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**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.**

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Abstract

This work shows the first analytical results obtained by X-Ray Fluorescence (XRF) (conventional and 3D) and Scanning Electron Microscopy with Energy Dispersive System (SEM-EDS) on original Portuguese ceramic pieces produced between the 16th and 18th centuries in Coimbra and Lisbon. Experts distinguished these productions only based on the color, texture and brightness, which originates mislabeling in some cases.

Thanks to lateral and spatial resolution in the micrometer regime, the results obtained with μ -XRF were essential in determining the glaze and pigment thicknesses by monitoring the profile of the most abundant element in each “layer”. Furthermore, the dissemination of these elements throughout the glaze is different depending on the glaze composition, firing temperature and on the pigment itself. Hence, the crucial point of this investigation was to analyze and understand the interfaces color/glaze and glaze/ceramic support.

Together with the XRF results, images captured by SEM and the corresponding semi-quantitative EDS data revealed different manufacturing processes used by the two production centers. Different capture modes were suitable to distinguish different crystals from the minerals that confer the color of the pigments used and to enhance the fact that some of them are very well spread through the glassy matrix, sustaining the theory of an evolved and careful procedure in the manufacturing process of the glaze.

Keywords: Portuguese ceramics, Polychrome glazes, Micro X-Ray Fluorescence, Confocal system, Scanning Electron Microscopy.

1. Introduction

Glazed ceramics are very challenging objects of study. By naked eye inspection, there are several characteristics about a certain piece, which one can extract immediately: the brightness of a glaze, the color palette, among others. Although these characteristics give hints about how the piece was produced, they are not sufficient to characterize it.

To extend knowledge about the manufacturing procedures involved in the glazing and surface decoration is the main goal of this investigation. The items, which served as object of study, were originally produced between the 16th and 18th centuries in two main centers in Portugal: Coimbra and Lisbon.

A glazed ceramic object can be divided in three main parts: (1) the ceramic support, (2) the glaze and (3) the surface decoration (Fig.1). The areas marked in red correspond to the interfaces color/glaze and glaze/ceramic support. Interface is defined here as an area where a mixture of two distinctive “layers” can be found. The surface decoration can be more or less dispersed within the glassy matrix, depending on the kind of glaze (in terms of chemical composition) and/or the firing temperature used. Information about the historical background of the pieces as well as the chemical composition that characterizes each part, including the pigments composition, is available in previously published works [1, 2].

According to the limited documentation about the possible manufacturing procedures involved in Portuguese glazed ceramics based on historical facts [3], several opinions have been developed about the raw materials, the glaze and color application as well as the firing stages and temperatures used at different centers of production, such as Coimbra and Lisbon.

It is known that Coimbra was a less wealthy center of production, when compared to Lisbon and, hence, the expensive raw materials were spared as much as possible. Therefore, one would find a broader range of elements used to confer the intended color. One example is given by the blue pigments, in which the source of cobalt (Smalt: a ground blue containing Co) is the main and expensive element. In the samples from Coimbra, additional elements can be found, such as Mn to spare the cobalt source. For that reason, in the samples from Coimbra the blue color has a kind of old-“pinkish” tone mixed to it. Further assumptions are related with the history of the country itself, particularly that Lisbon had more influence from the Muslim occupation than Coimbra, so the recipes may have kept rather different from each other [4].

There are several possibilities to obtain the final piece. In all cases, a firing process for the ceramic support took place and then, it may have happened just one firing process for the base glaze together with the decorative motives or a separate firing process for the decorative motives, after the firing for the base glaze. [5]. So, the piece may have been submitted to either two or three firing processes.

Regarding this study, we are interested in the interfaces: surface decoration/glaze and glaze/ceramic support, which helps us to distinguish differences in the manufacturing methods, as well as the chosen raw materials for the glaze formation in both production centers. Hence, a detailed study of the elemental profiles throughout the interface areas was carried out, by using laboratory X-Ray Fluorescence Spectroscopy techniques (conventional XRF and 3D Micro-XRF). To complement such qualitative data, elemental content of the surface decoration as well as the glaze beneath/within were also obtained by means of Scanning Electron Microscopy with an Energy Dispersive Spectroscopy system (SEM-EDS).

2. Experimental Methodology

A set of fragments from pieces originally produced in Coimbra (11 samples) and in Lisbon (9 samples) (fig.2) were collected for investigation. The art historians made the assignation to Coimbra and Lisbon on a stylistic basis. All of the fragments were cut with a diamond saw and polished in order to obtain flat cross sections for SEM and μ -XRF analyses.

The experimental approach was the following:

i) Conventional XRF measurements were carried out with a 45° tube-detector geometry setup enclosed in a chamber submitted to a 10 mbar vacuum, belonging to the Atomic Physics Centre of the University of Lisbon, and fully described in [1,2]. The X-ray tube is from Oxford Instruments (); the polycapillary optics are from XOS (New York, USA); and the detector is a Vortex-60EX from SII NanoTechnology USA Inc. (California, USA). The measurements were performed using a collimator, which allows an excitation area of about 1.2 mm², when the sample is placed at a 1.5 mm distance from the Kapton window, through which the excitation and fluorescence beams pass. The operating conditions were 50 kV and 1 mA, in order to excite the K-lines of such elements as Sn and Sb. Each spectrum was acquired for 300 s. Spectra were collected using a multichannel (4096 channels) and recorded both in binary mode and in ASCII data mode in order to perform their evaluation using the PyMCA software code [6].

With this spectrometer, measurements were performed perpendicular to the surface of each sample on each color and on the glaze. By using the collimator, a large area of analysis is obtained, which is more representative of the whole sample. Decoration and glaze areas are in all cases larger than 1.2 mm^2 .

The purpose of this investigation is to have intensity ratios for specific elements, which will provide us fingerprints of both production centers.

ii) *3D Micro-XRF* measurements were carried out with a tabletop setup from the Institute for Optics and Atomic Physics at the Technical University of Berlin. This system is a common development with ifG (Institute for Scientific Instruments). The X-ray tube is from Rtw Röntgen-Technik (Neunhagen, Germany); the polycapillary optics are from IfG (Berlin, Germany); and the detector is from Bruker nano (Berlin, Germany). The leading feature of this system is the ability to perform depth-resolving analysis as is fully described in [7]. Due to the high amount of lead in the samples, strong absorption effects took place. This leads to an information depth of several tens of micrometers, only, which prevents further depth resolution. Nevertheless, we took advantage of another feature of the confocal geometry, which is probing site selection. The probing volume created in the confocal geometry allows selective analysis in a certain volume in the micrometer regime, which reduces the amount of detected scattered radiation considerably. Therefore, scans just on the surface of the polished cross section of each sample were performed, in steps of $5 \text{ }\mu\text{m}$ (each during 60 s) through a length that varied according to the thickness of the relevant part of the sample. The operating conditions were the maximum for this system: 50 kV and $600 \text{ }\mu\text{A}$. The Full Width at Half Maximum (FWHM) of the probing volume obtained for Cu-K α (8.04 keV) was approximately $42 \text{ }\mu\text{m}$.

In addition to the measurements in confocal geometry (3D), Micro-XRF measurements (2D – with lenses in the excitation path only) were carried out at the same cross sections. Comparing scans along the same cross section obtained by the two methods, the confocal geometry enables a better resolving of the elemental profiles along the cross sections, as is shown in fig. 3. In this figure we see two scans performed along the cross section of the same sample (C29) capturing the pigment (purple), glaze and ceramic support, in 3D mode (a) and in 2D mode (b). In 3D mode, we can clearly see that there is an interface layer between the pigment and the base glaze, while with the 2D mode the transition is not so clear. This may lead to wrong conclusions about the pigment application on the glaze (see “Results and Discussion” section).

