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AZULEJO BLUES – AN ANALYTICAL STUDY OF THE BLUE COLOURS IN PORTUGUESE *AZULEJOS*

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ABSTRACT

This communication reviews the main variants of the blue colour found on glazed tiles (mainly of Portuguese manufacture) used in Portugal from the 16th to the late 18th centuries and discusses the composition of the pigments from which they result.

KEYWORDS: azulejos; cobalt pigment; blue colour in majolica

1. INTRODUCTION

Portuguese *azulejos* of the 17th century used a number of colours that were recently reviewed and analyzed [1]. Amidst those colours, blue is the only one that was used continuously since the earliest productions and throughout the whole *azulejo* chronology and is thus a prime subject for compositional research on the pigments, encompassing the whole production of historic tiles.

Well into the 19th century, the blue colour in *azulejos* derived exclusively from the use of cobalt pigments. From at least 1520 and throughout the classical period of Portuguese *azulejo* production, the cobalt originated from a region on the border between Saxony and Bohemia – the Erzgebirge (Ore Mountains) where it was a sub-product of the extraction of silver, copper, lead, bismuth and other metals [2]. The cobalt-bearing slags used in pottery and glassmaking were largely unrefined [2] and their compositions include, besides cobalt, other elements in an association that often characterizes their geographical provenance. For most of the Erzgebirge, the major association of cobalt is with iron, nickel, arsenic and bismuth [3] but their relative contents vary with the location and the chronology. In some cases those contents also bear on the colour [2; 8; 9].

When the blue colour is considered in a representative set of tiles it is easily recognized that its hue varies. This may result from the particular compositions of the pigment or of the glaze, or from the firing conditions. The counterpart of the pigment compositions on the blue hues has not, to our knowledge, been determined in Portuguese historic *azulejos*. That was the aim of our study.

2. SAMPLING

We started with more than 200 samples representing a period from the 16th century (six Hispano-Moresque tiles, two blue "enxaquetado" elements and a small set of "punta de clavo" [4] and other early patterns used around the turn of the century) to the late 18th century (represented by eight “pombalino” and “Dona Maria” samples). All samples were arranged in an approximately chronological manner. Some *azulejos* are painted with only one shade of blue; others with two. In this last case the composition of the pigment is the same, only the concentration changed and thus only the darker shade was considered. When these samples were reviewed, 50 were chosen for analysis in which sixteen different blue hues were tentatively identified. Specifically for the study of colour, this set was further filtered by removing very unusual hues occurring only once and unknown from architectural applications. Those are thought to derive mainly from pigment mixtures, trials, or the work of small workshops of lesser interest and were not considered in this study because of their lack of representativeness. Two hues of which we had only one sample were nevertheless kept because we know them from architectural applications.

After the filtering, the remaining samples were subsequently assessed by comparing them to a blue colour chart. The need for such a comparison comes from the fact that hues perceived as different may be judged essentially similar when compared to a standard and in that manner potential redundancies were avoided. Blue charts available commercially (RAL and BS) were not judged sufficiently varied and so we produced 40 different blue chips by printing 3x3cm squares from each of the 40 hexadecimal colour codes that corresponded to hues that might be expected to be found in *azulejos*. The chart was printed on Hewlett-Packard semi-glossy photo paper and each hue numbered with a new code. The fact that the blues obtained differ from one printer to the other is not relevant because our aim was solely to separate hues based on a comparison with some reference that might be confirmed by different observers.

Six main blues were thus identified which are represented in Figure 1 made from a single scanning, so that all samples were subjected to the same illumination and colour interpretation conditions (but please bear in mind that a scanner does not interpret colour the same way as an observer does). The image also includes the coded chips that best compared with each blue, noting that the colour chips are not exact equivalents but only the nearest matches found: 5.7 is the usual cobalt blue; 2.8 is a very distinctive blue-black; 5.6 is similar but somewhat muted - all *azulejos* of this hue have distinctive dimensions that characterize the Coimbra productions and so this hue is sometimes known as “Coimbra Blue”; 1.8 looks, at first, similar to 2.8 but depicts a greenish hue, best seen when the pigment is less concentrated; 5.5 is a light, opaque, slightly greyish cobalt blue; 5.2 is a very distinctive muted blue, only seen in non-majolica Hispano-Moresque tiles.

