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Morphological and Compositional Features of Portuguese Polychrome Glazed Pottery Investigated by SEM/EDX – Hints about the Manufacturing Processes

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This study addresses to the morphological and compositional features of polychrome glazed ceramic samples from Portugal by means of a SEM/EDX system (scanning electron microscopy with energy-dispersive X-ray spectroscopy).

Samples produced in the main pottery-making centers between the 16th and 18th centuries, from Portugal (Lisbon and Coimbra), were the object of study. The main question to be answered is whether there are differences or not in the manufacturing procedures employed. For this purpose, two types of samples were analyzed: faiences and wall-tiles (the famous "*azulejos*", in Portuguese). They all have a ceramic body, a "base" glaze and a surface decoration. The analyses were performed on the glaze and on every colored part of the samples. At first approach, the data obtained by SEM/EDX have revealed to be of great usefulness to identify heterogeneities on the samples' main parts.

Fig. 1 exhibits general morphological aspects of the glazes. The quartz grains are always observable as dark-grey areas and vary in shape from sphere-like to more oblong, with sizes up to 80 μm; Feldspars are identified with sizes up to 5 μm; Cassiterite (SnO_2) crystals are typically found in this type of ceramic glazes and the crystals size is around 1 μm or even down to the nanometer scale; With a high magnification we see that these crystals are well distributed in the glaze, forming agglomerates sizing micrometer range.

As a general feature of the glazes, the EDX spectra reveal the permanent presence of elements such as Si, Pb, Sn, Ca and K. Si is the network forming agent and Pb and K have a network-modifier (fuser) character in the glassy matrix, in order to lower the melting point of the Si-structure. Sn is found in these samples as an opacifier, which makes the glaze matte and allows a better application of surface decorations (Fig. 2).

As for the yellow pigment, Sb is the colour-carrier element (Fig. 3a) and its crystals have typically a hexagonal shape, which is an indicative of the firing temperature used. The crystals identified in both images (Fig. 3b and c) have a triangular and hexagonal shape, which is typical for the Naples yellow pigment [1]. Additionally, the shape of the crystals is also a hint to estimate the firing temperature. According to Ref. [2], from 950 °C up, some crystals start to form agglomerates, but in an irregular way (Fig. 3c, in Coimbra), and only from 1100 °C the nice hexagonal phase starts to appear (Fig. 3b, in Lisbon). Furthermore, from the table in Fig.3, the faiences from Coimbra seem to be characterized by a higher amount of Sb with respect to the yellow colour, than the wall-tiles.

References:

[1] A Guilherme, J Coroado *et al.*, Spectrochim. Acta B **66** (2011), p. 297.
[2] K. Sakellariou, C. Milian, *et al.*, J. Raman Spectrosc. **35** (2004), p.61.

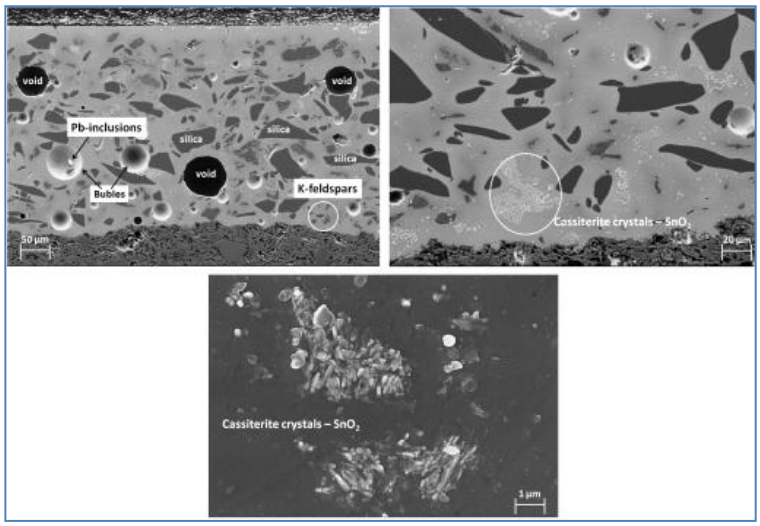


Figure 1. Morphology of the glaze. All micrographs were acquired on the cross-section of the samples. The quartz grains are always observable (dark-grey areas) together with bubbles and Pb-inclusions, on both upper pictures; SnO_2 crystal grains are observable on the upper right micrograph and well distributed in the glaze (lower micrograph).