With these results, we are able to monitor the profiles of certain elements through the interfaces color/glaze and glaze/ceramic support. It enables conclusions about the diffusion ability of elements, which give color, and about the fusibility of the glaze for these elements. These results also contribute to revelations on firing temperatures used in both manufacturing centers.

iii) *Examinations by SEM* were carried out with a Hitachi S4100 system from Bruker (Tokyo, Japan), equipped with Quantax 400 EDS system of Bruker AXS (XFlash Silicon Drift Detector) (Berlin, Germany). A 15 kV acceleration voltage and a current intensity of 32 μA were applied. The chemical information by EDS was taken from an area of $300 \times 400 \mu\text{m}^2$ selected regarding its homogeneity and lack of voids, with spectrum acquisition times of minimum 60 s. The semi-quantitative results were based on a peak-to-background ZAF evaluation method (P/B-ZAF), being ZAF a matrix correction, mainly based on analytical expressions for atomic number (Z), X-ray yield, self-absorption (A) and secondary fluorescence enhancement (F), provided by the Esprit software from Bruker AXS microanalysis. With these measurements, we obtain the distribution and morphology of certain compounds, which are crucial in the manufacturing process determination. In addition, the composition of color layer and glaze were obtained with the *EDS* coupling unit.

3. Results and Discussion

The results we present, are representative of the whole set of samples analyzed from both production centers. The measurements performed with all methods were carried out in all samples, and repeated in at least three spots.

3.1. The (white) glaze

In a common way, the glazes from both production centers belong to a class of “tin opacified lead glazes”, in which the main components are SiO_2 , PbO and SnO_2 . What differentiates the productions is the ratio between the amounts of these and other important oxides, such as Na_2O , K_2O and CaO .

With SEM-EDS, the uniform distribution of cassiterite crystals (SnO_2) throughout the glazes was evident. Tin and lead were usually burnt together and then added to the glaze. This way, tin oxide was first dissolved in a silica and lead vitreous matrix and during the firing process of the glaze, at a temperature of 650 $^\circ\text{C}$, it recrystallized in the cassiterite structure (SnO_2). Once in this form, SnO_2 becomes insoluble in the glaze [8].

As an example, fig. 4 displays an image taken perpendicular to the surface of the glaze (not colored) from the pieces (a) C41 from Coimbra and (b) AZLX1 from Lisbon. One can see how well distributed the tin oxide crystals are within the glassy matrix. Their length varies between 0.5-0.8 μm for the former (a) and between 1-2 μm for the latter (b). Furthermore, the EDS results (from SEM-EDS) in table 1 reveal some differences between the two production centers worth to discuss. The glazes produced in Coimbra reveal relatively high amounts of K_2O (8.1 – 9.3 wt %) and CaO (3.1 – 3.2 wt %) when compared with the ones from Lisbon (K_2O : 4.3 – 5.8 wt % and CaO : 0.8 – 1.1 wt %). This in addition to the amounts of Na_2O (0.8 – 1 wt %) and PbO (40.1 – 40.5 wt %) in Coimbra compared to the ones in Lisbon (Na_2O : 3.5 – 4.2 wt %, and PbO : 45.5 – 45.9 wt %), leads us to the preliminary conclusion that the glazes of Lisbon have more fusibility than the ones from Coimbra. The higher amounts of Na_2O and PbO indicate that the melting point of the glaze is lower than the ones where higher amounts of K_2O and CaO are present. It is already known that Na and Pb compounds, acting as dominant fluxes in the glaze, lower the fusion temperature [9].

Other significant results are the ones obtained with the cross section lateral scans performed with the 3D Micro-XRF setup. Figure 5a and b exhibit the profiles for one glaze from Coimbra (a: C41) and one from Lisbon (b: AZLX1), respectively, for the elements Pb, Sn and Ca. Scans performed in all the pieces from Coimbra showed that the glaze thicknesses vary between 150 – 350 μm , whereas the ones from Lisbon vary between 300 – 400 μm , by monitoring the energy line of the element, which mainly characterizes the glaze: $\text{Pb-L}\alpha$ (10.54 keV). These scans also support the results obtained by SEM-EDS: tin (Sn) is well distributed within the glassy matrix and the glazes from Coimbra reveal a higher concentration of Ca than the Lisbon ones, when compared to the other elements in the glaze of the same sample. Together with the images obtained by the microscope inside the confocal system, one can easily observe a very well defined interface glaze/ceramic support, being approximately 50 μm for the Coimbra sample and smaller than 30 μm for the Lisbon one.

3.2. Colors and pigments

Concerning polychrome glazed ceramics, some facts must be taken into account. The colors employed on the pieces were usually obtained by metallic oxides, which could have been used in a “pure” state or in a mixture called *frit*, which is a pre-melting of the pigment together with fluxes, such as Pb, Na, and sometimes even Sn (to make it more

opaque). After cooling down, this mixture (*frit*) was grinded until a powder was obtained and then applied over the “base glaze”. The brilliance or opacity and the migration ability of the elements, which grant the color, are some factors that help assigning the way the pigment was applied onto/within the glaze [10].

3.2.1. Blue

In general, blue is the most common color in glazed ceramics. The decorative motives as well as the tones used, make the difference. Measurements performed with the conventional XRF setup gave us the possibility analyzing bigger areas (due to the collimator) of the blue color from both production centers. These analyses were performed on the surface and, in order to identify the spectra from the blue color, spectra from the glaze next to these areas were subtracted. The typical elements detected were Fe, Ni, Co and As (Smalt) with the presence of Mn and Ba in certain cases mainly from Coimbra, as it was already discussed [2].

In Fig. 6 we can observe: a) comparison between spectra obtained on the blue color and the respective glaze of a sample from Coimbra (C34); b) comparison between spectra obtained on the blue color and on the respective glaze of a sample from Lisbon (AZLX1); c) comparison between the spectra obtained for the blue colors in Coimbra (C34) and Lisbon (AZLX1) and d) intensity ratios for the elements associated to the blue pigment (Smalt). From Figs.6a and 6b, we can see the elements that are associated to the blue color: Mn-Fe-Co-Ni-As are free from interference coming from the glaze, except Fe, which is also present in the glaze. Fig. 6c shows that the samples from Coimbra have higher content of Mn and Ba and less of Co than the ones from Lisbon, which supports the assumption that Coimbra was a less wealthy center compared to Lisbon. However, as we can see from fig.6d not only the ratios Mn/Co are higher for Coimbra, but also the ratios Fe/Co, due to less pronounced values for Co in these samples.

In addition to these results, we present also cross section scans by 3D μ -XRF together with pictures taken with the microscope. Figures 7a and b show an example of the different profiles obtained for a fragment from Coimbra (a: C34) and one from Lisbon (b: AZLX1). Due to the images provided by the microscope we clearly see two main differences: 1) the glaze of the piece from Coimbra is thinner ($\sim 150 \mu\text{m}$) than the one from Lisbon ($\sim 400 \mu\text{m}$); 2) by monitoring the Co K-line, the pigment distribution throughout the glaze is less in the Coimbra samples ($\sim 50 \mu\text{m}$) than the ones from Lisbon

(~100 μm). On one hand, either there is no interface between color/glaze in the sample from Coimbra or is less than the resolution allowed for the 3D Micro-XRF. This may indicate that glaze and pigment were applied together, as it is also proved by the Co-K β and Pb-L α profiles (fig.7a). On the other hand, there is an interface color/glaze in the sample from Lisbon (fig.7b). However, the pigment seems to disseminate quite well through the glaze, which is also proved by the profiles obtained for Co-K β and Pb-L α . In both cases the fact that Sn appears to be more abundant in the lower part of the glaze is noticeable (fig.7). In the case of the sample from Coimbra, it is evident that Sn is the dominant element on the lower part of the glaze (fig. 7a). This is in agreement with the assumption that tin crystals are very dense and tend to deposit on the lower part of the glaze [8].