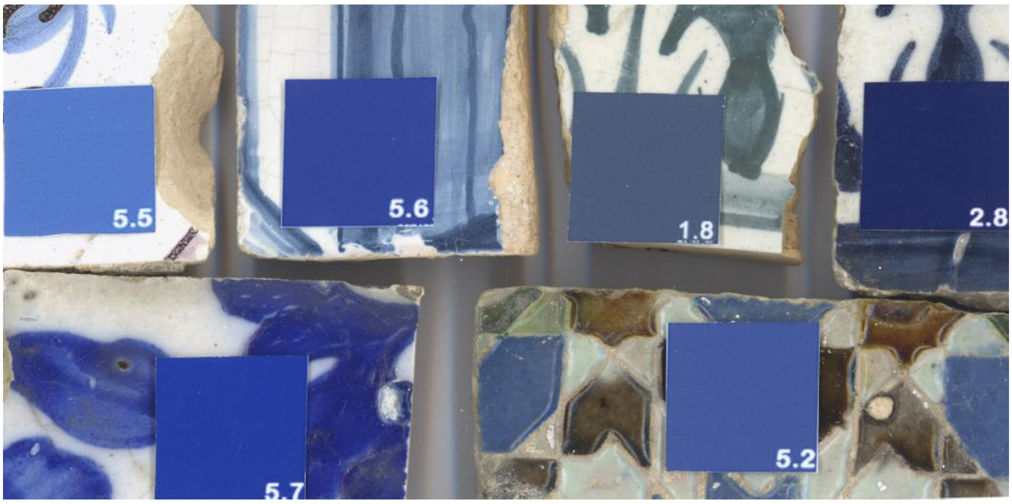


Fig. 1 - The six blue hues selected for the analytic study

Fifteen *azulejo* samples were finally selected representing the blues previously discriminated. Table 1 illustrates the samples chosen as well as their colour codes.

3. TECHNICAL

3.1. μED-XRF analysis

The main analytic study was made with an ArtTAX spectrometer (Intax GmbH), with a Mo anode (diameter about 70 μm) and an XFlash® silica detector. The measurement parameters were: 40 kV of voltage and 600 μA of current under a He atmosphere, the equipment can detect with acceptable accuracy elements with $Z > 13$ (aluminium). The acquisition time was always 300 s.

The blue in Hispano-Moresque tiles is made of coloured glass painted in partitions in the cloisonné style. All other tiles were manufactured by painting the blue over a white majolica that has to be analysed independently. For the white majolica glazes one spectrum was acquired. In doubtful cases a second spectrum was obtained. For the blue pigmented areas, two spectra were acquired. Both spectra were compared and whenever the measurements showed undue dispersion, a third spectrum was acquired. All the spectra obtained were considered when averaging the results.

For the calibration and assessment of the accuracy of the measurements an in-house manufactured white tin-lead-glaze reference material was used, as well as a glass standard CMOG C (The Corning Museum of Glass). No quantification was possible beyond that provided by the peak intensities for lack of a standard of blue-pigmented lead glaze.

The measurements on the blue areas in majolica tiles always carry the influence of the white glaze matrix. To filter off the matrix we used the *WinAxil®* software on each individual spectrum and then subtracted the peak areas corresponding to each element. This method is based on the fact that all the components of the matrix exist with approximately equal contents also on the pigment measurements and can be filtered off from the blue readings by subtraction.

In this study, and taking into consideration the limitations of the μED-XRF used, the following elements were detected: Si, Ti, Mn, Fe, Ni, Cu, Zn, As, Sn, Pb, Bi. Of these only Mn, Fe, Ni, Cu, Zn, As and Bi were considered to be potentially of value for the discrimination [3; 5; 6; 7] of the blue pigments. Given their recurrently low contents, often of the order of the background effect, we did not find the counts of Mn and Zn in our set of Portuguese samples to be useful to this research and so, for the sake of clarity, did not include them in the table of results. Lead has not been considered among the potentially characteristic elements of the pigment because it is not possible to discriminate whether the fluorescence counts come from residual contents in the pigment or from the glaze matrix, in which it is very significantly present. Tin is used at relatively high contents as opacifier in the glaze and thus is also unsuitable to characterize the blue pigment in majolica but was seen to be important in the case of the Hispano-Moresque non-majolica tiles. In these, Fe was not considered in the pigment because it is also part of the glaze composition.

