

On the use of glaze and ceramic body analytical spectra in heritage azulejos as beacons of provenance

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SUMMARY: A research group including Museu Nacional do Azulejo (Portuguese National Azulejo Museum), Laboratório Nacional de Engenharia Civil and Laboratório HERCULES of University of Évora joined forces to elucidate the beginnings of the production of faience azulejos in Lisbon during the mid-16th century. During the first part of the study SEM-EDS and XRF spectra were acquired from glazes and ceramic bodies of azulejos sampled from panels, single tiles from the Museum collections and archaeological finds. By comparing spectra obtained on significant areas it is possible to obtain a glimpse of affinity or of dissimilarity pointing to a similar or to a different officinal origin. In many cases such a preliminary approach is very important to orient the selection of cases for more detailed analytical examination. However, for that purpose it is necessary to consider the spectra taking into account the material, for instance considering what may be important and what should best be discarded and why, for the purposes of such a screening. This communication addresses the subject through exemplary cases.

KEY-WORDS: Provenance studies; majolica; archaeometry; tiles, XRF, SEM-EDS.

INTRODUCTION

Studies of provenance of ceramic items or most other heritage specimens usually rely on analytical quantification followed by some form of “objective” decision-making to aggregate clusters of (hopefully) objects with the same provenance. Such studies often produce an impressive array of instrumental results, out of which it is increasingly difficult to make sense, even when the researcher is personally certain that there must be some way to extract a measure of reasonably trustworthy conclusions from the data. Looking for objectivity to base the conclusions the researcher will apply a number of numerical methods some of which stemming from the statistical treatment of the data.

Three methods often encountered are the use of ternary plots, the calculation of Euclidean distances followed by an interpretative visualization through dendrograms and principal component analysis (PCA) or one of its specialized derivatives. In PCA an imaginary space of as many dimensions as one has variables is represented and the quantitative result of each item is

set as a single point in a system of orthonormal axes in that space. Then the mathematical approach will determine a direction in that space onto which the spread of the points will have a maximum extension, and other directions, orthogonal to the first, corresponding to the second, third, etc largest spread. All the points are now projected into a new reference system of axes following those directions and (hopefully) points that might otherwise be near one to the other or even superimposed are now spread well apart making it possible to define clusters (figure 1).

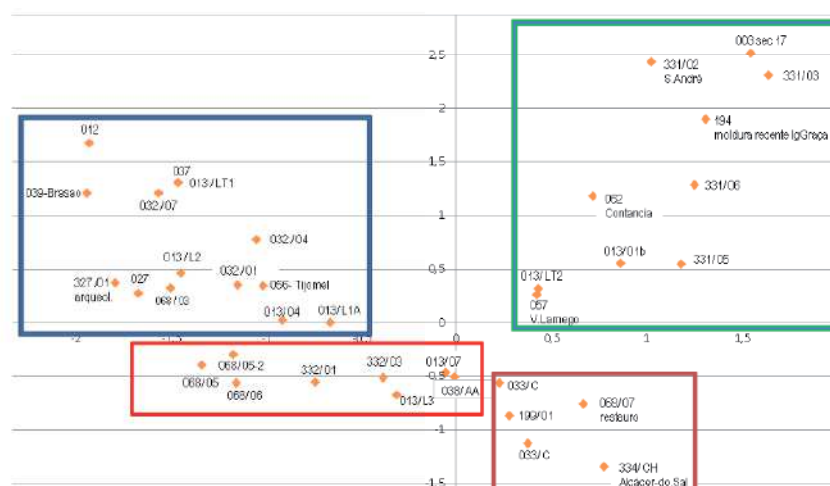


Figure 1: Tentative clustering after a Principal Component Analysis of azulejo ceramic body compositions defined by their contents in seven different chemical elements.

PCA is a powerful and impressive tool and its results can be very elucidative. However, there is a catch in all those methods and it is the same in all statistical decision-making: at some point the researcher is always called to make a subjective decision. Why exclude from a cluster another result very near its limits in the graphical representation? How to know whether a point included in a boundary is not actually an outlier from some other different cluster? Or, in general, what are the critical values of the test statistic that separate the rejection from the non-rejection region?

We are not going to propose a solution ruling away all subjectivity. On the contrary, we shall discuss another subjective approach to help cluster glazed ceramic specimens based solely on spectroscopic spectra but applicable to other analytically complex objects. A compelling feature is that it does not require quantification, resorting directly to the graphical spectra themselves and the subjectivity derives from the need to verify whether the closeness between spectral results is sufficient to grant tentative clustering. In this method special attention should be placed on using the same analytical equipment and the same conditions (e.g. the same acquisition time) to acquire the spectra and used under the same conditions. If conditions differ, they may affect the relative size of peaks and the evenness of the baselines making comparability more difficult.