3.2.2. Purple

Analyses performed with conventional XRF showed similar chemical composition in all purple colors from both production centers (fig.8). The dominant element to give the purple color is Mn, and the presence of Ba in both spectra indicates that the mineral *Psilomelane* [(Ba,H₂O)₂Mn₅O₁₀] was used as raw material to obtain Mn [11].

Further analyses performed by SEM-EDS perpendicular to the purple surface revealed that the crystals in the purple layer could be observed from both centers of production. However, the Mn crystals from Coimbra (fig.9a: C29) are more noticeable in comparison to the ones from Lisbon (fig.9b: AZLX2). The crystals formed on the sample from Lisbon appear to be more dispersed into the glaze matrix. The EDS results from these two samples were obtained by micro-spot analyses and are displayed in table 2.

Furthermore, interesting results were also obtained with 3D μ -XRF. The profiles in fig. 10 correspond to cross-section scans made on the same samples. In fig.10a, the Mn profile is similar to the one of Pb, where in the left side of the scan Mn corresponds to the purple color and in the right side it corresponds to the ceramic support. It is also evident that there is a drop in the Mn and Pb depth profiles between pigment and base glaze. This was a common result in all analyzed samples from Coimbra and it leads to the conclusion that the pigment was applied as a *frit*. The interface frit/"base glaze" was clearly remained after the firing process and the two "layers" (frit and base glaze) were practically kept individualized from each other, indicating that the glaze has low fusibility (due to the presence of Ca also). When we compare these profiles with the

ones from Lisbon (fig.10b), we see that the pigment is well dispersed into the glaze matrix. Furthermore, there is no accentuated drop in the Pb profile, revealing that the glaze is more fusible than the one in Coimbra, as it was already explained in Section 3.1: The (white) glaze. This allows a better dissemination of the frit in which the pigment was applied through the base glaze. Although we cannot compare the profiles of Ca obtained in both centers directly, when we evaluate the profiles Pb and Ca in each production center, the base glaze from Coimbra (fig.10a) has the same intensity in Pb and Ca. Conversely, the base glaze from Lisbon (fig.10b) has much less Ca in comparison to the Pb signal. This is in agreement with the higher fusibility of the glazes from Lisbon.

3.2.3. Yellow/Orange

From all the colors used in glazed ceramics, the yellow or orange comes out to be the most interesting one. By naked eye observation, we noticed that in Coimbra, this color tends to be orange and in Lisbon yellow.

The first results were obtained by conventional XRF, where different samples were analyzed from both centers and some differences are already to notice. Fig.11 shows a spectrum of glaze and yellow from Coimbra (a: C41) and from Lisbon (b: AZLX1). From the spectra, we see that this pigment comes from the same compound, which is a lead-antimony ($\text{Pb}_2\text{Sb}_2\text{O}_7$) composite called *Naples yellow* [12]. In fig.11c, we can see that the samples from Coimbra appear to have higher Fe and Mn count rate than the ones from Lisbon. This may be a justification for the orange tone exhibited by the samples from Coimbra. Furthermore, the ones from Lisbon revealed higher count rates in Sn and lower in Sb, which possibly indicates that Sn^{4+} , may have replaced the ion Sb^{3+} in the lead-antimony compound, provoking changes in the molecular structure [13].

Other relevant results are the ones we could obtain with SEM-EDS. Figs. 12a and 12b show images taken perpendicular to the surface of the yellow color in one sample from Coimbra (a: C41) and one sample from Lisbon (b: AZLX2). Figs.12c and 12d display images taken perpendicular to the cross section of the samples in order to evaluate the interfaces in Coimbra (c) and in Lisbon (d).

The crystals identified in both images (a and b) have a triangular and hexagonal shape, which is typical for the Naples yellow pigment [12, 14]. Additionally, the shape of the crystals is also a hint to estimate the firing temperature. According to [12], from 950 °C

up some crystals start to form agglomerates, but in an irregular way (as it might be recognized in fig. 12a, in Coimbra), and only from 1100 °C the nice hexagonal phase starts to appear (as it is shown on fig. 12b, in Lisbon). In sample C41 (from Coimbra) (fig.11a) the crystals are somehow irregular and still very small ($< 1\mu\text{m}$) in comparison to the crystals in sample AZLX2 (Lisbon) (fig. 12b), where they are very well shaped, having already a hexagonal shape.

Furthermore, the semi-quantitative results obtained from EDS (table 3) on these samples lead to the assumption that different firing temperatures were used. The values of Sb_2O_5 and SiO_2 obtained for Coimbra and Lisbon show great discrepancy. This is because in Coimbra, the values represent the yellow chromophore phases within the glassy matrix (small crystals) and in Lisbon, the values represent the yellow chromophore phase (just onto the crystal: hexagonal). These semi-quantitative data are an indication that in fact some differences between the chromophore phases exist when we compare the two production centers.

Now, looking to Figs.12c and d there are also some considerations. They both represent cross section images from sample C41 (c) and AZLX2 (d). The one from Coimbra (c) shows clearly an interface between color/glaze and glaze/ceramic support. These are characterized by a certain amount of bubbles, some of them contain *cerussite* (lead carbonate: PbCO_3) due to weathering. The picture from the Lisbon piece (fig.12d) is a magnification of the possible interface color/glaze and in this case, it is not as evident as in the case of the sample from Coimbra. These are all indicatives of different firing temperatures.

In complement to the results, we present also, the ones obtained with 3D μ -XRF relative to the cross section scans. Fig.13a represents a scan of the sample C41 (Coimbra) and fig.13b the sample AZLX2 (Lisbon). Once again, the profiles from the sample from Coimbra reveal a drop in the $\text{Pb-L}\alpha$ profile, which indicates non-homogeneity between base glaze and the frit in which the pigment was applied. The profiles of the sample from Lisbon show a higher homogeneity within all elements. However, the fact that the profile of Sb is more isolated from Pb suggests once again that the glaze in which the pigment is applied is more fusible than the one from Coimbra. In contrast, the Pb tends to go down the glaze due to its higher density. The Sn profiles indicate once again that the SnO_2 crystals tend to deposit on the lower part of the glaze.

4. Conclusions

It is clear that Portuguese polychrome glazed ceramics have an intrinsic value by the way they were produced: the broad polychromic pallet, the obtained tones or even the careful manufacturing procedure in order to achieve such slight differences.

Comparing the data obtained for the two main important production centers, Lisbon and Coimbra, new results about the raw materials used as well as the possible manufacturing techniques have been achieved. Due to the lack of archaeometric information on Portuguese ceramic production, we used the knowledge from previous works performed on Spanish and Italian glazed ceramics [4, 8, 10, 12-14], since we are dealing with similar types of samples. Hence, this work presents the first archaeometric results about Portuguese glazed ceramics produced in Coimbra and Lisbon as a comparative study.

The compositional and microtextural data obtained for both groups of samples revealed differences in the properties of the glazes: the ones from Coimbra are less fusible than the ones from Lisbon. This was noticeable by all the results obtained with the different techniques. Glazes with higher content of Na and Pb have a lower melting point than the ones with higher content of K and Ca. This was also evident when the pigments were applied to the glaze in the form of *frit*. For this manufacture procedure, a more pronounced interface between pigment and glaze was found in the SEM images. However, when the *frit* and the base glaze onto which the pigment was applied had higher fusibility and/or if the firing temperature was higher than in other cases, the interfaces were not so distinguishable. This could be detected by the 3D Micro-XRF scans. In all images correspondent to the samples from Coimbra the elements are less disseminated throughout the glaze than the ones from Lisbon. This means that the element that gives the color (Co in the case of blue, Mn in the case of purple and Sb in the case of yellow) is more concentrated on the surface of the sample from Coimbra than the ones from Lisbon. This lack of ability in going further down into the glaze is more related with the glaze composition than with the pigment itself. However, blue and purple pigments have in principle more ability of diffusion than the yellow ones when applied to the same glaze. This is due to the molecules size and ability in homogenizing themselves into the glassy matrix.

