Hispano-Moresque architectural glazes in the context of medieval glass technology

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Field of interest: technical art history / glazes

Introduction

Hispano-Moresque architectural tiles were extensively used in Portugal and Spain, during the 15th and the first half of the 16th centuries. Their rich patterns comprise mainly five colours – tin white, cobalt blue, copper green, iron amber, and manganese brown – which are all obtained from high lead glazes with the addition of specific metal oxides (Coentro *et al.*, 2014). These different coloured glazes are physically separated on the tile surface, either by a dark manganese-brown line (believed to contain a greasy substance such as linseed oil), which is known as the *cuerda seca* technique, or by a ridged contour line that acts as "wall" in the *arista* technique (*Figure 1*).From the study of two Portuguese Hispano-Moresque tile collections – the National Palace of Sintra (PNS) and the Monastery of Santa Clara-a-Velha (SCV), in Coimbra – the glaze technology is analysed in the context of coeval glaze, glass, and enamel production. Starting with the colour palette and with special emphasis on tin-opacified glazes, the aim of this communication is to present a short summary of the process of technological transfer that contextualises these glazes.

Keywords: Lead glazes, Tin-opacified glazes, Hispano-Moresque, μ-PIXE, LA-ICP-MS

Methodology

This work is part of a larger project aiming at characterising and comparing Portuguese and Spanish Hispano-Moresque tile collections. A multi-analytical, minimally invasive methodology was employed. Here, the results of two analytical techniques are discussed: micro-Particle-Induced X-ray Emission (μ-PIXE) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). The analyses were performed on glaze samples (1-3 mm wide) mounted as cross-sections in epoxy resin (Araldite® 2020) and polished in Micro-Mesh® sheets up to grit 8000. By analysing the glazes in cross-section, it was possible to avoid the corroded surface as well as the glaze-ceramic body interface layer.

Results and discussion

High-lead glazes (ca. 40-60 wt.% PbO) were identified in all analysed samples and can be divided into two types: "transparent" and tin-opacified. Silica (SiO_2) and lead oxide (PbO) are the major constituents of the glazes making up to 90 wt.% of the total composition. They show an inverse correlation, with higher SiO_2/PbO ratios for tin-opacified glazes (mostly white and blue ones). The decrease in PbO is compensated by a higher Na_2O content as a fluxing agent in tin-opacified glazes. Potassium, unlike sodium, was found to be present in variable amounts both in transparent and in tin-opacified glazes.

This is consistent with a glaze technology that followed the Islamic tradition introduced in the Iberian Peninsula from the 8th century onwards. The use of lead glazes is believed to have started in the Roman Empire or in China, between the 1st century BC and the 1st century AD, and then spread to Europe and the Middle East. Alkaline glazes and glasses were also used in Medieval Europe along with lead glazes. However, in the Iberian Peninsula only lead-glazed ceramics have been unearthed so far, the significant availability of galena (PbS) in the region being appointed as one of the major factors for this, along with the advantages that lead glazes present, such as less susceptibility to defects and a higher glaze brilliance (Tite *et al.*, 1998; Trindade, 2007).

The analyses of these Hispano-Moresque glazes have identified and quantified most SnO_2 contents between 6 wt.% and 10 wt.%, with variable degrees of homogeneity. Use of SnO_2 as opacifier represents the most important innovation brought by the Muslim occupation (8th-15th century) to glaze technology, turning the Iberian Peninsula into an important ceramic production centre from at least the 13th century onwards.

1 † *in memoriam* of our co-author and dear friend Vânia Solange F. Muralha

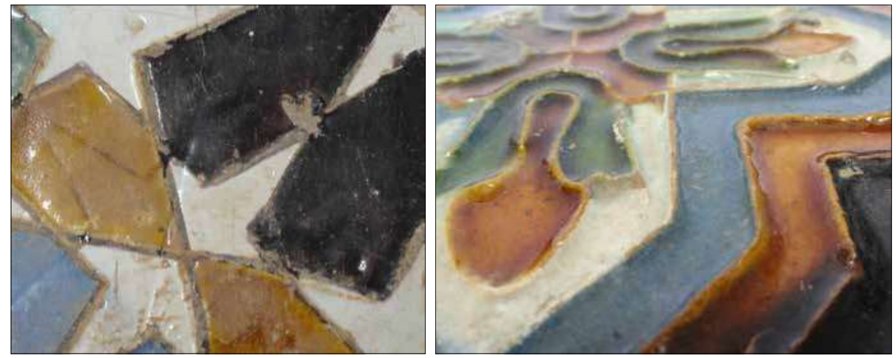

Fig. 1 **Details of a a *cuerda seca* (a) and an *arista* (b) tiles illustrating the five colours identified in Hispano-Moresque glazes: white, blue, green, amber and brown.**

However, tin-based opacifiers were used since Roman times and tin was used in white enamels and glass mosaics since the 4th century AD. The question remains on why this technology took almost five centuries to be adopted to ceramic coatings, since the earliest evidence of tin-opacified ceramics comes from the 9th century Iraq (Tite *et al.*, 2008).

The pictorial layer is composed of five colours: white, blue, green, amber and brown. The transition metals identified are those known to be responsible for the colours – cobalt for blue, copper for green, iron for amber and manganese for brown – the very same found in Byzantine glass mosaics, as well as in medieval Limoges enamels used on metal decoration (Drayman-Weisser, 2003; James, 2006).

The influence of metal decoration on ceramics is not restricted to the colours and one can see a parallel between *cloisonné* and *cuerda seca*, as well as between *champlevé* and *arista* techniques for separating the different coloured glazes. However, the *arista* technique appears as an innovation exclusive to architectural tiles as an evolution from 13th century Gothic lead-glazed monochromatic tiles used in France and England (Trindade, 2007).

