Instrumental techniques applied to the study of 16th century majolica tiles with examples from Spain and Portugal

Técnicas instrumentales aplicadas al estudio de azulejos del siglo XVI. Ejemplos en España y Portugal

João Manuel Mimoso (jmimoso@lnec.pt)

Department of Materials, LNEC, Av. Brasil 101, Lisbon, Portugal.

Abstract

The production of majolica tiles (azulejos) in Portugal is well documented from the second quarter of the 17th century through a succession of types of clearly local design and manufacture. However, the same cannot be said of the relatively few 16th century panels and patterned tiles hat were attributed to the workshops of Lisbon, whose provenance and chronology were often doubtful. This situation was the starting point of an ongoing research project aiming to shed light on the origin of majolica azulejo production in Lisbon and to identify local productions, separating them from imports from abroad. The research team includes art historians, geologists, chemists and engineers and the method calls for the support of instrumental analyses of glazes and biscuits using, mainly, Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDX).

The presentation will exemplify the results obtained with the instrumental techniques bearing on 16th century majolica tiles from the workshops of Talavera, Seville and Lisbon and the interlacing of the scientific campaign with the input of art historians which was the key for success.

Key-words: *azulejos; renaissance majolica tiles; Flemish potters in Iberia; glaze analyses; SEM-EDX*

Resumen

La producción de azulejos de mayólica en Portugal está bien documentada desde el segundo cuarto del siglo XVII a través de una sucesión de tipologías con origen claramente portuguesa. Sin embargo, no puede decirse lo mismo de los relativamente escasos paneles narrativos y azulejos de patrón del siglo XVI atribuidos a los talleres de Lisboa, cuya procedencia y cronología son a menudo dudosas. Esta situación fue el punto de partida de un proyecto de investigación en curso cuyo objetivo es aclarar el origen de la producción de azulejos de mayólica en Lisboa e identificar las producciones locales, separándolas de las importaciones. El equipo de investigación incluye historiadores del arte, geólogos, químicos e ingenieros y el método requiere el apoyo de análisis instrumentales de vidriados y bizcochos utilizando, principalmente, la microscopía electrónica de barrido y la espectroscopía de rayos X dispersiva de energía.

La presentación ejemplificará los resultados obtenidos con las técnicas instrumentales sobre azulejos de mayólica del siglo XVI de los talleres de Talavera, Sevilla y Lisboa y el entrelazamiento de la campaña científica con la aportación de los historiadores del arte, que fue la clave del éxito.

Palabras clave: *azulejos; mayólica renacentista; alfareros flamencos en Iberia; análisis de vidriados; SEM-EDX*

Foreword: The text is a short introduction to the methodology developed in Portugal by a team of researchers to study the production of majolica tiles in 16th century Lisbon. The oral presentation (in Spanish) will dwell mostly, not on the methodology itself, but rather on its results.

Prólogo: El texto es una breve introducción a la metodología desarrollada en Portugal por un equipo de investigadores para estudiar la producción de azulejos de mayólica en la Lisboa del siglo XVI. La ponencia (en español) se detendrá, sobre todo, no en la metodología en sí sino en sus resultados.

1. Introduction

Research on Portuguese azulejos in the field of Art History has, for the better part of a century, relied on documental sources, when available, and subjective appraisals based on stylistical considerations and personal experience. Those approaches allowed great steps into the establishment of the chronological succession of styles and authorships which Reynaldo dos Santos synthesized in his book of 1957 (Santos, R. 1957) There is, however, a period before the Portuguese productions became stylistically unique in the early 17th century, that presents specific difficulties to the researcher. Renaissance figurative panels and pattern tiles followed widespread models that do not allow a clear separation of Portuguese-made azulejos from Spanish and even, in some cases, Flemish productions. Amidst the well-known panels and pattern linings of the Bacalhôa Palace and Gardens near Lisbon (Pleguezuelo, A. et al., 2021) can be found striking examples of the situation.

Decisions on provenance were classically made from a subjective assessment, but let us consider the example of Figure 1, an interesting azulejo fragment found in an archaeological excavation at Terraços do Carmo in Lisbon. The study of 16th century ornamental designs is a domain of research in itself and this pattern, very similar to contemporary Flemish designs (Caignie, F. et al., 2012; Archer,M. and Wilson, T., 2010) may be of importance as one of the earliest manufactured in Portugal… if it is indeed of local manufacture. Was it made in Portugal, or imported? If so, from where? Antwerp, Talavera? And when? Can the reader try and reply to those questions? Are the replies subjective guesses, or is there some objectivity in the assessment? What objective proof may be offered?

Fig. 1. *A fragment found during an excavation at Terraços do Carmo in Lisbon (source of all images, unless otherwise indicated: LNEC)*

In this field opinions are traditionally based on what is seen and we only see what our eyes are able to see. Considering the electromagnetic spectrum (Figure 2) the range perceived by the human eye is small indeed when compared to the full electromagnetic range. 16th century tiles made in Lisbon are not distinguishable with any degree of assurance from most tiles of the period made elsewhere, when perceived with our eyes… but what if we could see in other ranges of the spectrum? Would they then be different? Modern instruments can enhance and expand perception by detecting and filtering radiation in many ranges that are not attainable by human vision, and then transform that detection into information that we can understand and allow us to perceive much beyond the range of our limited vision.