Another conclusion can be drawn from the analysis of the yellow pigment. Not only the dissemination of the pigment throughout the glaze is less in the samples from Coimbra but also the irregularity of the crystals in the yellow seen in these samples is higher in

comparison to the hexagonal shaped crystals from Lisbon. This indicates that the samples from Lisbon were submitted to a higher temperature than the ones in Coimbra. Summarizing, in this study, some questions mainly related to the glaze properties have been clarified by comparing the manufacturing centers of Coimbra and Lisbon as well as the pigments application and possible firing temperatures used. As a next step of the project, it becomes necessary to evaluate the surface composition of all samples with μ -XRD together with μ -Raman in order to know the local composition of the pigments, and their evolution along the time.

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References

- [1] A. Guilherme, J. Coroado, M.L. Carvalho. Chemical and mineralogical characterization on glazes of ceramics from Coimbra (Portugal) from the sixteenth to nineteenth centuries. *Anal. Bioanal. Chem.* 395 (2009) 2051-2059.
- [2] A. Guilherme, S. Pessanha, M.L. Carvalho, J.M.F. dos Santos, J. Coroado. Micro energy dispersive X-ray fluorescence analysis of polychrome lead-glazed Portuguese faiences. *Spectrochim. Acta, Part B* 65 (4) (2010) 328-333.
- [3] A. Pais, A. Pacheco, J. Coroado. *Cerâmica de Coimbra*. Ed. INAPA, Lisboa, (2007).
- [4] J. Molera, M. Vendrell-Saz, J. Pérez-Arantegui. Chemical characterization of Tin Glazes in Islamic Ceramics from Eastern Spain. *J. Archaeol. Sci* 28 (2001) 331-340.
- [5] Prudence M. Rice. *Pottery Analysis: A Sourcebook*. The University of Chicago Press, (1987).

- [6] V. A. Solé, E. Papillon, M. Cotte, Ph. Walter, J. Susini. A multiplatform code for the analysis of energy-dispersive X-ray fluorescence spectra, *Spectrochim. Acta, Part B* 62 (2007) 63-68.
- [7] I. Mantouvalou, K. Lange, T. Wolff, D. Grötzsch, L. Lühl, M. Haschke, O. Hahn, B. Kanngießer. A compact 3D micro X-ray fluorescence spectrometer with X-ray tube excitation for archaeometric applications. *J. Anal. At. Spectrom.* 25 (2010) 554-561.
- [8] J. Molera, T. Pradell, N. Salvadó, M. Vendrell-Saz. Evidence of Tin Oxide Recrystallization in Opacified Lead Glazes. *J. American Ceram. Society* 82 (10) (1999) 2871–2875.
- [9] A. Zucchiatti, A. Bouquillon, I. Katona, A. D’Alessandro. The ‘Della Robbia Blue’: A case study for the use of cobalt pigments in ceramics during the Italian renaissance. *Archaeometry* 48 (1) (2006) 131-152.
- [10] M.S. Tite. The production technology of Italian maiolica: a reassessment. *J. Archaeolog. Sci.* 36 (2009) 2065-2080.
- [11] Web Mineral Data. Psilomelane Mineral Data. Retrieved Friday, 18th November 2010 from <http://webmineral.com/data/Psilomelane.shtml>
- [12] K. Sakellariou, C. Milian, A. Morresi, M. Ombelli. Spectroscopic investigation of yellow majolica glazes. *J. Raman Spectrosc.* 35 (2004) 61-67.
- [13] 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 $Pb_2Sb_2O_7$ doped with tin and zinc. *J. Raman Spectrosc.* 40(1) (2009) 107–111.
- [14] G. Bultrini, I. Fragalà, G.M. Ingo, G. Lanza. Characterisation and reproduction of yellow pigments used in central Italy for decorating ceramics during Renaissance. *Appl. Phys. A: Mater. Sci. Process.* 83 (2006) 557–565.

Table 1 – Composition of the glazes from Coimbra and Lisbon (in % wt). Analysis perpendicular to the surface obtained with SEM-EDS. The uncertainty varies between 0.1 – 2.8 % (for the lowest and highest values, respectively).

Local	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	Fe ₂ O ₃	PbO	SnO ₂
Coimbra (N = 11)	0.8 – 1	0.2 – 0.3	2.8 - 3	31.3 – 31.9	8.1 – 9.3	3.1 – 3.2	3.6 – 3.7	40.1 – 40.5	10.4 – 10.8
Lisbon (N = 9)	3.5 – 4.2	0.6 – 0.8	3.1 – 3.7	28.9 – 29.4	4.3 – 5.8	0.8 – 1.1	2.1 – 2.5	45.5 – 45.9	9.8 – 10.3

Table 2 – Comparison between the purple chromophore phases from Coimbra (C29) and from Lisbon (AZLX2). Analysis perpendicular to the surface obtained with SEM-EDS.

Sample	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	MnO	Fe ₂ O ₃	PbO
C29 Coimbra	1.6 ± 0.1	0.6 ± 0.1	3.3 ± 0.2	28.4 ± 1.0	5.8 ± 0.2	2.9 ± 0.1	10.8 ± 0.3	4.0 ± 0.1	42.6 ± 2.6
AZLX2 Lisbon	0.7 ± 0.1	0.9 ± 0.1	3.2 ± 0.1	36.3 ± 1.1	5.4 ± 0.2	10.4 ± 0.3	24.7 ± 0.6	1.2 ± 0.1	18.3 ± 1.0

Table 3 – Comparison between the yellow chromophore phases from Coimbra (C41) and from Lisbon (AZLX2). Analysis perpendicular to the surface obtained with SEM-EDS.

Sample	Na ₂ O	Al ₂ O ₃	SiO ₂	K ₂ O	Fe ₂ O ₃	PbO	Sb ₂ O ₅
C41 Coimbra	0.8 ± 0.1	1.9 ± 0.1	20.8 ± 0.1	5.1 ± 0.2	6.7 ± 0.4	47.9 ± 1.6	16.7 ± 1.4
AZLX2 Lisbon	2.5 ± 0.2	1.6 ± 0.1	4.1 ± 0.2	---	3.7 ± 0.2	47.5 ± 2.8	40.1 ± 2.3

Figure 1 – Model of a polychrome glazed ceramic. The areas marked in red correspond to the interfaces color/glaze and glaze/ceramic support.

Figure 2 – Some analyzed samples: fragments from Coimbra and Lisbon.

Figure 3 – Comparison between 3D (a) and 2D (b) cross-section scans of the same sample (C29).

Figure 4 – SEM image perpendicular to the glaze surface of a sample from Coimbra (a: C41) and a sample from Lisbon (b: AZLX1).

Figure 5 – 3D μ -XRF cross section scans performed on glaze + ceramic support on a sample from a) Coimbra (C41) and b) Lisbon (AZLX1).

Figure 6 – a) Comparison between spectra on blue and glaze of a sample from Coimbra (C34); b) Comparison between spectra on blue and glaze of a sample from Lisbon (AZLX1); c) Comparison between spectra on the blue of the two samples; d) Intensity ratio of Fe and Mn with respect to Co, obtained on the blue in the set of samples from Coimbra and Lisbon.

Figure 7 - 3D μ -XRF cross section scans performed on blue + glaze + ceramic support of a sample from a) Coimbra (C34) and b) Lisbon (AZLX1).

Figure 8 - Comparison of spectra obtained with conventional XRF for a) Coimbra (C29) and b) Lisbon (AZLX2) samples on the purple color.

Figure 9 - SEM images perpendicular to the purple surface of a sample from Coimbra (a: C29) and a sample from Lisbon (b: AZLX2).

Figure 10 - 3D μ -XRF cross section scans performed on purple + glaze + ceramic support on a sample from a) Coimbra (C29) and b) Lisbon (AZLX2).