The blue glaze in *cuerda seca* and *arista* tiles is very characteristic with its light cerulean shade and opacity. The majority of the blue *cuerda seca* and *arista* glazes display a Fe-Co-Ni-Cu association, as determined by μ-PIXE and LA-ICP-MS. Copper may be linked with the raw material used for obtaining cobalt, or it could be added intentionally. As an example, a blue enamel recipe from Antonio Neri (*L'Arte Vetraria*, 1612) includes copper (*ramina di tre cotte*) along with cobalt (*zaffera*) (Vilarigues & Machado, 2015). During the 9th century, cobalt blue became profusely used by Muslim ceramists, who had the raw materials available "nearby" in one of the most important cobalt deposits in the world, Qamsar, in today's Iran. Cobalt is believed to have been introduced in the Iberian Peninsula during the 13th century, although its origin is still a matter of discussion. By then, both the Middle Eastern and the European (Saxony) cobalt mines were known in the Muslim Kingdom (which included part of the Iberian Peninsula), as referred by Abu l'Qasim's ceramic treatise (Kessler, 2012; Trindade, 2009). A small group of the blue glazes analysed displays arsenic contents above 1000 μg/g and bismuth contents above 500 μg/g. The presence of As is associated with cobalt exported as zaffre from the Saxony region (Germany) from the beginning of the 16th century onwards (Gratuze *et al.*, 1996). This is consistent with a later chronology attributed to these tiles, since the group is composed exclusively of *arista* samples.

Conclusions

Hispano-Moresque tiles represent a time of great cultural changes. Their technology incorporates Islamic and Christian influences, which is visible in the colours displayed and glaze compositions found, as well as in decoration techniques. To better understand the glaze technology and its evolution, one must look at the coeval glass and enamel technologies as well, as the colour palette is the same and even the methods for separating the colours are influenced by the metal arts.

References

Coentro, S., Trindade, R. A. A., Mirão, J., Candeias, A., Alves, L. C., Silva, R. M. C., & Muralha, V. S. F. (2014). Hispano-Moresque ceramic tiles from the Monastery of Santa Clara-a-Velha (Coimbra, Portugal). *Journal of Archaeological Science*, *41*, 21–28.

Drayman-Weisser, T. (2003). The Early Painted Enamels of Limoges in the Walters Art Museum: Historical Context and Observations on Past Treatments. *Journal of the American Institute for Conservation*, *42*(2), 279-312.

Gratuze, B., Soulier, I., Blet, M., & Vallauri, L. (1996). De l'origine du cobalt: du verre à la céramique. *Revue D'archéométrie*, (20), 77–94.

James, L. (2006). Byzantine glass mosaic tesserae: some material considerations. *Byzantine and Modern Greek Studies*, *30*(1), 29–47.

Kessler, A. T. (2012). *Song Blue and White Porcelain on the Silk Road*. *Studies in Asian Art and Archaeology* (Vol. 27). Leiden: Brill.

Tite, M., Pradell, T., & Shortland, A. (2008). Discovery, production and use of tin-based opacifiers in glasses, enamels and glazes from the Late Iron Age onwards: A reassessment. *Archaeometry*, *50*(1), 67–84.

Tite, M. S., Freestone, I., Mason, R., Molera, J., Vendrell-Saz, M., & Wood, N. (1998). Lead Glazes in Antiquity—Methods of Production and Reasons for Use. *Archaeometry*, *40*(2), 241–260.

Trindade, R. A. A. (2007). *Revestimentos Cerâmicos Portugueses. Meados do século XIV à primeira metade do século XVI*. Lisboa: Edições Colibri/Faculdade de Ciências Sociais e Humanas da Universidade Nova de Lisboa.

Trindade, R. A. A. (2009). Imagens de Azul. Evidências do emprego do azul cobalto na cerâmica tardo medieval portuguesa. *Revista de História Da Arte*, (7), 236–263.

Vilarigues, M., & Machado, A. (2015). Pintar com Luz: O Esmalte Azul na Pintura de Vitral. *Boletim Da Sociedade Portuguesa de Química*, *57*, 31–36.

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Investigating a Byzantine technology: experimental replicas of Ca-phosphate opacified glass

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Field of interest: archaeology/archaeometry

Abstract

The archaeometric examination of mosaic glass tesserae has recently become of great interest, and more attention is given to the textural examination. The glass coloring and opacification techniques so far identified in ancient glass are relatively homogenous from the early glassmaking until the end of the Roman empire, when a major change occurred. From the 5th century onward, Sb- based pigments were substituted by other compounds, such as Ca-phosphate, probably introduced in the form of powdered bones. This compound is found in Byzantine mosaic tesserae and associated to large quantities of gas bubbles; a previous study aimed at the characterization of the opacifier highlighted the presence of a reaction rim enriched in sodium at the glass/inclusion interface, but to date little is known about the technology of production of this specific kind of opacifier.

To understand the production technologies of glass opacified with bone powder, experimental replicas were made under laboratory conditions using a silica-soda-lime base glass. Bovine bones were selected in order to minimize the variables depending on the species or the individuals; both cortical and trabecular portions were selected. Different thermal pre-treatments of the bones were tested, and batches were melted with different firing and cooling rates at different temperatures. The experimental samples thus obtained were prepared in polished sections and analyzed by means of optical microscopy (OM), scanning electron microscopy (SEM-EDS) and Raman spectroscopy in order to guarantee the textural, mineralogical and qualitative chemical analysis of the opacifying phase and the comparison with the archaeological samples.

Keywords: bones; Ca-phosphate; opaque glass; Byzantine