Glazed ceramics offer at least two different spectra for comparison, those acquired from the glaze and those acquired from the ceramic body. Information from both can be useful to attribute the geographical their provenience. A similarity of ceramic bodies might suggest a same geographical origin and a similarity of glazes might point to the use of a same formulation or workshop.

But spectra are not just graphs in an x-y coordinate system - peaks have a chemical meaning and can be translated into elemental contents if one knows the material and has the means for that second step. In all cases they offer a wealth of information but it is necessary to know how to interpret them and for that it is necessary to have knowledge about the materials, the analytical techniques used, and the counterparts of the analytical results.

In this paper, we discuss the elemental nature of glazes and ceramic bodies and explain their consequences on the approach proposed. Although we have also successfully used this approach with spectra obtained on sites with an energy-dispersive X-ray fluorescence (ED-XRF) portable analyser, we shall exemplify it solely with spectra acquired by scanning-electron microscopy coupled with energy-dispersive spectroscopy (SEM-EDS). The examples pertain to our on-going research with faience azulejos.

THE MATERIAL OF FAIENCE AZULEJOS

The glaze

Faience azulejos (figure 2) are a layered material in which a previously fired ceramic base (the ceramic body) is overlaid by a glass layer eventually painted with pigments able to withstand temperatures of over 1,000 °C and then fired a second time. During this second firing, pigments become encased in the glass, which becomes a glaze by connecting to the ceramic body in a very durable manner, as long as there is a degree of compatibility between them.



Figure 2: Part of an azulejo panel at Igreja da Graça in Lisbon. At the corners where the glaze detached, the underlying cream or reddish ceramic body became visible.

The main components of a tin glaze, traditionally used in faience azulejos, are, by atomic number (Z): sodium (Na, Z=11); magnesium (Mg, Z=12); aluminium (Al, Z=13); silicon (Si, Z=14); phosphorus (P, Z=15); potassium (K, Z=19); calcium (Ca, Z=20); titanium (Ti, Z=22); iron (Fe, Z=26); tin (Sn, Z=50); and lead (Pb, Z=82). Of those, the main elemental components of the glaze are Si (the amorphous glass is formed from silica), Pb (a fusing agent that lowers the fusion temperature of silica from ca. 1900 °C to about one third of that value), and K or Na or both (also fusing agents that are incorporated into the glass structure altering the viscosity of the molten glass and its rate of retraction during the cooling phase). The content in Sn derives from the use of tin oxide as opacifier, turning the otherwise translucent glaze into an opaque white “canvas” over which a decoration may be painted.

Any other elements “found” in the glaze with the average XRF or EDS instruments must be viewed with the utmost caution particularly when one presses a button and accepts flatly an

instrumental quantification. For instance, the presence of sulphur ($K\alpha_1$ 2.309 and $K\beta_1$ 2.465 emission lines) in glazes is usually an artefact resulting from confusion with peaks of lead ($M\alpha_1$ 2.342 and $M\beta_1$ 2.444 emission lines) and there are also a number of mystifying artefact peaks resulting from the elements constituent of the analytical instrument or unavoidable atomic phenomena such as escape and sum peaks. However since the method of directly analysing the spectra profiles is purely comparative, one do not have to be much concerned with recurring misidentifications or repetitive technologic artefacts.

We should have in consideration that from the elements mentioned above, the size of Sn peaks or the resulting quantifications by non-destructive XRF are not to be trusted unless the acquisition area is very considerable. Sn crystals form during firing of the glaze and often aggregate in a manner that, with small measuring areas as imposed by the size of most samples, the acquisition may fall on an area with no Sn at all or, on the contrary, where a high content is concentrated. Sn ($L\alpha_1$ 3.444 and $L\beta_1$ 3.663 emission lines) also interferes with the main peak that should be used to identify Ca ($K\alpha_1$ 3.692 emission line), rendering this element much less valuable in the characterization of glazes than it is in ceramic bodies from which Sn is absent. Often it is better to do without considering the low Ca content at all.

Sometimes a comparison of spectra gives an hypothetical insight into workshop practises: i) a high Na content may mean that sea salt was added to the glaze; ii) relatively high contents in K and Al together suggest an addition of K-feldspars; iii) P and Ca together suggest an addition of bone dust, maybe to increase the opacification iv) concomitantly high contents of Mg, Al, K and Ca may mean that the workshop master added some clay to the glaze components maybe in hopes of improving its compatibility with the ceramic body.

An important reminder is that when the glaze is fired over the ceramic body and the surface of the ceramic is partially digested by the molten glaze [1] many alien elements, and also more Na, Mg, Al, P, Ca, Ti and Fe are incorporated into the glaze (figure 3). Ti, Fe and other minor-content elements may also be introduced as contaminants e.g. of the sand. Pinpointing a geographical origin from the glaze may be possible if there is information on recognizable patterns in the composition in major elements but resourcing to low-content elements may be problematic because lead and tin oxides were usually not of local origin and a number of sources could be used for the alkali oxides, all of them affecting the chemical composition as far as minor or trace elements are concerned.