The analyses were carried out calculating the peak intensities of the elements ($K\alpha$ & $K\beta$ for Fe, Co, Ni, and As, and $L\alpha$ & $L\beta$ for Bi) with the WinAxil® software. Arsenic is a very important element to characterize the blue pigments, namely those coming from Germany [2; 3; 5]. There is however an overlap of its $K\alpha$ peak with the $L\alpha$ of Pb and because of this its presence is better characterized by the $K\beta$ peak.

After the calculation and elimination of the background, the results of the averages of each relevant element for each sample were normalized by calculating the ratios of their values to the value of the Co. It must be pointed that the values represent areas in the spectra and not necessarily contents, but they are related to the individual contents. By calculating the ratios of the areas of the individual elements to cobalt, the rates in individual samples are made comparable to the same rates in other *azulejos*. The ratios of Fe/Co, Ni/Co, As/Co, Cu/Co and Bi/Co allowed us to make a first characterization of the compositional groups potentially present, and thus made it possible a preliminary assessment of the chemical associations in the cobalt pigments used in the samples.

3.2. WD-XRF semi-quantitative analysis

The main results that might be considered doubtful or needed clarification were re-checked by ablating 20 mg of the blue-pigmented majolica and pressing the samples on pellets of *Suprapur* boric acid from *Merck*. Their chemical composition was then evaluated by semi quantitative analysis using a sequential wavelength dispersive X-ray fluorescence spectrometer, AXIOS PW 4400/24, from PANalytical. This equipment allows the analysis of elements from Z=4 in the Periodic Table (beryllium) to Z= 92 (uranium). The measurements were carried out using a 4 kW rhodium tube as a source of X-ray radiation. The IQ+ software, version 4.0G, was used to analyze the results. After a peak search procedure, the peaks identified were used to calibrate the system by performing a regression against theoretical intensities from a fundamental parameters program. For operational reasons only the blue pigmented glaze could be analysed with two measurement runs and the results assessed on the basis that the contents measured referred to elements not present in the white majolica. This supposition is not valid for Fe and so these results do not include iron because part of the contents measured may be attributable to the matrix. The results are given in Table 1 as a cross-check of the μED-XRF counts but because they do not cover the whole set of samples, they were not used to draw conclusions.

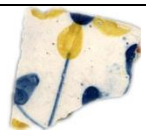
4. RESULTS

Table 1 illustrates the samples and includes the results relative to the most relevant elements present in the blue pigment. For elements with low readings, these were only considered when found to be significant at the 97.5% level when compared to the background noise, otherwise they were made nil. All the results are on an elemental basis and normalized to the cobalt content.

Table 1 - Fe, Ni, As, Cu and Bi association with Co for each sample, normalized to the cobalt content and corresponding blue hue

sample	ID ref	chronology	hue	Fe/Co	Ni/Co	As/Co	Cu/Co	Bi/Co
	MM03	cuerda seca late 15th - - early16th centuries	code 5.2	-	0.4	0.0	1.0	0.1
same sample by WD-XRF	MM03			-	0.60	0.00	0.61	0.00
	MM01	arista 1st half 16th	code 5.2	-	0.4	0.6	1.0	0.2
	MM02	arista 16th cent	code 5.2	-	0.3	0.9	1.4	0.2

sample	ID ref	chronology	hue	Fe/Co	Ni/Co	As/Co	Cu/Co	Bi/Co
	PT10	majolica ca. 1620-1660	code 5.7	0.9	0.3	0.5	0.0	0.1
	PT11	majolica ca. 1620-1640	code 5.7	0.7	0.4	0.3	0.0	0.0
	PT15	majolica ca. 1620-1680	code 2.8	0.3	3.5	2.4	0.0	0.2
	PT30	majolica ca. 1650-1700	code 5.7	0.9	0.4	1.7	0.0	0.2
same sample by WD-XRF	PT30			-	0.43	1.78	0.06	0.80
	PT31	majolica ca. 1650-1680	code 2.8	0.6	2.9	1.5	0.0	0.2
	PT37	majolica ca. 1680-1730	code 1.8	0.8	3.5	1.2	0.0	0.1
same sample by WD-XRF	PT37			-	2.27	0.91	0.09	0.66
	PT38	majolica ca. 1680-1730	code 2.8	1.0	3.0	0.4	0.0	0.0
	PT39	majolica ca. 1700-1720	code 5.7	1.0	0.7	3.2	0.0	0.2
	PT41	Coimbra majolica 1700-1715 ca.	code 5.6	0.6	1.0	0.1	0.0	0.0

sample	ID ref	chronology	hue	Fe/Co	Ni/Co	As/Co	Cu/Co	Bi/Co
	PT44	Coimbra majolica ca. 1715-1750	code 5.6	0.3	1.2	0.2	0.0	0.0
same sample by WD-XRF	PT44			-	0.77	0.00	0.17	0.32
	PT45	majolica ca. 1780-1810	code 5.5	1.6	0.7	0.0	0.0	0.0
	PT46	majolica ca. 1790-1810	code 2.8	1.1	2.1	1.3	0.0	0.1