Figure 11 – a) Comparison between spectra on yellow and glaze of a sample from Coimbra (C41); b) Comparison between spectra on yellow and glaze of a sample from Lisbon (AZLX2); c) Comparison between spectra on the yellow in the two samples.

Figure 12 - SEM images perpendicular to the yellow surface of a sample from Coimbra (a: C41) and a sample from Lisbon (b: AZLX2). SEM images perpendicular to the cross section of sample C41 (c) and sample AZLX2 (d).

Figure 13 - 3D μ -XRF cross section scans performed on yellow + glaze + ceramic support on a sample from a) Coimbra (C41) and b) Lisbon (AZLX2).

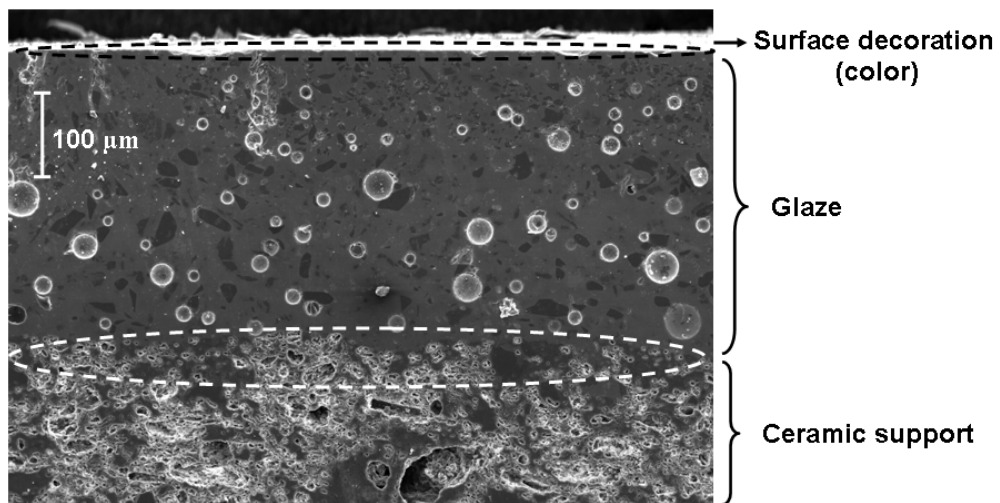


Figure 1

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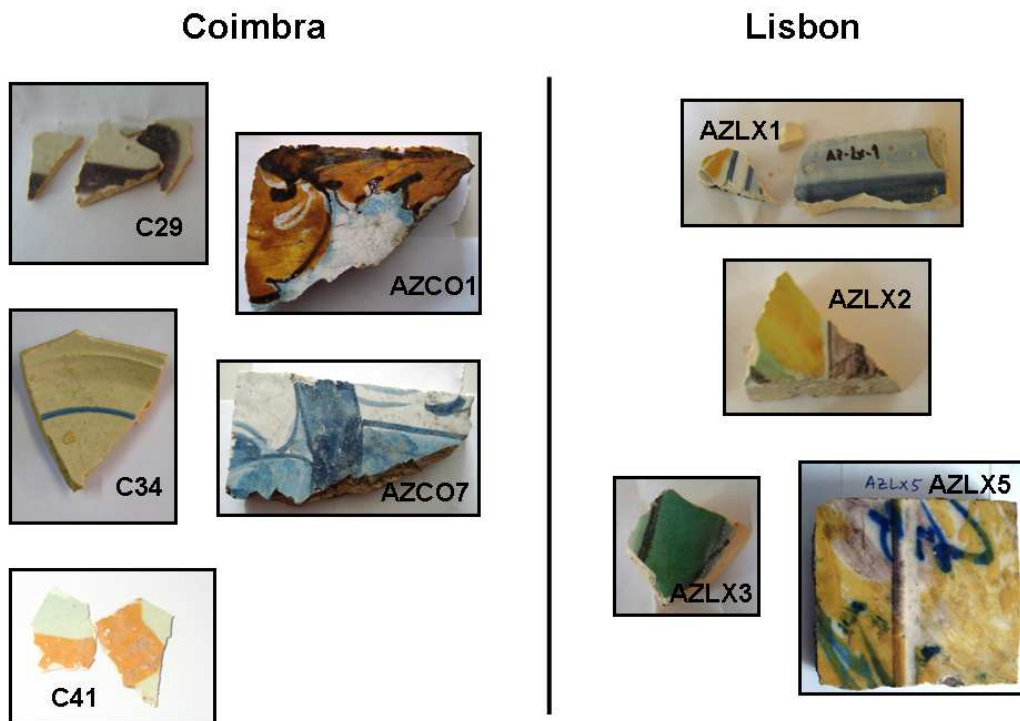


Figure 2

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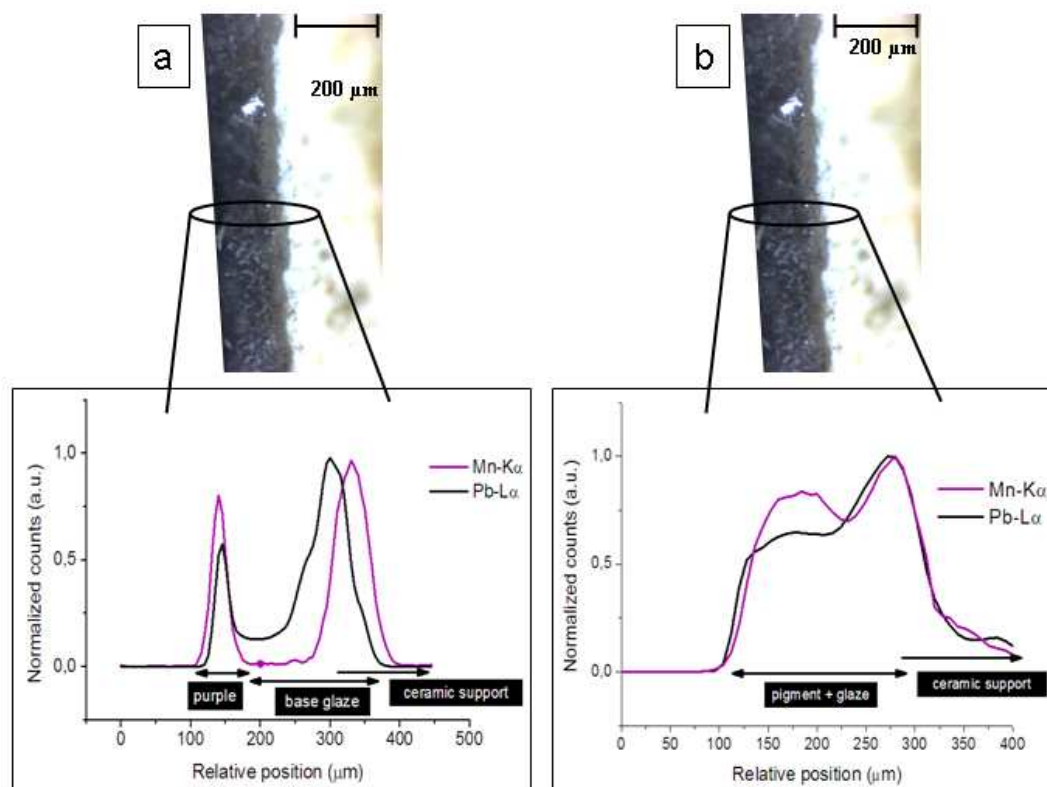