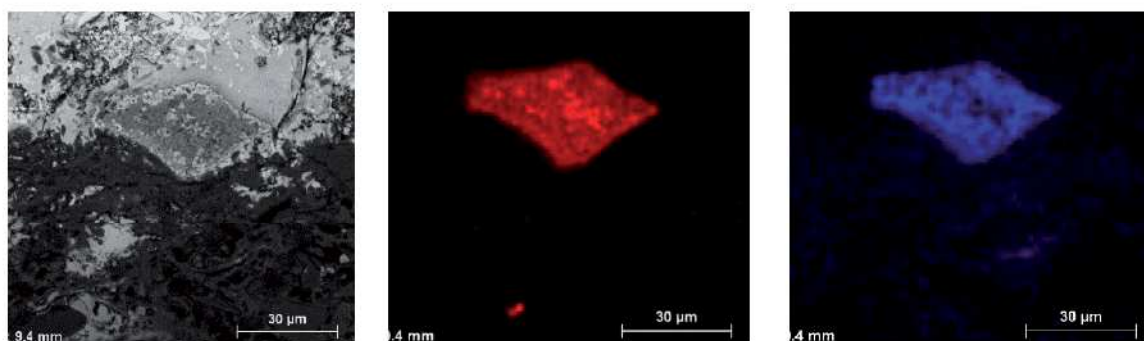


Figure 3a, b, c (left to right): A crystal of ilmenite ($FeTiO_3$) in the process of detaching from the ceramic body and interacting with the glaze. 3a) BSE image of the glaze-ceramic body ceramic body interface; 3b) map of Ti; 3c) map of Fe

The ceramic body

Analysing the ceramic body is rather more complicated than the glaze because the raw materials are often sedimentary marls where many chemical elements are found, including rare-earths brought (in the case of Lisbon) by the rivers from the granite hinterlands of the Peninsula. The major elements routinely found are the main components of aluminium silicates (Na, Al, Si and K) plus P, Ca, Mg, Ti and Fe. Given certain technological procedures, the ceramic body may also incorporate a significant amount of Pb (in some cases up to 8%), particularly in the region nearest to the interface with the glaze. While analysing the ceramic body Pb should be neglected when comparing spectra because of its space-dependence but the fact that a high content of Pb is present may itself be a relevant piece of information on the technology used.

Of the utmost importance when studying the provenance of glazed ceramics is the notion of where the materials were obtained from. For instance due to the good sources of marl clays and sand close to Lisbon it is highly probable that they were obtained locally. In other cases such as with the tiles from Flandres, information exists about the import from other countries of their clays and marls and this information should be therefore taken into consideration ⁽¹⁾.

INSTRUMENTAL MEANS AND SOFTWARE

The direct comparison of spectra can be applied with any instrumental means returning reproducible area or volume compositional spectra, although some technologies are more appropriate than others for the specific purpose pointed here. Energy-dispersive X-ray fluorescence (ED-XRF) is better adapted for the quantification of elements starting with $Z=13$ (aluminium) and therefore misses or is not sufficiently accurate in the cases of $Z=11$ (sodium) and $Z=12$ (magnesium) which are important for clustering, as will be seen. However even XRF spectra obtained with hand-held analysers from the face of tiles can be used, and we have applied that method in a preliminary study (unpublished) aimed at tentatively selecting the cases that would be more thoroughly studied within the present research project. During that preliminary phase we observed that a good fit of replicated XRF surface spectra obtained from white areas of different 16th century azulejo panels was a quite reliable means to pinpoint possible common workshop provenances. The technology has the advantages of application on site and of being wholly non-destructive.

SEM-EDS, with its confirmed repeatability in the quantification of low- Z elements such as Na, Mg and Al, was, however, the preferred technique. However, for it to be useful in graphical comparisons it is very important to consider the peaks of several low-content elements in detail and therefore we should depict the SEM-EDS spectra in a logarithmic scale.

Azulejo panels, loose tiles and fragments were sampled by removing small fractions of the glaze with ceramic body attached. All samples were identified with a code of the type "Az abc/de, in which "abc/de" is a unique alfa-numerical code. The samples were stabilized in resin, cut to obtain a flat section, polished for SEM observation and analysed with EDS.

SEM-EDS observations and analyses were made at the HERCULES Laboratory in Évora using a HITACHI 3700N SEM coupled to a BRUKER XFlash 5010 EDS. The specimens were uncoated and the selection of areas was made in back-scattering mode (BSE) with air in the chamber at a pressure of 40Pa and at an accelerating voltage of 20.0 kV. The acquisition of spectra was done in the same conditions with the detector set at ca. 8 mm distance from the surface of the specimens.