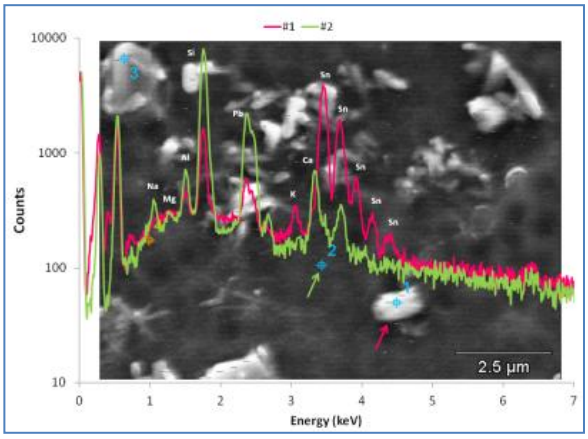
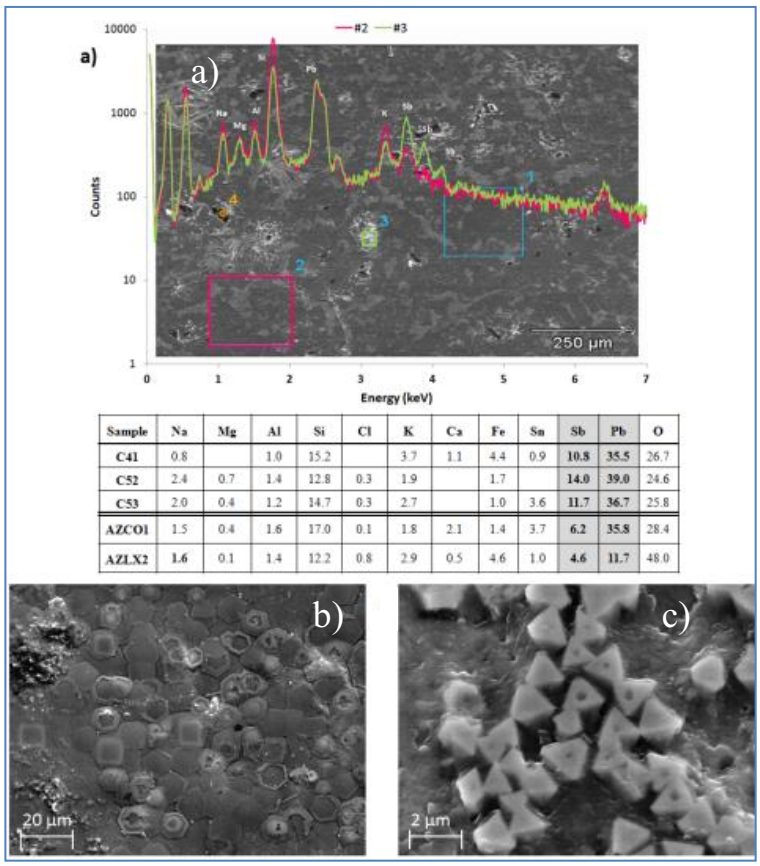


Figure 2. Micrograph of the glaze of a sample from Coimbra with the respective EDX spectra onto two marked spots. The bright areas correspond to cassiterite crystal.



Sample	Na	Mg	Al	Si	Cl	K	Ca	Fe	Sn	Sb	Pb	O
C41	0.8		1.0	15.2		3.7	1.1	4.4	0.9	**10.8**	**35.5**	26.7
C52	2.4	0.7	1.4	12.8	0.3	1.9		1.7		**14.0**	**39.0**	24.6
C53	2.0	0.4	1.2	14.7	0.3	2.7		1.0	3.6	**11.7**	**36.7**	25.8
AZCO1	1.5	0.4	1.6	17.0	0.1	1.8	2.1	1.4	3.7	**6.2**	**35.8**	28.4
AZLX2	**1.6**	0.1	1.4	12.2	0.8	2.9	0.5	4.6	1.0	**4.6**	**11.7**	48.0

Figure 3. a) Micrograph of the yellow of a sample from Coimbra with the respective EDX spectra onto two marked spots. The bright areas correspond to agglomerates of Sb-crystals. The table shows the rough composition of yellow surface areas of samples from Coimbra and Lisbon; b) hexagonal-shaped crystals on a sample from Lisbon and c) triangular-shaped crystals on a sample from Coimbra.

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