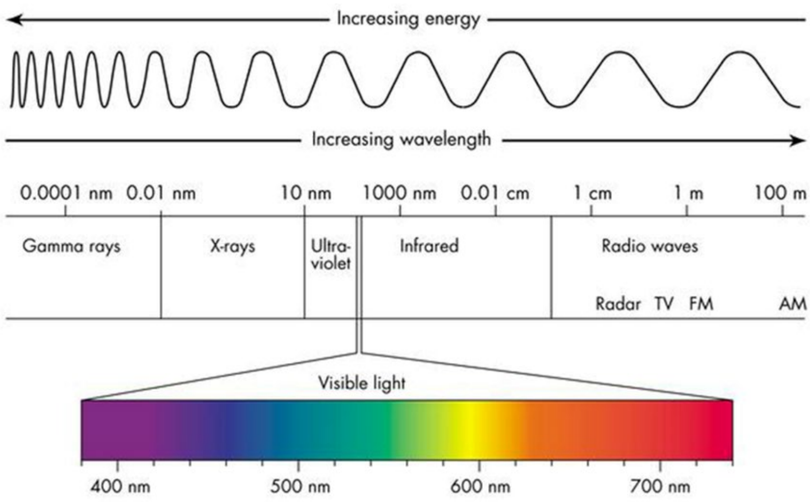

Fig. 2. *The electromagnetic spectrum- visible light corresponds to the very narrow domain between infrared and ultraviolet radiation.(Source: Wikimedia Commons, Ziortza Agirrezabala - Own work, CC BY-SA 4.0)*

2. The Scanning Electron Microscope (SEM)

The most readily available, flexible and all-round useful instrument in the study of azulejos is the Scanning Electron Microscope (SEM- Figure 3). Using it is like Alice going through the mirror: you enter a new world where things may still be recognizable but certainly look different. And one immediately gets two powers from the images: perception is increased to the tune of a 20,000 magnification or more; and, if the user is knowledgeable on the materials with which he is dealing, he will be able to have a notion of the elemental chemical composition of the samples being observed.

Fig. 3. *A scanning-electron microscope manufactured by Tescan in the Czech Republic, similar to the unit used at LNEC (source: Tescan)*

I do not want to go into atomic physics, and so I shall only say that an electron beam, as thin as 1.3 nm across, scans the object pixel by pixel and line by line and then composes an electronic image of what it "sees". Figure 4 compares sectional images of a glaze seen in a plain microscope with that of an electron microscope, representing both sides of the mirror through which we go when we turn the beam on. This image is made of electrons that go into the object and return without losing any energy- they are called back-scattered (BS) electrons. Few electrons are backscattered by light atoms, while heavier atoms backscatter more electrons according to their atomic weight. If you imagine that to each electron will correspond a quantum of white light against a black background, when the electronic beam "finds" light atoms such as aluminium, silicon or calcium, only a few electrons will be backscattered; when the beam "finds" a concentration of large and heavy atoms, such as lead, many will be backscattered, forming an image with an intensity in the white-black range proportional in terms of white intensity to the atomic weigh of the atoms they encountered on that particular pixel. In the image of Figure 5, the difference in terms of intensity in the white/black range between the glaze and the biscuit is evident and stems from the fact that all faience glazes up to the 20th century are tin-opacified lead glasses. Their main elemental components introduced by the recipe are sodium (Na), silicon (Si), potassium (K), tin (Sn) and lead (Pb) while the presence of elements such as magnesium (Mg) or aluminium (Al) derive from associated impurities. Of the recipe elements, lead (a strong fusing agent to lower the fusing point of silica) and tin are elements of high atomic weight and the higher the content in lead, the lighter the colour of the SEM-BS image. Tin crystalizes as the glaze cools down and can often be seen as small white specks spread through the section.

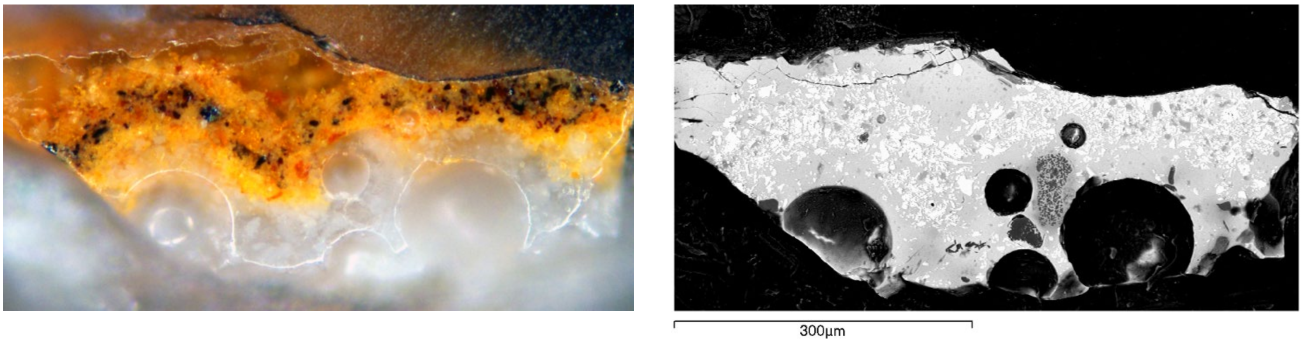

Fig. 4. *A small scale about 0.6mm long sampled from a 16th century Flemish tile. The sample was stabilized in epoxy resin, lapped and polished to obtain a flat cross-section. Left side: image taken through an optical microscope; Right side: SEM-BS image*