The back-scattering mode relies on electrons from the incident beam that are back-scattered out of the specimen without losing their initial energy. Since heavy elements (those with higher atomic numbers in the Periodic Table) backscatter more electrons than light elements (those with low atomic numbers), areas with heavier elements in their content appear brighter (or "whiter")

in a back-scattered image and thus give information about the composition of the specimen under observation. Since the glaze of an azulejo has a high lead-content and the tin oxide opacifier or the yellow pigments have a still overall higher atomic mass, their image is much whiter than the image of silica or feldspar inclusions in the glaze, or the ceramic body that contain mostly low-atomic weight elements such as silicon, aluminium, potassium and calcium. BSE imaging is therefore ideal to select areas of the glaze as free of inclusions as possible as well as areas of the ceramic body where the glaze has not penetrated.

All EDS spectra acquired were saved in XY-ASCII format (.spx file extension), opened and saved as a graph with the Artax™ spectral analysis PC software as used with the Bruker Tracer III and other XRF analysers of the same brand. All other alternatives are acceptable as long as they allow the saving of an EDS spectrum on a logarithmic scale.

OBTAINING AND INTERPRETING SPECTRA

The glaze

Figure 4 depicts the section of a late 16th century or early 17th century azulejo ready for the acquisition of a compositional spectrum of the glaze by EDS. The rules when choosing the area are three:

- avoid, if possible, areas where the glaze is not perfectly clear (avoid e.g. pigmented or corroded areas);
- avoid as much as possible all inclusions (the darker inclusions are grains of sand and feldspars and if a significative percent of the test area includes e.g. grains of sand that did not take part in the formation of the glaze, then the acquisition will lose reproducibility and any clustering may be less reliable for that reason);
- avoid using point quantification but always area quantification- try and choose a significative area. An area of ca. 0.04 sq mm (200 x 200 μm) or larger would be excellent but areas equivalent to 100 x 100 μm are often satisfactory in a clean glaze- “satisfactory” means that if the acquisition is repeated in a different day, on a different area of the same glaze, with the same instrument within the same operational parameters, the result will be practically the same (“practically the same” being judged by experience, given the uncertainties involved in the acquisition procedure).

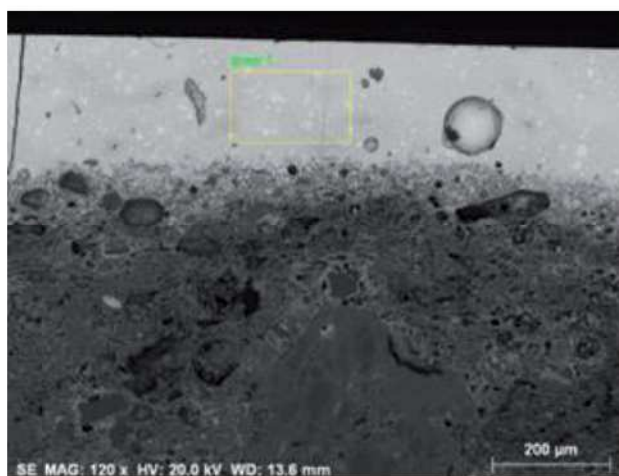


Figure 4a, b (left to right): Tile Az008 and selection of an area ca. 200 x 150 μm for EDS acquisition. Albeit including some tin crystal agglomerations, the selection avoids the darker inclusions and is satisfactory because the tin content will not be used anyway.

