: *i)* Group A, which includes nine samples dating from the 13th century to the second half of the 14th century; *ii)* Group B, comprising six samples from the first half of the 14th century to the early 15th century. In contrast, the samples from Catalonia and Valencia (14th century) display a very homogeneous lead isotope composition, indicating the use of the same sources.

A preliminary comparison with Pb ore deposits from the European and Circum-Mediterranean regions, exploited between the 13th and 15th centuries and included in the reference database, enables the selection of some Pb districts for further evaluation, including those in France, Germany, Italy, Poland, Slovakia, Spain, and Switzerland. The evaluation of compatible deposits starts with those from Italy and Spain, where the tin glazes studied were produced. In Italy, Pb-Ag-Zn mineralisations occur in Tuscany (southern Tuscany and the Apuan Alps) and Sardinia (see Fig. 2) and were mined during the Middle Ages. Samples from Group A overlap with the Sardinian deposits, particularly those from the Sulcis–Iglesias region. In contrast, samples from Group B do not match Italian deposits. Historical records indicate that the Sulcis–Iglesias region was extensively exploited by the Republic of Pisa for Pb and Ag since 1326, when this region was transferred to the Crown of Aragon (Mezzolani & Simoncini, 2001; Poisson, 2019), marking the start of Pisa's decline. This event aligns with the isotopic findings, as Group B, including samples from after the mid-14th century, exhibits isotopic differences compared to Sardinian deposits. This likely suggests a shift in the Pb sources employed by Pisan potters and the emergence of new trade routes, potentially due to the loss of Sardinian deposits. Moreover, the isotopic signature of Catalonian and Valencian ceramics does not match Sardinian deposits, suggesting that the Aragonese Crown ceased exploring Pb ore sources after conquering this region (Poisson, 2019). Instead, the comparison with the Iberian Peninsula deposits indicates that the samples are consistent with those from the Catalan coastal ranges, Sierra de Cartagena, and Mallorca Island (see Fig. 2). Among these, the most notable is the match with the Catalonia deposits (Molar, Bellmunt, Falset), which were mined during Arab rule (from the 8th to the 12th centuries) due to the abundance of galena (Martínez Elcacho, 2019). Pb from these deposits was used to produce glazed ceramics and traded as lead oxide (Rafel et al., 2003). Starting in 1342, Sardinian miners from Iglesias were appointed by Prince Peter of Aragon and Anjou to assist in managing and exploiting these mines (Rafel et al., 2003; Martínez Elcacho, 2019). Between 1365 and 1367, King Peter III expanded exports of galena and lead (Peix Virsedo, 2022). In the following century, the Falset region focused on exporting internationally through routes linking Barcelona to North Africa (Peix Virsedo, 2022). Consequently, it is very probable that the lead found in samples from Catalonia and Valencia originates from this region. Finally, other Pb deposits that align with the analysed tin glazes have been considered, especially those of the Massif Central in France, the Rhine Massif and the Upper Harz in Germany and Banská Štiavnica in Slovakia. The match with these deposits will be discussed in more detail in the following section, as a correlation with the Montelupo samples' signature has been demonstrated.

From Pisa to Montelupo: the transition in tin glaze production from the 14th to the 18th centuries CE

The ceramic bodies from Pisa and Montelupo exhibit different chemical compositions, particularly in CaO content. Samples from Pisa and Montelupo (late 14th century) feature a non-calcareous matrix with CaO content below 10 wt.%. In contrast, samples from Montelupo dating to the 17th–18th centuries show a low-calcareous matrix with CaO levels ranging from 10 to 15.3 wt.%. Finally, samples from the 15th and 16th centuries have a CaO-rich matrix.