Figure 5 identifies common inclusions and other features in the glaze that are often unclear or even invisible under a plain optical microscope.

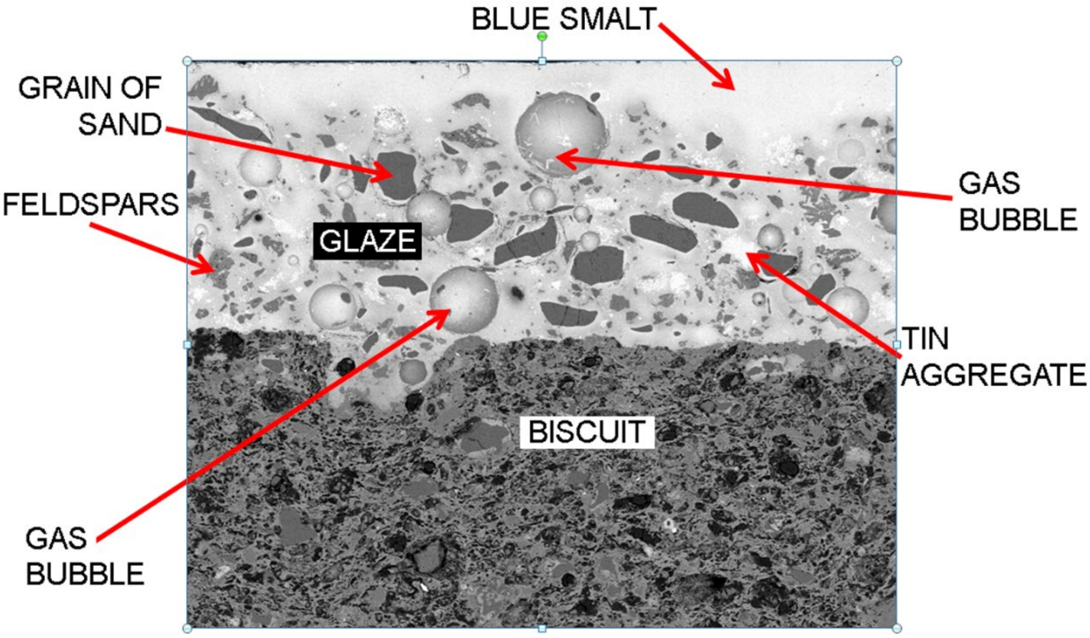

Fig. 5. *Section of a 17th century Portuguese azulejo seen under the SEM at backscattered electrons mode*

Practically all SEMs have an energy–dispersive spectrometer (EDX) coupled to them. Electrons from the SEM beam often collide with electrons of the atoms of elements in the sample, causing transitions from high-energy to lower-energy levels and an emission of photons. The EDX is able to detect those photons whose wavelengths are within a region of the X-rays range, measure the energy associated to them and count the detections per each class of energy. This is an extension of our vision into the X-ray range and it is all-important because the atoms of different elements emit photons with specific energies and the contents of the sample in those elements may therefore be quantified with an acceptable accuracy by the number of characteristic photons that are detected. Figure 6 depicts artificially colorized elemental mappings of an area of an azulejo glaze: elements are identified from the energies of the characteristic photons emitted and a counting of those photons is related with the content of the element in any pixel of the image. Figure 7 combines the four images in Figure 6, allowing a visualization of the nature of the glaze inclusions through their elemental composition.