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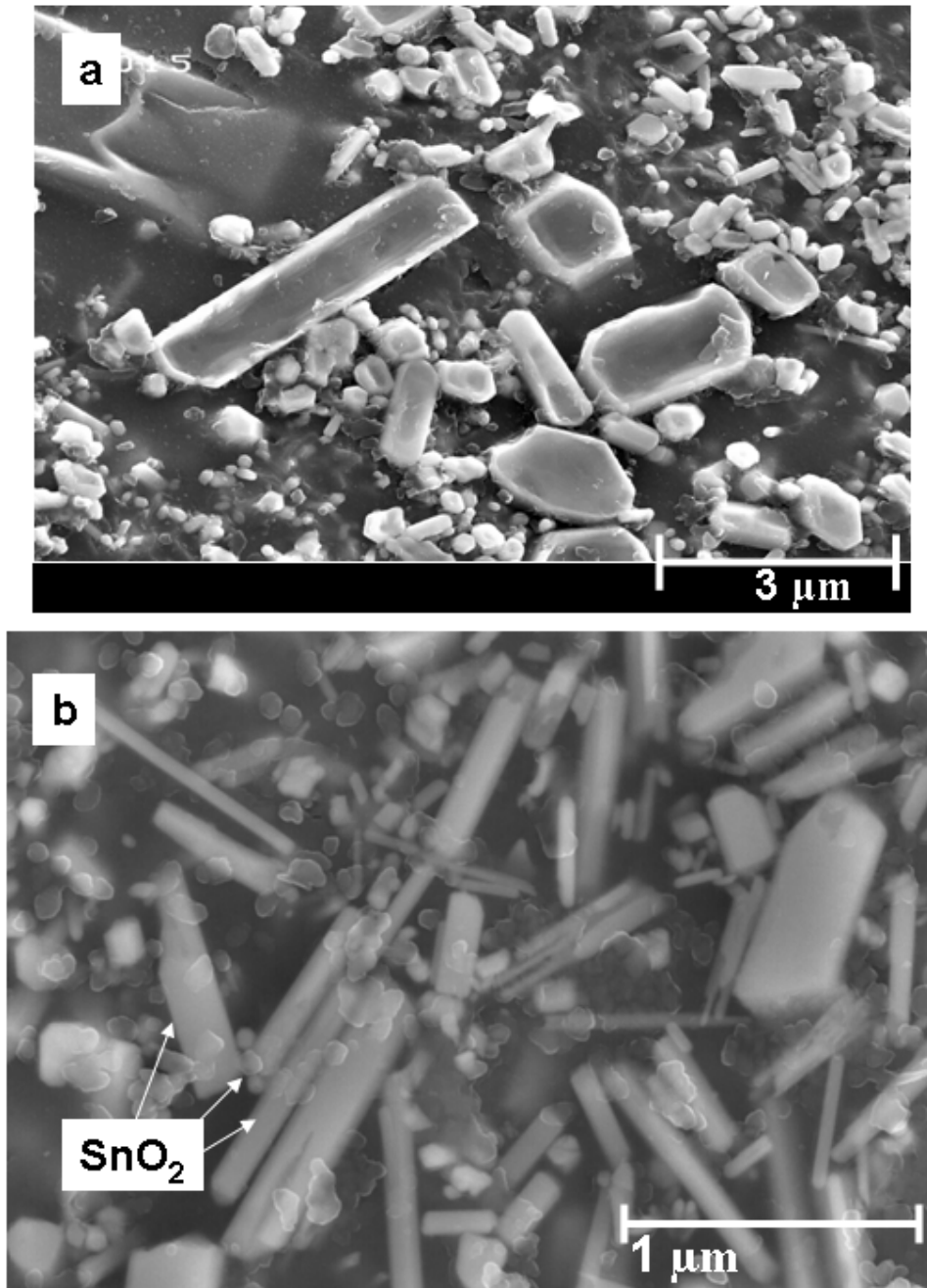


Figure 4

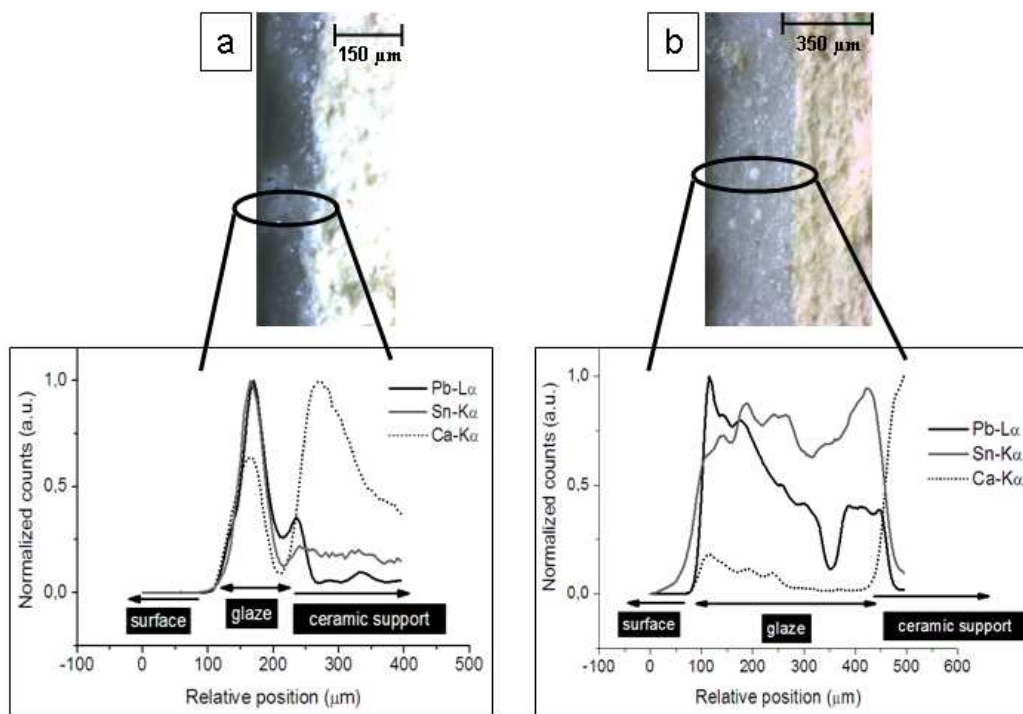


Figure 5

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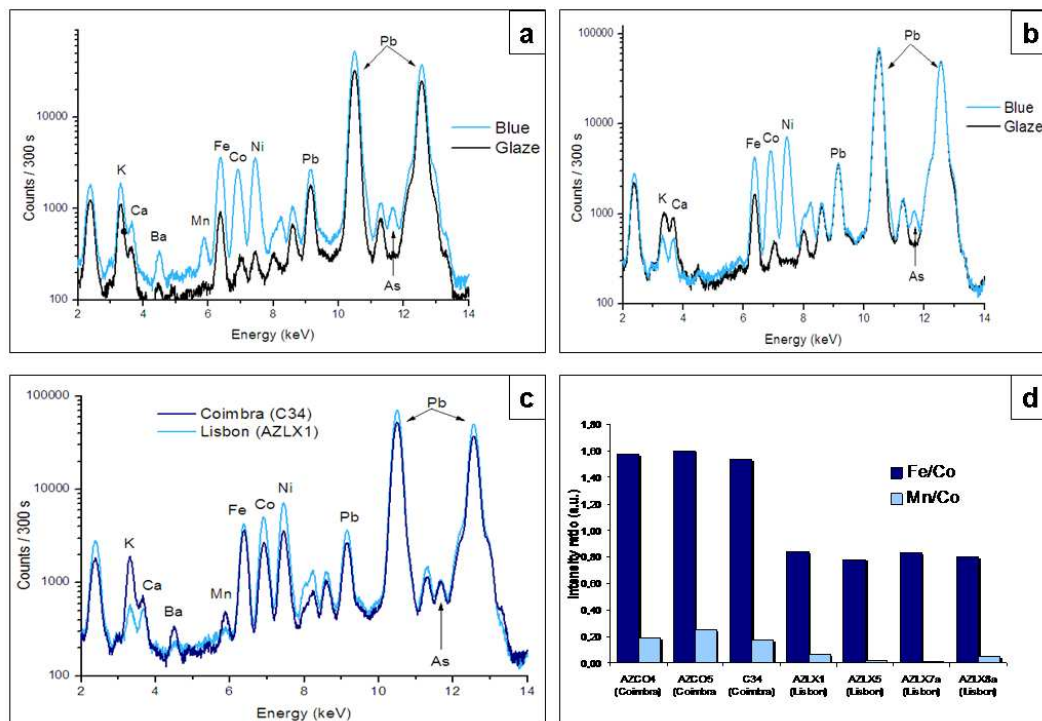