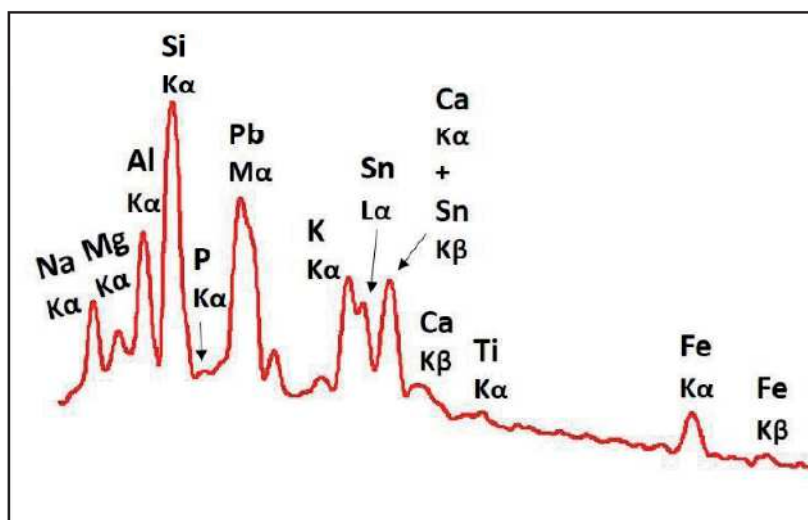
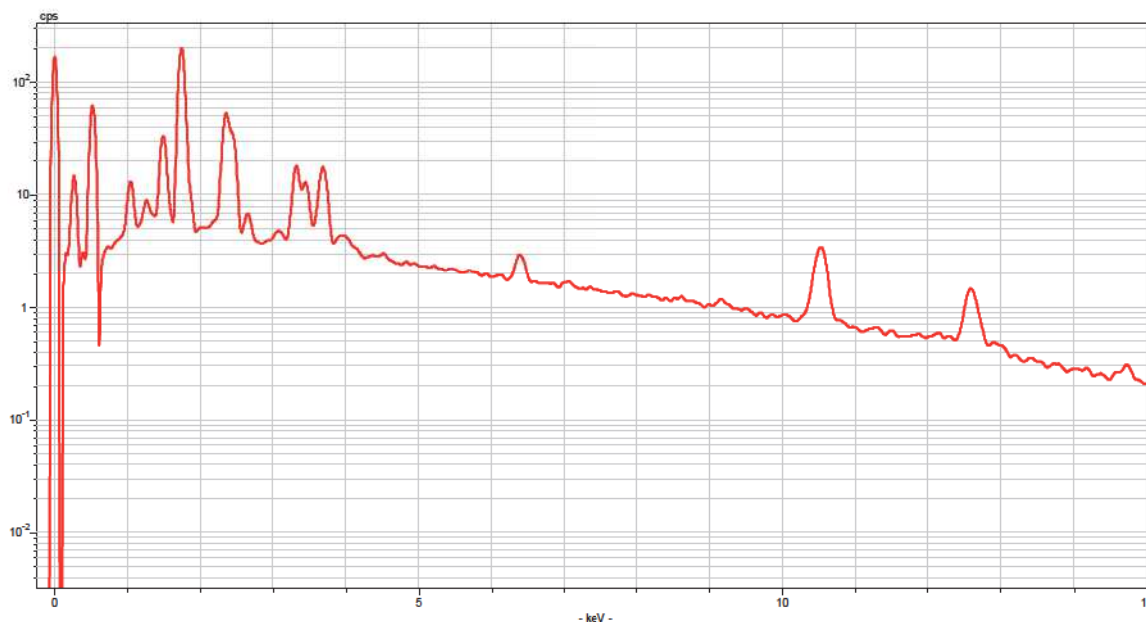


Figure 5a, b (top to bottom): 5a Image of the EDS spectrum of the glaze of a 17th century tile (Az008) from Lisbon workshops; 5b) Span of interest in the spectrum with peaks identified (Sn and Ca will usually not be used).

Figure 5a: depicts the spectrum acquired after smoothing (not strictly necessary) and exporting as indicated before. The relevant part of the spectrum with the peaks that define the elements of interest to our discussion are identified in figure 5b. As explained before, Sn and Ca peaks will not be used in our presentation.

The ceramic body

Figure 6 depicts the section of a specimen obtained from tile Az031A, a fragment of an azulejo from the 1558 Antwerp panels of the Palace of Vila Viçosa, ready for the acquisition of a compositional spectrum of the ceramic body by EDS. The rules when choosing an area are set by the same concerns as for the glaze. Here we should avoid all larger inclusions (small pebbles included in the ceramic bodies are usually no larger than a length of 300 μm in Portuguese azulejos of the late 16th century and the Flemish samples are similar). The size of the area is determined by the size of the inclusions that cannot be avoided. We did a blind test by acquiring spectra for three 500 x 500 μm ceramic body areas of a Portuguese ca. 1570 azulejo without concern for any inclusions and the spectra superimposed almost perfectly. So:

- avoid, if possible, areas including inclusions any of which represents more than ca. 5% of the full area;
- avoid areas too near the glaze-ceramic body interface where the lead may have penetrated (noticeable by the incipient formation of glass or the strikingly lighter colour of the boundaries of inclusions when seen in the back-scattered electrons mode of the SEM);
- never use point quantification but always area quantification- try and choose a significant area. An area of ca. 500 x 500 μm would be excellent but areas equivalent to 300 x 300 μm or even less are often satisfactory.