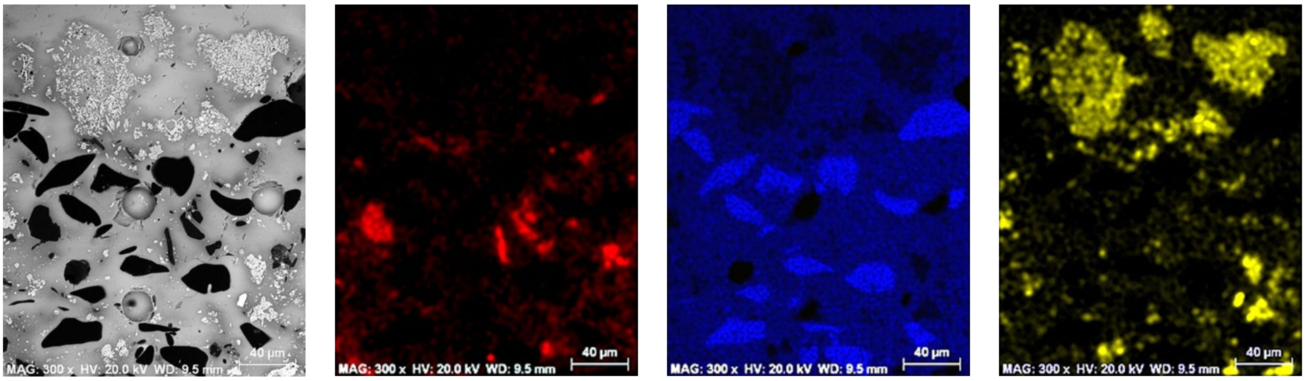

Fig. 6. *Sectional area ca 0.3 mm across in a glaze. Left to right: SEM-BS image; red map of the contents in aluminium (pin-pointing feldspars); blue map of the contents in silicon (pin-pointing grains of sand); yellow map of the contents in tin (pin-pointing aggregations of crystals of the opacifier tin oxide)*

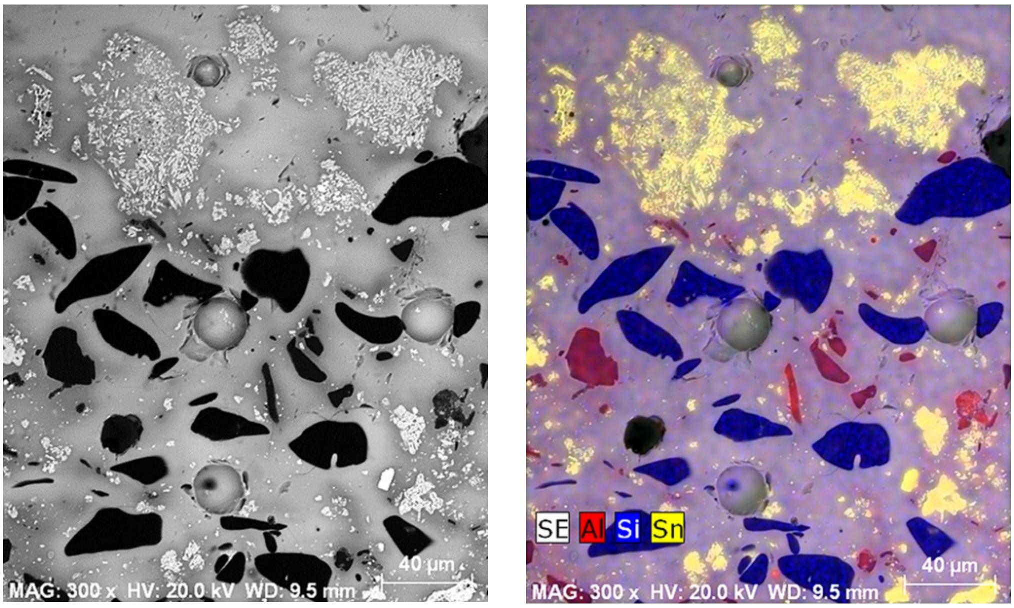

Fig. 7. *Superposition of the coloured maps in Figure 6 to form a partial analytical map of the sample*

The ability to measure the energy associated to photons and through it identify the elements whose atoms emitted them and count the number of such emissions, allows also a semi-quantitative analysis. Figure 8 shows an area in a glaze section and the spectrum resulting from the analysis. The spectrum is a sort of fingerprint of the composition and its peaks above a background of noise can be related to elements that emit photons with that energy. The spectrum is raw information, but from the areas of relevant peaks the equipment can offer a best-estimate of the composition. The selection of elements is not fully automatic: the operator must have an accurate idea of what elements are present and the equipment offers a quantification of only those elements selected which shows that human interaction is necessary and knowledge both of the instrumental process and of the material being analysed are essential. There are several possible sources of error in the numerical process of quantification, stemming from the operator and from the software that interprets the spectrum. However, the spectrum itself is free of such errors and may be used for comparisons, much as pictures of fingerprints or facial features may be compared to identify a person.