The two productions also exhibit notable differences in the white glaze, both in microstructural and chemical composition. The glazes produced in Montelupo are generally thicker than those from Pisa. The reaction layer between the glaze and the ceramic body is less than 15 µm thick, indicating a double-firing process (Molera et al., 2001). Silicate inclusions, such as quartz and K-feldspar, are rare or absent in Pisa samples, and SnO_2 crystals occur as large clusters (15–50 µm in length). In Montelupo, the glazes contain varying amounts of silicate crystals, while SnO_2 appears as small crystals measuring 2–50 µm.

Regarding glaze composition, Pisa glazes are of the high-lead type, whereas those from Montelupo are of the alkali-lead type (Tite, 2009). Pisa samples contain higher amounts of PbO (averaging 42.1 wt.% vs 31.7 wt.%) and SnO_2 (averaging 11.2 wt.% vs 3.9 wt.%). In contrast, Montelupo glazes are rich in alkali (averaging 3.8 wt.% compared to 2.3 wt.%) and SiO_2 (averaging 56 wt.% vs 36.8 wt.%). These compositional differences suggest the use of different recipes for producing the glazes. We can propose that there was no technological transfer from Pisa to Montelupo during the 14th to mid-15th centuries, coinciding with Florence's rise. Although connected by the Arno River, a trade route that could easily facilitate ceramic exchange, this study's data indicates that these two centres probably developed their technologies separately. Finally, five Montelupo samples from the 15th-16th century display a transparent overglaze layer measuring 5–50 µm in thickness. This layer, common in Renaissance and Late Renaissance ceramics (Tite, 2009; Di Febo et al., 2025), has not been previously documented in Pisa tin glazes.

As concerns the colours, green and brown have similar compositions: CuO content ranges from 1.0 to 2.4 wt.%, and MnO from 1.1 to 3.2 wt.%. They were applied using an overglaze technique, which is highly attested in Italy (Pradell & Molera, 2020; Di Febo et al., 2025). Montelupo also displays a broader colour palette: alongside turquoise-green and brown, violet, blue, yellow, orange, and red were also utilised.

Lead isotope analysis revealed that the Montelupo samples have an isotopic composition consistent with that of Group B from Pisa, suggesting the use of similar Pb sources. It is possible that, after losing Sardinia, Pisa established new trade routes for raw materials in the 14th century, which were subsequently used by other Tuscan manufacturing centres, such as Montelupo, in later centuries (Caroscio, 2009). An initial comparison with the Pb ore deposits from the European and Circum-Mediterranean regions exploited between the 14th and 18th centuries enabled us to identify specific deposits compatible with our samples, particularly those from England, France, Germany, Poland and Slovakia (Fig. 3).