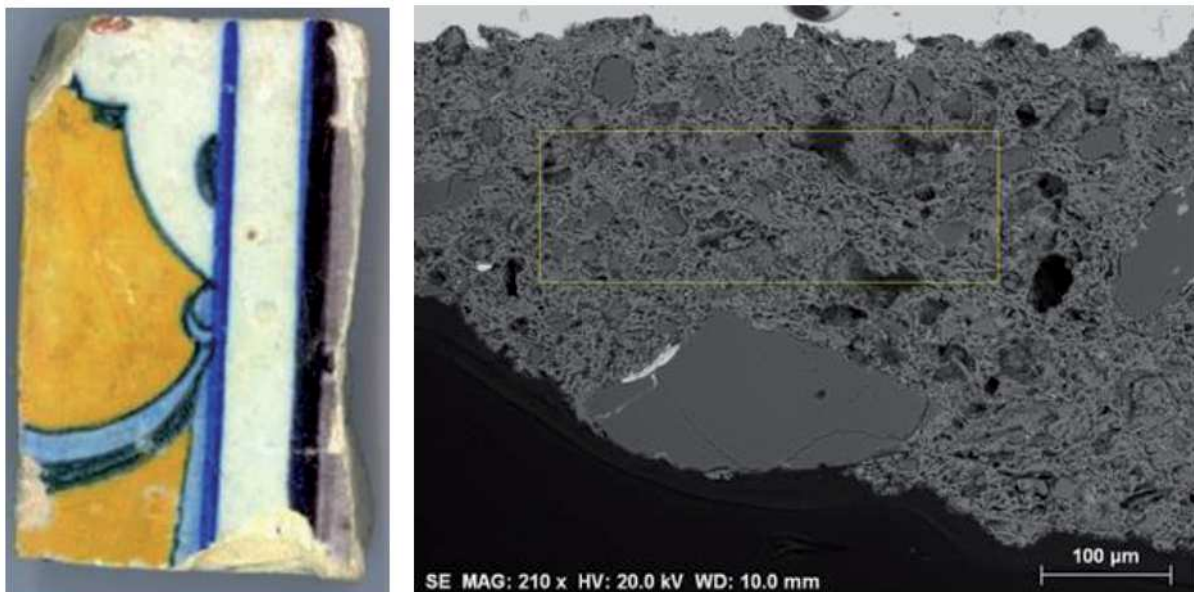


Figure 6a, b (left to right): Tile Az031A and selection of a ceramic body area ca. 350 x 110 μm for EDS acquisition. Albeit including some tiny inclusions, the larger ones were avoided.