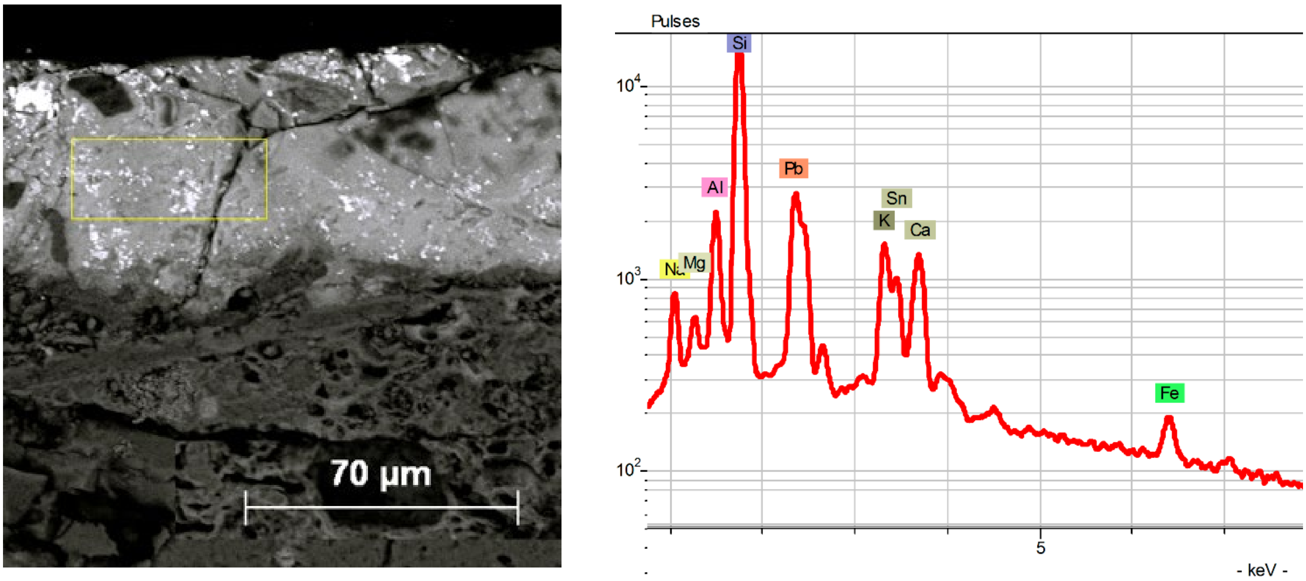

Fig. 8. *Selected area of the glaze of a 17th century Portuguese tile (left side) and part of the analytical spectrum. The area of each peak is related with the contents in the element indicated. The peaks in this spectrum are, from left to right: sodium (Na), magnesium (Mg), aluminium (Al), silicon (Si), lead (Pb), potassium (K), tin (Sn), calcium (Ca) and iron (Fe)*

3. Comparing two different productions with SEM

Figure 9 depicts images of part of a Portuguese panel (called *de Nossa Senhora da Vida*) from the collections of *Museu Nacional do Azulejo* (MNAz) in Lisbon, dated from the 1570s or early 1580s, attributed, from the signature, to the Lisbon workshop of João de Góis (Pais, A. et al., 2019) and on the right side four tiles also from the collection of MNAz, of a pattern used at *Convento Santa Clara* in Seville, dated ca. 1575 (Sancho, A. 1948).

Fig. 9. *Azulejos to be compared. Left side: Lisbon, Portugal late 1570s-early 1580s; Right side: Seville, Spain ca. 1575 (source: MNAz, Lisbon)*

Figure 10 compares images at the same scale of the glazes, while Figure 11 compares the relevant parts of both spectra representing the composition of the glazes. The interfaces in the lower row of Figure 10 and the spectra depict substantial differences.