Figure 6

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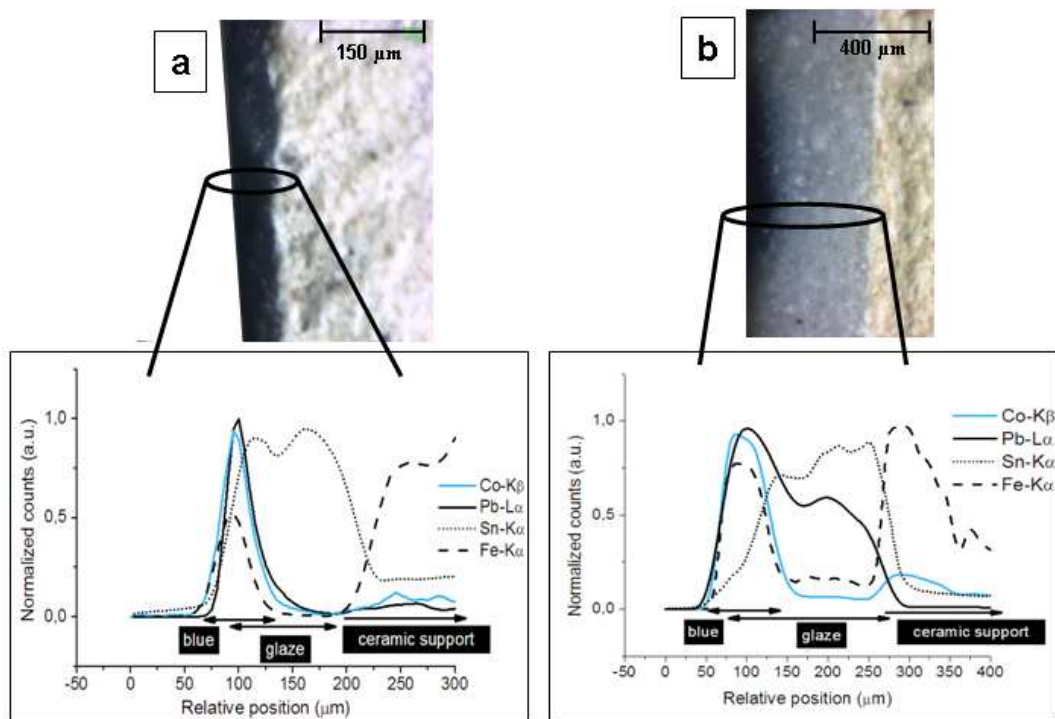


Figure 7

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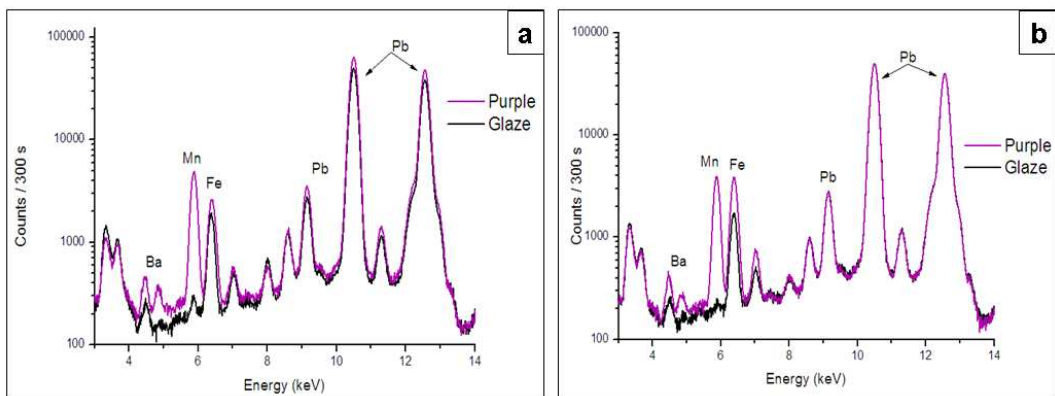


Figure 8

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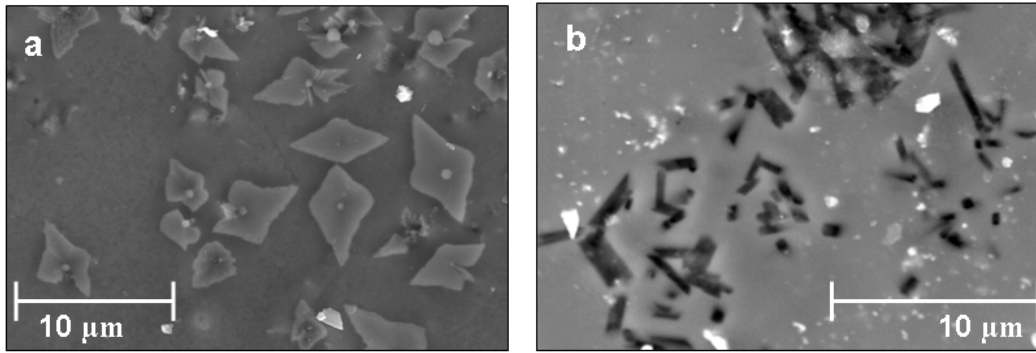


Figure 9

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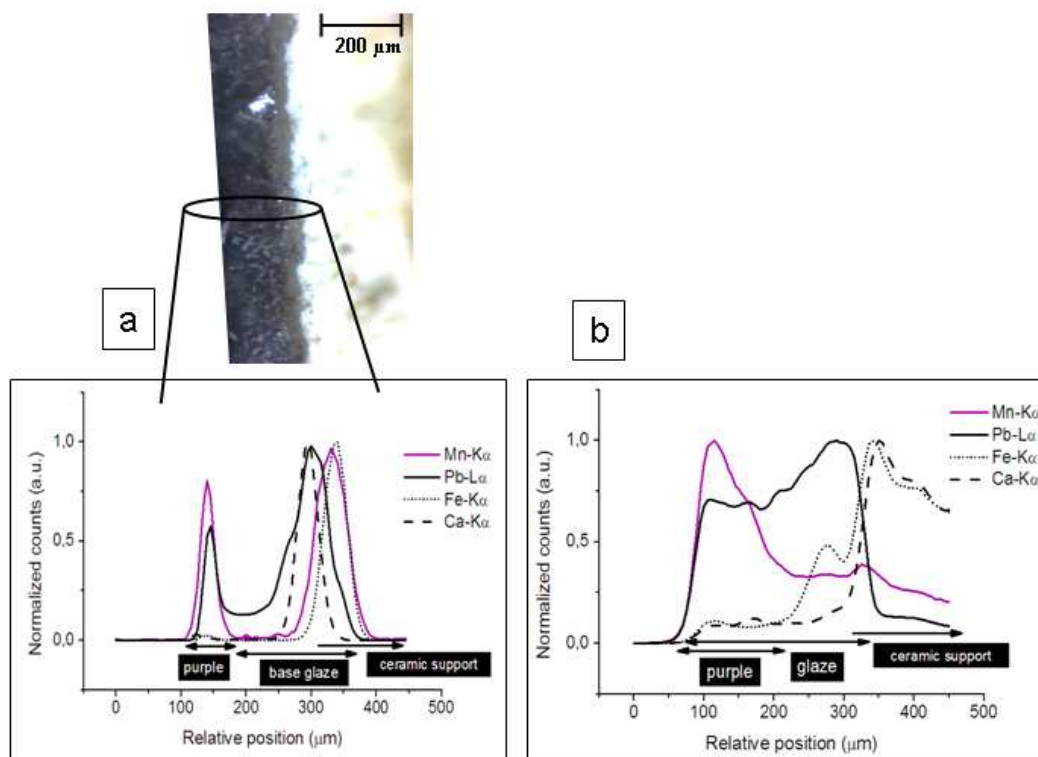