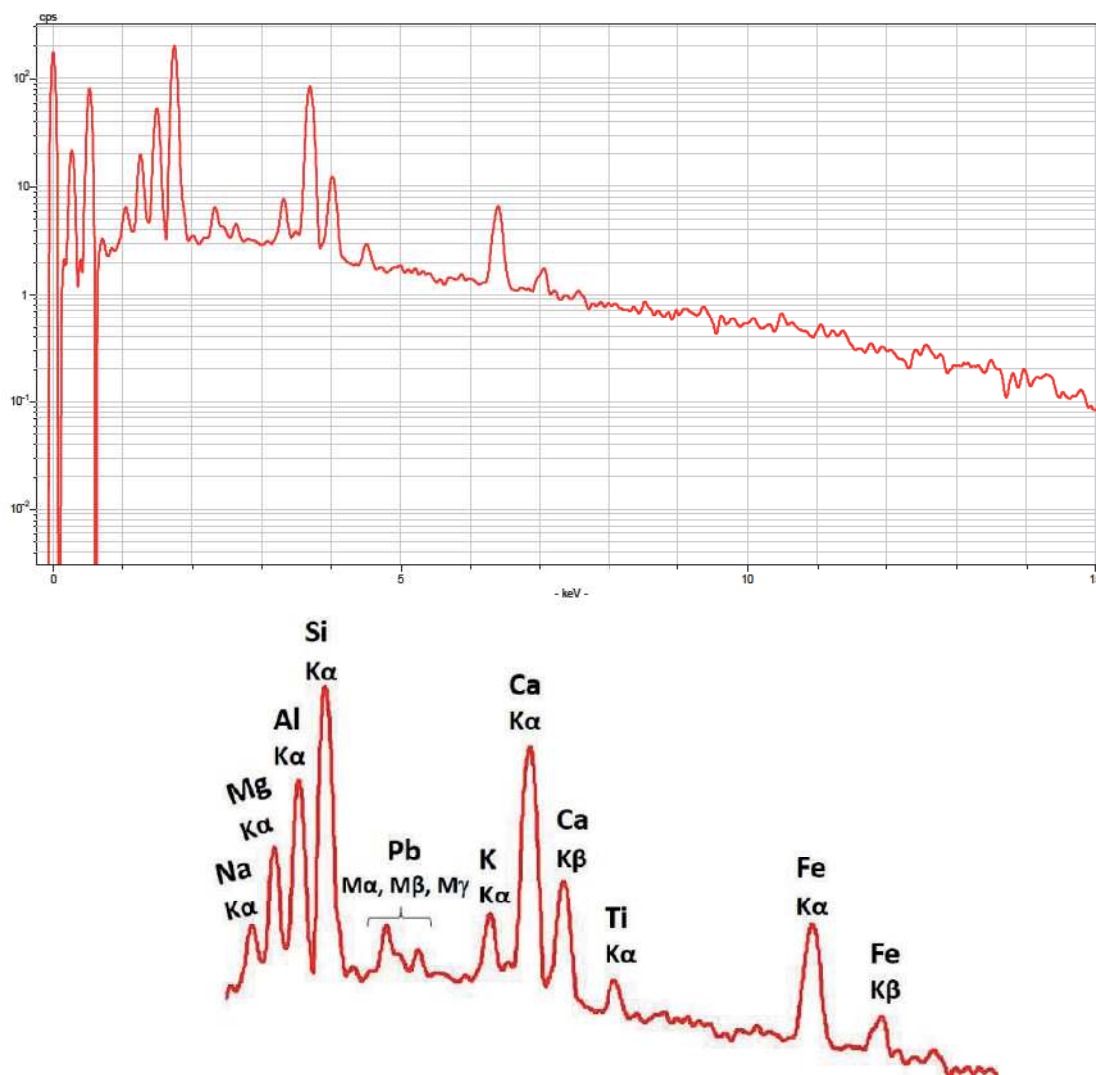


Figure 7a, b (top to bottom): 7a) Image of the EDS spectrum of the ceramic body of a 1558 tile from the workshops of Antwerp (Az031A); 7b) Span of interest with peaks identified. The region marked Pb includes several transitions of the element and should not be considered since it results from the penetration of the glaze into the ceramic during the firing process.

USING SPECTRA

Figure 8 depicts two different Hispano-Moresque tiles (Az65 e Az66) with no relation between them except that they are in the archives of the *Museu Nacional do Azulejo* without a register of the site from which they were removed (the museum was formed much after the tiles were removed from convents and churches sold to private parties in the mid-1800s) and are thought to count amidst the latest to have been imported from the workshops of Seville. The spectra of the two glazes are depicted in figures 8a1 and 8b1. Figure 8c depicts both spectra superimposed. For this purpose, they were made comparable by exactly adjusting the height of the Si peaks and since the baseline differed as a consequence of the varying duration of both acquisitions, the blue spectrum of Az066 was sectioned in two halves just after the Pb peak and without any alteration of the scale the baselines were brought to coincide as closely as possible. After some experience

by the reader about the consequences to spectra of the variability of the glaze compositions, a close observation of figure 8c will strongly suggest, notwithstanding the relevant different in the K contents, that unless direct proof on the contrary (e.g. from historical sources) is available, both tiles should be tentatively clustered together as coming from the same production centre and maybe even the same workshop.