4. DISCUSSION

4.1. Hispano-Moresque tiles

The Hispano-Moresque tiles have to be discussed separately because of their specificity – they were not manufactured by the majolica technique but rather by depositing coloured glaze into cloisonné areas of the surface. The blue pigment is not a good opacifier of glass and used by itself would result in a transparent glaze, showing the colour of the biscuit, or else too much pigment would have to be used, making the glaze very dark. To obtain the opaque aspect and rather light colour seen in practically all Hispano-Moresque blues, at least another component was needed. Table 2 depicts the full analytical results (in terms of count intensity of the main lines) for those tiles by μED-XRF while Table 3 depicts the semi-quantitative results by WD-XRF for MM03 in terms of common oxides.

Table 2 - Results of the μED-XRF analytic procedure (counts) for the Hispano-Moresque tiles

	Kα Si	Kα Ti	Kα Mn	Kα Fe	Kα Co	Kα Ni	Kα Cu	Kα Zn	Kα As	Lα Pb	Lα Bi	Lα Sn
MM03	2223	177	1096	25978	9294	3925	9525	415	0	214841	727	3400
MM01	7234	396	857	37068	9308	3738	9001	917	5967	445521	2203	4479
MM02	5734	485	871	22638	12521	4068	17022	535	11171	492282	2926	4911

Table 3 - Contents in terms of oxides of the analysis of the blue glaze in tile MM03 by WD-XRF

MM03	Na2O	MgO	Al2O3	SiO2	P2O5	SO3	K2O	CaO	TiO2
%	4.53	0.51	2.43	41.97	0.10	0.22	2.09	3.27	0.20
	MnO	Fe2O3	Co3O4	NiO	CuO	ZrO2	SnO2	PbO	Cl
%	0.08	2.56	0.55	0.30	0.31	0.12	4.46	35.60	0.60

The results in Tables 2 and 3 show that the blue glazes of all Hispano-Moresque tiles contain a considerable content of tin oxide (over 4%) which was not needed for a coloured, non-majolica glaze and this can only have been added to increase the opacity and ensure the clarity of the colour. The tin-cobalt mixture must then be responsible for the rather hazy blue seen in those tiles. All items have also a relatively high content in copper. This has been noticed by other authors [6, 7] and we cannot state based solely on the present data whether the copper is associated to the cobalt in the pigments or whether it is associated with a component of the glaze, or even has been added purposefully to alter the blue [8].

4.2. Portuguese tiles

Figure 2 plots the results of the Portuguese *azulejos* in terms of the normalized iron, nickel and arsenic contents alone. As seen, the two main groups, “cobalt blue” (5.7) and the “blue-black” (2.8) occupy two defined areas in the diagram, ruled by the third axis: the first area (marked in red) corresponds to a relatively low content in nickel; the second (marked in blue) corresponds to a relatively high content in nickel. In the full set of 50 samples tested, of which the present 15 are a sub-set, there are cases of simultaneously Fe/Co<<1 and Ni/Co<<1, Fe/Co<<1 and Ni/Co>>1, Fe/Co>>1 and Ni/Co<<1, but none with both Fe/Co>>1 and Ni/Co>>1. In all cases the hue of the blue colour does not seem to be particularly affected by the content in iron associated with the cobalt. It is the relatively high nickel content that sets the dark 2.8 blue apart from the 5.7 blue, with a divide around the 40% Ni/Co content when only the three main normalized rates are considered. As an additive, nickel oxide is known to potters as a means to impart a grey hue to cobalt blue [8].