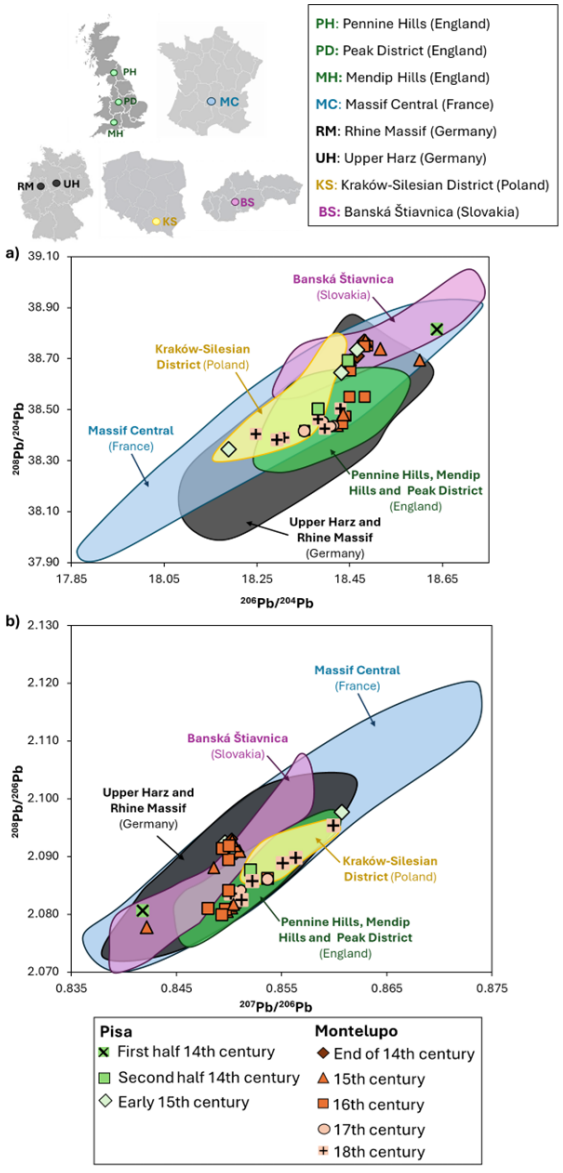

Figure 3 Lead isotope composition of the investigated samples from Pisa and Montelupo compared with the Pb ore deposits of Germany, England, France, Poland and Slovakia: **a)** $^{206}Pb/^{204}Pb$ versus $^{208}Pb/^{204}Pb$; **b)** $^{207}Pb/^{206}Pb$ versus $^{208}Pb/^{206}Pb$.

It is notable that we can exclude the Italian deposits of Tuscany and Sardinia, as none of the Pisa group B or the Montelupo samples matches the isotopic composition of these deposits. Although the Pb-Ag-Zn deposits of Tuscany were extensively exploited during the 15th and 16th centuries by the Grand Dukes of Tuscany (Biagioni et al., 2018), lead was apparently not used to produce Montelupo glazes, and this centre probably employed "foreign" sources.

Among the selected Pb deposits, the most significant ones are in Germany (Fig. 3), as this region is mentioned in a notable historical reference: the proverb by Cipriano Piccolpasso in his 1557 treatise "piombo todesco, stagnio fiandresco" ("German lead, Flemish tin") (Lightbown & Caiger-Smith, 2007). The Upper Harz and Rhine Massif districts host Pb-Zn-Cu-Ag mineralisations that were highly active in producing Ag and Pb during the Middle Ages (Kershaw & Merkel, 2023). In the 15th century, the Upper Harz mines dominated the Pb supply in Central Europe (Monna et al., 2000). This metal was subsequently exported to Lower Germany and Flanders, where it entered the broader European market (Blanchard, 2001). Flanders' crucial role in European maritime trade during the 14th and 15th centuries is well documented (Caroscio, 2009). Consequently, it is likely that Pb from German deposits reached Italy via trade routes through Flanders.

Furthermore, samples from Pisa and Montelupo also fall within the isotopic field of English deposits, especially those of the Peak District in Derbyshire, the Mendip Hills in Somerset, and the Pennine Hills in Cumberland, Northumberland, and Durham (Fig. 3). These districts were exploited to extract Pb, Ag, and other metals from the 12th century onwards, playing an important role in the European trade from the 13th to the 18th centuries (Fusaro, 2015; Kershaw & Merkel, 2023). Pb mined from English deposits reached Flemish markets (Kershaw & Merkel, 2023) and was then exported from Antwerp (in the Netherlands) to Germany, Eastern Europe, Italy, and the Iberian Peninsula. During the 15th century, Italian traders controlled most of the exports from English ports such as London and Southampton (Blanchard, 2001; Caroscio, 2009).

The isotopic compatibility with deposits in the Massif Central in France, Kraków-Silesian District in Poland, and Banská Štiavnica in Slovakia (see Fig. 3) was also investigated. The Massif Central in France hosts numerous Pb-Zn-Ag deposits that were mined from the 11th to the 14th century primarily for monetary purposes (Baron et al., 2006). Activity declined sharply between the 14th and 15th centuries, likely due to the exhaustion of shallow veins and the demographic and economic crises caused by the Black Death. Mining recommenced in the 15th century and continued until the 17th century (Thuaudet, 2019). In the first half of the 17th century, the Pb obtained was mainly used in ceramic glazing (Thuaudet, 2015).