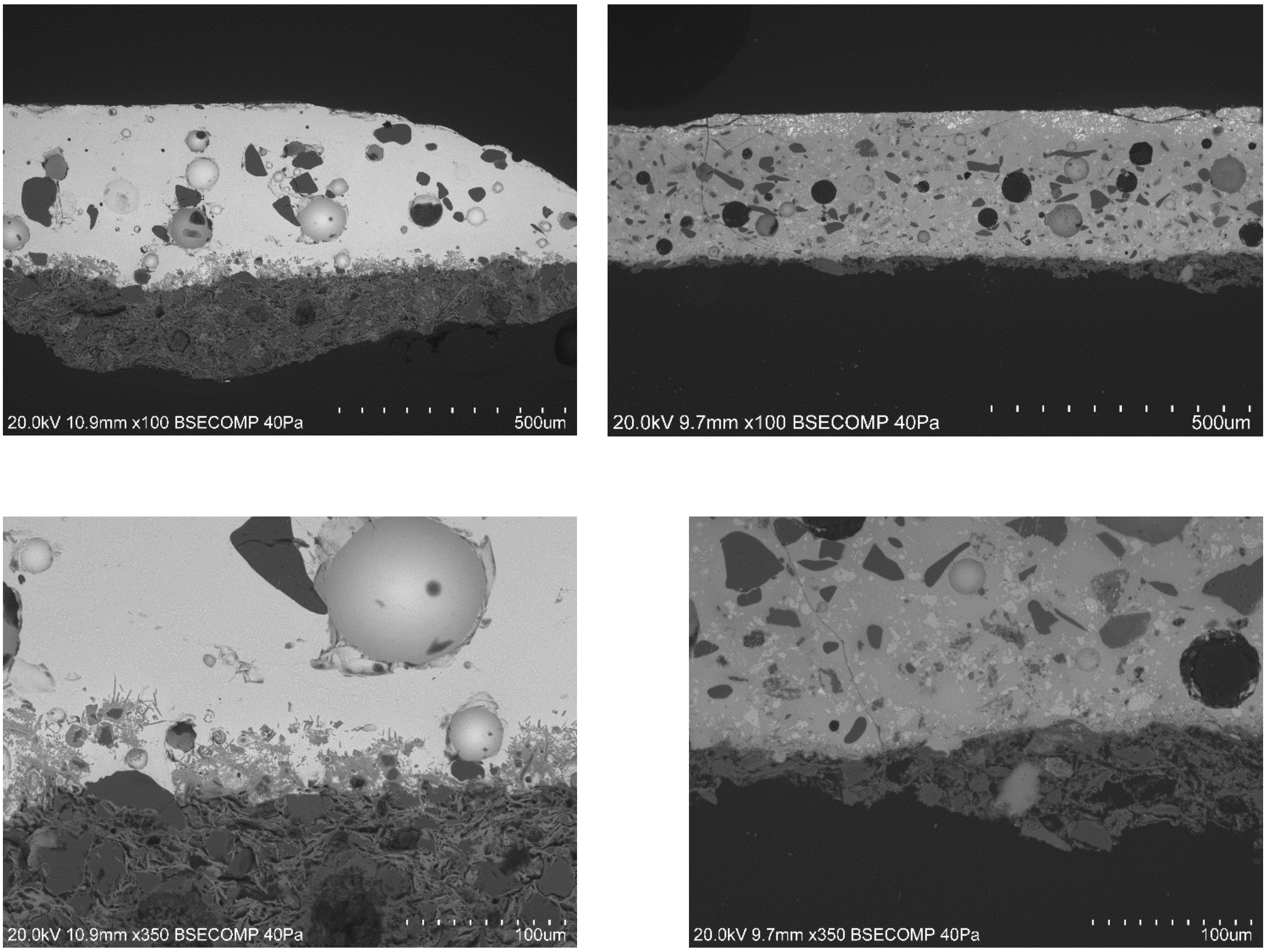

Fig. 10. *Comparison of the glazes of the azulejo panels in Figure 9. Left side: Lisbon, Portugal late 1570s-early 1580s; Right side: Seville, Spain ca. 1575. The top images depict the glazes at a magnification of 100x; the lower images depict the glaze-biscuit interfaces at 350x. There are differences in the morphology of the glaze inclusions (top two images) but they are not sufficient to assert a distinction; however, the differences in the interfaces (lower images) are related with both the composition of the glazes and the firing cycle, pointing to a definite distinction between the two panels*

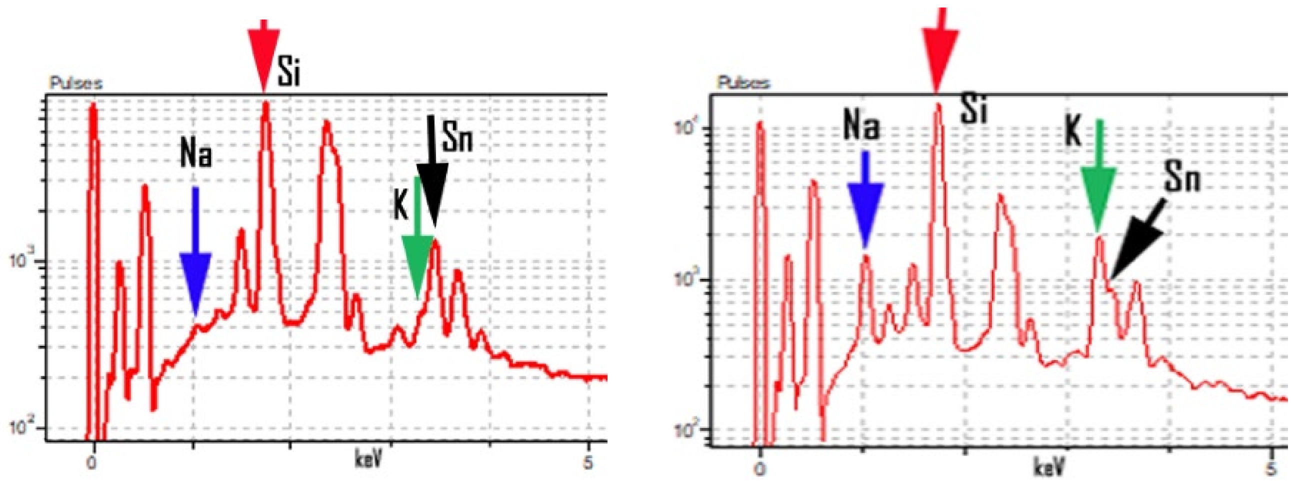

Fig. 11. *Comparison of the analytical spectra of the glazes of the azulejo panels in Figure 9. Left side: Lisbon, Portugal late 1570s-early 1580s; Right side: Seville, Spain ca. 1575. The arrows mark the most substantial differences: blue arrows- contents in sodium; red arrows: lead; green arrows: potassium; black arrows: tin*

4. Assessing the provenance of a tile fragment

Let us now return to the quiz about the fragment in Figure 1. Figures 12 and 13 compare images of the glaze sections and spectra of the fragment with the panel *Nossa Senhora da Vida*, showing that, both the morphology, and the composition suggest a similar provenance: if the panel is from the workshop of João de Góis and datable to the late 1570s, then the fragment may well have the same provenance - either the workshop of João de Góis, or another of the same technological circle. In that case its chronology should also be from the period when that technology was used in Lisbon, seemingly from the mid-1560s to the mid-1580s.