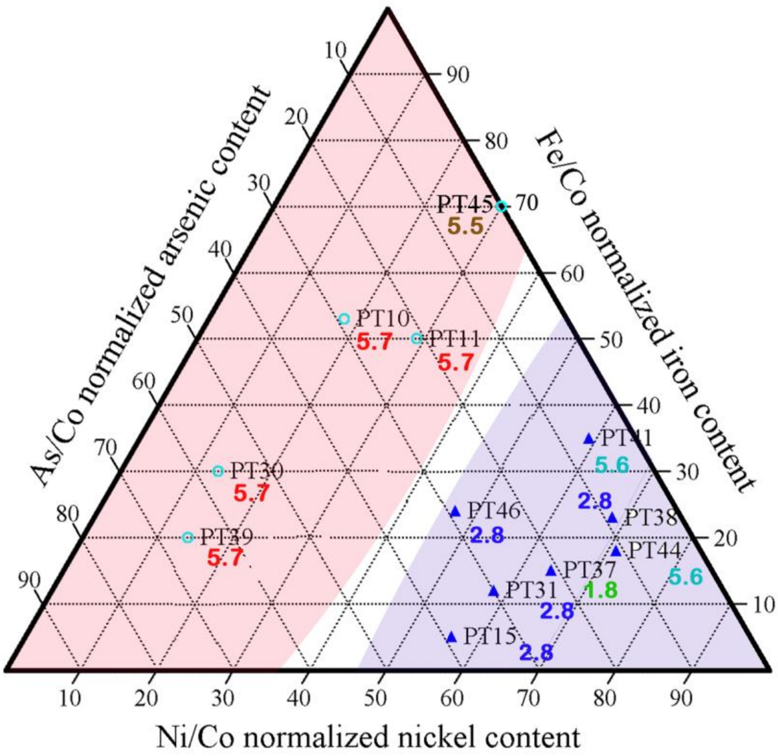


Fig. 2 - Ternary plot of the results in terms of As/Co, Ni/Co and Fe/Co contents

The Coimbra productions (branded “5.6# in the ternary plot of Figure 2) are within the “high Ni area” (together with PT38 branded “2.8# – which may also stem from Coimbra) and somewhat set apart there only because of their low relative As content. They are undoubtedly of the “blue-black group” but more samples are needed for an appraisal of their eventual specificity, both in terms of composition and colour, as well as to establish the chronology of the use of pigments imparting this particular blue by the workshops of Coimbra.

PT45, although clearly a part of the “cobalt blue group”, is set in an area of the plot apart from the rest, because no As was found in it and its iron content is relatively high. Again its status will have to stay unresolved until more samples can be obtained for analysis.

The most interesting case is arguably that of the PT37 “blue 1.8” (Figures 1 and 2). This hue is very clearly greenish and quite unlike any other blue. We know other *azulejos* with precisely this blue although we could not obtain further specimens in time for the analytic program. What makes it particularly interesting is the fact that the composition of the blue pigment in terms of the major elements is very similar to sample PT 31, as may be verified through Table 1, but PT31 does not show any hint of green.

Table 4 depicts the semi-quantitative results by WD-XRF of the main blue-pigmented glaze components for PT30, PT37 and PT44 in terms of common oxides, while Table 5 compares their contents in sodium and potassium normalized to the cobalt content. As seen, PT37 has comparatively high contents of the alkaline metals, particularly of sodium when normalized to the cobalt content. This result suggests that the sodium content, or else the combined sodium and potassium contents may be the key to explain the peculiar hue, and not a compositional particularity of the pigment. Another alternate hypothesis is that due to the asymmetries in firing conditions this particular tile and all others exhibiting the same greenish blue were fired in a partially reducing environment [8].

Table 4 - Percent results (oxides) of the WD-XRF analysis of the blue glaze in PT44, PT30 and PT37

%	Na2O	MgO	Al2O3	SiO2	P2O5	SO3	K2O	CaO	TiO2	MnO	Fe2O3
PT44	2.96	0.66	3.77	51.45	0.20	0.13	2.60	1.46	0.25	0.10	1.11
PT30	2.67	0.17	6.04	69.73	0.07	0.33	6.71	0.83	0.21	0.18	1.24
PT37	4.97	0.32	7.49	65.22	0.11	0.14	4.00	0.96	0.27	0.03	0.78
%	Co3O4	NiO	CuO	ZnO	As2O3	Rb2O	ZrO2	SnO2	PbO	Bi2O3	Cl
PT44	0.39	0.28	0.06	0.00	0.00	0.08	0.10	3.94	30.08	0.10	0.29
PT30	0.51	0.21	0.03	0.00	0.87	0.04	0.02	0.64	8.96	0.33	0.24
PT37	0.25	0.53	0.02	0.02	0.22	0.04	0.06	1.46	12.75	0.14	0.25

Table 5 - Normalized contents of Na and K

	Na/Co	K/Co
PT44	7.6	6.7
PT30	5.2	13.2
PT37	19.9	16.0

5. CONCLUSIVE NOTES

Azulejos used in Portugal depict a number of different blue hues that we tried to systematize and explain based on the pigment composition.