Figure 10

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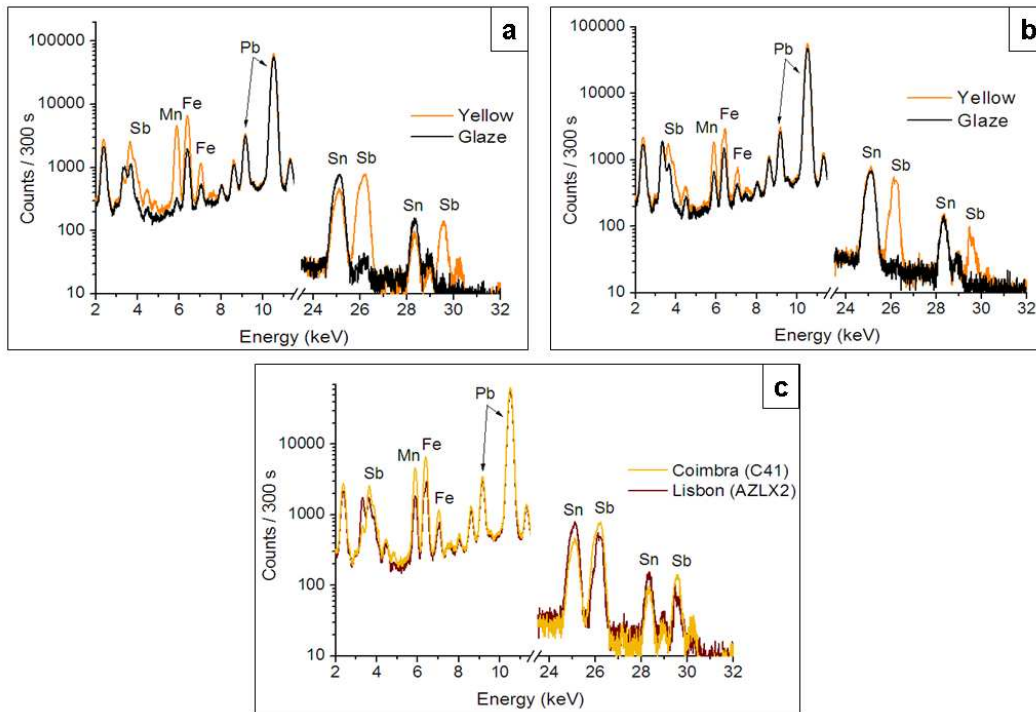


Figure 11

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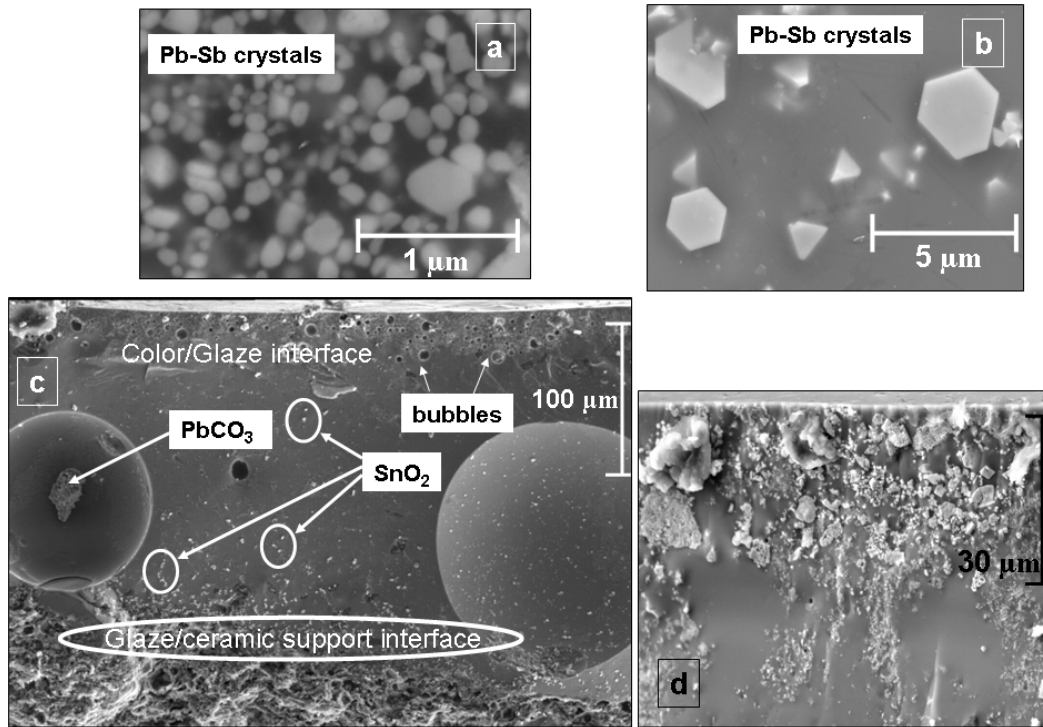


Figure 12

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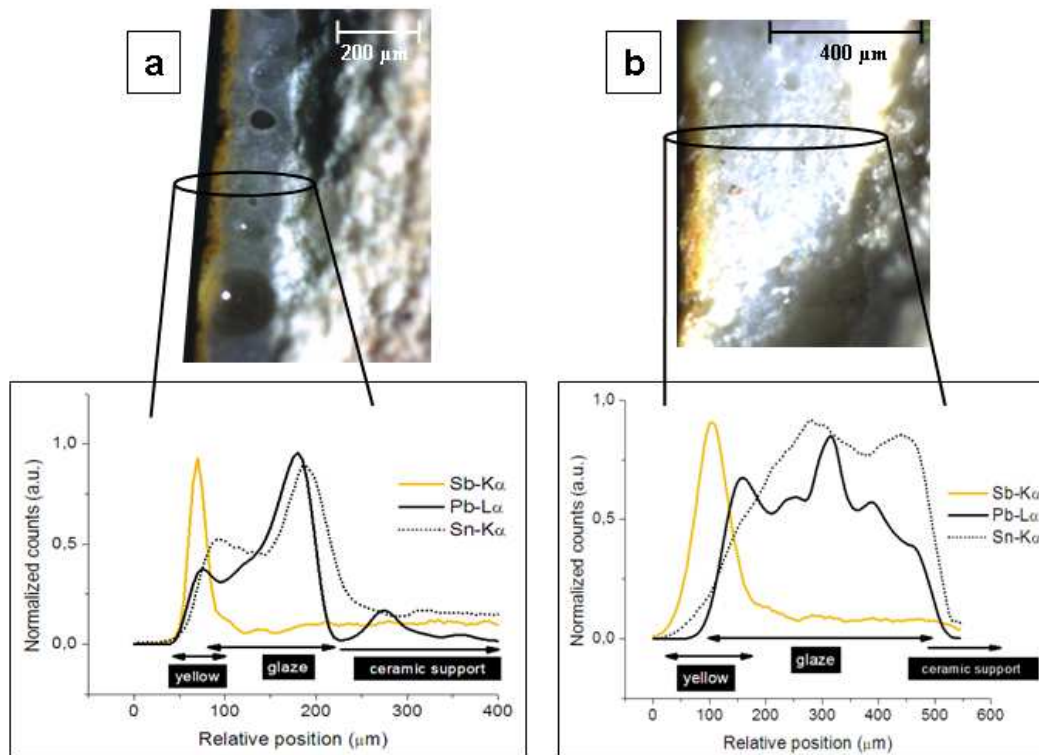


Figure 13

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