In the Kraków-Silesian District of Poland, Pb and Ag extraction started around the 12th century (Miazga et al., 2022) and mainly served local markets. Large-scale production grew in the 13th century, beginning with exports to Upper Hungary, Bohemia, Germany, and Flanders (Miazga et al., 2022). These routes remained active from the 13th to the 15th centuries. Italian merchants dominated the Polish lead trade in the 15th century.

Metal deposits in Slovakia played a central role in European trade during the Middle Ages. Ag and Pb mining and trade in the kingdom of Hungary were conducted by Italian merchants, primarily from Venice and Florence, between the 13th and 15th centuries (Stefánik, 2011). During this period, the Banská Štiavnica district became one of the largest silver and lead-producing areas (Stefánik, 2011). Nonetheless, historical records do not indicate that lead was directly imported into the Florence production region.

Hyperspectral imaging (HSI) of Italian tin-glazed ceramics

HSI has proven to be a quick, non-destructive method for examining highly refractive, three-dimensional tin-glazed wares, confirming previous findings (Galluzzi et al., 2024; Sciuto et al., 2022). The SPECIM IQ and the SPECIM HS-XX-V10E camera detected the same chromophores, providing comparable results and demonstrating the effectiveness of both devices in characterising the colours of glazed ceramics. The findings align with those obtained from previous analyses (MA-XRF, micro-Raman, PIXE-PIGE, and SEM-EDS) by Mangani (2024) and the SEM-EDS analysis conducted in this study, with the added advantages of being non-invasive, portable, very rapid, and enabling immediate analysis of the entire surface of the sherds.

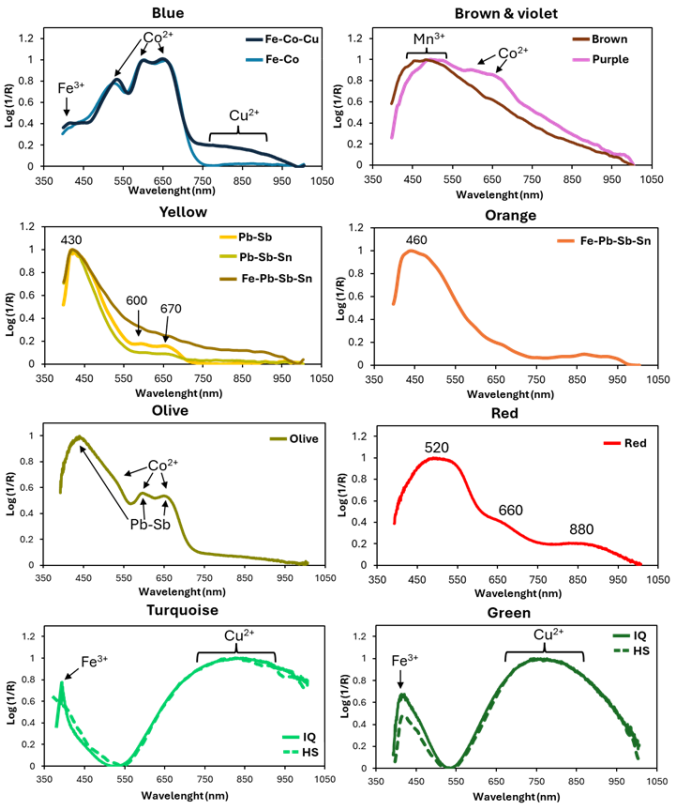

Figure 4 *Absorbance spectra obtained for the colours of Montelupo tin-glazed ceramics.*

HSI proved highly effective at detecting cobalt in blue decorations made with a cobalt-based colourant. Co is usually difficult to identify with other techniques, such as SEM-EDS, due to its low concentrations in the blue colour, often below the detection limit. Furthermore, HSI investigations detected Fe^{3+} in all blue decorations and Cu^{2+} in samples from before 1500–1520 CE, consistent with the literature (Seccaroni & Haldi, 2016; Colomban et al., 2021; Fig. 4). No additional compositional information could be obtained concerning the technological change in blue glaze production that occurred after the early 16th century.