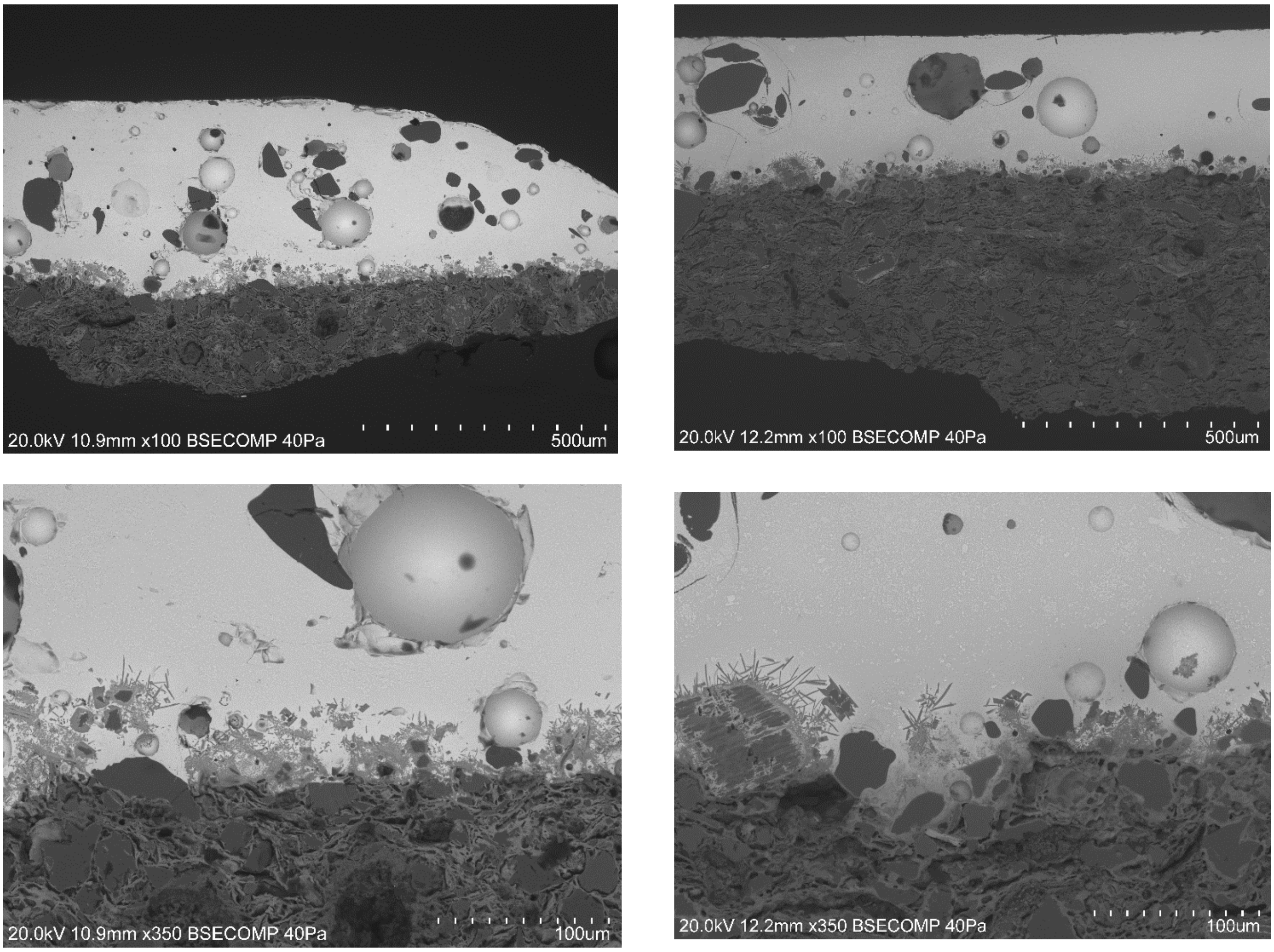

Fig. 12. *Comparison of the glazes of the Nossa Senhora da Vida panel in Figure 9 (left side) with the unknown fragment of Figure 1 (right side). The top images depict the glazes at a magnification of 100x; the lower images depict the glaze-biscuit interfaces at 350x. The morphologies of the glazes are similar and the crystallizations in the interfaces are equally well-developed*