The Hispano-Moresque tiles always depict the same very distinctive muted blue, sometimes lighter, sometimes darker, but always different from true cobalt blue (Figure 3). This hue is most likely a consequence of colouring the glaze with a mixture of blue cobalt pigment and white tin oxide (instead of painting with blue pigment over a tin-opacified glaze). We call this particular hue “Moresque Blue”.

The blue more readily associated with Portuguese azulejos is based on a pigment whose composition depicts the common association Co+Fe+Ni+As but is relatively poor in nickel. We call this hue “Portuguese Blue”.

Another very distinctive hue is characterized by a less rich blue colour, unlike true cobalt blue, but, when diluted, similar to the famed Delft blue. When used in concentration, the pigment returns a blue-black without any hint of true cobalt blue. The analysis of tiles using this pigment revealed the same element association Co+Fe+Ni+As but in this case the nickel content was relatively high. We call this "Nickel Blue". Figures 4 a, b, c illustrate locations where both blues are used side to side. The fact that they are set together suggests that the tiles were brought from other locations and re-used here at a later time.

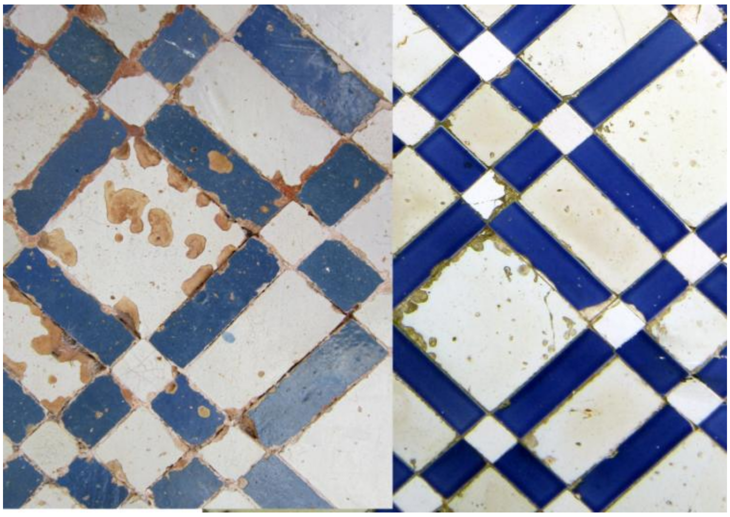


Fig. 3 - *Moresque Blue* 16th century chess-like pattern (left side) compared to a cobalt blue 20th century integration (right side) on the streets of Vila Viçosa

Fig. 4 - Simultaneous use of *Portuguese Blue* and *Nickel Blue* (4a. Ducal Palace of Vila Viçosa; 4b. Cloister of Convento da Conceição in Beja; 4c. *Loggia* of the Igreja da Misericórdia de Beja)

There is, we think, an interesting field of research for the art historian stemming from the results presented. All early azulejos we located that used the Nickel Blue seemingly date from after 1640 (some from shortly after that date), when the 28-year long War of Restitution broke between Portugal and Spain. That fact suggests the hypothesis that Nickel Blue, returning a clearly inferior colour, was cheaper and because of that was used for some workshops during the dire years when the country was in great financial strain. By the end of the century and for most of the 18th century, "Nickel Blue" seems to have fallen from grace everywhere except in Coimbra. So, maybe the Coimbra Blue of the first half of the 18th century, exemplified here by samples PT41 and PT44, is nothing but a continuing acquisition of pigment from a cheaper source that the workshops of Lisbon had waved aside. The pigment seems to reappear in Lisbon around 1800 (PT46) at the time of still another war: the Peninsular War, which drove the Royal Family to abandon Europe with their entourage and set their capital in Brazil. It was not seen afterwards

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Operators at LNEC: António Carvalho (WD-XRF) and Luis Nunes (ablation of the blue glaze).

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