Analysis of brown and violet colours revealed that Mn^{3+} was the main chromophore. In eight violet samples, the presence of Co^{2+} was also detected by HSI, thanks to the exceptionally low detection limit of UV-Vis-NIR spectroscopy for Co^{2+} in tetrahedral coordination in glass materials (down to 18 ppm) (Patin et al., 2022; Fig. 4). Co oxide was probably used to achieve a deeper violet shade.

For the yellows, it was possible to distinguish between the pure antimony yellow pigment ($Pb_2Sb_2O_7$), characterised by three distinct absorption peaks (around 440 nm, 600 nm, and 670 nm), and the modified antimony yellows with Sn only or with Sn and Fe, where the two peaks at higher wavelengths are attenuated (Fig. 4). Orange is further characterised by a single, large, and distinct absorption band at 450 nm (Fig. 4).

The olive colour results from mixing antimony yellow with a cobalt-based blue (Fig. 4).

The red hue was achieved using a hematite-based pigment (α-Fe_2O_3), identifiable by a strong absorption band at 455–500 nm, a shoulder at 650–670 nm and another absorption band at 865–880 nm.

A copper-based colourant was used to create green and turquoise shades. When comparing the two colours, a shift in absorption is seen in the Cu^{2+} ion band (around 800–840 nm for turquoise and 770–815 nm for green). An additional peak at 420 nm, characteristic of Fe^{3+}, was also observed in the green (Fig. 4). This peak was not detected in the turquoise sample by the SPECIM HS-XX-V10E camera. The SPECIM IQ camera shows a peak around 420 nm in both green and turquoise, which is likely an artefact in the turquoise. Finally, no particular peaks were identified from the white glaze.

CONCLUSIONS

This study, for the first time, reveals the existence of a commercial network that, beyond circulating tin-glazed ceramics decorated in green and brown, also facilitated the exchange of recipes, production techniques, and technological knowledge between Italy and Spain in the 14th century. While in Tuscany, Montelupo tin glazes differ from those of Pisa, indicating distinct channels and traditions.

Regarding lead provenance, the samples' isotope signatures indicate that the lead used in Pisan production before the second half of the 14th century came from Sardinian deposits, which were indeed under the control of the Republic of Pisa at that time. Similarly, tin glazes from Catalonia and Valencia exhibited an isotopic signature consistent with local deposits in Catalonia, exploited in the mid-14th century for lead production. Conversely, the samples from Pisa, dating to the second half of the 14th century, and those from Montelupo Fiorentino display isotopic compositions that do not match those of local Italian lead deposits, highlighting the existence of long-distance trade in lead. The samples are compatible with German deposits, supporting the proverb reported by Cipriano Piccolpasso in his treatise (1557), which mentions "German lead". Moreover, the lead deposits of Somerset and Derbyshire (Great Britain) align with the analysed samples. Lead from England was extensively mined and exported from the 13th to the 18th centuries, with Italian traders dominating exports from English ports. Other European deposits are also isotopically consistent with the analysed glazes and cannot be ruled out as potential sources, even in the absence of supporting historical records.

HSI has proven to be a rapid, non-invasive, and portable method for colour characterisation of ceramic artifacts. The results obtained with the two SPECIM cameras (IQ and HS-XX-V10E) showed good agreement with those obtained using more traditional microanalytical techniques (MA-XRF, PIXE-PIGE, micro-Raman, SEM-EDS), confirming the reliability of the HSI approach and its potential for museum and conservation applications. All data generated in this study have been published in Paghi et al. (2025), uploaded to the open-access repository ZENODO (*https://zenodo.org/records/17123249*), and are available to support future research.

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