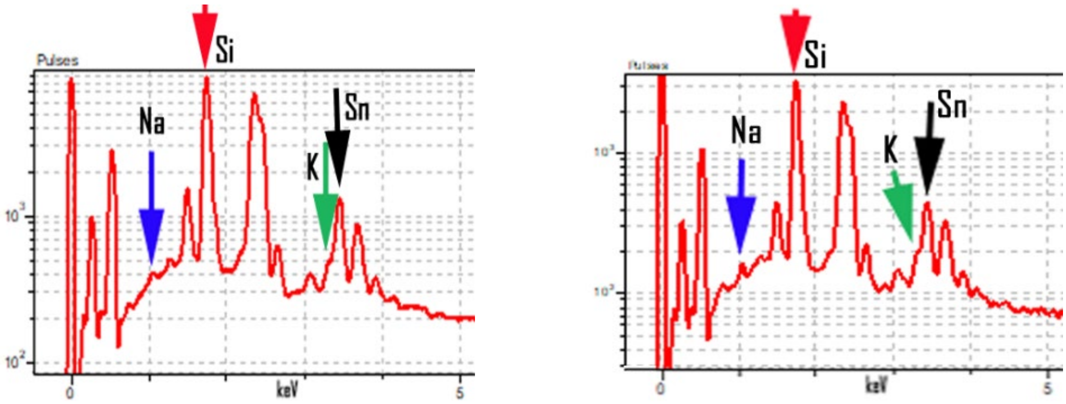

Fig. 13. *Comparison of the analytical spectra of the glazes of the Nossa Senhora da Vida azulejo panel (left side) with the fragment in Figure 1 (right side). Comparison with Figure 11 shows that those contents that were discordant are now very similar: blue arrows- sodium; red arrows: lead; green arrows: potassium; black arrows: tin*

Obviously, analytical results obtained from tiles of two different panels are never exactly the same and the relevance of the differences has to be assessed to sustain a decision. Very often the process leading to a conclusion on provenance is more elaborated than suggested above, involving the separate application to glazes and biscuits of a mathematical tool called *Principal Component Analysis* (PCA) whose explanation is beyond the aims of this text, but in all cases, it may well be asked: "How sure are you of a conclusion on provenance?". Notwithstanding the apparent objectivity of results, all scientific work has a degree of uncertainty associated, which should always be unequivocally conveyed - that is the reason why we say that our approach "suggests a similar provenance" but can never assure that the provenance is actually the same, even after exhaustive research. Those interested in the application of the full methodology to the fragment in Figure 1 may read the 15-page results and conclusions of the multidisciplinary study in a paper (Mimoso, J.M. et al., 2019) available on the internet.

5. The role of the art historian

I explained our method in broad lines and the roles of the scientists involved in the studies derive from the needs to determine the analytical requirements, select the technologies to be used, obtain data and interpret the results. Because the biscuits are made of clay, the role of the geologists is obvious; so is the role of the materials engineers in dealing with the characteristics of glazes, the role of the chemists in dealing e.g. with the interactions between the glazes and the biscuits and the role of the instrumentalists in determining the best analytical technologies for each purpose, making sure that they are properly applied. I also implied the role of archaeologists by depicting in Figure 1 a shard dug in Lisbon and exemplifying some of the information that may be extracted from it (see also Mimoso, J.M. et al., 2019). But the art historians were never mentioned... Yet, they are a *sine qua non* part of the research team, capital at the beginning of a project because it falls to them to select the tiles and panels whose provenance and chronology can be ascertained beyond a reasonable doubt. Samples from those tiles are used to build up a database of "anchors" against which samples of the tiles to be studied will later be compared. Art historians are the source of questions based on which the team produces hypotheses which the instrumental research must verify or reject. Finally, art historians are those who give meaning to results because, once these are available, they will interpret them to integrate with what is already known in a coherent and logical construction.

Nothing in our method is new in the sense that it has never been done before. The innovation lies in the fruitful cooperation of so many fields and, capital among them, art history imbricated with scientific domains through which we achieved results that are finally offering a clear vision of the early production of majolica tiles in Portugal, determining what was made in the country (and, often, when it was made) and what was imported (and from where). And in this respect, it is important to note that we worked with two distinguished art historians: Dr Alexandre Pais, until recently Director of MNAz, with whom we developed the method and achieved the first successes, and Prof. Alfonso Pleguezuelo of the University of Seville, with whom we are disentangling the previously inextricable linings of *Palácio e Quinta da Bacalhôa* (Pleguezuelo, A. et al., 2021) a study calling for knowledge on the productions of Antwerp, Talavera, Seville and Lisbon.

This paper pertains to the 16th century, when productions from several countries including Portugal were stylistically similar and therefore difficult to separate resourcing only to the tools of an art historian. Still, it heralds a time when cooperation between art historians and scientists in the fields of analytical chemistry, geology and materials engineering may potentially reply or help in the replying to questions that could only until now be approached through subjective argumentation. And the potential of this and other more sophisticated instrumental methodologies is not exhausted in the renaissance productions. On dealing with azulejos from the 17th, 18th and 19th centuries, it may help to group panels according to their workshop provenance, it may help resolve doubts pertaining to dispersed tiles or panels that may, or may not, have once been part of the same lining, and it may indicate e.g. which 19th century façade tiles were manufactured by what factory, which is a relevant subject in the Portuguese context given the number of 19th century edifications with tiled façades throughout the country.

Acknowledgements

The fragment illustrated in Figure 1 was exhumed from the grounds of the ancient *Convento do Carmo* in Lisbon during campaigns in 2013-15 led by António Marques of the *Centro de Arqueologia de Lisboa*.

The author thanks *Museu Nacional do Azulejo* in Lisbon for authorization to use images and instrumental results of azulejos in its collections.

Paper written at *Laboratório Nacional de Engenharia Civil* in under LNEC Research Project 0202/1101/19014.

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