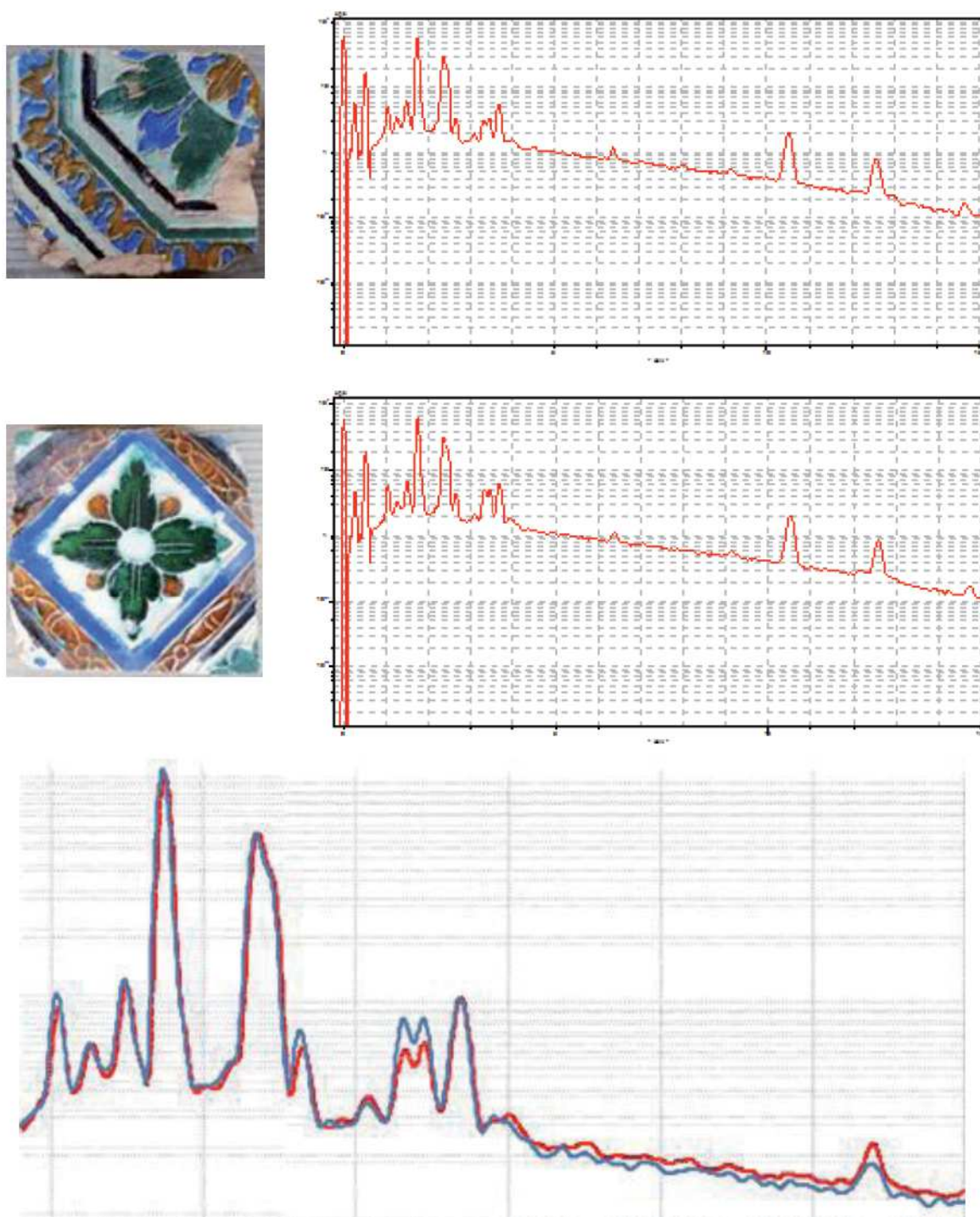


Figure 8 a, a1, b, b1, c (left to right and top to bottom). 8a, a1) Sample Az065 and glaze EDS spectrum. 8b, b1) sample Az066 and glaze EDS spectrum. 8c) EDS Spectrum of Az066 (blue) superimposed over Az065 (red).

On the other side, EDS spectrum of sample Az065 can be compared with the spectrum of Az008 in figure 5a to verify that they are indeed different (Figure 9).

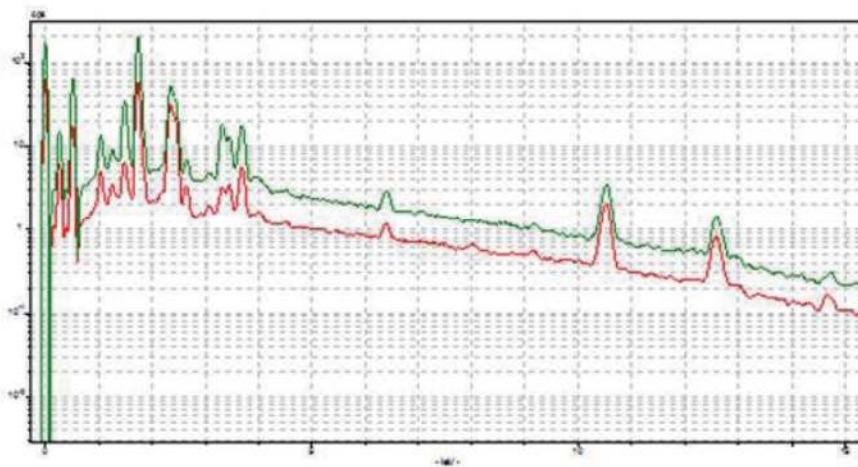


Figure 9: EDS spectra of samples Az065 (red) and Az008 (green)- the peaks of Si have been equalized and, as can be seen, the peaks of Al, Pb and K differ substantially.

CONCLUDING REMARKS

In this communication, we discuss material aspects of glazed ceramics having a counterpart in SEM-EDS spectra and how they should be acquired, interpreted and possibly used as the first stage of a study on provenances without resorting to elemental quantification.

The ceramic bodies of azulejos are made, in most cases, from raw materials locally sourced but clays from the same geologic strata could be used by many workshops. The glazes seem to be more promising whenever it is desired to identify specific workshops or, at least, technological circles sharing the same technology.

This is not a solve-all method but rather one that has borne fruit for an initial screening and the formulation of arguable hypotheses as to the possible clusters. The full method proceeds with a study of the morphology of the glazes, their composition as pertains the Si/Pb ratio, the ceramic bodies again based on the simple but highly significant ratio Ca/Si and the mineral inclusions found in them. But that is a subject needing a few more papers to develop...

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Notes to the text

1. A marl compatible with the glaze is not available everywhere, nor easily recognizable when available. For a time, manufacturers were not aware that they could improve the characteristics

by mixing several clays and adding calcite and sand. In the case of Flanders, local researcher Kate van Lokeren Campagne has found proof that for a time marl was even imported from England [2]. But in the case of Lisbon and Seville there were ample sources of adequate marl available locally and they had been known and used well before faience azulejos were first manufactured.

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